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FOREWORD

The Twenty First Annual Research Review describes the ongoing research programme in the School of Biosystems and Food Engineering at University College Dublin from over 83 researchers (11 academic staff, 1 technician, 4 postdoctoral researchers and 67 postgraduates). The research programme covers three focal areas: Food and Process Engineering; Bioresource Systems; and Bioenvironmental Engineering. Each area is divided into sub-areas as outlined in the Table of Contents which also includes the name of the research scholar (in bold); the research supervisor(s); the title of the research; the nature of the research programme; and the research sponsors. It also includes the noting of four awards for presentational excellence at the Twenty First Annual Biosystems and Food Engineering Research Seminar held in University College Dublin on Monday 14th March 2016.

The six Appendices in the Review provide:

- a listing of research projects in progress which were not included in the Review;
- profiles of Postdoctoral Research Scholars;
- a photographic record of postgraduate students;
- a photographic record of full-time staff; and
- links to Postgrad Research Activities with YouTube Videos

The Editors gratefully acknowledge the dedicated work of the individual research scholars, their research supervisors and the financial support of research sponsors. Suggestions as to how future editions might be improved in presentation, style or content would be greatly appreciated. A copy of this book is available to download from the UCD Research Repository at: http://researchrepository.ucd.ie

The review also includes papers from the School’s Taught Masters Programmes as follows:

ME - Biosystems and Food Engineering
http://www.ucd.ie/eacollege/studywithus/engineering/biosystemsfood/biosystems.html

MEngSc – Food Engineering
http://www.ucd.ie/eacollege/studywithus/engineering/biosystemsfood/food.html

MSc – Environmental Technology
http://www.ucd.ie/eacollege/studywithus/engineering/biosystemsfood/environmental.html

MSc – Sustainable Energy and Green Technologies
http://www.ucd.ie/eacollege/studywithus/engineering/biosystemsfood/sustainable.html

ENDA CUMMINS and TOM CURRAN 14th May 2016
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PRELIMINARY ANALYSIS OF CORRELATIONS BETWEEN XRD AND IR SPECTRA OF BONE CEMENT BIOMATERIALS

Ronan Dorrepaal, Aoife Gowen
UCD School of Biosystems and Food Engineering, University College Dublin, Belfield, Dublin 4, Ireland

Abstract

X-ray Diffraction (XRD) and infrared (IR) spectroscopy techniques can be used to determine aspects of the physical and chemical nature of substances beyond that visible to the naked eye. XRD provides information regarding the crystal structure of a material, through the diffraction of incident x-rays upon its surface at different angles, whereas IR spectroscopy provides information of molecular functional groups within a material. This preliminary study investigated the correlation between the two modalities in order to see whether the spectroscopic features of one modality may be indicative of features of the other. The study was conducted on a range of Sorel cements at 3 days, 7 days and 14 days.

Introduction

Sorel cements (also known as magnesium oxychloride cements) show great mechanical strength and low porosity. They can be manufactured in four crystal structures known as Phase 2, Phase 3, Phase 5 and Phase 9, though Phases 2 and 9 are only possible above 100°C (de Castellar et al. 1996). Phase 5 Sorel cements are stronger than Phase 3 cements and the creation of one in preference to the other is dictated by the ratios of the three constituent components: magnesium oxide (MgO), magnesium chloride (MgCl₂) and water (H₂O) (Li and Chau 2007). This study sought to analyse varied component ratios in the interest of spectral variation.

The use of Sorel cements has been limited to date, particularly in the field of biomaterial research, due to their instability in water. However, additives have been proposed which stabilise the cements with respect to water, resulting in renewed interest (Tan, Liu and Grover 2014; Tan, Liu, Zhao, et al. 2014). While Sorel cements have been studied through the use of both XRD and IR spectroscopy previously, it appears that chemometric correlations have not previously been considered.

The objective of this study was to investigate correlations between XRD and IR spectra of Sorel cements biomaterials at different setting times.

Materials and Methods

Sample Preparation: Three Sorel cement sample types were prepared by first dissolving MgCl₂.6H₂O in deionised water. MgO was added to this solution, followed by rapid mixing until a homogenous paste formed. The cements were then spread on glass slides and allowed to set in air. Three batches of cement were made by combining the constituent components at different ratios according to the literature (Li and Chau 2007) as displayed in Table 1.
Table 1. Table displaying the component weights of the three Sorel cement types used.

<table>
<thead>
<tr>
<th>Name</th>
<th>MgO</th>
<th>MgCl₂·6H₂O</th>
<th>H₂O</th>
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<tr>
<td>M13H12</td>
<td>17.1133g</td>
<td>6.6408g</td>
<td>7.0551g</td>
</tr>
<tr>
<td>M07H10</td>
<td>9.1889g</td>
<td>6.6218g</td>
<td>5.8621g</td>
</tr>
<tr>
<td>M19H18</td>
<td>14.9641g</td>
<td>3.9726g</td>
<td>6.34g</td>
</tr>
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</table>

Spectral Acquisition: A sample from each batch was analysed after 3 days, 7 days and 14 days. At each time point, diamond crystal ATR-FTIR spectroscopy was performed on the sample using a Nicolet iS50 FTIR spectrometer over a range of 4000 cm⁻¹ to 650 cm⁻¹. The sample was then pulverised into a fine powder and mixed with a small amount of silicon powder (used as a known standard to monitor spectral drift). XRD was then performed using a Siemens D500 Bragg diffractometer at 20 from 10° to 90° with a step size of 0.4 and an acquisition time of 1.5 seconds.

Pre-Treatment: Before beginning analysis of the spectra, some pre-treatments were performed.

IR pre-treatments: The IR range of acquisition was 4000 cm⁻¹ to 650 cm⁻¹, however it was found that extremities of the spectra were quite noisy. The spectra were therefore cut such that the range for analysis was 4000 cm⁻¹ to 782 cm⁻¹. The standard normal variate (SNV) of each spectrum was then calculated resulting in spectra with the same mean and variance. These spectra were used for correlation analysis.

XRD pre-treatments: The SNV of each XRD spectrum was calculated resulting in spectra with the same mean and variance. As stated above, when the cement samples were pulverised, a small amount of silicon powder was added as a known standard before XRD analysis was performed. This known standard was useful when assessing whether the acquired spectra drifted from the true diffraction angles. By using silicon as a reference, it was found that the spectra of day 3 were offset by ~15°, while the spectra of days 7 and 14 drifted very little. All spectra were then shifted along the X-axis such that the known reference silicon peaks were in the correct positions. The spectra were subsequently cut to remove spectral ranges not found in all nine acquisitions (resulting from spectral drifting). The XRD range after spectral cutting was 25.52° to 90°. The SNV of each spectrum was calculated again and these spectra were used for further analysis.

Results and Discussion

The resultant spectra were analysed using Matlab 2015b with the Statistics and Machine Learning Toolbox, the Signal Processing Toolbox as well as in-house functions.

Analysis of the spectra included the following:

1. Concatenating the IR spectra into a single matrix, where the rows were the spectra and the columns were the wavenumber acquisitions.
2. Concatenating the XRD spectra into a single matrix, where the rows were the spectra and the columns were the angle readings.
3. Preparation of a Pearson correlation matrix from the concatenated spectra.
4. Plotting a bar indicating a region of the IR and XRD spectra which correlate strongly.
5. Performing partial least squares (PLS) using IR spectra to predict XRD spectra.
6. Performing PLS on IR using XRD spectra to predict IR spectra.

Notable strong IR bands are present between 3727 cm\(^{-1}\) to 3672 cm\(^{-1}\) and 3630 cm\(^{-1}\) to 3598 cm\(^{-1}\), which according to the literature, are indicative of magnesium oxychloride cement crystal structure (Tan, Liu, and Grover 2014). -OH bands between 3571 cm\(^{-1}\) and 2857 cm\(^{-1}\) as well as 1648 cm\(^{-1}\) to 1600 cm\(^{-1}\) are also visible.

Silicon reference peaks are visible at ~28°, 47° and 56°. Sample peaks are found at 43° (MgO), 46° (Phase 5). Other notable variation in the XRD spectra is visible at about ~38° which is reported to be indicative of the crystal structure (Li and Chau 2007). This was in line with the correlation found between the IR wavenumber 3700 cm\(^{-1}\) and the XRD reading at ~38°, as shown in Figure 2.
**Correlation:** It was found that there was a strong inverse correlation between IR wavenumber 3700cm$^{-1}$ and XRD angle 38°. As shown in Figure 1, larger peaks at 3700cm$^{-1}$ for a given sample on the IR appears to relate to inverted larger peaks for the XRD spectra at 38°. These preliminary results suggest that the peaks provide information of the same physical or chemical properties, though larger datasets are needed for confirmation purposes.

**PLS:** Both XRD prediction of IR spectra and IR prediction of the XRD spectra look very promising as shown in Figure 2. It can be seen that predictions almost perfectly mirror the true spectra.

**Conclusions**

This preliminary study showed very promising results, however some caveats must be considered. Firstly, the dataset is relatively small in this preliminary study, meaning issues with overfitting are possible. Further, the training set used to create the model through PLS was later used for spectral prediction. Ideally different datasets would be used for training, testing and validation. Finally, features visible to one modality can only be predicted by a second modality if those features are also visible to the second modality.

**Acknowledgements**

The authors would like to thank the European Research Council (ERC), who funded this research. The authors would also like to thank Dr Kenneth Stanton, Dr Kevin Doherty and the UCD School of Mechanical and Materials Engineering for use of the XRD diffractometer.

**References**


EXPLORING THE EFFECT OF ATTENUATED TOTAL REFLECTION FOURIER TRANSFORM INFRARED (ATR-FTIR) CRYSTAL PRESSURE ON IR SPECTRA OF THE WATER-POLYMER INTERFACE OF HYDROPHOBIC POLYMERS

Sinduraj Mukherjee, José Ángel Martínez González, Aoife Gowen
School of Biosystems Engineering, University College Dublin, Belfield, Dublin 4, Ireland

Abstract
This paper describes the effect of Attenuated Total Reflection (ATR) crystal pressure on the spectral quality of the infrared (IR) spectra water-polymer interface. Three commercially available polymers, polytetrafluoroethylene (PTFE), polyethylene terephthalate (PET) and ultra-high molecular weight polyethylene (UHMPE) were analysed using Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) imaging and contact angle (CA) measurements. Four different ATR pressure percentages (5%, 10%, 15%, and 20%) were selected for comparison. Dry and wet spectra were collected from each polymer and the OH stretching vibration \( v_S \) (3800-2800cm\(^{-1}\)) band area was extracted and compared. A 1-way ANOVA analysis was carried out on this band area acquired using different ATR crystal pressures to investigate differences in water-polymer interaction spectra.

Introduction
PTFE, PET and UHMPE are commonly used polymers for a wide variety of commercial applications e.g. packaging, medical industry. Depending on the surface properties of the polymer, phenomena such as permeability, diffusion, and degradation may occur to varying degrees. An understanding of the extent to which these phenomena are affected by the nature of interaction of polymers with water is desirable to further understand lifespan and operational limitations for different applications. A material’s hydrophobicity is one of the factors which influences the availability of water for surface interactions. ATR-FTIR is a suitable tool to investigate this interaction as it is sensitive to water and solid polymer forms. However, the spectral quality of the polymer-water interface is affected by sample presentation and appropriate data collection among other factors. Appropriate ATR pressure is necessary to achieve optimal contact with the polymer, which affects the spectral quality. Therefore, investigating the optimal ATR pressure is an important task in order to understand water-polymer interactions.

The objective of this paper is to explore the effect of ATR crystal pressure on the spectral quality of the polymer-water interface.

Materials and Methods
Contact Angle Measurements
Three commercial test samples of polymers PTFE, PET and UHMPE (CS Hyde Company, 1351 N. Milwaukee Avenue, Lake Villa, Illinois, USA) were tested using a dynamic contact angle measurement system, the Dataphysics OCA™. Contact angles using sessile drops are a very simple measure to determine a surface’s hydrophobicity(Butt et al. 2014). A droplet of deionised water was placed onto the polymer sample surface using a syringe, and the shape of the sessile droplet, was captured using a high speed camera (Fig. 1). CA measurements were collected at three separate locations focused in the central region of each polymer at room temperature (25°C).
Figure 1. These images show the (a) Dataphysics OCA™ system, (b) a droplet of DI water dispensed using a syringe on the surface of a polymer exhibiting hydrophobic properties and, (c) the shape of the droplet with respect to the wafer surface, (d) schematic representation of surfaces with different hydrophobicity.

**ATR-FTIR spectra acquisition**

A Thermo Scientific™ Nicolet™ iN™10 Infrared Microscope offering a fixed 10x magnification, fitted with a Mercury-Cadmium-Tellurium (MCT) detector, capable of imaging in the 7800–650 cm\(^{-1}\) range (4 cm\(^{-1}\) spectral resolution) with a germanium crystal (refractive index = 4) was used to collect spectra in Attenuated total reflectance (ATR) mode. 16 scans were co-added to increase the SNR (signal to noise ratio) and the scans were collected in the 4000-750 cm\(^{-1}\). Deionised (DI) water sourced from a Thermo Scientific™ Barnstead™ Smart2Pure™ water purification system producing Type I ASTM water, with a resistance of 18.2M \(\Omega\) cm at 25.6°C. Wetting of polymers was accomplished using Blu Tack™ to make a well on each polymer, which served as a water trap. Wet spectra was captured after hydrating the polymers with an equilibration time of at least 1 minute. A total of 91 spectra for each polymer were captured in dry and wet state in the form of hypercubes or spectral data cubes. ATR pressure was controlled using inbuilt pressure controls offered by the Omnic™ Picta™ and spectra were collected at four different pressure percentages (5%, 10%, 15% and 20%).

Figure 2. This figure shows the (a) use of a well to trap water on the polymer to be tested and (b) the data acquisition setup using the ATR slide on attachment (glass slide as a representative surface)

**Data Analysis**

All wet spectra hypercubes were unfolded, and the band area of the OH stretching vibration OH \(\nu_S\) (3800-2800 cm\(^{-1}\)) for each polymer & each pressure were compared. A 1-way ANOVA test was carried out at a 5% significance level to explore the effect of ATR pressure on the band the band area of the stretching vibration OH \(\nu_S\) (3800-2800 cm\(^{-1}\)). All spectra were visualised and processed using a combination of Origin 9.0 (OriginLab®, Northampton, MA) and Matlab® 2013 (The MathWorks, Inc., Natick, Massachusetts, United States).

**Results & Discussion**

*Contact Angle Measurements*
The contact angle values of the polymers (Table 1) indicated that the polymers tested were hydrophobic in nature. Variation in CA values over different points of the polymer surface indicated that surface hydrophobicity of these polymers across different data points exhibited large variations.

Table 1 This figure quickly summarises the contact angle measurements for each polymer tested. The higher the angle at which the water droplet contacts the surface of the polymer, higher the hydrophobicity of the polymer surface (Butt et al. 2014).

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<td>0.08</td>
<td>0.060277</td>
<td>SD %</td>
<td>0.040415</td>
<td>0.147422</td>
<td>0.052915</td>
<td>SD %</td>
<td>0.058595</td>
<td>0.087178</td>
<td>0.035119</td>
</tr>
</tbody>
</table>

ATR-FTIR Dry & Wet spectra

Mean dry and wet spectra from Images at 5% pressure at 0–1 minute wetting time are shown in Fig. 3. The main spectral features of the wet polymer are the OH bending $\nu_B$ at 1640 cm$^{-1}$ and the OH stretching vibration $\nu_S$ (3800-2800cm$^{-1}$) (Socrates 2004).

Figure 3. This figure shows the representative dry and wet spectra (~1 min hydration time) for the three polymers tested (top portion) at 5% ATR crystal pressure. The lower section of the figure shows the subset of the spectra focussed at the OH stretching vibration $\nu_S$ (3800-2800cm$^{-1}$) region. Please note that the Y axis (Transmittance %) has been scaled differently for convenience and the X-axis denotes Wavenumber cm$^{-1}$.

One could choose the OH bending $\nu_B$ at 1640 cm$^{-1}$ to study water-polymer interactions as well. However the peak position for this band overlaps with one of the peaks of PET and has a weak transmittance compared to the $\nu_S$ band, making it an unsuitable spectral feature for further analysis. Therefore, we proceeded to extract the $\nu_S$ peak area for different pressures, i.e., 5%p, 10%p, 15%p,
20\% p for each of the polymers. **Fig. 4** shows the comparison of the band area of the OH stretching vibration OH $\bar{\nu}_S$ (3800-2800 cm$^{-1}$) for each polymer over different ATR crystal pressures. In each case, the band area of the OH stretching vibration OH $\bar{\nu}_S$ seemed to decrease as we increase the ATR crystal pressure. This makes sense in light of the fact that, as the ATR pressure increases, there is less water available at the water-polymer interface.

![Figure 4](image.png)

**Figure 4.** This image compares the band area of the OH stretching vibration OH $\bar{\nu}_S$ (3800-2800 cm$^{-1}$) for each polymer over different ATR crystal pressures (5\%, 10\%, 15\%, 20\%). The error bars represent the standard deviations in values of band area of the OH stretching vibration OH $\bar{\nu}_S$.

Furthermore, when a 1-way ANOVA test was applied on the band area of the OH stretching vibration OH $\bar{\nu}_S$ (3800-2800 cm$^{-1}$) for each polymer to compare different crystal pressures, the p-value of the ANOVA was 0, implying that there are significant differences in the usage of different ATR crystal pressure on spectral quality of water interacting with these particular polymers.

**Conclusions & Future Plans**

In case of all the polymers tested, as the ATR crystal pressure increases, the $\bar{\nu}_S$ band area decreases, because of lesser amount of water available for water-polymer interaction. 10\%-15\% ATR crystal pressure results in similar $\bar{\nu}_S$ area while 20\% ATR crystal pressure maybe too high for studying water-polymer interaction as it may damage soft polymers. Since the contact angle measurements indicate that, different parts of the polymer surface exhibit differential hydrophobicity, i.e., have different surface characteristics, one can start with 5\% ATR crystal pressure for optimal contact. We plan to expand this study to other polymers to have a systematic understanding of water-polymer interaction. In the future we also plan to study other factors affecting water-polymer spectral quality such as optimising effective hydration time and controlling the mode of wetting using a Relative Humidity chamber for a more defined water-polymer interaction.

**Acknowledgements**

The authors acknowledge funding from the EU FP7 under the European Research Council Starting Grant programme and thank Prof. Denis Dowling and Dr. Charlie Stallard for use of the CA measurement system.

**References**


APPLICATION OF HYPERSPECTRAL IMAGING ON QUALITY ASSESSMENT OF FRUITS: A BRIEF REVIEW

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Abstract
Hyperspectral imaging (HSI) has gained wide recognition as a rapid, chemical-free, and non-destructive quality and safety analysis method for a wide range of food products, by simultaneously offering both spatial information and spectral signals from one object. This study focuses on the recent applications of hyperspectral imaging on quality assessment for fruits. First, the fundamental principles, major instrumental components and data analysis methods of hyperspectral imaging are presented. Second, applications of hyperspectral imaging on quality inspection of fruits are reviewed specifically summarized into bruise, moisture content and fruit fly/insect infestation.

Introduction
Fruits with superior quality are always expected and demanded by consumers. It is a big concern to analyse and assess quality attributes of fruits throughout the processing operations. Quality assessment of fruits integrates determination of the external defects and internal features. The external defects, such as bruise and chilling injury, can drastically lower the quality level, causing great economic loss (Ariana et al., 2006; Lu and Tang 2012; Velez et al., 2014; Lee et al., 2014). The internal features in fruits, with a high connection with product aroma and taste, implicate a key role in quality assessment (Rajkumar and others 2012; ElMasry et al., 2007).

Currently, human visual inspection is still widely used, which, however, is subjective, time-consuming, laborious, tedious and inconsistent; therefore, the development of accurate, rapid and objective quality inspection systems is an urgent need for the food industry to ensure the safe production of food products. Recently, with the integration of two mature technologies of imaging and spectroscopy, hyperspectral imaging techniques have been investigated as a potential analytical tool for non-destructive analysis and assessment for food products quality. Many studies have applied HSI in quality assessment of different fruits, such as apples (Xing et al., 2005), mangos (Velez et al., 2014), kiwi fruit (Lu and Tang, 2012), pears (Lee et al., 2014), strawberries (Nanyam et al., 2012), bananas (Rajkumar et al., 2012), tart cherry (Xing et al., 2008) and many other fruits, which shows the great capability of HSI for the quality assessment of fruits.

The objectives of this study are (1) to provide the fundamental principles of hyperspectral imaging and the key methods for data analysis; (2) to summarize the application of this technique for the quality assessment of fruits.

Hyperspectral imaging
Principle of hyperspectral imaging
Hyperspectral imaging is a platform technology that integrates conventional imaging and spectroscopy to attain both spatial and spectral information from one object (Gowen et al., 2007). Hyperspectral images are three-dimensional hyperspectral cube, which are composed of two-dimensional spatial information and one-dimensional wavelength information. Since regions of a sample with similar spectral properties would have similar chemical composition, HSI can visualize the biochemical components of a sample by applying the developed prediction model on particular areas of the image (Wu and Sun, 2013).

Instrumentation
Instrumentation of HSI is the basic and essential step to acquire high quality images with high reliability, which requires a good understanding of the configuration and calibration of the system (Wu and Sun, 2013). The essential elements for constructing HSI system generally contain the
following components: light sources (to illuminate the target), wavelength dispersion devices (to disperse broadband into different wavelengths), detectors (to quantify the intensity of the acquired light), and calibration of HSI system (to ensure the reliability of the acquired hyperspectral image data and the performance of the system). Figure 1a displays the components of a HSI system.

**Data analysis**

In order to acquire useful spatial information from the hyperspectral images, the problems related with bad illumination, the presence of artefacts or noise in the images and the selection of regions of interest need to be corrected in pre-processing steps; therefore, a series of image processing methods and algorithms are necessary (Lorente et al., 2012). Typical steps followed in analysing hyperspectral images are showed in Figure 1b. The most commonly used statistical techniques found in the scientific literature for classification or regression include principal component analysis (PCA), linear discriminant analysis (LDA), partial least square (PLS), artificial neural network (ANN), support vector machine (SVM), and cluster analysis (CA).

**Application of HSI on quality assessment of fruits**

As a rapid and non-destructive technology, hyperspectral imaging has found increasing utilization in the quality assessment of fruits. This part of the review categories the recent applications of hyperspectral imaging into three aspects: bruise, moisture content and fruit fly/insect infestation.

**Bruise**

Bruise damage, as the most significant external defect of fruits, has gained a great deal of attention from researchers since it can lower the quality of the fruit and thus cause significant economic losses (Wu and Sun, 2013; Pu et al., 2015). Detection of a bruise on apples using HSI is the main research investigation in the last decade (Lorente et al., 2012; Wu and Sun, 2013). Many studies have shown apple bruises could be detected by HSI effectively with promising results, such as bruising of ‘Golden Delicious’ apples had been detected by hyperspectral reflectance imaging with a classification accuracy of 86% (Xing et al., 2005). However, some apple cultivars are hardly detected by using HSI with the lowest detection accuracy of 63% (Soliva-fortuny et al., 2001), and fresh and small bruised regions which have the similar hyperspectral images with the healthy regions are often undetected (Kleynen et al., 2005). In order to build a system which can detect fresh and small bruises while handling different apple varieties, several setups have proposed in many research. Ariana and Lu (2010) stated that using hyperspectral imaging in the visible and near infrared range for model building can detect different apple cultivars with better bruise detection. Baranowski et al. (2012) investigated the effective application of short wave infrared HSI for early bruits detection in apples. Keresztes et al. (2016) developed a real-time pixel based early apple bruise detection system based on HSI in the shortwave infrared range which was able to detect fresh bruises in thirty apples with 98% accuracy. Hyperspectral imaging has also been applied for bruise detection of many other fruits including mango (Velez et al., 2014), kiwi fruit (Lu and Tang, 2012), pear (Lee et al., 2014) and strawberry (Nanyam et al., 2012), as shown in Table 1.
Table 1. Applications of reflectance HSI in bruise detection of some fruits

<table>
<thead>
<tr>
<th>Species</th>
<th>Range (nm)</th>
<th>Image processing</th>
<th>Accuracy</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pear</td>
<td>950 to 1650</td>
<td>Band ratio</td>
<td>92%</td>
<td>(Lee et al., 2014)</td>
</tr>
<tr>
<td></td>
<td>/</td>
<td>PCA</td>
<td>93.8%, 95%</td>
<td>(Zhao et al., 2010)</td>
</tr>
<tr>
<td></td>
<td>949 to 1666</td>
<td>Band ratio</td>
<td>/</td>
<td>(Dang et al., 2012)</td>
</tr>
<tr>
<td>Mango</td>
<td>650 to 1100</td>
<td>/</td>
<td>67.46% to 98.13%</td>
<td>(Velez et al., 2014)</td>
</tr>
<tr>
<td>Kiwi fruit</td>
<td>600 to 1000</td>
<td>PCA</td>
<td>85.5%</td>
<td>(Lu and Tang, 2012)</td>
</tr>
<tr>
<td></td>
<td>600 to 900</td>
<td>PCA</td>
<td>87.5%</td>
<td>(Lu et al., 2011)</td>
</tr>
<tr>
<td>Strawberry</td>
<td>960 to 1700</td>
<td>Multiband segmen</td>
<td>85.3%, 97.67%</td>
<td>(Nanyam et al., 2012)</td>
</tr>
<tr>
<td></td>
<td>650 to 1000</td>
<td>/</td>
<td>/</td>
<td>(Nagata et al., 2006)</td>
</tr>
</tbody>
</table>

Moisture content

Fruits are usually sorted either manually or mechanically based on the external quality features. However, the internal quality attributes such as moisture content, total soluble solids and acidity are increasingly significant in the growing trend. According to the research, the moisture content of fruits has a critical impact on quality evaluation. Rajkumar et al. (2012) investigated the relationship of moisture content and maturity stages in banana fruit at 3 different temperatures using HSI with reflectance mode in 400 to 1000 nm spectral domain. Optimal wavelengths were selected for predicting moisture content using an exhaustive search with b-coefficients from PLSR models, resulting in coefficient of determination of 0.87. The result showed the change in moisture content followed a linear relationship at different maturity stages. ElMasry et al. (2007) studied the moisture content in strawberries by HSI in a range between 400 and 1000 nm, in which it showed a good prediction performance ($r = 0.91$) and the strawberries in deep maturity stage showed higher moisture content and lower relative reflectance. In Table 2, it summarizes the applications of HSI in quantitative analysis of moisture content in fruits.

Table 2. Applications of HSI in quantitative analysis of moisture content in fruits

<table>
<thead>
<tr>
<th>Species</th>
<th>Range (nm)</th>
<th>Data analysis</th>
<th>Accuracy</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Banana</td>
<td>400 to 1000</td>
<td>PLS, MLR</td>
<td>$R^2 = 0.87$</td>
<td>(Rajkumar et al., 2012)</td>
</tr>
<tr>
<td>Strawberry</td>
<td>400 to 1000</td>
<td>PLS, MLR</td>
<td>$R^2 = 0.87$ to 0.90</td>
<td>(ElMasry et al., 2007)</td>
</tr>
<tr>
<td>Mango</td>
<td>400 to 1000</td>
<td>PCA, PLS, ANN</td>
<td>$R^2 = 0.81$</td>
<td>(Servakaranpalayam, 2006)</td>
</tr>
</tbody>
</table>

Fruit fly/insect infestation

Detection of fruit fly/insect infestation is significant as it can lead to serious economic loss (Wu and Sun, 2013). HSI has been used to detect not only external infestation such as in jujube fruit (Wang et al., 2011) and mango (Haff et al., 2013), but also internal infestation such as in tart cherry (Xing et al., 2008). Reflectance mode was applied in the jujube fruit. Both reflectance (590-1550 nm) and transmittance (580-980 nm) modes were used for image acquisition in tart cherry. HSI had satisfactory detection results for jujube and mango, which are overall classification accuracy of 97.0%, and 0.9% false negatives for infested fruit misclassified and 5.7% false positives for control fruit misclassified, respectively. Table 3 summarizes the applications of HSI in fly infestation inspection of fruits.

Table 3. Applications of HSI in fly infestation inspection of fruits

<table>
<thead>
<tr>
<th>Species</th>
<th>Range (nm)</th>
<th>Data analysis</th>
<th>Accuracy</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jujube</td>
<td>400 to 720</td>
<td>SDA</td>
<td>94% to 97%</td>
<td>(Wang et al., 2011)</td>
</tr>
<tr>
<td>Mango</td>
<td>400 to 1000</td>
<td>Multialgorithms scheme</td>
<td>79.7% to 98%</td>
<td>(Haff et al., 2013)</td>
</tr>
<tr>
<td>Tart cherry</td>
<td>580 to 980</td>
<td>GA, PLS-DA</td>
<td>81.3 to 95.76%</td>
<td>(Xing et al., 2008)</td>
</tr>
</tbody>
</table>

Conclusion

Integrating the benefits of computer vision and spectroscopy through hyperspectral imaging has the potential as an analysis and assessment tool for qualitative and quantitative determination of many food products. This review summarizes the recent application of hyperspectral imaging in quality assessment of fruits in the aspects of bruise detection, moisture content and fruit fly/insect infestation.
Acknowledgement
The authors would like to thank the financial support from the Chinese Scholarship Council (CSC) and University College Dublin (UCD).

References


APPLICATION OF HYPERSPECTRAL IMAGING FOR AUTOMATIC DIFFERENTIATION OF ORGANICALLY AND CONVENTIONALLY FARMED SALMON

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Abstract

This study was carried out to investigate the potential of short-wave near infrared (400-1000 nm) hyperspectral imaging (HSI) system for differentiation of organic and conventional farm-raised salmon fillets in fresh and chill-stored conditions. Hyperspectral cubes were acquired and their corresponding spectra data were extracted. Principal component analysis (PCA) was applied to explore the variance between different classes of salmon. Partial least squares-discriminant analysis (PLS-DA) was used to build classification models for recognition and authentication of the tested samples. The best results were obtained with the correct classification rate (CCR) of 98.2% in validation and CCR of 97.1% in cross-validation, which suggested the capability of the hyperspectral imaging for objective and rapid categorization of the two salmon varieties under circumstances of fresh and chill-stored conditions.

Introduction

When most consumers see the organic label, they think of a superior product compared to conventionally raised varieties, from an environmental, health, and animal welfare perspective. In Europe, the leading product in organic aquaculture is Atlantic salmon, followed by the Mediterranean species seabass and seabream, freshwater salmonids, and carp (Szeremeta et al. 2010). Due to the natural and healthy environment and low population density, organic salmon are well recognized as having good muscle tone and body shape, which makes organically farmed salmon a superior product with higher price. However, since there was little distinction in appearance, texture or flavour between the two varieties of the farm-raised, it is not reliable to depend on human vision detection, especially not suitable in the fish industry when tons of products are involved during a short period. As a result, appropriate methods that are applicable for online inspection are required.

Partial least squares-discriminant analysis (PLS-DA) is a popular chemometric technique for supervised classification of the spectra and it is increasingly-used in hyperspectral data analysis for classification and discrimination problems (Chevallier et al. 2006). Meanwhile, hyperspectral imaging (HSI) has established itself as one of the most versatile tools in food quality and safety analysis. However, to the best of our knowledge, no research endeavours have been reported for differentiation between conventionally and organically farmed salmon using hyperspectral imaging technique. Therefore, the objective of this study was to investigate the suitability of using short-wave near infrared (400-1000 nm) hyperspectral imaging for authentication of organic salmon in fresh and chill-stored conditions.

Materials and Methods

Fish sample preparation

A total of 80 organic and 80 conventional farm-raised Atlantic salmon (Salmon salar) fillets originated from a farm in Ireland were labelled and then transported to laboratories of Food Refrigeration and Computerized Food Technology (FRCFT), University College Dublin (UCD), Ireland. Each fillet was about 200 grams in different sizes and no any two fillets were
Organic salmon samples are provided with special diets that contain only organic, natural ingredients from sustainable sources and reared in large pens which allow them to follow their natural shoaling behaviour, with the stocking density less than 10 kilogram per cubic meter – less than half that of conventional farms. Upon arrival, samples were randomly divided into four groups with equal numbers: fresh organic (Group 1), fresh conventional (Group 2), chill-stored organic (Group 3) and chill-stored conventional (Group 4) samples, where chill-stored groups (Groups 3 and 4) refer to the samples subject to storage for 5 days at controlled refrigerated condition.

Hyperspectral image acquisition and calibration

The specific description of HSI system can be found elsewhere (Xu et al. 2016). Each salmon fillet was firstly placed on the translation stage and then conveyed to the field of view (FOV) of the camera to be scanned line by line.

Multivariate exploration of images

The final result of measuring a hyperspectral image is a 3-D dataset named as ‘hypercube’ with one spectral dimension (λ) and two spatial dimensions (x, y). Each hypercube in this study contains one class of salmon fillet and background. It usually comprises thousands of spectra (spectral signature) distributed over the measured area (spatial signature). Thus, it is essential to explore and understand the structure of the hyperspectral image in order to select the proper tools for dealing with the final aim. Among all the methods for multivariate exploration, principal component analysis (PCA) is the most versatile and widely-used. It aims at studying the variability (variance) by dividing the hypercube into a set of surface scores and spectral loadings.

Data partition

In this work, the calibration model was strictly built using the calibration (or training) set and validated by an independent set (validation or prediction set). Kennard-Stone (KS) algorithm (Kennard and Stone 1969) was applied to automatically split all samples into different calibration and validation subsets for each system. Specifically, 160 salmon samples were divided into two groups: 105 samples (approximately 2/3 of all samples) were selected as the calibration set and the remaining 55 samples (approximately 1/3 of all samples) were used as the validation set. In this way, it was ensured that both sets covered appropriately and consistently all the categories. Before models were established, several spectral pre-processing methods, including mean centre, multiple scatter correction (MSC), and extended mixture model (EMM) filter were applied.

Results and Discussions

Image exploration by PCA

A PCA model of the big hypercube with four classes of salmon samples randomly selected is shown in Fig. 1. This PCA model was performed based on spectra in the range of 400-1000 nm and pre-processed by multiple scatter correction (MSC) and mean centre. The total amount of variance explained by the first four principal components (PCs) was higher than 97%, indicating that the main differences are presented within these four PCs. Since each material has a unique spectral signature based on its physicochemical properties, the white stripes display distinctive spectral signatures compared with that of muscles within the same fillet. It is found in score images that each class of salmon fillet contains big variance so it is not possible to differentiate these four classes of images by simply applying PCA on images. However, each class of image contains the variance in different ratios, which means it is possible to differentiate if appropriate classification methods were applied.
Figure 1. PCA model of the hypercube in the full range of 400-1000 nm. Top: Score images at PC1, PC2, PC3 and PC4. Bottom: the corresponding loadings. 1: Fresh organic; 2: Fresh conventional; 3: Chill-stored organic; 4: Chill-stored conventional samples.

Qualitative modelling based on PLS-DA

Specifically, MSC, EMM filter and mean center were employed as pre-processing techniques to build a robust PLS-DA model. PLS-DA classifier demonstrated good prediction performance based on the full 400-1000 nm spectrum, resulting in the satisfying result with CCR of 100% for calibration, 98.2% for validation and 97.1% for cross-validation, which meant that all the 105 samples were correctly classified in the training set and 54 out of 55 samples were correctly identified in the prediction set. The predictive result in Table 1 further presents that only 1 chill-stored conventional sample was misclassified into chill-stored organic group.

<table>
<thead>
<tr>
<th>Actual Group</th>
<th>Predicted as Group 1</th>
<th>Predicted as Group 2</th>
<th>Predicted as Group 3</th>
<th>Predicted as Group 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group 1</td>
<td>14</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Group 2</td>
<td>0</td>
<td>14</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Group 3</td>
<td>0</td>
<td>0</td>
<td>11</td>
<td>1</td>
</tr>
<tr>
<td>Group 4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>15</td>
</tr>
</tbody>
</table>

Table 1. Confusion matrix obtained from PLS-DA model.

Notes: Group 1: Fresh organic; Group 2: Fresh conventional; Group 3: Chill-stored organic; Group 4: Chill-stored conventional samples.

In this model, 2 latent variables (LVs) were selected by checking the evolution of the classification error (class error) for calibration, cross-validation and validation set. LV 1 and LV 2 were particularly representative of the spectral information and contributed to 81.33% of the total variance (LV 1 - 43.75% and LV 2 - 37.58%). The score plot displayed in Fig. 2 confirmed that the tested salmon groups had different spectral patterns and could be easily distinguished into four separate groups. Interestingly, organic and conventional salmon fillets both in the chill-stored condition were much closer to each other whereas the fresh conventional (Class 2) and chill-stored organic samples (Class 3) were quite far away, implying that freshness degree enlarged the spectral difference between conventional and
organic salmon. Meanwhile, most organic samples had negative scores on LV 1 and most conventional ones were situated on the positive side, testifying the possibility to classify between conventional and organic samples no matter if samples were fresh or not. Additionally, LV 2 proved the capability of discriminating between fresh samples and the chill-stored ones, with most fresh samples locating at the negative side and the chill-stored ones on the other side. Overall, Fig. 2 strongly suggested that tested samples had reasonable variation in their spectral patterns, which led to the successful discriminant analysis based on the full 400-1000 nm range.

![Figure 2. Score plot with 2 latent variables from PLS-DA.](image)

**Conclusions**

This study demonstrated the great potential of hyperspectral imaging for rapid and non-invasive discrimination between organic and conventional varieties of farm-raised salmon at different freshness stages. The successful outcome of this study would be very advantageous to assure consumers and buyers of authentic organic salmon fillets.

**Acknowledgements**

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**Reference**


POTENTIAL OF TIME-SERIES HYPERSONTICAL IMAGING FOR FRESHNESS DETECTION IN SALMON DURING COLD STORAGE

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Abstract

Freshness is a primary attribute of consumers’ acceptance to evaluate quality of fish fillets. This experiment investigated the potential of using near infrared hyperspectral imaging (900-1700 nm) for rapid and non-destructive prediction of freshness in Atlantic salmon (salmon salar) fillets during cold storage. One salmon fillet was stored in the refrigerator at controlled temperature of -1°C over 12 days. Hyperspectral images were obtained at 0, 3, 6, 9 and 12 days and their corresponding spectral data were extracted. Savitsky Golay smoothing and derivatives (SG) and standard normal variate (SNV) were used as spectral pretrement methods, principal components analysis (PCA) was applied for exploration of image variance. The results demonstrated that hyperspectral imaging technique has the potential to present and classify the differences of salmon samples with different storage days.

Introduction

Nowadays, food safety and quality has been receiving increasing attention from consumers as well as from producers. Freshness is a vital determination for food quality, especially for fish. It has been acknowledged that fish is an extremely perishable and vulnerable food, because of high moisture content, rich nutrition and neutral or slightly acid pH. All of these characteristics provide a comfortable and suitable environment for various kinds of microorganisms. The spoilage of fish is a complex process (Benjakul et al., 2003) which is implicated in physical, chemical and microbiological mechanisms and can lead to loss of freshness, change of texture, even slime and sensory rejection. Salmon is one of the most popular fish in coastal countries and areas. Therefore, the investigation of freshness in salmon is of great significance not only to consumers’ health but also to international fishery.

As for the freshness detection of fish, there are many traditional methods, such as the detection of change in color and firmness, the oxidation of lipid, the decomposition of protein and the activity of microorganisms. These methods are generally labor-intensive, destructive and time-consuming. Therefore, the development of rapid, objective and non-invasive technology is desperately needed. As an innovative tool, hyperspectral imaging techniques merged traditional spectroscopy and computer vision technology into one system, providing a three-dimensional hypercube (x, y, λ) which includes spatial (x and y) and spectral (λ) information simultaneously. The obtained hypercube is composed of hundreds of wavebands for every spatial position of a sample target. In recent years, this promising and powerful technique has been intensively used for quality inspection and safety control in food industry, such as red meat, fish, fruits and vegetables and cereals(Cheng and Sun, 2014, Nicolaï et al., 2007, Wu and Sun, 2013). At the same time, these products’ physical, chemical and microbial attributes have also been investigated. The objective of this study was to explore the potential of using time-series hyperspectral images for freshness detection in salmon during cold storage at -1°C for 0, 3, 6, 9 and 12 days.
Materials and Methods

Sample preparation
One fresh Atlantic salmon (*salmon salar*) originated from Norway was transported to laboratory of FRCFT at UCD, and then stored at -18 ℃ for three months. After frozen treatment, it was stored at -1 ℃ for 0, 3, 6, 9 and 12 days.

Hyperspectral imaging system
Spectral images of the salmon fillet stored for different days were acquired in reflectance mode by using a laboratory-based pushbroom hyperspectral imaging system (Xu et al., 2016). The system is made up of a camera with a C-mount lens (Xeva 992, Xenics Infrared Solutions, Leuven, Belgium), a spectrograph (ImSpector, N17E, Spectral Imaging Ltd, Oulu, Finland) with a near infrared wavelength from 900 to 1700 nm, two tungsten illuminating lamps (Vlight, Lowel Light Inc., New York, USA) positioned at an angle of 45° to light up the translation stage, which was operated by a stepping motor (GPL-DZTSA-1000-X, Zolix Instrument Co. Beijing, China), and a computer system consisting of imaging data acquisition software (Spectral Cube, Spectral Imaging Ltd., Oulu, Finland). The wavelength interval is 3.34 nm between contiguous bands and produce 256 bands in total.

Hyperspectral image acquisition and calibration
After the salmon fillet was taken from the refrigerator, thawed at room temperature for about 20 minutes, then put on the translation stage and conveyed the fillet to the field of view (FOV) of the camera at a speed of 2.7 cm/s to be scanned line by line. Exposure time of the camera, speed of the motor were carefully selected to avoid distortion of images. Two standard images, the dark current (0% reflectance) and the white Teflon tile (99% reflectance) were obtained firstly in order to correct the raw images (R₀). The calibrated image (R_c) of sample was calculated using the formula below:

\[ R_c = \frac{R_0 - R_d}{R_w - R_d} \]

where R_d is the dark reference image with the camera lens covered with its non-transparent cap and R_w is the white reference image obtained from a white Teflon tile as reference.

Data analysis
After image acquisition, Matlab R2015a software (The Mathworks Inc., USA) was used for image processing. Prior to data analysis, Savitsky Golay smoothing and derivatives (SG) and standard normal variate (SNV) were used as spectral pretreatment to remove the undesired effects in sample measurements, such as random measurement noise, interfering effects of unwanted chemical and physical variations. Then principal components analysis (PCA) exploration was applied for spectral analysis.

Results and Discussion

Results of SG and SNV pretreatment
50 pixels were chosen from the 5 images randomly, as seen from Fig.1-a, before SG pretreatment, there were some spikes detected, after the pretreatment, these spectra became quite smooth. From Fig.1-b, after SNV pretreatment, the offset and multiplicative effects were removed, but there were still spikes. So in Fig.1-c, the two methods were integrated together and desired effects were obtained.
Figure 1. Comparison of pretreatment of (a) Savitsky Golay (SG) (b) standard normal variate (SNV) (c) SG-SNV.

Results of PCA analysis
PC 1, PC 2, PC 3 interpret 93.74%, 4.74% and 1.15% variance respectively. The blue part in the red circle became smaller and smaller during the cold storage in Fig.2-a, which can be used as an indicator of freshness. However, Fig.2-b didn’t show much difference. Although Fig.2-c had quite a small percent of variances, it demonstrated a big difference in the period of storage time. As seen from the black circle, the yellow stripes faded with storage time going by.

Conclusions
The combination of SG and SNV showed satisfactory effects for spectral pretreatment, PCA was appropriate for hyperspectral image analysis. NIR hyperspectral imaging (HSI) from 900 to 1700 nm shows the potential to detect the difference in salmon during cold storage.
Figure 2. (a), (b), (c) present PC 1, PC 2 and PC 3 after principal components analysis (PCA) exploration respectively.

Acknowledgements

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References


Migration assessment of chitosan nanoparticles from an experimental nanoparticle/dip and spin coated food packaging

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Abstract

The use of non-metal nanocomposites in food packaging applications may present solutions to specific issues associated with metal nanoparticles (NPs) (e.g. public acceptance) as they are perceived as more natural and less toxic. In this study the migration of chitosan nanoparticles (CsNPs) is assessed from a dip and spin coating into distilled water (dH\textsubscript{2}O) as a food simulant. Migration amounts were 1 µg/kg\textsubscript{food} and 20 µg/kg\textsubscript{food} for the spin and dip coating, respectively. The presence of NPs was confirmed in the packaging by scanning electron microscopy (SEM) and in the food simulant by NTA, however, fewer NPs were observed in the dip coating. Based on the regulatory migration limit of 0.01 mg/kg\textsubscript{food} established by the European Commission (2011) only the CsNP spin coated material was found to fall below the limit, with the dip coating having two-fold higher migration than the limit. From these findings, more focus will be placed on the dynamic migration behaviour of the spin coated samples.

Introduction

Food packaging materials containing particles with at least one dimension in the size range 1-100 nm (nanoparticles), exhibiting novel antibacterial properties have the potential to alleviate some of the world’s food waste issues whilst improving food safety. The antibacterial properties that are associated with NPs reduced particle size and subsequent increased reactive surface area, are also the leading mechanism suspected for their potential toxicity (Hannon et al., 2015). In the literature, a lack of studies documenting the toxicity, exposure and fate of NPs in the environment and human gastrointestinal tract has added to concerns related to the safety of food packaging materials containing NPs. There has been increasing attention on the release of a select group of engineered nanomaterials (ENMs) from solid nanocomposites, particularly Ag, carbon nanotubes, TiO\textsubscript{2}, SiO\textsubscript{2}, clay, ZnO, Fe\textsubscript{2}O\textsubscript{3}, Al\textsubscript{2}O\textsubscript{3} and CuO (Mackevica et al., 2016). Few studies have focussed on the release of NPs from food packaging coatings, and fewer studies have investigated the release of non-metal nanoparticles such as CsNPs from coatings (Hannon et al., 2015). To the best of the author’s knowledge this is the first study to report the migration of CsNPs from a food packaging material.

The objective of this study was to characterise and quantify the level of migration of chitosan nanoparticles from an experimental dip and spin coated food packaging material.

Materials and Methods

Nanocomposite manufacture

Substrates of silicon and glass were cut into 2 × 2 cm\textsuperscript{2} and 1 × 1 cm\textsuperscript{2} squares, followed by cleaning in EtOH solution under ultrasonication for 30 mins and then dried under a stream of N\textsubscript{2} gas. The substrates were then cleaned in a piranha solution (1:3 %v/v, 30 % H\textsubscript{2}O\textsubscript{2}:H\textsubscript{2}SO\textsubscript{4}) at 90 °C for 40 mins, washed with deionised water and dried under a stream of N\textsubscript{2} gas. A 1 wt.% solution of PEO in chloroform was spin-coated (G3P-8 Spincoat, Cookson Electronic Equipment) onto the substrates at 3000 rpm for 30 s. The coated samples were then annealed at 60 °C for 8 hrs at a reduced pressure of -83 kPa in a vacuum oven (Townson and Mercer EV018). Any unbound polymer was removed by washing with deionised water. CsNPs were synthesised in solution from a modified method set out by
Calvo et al. (1997). The modified substrates were dipped into CsNPs solutions three times using a PTL-MM01 desktop dip coater at a withdraw rate of 5 mm/min and then allowed to dry at ambient temperature. CsNPs were also spin-coated onto the modified substrate surface at 3000 rpm for 30 s.

**Scanning electron microscopy – nanocoating characterisation**

Characterisation of the CsNPs size and shape was investigated using SEM (Hitachi S-4300 field emission SEM, USA). Prior to SEM analysis, the nanocoated glass slides were mounted with double sided carbon tape to a SEM stub and sputter coated (Agar sputter coater with gold target, UK).

**Migration experiments**

To investigate the migration potential of chitosan from a CsNP coated glass slide, samples were tested using an accelerated time/temperature scenario (2 hours at 70 °C) according to European Regulation (2011) No. 10/2011. A 2.5 × 2.5 cm² sample (dip or spin coated) was immersed in 10 ml dH₂O and placed in an oven for 2 hours at 70 °C.

To investigate the dynamic behaviour of CsNP release, a time series experiment was performed. A 1 × 1 cm² sample (spin coated) was placed coated side up in 5 ml of HPLC grade water and 1 ml of sample was removed (with replacement) and tested using the NTA technique at each time interval (0, 30 and 90 minutes). The subsequent migration readings were then fit with a power function by adjusting the constants a and b as seen in Equation (1).

\[
\text{Particle concentration} = a \cdot \text{time}^b
\]  

(1)

**Nanoparticle tracking analysis**

The level of chitosan migration was quantified using a NanoSight NS300 fed by a syringe pump. Following migration studies, samples were aspirated using a 1 ml syringe and loaded on the syringe pump. 0.5 ml of sample was passed through the NTA before recording was initiated. Each sample was manually focused and the camera level set to 14. Recordings were carried out for 15 minutes at a pump rate of 50. Video files were processed in the NTA 3.1 program using a detection threshold of 5, followed by post processing in MS Excel 2013 (Min. track length = 10). Before and after each analytical run the NTA was cleaned with 1 ml of 10% EtOH in HPLC grade water followed by 2 ml of HPLC grade water (pump speed = 1999).

**Results and Discussion**

**Experimental migration**

The migration levels observed for both the accelerated test and time series can be seen in Figure 1. From the migration studies for 2 hours at 70 °C the dip coating was identified to have the poorest CsNP attachment, having four times the particles per ml present in the food simulant compared to the spin coating (see Figure 1a).

![Figure 1. NTA particle concentration for a) all samples tested (dip and spin coated) and b) migration time series fitted with power function.](image-url)
From the time-series migration experiment investigating the dynamic behaviour of the spin coated CsNPs sample (Figure 1b), it can be seen that there is an initial release of CsNPs, followed by a slow release thereafter as migration approaches equilibrium. This dynamic behaviour was fitted with a power function (Equation 1) using fitting parameters \( a = 70 \times 10^6 \) and \( b = 0.12 \). The power function produced a satisfactory fit \( R^2 = 0.98 \).

On inspection of the size distributions generated from the NTA particle concentration measurements (Figure 2b), it is difficult to differentiate the CsNP coating size distributions from the blank dH_2O size distribution. The peak present at approximately 360 nm are not present in the blank reading, however, these peaks do not appear in the size distributions for the CsNP spin coated samples used for the time series (Figure 2a). This would suggest that the micro particles found at 360 nm are contamination introduced during the migration experiments. An important finding obtained from the NTA size distributions is the similarity between the CsNP coated samples and blank. This implies that there is a lack of CsNPs in the dH_2O. The only significant peak that does not appear in the blank is marked X-X in Figure 2a. This peak particle concentration which occurs at approximately 73 nm increases with time, potentially explaining the increasing concentration obtained from the time series experiment (Figure 1b). This finding merits further investigation in order to characterise this NP population (X-X), but also quantify migration at longer migration periods.

![Figure 2. NTA size distributions for a) spin coating time-series and b) accelerated migration study](image)

From the NTA size distributions it could be deduced that a portion of the chitosan which migrates from the food packaging coating is in the nanoscale. Therefore, the packaging coating must be assessed for migration as a nanomaterial, for which no specific migration limit exists. As a result, a generic migration limit for unauthorised substances of 0.01 mg/kg food is used to evaluate the migration (European Commission 2011). To compare the nano portion of migrant chitosan to the regulatory limit, the particle concentration was converted to mg/kg food. The migration quantities from the spin coated samples was found to fall below the regulatory limit with migration of 1 µg/kg food, however, the dip coating was found to exceed the limit with migration of 20 µg/kg food.

**Nanocomposite characterisation**

The use of SEM was essential for the successful characterisation of both spin and dip CsNP coatings. Nanoparticles were identified in the spin coating with a characteristic aspect ratio of CsNPs which
have been witnessed in a study by (Souza et al., 2013). Far fewer particles were observed in the dip coating, particularly in the nano size range. Microparticles similar to the ones seen in Figure 3b could explain the peaks observed from NTA analysis at 360 nm (see Figure 3b)

![Figure 3. SEM images of a) CsNP spin coating, b) CsNP dip coating.](image)

**Conclusions**

Following studies assessing the migration of CsNPs from an experimental food packaging under accelerated conditions and at different time intervals under ambient conditions using NTA, migration amounting to 1 µg/kg_{food.} from the CsNP spin coating was found to fall below regulatory limits. The CsNP dip coated samples produced four times the migration than the spin coating, exceeding the regulatory limit with mass concentrations of 20 µg/kg_{food.} A time series experiment confirmed that the majority of CsNP migration from the spin coating occurred rapidly after exposure to the food simulant and that migration after 1.5 hours approached equilibrium. NPs were confirmed in both food packaging coatings using SEM, however, few NPs were witnessed in the dip coating. These findings call into question the effectiveness of the dip coating as a method of immobilising CsNPs onto food packaging. Further investigations will be carried out to identify the dynamic migration behaviour of CsNPs in the dip coating over longer periods of time above 1.5 hours.

**Acknowledgements**

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**References**


MICROBIOLOGICAL METHODS OF SPORE ANALYSIS FOR DAIRY POWDERS AND HEAT RESISTANCE UNDER DIFFERENT TEMPERATURE

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Abstract
Given the fact that some heating processes or pasteurization used in dairy industry are mild which are not effective to kill those highly heat-resistant spores, it is very critical to develop novel methods to eliminate the spore numbers in milk powder products, and simultaneously to maintain the nutritious compounds and sensory qualities at the maximum level. In this study, we investigated the spore behaviours in response to different heating procedures via microbiological spore analysis. We used total powder weigh in a double-layer bag of whey protein isolate (WPI) 35 stored in the storage room since 2012. This powder was the sources of spore-forming bacteria from previous spore detecting tests. A microbiological spore analysis was undertaken for the distribution of spores in the bag. We also wanted to find the influence of different reconstituted percentages and holding temperatures and to use them in the following experiment as the optional conditions. The spore growth curve was taken under the most problematic holding temperature at 55°C in which has the highest spore counts.

Introduction
The safety of dairy products has been challenged by spore-forming bacteria for a very long time, as it can not only reduce the quality and shelf life of the products, but also be able to introduce potential risks to the consumer health. The multilayer structure of spores provides them with extra resistances to different environmental stresses, including desiccation, high pressure, low temperature, heat, UV, and extreme chemical resistance. Some pieces of spores can even have a prolonged life up to millions of years under certain favorable conditions (Reineke, 2012, Nguyen Thi Minh et al., 2010, Watterson et al., 2014).

It has been reported that the spores and spore-foaming bacteria were detected in many steps throughout the processing chain in the dairy powder manufacturing plant, including the pasteurization process, cleaning-in-place (CIP), drying process, and the storage period (Scott et al., 2007). Additionally, the high heat resistance of the spores and biofilm largely increase the difficulties to remove the spores and to prevent the products from contamination. The wide distribution of spore-foaming bacteria has been reviewed from dairy farm to dairy industry by (Gleeson et al., 2013, Gopal et al., 2015), in which they found teat skin and milking equipment were significant sources of thermuduric bacteria in raw milk. They also pointed out that two major groups of spore-foaming bacteria were Bacillus cereus group and Sulphite-reducing clostridia (SRC) based on the growth at high temperature and high prevalence in the farm and milk products. Another paper (Miller et al., 2015) claimed they found significant differences of spore population in raw milk tank and dairy powder and Bacillus was the predominant spore specie in both raw milk and dairy powder.

In recent years, there have been many studies focusing on the B. cereus group in the dairy production because of aforementioned reasons. Apart from the common characters as spore-forming bacteria, B. cereus group also has some specific features, for example, they can be easily isolated from other species when using some selective agar, which makes the B. cereus group a better research object. They can grow pink or orange colonies on the mannitol egg yolk polymysin agar (MYP agar) or on the FDA recommended BACARA plate (Gleeson...
et al., 2013). It has been noticed that the spores of B. cereus group can be activated to germinate instead of being destroyed when heated between 70~80°C for several minutes (Reineke, 2012). The pasteurization used in dairy industry also lies in the same temperature range.

Materials & Methods

Sample collection and preparation
The powder samples were aseptically collected in sterile sample containers. In order to explore the spore distribution in the powder bag, we manually selected three points from each position, namely, the top, the middle and the bottom, nine sampling points in total. The method used to prepare the rehydrated sample solutions was similar as described in the papers of (Watterson et al., 2014). 20 grams of powder samples were reconstituted with sterile distilled water in the 250ml sterile bottles (SCHOTT, Germany) at the ratio of 1:10 (w/w). This reconstituted ratio was changed to 20% and 30% in the study of optional reconstitute condition for spore growth. The whey protein solution could be used for the next heating step or be held at different temperatures for 24 hours if a holding step was needed.

Heat treatment
The heating step was to eliminate the normal bacteria (vegetative cells) in the solution and there are various combinations of heating time and temperatures for different types of spores (Reineke, 2012, Nguyen Thi Minh et al., 2010, Sumana et al., 2009). The heating procedures were performed separately for general spore pasteurization at 80°C for 10 min and for highly heat resistant spores at 100°C for 30 min in water bath. 10 ml of rehydrated milk from the bottle was added into the 50 ml tube (SARSTEDT, Germany) for heating and followed by an immediate cooling with running water.

Enumeration of spores
One ml of each heated sample was examined for the spore counts with pour-plate technique of PCA (skim milk plate counting agar). Serial 10-fold dilutions were applied by adding 1ml of sample in the MRD (Maximum Recovery Diluent) tube if the plate count was over 1000. The incubators were set to 55°C and 30°C for the growth of thermophilic spores and mesophilic spores for 72 hours respectively. To obtain a better understanding of the profile of spore-foaming bacteria in the whey powder, we also tested the number of aerobic and anaerobic spores by comparing the plates incubated in the anaerobic jar (Merck, Germany) with normal ones.

Results and Discussion

Distribution
From all the nine samples we collected for different positions in the powder, we found no significant difference in the spore count, which indicated that the spores were evenly distributed and there was no spore contamination from the outside. The tests covered four categories, thermophilic aerobic (T/A) plating, thermophilic anaerobic (T/NA) plating, mesophilic aerobic (M/A) plating, and mesophilic anaerobic (M/NA) plating. The results showed that T/A plates had the highest count among the rest of groups. Thus, we paid more attention on T/A spores in the following tests.

Optional reconstituted ratio
The most common ratio used to rehydrate whey powder was 10% (w/w). We added 20% and 30% in the experiment to find how the reconstituted ratio would influence the spore number. There was a reasonable increase of spores with the increasing of reconstituted ratio, which was quite understandable as more powder was added and it was more likely to contain more spores. However, we discovered that the higher ratio of whey powder would also increase the protein coagulation during the heat treatment, which might influence the following counting
step. In that case, the sterile filter bags (Whirl-Pak, US) were used to remove the coagulated protein. The optional ratio should be 1:10 in order to have the best results in the future experiments.

**Holding temperature**

In the industrial processing plants, it is possible to have reconstituted dairy solution held in the tank for around 24 hours before the next processing step. The holding temperature may stimulate or suppress the germination of spores or change the heat resistance. We held the reconstituted milk for 24 hours separately in a wide temperature range from 5°C up to 72°C, which started from the common cold storage temperature and ended up with the pasteurization temperature. The temperatures we selected were 5°C, 20°C, 30°C, 37°C, 55°C, and 72°C which were based on the consideration of standard spore incubation temperatures, common bacteria optional growth temperature, and the possibility of temperature abuse that may happen in real life. The results were showed in the figures below.

![Figure 1](image1.png)

**Figure 1.** Spore count of T/A and M/A at various holding temperature and reconstitution percentage

![Figure 2](image2.png)

**Figure 2.** Spore growth curve at 55°C within 60 hours

The results in figure 1 suggested that there was a critical increase of heat resistance at the holding temperature of 55°C, which was also the incubation temperature for thermophilic spore. Accordingly, we used 55°C as the optional holding temperature for thermophilic spores and profiled a growth curve (figure 2) within 60 hours. The growth curve showed a second peak after 40 hours, which may explain the recovery of spores after the CIP in some food manufacturing industry.

**Conclusions**

In this study, we used one bag of WPI 35 as the research material and classical microbiological spores analysis methods to learn the change in pores behavior when common
conditions vary, including the reconstitution percentage and holding temperature. We found that the spore count of thermophiles reached a highest point when holding at 55°C for 24 hours, which implied that the risk of being contaminated by spores could be introduced through inappropriate holding.

Acknowledgement

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References


MIGRATION POTENTIAL OF SILVER NANOPARTICLES IN FOOD PACKAGING

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Abstract

Due to the increased use of nanoparticles in food packaging globally there has been growing concerns surrounding the risks associated with migrating nanoparticles from the packaging into the food product. The European legislation EC No. 10/2011 advises on the simulants to be used when testing plastic materials in contact with food products. The use of spectrophotometry will detect the silver particles which have migrated from the specimen into the simulants. The effect of time and temperature on the migration potential of nanoparticles are examined in this study. The results found that an increase in temperature, increases the level of nanoparticles migrating from the packaging to the food product. Increasing the time the specimen was in contact with the simulant increased the migration potential for the refrigerated samples however there was a slight reduction in the oven stored simulants. The results showed that migrated silver does not exceed that of the toxic levels in humans of 10 mg/l.

Introduction

Due to population growth, increased wealth and the increase in trade markets across the world, the consumption of food globally has increased dramatically (Wilkinson, 2013). To meet these demands and also the demand for transportation of products further across the world than ever before there is an increase in the need for new technologies and processes to increase shelf life in food to avoid wastage (Hannon et al., 2015). Among the most common methods for preserving food for transport is packaging. To improve the efficiency of the simple packaging on shelf life novel materials are being applied to the containers. Examples of these novel materials are nanoparticles.

A definition for nanoparticles is "an insoluble or biopersistant and intentionally manufactured material with one or more external dimensions, or an internal structure, on the scale from 1 to 100 nm"(Union 2009). Nanoparticles have highly reactive properties due to their high surface area, although these properties are useful for some applications they may also have harmful consequences (Metak et al., 2015). Nanoparticles can have numerous applications ranging from incorporation in medical products, textiles and in the food industry

Nanoparticles have been applied to the food industry through food packaging due to their degradation as well as their antimicrobial properties (Echegoyen and Nerin, 2013). There are numerous types of nanoparticles which all have different applications. Silver nanoparticles are the most commonly used in packaging due to their antimicrobial properties (Bouwmeester et al., 2009). There is enough silver in a concentration of 10 µg/l of water to be effective against the reduction of bacteria in the solution (Jokar and Rahman, 2014). This level of silver is much lower than the toxicity level for human consumption. However there are risks associated with the use of nanoparticles. These risks include the potential of nanoparticles to migrate from the food packaging into the food product which could lead to direct exposure to human through consumption. And after direct exposure there is a risk of the nanoparticles being toxic to humans.

The objective of this study was to determine the migration potential of silver nanoparticles from food packaging using analytical methods. From this an exposure model will be used to determine the risk from human consumption.
Materials and Methods

Sample Preparation
Legislation EC No. 10/2011 (plastic materials in contact with food products) provides the list of simulants which may be used to represent food products during experimentation (Table 1). A solution of 50% ethanol was used as a fatty food. A second solution of 3% acetic acid represents acidic food products. The test specimen for this experiment was low density polyethylene (LDPE) film with a 2% coating antimicrobial coating. This 2% coating is achieved by dipping the film into a bath containing 2% silver nitrate and treating with ozone for 30 minutes. This provides the film with its antimicrobial properties. The rate of film to solution is 100 ml of food simulant for every 1 dm$^2$ of film. Two samples of each simulant will be placed in an oven at 70°C for 2 hours. Three samples of each simulant, were placed in a fridge at 4°C for 2 hours to determine the effects of temperature. To determine the effect of time the previous steps were repeated however the samples were left in the fridge and oven for 3 hours. After this process the samples were prepared for the Hach Lange Spectrophotometer using a silver testing kit. They were then tested in the Hach Lange. All samples were tested in duplicate form to ensure accurate results.

<table>
<thead>
<tr>
<th>Food Simulant, Regulation (EC) No 10/2011</th>
<th>Abbreviation</th>
<th>Used for</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol 10% (v/v)</td>
<td>Food Simulant A</td>
<td>Aqueous Foods</td>
</tr>
<tr>
<td>Acetic Acid 3% (w/v)</td>
<td>Food Simulant B</td>
<td>Acidic Foods</td>
</tr>
<tr>
<td>Ethanol 20% (v/v)</td>
<td>Food Simulant C</td>
<td>Alcoholic Foods</td>
</tr>
<tr>
<td>Ethanol 50% (v/v)</td>
<td>Food Simulant D1</td>
<td>Fatty Foods</td>
</tr>
<tr>
<td>Vegetable Oil</td>
<td>Food Simulant D2</td>
<td>Fatty Foods</td>
</tr>
<tr>
<td>Poly(2,6-diphenyl-p-phenylene oxide)</td>
<td>Food Simulant E</td>
<td>Dry Foods</td>
</tr>
</tbody>
</table>

Determination of silver migration
All samples were tested using a Hach Lange Spectrophotometer to determine the levels of silver nanoparticles which may have migrated. They were prepared for the testing using a silver testing kit LCK 354. A standard was carried out by testing a 0.1 mg/l silver solution using the Hach Lange to determine if the readings were accurate.

Data analysis
After the samples were tested using the Hach Lange Spectrophotometer a t-test was carried out to test the migration potential of the silver nanoparticles from the food packaging into the product. The t-test will statistically differentiate between all the various samples that were tested.

Determination of nanotoxicity from exposure through consumption
From the results of the Hach Lange Spectrophotometer, an exposure model was used to determine the toxicity to humans through the consumption of the effected food products. The model used to determine the exposure was:

\[ E = M \times C \]

Where:
E  Silver nanoparticle exposure level (mg/l)
M  Mass of silver nanoparticles (mg)
C  Amount of product containing nanoparticles consumed (l)
Results and Discussion

Effect of Temperature on Migration
The amount of silver migrating varied, depending on the temperature of the storage medium, i.e. oven or fridge. The migration level of silver in the distilled water simulant showed 0.799 mg/l in the oven at 70°C for two hours, compared to just 0.067 mg/l and 0.075 mg/l in the fridge at 4°C for the same time. The 3% acetic acid solution and 50% ethanol solution did not provide any results as the silver testing kit LCK 354 was a water based kit. Therefore another an alternative method of testing with a UV-VIS Spectrophotometer will be used to test these simulants for the migration potential of nanoparticles.

Figure 1. Shows the results from the Hach Lang Spectrophotometer. The detected levels of silver migrated (mg/l) is higher when exposed to a higher temperature.

Effect of Time on Migration
Time was found to have a significant effect on the migration levels of silver nanoparticles. The 3 hour refrigerated samples showed an average increase in migration of 0.099 mg/l compared to the 2 hour samples. The samples left in the oven @70°C actually had a lower overall migration of silver compared to the 3 hour samples. However when looking at the samples closer there is only a reduction of 0.082 mg/l which may have been due to experimental error. Further repetitions will be carried out to determine the cause for this reduction.

Figure 2. (a) Effect of time on migration @70°C (b) Effect of time on migration @4°C. Average migration over 2 hours (black). Average migration over 3 hours (grey). We can see the migration increases slightly in the refrigerated samples and reduces slightly in the oven stored samples.
Nanotoxicity of migrated silver

An exposure model was carried out to identify the risks the toxicity of the particles had on humans through consumption. The model found that sample which contained the highest overall migration had an overall exposure level of 2.397 mg/l when consuming 3 litres daily of a product packaged in nanopackaging e.g. bottled water. This is below the toxicity levels which have been found to be harmful for human consumption of 10 mg/l, however continuous exposure and cumulative effects would need to be investigated further.

Conclusions

It can be concluded from the results shown that the migration of silver has occurred. However the levels of migration are not at the levels which may be toxic to humans following consumption. Increasing the time the nanopackaging is in contact with the product has been proven in the refrigeration case to increase the migration levels slightly, however the oven samples showed a slight reduction. Further repetitions will have to be carried out to determine the overall effect time has on migration potential. However, as the temperature is increased the migration levels also show an increase. Therefore consumers putting food packaging through temperature abuse may lead to further migration potential. However, due to the difficult nature of differentiating between nanoparticles and ionic particles further research needs to be carried out to ensure that the use of silver nanoparticles in food packaging is commercially safe.

References


Abstract

Cronobacter spp. (formerly Enterobacter sakazakii) in powdered infant formula (PIF) has in the past been associated with illness and deaths in neonates. The sampling plans associated with MCs need to provide a high level of protection to insure a safe product. As part of a bigger project and sampling strategy at a dairy powder plant, a number of powder samples were taken for RT-PCR analysis. These samples were first tested with the classical culture based approach to identify Cronobacter spp. colonies. The presumptive positive colonies were then analysed with RT-PCR. All positives from the classical method were confirmed in the RT-PCR analysis. Further analysis of the data will allow an examination of temporal and spatial patterns in the dairy powder contamination.

Introduction

Cronobacter spp. (formerly Enterobacter sakazakii) is an opportunistic pathogen widely associated with powdered infant formula (Healy et al. 2009, Yan et al. 2012). Its high mortality rate in neonates makes it a pathogen of concern for the PIF industry. Microbiological Criteria (MC) are one of the potential tools in evaluating a food safety risk management system. They can help decide the acceptability of a product or food lot, based on whether a specific microorganism is present or absent, and in what quantity (van Schothorst et al. 2009). The MC as specified under the Commission Regulation (EU) 2073/2005 (FSAI 2015) for PIF are absence in thirty 10g samples. The (ISO 2006) is used for Cronobacter spp. detection as part of the MC.

Because of the EU MC, PIF manufacturers carry out a considerable amount of quality control (QC) monitoring for Cronobacter spp. Historically, manufacturing companies have had periods of high incidence of detection, but with the introduction of enhanced biosecurity and cleaning processes, levels have reduced. However, sampling by its nature only tests a very small proportion of the total production and there is always the possibility of defective material slipping through.

Chromogenic Cronobacter Isolation Agar (CCI) is a selective agar used as part of the isolation and the identification of Cronobacter spp. It uses the physical attributes of Cronobacter spp. to differentiate it from other bacteria such as E.coli (Iversen et al. 2008, Druggan and Iversen 2009, Ye et al. 2014). Results attained by this method can be seen as presumptive positives. Further molecular analysis such as real-time polymerase chain reaction (RT-PCR) is often used to confirm these results. RT-PCR has been established as a reliable method for the detection and confirmation of Cronobacter spp. (Seo and Brackett 2005, Mullane et al. 2007). It uses a segment of DNA unique to a specific species to confirm whether the tested bacteria is present.

The objective of this study is to assess RT-PCR for confirming the presence of Cronobacter spp. identified with CCI agar.
Materials and Methods

Chromogenic Cronobacter Agar Isolation
As part of a bigger project and an intensive amount of sampling from a dairy powder plant, 54 of those samples were taken to develop a sampling protocol.

For each sample taken, 10 g of powder was weighed out and suspended into 90 ml of buffered peptone water (BPW). This was then incubated at 37°C for 18-24 hours. 100 µl of BPW were then inoculated into 10ml of Cronobacter screening broth (CSB) and incubated at 42°C for 18-24 hours. A colour change from purple to yellow indicates the presence of Enterobacteriaceae. Samples that did not undergo a colour-change can be deemed to be Cronobacter spp. negative. 10µl of the enriched sample were streaked onto a Chromogenic Cronobacter Isolation agar (CCI) and incubated at 37°C for 18-24 hours. Cronobacter colonies appeared as blue/green colonies and E.coli appeared as yellow colonies. This can be accepted as a presumptive positive result for Cronobacter spp. but molecular analysis can be used to confirm. To facilitate this a well isolated Cronobacter spp. colony was picked and streaked onto Tryptic Soy Agar (TSA). These were then incubated at 37°C for 18-24 hours to grow pure colonies. The colonies were then re-suspended in Tryptic Soy Broth (TSB) with 20% Glycerol solution and frozen until further analysis.

Real-Time PCR
RT-PCR analysis was used to confirm the isolated colonies as being Cronobacter spp. The frozen cultures were revived overnight on a TSA plate. For each isolate being tested 50 µl of 18MΩ water was added to a 1.5 ml centrifuge tube. One colony was picked from the TSA plate and homogenised into the sterile water. The tubes were boiled on a heating block at 90°C for 10 minutes and then briefly vortexed. The samples were then spun at 10,000 rpm for two minutes. The RT-PCR reagents were removed from the freezer and added to the 0.2 ml PCR tubes. The samples were also added to the 0.2 ml tubes. Finally the samples were centrifuged briefly on a mini benchtop centrifuge. A negative and positive control were also prepared. A Rotorgene R-3000 instrument and Rotor Gene 6 software were used for the RT-PCR. The samples were put into the Rotorgene and the details entered into the rotor gene 6 program.

Results and Discussion
Taking 10 g samples from each of the 250 ml samples yielded six presumptive positive colonies. Each of these positives was regrown on a TSA plate and underwent RT-PCR. All green CCI colonies were confirmed as Cronobacter spp. by the RT-PCR. In addition to this, one sample which appeared darker than the other non-Cronobacter colonies was also tested with RT-PCR. This sample was confirmed as being negative. The RT-PCR confirmed all of the presumptive Cronobacter spp. colonies isolated from the CCI agar.

<table>
<thead>
<tr>
<th>Table 1. Number of samples taken and positive results.</th>
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<tr>
<td><strong>Number of Samples</strong></td>
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<tr>
<td>54</td>
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</table>

Conclusions
The RT-PCR confirmed the viability of the classical culture based approach for identifying Cronobacter spp. in dairy powders. Further work is to be done on this including sequencing to fingerprint the isolates. This would allow the temporal and spatial mapping of the identified
Cronobacter spp. strains and allow a deeper analysis of how the dairy powder is contaminated with the Cronobacter spp.

Acknowledgements

This project was part financed by the Irish Department of Agriculture, Food and the Marine Food Institutional Research Measure.

References


INVESTIGATION OF SPECTROSCOPIC TECHNIQUES FOR ADULTERATION DETECTION IN FOOD INGREDIENTS

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Abstract

Near Infrared – Hyperspectral Imaging (NIR-HSI), an emerging analytical technique for non-destructive fast analysis, was investigated in combination with chemometric techniques, (Principal Component Analysis (PCA), Partial Least Squares Discriminative Analysis (PLS-DA), Partial Least Squares Regression (PLS-R)), to assess their potential to detect adulteration in powder food ingredients. NIR-HSI images were acquired in the wavelength range of 880 to 1720 nm at 7 nm intervals using a line scanning NIR-HSI system. In the first experiment NIR-HSI of corn flour (CF), icing sugar (IS), poorly and well mixed samples (50:50 w/w) were analysed. Histograms of first principal component scores (PC1 75.85%) and PLS-DA (100% right classification for both classes, 1 latent variable) predictions of pure components were sharp and narrow while the histogram of poorly mixed was flat and wide, demonstrating strong potential to evaluate mixture homogeneity of seasonings and food ingredients. In the second experiment binary mixtures of CF-IS, were made by mixing at different concentrations (0, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 % (w/w)). PLS-R model predicted accurately concentration of icing sugar in corn flour (RMSECV 4.58%, RPD 6.59, R² 0.977); showing the potential of NIR-HSI to detect adulteration in powdered mixes like food seasonings and food ingredients.

Introduction

Food adulteration, whether economically motivated (EMA) (Everstine et al. 2013 and Srivastava et al. 2016) or accidental, can lead to chemical, physical and microbiological hazards that could put consumers’ health at risk. Regulation (EC) No 178/2002 outlines the principles to protect food consumers from adulteration. Manufacturers rely on certificates of analysis provided from their supplier and may also perform additional analytical tests. These analytical methods include high performance liquid chromatography (HPLC), gas chromatography – mass spectrometry (LC-MS/MS), isotope ratio mass spectrometry (IRMS), ELISA (Eksi-Kocak et al. 2016); which are expensive, time consuming and require sample preparation. Some notorious examples of EMA include the deliberate adulteration of infant milk formula with melamine in China in 2008 (Srivastava et al. 2016) and the horsemeat scandal in Europe in 2013 (Everstine et al. 2013).

NIR-HSI is a powerful, rapid and non-destructive vibrational method that provides chemical and molecular information of a sample, it combines spectroscopy techniques and conventional imaging to achieve both spatial and spectral information from an object, originally developed for remote sensing applications nowadays is widely used in medicine, pharmacy, astronomy, agriculture and it is being explored in food industry (Gowen et al. 2007).

The objective of this work is to investigate the feasibility of NIR – HSI and chemometric analysis to identify adulteration in powdered food ingredients.

Materials and Methods

Sample preparation and NIR Hyperspectral Imaging:
Samples of corn flour (CF) and icing sugar (IS) with very similar characteristics in colour and particle size were bought at a local store. Approximately 8.5 g IS and 8.9 g CF were placed in
separated containers and their NIR-HSI spectra were obtained. 25g of both samples in 50:50 w/w proportion were slightly shaken and 8.3g was placed in a container, the spectra of this sample corresponds to poorly mixed sample (PM), the mixing process was repeated, but this time it was strongly shaken, the resulting spectra corresponds to well mixed sample (WM). NIR-HSI images were acquired from CF-IS mixtures mixed at different proportions (0, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 % (w/w)).

**NIR Hyperspectral Image Acquisition**

All samples were scanned using a line scanning near infrared hyperspectral imaging system (DV Optics, Padova, Italy), NIR – HSI images were acquired in the wavelength range of 880 to 1720 nm at 7 nm intervals and data were recorded as hyperspectral image and reflectance in ENVI format for further multivariate data analysis in Matlab (The MathWorks, Inc., Natick, MA, USA).

The system consists mainly of an illumination source, diffuser, moving base, optics, spectrograph and camera. The moving base speed set at 20 mm/s to obtain pixels of approximate size 0.3 × 0.3 mm. Before starting calibration and image acquisition, the system was turned on and allowed to stabilise for around 30 min. The calibration procedure was as follows: 100 scan lines of a black reference (Ib) were acquired and averaged by taking a measurement after covering the spectrograph lens with a cap; a white tile with a known reflectance (Rw) was placed on the moving base and used as a “white” reference (Iw) by averaging 100 scan lines and finally the signal from the sample (Is) was converted and stored as reflectance (R) according to Equation (1):

\[
R = \frac{I_s - I_b}{I_w - I_b} \times \frac{R_w}{R_w}
\]  

(1)

**Chemical image analysis**

NIR Hyperspectral images of CF, IS and CF:IS mixtures were imported from ENVI formatted files into Matlab. Data analysis was performed with in-house developed codes and scripts, spectral data were trimmed owed to great noise level before band 11 and after band 113. Hypercubes obtained were treated as follow:

a) A region of interest (ROI) were cropped from each sample and stacked in one file.
b) Logarithmic transformation log (1/R) were done.
c) PCA and PLS discriminative Analysis were done for the first experiment, PCA and PLS regression were performed for the second experiment. The effect of pre-treatments (SNV, first derivative, second derivative and lineal detrending) and combinations of two of them were also tried.

To build the PLS-DA model, the spectra of 100 random selected pixels of each pure component were employed. For built the PLS-R model, the mean spectra of each sample were used. The numbers of latent variables (LV) were selected by analysis of RMSECV (using 10 fold cross validation and leave one sample out cross validation) and roughness of the regression vector (Gowen et al. 2011)

**Results and Discussion**

a) **Experiment 1: Well mixed – poorly mixed detection:**

The first part of the experiment evaluated if NIR-HSI could determinate mixing ratios in samples. Scores image in Figure 1 clearly shows that NIR-HSI could differentiate between WM and PM mixtures of similar components (CF/IS).

b) **Experiment 2: Concentration detection:**

The second part of the experiment was to assess the feasibility of NIR-HSI in conjunction with chemometric analysis to quantify the concentration of the mixture of CF and IS. Figure 2 shows that the best PLS regression model was developed with log (1/R) SNV + second order lineal detrending (RMSECV 4.58%, RPD 6.59, \(R^2\) 0.977) pretreatments.
Figure 1. Image analysis of experiment 1: a) mean spectra of pure components: corn flour, icing sugar and poorly mixed and well mixed samples. b) scores image of the four samples. After PCA and SNV + Second order linear detrending pretreatments. c) PLS – DA histograms, predictions of pure components are sharp and narrow, PM flat and wide and WM also sharp and narrow.

Figure 2. Image analysis of the second experiment: a) mean spectra of mix concentrations of corn flour: icing sugar (0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 %) b) scores image of the eleven samples c) PLS – R showing accurately concentration of icing sugar in corn flour (RMSECV 4.58%, RPD 6.59, R² 0.977).
Conclusions

In this preliminary study it was possible to evaluate the homogeneity of a mixture of corn flour and icing sugar by PCA of NIR-HSI data, demonstrating the strong potential of NIR-HSI to evaluate mixture homogeneity in preparation of seasonings and food ingredients. PLS regression models developed accurately predicted the concentration of icing sugar in corn flour, showing the potential of NIR-HSI to detect adulteration in powdered food ingredients.

Acknowledgements

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References


EXPOSURE ASSESSMENT OF ACRYLAMIDE FOR THE IRISH CONSUMER

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Abstract

Researchers in Europe and the United States have discovered acrylamide in certain foods that are heated to a temperature above 120 °C. Potato chips and French fries are known to contain higher levels of acrylamide in comparison with other foods. Both the World Health Organization and the Food and Agriculture Organization of the United Nations have stated that the levels of acrylamide in foods pose a major concern as a possible human carcinogen and that more research is required to determine the risk of dietary acrylamide exposure. The evidence from human studies however is still incomplete and toxicology studies have shown differences between humans and rodents in acrylamide absorption rates. This study will evaluate the likely human consumption of different food products with the Irish Universities Nutritional Alliance Survey and evaluate the likely human health risk posed by acrylamide in the diet. A risk assessment model will be developed based on the principles of qualitative/quantitative risk assessment with Monte Carlo simulation modelling to determine how predicted exposure concentrations relate to the regulatory requirements set out by WHO of a safe level of 1 μg/kg body weight per day and a maximum level of 4 μg/kg body weight per day. The model developed in this study will be useful to government agencies and Irish consumers.

Introduction

A report by the world health organisation in 2002 found that Acrylamide is mostly found in certain foods that have been cooked and processed at high temperatures, and the levels of acrylamide increase with the time of heating. The World Health Organization stated that the levels of acrylamide in foods pose a “major concern” and that more research is needed to determine the risk of dietary acrylamide exposure.

Asparagine is a type of amino acid that is found with high concentrations in some varieties of potatoes but also in some other vegetables. When heated to high temperatures through methods such as frying, baking or broiling in the presence of sugars, asparagine can form acrylamide (Mottram et al., 2002). Although boiling and microwaving appear less likely to do so. Longer cooking times can also increase acrylamide production when the cooking temperature is in excess of 120 °C.

Studies in rodent models have found that acrylamide exposure poses a risk for several types of cancer. The evidence from human studies still remains incomplete. The National Toxicology Program and the International Agency for Research on Cancer both consider acrylamide to be a probable human carcinogen, this is based on studies in laboratory animals given acrylamide through their drinking water. However, toxicology studies have shown differences in acrylamide absorption rates between humans and rodents (Fuhr et al., 2006). This study was carried out to accurately assess a number of different age groups within Ireland including 10 year olds, 20 year olds and 65 year olds for both male and females. The exposure to acrylamide in food was determined using the Irish Universities Nutritional Alliance Survey for each age group. The information is analysed using the Monte Carlo simulation modelling system. The most at risk group may be the 10 year olds due to a significantly higher acrylamide to body mass ratio.

The objective of this study is to develop an exposure assessment for acrylamide and evaluate whether exposure poses a health risk to Irish consumers.
Materials and Method

Data inputs and model development

Food is known to make a significant contribution to total exposure of the general public to acrylamide, the other major contributor is smoking (Urban et al., 2006) but will not be analysed in this study. Levels of acrylamide can vary considerably in different foods, this is due to the processing or cooking conditions used and the temperature achieved. Potato chips and French fries contain higher levels of acrylamide compared with other foods as determined by the World Health Organisation. Bread, cereals, popcorn, pizza bases and coffee are also examples of foods high in acrylamide so these foods will be focused on during the analysis of the Irish person’s diet. The average intake for the general population are estimated to be in the range of 0.3 to 0.8 microgram of acrylamide intake per kilogram of body weight per day as set out by the WHO. Within a general population, it is anticipated that children will generally have a higher level of intake two to three times that of adults when expressed on a body weight basis. Dietary intakes of acrylamide by some individual consumers may be several times higher than the average. Using the Irish Universities Nutritional Alliance survey the participants were analysed for both male and female in the 10, 20 and 65 year old age groups.

Table 1. Acrylamide content of several typical food categories μg/kg (EFSA 2010)

<table>
<thead>
<tr>
<th>Food Type</th>
<th>Minimum</th>
<th>Mean</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biscuits</td>
<td>15</td>
<td>300</td>
<td>4200</td>
</tr>
<tr>
<td>Bread</td>
<td>5</td>
<td>60</td>
<td>910</td>
</tr>
<tr>
<td>Cereals</td>
<td>15</td>
<td>140</td>
<td>1600</td>
</tr>
<tr>
<td>Coffee</td>
<td>15</td>
<td>260</td>
<td>1158</td>
</tr>
<tr>
<td>French Fries</td>
<td>15</td>
<td>355</td>
<td>2668</td>
</tr>
<tr>
<td>Potato Crisps</td>
<td>10</td>
<td>564</td>
<td>4180</td>
</tr>
<tr>
<td>Potato’s</td>
<td>17.5</td>
<td>270</td>
<td>2175</td>
</tr>
</tbody>
</table>

Data from the mentioned sources above were used in the RASP system with a Monte Carlo simulation and run with 1000 iterations and 20 bins. The calculation involved is based as follows: Exposure = Level X Consumption. Where exposure is measured in μg/kg/bodyweight/day. Level is μg/kg per population studied. Consumption is (μg/kg)/(bodyweight).

Analysis of Diet

A Monte Carlo simulation using the RASP system or Risk Assessment Software Package is used during the analysis. Since any level of exposure to a genotoxic substance could potentially damage DNA and lead to cancer, EFSA’s scientists conclude that they cannot set a tolerable daily intake of acrylamide in food. The World Health Organisation however estimates that human exposure should
not exceed 1 \( \mu g/kg \) body weight per day with a maximum level set at 4 \( \mu g/kg \) body weight per day. The results will be presented in a probability density versus acrylamide exposure curve graph.

**Results and Discussion**

The importance of this study is its sole focus on the Irish diet in relation to acrylamide exposure. This is significant to other similar European studies mainly due to the dependency on the potato crop as a food source which may be consumed on a more regular basis than in other European countries. Initial results show the mean acrylamide exposure for adults at 20 years old was estimated to range between 0.33 and 1.18\( \mu g/kg \) body weight per day. High exposure reached 2.1 \( \mu g/kg \) body weight per day with french fries, coffee, bread and biscuits as the main contributors. In this study French fries, crisps, soft bread, coffee, potato’s and biscuits are most likely to contribute highly to the adult population.

Based on data available in Europe, child exposure was two times higher than those of adults (Bolger et al., 2010). In the EFSA study, based on data from 17 different surveys, mean exposure for children 3 to 10 years old category, and toddlers 13-36 months old category were estimated to range between 0.70 and 2.05 \( \mu g/kg \) body weight per day and 1.2 to 2.4 \( \mu g/kg \) body weight per day, respectively, with 95th percentiles ranging between 1.5 and 4.2 \( \mu g/kg \) body weight per day and 2.4 and 6.5 \( \mu g/kg \) body weight per day respectively. These results are expected to be replicated in this study due to the difference in body weight between adults and children. There is also an increased likelihood of children consuming crisps, breakfast cereals and possibly French fries due to dietary trends and children having a lower standard of education and desire to eat a more balanced diet. As shown toddlers are most at risk of exceeding the upper limit of 4 \( \mu g/kg \) body weight per day however all groups exposure to acrylamide levels are expected to fall below this threshold in this study based on information from the EFSA report 2007-2009.

**Conclusions**

Exposure estimates across the different population groups are similar to other European studies on acrylamide exposure due to a similar high carbohydrate based diet across much of Europe. It’s obvious that in order to reduce the acrylamide intake in Ireland we must firstly reduce the acrylamide levels in foods high in its concentration such as French fries, crisps, cereals and coffee. Although studies in rodent models do suggest that acrylamide is a potential carcinogen, additional studies on humans are needed to help determine any effects of dietary acrylamide intake on human cancer risk. It is also necessary to determine how acrylamide is formed during the cooking process and if acrylamide is present in other foods than those already tested. This information will then allow more accurate and comprehensive estimates of the Irish dietary exposure. Although results do show that we safely fall within the boundaries of the WHO limited maximum exposure of 4 \( \mu g/kg \).

**References**


ADULTERANT DETECTION IN WHISKEY USING NIR SPECTROSCOPY AND CHEMOMETRIC METHODS

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Abstract

Whiskey adulteration is a common problem. Adulterants include methanol, ethanol and water. NIR technology in the wavelength range of 780~2526 nm combined with PCA and SIMCA models has been applied to distinguish whiskey samples at different levels of adulteration. It is expected that the technology investigated in this study will be demonstrated to be suitable for adulterant detection in whiskey samples.

Introduction

Adulteration of whiskey, which is a high-end liquor has long been associated with significant adulteration issues. As a Brazilian researcher reported, in the beginning of nineties, adulterated alcohol drinks are frequently presented in the markets (Pontes et al. 2006). Some clandestine producers refilled the branded barrels or bottles with water-diluted genuine whiskey or with chemical components (such as methanol and ethanol) (Henderson 2015). During the normal drink production, methanol and ethanol exist at a safe content. However, there is no quality control of adulterant whiskey. Based on health studies, high methanol intake will cause headache, nausea, vomit and even blindness. Old Forester 1897 comes from the first distillery which bottled spirits and is still operating (Best 2016) and addressing the counterfeit problem successfully. However, the composition could not be identified before the detection technology was developed.

Spectroscopy is more and more widely applied in component analysis for rapid, reagent free and non-destructive results. Near infrared spectrometry (NIR) is in the wavelength range of 780~2526 nm. Each whiskey sample will have a unique Near infrared (NIR) absorption spectral signature which is different due to various mixed compositions like alcohol and water. Chromatography technology like principal component analysis (PCA) and soft independent modelling of class analogy (SIMCA) models built with NIR spectroscopy have been considered to classify and analysis the data in a multidimensional space and a clear way. SIMCA model is applied for judging the prediction of PCA models. Calculated value (Vcal) in a SIMCA model will be compared with critical value (Vcrit) of a group. If Vcal is lower than Vcrit, the sample locates in that group. To reduce noise in the spectra multiplicative signal correction (MSC) is used to pre-treat data.

The objective of this study is to differentiate adulterated whiskey samples using NIR spectroscopy and chemometrics.
Materials and Methods

The equipment and materials include NIR spectroscopy equipment placed at the food engineering laboratory of UCD, deionized water prepared in the laboratory, cheap whiskey, and premium whiskey obtained in the supermarket, 100 g containers and pipettes. Two subtopics are studied with a PCA/ SIMCA model. The first one is to find the influence of value on diluting with water (Weight ratio: 0, 1, 2, 4, 8, 16%). The second one is to detect the change by adding cheap whiskey (adulteration ratio: 0, 2.5, 5, 10, 20, 40% w/w) into the original samples. Experiments will be repeated to prevent the error caused by inhomogeneous mixing. Before setting up the models, MSC is required for data pre-treatment to reduce the error effect causing by various components. The Unscrambler X software (v10.4, CAMO Software AS, Oslo, Norway) has been applied to build the PCA and SIMCA model. The model should be adjusted constantly.

Predicted Results and Discussion

The predicted results should be grouped into different groups based on the various concentration of additives. After data pre-treated, a 3-D plot will be built as Pontes has done in 2006 (Fig 1). The first principal component, PC1, can influence model more obviously than other components like PC2, PC3. PC1 accelerates the distinction of whiskey and brandy to rum and vodka which means without PC1, the boundaries of two groups will be fuzzy. PC2 represents nearness between whiskey and brandy as well as between rum and vodka. Based on Fig 1, the two almost perfect circles show that PC1 and PC2 are enough to describe whiskey and vodka. The value of brandy and rum need to be distinguished by three PCs which represents the first three variances of data. The selection of PC is very important which can influence the PCA result dramatically.

Four types of beverage are placed separately which proves a wide application of Pontes’ model including the detection of rums, whiskeys, vodkas and brandies. As can be seen in Fig 1, a clear linear relation of points can be found in whiskey samples which spread in a middle size circle. It is a very small group of rum samples which means discrimination among samples should be poor and a sensory model needs to be improved by narrowing units. The difference of each rum sample should be smaller than the other groups. Vodkas are spread into a line showing a strong connection. The ellipse shape of Brandies group means three-dimensional space is required in which the points spread perfectly. A positive correlation has been presented on the plot. The distance between whiskey group and brandy group seems to be small which might have a possibility of mutual interference. Except whiskeys group, the rest groups (rums, brandies and vodkas) have low sensitivity on PC1. Maybe another model with small units of PC1 is suitable to describe these samples.
**Figure 1.** Plots of different liquors (• – rums; + – whiskeys; ▴ – vodkas; * – brandies).

**Conclusions**

Using NIR spectroscopy analysis data, the researcher has built a sensory model of adulterant whiskey. This study shows that NIR with PCA and a SIMCA model can be applied to detect adulterant information. By using this model, a further series of experiments to predict adulteration in bar served samples will be investigated. Upon completion of the proposed study, the authenticity whiskey sold in selected Dublin bars will be determined.

**References**


USE OF MIR TO DIFFERENTIATE SKIM MILK POWDER SAMPLES BY HEAT SPECIFICATION

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Abstract

MIR spectral (4,000-400 cm\(^{-1}\)) can reflect the protein (peptide bounds) structures. Skimmed milk powder treated by different temperatures (none-treatment, 72 °C, 95 °C, 115 °C) were tested by FT-IR; the spectra between 800 to 1800 cm\(^{-1}\) were selected as fingerprint region and used to all chemometric operations; the PLS scores showed better separation clusters than PCA scores after MSC and 2\(^{nd}\) derivative of Savitzky-Golay. The whole PLS discriminant model developed with 4 loadings, which was quite accurate to discriminate the samples with the different heat treatments.

Introduction

Following the recent abolition of EU milk quotas, it provides developing opportunities to dairy product exports particularly to them with high added-value such as infant formula milk powder. Irish producers require to build up an implement system to ensure and control the quality and properties of dairy products, which is a major challenge due to the high-degree variations in dairy processes. However, PAT tools (Process Analytical Technology) can improve the real-time monitoring capacity during the producing process \textit{via} spectroscopic measurement. These spectroscopic measurement technologies generally include NIR (Near-infrared), MIR (Mid-infrared), FIR (Far-infrared), GMS (Guided Microwave spectroscopy) and Fluorescence Spectroscopy \textit{et al}. All of them, combined with chemo-matric modelling to analyze, control or improve the product quality are widely used in pharmaceutical industries and dairy manufacture industries (Reid, L. M \textit{et al}., 2006).

Generally, milk powder is preheated at different temperatures depending on final use of powder; protein secondary structure in dairy products is sensitive with the drying temperature (heat treatment); meanwhile, protein has obvious absorbance in MIR spectra (4000-400 cm\(^{-1}\)) (Karoui \textit{et al}., 2003; Karoui and De Baerdemaeker, 2007). Karoui \textit{et al} (2003) summarized that peptide bond of protein had absorbance during the range from 1700 to 1500 cm\(^{-1}\) in mid-infrared spectra as well as C=O group has absorbance in approx. 1750 cm\(^{-1}\). Theoretically, it is valid to set up the discriminant model to identify different heat treatments \textit{via} MIR Spectra. The main project objectives of this study try to use the spectral data in fingerprint region (800-1800 cm\(^{-1}\)), I) to range samples by Principal Component Analysis (PCA) and Partial Least Square discriminant (PLS) scores; II) to develop PLS discriminant modelling to MIR spectroscopy application to milk powder heat treatment investigation.
Materials and methods

Skimmed milk powder samples were prepared depending on the treated temperature; non-heat treated samples were prepared 2 trials (T1 & T3); the heat treated samples under 72 °C & 95 °C & 115 °C respectively were prepared 4 trials (T1 & T2 & T3 & T4) for each temperature.

Spectra were collected on a Bio-rad Excalibur series FTS 3000 FT-IT spectrometer (Analytica Ltd. Dublin, Ireland.) Instrument control and spectral collection were performed using WIN-IR Pro (v. 3.0) software supplied by the instrument manufacturer. 128 scans were co-added at a nominal resolution of 4 cm⁻¹. A single beam spectrum of each sample was collected and rationed against a background of air. Spectra were truncated to 4,000-600 cm⁻¹. Two sub-samples and triplicate scans were taken for each trial; all spectra were recorded at room temperature. The mean of these triplicates was used in later chemometric operations. Spectra were exported from EIN-IR Pro as FRAMS files (ThermoGalactic, Salem, MA, USA) and imported directly into The Unscrambler 9.7 (CAMO PROCESS AS, OSLO, Norway).

The raw MIR spectra of samples (4,000-600cm⁻¹) was showed in Figure 1, CO₂ noises occurred during 2100 to 2500 cm⁻¹ should be removed, as well as the main variables of spectra were before 1800cm⁻¹; removing the first 20 unstable variables, the fingerprint region was selected from 800-1800 cm⁻¹ (520 variables) and used in all chemometric operations.

![Fingerprint region (800-1800cm⁻¹) CO₂ Noises (2100-2500cm⁻¹)](image)

Figure 1. Raw MIR spectra of samples (4,000-600 cm⁻¹)

Data analysis was preliminary performed by principal component analysis (PCA), models were constructed using raw spectra and after pre-process by multiplicative scatter correction (MSC) and Savitzky-Golay derivatisation (2nd derivative with 5 points). The pre-treatments were able to remove baseline shifts, slope changes, scatter and other effects from spectral data.

Due to less samples, a whole discriminant model was developed using full cross validation (leave-one-out cross validation) and the best model was selected based on a number of criteria including the position of the first local minimum in the leverage and residual X-variance plot. A dummy Y-value was given to each sample- value 1
was given to the control sample set; values 2, 3, 4, were given to the sample sets treated at 72 °C, 95 °C, 115 °C respectively. If the samples’ Y-value were above or below the original value for 0.5, then these samples were identified as miss classifications.

Results and discussions:

PCA and PLS scores:
The PCA results showed poor separation clusters of each temperature samples using both raw data and data after MSC and 2nd derivative pre-treatments (not shown here). The Figure 2 showed the result of PCA via using MSC and 2nd derivative of Savitzky-Golay in fingerprint region. 4 clusters based on treat temperature along 4 directions were basically separated.

![Figure 2. PLS scores plot, fingerprint range 800-1800cm⁻¹, 520 variables, MSC & 2nd dev, PC1 vs. PC2. (1: no heat treatment; 2: heat treatment at 72 °C, 3: heat treatment at 95 °C 4: heat treatment at 115 °C).](image)

PLS modelling:
As the Figure 3 showed, the PLS model was developed with the 4 loadings; models with fewer loadings are preferred because they are likely to be more robust i.e. stable. The samples with different heat treatments were separated. The samples at control, 95 °C & 115 °C sets were separated with 100% accuracy; for the 72 °C set, 2 samples were missed classification (T3 sample 2 & T5 sample 2), it was probably because the poor temperature control in 72 °C heat treatment process or influences of properties of milk powder (i.e. particle size).
Figure 3. Left: PLS discriminant model (Measured Y vs Predicted Y); Right: the leverage and residual X-variance plot.

Acknowledgements:

The authors would like to thank PhD student Xiao Wang and Ms. Ming Zhao who give me lots of helps in this subject.

Conclusions:

In this project, based on the MIR spectra, skimmed milk powder samples with different heat treatment can be obviously separated by PLS discriminant analysis, which meant the better temperature controls were performed in the different heat treatment processes. However, due to less samples involved in this project, validation set were not set up, therefore, the accuracy of PLS model can not be validated.

References:


VALIDATION STUDY TO MONITOR THE COAGULATION OF MILK AND CUTTING TIME IN CHEESE-MAKING USING PAT TOOLS

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Abstract
Process analytical Technology (PAT) is used in various processes to control the process and ensure the quality and the safety of the product being manufactured. PAT is an online measurement system that monitors and controls various steps in a process. The present study is focused on the application of PAT in cheese making and a validation study was carried out to monitor the coagulation time and the cutting time in cheese making using different PAT tools – fibre optical sensors, hot wire and Rheometer as a reference method. The methods were validated in a repeatability study and excellent results were obtained for all the three PAT techniques, with the optical techniques performing better than the hotwire.

Introduction
The quality of the product is a major concern for the manufacturers as well as the consumers. The main focus is shifted from the production rate and the quantity to ensuring the quality of the product. The current trend is focused towards Quality by Design (QbD) which is facilitated by Process analytical Technology (PAT), a key enabler to ensure that the quality is built into the process rather than quality tested on the product. It is the system used to design, analyse and control the manufacturing processes to ensure the quality of the product online during the production. It is integrated in the process line facilitating continuous measurements of the samples without interfering the process. The idea is to be sure that the product is being manufactured meeting all the standards and the quality aspects (Simon et al., 2015). PAT is a well-known concept in the pharmaceutical industry which is now applied to the food industry. Food industry is facing a demand of strict regulation to be followed in terms of quality control, safety and traceability. The existing offline laboratory analytical methods are not sufficient to meet these demands considering the complex nature of food and the high degree of variation and influencers in most biological processes. The implementation of PAT in food industry will lead to improved control, rapid final product quality evaluation and increased productivity (van den Berg et al., 2013).

Dairy is one of the essential and a fast growing sector of food industry. The development and application of the process control techniques and product analysis in the dairy product manufacture has been influenced by the consolidation and the increased scale of dairy product manufacture (Fagan et al., 2008). Cheese is one of the major dairy product worldwide. Cheese making involves various different steps which influence the quality of the end product. Coagulation of milk is one of the important steps deciding the quality of the cheese. It is the phase where the liquid milk converts to the gel phase. Taking into account of the importance of coagulation point of milk in the cheese making, the present review is focused on the PAT techniques available to monitor the milk coagulation kinetics for cheese making. The objective of the study is to validate the performance of the Hotwire sensor and the CoAguLite II sensor in monitoring the milk coagulation with Rheometer as a reference method.
Material methods
There are a number of tools available to monitor the coagulation of milk. The coagulum is formed when the rennet interacts with the milk proteins leading to the formation of the gel. The coagulum is cut when the gel is found to be firm enough into discrete particles capable of expelling whey without fragmentation (O’Callaghan et al., 2002). The tools used in the present study was the Rheometer, fibre optical sensor ‘CoAguLite II’ and the ‘Hot wire’ sensor. The Rheometer was used as the reference method to monitor the milk coagulation. The experiment was carried out in a jacketed 12 litre laboratory cheese-making vat was fitted with the fibre optical sensor and the hot wire sensor. Commercial skim milk with 0.34% fat, 3.58% protein, 2.66% casein, 4.96% lactose, 9.67% total solids was used for the study. The vat was filled with 10kg of milk and heated to 32°C. The pH of the milk was not adjusted and the recorded pH at the time of renneting was 6.58. 2.72 gm of enzyme (CHY-MAX Plus 200 IMCU/ml) was added and agitated for 3 minutes and 20 ml of the milk was added to the sample holder of the Rheometer (AR 2000 Ex) and the data was recorded. The data from the optical sensor was recorded and collected using the Milk coagulation software. The hot wire data was recorded manually. The data was recorded till the coagulation point was attained and the gel firmness reached 35 Pa in the rheometer. The data points corresponding to different gelation points 0.5 Pa, 5Pa, 20Pa and 35Pa were obtained and analysed.

Figure 1: Graph obtained from the Rheometer data

Figure 2: Graph obtained from the Hotwire data

Figure 3: Graph obtained from the CoAguLite II optical sensor

Results and discussion:
The data obtained from the rheometer was used as the reference to compare the data obtained from the optical sensors and the hotwire. The data points had good repeatability with Standard deviation ranging from 0.1 to 0.9. The repeatability of the optical sensors was comparatively better than the hot wire and the Rheometer.
Table 1. Time (in min) recorded for different firmness from the Rheometer and the point of maximum inflection from the sensors

<table>
<thead>
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<th>DesignCode</th>
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<th>tcut @ 5Pa, min</th>
<th>tcut @ 20Pa, min</th>
<th>tcut @ 35Pa, min</th>
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<th>F t1min</th>
<th>F t2min</th>
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<td>20.34</td>
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<td>18.25</td>
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<td>0.53</td>
<td>0.81</td>
<td>0.89</td>
<td>0.15</td>
<td>0.25</td>
<td>0.28</td>
<td>0.24</td>
<td>0.60</td>
</tr>
<tr>
<td>SD/mean</td>
<td>1.6%</td>
<td>1.9%</td>
<td>2.1%</td>
<td>1.9%</td>
<td>1.0%</td>
<td>1.2%</td>
<td>1.5%</td>
<td>1.1%</td>
<td>3.3%</td>
</tr>
</tbody>
</table>

Further work will be carried out to validate the performance of the sensors at various conditions like temperature, enzyme concentrations, proteins etc.

References


WHISKEY AUTHENTICATION USING RAMAN SPECTROSCOPY

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Abstract

Irish whiskey and Scotch whisky are two of the most popular and famous whiskey types around the world due to the excellent flavour brought by their high quality raw materials and specious process techniques. However, the high popularity also brings counterfeiting of these spirit drinks, and it is a worldwide problem to authenticate whiskey. The normal customers usually do not have professional ability to authenticate the whiskey based on the test and the traditional analysis technologies such as gas and liquid chromatography need sample preparation and some time to get results. For that reason, a rapid and non-destructive technology could be very useful for whiskey authentication. This project will use Raman spectroscopy to construct a model for rapid detection system for whiskey authentication and evaluate its specificity, accuracy and sensitivity.

Introduction

Whiskey, is known worldwide as a high value alcoholic drink, which is produced via distillation of fermented mash made from malted grains or from grains which have been saccharified by the diastase of the malt contained therein. Whiskies’ categories are different by raw materials configuration, water, fermentation technologies, distillation processes and maturation conditions (Piggott et al. 1989). Scotch whisky and Irish whiskey are two of the most popular whisky types, and the high popularity of products usually causes a potential risk of adulteration. Thus authenticity assessment is one of the key elements of food product marketing.

Raman scattering is an inelastic phenomenon. Although its cross section is very small, recent advances in electronics, lasers, optics, and nanotechnology have made Raman spectroscopy suitable for analysis in a very wide range of research fields, such as microbiology, geology, pharmaceutical industry, forensic science and food industry (Li and Church 2014). Raman spectroscopy as a process analytical technology is applied in food industry mainly for detect food nanomaterials, pesticides, fungicides and bacteria in food. So it suits for whiskey authentication by comparing the composition of this alcohol with other spirit drinks. Alison Nordon et al. (2005) investigated Raman spectroscopy for determination of alcohol content of spirits.

Objectives of this study are to (I) differentiate Irish whiskey and Scotch whiskey from non-branded cheap whiskey and (II) identify adulterated whiskey.

Materials and Methods

Samples

There will be a total 19 samples used in experiment as shown in Table 1. Three different brands’ samples for Scotch whisky and Irish whiskey respectively and another sample is non-branded cheap whisky. They are all purchased from the local market. The branded samples can represent high value whisky produced through the specific process and the low price whisky stands for those products with low quality raw materials or poor technique. So they are supposed to show different results by Raman spectroscopy which could use to construct a model with data analysis.
Raman Instrumentation

Optical fibres can be used to transmit light from one place to another based on the principle of total internal reflection. The major function of the optical fibre in the Raman spectrometer is to transmit the excitation laser light, Raman scattering light, or both. There are three different fibre optic probes as shown in Fig 1 (Li and Church 2014). They are based on the use of different fibres for sample excitation and scattering collection.

![Figure 1](image)

**Figure 1.** Three different types of fiber optic probes: (A) fiber bundle probe, (B) double-fiber probe, and (C) single fiber probe. The lower images represent the cross-sectional view. The shaded fiber represents the excitation fiber in (A) and (B).

In this project, Raman spectra will be collected on a DXR SmartRaman spectrometer (ThermoFisher Scientific UK Ltd., Loughborough, UK) as shown.

### Table 1. Composition of the experimental samples

<table>
<thead>
<tr>
<th>Types</th>
<th>Brands</th>
<th>Original</th>
<th>20% blended</th>
<th>40% blended</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irish whiskey</td>
<td>Brand 1</td>
<td>b/o</td>
<td>b/1</td>
<td>b/2</td>
</tr>
<tr>
<td>Scotch whiskey</td>
<td>Brand 1</td>
<td>d/o</td>
<td>d/1</td>
<td>d/2</td>
</tr>
<tr>
<td>Low price whiskey</td>
<td>Brand 1</td>
<td>g/o</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Data analysis
The use of full spectra or specifically selected regions is now commonly carried out using multi-variant approaches, such as principal component regression (PCR) and partial least squares (PLS) regression. PCR is a regression analysis that uses principal component analysis (PCA) when estimating the regression coefficients. PCA uses an orthogonal transformation to decompose the spectral data set into a set of linearly uncorrelated variables or principal components (PCs) and a set of scale factors or scores (Zhao et al. 2015). The applications of these techniques are generally preceded by the pre-processing of the data sets. Common methods applied include taking second derivatives and normalization based on either total area or peak intensity.

Expected Results

With the determination of Raman spectroscopy, the data collected from different samples will show the different curves of intensity which is similar as Fig. 2 (Nordon et al. 2005).

![Graph showing Raman spectra](image)

**Figure 2.** Raman spectra of: (a) whisky (56.7% (v/v)), (b) vodka (37.7% (v/v)), (c) a sugary drink (20.0% (v/v)) and (d) an empty glass bottle

The expected result of this project is constructing a model which can classify samples to relevant groups shown in table 2 with high accuracy. Basically, the model with Raman spectroscopy will be able to detect different whisky types and adulterated products.

<table>
<thead>
<tr>
<th>Types</th>
<th>Original</th>
<th>Adulterated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irish whiskey</td>
<td>A/O</td>
<td>A/A</td>
</tr>
<tr>
<td>Scotch whiskey</td>
<td>B/O</td>
<td>B/A</td>
</tr>
<tr>
<td>Low price whiskey</td>
<td>C/O</td>
<td>/</td>
</tr>
</tbody>
</table>

Table 2. Different sample groups

Conclusions

The objective of this project is to ensure the authentication of valuable branded Irish whiskey and Scotch whisky within a rapid and non-invasive technology, Raman spectroscopy. The expected results will be obtained by collecting data with different samples and multi-variant data treatment approaches like PCA.
References


USING PREDICTIVE MICROBIOLOGY TO EVALUATE THE SAFETY OF CHEESE WITH RESPECT TO \textit{L. monocytogenes}

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Abstract

This study covers the application of predictive microbiology to model the safety of cheese with respect to bacteria \textit{L. monocytogenes} during storage at temperatures ranging from 5 to 20°C. Primary models used in this study were prepared from data available on the ComBase, a web-based system. The observed growth rate of \textit{L. monocytogenes} in cheese was compared with respect to temperature, pH and water activity. In further studies a Barayni model will be fitted to obtain growth curves and goodness of collecting data will be compared. Next, the secondary models will be developed and validated, which are expected to highlight the use and validity of predictive models in food operating industry.

Introduction

Listeriosis is a serious foodborne disease caused due to rods of \textit{Listeria} genus, especially the \textit{Listeria monocytogenes} species. Food safety authorities recognize it as a major issue and aims to regulate the occurrence of this pathogen in food due to it’s high (30%) mortality rate in susceptible groups, such as pregnant women, neonates, children, elderly people, and immunocompromised patients (Schvartzman \textit{et al.} 2014). In the past three decades, after the detection of listeriosis as a foodborne disease, a large number of listeriosis outbreaks and erratic cases of varying level have been reported in Europe. A number of outbreaks have been related to the consumption of dairy products, particularly cheese. In European countries, the annual occurrence of reported listeriosis cases fluctuates between 0.3 and 7.5 cases/ million (Melo \textit{et al.} 2014).

Food safety norms for the presence of \textit{L. monocytogenes} are regulated in the European Union. Ready to eat foods (RTE) that allow the growth of pathogen a limit of 100 CFU/g is set up throughout their shelf life or is absent in 25g before the food has left the control of food business operator (European Commission 2005). Hence, such legislation and guidelines increase the demand on food operators to observe this pathogen both at production and storage levels (Melo \textit{et al.} 2014). Currently, the importance of developing mathematical models to trace the development of micro-organisms by utilizing controlling factors such as water activity (aw), pH, temperature and oxygen availability has increased (Giffle and Zwietering 1999). Predictive models displaying growth over time of pathogen \textit{L. monocytogenes} in soft blue, white cheese (Rosshaug \textit{et al.} 2012) in addition, subsistence in soft and semi-soft cheeses (Campbell \textit{et al.} 2006) have been developed.

In this study, data will be obtained from the ComBase computer software to build primary models and secondary models (combase.cc). A primary model measures response over time, for instance, lag phase duration, specific growth rate, and death rate. A secondary model is then combined with the primary model to illustrate reliance of these factors on environmental conditions (Schvartzman \textit{et al.} 2014)

The objective of this study is to predict the growth of \textit{Listeria monocytogenes} during storage conditions of cheese and to calculate the impact of various factors to reduce the risk.
Materials and Methods

Data collection and analysis
ComBase is a web based system which includes more than 50,000 records of quantified microbial response to the food environment and based on this data, predictive models for growth or inactivation of a microorganism can be obtained. It has 443 records of *L. monocytogenes* in different types of cheese for example cottage cheese, processed cheese slices, Camembert cheese. All of these records represent different conditions and temperatures, pH and water activity in which *L. monocytogenes* can nurture. Gathered data show a wide range of pH and water activity, 4 to 6 and 0.93 to 0.99 respectively. Data are also collected for survival or growth of *L. monocytogenes* in cheese such as time and log CFU/g which will be used to build primary models (combase.cc).

Primary models will be fitted to Baranyi function and goodness of data will be evaluated.

Results and Discussion

Prediction of Primary Model
The behaviour of *L. monocytogenes* during storage temperatures of cheese was studied at different temperatures. During cold storage of cheese pathogen multiplies intensively, changing according to the applied temperature. The increasing temperature reduced the period of lag phase, reaching values of 192, 72, 48 and 30 for temperatures 5, 10, 15 and 20°C respectively. The maximum density of the cells does not go beyond 8.87 log CFU/g and was, on average, 7.84 log CFU/g. Initial values of parameters such as pH and water activity ($a_w$) are 6.8 and 0.971 respectively. The maximum density of bacterial cells increased as the temperature of storage unit arose.

![Figure 1](image_url)

*Figure 1.* Primary modelling results describing the growth of *L. monocytogenes* in cheese at (A) 5°C, (B) 10°C, (C) 15°C and (D) 20°C over the time (h).
Conclusions

Through present study, it was proven that a well-functioning predictive model describing the growth of *L. monocytogenes* in cheese as a function of temperature, pH and water activity can be developed. The model can be built by validating the data which will predict the growth of *L. monocytogenes* in cheese under dynamic pH and temperature precisely.

References


Institute of Food Research, the USDA Agricultural Research Service (USDA-ARS) and the University of Tasmania Food Safety Centre (2004) ComBase [online], available [http://browser.combase.cc/](http://browser.combase.cc/) [Assessed date 2 Mar 2016].


USE OF NIR SPECTROSCOPY TO DETERMINE THE MOISTURE CONTENT OF CHEESE

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Abstract

This study focuses on the determination of moisture content of cheese by near infrared spectroscopy. To ensure reliable results, reference duplicate results will be set by predicting moisture content in cheese by the air-oven method. Partial least square regression (PLSR) and principle component analysis (PCA) will be used for multivariate analysis of the chemo-metrics data. The moisture content prediction in cheese may vary in the range of 20-70% (González-Martín et al., 2008). This is the online sensing technique and a reflectance fiber-optic probe will be used to do the qualitative analysis of cheese.

Introduction

Near infrared spectroscopy (NIRS) has been used to determine various compositional factors or specifications of many dairy products in the industry. Cheese industry requires real-time controlled processing lines and NIRS is a real-time, rapid, non-destructive, powerful information gathering tool, which is suitable for on-line process control. The NIRS works on the principle of the interaction between photons of radiations and molecules in the cheese. Since it is a molecular interaction, where vibrating molecules in the cheese allow extracting of molecular information from the cheese. Chemical bonds absorb the radiations and are shown in terms of absorbance whereas non-absorbed radiations are shown in terms of reflectance or transmittance. The absorption data provides the chemical composition, which includes the moisture content in cheese.

Cheese production can be summarised in four main processes as milk coagulation, syneresis, salting, and cheese ripening. On-line or at-line NIRS can be used in controlling all these processes along the production line. The expected data or spectra will be very rich and complex with band combination and overtones hence partial least square regression (PLSR) or principle component analysis (PCA) will be used for multivariate mathematical analysis. The reflectance fiber-optic probe will be able to conduct the compositional measurements directly. The final results from the NIRS will be assessed with the reference duplicate results from air-oven method to confirm the reliability of the entire analysis.

The objective of this study is to determine the moisture content of cheese by Near infrared spectroscopy (NIRS).

Material and methods

Sample analysis
The cheese samples will be selected on its physical and chemical aspects. In this study, initially the moisture content in cheese samples will be determined by using the air-oven method the sample will be heated under specified conditions and the weight loss is measured to find the moisture content of the cheese sample.

NIR Spectroscopy
The sample will be assessed by NIRS where the spectra will be recorded at specific intervals with direct application of fiber-optic probe. The detailed procedure will be as follows: After recording the
spectra the spectral mean will be taken. Furthermore, it will be calibrated using the multivariate mathematical software followed by respective chemical analysis. The principle component analysis (PCA) and partial least square regression (PLSR) will be used in multivariate mathematical or statistical analysis. PCA is sufficient only to compress data and analyse it thoroughly and PLSR explains the chemical data and does respective mathematical interpretations. This analysis will explain the spectral variability and also the principle components required for moisture content determination.

Expected results and discussion

Chemical analysis and spectral information
The expected results of the chemical analysis will be shown in tabular form as a statistical overview of the data. To simplify this analysis, the spectral variability enables development of calibration equation. The fig.1 below shows the spectrum of cheese with the fiber-optic probe.

![Figure 1. Raw NIR Cheese spectra and Pretreated Cheese Spectra Source- (Gonzalez-Martin et al)](image)

Calibration equation and validation
The anticipated outcomes will be reported in tabular form showing the choice of principal components in multivariate analysis and calibrations by NIRS. Figure 2 explains how the predictions of reference values and NIRS values will be plotted. This comparison will give the acceptable, reliable and valid outcomes. The moisture content can vary in the range of 20-70% of the total weights of the sample.

![Figure 2. Comparison of reference and predicted NIRS values. Source- (Gonzalez-Martin et al)](image)
Conclusion

The expected results of moisture content in cheese by NIRS will be in the range of 30-40% of the sample weight. The expected results from the reference method (air-oven method) will be determined with respect to the appropriate temperature and time. Both the results will be compared and predictions will be on the basis of those observations. The role of spectroscopic sensors in quantifying major components of cheese and the use of near infrared spectroscopy (NIRS) in cheese manufacture will be explained briefly to give an overview of this technology.

References

Downey, G., Spectroscopic sensors technology for PAT systems in industry, Class notes.


USE OF NIR SENSOR TO INVESTIGATE MILK COAGULATION KINETICS

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Abstract

Milk coagulation is a critical control point in cheese making, this process is followed by curd cutting and the quality of the cheese is determined by cutting curd at the right time. Near Infrared (NIR) spectroscopy has emerged as a robust and accurate analytical tool compared to traditional methods. Commercial dairy plants process milk in large quantities and it is difficult to implement offline methods to observe milk coagulation. NIR spectroscopy is a real time, non-destructive and efficient inline way of milk coagulation monitoring. NIR is used as a process analytical tool in many food products, experiments conducted to study use of this optical spectroscopy to monitor milk gelation have produced successful results. The aim of this study is to observe spectroscopic response of a proposed near infrared sensor towards the milk coagulation process, using different milk types and Glucono-δ-Lactone as a milk acidifying agent.

Introduction

Fermented milk products are one of oldest and popular food items produced around the world. The variety of product range and nutritional benefits are the reasons behind the popularity of cheese and yogurt products. Milk coagulation is an initial stage in the production of cheese products, it is typically induced by enzymatic action or acidification to form a continuous solid curd that ensnare fat globules and moisture (Castillo et al 2006). After achieving certain firmness of curd syneresis is induced by cutting curd gel into small pieces. This process helps whey to escape while gel structure is reconstituting. Traditionally cutting of the gel is carried out after a fixed time interval or following expert’s judgement on firmness and visual inspection. These methods are uncertain as milk composition differs in every batch. Process control and prediction of curd cutting time is essential in cheese production as it carries significant impact in both cheese quality and yield (Bakkali et al 2001).

Many instruments have been built and proposed in the last few decades to monitor rheological properties of curd setting but those systems are destructive and cannot be applied as an inline method. In 1993 Payne et al built an inline optical sensor to monitor physiochemical changes in coagulation process based on backscatter phenomena of infrared light, this method efficiently provides close results to optimum cutting time. This technology successfully developed and implemented by Castillo in 2001. Previous studies have proved that light backscatter phenomena depends on milk composition. However, due to the complexity of the curd formation process, adaptability of optical spectroscopy to study factors influencing coagulation are yet to be studied. Formation of micelles clusters and kinetic profile of gel setting is different for enzymes and acids used to initiate proteolysis. Recently Glucono-δ-Lactone (GDL) is used as a popular milk acidifying agent. After heat treatment GDL hydrolyze to gluconic acid and drops pH to start curdling, it is a rapid way to get quality product consistently.

The objective of this experiment is to study the kinetics of milk coagulation induced by Glucono-δ-Lactone and develop a model to predict gel strength.
This paper briefly describes NIR methods developed to predict gel cutting time. Details of near infrared spectroscopic system to examine gelation process of coagulate formed using Glucono-δ-Lactone on real time basis are described with expected results.

Materials and Methods

Experimental Design

This experiment is designed to understand and study the effect of different milk types, Glucono-δ-Lactone concentration levels and milk coagulation temperatures on the Near Infrared blight backscatter profile during milk gel formation and on the kinetics of the coagulation process. To achieve the study objectives different levels of experimental factors are going to be selected. Milk coagulation will be monitored using small amplitude oscillatory rheometry (SAOR) and NIR light backscatter, concurrently clotting time will be visually determined.

Materials

Different types of milk with different composition obtained from supplier will be used in this experiment. For acidification of the milk Glucono-δ-Lactone will be used as acidifier. Collected milk will be pasteurized to eliminate bacterial growth in a sample, then milk will be stored at 4ºC to equilibrate. At the time of sample preparation measurement of initial milk composition is essential. Using lab methods pH, fat, protein, total solids and ash content in milk will be calculated. Milk samples with different fat content are prepared. Then samples are then heated at 65ºC for 30 minutes to reach optimum temperature of coagulation process. After heating milk is rapidly cooled at 30ºC. Glucono-δ-Lactone (GDL) is an acidifier and act as a catalyst in coagulation process, different concentrations are used to study effect of GDL on milk coagulation. Constant temperature is maintained usually between 30ºC to 38ºC throughout the process. pH is measured constantly.

The near infrared light backscatter profile of milk coagulation for every sample will be obtained using the method described by Castillo et al (2000). The response data is generally collected in the form of voltage every after 6 s. By using linear-least square regressions derivatives of light backscatter profile can be calculated. Table 2 shows different derivatives required to be obtained as optical time parameters.

Table 2: Main optical parameters need to be derived from the light back scatter ratio profile

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Definition</th>
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</thead>
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<td>t&lt;sub&gt;max&lt;/sub&gt;</td>
<td>min</td>
<td>Time to the first maximum of R'</td>
</tr>
<tr>
<td>t&lt;sub&gt;max2&lt;/sub&gt;</td>
<td>min</td>
<td>Time to the second maximum of R'</td>
</tr>
<tr>
<td>t&lt;sub&gt;2max&lt;/sub&gt;</td>
<td>min</td>
<td>The time to the first maximum of R''</td>
</tr>
<tr>
<td>t&lt;sub&gt;2min&lt;/sub&gt;</td>
<td>min</td>
<td>Time to the first minimum of R''</td>
</tr>
<tr>
<td>t&lt;sub&gt;2max2&lt;/sub&gt;</td>
<td>min</td>
<td>Time to the second maximum of R''</td>
</tr>
<tr>
<td>t&lt;sub&gt;2min2&lt;/sub&gt;</td>
<td>min</td>
<td>Time to the second minimum of R''</td>
</tr>
<tr>
<td>R'&lt;sub&gt;max&lt;/sub&gt;</td>
<td>min&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>Value of R' at t&lt;sub&gt;max&lt;/sub&gt;</td>
</tr>
<tr>
<td>R''&lt;sub&gt;max&lt;/sub&gt;</td>
<td>min&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>Value of R'' at t&lt;sub&gt;max&lt;/sub&gt;</td>
</tr>
</tbody>
</table>

R, light backscatter ratio; R', first derivative of R as a function of time; R'', second derivative of R as a function of time. (Ref. A.R. Abdelgawad et al 2014)
Small amplitude oscillatory rheometry (SAOR) will be performed as described by A.R. Abdelgawad et al (2014). Different rheological parameters like elastic storage modulus ($G'$), viscous or loss modulus ($G''$) are determined to estimate get cutting time. Operator visual inspection of coagulum is carried out by inserting spatula into gel to monitor satisfactory density of casein flocks is obtained. Acquired data is analysed using Statistical Analysis System (SAS 9.2.3., 2009) and software like Unscrambler X software (v10.2, CAMO Software AS, Oslo, Norway). Software produce graphical representation of gel formation kinetic models for different milk compositions.

Expected Results

Previous experiments conducted to study similar attributes of milk coagulation process give idea about expected results. A.R. Abdelgawad et al (2014) has given detailed comparison between optical and rheological methods to study milk coagulation kinetics. The light backscatter ratio increases with increasing particle size of casein network. Temperature at which coagulation is carried out determines kinetics of the process. NIR is more sensitive to chemical changes occurred during process, this helps to provide real time coagulation process kinetic model and predicting cutting time. For rheological cutting time prediction SAS system can be implement to determine descriptive parameter for process e.g. enzymatic concentration. Figure 1 shows typical results obtained from NIR light back scatter readings in milk coagulation process.

![Figure 1: Typical LB profile and its first and second derivatives as a function of time. $t_{max}$, inflection point of the light backscatter ratio; cutting time, here defined as the time when the gel reached $G_0 =30$ Pa. (Source: A.R. Abdelgawad et al 2014)](image)

Arango et al (2015) carried out an experiment to predict coagulation and syneresis parameters of milk gels when inulin is added as fat substitute using infrared light backscatter, the coagulation process was monitored using near infrared spectrometry, small amplitude oscillatory rheometry and visual coagulation indexes. The extent and kinetics of syneresis was evaluated by volumetric methods. The results demonstrated that it is possible to obtain models for the prediction of coagulation and syneresis parameters in milk gels when inulin is added as a fat substitute using a fiber optic light backscatter sensor. Fig. 2 shows one of the cutting time prediction model result based on NIR light backscatter. This clearly indicates that real
time monitoring of coagulation process using different milk compositions is possible using NIR sensor.

![Figure 2. Comparison of predicted milk gel cutting time using NIR and actual cutting time (Arango et al, 2015).](image)

**Conclusion**

It is evident that Near Infrared spectroscopy is an effective inline method to predict milk gel formation dynamics. Previous research experiments have proved that optical sensors are sensitive to process chemical reaction and temperature. This indicate that NIR sensor can interpret real time compositional and chemical changes occurred in milk sample. Effect of different types of milk on GDL acidified milk coagulation process kinetics can be successfully investigated by using NIR spectroscopy.

**References**


ANTIMICROBIAL USE OF OZONE IN PROCESSING OF DRIED FOOD INGREDIENTS

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Abstract

Dried food Ingredients (DFI) such as spices, herbs, flour and milk powders are extensively used in domestic and commercial culinary practices globally. These are frequently exposed to a wide range of microbial contamination during pre- and post-harvest processes. Aerobic spore formers are found to cause spoilage in DFI. Numerous studies on removal of these sporeformers exploiting novel strategies were conducted but none of them seems to be encouraging in terms of preserving organoleptic properties and texture of DFI. Ozone with its antimicrobial potential and unique capability of keeping the sensory attributes of food intact is found promising against these sporeformers in DFI. This paper discuss about the potential of ozone technology in inactivation of sporeformers prevalent in DFI.

Introduction

Dried food ingredients play a significant role in food industry. They are used in preparation of variety of food items in domestic and commercial settings. Spices ($a_w$ 0.3-0.6) used for their flavouring properties and herbs for imparting aroma to food. Herbs($a_w$ 0.4)  are usually added after food has been cooked or served considered to be in ‘ready to eat state’(Little et al. 2003). Flour (wheat and rye $a_w$ 0.87) is an active ingredient used for production of commercial and artisan breads consumed directly after milling whereas milk powders ($a_w$ 0.2) have variety of culinary uses in production of range of sweets, cakes and cheese sauces. Since they are produced naturally they get exposed to environmental microbial contamination during collection, processing, packaging and distribution(Banerjee and Sarkar.; García et al. 1985; De Boer, E. W.; Spiegelenberg, M.; Janssen 1985; McKee 1995). Microbes including *Bacillus cereus*, *Yeast & Moulds*, *Clostridium perfrigens*, *Escherichia coli* and *listeria monocytogenes* are found associated with DFI contamination which can lead to increased number of food-borne infections and intoxications.(Rendlen et.al 2004).

DFI are often burdened with heavy loads of vegetative cells and spores of aerobic sporeforming bacteria because most of these products are in powdered forms with low water activity favourable for bacterial spore’s survival and increased resistance to thermal treatments (Laroche et al. 2005) as shown in Table 1. Bacterial spores are highly resistant to heat treatment because of the dehydrated state of protoplasm and multi-layered spore coat (Leuschner and Lillford 2003; Desai and Varadaraj 2010).The low water and mineral content of spore coat is another factor causing them resistant to radiation whereas spore’s inner membrane, exhibiting extremely low permeability to small hydrophilic and hydrophobic molecules forms the basis of chemical resistance.(Belliveau et al. 1990; Nicholson et al. 2000; Young and Setlow 2003).Various safe decontamination strategies have been adopted Table 2, but these are not found suitable for DFI decontamination.

Ozone is one of the most potent sanitizers known, excess ozone auto-decomposes rapidly to produce oxygen, and thus it leaves no residues in food. The sanitizer is active against all forms of microorganisms at relatively low concentrations. (Khadre et al. 2001). It is effective against Gram positive, Gram negative bacteria, fungi and viruses. (Restaino et al. 1995).Ozone is extensively used as a disinfecting agent in food industries and possess antimicrobial properties which can be exploited for decontamination of DFI. (Restaino et al. 1995; Guzel-Seydim et al. 2004)

The objective of this study is to test the efficacy of ozone technology for inactivation of *bacillus* sporeformers in dried food ingredients.
Table 1. Spore counts in different food ingredients.

<table>
<thead>
<tr>
<th>Dried Food Ingredient</th>
<th>Spores Count (cfu/g)*</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spices</td>
<td>&gt;10^5</td>
<td>(Sagoo et al. 2009)</td>
</tr>
<tr>
<td>Herbs</td>
<td>10^2 - 10^3</td>
<td>(Aksu, H., Bostan, K. and Ergün 2000)</td>
</tr>
<tr>
<td>Flour</td>
<td>10^5</td>
<td>(Yibar et al. 2012)</td>
</tr>
<tr>
<td>Milk Powder</td>
<td>10^4</td>
<td>(Rueckert et al. 2005; Seale et al. 2015)</td>
</tr>
</tbody>
</table>

*Aerobic sporeformers strains may vary with food component such a Bacillus subtilis, Bacillus cereus and Bacillus amyloliquefaciens*

Table 2. Strategies adopted for DFI decontamination (Personal communication with Dr. Amalia Scannell)

<table>
<thead>
<tr>
<th>Existing Strategies</th>
<th>Issues related with DFI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non Thermal Technologies</td>
<td></td>
</tr>
<tr>
<td>Steam</td>
<td>Low microbial reductions (&lt;3 log CFU/ml), loss of heat sensitive substances and volatiles. (Almela et al. 2002)</td>
</tr>
<tr>
<td>Irradiation</td>
<td>Can cause rancidity, potentially harmful radiolysis products from packaging material. (Goulas et al. 2003; Chytiri et al. 2006)</td>
</tr>
<tr>
<td>Chemical Fumigation</td>
<td>Fomaldehyde, Methyl Bromide, Ethyl Alcohol may leave residual chemical residues, reduce bioactive content. (Brodowska 2014)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Novel Technologies</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>High Hydrostatic Pressure</td>
<td>Limited to liquids not effective against spores. (Devlieghere et al. 2004)</td>
</tr>
<tr>
<td>Pulse Electric Fields</td>
<td>Not suitable for DFI due to low a_w homogenous treatment not guaranteed. (Butz P, Heinisch O 1994)</td>
</tr>
</tbody>
</table>

Material and Methods

Sample Preparation
Sample include flour from bread factory based in Cork, Ireland with long reputation in artisan bread production. 100 gm of flour was reconstituted in 100 ml of sterile water and 1 ml from this suspension was plated on Bacillus cereus selective agar (Oxoid CM0617). Serial dilutions of the suspension was prepared up to 10^6 dilution and sample is then spread plated on solidified agar plates including control. Bacillus counts obtained after incubating the agar plates for 48 hours in 37°C. Bacillus sp. obtained on the plates was cultured on 100 ml of tryptone soya broth (Oxoid CM0129) (TSB) to get liquid suspension for ozone treatments. Spores for ozone treatment will be 10^8 CFU/ml considered as control. For obtaining spores the bacterial suspension will be heated on a water bath at 80°C for 15 minutes. Petroff-Hausser chamber was utilized to count the spores before ozone treatments.

Staining of bacterial Endospores
In order to visualize spores from prepared samples Schaeffer-Fulton staining was adopted. (Knaysi 1948; Murray et al. 1981).

Ozone Apparatus
It includes 100 ml bubble column reactor with inbuilt diffuser (Ozone Labs TM, Ozone Services, Burton, B.C., Canada as shown in Figure 1). Ozone is generated using a corona discharge ozone generator (model OL80A/DLS, Ozone Services, Burton, B.C., Canada). Pure oxygen is supplied via an oxygen cylinder (Air Products Limited, Dublin, Ireland) and the flow rate is controlled using an oxygen flow regulator. The presence of ozone is detected by using an ozone sensor (Model OS-3, Eco Sensors, INC) which is placed above the bubbling fluid column. Ozone gas concentrations is determined using an ozone gas analyser (Figure 1).
Experimental parameters for the present study are adopted from (Akbas and Ozdemir 2006; Rosenblum et al. 2012) for flow rates, time of exposure and concentration of ozone but difference lies in sample type and bacillus spores in question. Ozone was diffused through 50 ml bacterial spore culture samples.

![Diagram of ozone apparatus]

**Figure 1.** Schematic arrangement of Ozone apparatus for disinfecting food items (Liquid, Solids)
Adapted from Ozone Services & OzoneLab™
(a) A: Oxygen cylinder with flow rate regulator (b) B: Ozone generator (c) C: Ozone bubble column reactor for different test materials

*Microbiological analysis*
Following ozone treatment all ozonated samples were diluted up to $10^{-4}$ under a laminar hood. To ensure proper mixing the test tubes were placed on a vortex (Scientific Industries, INC, USA). 100 µl of each dilution was surface spread onto labelled agar petri plates. All completed plates were placed into an incubation chamber (Thermo Scientific, Precision compact, Cambridgeshire, England) set at 37°C for 48 hours. The efficacy of treatments is determined in terms of viable cell counts following the 48 hour period in the incubation chamber. After 48 hours the incubated plates were manually counted. The results were reported as colony forming units (CFU mL$^{-1}$). The data was converted exponentially using Microsoft Excel for all graphical representations.

**CFU/mL** = no. of colonies x vol. of cultured sample x dilution of sample

*Results*
Ozone potential for spores population reduction largely depends upon the contact time and concentration used which can be predicted analysing the graph obtained. According to this preliminary study 4 log reduction in spore count is received in 30 mins at 1.5 ppm of ozone exposure but data stands insufficient to obtain a curve predicted as (Akbas and Ozdemir 2006; Rosenblum et al. 2012) shown in Figure 2.
Discussion

Microbial inactivation by ozone is a complex process and depends upon cell wall and spore water content in bacterial spores, particularly for cells they are inactivated by disruption of the cell envelope or disintegration leading to cell lysis. Both molecular ozone and the free radicals produced by ozone breakdown play a part in this inactivation mechanism but still investigation is needed on elucidating the definite mechanism of ozone killing the spores which can be addressed in our future studies.

Conclusions

The preliminary observatory indicates ozone technology as an efficient novel food processing technology for decontaminating dried food ingredients.

Acknowledgements

The authors acknowledge the support of Department of Agriculture Food and Marine Ireland for the project.

References

INVESTIGATION OF SELECTED PARAMETERS INFLUENCING THE DISSOLUTION RATE OF MILK POWDERS

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Abstract

The effect of several selected parameters (i.e. temperature, mixing speed, ultrasound power) on milk powder dissolution behaviour was investigated. Milk powder samples were subjected to one of the four different reconstitution conditions: high speed stirring high temperature, high speed stirring low temperature, low speed high temperature, or use of sonication. FBRM was used as the tool for monitoring the reconstitution process. The results showed that the reconstitution process can be accelerated by increasing the reconstitution temperature and mixing speed. Also, the results of using ultrasound presented the ability to further reduce the particle size of milk powder dispersions by breaking apart some of the larger particles into smaller ones.

Introduction

In the food industry, powdered dairy products with rapid dissolution behaviour are desirable; it could avoid prolonged processing time, decrease production costs and increase product quality (Fang et al. 2011; Chandrapala et al. 2014). Reconstitution of milk powders is significantly influenced by several parameters, such as protein and mineral content, heat treatment histories, spray drying temperature, reconstitution process and storage conditions of powder samples (Koh et al. 2014; McCarthy et al. 2014). In recent years, more studies have been conducted to characterize the dairy powder reconstitution properties (Martin et al. 2010; Jeantet et al. 2010; McCarthy et al. 2014; Chandrapala et al. 2014), and for these studies, the reconstitution properties of dairy powders were normally characterized using Malvern Mastersizer, a light scattering technique. However, this technique requires sample preparation and is restricted to a very dilute concentration of milk powder (<0.1%) (Fang et al. 2010). In comparison to Malvern Mastersizer, Focused Beam Reflectance Measurement (FBRM) can be directly used in situ without any further sample preparation, and it has been proven as a suitable tool for dairy powder solubility characterization (Fang et al. 2010; Fang et al. 2011).

The objective of this study was to investigate the effects of selected parameter on the dissolution rate of milk powders.

Materials and Methods

Reconstitution of powders

The reconstitution experiments were carried out using a 500 ml jacketed glass vessel with a recirculating water temperature control system, and a 4-blade impeller mounted vertically and centrally. FBRM (model D600L, by Mettler Toledo) was placed in the vessel to monitor the reconstitution process. A 1.5 kW ultrasonic processor (VC 1500, Sonics and Materials Inc., Newtown, USA) with a 19 mm diameter probe was used for sonication. Milk powder were reconstituted in deionized water to make a 300 g solution with 12% total solid at 30 and 50 °C for the study of temperature effect. The influence of impeller stirring speed (rpm) was studied by the speed of 400 and 200 rpm at 50 °C, samples reconstituted by 200 rpm will be directly applied for ultrasound for 1min with pulse durations of 3s on and 3s off. The milk powder dispersions were then initially stirring for 30s at 200 rpm, and the next 5 min of readout from
the FBRM was averaged and defined as the final particle size after ultrasound treatment. All experiments were performed in triplicate and the reported values are the mean of the three experiments.

**Results and Discussion**

**Effect of reconstitution temperature**

The speed of reconstitution was compared for high (50 °C) and low (30 °C) reconstitution temperature (Figure 1), here, the particle size was used as a parameter of reconstitution behaviour (Fang et al. 2011). Under both temperatures, the particle size exhibited a significant decrease in the first 30 s rapidly and reached to a plateau. For the next 29.5 min, mean particle size changes were minor. Although under a lower reconstitution temperature, the reconstitution of milk powder is still a rapid process; the processes were slowed down, since the rates of the particle size decrease were slower in the first 10s, as shown in Figure 1. Furthermore, higher reconstitution temperature not only accelerates the reconstitution process, it also affects the final particle size after reconstitution. Powders dissolved in higher temperature water presented smaller particle size, however the differences were minor. This also proved that powder can be rapidly solubilized by increasing the temperature during reconstitution (Martin et al. 2010; Chandrapala et al. 2014).

![Figure 1. Mean particle size change with time at 30 °C and 50 °C.](image)

**Effect of mixing speed**

When reconstituting milk powder used high mixing speed (400rpm), powders usually instantly sank and dispersed into water, but it be found that slowing down the stirring speed leads to slower sinking and dispersing procedures. Therefore, the particle size distribution reached a plateau in a very short time for samples reconstituted with a high mixing speed, but on the other hand, it took much longer time using low mixing speed (Figure 2). In addition, the changing trends of each particle group’s population also confirmed this phenomenon. As described in Figure 2, for low mixing speed tests, fines particles (particle size less than 10 μm) experienced a significant fluctuation during the first 10 min. Moreover, during the reconstitution process, large particles (particle size between 150-300μm) occasionally appeared, which synchronously caused the increase of the mean particle size. In this case, it can be noted that increasing the stirring speed leads to faster sinking and dispersing steps of reconstitution.

Figure 3 presented the particle size change during reconstitution process, as expected, particle size experienced a fluctuation phase until it reached plateau. This proved previous results, but unlike the temperature effect, final particle sizes were not decrease as the reconstitution process
accelerated. Powders reconstituted with lower mixing speed showed even smaller particle size after reconstitution (Figure 3). After reconstitution, some sediment could be found when mixing by lower speed. Hence, some of the larger particles sank at the bottom of the vessel, which meant the stirring power was not strong enough to bring them under the FBRM probe to be determined. Although with the increase of final particle size, increasing the mixing speed still accelerated the overall reconstitution process of milk powder.

**Figure 2.** Trends of the number change of each particle size range.

**Figure 3.** Mean particle size change with time under different mixing speed.

**Effect of ultrasound**

The use of high shear techniques, such as ultrasonication, has proved to greatly accelerate the solubilisation of dairy powders (Chandrapala et al. 2014; McCarthy et al. 2014). In our case, it was found that applying an ultrasound treatment could continually decrease the particle size of milk powder dispersions (Figure 4). After ultrasound treatment, the population of fines particles (particles less than 50μm) increased, in the meantime, the population of large particles (particle size between 50 and 150μm) decreased. Some of the large particles were physically broken apart by the ultrasound power (Chandrapala et al. 2014), leading to the decrease of mean particle size of milk powder dispersions (Figure 4).
Conclusions

In this study, the effect of reconstitution temperature, mixing speed and application of ultrasound were investigated. The reconstitution process was accelerated and the final particle size was decreased by increasing the reconstitution temperature. High mixing speed was also able to accelerate the rehydration process, but increase the particle size after reconstitution. Moreover, ultrasonication can break larger particles into smaller ones, and further improve the reconstitution process after conventional mixing.

Figure 4. Particle amounts change with different size ranges.

Acknowledgements

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References

THE USE OF PREDICTIVE MICROBIOLOGY TO MODEL LISTERIA MONOCYTOGENE’S GROWTH IN COLD SMOKED SALMON

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Abstract

Recent *Listeria monocytogenes* outbreaks linked to ready to eat fishery products underscore the importance of understanding the growth kinetics of *L. monocytogenes* in these products at different temperatures. Predictive microbiology provides a powerful tool to aid assessment of human exposure to microbial pathogens and their growth kinetics in foods. Using predictive models changes in microbial populations on foods between the points of production/harvest also, the point of eating can be evaluated from changes in product parameters (temperature, pH, salt/water activity, storage atmosphere and so on.). In this way, it is conceivable to derive exposure to *Listeria monocytogenes* at the time of consumption from the starting microbiological state of the food and its history from production to consumption. Furthermore cold smoked salmon is a high risk product with respect to listeriosis because there is no point during the processing of fish which can ensure the absence of *L. monocytogenes* in product. Moreover it’s not even heated prior to consumption. Therefore, this paper reviews the gathering of data and development of model for *L. monocytogenes* in cold smoked salmon by using knowledge available such as literature review and ComBase.

Introduction

*Listeria monocytogenes* is a food borne pathogen which is mainly found in soil, water and on plant material. *Listeria monocytogenes* is ubiquitous in nature which makes fish or sea foods harvested from natural environment to be the potential sources of this pathogen.

The presence of *Listeria* in smoked salmon is often a concern because smoked salmon are commonly eaten without further heating. Cold smoked salmon is produced by filleting raw salmon, which is then salted, dried and smoked at a temperature < 30ºC. The salmon fish is then vacuum packed when cooled. Because of the low temperatures that are involved, cold smoking is not regarded as a cooking step. During cold smoking process, there is no point of the process that can fully ensure the absence of *L. monocytogenes*. Neither the smoking temperature nor the salt content is enough to kill the bacteria. Therefore it makes it an issue for food industry to continuous research *L. monocytogenes* in cold smoked salmon.

Predictive microbiology is one of the reliable and effective tool of describing the responses of microorganism's to specific environmental conditions such as temperature, pH and water activity, smoking. Predictive microbiology aid in assessing the human exposure to *L. monocytogenes* in foods. Models that have already successfully developed or validated enable changes in microbial populace on foods, between the point of production/harvest and the point of eating is to be estimated from product, storage and processing parameters i.e. temperature, pH, salt/water activity, storage atmosphere, smoking etc.). These models can also be used to evaluate the microbial consequences to fluctuating conditions.

The objective of this review is to study the growth and survival characteristics of *listeria monocytogenes* in cold smoked salmon during storage and to develop a model by gathering data from literature review and using ComBase.
Methods

ComBase microbiological model was used for gathering the data for studying the growth and survival characteristics of *L. monocytogenes* in cold smoked salmon at different temperatures and will also be used in future for the development of the final model. ComBase is an online tool for quantitative food microbiology. Its focus is to study and predict how microorganisms grow and survive under various conditions. This web searchable database provides support for predictive microbiology approaches. Predictive microbiology involves the systematic development of description of microbial growth responses to environmental factors relevant to food and their summary as mathematical models. The models can be used to interpret the effect of processing and distribution practices on microbial growth in food or to design food or food processes and to meet required level of shelf life and or safety.

ComBase is based on the combined data sources of Food micromodel FMM, Pathogen modeling program (PMP) and publicly available scientific literature. It contains over 50000 records on growth, survival and inactivation rate data for food borne pathogen and spoilage microorganism. It is used for predicting and improving the microbiological safety and quality of food, designing, producing and storing foods economically and assessing microbiological risk in foods. It has two main components- ComBase database and ComBase Predictor. ComBase Predictor is a free on-line tool for predicting the response of a range of pathogens and spoilage microorganisms to key factors (temperature, pH and salt concentration, etc.) characterizing the food environment.

Modelling background of Combase predictor

Predictive models for ComBase Predictor are based only on output from laboratory experiments observed in culture media under well controlled laboratory conditions. Variation of cell concentration is described by a mathematical (growth or survival) curve and this is called a primary model. Secondary models describe how the parameters of primary models depend on environmental factors such as temperature, pH and water activity. These are described by mathematical functions, and, by interpolation, the cell concentration against time can be predicted for any combination of conditions. ComBase Predictor uses the model of Baranyi and Roberts (1994) as the primary model. To create the secondary models, the logarithms of the specific growth rates were described as a function of the (possibly rescaled) environmental factors by a standard quadratic multivariate polynomial. For the models of ComBase Predictor, standard second order polynomials model the effect of temperature, pH, and Aw values on the logarithm of the growth rate. The maximum specific growth rate is the main model parameter for ComBase Predictor. The other key parameter (in place of lag) is the ‘initial physiological state’ (phys. state). The phys. state value is a dimensionless number between 0 and 1; if phys. state= 0, then there is no growth and the lag time is infinite; if phys. state=1, there is no lag and growth will commence immediately. It has a similar role to the inoculum size but is an initial parameter quantifying the history of the cells. The value for this parameter can be selected by the user but because the user is rarely able to provide its true value, a typical value is used as the default phys. state. It is advised that users try different values for the physiological state, to study its effect on the growth curve. For further information regarding this ‘initial physiological state’ parameter, see Baranyi and Roberts (1994).

Results and Discussion

Primary model is growth and survival findings of this bacterium in smoked product at two temperatures which are generally storage temperature of cold smoked salmon i.e. 4°C and 8°C. For this study ComBase databases were used, there are almost 900 records for *listeria* in seafood’s in ComBase database.
Figure 1. Graphical representation of growth and survival of *listeria* in cold smoked salmon at two different temperatures. (Source- ComBase database available at http://browser.combase.cc.)

As it is clearly visible from the graph there is a survival of this bacteria in cold smoked salmon during storage and sometimes it has growth as well. Therefore a potential risk to consumers of this product and makes it necessary for researcher to study this topic further.

In Future all the available data will be draw together to generate final models that encompass all factors that may affect the fate of *L. monocytogenes* in cold smoked salmon. The developed model will predict both the growth boundary and growth rate of *L. monocytogenes* and will be useful for the risk management of lightly preserved cold smoked salmon. Particularly, the model will encourage the identification of product characteristics needed to prevent the growth of *L. monocytogenes*, thereby will make it possible to identify critical control points, and will be useful for compliance with the new European Union regulation on ready-to-eat foods (EC 2073/2005).

Conclusions

Currently, there exists a wealth of data and models that can be used to predict the growth kinetics of *L. monocytogenes* in fish products for the human consumption. Out of which, ComBase is used for this study because of its wide ranging database, reliable results, easy to use and simple. Primary findings have been evaluated using ComBase database in order to develop a future model.

References


A BRIEF REVIEW: EFFECTS OF DIFFERENT DRYING METHODS ON QUALITY CHANGES OF FRUITS

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Abstract

Drying is a conventional food preservation method that inhibits the growth of microorganism in perishable products, such as fruits. The dried fruits qualities are influenced by different dehydration processes, and the most common quality damages are color change, nutrients loss and texture shrinkage. Generally, the hot air drying results in bad product quality, and the products dried by microwave drying are better than the hot air dried products but worse than the freeze dried products. Novel drying methods can lead to similar final quality with a lower process cost.

Introduction

Drying is a thermal process for preserving food products by removing water from the products, extending their shelf life (Maskan 2000). As the water removed during the dehydration process, the water activity of the food decreases gradually, the metabolic activities of microorganism was inhibited. As a result, the shelf life of the food was extended (Nielsen et al. 2012). Among all of the food products, fruits are regard as healthy food for its rich content in vitamins and antioxidant which can help to lower the rate of aging process, cancer risk, and heart disease (Fernandes et al. 2011). Nowadays, the dried fruits products become popular snacks, attractive to both of children, adults and the old. However, the selection of different drying methods is essential for the dried fruits’ quality. Different drying methods can cause different levels of fruits damage, such as the color change, texture shrinkage and nutrients loss (Vega-Galvez et al. 2009).

Conventional drying methods for fruits include sun drying, hot air drying, and microwave drying. Though these methods are cheap, they are time consuming and high process temperature are needed, which will lead to poor quality attributes. Freeze drying and vacuum drying can produce high quality products, but they need high capital cost and electricity consumption. Therefore, some novel fruits drying methods are proposed to reduce the process cost with similar products quality. Such as microwave-freezing drying (Duan et al. 2010), microwave-vacuum drying (Maskan 2000) and ultrasound assisted hot air drying (Ortuno et al. 2010).

The objective of this study was to review different dry methods and investigate their effects on fruit qualities during dehydration process.
**Hot air drying**

Hot air drying is the simplest drying technique, taking place in an open and heated chamber. The hot air works as drying medium. This drying process is accomplished by passing hot air (at designed temperature and humidity) through the food, which is often used for the food products with low value (Rahman 1999). Long drying times and high temperatures are required in this conventional drying method, as the thermal conductivity of food product is low and the heat transfer from the food surface to its center (Maskan 2000).

As the food product exposed to a high temperature for a long time, serious damage occurred on their color, nutrients, flavor, bulk density and rehydration capacity (Maskan 2000). High water content fruits are not suitable for hot air drying due to the long drying time and serious quality damages (Vega-Galvez et al. 2012).

**Microwave drying**

Microwave is a form of the electromagnetic waves that have a frequency from 300 MHz to 30GHz (Sun 2012). It penetrates the food material from inside to the surface first, then the microwave energy transformed to thermal energy and dry the food materials (Mujumdar, 2001). This drying process are composed of three steps. First, in the heating period, the microwave energy transform to thermal energy, then under the high temperature and pressure conditions the moisture loss begins, finally local moisture reduced in a high rate and overheating might occurred.

Compared to the conventional hot air drying, microwave drying is more rapid, uniform and energy efficient. Both of the drying rate and quality of the food products are affected by microwave. As the water molecules can absorb this energy in a very short time and evaporate rapidly, the microwave drying has a high drying rate (Maskan 2000). The drying time decreased from 34 to 8 min by increasing the microwave power output from 180 to 900W (Sun 2012). When increasing the microwave power level from 1.2 to 2.5 W/g, the retention of Vitamin C increased by 87.9% and the density increased by 14.6 in Chinese jujube fruits (Fang et al. 2010). However, the disadvantages for MVD is the uneven heating which might caused by the uneven moisture distribution (Sun 2012).

**Freeze drying**

Freeze drying process takes the advantages of conduction, convection and radiation, forcing the water to evaporate (Sagar and Kumar 2010). During the process, the water of food products is removed under a reduced pressure through sublimation, water removed from solid phase as vapor phase directly. It can be divided into three steps, freezing, primary drying and secondary drying (Mujumdar, 2001). In the freezing stage, the freeze concentration happened and the glassy materials is generated by the ice crystallization, then the water sublimation take place in the primary drying process, finally more water will be lost during the secondary
drying where structure collapse might occur particularly when the products have high moisture content.

Since the food ingredients remains frozen, the freeze drying happened at low temperature, there is no heat damage occurred (Rahman 1999). This process is widely used in the dehydration process of heat sensitive products to maintain a high quality, such as fruits and vegetables. It can result in a high retention of nutrients and a better maintained food texture, and the porous cased by the ice crystal leaving can allow a rapid rehydrate of products. However, freeze drying process has a slow drying rate and a high energy consumption caused by its vacuum and refrigeration system, which means a high capital costs are required for small throughputs (Huang et al. 2012). And the open porous food structure might cause lipid oxidative degradation. Therefore, the processed food products need to be packaged in inert gas.

**Novel drying methods**

In order to prevent the disadvantages of a particulate drying methods, the combination of different drying methods are innovated to optimize the dehydration process, such as reducing drying time, improving energy efficiency and enhancing rehydration capacity (Huang et al. 2012).

Microwave-freezing drying (MFD) is the combination of microwave drying and freeze drying, which can be used to reducing the drying time for high quality product. (Maskan 2000). Because of the moisture remove during the freeze drying process, the thermal conductivity of food ingredient become lower, drying rate decreases along with the drying time increasing. MFD is a promising technique that can accelerate freeze drying process significantly, as the microwave energy can pass through hard material without heating its outer surface. Compared with single freeze drying, MFD can reduce the drying time by 50% with similar product quality (Duan et al. 2010). However, the drying rate for MFD can only be improved slightly when the food ingredient have high water content (Sun 2012).

Microwave-vacuum drying (MVD) is an alternative combining the advantages of low temperature evaporation for vacuum drying and the rapid volumetric heating for microwave drying. It has been widely used for the heat sensitive food products (Maskan 2000). As it takes place at a low pressure, the boiling point of water in the material is reduced, heat damaged could be avoided. Therefore, MVD can achieve fast drying for the heat sensitive products with high quality, compared with the conventional drying methods. Ultrasound assisted hot air drying is also an novel drying method to improve the drying process, the ultrasound can enhance the water transportation process during the orange peel hot air drying so that to reduce the drying time and energy use. (Ortuno et al. 2010).

**Conclusion**

This paper reviewed the process of hot drying, microwave drying, freeze drying and some novel drying methods. The effects of these drying methods on the fruits quality attributes are
different due to their different processing conditions. Generally, the quality of the freeze dried products is the best, the microwave dried products are better than the hot air dried products. Novel drying methods are the combination of two typical drying methods, aiming to reducing the process time but obtain similar products’ quality. The technique selection for the drying process depends on both of food properties and process purpose.

Reference


PULSE ELECTRIC FIELDS AS AN ANAEROBIC DIGESTION PRETREATMENT TO INCREASE THE BIOAVAILABILITY OF LIGNOCELLULOSIC BIOMASS

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Abstract

Anaerobic Digestion (AD) is a versatile conversion technology for converting biomass to biogas. However, pretreatments are needed to make the process more efficient and more viable. The recalcitrant nature of lignocellulosic biomass impedes the hydrolysis stage of AD, this needs to be overcome to be able to efficiently use the cellulose locked inside lignocellulosic biomass such as crop residuals, paper waste and wood residuals. This study aims to investigate whether or not pulse electric field (PEF) treatment will increase the bioavailability of lignocellulosic biomass and look at its potential as a pretreatment for AD.

Introduction

Non-petroleum based fuels are gaining more and more interest in terms of development and utilisation. Biogas from AD is one such fuel. During hydrolysis, the first stage of AD, long chain polymers in the biomass are depolymerised and the subsequent polymers and monomers are solubilised ready to be converted into biogas during the remaining stages. Cellulose is the most abundant biopolymer on the planet and is contained in many forms of lignocellulosic biomass such as crop residuals, paper waste and wood residuals. These are available in large quantities around the world but are mostly unused for AD (Teghammar et al 2012). This is because lignocellulosic biomass is not easily converted to biogas by AD which results in prolonged digestion or hydraulic retention times (HRT) (Jeihanipour et al 2011). Cellulose, hemicellulose and lignin form a complex structure which accounts for some of the difficulty in hydrolysing lignocellulosic biomass. Hydrolysis is the rate limiting step for AD when it comes to lignocellulosic biomass (Ariunbaatar et al 2014). Pretreatment techniques are commonly used with AD to increase the hydrolysis rate and overall efficiency of the process and are a widely researched topic. Pretreatments work in different ways but the main objective is to open up the structure of the biomass to make it less crystalline, this will then leave it more susceptible to enzymatic attack (Carrere et al 2016). According to research by Monlau et al (2012), lignocellulosic biomass will produce higher yields of methane if lignin content is reduced, sugars solubilisation is increased and cellulose crystallinity is reduced. One technology which could have the potential to improve the bioavailability of lignocellulose is pulse electric field treatment (PEF). PEF uses strong electrical fields that are pulsed on and off to influence polar groups such as phospholipids in the periplasmic membrane and peptidoglycan in the cell wall. The pulse shape, frequency and voltage of the electric fields determine how these polar groups are influenced. PEF has been used in medical and food processing studies and applications to create pore openings in cell membranes to increase molecular transport (Lindmark et al 2014). When PEF is used for increasing molecular transport the parameters are selected to keep the voltage across the cell membrane below the critical membrane potential level, this will ensure that the process is reversible. If the voltage across the membrane exceeds the critical limit much larger pores will form and osmotic pressure can provide enough force to lyse the cell. This is irreversible and will usually cause the cell to disintegrate and release the soluble components of the cytoplasm (Zimmerman et al 1974, Zhang et al 2009). It is this action of cell disintegration and the subsequent increase in bioavailability that is of interest when considering PEF as a pretreatment for AD.

The objective of this study is to investigate the application of pulse electric field treatment on lignocellulosic biomass to increase the bioavailability and its potential as a pretreatment for anaerobic digestion.
Materials and methods

Raw materials

Ensiled maize, harvested in November 2015, will be obtained from UCD Lyons Research Farm (Newcastle, Co. Kildare). Freshly harvested Miscanthus will be obtained from the Teagasc Crops Research Centre (Oakpark, Co. Carlow). Rooster potatoes will be obtained from a local supermarket. All samples will be milled to approximately 2mm using a small sample mill, sealed in airtight plastic bags and stored at 4°C prior to treatment.

Proximate analysis

Total solids, volatile solids and ash content of the samples will be analysed using standard procedures as described by the National Renewable Energy Laboratory (NREL) (Sluiter et al. 2008b, Sluiter et al. 2008a).

Pulse electric field treatment

The homogenous samples will be subjected to PEF treatment using a pilot-scale PEF system (ELCRACK HVP-5, DIL, German Institute of Food Technologies). The system will be operated in batch mode, field strength and frequency will remain constant for all treatments, 5kV/cm and 1Hz respectfully. The number of pulses will be varied from sample to sample, 300, 600 and 900 pulses will be used.

Post treatment analysis

The same proximate analysis mentioned above will perform on the samples after treatment as well as a number of other tests selected to indicate if there has been an increase in bioavailability due to PEF treatment.

For the dye uptake test samples will be added to a solution of neutral red dye (molecular weight: 289 g/mol) of known concentration. The samples will be continuously stirred using a magnetic plate stirrer. The concentration of the solution will be measured every 20 minutes for the first hour and every 40 minutes for the next two hours using a Hach Lange Spectrophotometer.

Soluble chemical oxygen demand (SCOD) will be measured using the Lange LCK 114 reagent kit after the samples have been diluted appropriately, stirred for one hour and filtered through a 0.45 μm filter.

Images at x650 magnification of the treated and control samples will be taken using a scanning electron microscope (SEM). The samples will be prepared onto adhesive carbon tape followed by a gold sputter coating.

Results and Discussion

As experimental analysis and preparation is currently ongoing, expected results are discussed here. Many other studies have shown that plant cells can be altered and disintegrated after PEF treatment under certain parameters. It is expected that the parameters used in this paper will disintegrate some cells within the biomass especially the PEF treatment using 900 pulses. The purpose of the three tests that will be carried out on the samples are to show that cells have been disintegrated and that the lignocellulose may be more bioavailable as a result of this.

Kumar (2011) performed the dye uptake test on switchgrass and showed that the concentration of dye in the solution decreased faster for samples that received a more severe PEF treatment. Neutral red dye is a large molecule so any increase in migration of this large molecule from the solution into the biomass suggests an increase in porosity. This increase in porosity would be as a result of
disintegrated cells. Any increase in porosity would improve the bioavailability of the sample by opening it up and increasing surface area for enzymatic attack. Figure 1 is taken from the Kumar (2011) paper and shows the reduction in concentration of neutral red dye over time.

Figure 1. Concentration of neutral red dye for untreated (fresh) switchgrass and switchgrass treated with PEF at 8 kV/cm and 10kV/cm (Kumar et al 2011).

A chemical oxygen demand test is used to test for organic compounds. If cell disintegration occurs there should be a release of intracellular material, mixing the samples in water will allow any of the soluble material to dissolve and therefore pass through the 0.45 μm filter. An increase in SCOD for treated samples compared to the control could suggest that cells have been disintegrated.

Finally, the SEM analysis should give an indication of any changes that are taking place structurally. As mentioned earlier the complex structure of lignocellulosic biomass is one aspect that adds to the recalcitrant nature of it. If SEM images show that the structure has been changed, broken up or that perhaps the structure looks more easily accessible it would suggest an improvement of the bioavailability of the biomass.

The results of these three tests will indicate whether or not the biomass will be more bioavailable after PEF treatment. If the results suggest that the samples are more bioavailable after the treatments it would mean that PEF has potential to be a useful pretreatment for anaerobic digestion by reducing enzymatic hydrolysis times and increasing efficiencies of the process.
Conclusions

If results are seen from theses treatment intensities it could be quite significant and be seen as reasoning to investigate certain aspects of PEF and AD. Kumar et al. (2011) showed an increase in porosity of switchgrass and wood chips using 8kV/cm and 1 kV/cm respectfully after 1000 pulses at 3 Hz. Lindmark et al. (2014) noticed that lower frequency PEF treatment had more of an impact on lignocellulosic biomass but this could not be statistically verified. Although miscanthus and maize are not comparable to switchgrass and wood chips, there could be an argument for more research into the effect of low frequency PEF on lignocellulosic biomass if results show an increase in bioavailability at 300, 600 or 900 pulses at 1 Hz.

References


FEASIBILITY STUDY OF APPLYING CYNAR TECHNOLOGY IN THE GULF COOPERATION COUNCIL COUNTRIES

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Abstract

Waste management is a cross-cutting issue impacting on many aspects of society, environment and the economy. It constitutes one of the greatest challenges facing authorities in the Gulf countries. Plastics waste represents an average 13% of waste in the Gulf countries. Most of the plastic waste is disposed of in landfills without exploiting it. This study is designed to investigate the viability of applying plastics-to-fuel (PTF) technology provided by Cynar Plc. company in the Gulf Co-operation Council.

Introduction

Today, the Gulf Cooperation Council (GCC) countries (the Kingdom of Saudi Arabia, United Arab Emirates, State of Kuwait, State of Qatar, Kingdom of Bahrain, and Sultanate of Oman) have some of the highest per capita waste generation rates worldwide because of fast-paced industrial growth, recent booms in construction, increasing population sizes, rapid urbanization, and lifestyle improvements (Al Ansari 2012). Although most of the waste produced in these countries are largely decomposable and recyclable, the majority of the waste is disposed of in landfills and little is recycled or even managed (Al Ansari 2012). This is not likely to be sustainable over the long term, as preliminary estimates put the total volume of solid waste generated in the GCC states at approximately 120 million tonnes per year (Palanivel and Sulaiman 2014). However, GCC countries have been active in symposia, conferences, and initiatives aimed at combating global warming. Nonetheless, opportunities in the waste sector are still largely unexploited (Al Ansari 2012).

As shown in Table 1, plastic waste ranged between the second and third most represented waste component in the GCC countries, with the proportion ranging from 7.4% to 14%. Currently, most of the plastic waste are disposed of in landfills where the resources it contains are wasted (Alhumoud 2005). Furthermore, the municipalities in this region have not made plans for the recycling of plastics; the only comprehensive form of recycling available within the GCC member states is the recycling of paper and cartons (Alhumoud 2005). However, some of the plastics waste materials of all types are being collected and exported to other Arab countries such as Lebanon, and Egypt for further processing (Alhumoud 2005). It is clear that opportunities for using plastics waste as valuable resources are still to a great extent unexploited in the GCC countries.

According to UNEP (2009), waste plastics are one of the most promising resources for fuel production. Over the past few years, plastics-to-fuel (PTF) technologies have emerged as one potential solution to reducing plastic waste and the landfilling of end-of-life plastics (Ocean Recovery Alliance 2015). Cynar Plc., a PTF company, was established in 2004, with a focus on finding solutions for end of life plastics (Cynar Plc. 2016). Cynar has developed and has patented technology, which efficiently and effectively converts a wide range of waste plastics into useable liquid fuels, mainly diesel (Figure 1). Cynar’s unique technology produces synthetic fuels that considerably reduce greenhouse gas emissions (Cynar Plc. 2016).

The objective of this study is to investigate the feasibility of importing and applying Cynar Plc. plastics-to-fuel technology in the GCC countries.
Materials and Methods

Data illustrated in Table 1 was calculated by taking the average values from the following sources: Al Ansari 2012, Al-Maadeed et al 2012, Urban Environment Team 2013, Hakami and Abu Seif 2015.

<table>
<thead>
<tr>
<th>County</th>
<th>Waste Generation (kg/per capita/day)</th>
<th>Organic</th>
<th>Paper</th>
<th>Plastic</th>
<th>Glass</th>
<th>Metals</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saudi Arabia</td>
<td>1.42</td>
<td>47</td>
<td>21</td>
<td>14</td>
<td>4</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>UAE</td>
<td>1.60</td>
<td>45.5</td>
<td>6</td>
<td>12</td>
<td>9</td>
<td>6</td>
<td>21.5</td>
</tr>
<tr>
<td>Oman</td>
<td>0.85</td>
<td>60</td>
<td>8</td>
<td>12</td>
<td>10</td>
<td>9</td>
<td>1</td>
</tr>
<tr>
<td>Kuwait</td>
<td>1.40</td>
<td>51</td>
<td>19</td>
<td>13</td>
<td>4.5</td>
<td>5</td>
<td>7.5</td>
</tr>
<tr>
<td>Bahrain</td>
<td>1.83</td>
<td>59.1</td>
<td>12.8</td>
<td>7.4</td>
<td>3.4</td>
<td>2.1</td>
<td>15.2</td>
</tr>
<tr>
<td>Qatar</td>
<td>1.37</td>
<td>57</td>
<td>11</td>
<td>14</td>
<td>4</td>
<td>9</td>
<td>5</td>
</tr>
</tbody>
</table>

![PTF technology designed by Cynar Plc. Company](image_url)

**Table 1. Solid waste generation and composition in the GCC countries**

**Research questions**

The research question is: ‘To what extent is the Cynar PTF technology applicable to GCC market and is it a profitable business?’ All activities in the study are directed toward helping answer this question.

**Research objectives**

The key research objectives are:

a) literature review of the Cynar PTF technology; b) identification the opportunities that exist for creating favourable conditions for commercializing this technology in the GCC market; c) assessment of the types and sources of available waste plastics, the supply chain for delivery of these plastics and end-markets for oil products; d) market, technical, financial, economic and legal assessment of applying Cynar technology in Gulf market; e) investigation into barriers that could present challenges for the implementation and commercialization of the Cynar PTF
technology in GCC market; and f) identification and description of alternative business scenarios and models.

Research design
The research is designed to test the applicability and feasibility of importing Cynar PTF technology to the GCC market. This research is designed as a sequential mixed methods research project and consists of a number of stages:
1) A literature review of the Cynar PTF technology and plastics waste market in GCC countries: the review will be carried out through internet research focused on key websites including those of universities, peer-review journals, industry associations and research bodies, as well as information provided by Cynar Plc. Company;
2) Identification and exploration of business scenarios and selected the scenarios that appear to have potential for further exploration; and
3) Assessment of selected business scenarios and models in terms of market, technical, financial, economic and legal aspects: to carry out such investigations, several questionnaires will be prepared, pilot-tested, and provided to solid waste program operators and municipalities in selected cities from the Gulf States. The questionnaires aim to collect the information about the locality type; plastics waste quantities and characteristics collected, collection fees, collection service availability, collection equipment and vehicles, cost and type of fuel use in facilities and vehicles, final disposal methods, location/type of dumping sites, partnership opportunities with Cynar Plc. Company and potential alternative business scenarios and models. Moreover, meetings with decision makers and workers in this field will be arranged.

Results and Discussion
The main results expected from this study are:
   a) Identify and describe alternative business scenarios and models of applying Cynar PTF technology in the GCC countries.
   b) Compare and contrast business scenarios and models based on analytical assessment of market, technical, financial, economic and legal aspects.
   c) Outline criteria for decision making among alternatives.

Conclusions
Today, a large portion of the plastic waste in the GCC is disposed in landfills, where the resources it contains are wasted. Cynar PTF technology has a potential solution not only to reducing plastic waste and the landfilling of end-of-life plastics but also converts a wide range of waste plastics into useable liquid fuels. This study is an analysis of the viability of applying Cynar PTF technology in the GCC countries. The study provides all data necessary for an investment decision on this field. The market, technical, financial, economic and legal prerequisites for an investment project are defined and critically examined on the basis of alternative selected business scenarios and models.

Acknowledgements
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References


Urban Environment Team (2013) *Guidelines for the management of municipal solid waste in the Gulf Cooperation Council (GCC)*, Riyadh: General Secretariat Press of the GCC.

ECONOMIC VIABILITY OF DOMESTIC MICROGENERATION OF ENERGY THROUGH SOLAR PHOTOVOLTAIC IN IRELAND

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Abstract

The use of Solar PV as an energy source has been slow to develop in Ireland in comparison with its European neighbours. Previous studies have suggested that the market has not developed due to solar PV’s economic inefficiency in a country like Ireland and so focus has been placed on other sustainable energy development in order to reduce reliance on conventional fossil fuel energy and reduce greenhouse gas emissions. This study will assess the economic viability of the use of solar photovoltaic energy as part of a micro generative energy system for a domestic setting and whether it is a viable option for energy consumers around Ireland. This will be done by undertaking a cost analysis from the results of software models that focus on optimisation of energy systems from an economic view. As the project is ongoing only expected results have been offered in this paper, where it is believed that the economic viability will be dependent on factors such as market intervention, conventional energy cost and availability of financial support.

Introduction

Based on the Renewable Energy Action Plan (The National Renewable Energy Action Plan for Ireland 2010) it is clear that it is not felt by policy makers that solar photovoltaic will have a significant contribution to Ireland possibly reaching its 2020 targets for renewable energy contribution and reduction of greenhouse gases. This is made clear by the relatively small target of 5MW of solar PV installed capacity in Ireland by 2020. Many critics currently believe we will fall short of the minimum requirements set out by the EU Renewable Energy Directive 2009/28/EC (EU 2009), which demands that 16% of energy consumed being from renewables as well as a reduction of greenhouse gas (GHG) Emissions by 20%. The question is why in Ireland’s renewable energy policy is solar PV left in the wake of alternatives. Previous studies have suggested that it is not yet financially feasible in Ireland. Ayombe et al (2010) state that PV costs are 50% higher in Ireland than other areas with similar climatic conditions, this is mainly due to a lack of financial assistance aimed towards promoting solar PV, which leaves the consumer with very high capital costs to invest in the technology and so acts as a disincentive. Those authors also suggest a need for market intervention through higher feed-in tariffs (FITs) and regulation. This sentiment is also suggested by Li et al (2011) who wrote specifically on the economic viability of domestic applications of solar PV in Ireland. Due to this most papers have suggested that it has not been economically viable, at least at the time those studies were carried out. Following the publication of these papers the cost of PV panels has decreased significantly with mass production and distribution of solar PV panels occurring in the global market, as well as steady increases in efficiencies in various types of solar cells. With this in mind, the question about whether these continuously changing factors have influenced the economic viability of Solar PV in Ireland in 2016 or whether the economic viability is still dependent on external factors like market intervention will be addressed in this study.

The objective of this study is to determine whether the microgeneration of electricity through solar photovoltaic is economically feasible for a domestic consumer in Ireland at present.
Materials and Methods

Data Accumulation
This paper will examine the current PV market in Ireland and globally in order to find the real current costs to the average domestic consumer. At the same time, factors such as legislation, tax incentives, grants and current conventional energy pricings will also be incorporated to create a viable data set for analysis to be carried out on. A broad spectrum of types and sizes of PV systems as well as various locations around Ireland will be taken into account in the data accumulation phase of the project. All these factors will then be placed into a relevant energy system optimisation model in order to assess the economic viability of solar PV being used in a microgeneration setting in comparison to conventional & alternate energy sources.

Optimisation Models
Optimisation models will be built using energy system modelling software, examples of possible software to build an appropriate model are HOMER (Legacy/Pro) and RETScreen. HOMER is a microgrid software developed by the National Renewable Energy Laboratory and used globally for optimizing microgrid design. While RETScreen is a clean energy management software system for energy efficiency renewable energy and cogeneration project feasibility analysis provided by Natural Resources Canada. Some accumulated data such as relevant grants, tax incentives and tariffs or other external duties and benefits that would affect overall cost to the consumer may not be able to be inputted into these software models due to software limitations. In this case a tailored micro energy system model will be constructed using other software such as Microsoft Excel from a combination of the data acquired from the software models discussed as well as external relevant data that was not possible to include in the original models.

Through HOMER and RETScreen, average electrical loads will be generated that are consistent with the theme of the research project, this will be combined with the power output of the solar PV microgenerative energy systems to create models highlighting the optimal energy systems from an economic point of view.

Solar PV Cost Analysis
Following these steps a cost analysis will be undertaken based on the results of the various software models. This will be done by using a number of techniques used commonly to assess economic viability of energy projects. These are Net Present Value (NPV), Internal Rate of Return (IRR) and Payback Period (PBP).

NPV is the sum of present value costs associated with the PV module, initial balance of system, replacement costs and variable costs. It simply assesses a project by comparing future cash flows with initial investment, if the values gained are positive then the project can be deemed economically viable due to the creation of profit. NPV is simplified by the following equation:

$$NPV = R_t - C_t$$

where $R_t$ is the present value of total revenue form the system during its useful life and $C_t$ represents the total system cost (Ayompe et al, 2010). It can also be expressed in a more thorough equation as seen in a paper by Dusonchet and Telaretti (2015) and represented below.

$$NPV = \sum_{t=1}^{N} \frac{C_t}{(1 + i)^t} - C_0$$
The Internal Rate of Return is the rate of return that forces the NPV of the investment to equal zero (Swift 2013). IRR is commonly described using the following formula:

$$C_0 - \sum_{t=1}^{N} \frac{C_t}{(1 + IRR)^t} = 0$$

where $C_0$ is the up-front cost of installation, $N$ is the lifetime of the investment and $t$ is time represented in years (Dusonchet and Telaretti 2015). Analysing the payback period will also be done as part of the cost analysis, with a general view being that the longer the payback period the greater risk to investors.

Comparative analyses will also be undertaken in order to ascertain the differences if existent of costs between other countries with similar endowments of solar insolation and population levels. This will be used to highlight what makes solar PV economically viable in some states and not others and provide a basis for further research into measures to ensure economic viability in the future.

**Expected Results**

The project is still in the data accumulation stage and so it is unclear what the exact results will be so far. Speculation can only be stated based on previous literature and comparisons to countries with similar resource potential. Seeing as other EU countries such as Denmark, which has a similar population and solar insolation to Ireland has reached ‘socket parity’, which is defined by (Bazilian et al. 2013) as the point where a household can make 5% or more return on investment in a PV system just by using the energy generated to replace household energy consumption, it is felt that the factors used to encourage this market to grow in these countries will be the factors that will help Ireland’s PV market grow or stagnate. These factors are generally the level of market intervention stemming government policies, grants, tax incentives and financial assistance available to energy consumers who wish to invest in solar PV, as well as the price of electricity from the standard grid, which can vary considerably for countries that rely on energy imports.

Although it is felt that the price gap between conventional energy and energy from solar PV has been narrowed considerably in recent years, it is felt so far that the level of market intervention favouring solar PV in Ireland will be the deciding factor in its potential economic viability at the domestic energy consumer scale.

**Conclusions**

In conclusion, this study aims to analyse the potential for solar PV in Ireland by looking at it from a cost perspective. It will do this through careful and accurate analysis of various types, sizes and energy levels produced by PV in Ireland at a microgeneration level and cross-analysing this with conventional energy to find which is the optimal energy system for a domestic energy consumer and whether PV can economically fit into that mix. Various energy systems will be analysed in this process, including various types of co-generative systems both including and excluding solar PV. By the end of the study an accurate representation of whether PV is economically viable will be presented and analysed to find the factors effecting PV economic viability. Currently, it is expected that external factors such as those discussed in the Expected Results will be the deciding factor in this analysis based on literature and comparisons to other countries where solar PV has a large market share of energy production.
References


AN ECONOMIC MODEL OF ENHANCED GEOTHERMAL SYSTEMS IN CHINA

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Abstract
Enhanced geothermal is a technology which has the potential to replace coal as the biggest source of base load electricity in the world. Over 65% of China’s primary energy comes from coal and needs to be replaced in order to improve their air quality and to reduce carbon dioxide emissions. The aim of this study is to find coal power plants in China that are located in areas which have a heat gradient good enough to extract geothermal energy. The top five power plants will be chosen for an economic assessment using the Geothermal Energy Technology Evaluation Model (GETEM) to see how much it costs to install and run the EGS project over its lifetime using Levelised Cost of Electricity (LCOE). Northern provinces in China seem like the most suitable areas for EGS projects due to their high coal consumption and high heat gradients.

Introduction
Climate change has become one of the world’s biggest challenges to overcome in our time. It has been estimated that China is responsible for 25% of the world’s CO₂ emissions. The Chinese National Bureau of Statistics has calculated that coal has made up 65% of China’s primary energy consumption since 1978. In a report written by Hao et al. (2015), they state that the provinces with the highest coal consumption were Shanxi, Inner Mongolia, Hebi, Liaoning, Shandong and Jiangsu. It was also stated in the report that Shandong, Guangdong and Jiangsu had the highest amount of thermal power plants with a combined capacity of over 100 billion KWH per year. Hao et al. (2015) believe that the overall coal consumption in China will slow down with annual growth averaging 1.1% between 2018 and 2020. In another study it was shown that the level of PM₁₀ in the 32 largest Chinese cities was 98ug/m³ on average while the World Health Organisation recommends PM₁₀ should not exceed 20ug/m³, which poses a major health hazard for the people living there. In the Northern cities during the Winter, PM₁₀ can average 125ug/m³ and the authors estimate that if that value was dropped to the Los Angeles average of 25ug/m³ then the elderly mortality rate would drop by 15% (Zhou et al. 2015). It is clear that a cleaner solution must be found.

Accord the US Department of Energy, Enhanced Geothermal Systems is defined as ‘engineered reservoirs that have been created to extract economical amounts of heat from low permeability and/or low porosity geothermal resources (Idaho National Laboratory, 2006). In order to extract usable heat (+175°C), a well must be drilled 3-10 km deep depending on the thermal gradient of the area, it must then be stimulated which involves fracturing the rock or opening already existing fractures (hydrosearing), this is then followed by drilling a second well which is used to bring the heated fluid to the surface (producer well). The hot pressurized water is then brought through a power plant (binary, flash or steam) to convert the thermal energy into electrical energy; the fluid is then pumped down the injector well that continues the cycle. The total amount of thermal energy within the earth’s crust is around 540 X 10¹⁷EJ (1 exajoule is equivalent to 10¹⁸ joules), assuming all the energy we consumed came from geothermal, 1% of the energy within the earths crust would provide all our energy needs for 2800 years assuming 500EJ consumption per annum, considering that the earth produces around 660EJ of heat per year, it becomes obvious that EGS is a renewable energy source (Olasolo et al. 2016).

The aim of the study is to locate coal power plants in China that can be economically replaced by enhanced geothermal systems using the GETEM model.
Materials and Methods

Mapping overview
This study has been based on the work of Susan Petty from Alta Rock Energy (Petty 2016). The methods chosen in this study have been taken from the methodology used in her report. A resource assessment must be carried out to see how the thermal heat gradient varies across China. A GIS map will be created which includes a thermal gradient layer, the location and power output of the coal power plants across China and a final layer that shows the relative water scarcity across the country. Once the mapping aspect of the project has been completed, five coal power plants will be selected for modelling.

GETEM Model drilling cost
The Geothermal Energy Technology Evaluation Model (GETEM) will be used to assess the levelised cost of electricity (LCOE) for each site. The price of a barrel of oil (Brent) has dropped significantly $111.87 in June 2014 to $33.2 in February 2016. This has caused a reduced demand for drilling rigs as the oil has become less profitable. Drilling rig rental prices in the US have gone from $35,000 to $15,000 per day since last year (Mallin 2016). As oil drill rigs can be used to drill for geothermal, these prices will be used in the GETEM model. It has been shown however that the conventional rotary drilling technology has a very slow rate of penetration (ROP) in metamorphic and igneous rocks (Yost et al 2015). Down The Hole (DTH) hammer drilling is an alternative way of drilling through igneous rock which is more fuel efficient and ten times faster than rotary mechanisms (Mallin 2016). A new company called Strada Energy has a DTH hammer drill in operation, their company will drill the well, insert the casing pipe, concrete and surface coverage for a price of $2,000/m drilled. The cost of drilling using both rotary and percussion methods will be compared.

Well orientation
It will be assumed in the model that every injector well will have three producer wells each producing between 35-105kg/s, this will be compared to a doublet horizontal well system which have not been used in any EGS project before, however a lot of research has shown that it can increase the volume of the reservoir thus minimising the drawdown temperature over a 30 year life time and it also reduces the investment costs as only two wells are needed (Lowry et al 2014). A schematic of the well orientations can be seen in figure 1. The model assumes that the owner of the plant has access to 40 km² underground, a reservoir thickness of 1,000m and a drilling depth dependant how deep you need to drill to reach 175°C.

The power plant
The model will assume that each EGS power plant has a capacity of 100MW, the injector well needs to be pumped to maintain flow and the plant uses binary technology. The water required to stimulate the well will be derived from the coal power plant’s waste water and the power plant operation requires minimal water because it will be cooled using air. The electricity transmission cost is excluded from the model, as it is right beside a grid connected coal power plant. The siting and permitting time for the project will be reduced significantly as it will be located in an electricity generation zone. Land preparation will also be reduced, as a coal power plant will already have road access and a flat surface area to work with. China was the fastest growing market for district heating systems in the world with surface heating area increasing eight times and pipe length increasing seventeen times between 1995-2012 (Gong et al 2015). District heating will be assessed as a way to increase the efficiency of the system and reduce the LCOE.

Stimulation
Enhanced Geothermal Systems is a technology that is still in its development phase, which means that research being conducted now could have a massive effect on the LCOE in the future. It has been discussed in numerous papers that advances in stimulation techniques can
reduce investment costs as it can increase the reservoir size and conductivity without the need for added drilling. Conventional stimulation techniques such as acid dissolution (McClure and Horne 2014) and new techniques like PAA-CO2 along with other methods will be considered when calculating the cost of the project. PAA-CO2 will require the use of a carbon dioxide pump similar to the ones used in Enhanced Oil Recovery (EOR) projects in the oil industry (Shao et al. 2015).

Operation and Maintenance

One of the biggest cost of an EGS project according to (Lowry et al. 2014) is the operation and maintenance of the facility, this has a lot to do with the labour costs of running and maintaining the power plant however, the labour cost used in the default GETEM model assumes American labour costs which must be changed to account for Chinese labour. Taxation and insurance is also included and must be adjusted accordingly. The cost of building a geothermal power plant is capital intensive which is why a loan will need to be taken out to cover the cost of the project, the rate of interest from a Chinese bank will need to be considered to make an accurate location based assumption of the cost of capital. Other financing options will also be considered to minimise costs.

![Figure 1.](image)

**Figure 1.** Left: Geothermal heat gradient °C/km of China (source (Feng et al. 2014)); Right: Well orientation schematic (source Lowry et al. 2014)

**Expected Results**

The aim of the project is to locate the best place to install an EGS power plant where a coal power plant already exists purely based on the LCOE of the project. There are many factors which need to be considered before making an accurate assumption however the most important one for this project is the thermal gradient of the chosen site as it will affect the drilling cost. The utilisation of geothermal energy in Inner Mongolia, Shanxi and Liaoning seem like the best places to drill due to high thermal gradients as seen in figure 1 and because of their high demand for coal use in those provinces. EGS is highly dependent on water for initial stimulation and for topping up the reservoir due to losses in the system which means that the optimal location will be in an area with low water stress. It has been shown in numerous reports that a doublet horizontal well orientation has a reduced temperature drawdown and lower LCOE compared to vertical or inclined wells, which is why this method might be chosen in the GETEM model. PAA-CO2 seems like a highly promising stimulation technology and it will be assumed that it will increase the energy output. Costs of labour should be cheaper in china and the rate of tax will be less, as it is a developing technology that will reduce the operating and management expenses. The cost of capital is a major issue for a project of this scale due to the very high initial investment costs, a loan from the government or money from the nations pension fund could be used, as they will require a lower rate of interest compared to a bank.
Conclusion
EGS must be nurtured in China as it is in Europe, Australia and the United States due to their demand for base load electricity and need for a low carbon energy source. Using a combination of new drilling technologies, innovative stimulation techniques, cheaper operating and management costs and creative financing it could be possible to produce electricity from EGS economically in the future. It will probably not be the cheapest source of renewable energy available within the country however the advantage of continuous power will appeal to a nation that sources 65% of its energy from coal power stations.

Acknowledgements
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References
DEVELOPING AN ANALYSIS OF FRENCH COASTLINE PROTECTION FROM EROSION USING WAVE ENERGY CONVERTERS

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Abstract
Erosion is a major concern for French coastlines and the government has difficulties in dealing with it. At the same time, renewable energy is a growing sector pushed by European and national legislations and energy demand. This thesis aims to develop a tool in order to analyse the utilization of wave energy converters for protection of French seashores and energy recovery. A combination of two models will be built to estimate the coastline evolution according to the sea state of a specific site and the amount of generated energy: a wave propagation model and a morphodynamic one. Wave energy converters will then be implemented into this combination, and the sensitivity of the results to several parameters (type of wave energy converters, positioning, etc.) will be analysed and discussed.

Introduction
Research and experimentation on wave energy is developing rapidly worldwide. It is especially true in Europe where 45% of the wave energy developers and most infrastructures are situated. This interest in wave energy is stimulated by a considerable amount of available energy but also by European and national policy actions. In 2009, the EU’s Renewable Energy Directive (2009/28/EC) introduced the well-known “20-20-20” targets and gave a legal framework for promoting renewable energy. It also required every member state to define specific objectives in National Renewable Energy Action Plans to detail their commitment in this ongoing process of reducing greenhouse gases emissions (Magagna and Uihlein 2015; O’Hagan et al. 2015). As regards France, 23% of the total consumed energy and 27% of electricity must be provided by renewable energies by 2020. The induced emissions saving is not the only purpose of this target. France is greatly reliant on fossil fuels imports, and developing renewable energies such as wave energy will reduce this reliance and therefore increase energy security. France intends to become a major actor in the renewable energy sector which is growing rapidly, encouraging technological innovation and constituting an economic boost. As concerns wave energy, the French government has evaluated a potential of 200 MW operating 4,000 hours each year. Considering that this technology is in its early stage of development and other associated barriers, the retained objective for 2020 is 200 GWh which is 0.13% of the total renewable target of 27% for electricity (Ministère de l’Ecologie, de l’Energie, du Développement durable et de la Mer 2009).

Erosion has been a major problem for French coastlines. About one quarter of the coastlines are eroding and this has been recognised since 1987, however the French government has had difficulties dealing with this problem. Two main reasons can be highlighted when stressing the need for its protection. More than 25% of the terrestrial land within 500 metres of the seashore is built upon, compared to only 5% for the overall French territory. The second reason is the biological diversity of the French seashore, which needs to be preserved (Institut Français de l’Environnement 2006). Combining the generation of electricity with the need to protect the coastline from erosion can strongly push the development of wave energy, which is needed and an opportunity for France. It would provide renewable electricity for an always developing area and reduce the energy cost of wave energy, which is currently a major barrier to the development of this technology (Mendoza et al. 2014).

The objective of this thesis is therefore to analyse the possible utilization of wave energy converters to protect the French coastline from erosion.
Materials and Methods

Site selection
The first step of this thesis is the choice of a specific site to study. Figure 1 is a map of France which displays the coastline evolution of each state. What can be underlined, using this map, is that the northern seashores are highly subjected to erosion. The average percentage of the seashore endangered by erosion in each state is 31% whereas it reaches 85% and 92% respectively in the Pas-de-Calais state and the Seine-Maritime one. The specific site which will be studied in my thesis will therefore belong to one of these two states (Institut Français de l'Environnement 2006).

Figure 1. Coastline evolution in France (Institut Français de l'Environnement 2006)

Sensitivity to erosion depends on the nature of the considered coastline. Chalk cliffs are the type of seashore that are the most affected by erosion and nearly all of them are moving back through the years. Erosion also constitutes a meaningful concern for beaches composed of sand, as two thirds of them are reported to recede each year. However, granite and metamorphic rocks coastlines are stable for the great majority. Muddy seashores, that is to say bays, estuaries and seaboard swamps, are even known to generally be sedimentation areas. Accommodation, industry and tourism facilities are being developed more on sand coastlines than on chalk cliffs. A sand beach will therefore be considered in this study (Institut Français de l'Environnement 2006).

Wave propagation model
Two models will be required to meet the objective of this study. The first model is a wave propagation model and is used to simulate the evolution of the wave status while spreading from the open sea towards the coastline. The main required data for this model, concerning the waves, is height, period and direction. This data can be collected from a combination of existing large wave models (for offshore data) and physical sensors (for nearshore data). Considering the limited available time and means for this thesis, using physical sensors is obviously impossible. The choice of the studied site will therefore rely on previous scientific studies in which nearshore data is available and can be directly used (Abanades et al 2014). Different scenarios will then be required to best represent the reality due to the potential high variability of the data. The studied period will be divided according to the dominant sea state in the considered site. Constant inputs for wave data will be given to each scenario. Consequently, a complex variable reality is transformed into a sequence of scenarios to simplify the model (Mendoza et al 2014).

There are several scientific methods to deal with propagation model, such as analytical models or boundary element methods. A review of all those methods can be found in Babarit (2013). In this study, a specific software will be used and described as a later stage.

If the available data enables it, there will be 2 different resolutions concerning the computational grids of this wave propagation model. The onshore grid will have a higher resolution than the offshore one due to the requirement of having an accurate evaluation of the impact of the wave energy converters on wave energy status in this area (Abanades et al 2014).
Boundary conditions will then be implemented in the wave propagation model, depending on the studied site. The open sea edges of the model will be defined as open boundaries, whereas the edges in contact with a land will require a reflection coefficient of 0.3 (Mendoza et al 2014).

**Morphodynamic model**

The second model to be built is a morphodynamic model. This model will be used to evaluate the modification of the beach profile over the studied period. The inputs are obviously the original shape of the seashore, but also the propagation cartography generated by the wave energy model. Correlations describing sediment transportation are then resolved to model the morphological changes of the considered coastline. The software which will be used in this study will be described at a later stage. For this kind of model, the results on the shore can be analysed on an imaginary line moving toward the land, one parallel to the land, or on each point of the coastline (Abanades et al 2014; Abanades et al 2014; Mendoza et al 2014). One of these options will be selected for this thesis depending on the available data, even if the last option would be preferred as it will obviously give a more detailed overview of the results.

**Wave energy converters**

After the combination of the wave propagation model and the morphodynamic one, wave energy converters will be implemented into the first of the two models. The influence of wave energy devices on wave height is illustrated in figure 2, which is a wave propagation cartography, in which wave energy converters have been implemented. Each type of wave energy converter has a different impact on wave energy, and therefore on wave height, due to its specific transmission coefficient, defined as:

\[ K_T = \frac{H_T}{H_I} \]

where \( H_T \) is the incident wave height and \( H_I \) the wave height behind the WEC (Zanuttigh and Angelelli 2013).

![Figure 2. Propagation cartography with wave energy converters (Abanades et al 2014)](image)

Each type of wave energy converter is also able to generate a certain amount of electricity with a given wave energy. To evaluate the absorbed wave energy by a specific kind of device, its power matrix must be multiplied by the scatter diagrams of wave statistics (Babarit et al 2012). The considered device is therefore an important factor for the two main overall results of this thesis, which are energy generation and coastline protection. Other parameters have an impact on these results such as the number of devices, their positioning and the distance between them and the coastline. All these factors will be taken into consideration in this thesis.

**Expected results**

The coastline evolution will firstly be compared with and without the presence of the wave energy converters. In a second time, the factors relating to the wave energy converter, which are mentioned in
the previous paragraph, will be modified to analyse their influence on electricity generation and the degree and area of protection. Several indicators will be used to analyse the results concerning erosion: bed level impact, eroded area, non-dimensional erosion reduction, and mean cumulative eroded area (Abanades et al. 2014). It can be assumed that the size of protected area and the amount of generated energy will increase with a growing distance between the wave energy converters and the coastline, whereas the degree of protection will decrease. This is due to the higher available energy in offshore areas and to the redistribution of energy into the shadow generated by the wave farm (Abanades et al. 2014). The influence of the number and positioning of the wave energy converters is less obvious to predict because of the possible park effect. The park effect is the interaction between each wave energy device, due to the diffracted waves they produce. It can be neglected from a certain distance between the several devices (Babarit 2013). In this study, it will first be not considered and may be taken into consideration in a later stage.

Conclusion

This thesis addresses two challenges that France is currently facing: the protection of the coastline against erosion and the development of wave energy. A parametrized model will be built to study the influence of several wave energy converters’ parameters on the generated energy, and the area and degree of protection they can provide. With this tool, two practical applications will be possible:
- For a required area and degree of protection, determine the best set of parameters to maximise the amount of generated electricity
- In other situations, find the best trade-off between protection of the coastline and generation of electricity

References

FEASIBILITY STUDY OF AN OFFSHORE WIND FARM TO BE LOCATED IN THE TURKISH SEAS

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Abstract

Offshore wind power will potentially play a key role for Turkey to achieve 2023 targets due to its favourable geographical location. However, there are currently no offshore wind farm projects. The aim of this study is to determine the feasibility of an offshore wind farm on Turkish seas. Current status regarding the market, wind power potential, and policy will be overviewed. Considering the wind speeds and other factors, a location will be proposed. Issues with the current supporting mechanism are identified, and solutions are proposed for the future development of offshore wind farms in Turkey.

Introduction

With the accelerated industrialization and increased population trends all over the world, many concerns, such as energy security, fossil fuel depletion, environmental issues, and the increase in energy demand have led countries to search ways of deploying the renewable energy potentials. Among the alternatives, wind energy is a promising source and has been exploited for over a century. Research on wind energy has gathered momentum, and wind energy penetration started first in USA after the oil crises in 1970s (Kaldellis and Za 2011). Then, it has shifted to Europe; making Europe the leading market on the global scene for wind energy since 1990s (Kaldellis and Za 2011). The EU has set the 2020 targets to increase the use of renewable energy to 20% under the Directive 2009/28/EC. Today, one of the candidate countries for the EU, Turkey, has been a part of the G20 forum with a fast emerging economy, with its GDP ranked 18th in the world (IMF 2015). All of this enables Turkey to be a major regional power. Regarding the 100th anniversary of the foundation of the Republic of Turkey, Turkey has set ambitious goals targeting the share of 30% renewable energy sources of total electricity generation and building 20 GW capacity of wind energy (Melikoglu 2013).

Wind energy can be exploited in two ways: onshore and offshore. While onshore wind turbines have been utilized for over a century, offshore wind power is fairly new; with the world wind energy market having a transition to offshore sites recently (Markard and Petersen 2009). Higher wind speeds and more stable wind flows beyond the coasts, due to the absence of the obstacles at sea capable of disrupting the wind flow, result in higher power potential compared to onshore. Also, larger turbines capable of generating more power can be installed on the sea due to the ease of transportation of larger equipment by ships, whereas logistic challenges and physical barriers are encountered on onshore wind projects, such as relatively smaller roadways, bridges, etc. Larger turbine sizes reduce the costs of non-turbine project elements considerably, however offshore wind power is still more capital intensive compared to the onshore counterpart (Sun et al 2012).

In 2015, led by the UK, installed offshore capacity in the EU reached 7748 MW, starting in 1990 (Rodrigues et al 2015). Even though Turkey is surrounded by sea on its three sides, which makes it conducive to offshore wind energy, Turkey has not started to contribute to this capacity yet (Kaplan 2015). Moreover, there is a lack of research in offshore wind in Turkey.

The objective of this paper is to evaluate the feasibility of an offshore wind farm to be located in the Turkish seas regarding technical, economical and policy aspects.
Materials and Methods

Current market
Total gross electricity generation in Turkey was 251,962.8 GWh in 2014, 21% of which was from renewable energy sources (TETC 2016). As of the beginning of January 2016, cumulative installed wind power capacity was 4.718 GW (TWEA 2016).

Offshore power potential
According to the study of Malkoc (2007), Turkey has economically viable wind power potential of 47,849 GW, 10,463 GW of which is from offshore wind as shown in Table 1. Currently, installed wind capacity is 9.6% of the total potential, but none of this is from offshore projects.

Table 1. Onshore and offshore wind power potential of Turkey (Malkoc 2007)

<table>
<thead>
<tr>
<th>Wind Power Class</th>
<th>Resource Potential</th>
<th>Wind Power Density at 50 m (W/m²)</th>
<th>Wind Speeda at 50 m (m/s)</th>
<th>Total Power Potential (MW)</th>
<th>Total Offshore Power Potential (MW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Good</td>
<td>400-600</td>
<td>7.0-7.5</td>
<td>29259</td>
<td>5133</td>
</tr>
<tr>
<td>5</td>
<td>Excellent</td>
<td>500-600</td>
<td>7.5-8.0</td>
<td>12994</td>
<td>3444</td>
</tr>
<tr>
<td>6</td>
<td>Outstanding</td>
<td>600-800</td>
<td>8.5-9.0</td>
<td>5399</td>
<td>1742</td>
</tr>
<tr>
<td>7</td>
<td>Superb</td>
<td>&gt; 800</td>
<td>&gt; 9.0</td>
<td>195</td>
<td>142</td>
</tr>
</tbody>
</table>

*aWind speeds are based on a Weibull k value of 2

Offshore wind speeds
Wind power speeds around Turkey are published by Wind Power Potential Atlas (REPA) prepared by EIE (currently called YEGM, General Directorate of Renewable Energy). YEGM is the sole governmental body in Turkey for the development of renewable energy policies. In Figure 1, majority of the high wind speeds are observed in throughout the Aegean Sea, and partially in Marmara Sea, central North Sea and Mediterranean Sea.

Current regulatory environment
Even though Turkey has high renewable energy potential, only a few promotional measures were proposed, and no financial support was available until the early 2000s. The priority was only given to large hydropower projects (Murat Sirin and Ege 2012). With the enactment of the Law on Utilization of Renewable Energy Resources for Generating Electrical Energy (the RER Law, Law No. 5346) in 2005 which aims to expand renewable energy utilization by various mechanisms, the licence applications to renewable energy projects increased notably. One of the mechanisms the law introduced was fixed feed-in tariff (FiT) for all types of sources. After 2005, unit capacity of wind turbine increased from kilowatts to megawatts, and since 2006 the installed wind power capacity underwent a rapid increase (Dursun and Gokcol 2014). The second important legislation is the amendment to the RER Law which was
promulgated in 2010 (Law No. 6094). The Renewable Energy Support Mechanism was introduced, priority was ensured for grid connection to renewables, and FiT rates was regulated according to the source type to be applied for first 10 years of the operation. FiT for wind energy project is regulated as 7.3 USD cent/kWh. Also, incentives for local content is introduced. According to this, a bonus to FiT is applied for locally manufactured electro-mechanical equipment used in power generating systems. Regarding the wind turbines, for locally manufactured turbine blades, turbine tower, generator and power electronics, and mechanical equipment in rotor and nacelle groups, a maximum FiT of 11 USD cent/kWh is applicable for 5 years. Also, the law exempts individuals and corporate entities from licencing for maximum installed capacity of 1 MW.

**Economical aspects**

Offshore wind farm economics is based on two main factors (Pantaleo et al., 2005). First is the annual energy yield, considering the wind farm design, wind flow predictions, capacity factor, and electrical transmission system. The other one is the investment and O&M costs. The major factor on costs is the number and size of the turbines. Support and installations costs are correlated with sea depths, and distance to transformer station on the shore is effective on the grid connection costs. Although offshore wind investors have little influence on these factors, proper site selection can increase the profits (Snyder and Kaiser 2009).

**Results and Discussion**

**Proposed offshore wind farm location**

The proposed location in Figure 2 is 1.5 km away from Bozcaada, an island 8 km away from the mainland. According to the nautical charts of the Turkish Office of Navigation, Hydrography and Oceanography, proposed location has an average sea depth of 10 m. There is already an onshore wind farm with a capacity of 10.2 MW located on Bozcaada, therefore existing electricity transmission infrastructure may reduce the costs. Also, since there is no Greek Island in the vicinity of that region, territorial waters are not an issue.

![Figure 2. Proposed offshore wind farm location (left), zoomed out location of the offshore wind farm in Aegean Sea (right)](image)

**Analysis of the support mechanism**

From the insights developed during this still-ongoing study, the current FiT for wind energy projects is found to be insufficient for offshore wind power development in Turkey. The comparison of the current supporting mechanism with the EU countries presented in the study of Green and Vasilakos (2011) reveals that a separate, higher FiT is required for offshore wind power than the onshore counterpart. Considering the long return of investment due to capital intensive nature of offshore wind power, the current validity of 10 years for FiT is making the offshore investment unattractive in Turkey. After 10 years, profitability of the offshore wind projects may be based on the price set by the market which results in a risk. Considering the inadequacy of the current support mechanisms, it can be interpreted that there is a lack of interest by the government to the offshore wind projects.
Conclusions

Offshore wind power is shown to be a very promising source of renewable energy for Turkey on its way to achieve 2023 targets. In this regard, Bozcaada region on Aegean Sea is proposed for the development of an offshore wind farm due to high wind speeds, and other important factors. The assessment of the power capacity to be proposed, and economical and technical analysis of the offshore wind farm will be carried out at a later stage of the study. Regarding the policy, current support mechanism in Turkey is not sufficient, and an amendment is required to the RER Law for making offshore wind power investments to be feasible and attractive. Fiscal incentives and public finance which are widely employed in the EU countries should also be introduced in Turkey by the government to support offshore wind power projects.

References

INVESTIGATION OF POST-HARVEST LOSSES IN THE TOMATO SUPPLY CHAIN IN THE NASHIK DISTRICT OF INDIA

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Abstract

The reduction of post-harvest losses is an urgent need for a country like India whose population is 1.252 billion and it is increasing with annual population growth rate of 1.2%, so if the food losses will continue then it will be a big challenge for India to feed such a big population. The major post-harvest losses occur in fruits and vegetables as their life cycle is very short. The tomato has a very short shelf life and the chances of post-harvest losses are very high if compared with other vegetable crops. To calculate the exact post-harvest losses of tomatoes, a micro level investigation was done by choosing Nashik district which is the major tomato producing region in India and exact losses were calculated. The results showed that the post-harvest losses of tomatoes increase with the increase of intermediaries in the supply chain, also other problems such as lack of low cost cold storage facilities and improper packaging techniques at farm level lead to high post-harvest losses.

Introduction

The Global Hunger Index places India 55th out of 76 countries, so food security is a very important issue as many people are dying due to starvation. India ranks fourth in the worldwide production of tomato and tomato is the second largest produced vegetable after potato in India (Kalidas et al 2014). The tomato is scientifically a fruit but in culinary terms it is considered as a vegetable. The production of tomato in the year 1991 was 4,243,000 metric tones and as per latest data it was 18,735,000 metric tones in the year 2013 (NHB 2015), so statistics show that the production is increasing every by year. The Nashik district is the biggest market for tomato in India and the tomato is grown over an area of nearly 125,000 hectares, where climate conditions are such that the tomato can be cultivated in any month of the year (NHB 2015). In the Nashik district, there is adequate attention paid by the government or the National Horticultural Research and Development Foundation at the pre-harvest stages for boosting the levels of tomato production by training or guiding farmers about plant protection, soil conservation, pest control, fertilisers, etc., but after harvesting, it is necessary to have further training and guidance for farmers about the optimum manner to sell produce to maximise profits; at the moment due to improper management, some tomatoes get spoiled before reaching consumers.

The major post-harvest losses of tomatoes occur at each stage of its supply chain, which includes producers, commission agents, traders, wholesalers and retailers. At each point, there is storage as well as transportation, so even a small mistake can lead to post-harvest losses (Halder et al 2011). The average land per farmer in India is less than one hectare and because of this, the farmer sells the produce to the trader at the price set by the trader. Another reason for selling the produce at low cost is because the farmer does not have access to cold storage and he has to sell his produce as early as possible to support his family; this forces him to sell his produce at the price fixed by the trader which results in traders, wholesalers and retailers earning more profit than the farmer (Sazzad 2014). A small improvement can stabilise food prices as well as reduce the post-harvest losses of tomato and save lives of many people (Adepoju 2014). Therefore, the entire supply chain of tomato in the Nashik district and post-harvest losses of tomatoes at each stage of that chain have been studied for identifying the hotspots that lead to post-harvest losses.

The objectives of this study were to identify the different channels through which tomatoes reach consumers in India, to determine the post-harvest losses occurring at each stage, and to devise appropriate solutions to reduce such losses.
Materials and Methods

The Nashik district of Maharashtra state was selected for this study because Nashik district produces tomatoes all year round and it supplies tomatoes to different states of India and exports it to the neighbouring countries when there is an increasing demand. The study was done by randomly selecting 2 tomato growers from different places of Nashik district. The channels through which they sell their tomato after harvesting were studied and the data for profits received by each stakeholder in that channel was collected for analysis. Further to this, data was collected by studying each channel and the post-harvest losses occurring in each stage of that channel. The questionnaire technique was also used to take feedback from each stakeholder involved in the supply chain of tomatoes. The survey was done to identify problems faced by each stakeholder and then this feedback can be used to develop new practices to minimise post-harvest losses.

Results and Discussion

Preferred varieties
Pusa Hybrid 2 and Pusa Hybrid 4 are the most widely preferred variety by more than 70% of the tomato producers in the Nashik district because the yields are very high (NHB, 2015).

Market price
The data for monthly average price (Rupees/quintal) given for the tomato produce by the registered middlemen in markets of Nashik district was taken from the National Horticulture Board, Ministry of Agriculture, India (NHB, 2015) and the details are shown in Figure 1.

![Figure 1. Average monthly price at markets in the Nashik district for tomato produce in 2014](image)

Distribution channel for tomato produce
The distribution channel for tomato produce was studied by comparing two different farmers producing tomatoes. The channel used by the first farmer is shown in Figure 2 and from that it can be seen that the produce is exchanged through many different intermediaries before reaching the consumer. The channel used by the second farmer is shown in Figure 3 and from that it can be seen that there are no intermediaries.

![Figure 2. Channel used by farmer 1 to sell tomato produce](image)

![Figure 3. Channel used by farmer 2 to sell tomato produce](image)
Post-harvest losses
At farm level the post-harvest losses are due to mechanical damage to the produce during harvesting, packaging and transportation. The main problem that was seen at the farm level was that farmer 2 used wooden crates for packaging and then transporting it to the nearest market to sell it directly to consumers, but the wooden crates had sharp edges as well improper ventilation leading to further post-harvest losses. The whole produce was sold after 4 days and within those 4 days, farmer 2 always had some unsold tomatoes that were brought back from market to his warehouse. This transport and lack of cold storage at his warehouse resulted in high post-harvest losses. Farmer 1 had post-harvest losses due to damage, and harvesting at the wrong time. On the first day i.e. after harvesting, market demand was poor; meaning farmer 1 had to return the unsold tomatoes back to his warehouse which lacked cold storage, resulting in further losses. On day 2, he returned to the market, selling the produce to the trader.

Table 1. Total calculated post-harvest losses (Kg/100 Kg of production) at each stage of distribution channel

<table>
<thead>
<tr>
<th>Stages</th>
<th>Farmer 1</th>
<th>Farmer 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total quantity</td>
<td>Total quantity</td>
</tr>
<tr>
<td></td>
<td>remaining after</td>
<td>remaining after</td>
</tr>
<tr>
<td></td>
<td>post-harvest</td>
<td>post-harvest</td>
</tr>
<tr>
<td></td>
<td>losses (Kg/100 Kg)</td>
<td>losses (Kg/100 Kg)</td>
</tr>
<tr>
<td>Farm level</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>(Collection + Packaging +</td>
<td>90</td>
<td>80</td>
</tr>
<tr>
<td>Transportation + Unloading)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trader level</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>(Sorting + Repacking +</td>
<td>86</td>
<td>-</td>
</tr>
<tr>
<td>Transportation + Unloading)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wholesaler level</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>(Sorting + Repacking +</td>
<td>82</td>
<td>-</td>
</tr>
<tr>
<td>Transportation + Unloading)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Retailer Level</td>
<td>6</td>
<td>-</td>
</tr>
<tr>
<td>(Sorting + Repacking)</td>
<td>76</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>24</td>
<td>20</td>
</tr>
</tbody>
</table>

The trader who purchased the tomato produce from farmer 1 carried out repacking because he sold it to different wholesalers in different quantities, so the post-harvest losses occurred due to repacking, transportation and environmental conditions. The losses at wholesaler level occurred due to repacking of the tomato produce as he sold to different retailers in different quantities and again the packaging was inadequate. The retailer received the tomatoes but some tomatoes were damaged in transportation and that quantity was disposed. Again, there was a lack of cold storage facilities at the retailer level and if the customer does not purchase tomatoes early, the retailer will have further losses.

Lack of low cost cold storage facilities
The Nashik district has cold storage facilities for nearly 70% of the overall tomato produce, but all the facilities are private and very expensive, so farmers end up selling it to traders at low cost rather than keeping the produce in cold storage facilities. There is an urgent need to educate farmers about the available techniques for building low cost cold storage facilities to avoid post-harvest losses; also the government could build cold storage facilities for tomato producers where they could keep their produce at lower cost.
Losses due to improper packaging of tomatoes

Nearly 75% of Indian tomato producers use wooden crates to minimize overall cost as they are cheaper than plastic crates, but this material difference leads to more post-harvest losses. When the total cost of plastic and wooden crate was calculated by contacting suppliers, it was proven that with the use of wooden crates the post-harvest losses are high. Therefore, it is better to use plastic crates from a long term point of view and post-harvest loss perspective. However, this does not take into account the environmental sustainability of the materials used.

<table>
<thead>
<tr>
<th>Table 2. Analysis of packaging material for tomatoes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Details</td>
</tr>
<tr>
<td>--------------------------</td>
</tr>
<tr>
<td>Cost (Rupees/crate)</td>
</tr>
<tr>
<td>Capacity (kg)</td>
</tr>
<tr>
<td>Life (year)</td>
</tr>
<tr>
<td>Cost (Rupees/qtl)</td>
</tr>
<tr>
<td>Post-harvest losses (%)</td>
</tr>
</tbody>
</table>

Conclusions

The study was done by comparing the distribution channels used by two tomato producers of the Nashik district in India. The overall post-harvest losses calculated were 24% and 20%, respectively. The post-harvest losses for the first producer were mainly because of a lack of cold storage facilities, improper handling of produce and a very high number of intermediaries involved in the distribution chain. The data analysis for second producer concluded that the lack of cold storage facilities and improper packaging material (wooden crates) lead to high post-harvest losses. The data analysis concluded that the losses increase with the addition of more intermediaries. It was also shown that the use of plastic crates is the best solution for avoiding post-harvest losses due to packaging.

References


ASSESSING THE IMPACT OF AMMONIA EMISSIONS FROM COUNTY LIMERICK BROILER HOUSES BELOW THE EPA LICENSING THRESHOLD

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Abstract

Guidelines set by the Irish Environmental Protection Agency (EPA) require intensive poultry units with over 40,000 birds to require IED/IPPC licences. Each farm is licensed to contain a maximum number of chickens, though this maximum may not always be met. Licensed farms submit records of ammonia emissions based on emission factors per bird, whereas farms which fall below 40,000 birds are not required to report data. Farms which are below the EPA licensing threshold also produce ammonia which influences the neighbouring environment, although the extent of such impacts has heretofore not been assessed.

Introduction

Agriculture is the primary source of atmospheric ammonia. Cattle production accounts for 80% of ammonia emissions (EEA 2016) and is regarded as its largest source (Bussink and Oenema 1998). The pig production industry is ranked second when compared to cattle farming, accounting for 7% of national emissions. Poultry are relatively insignificant when compared to ammonia emissions from pigs and cattle (EEA 2016), accounting for 2% of Ireland’s emissions. Although poultry farms have relatively low emissions when compared to pigs and cattle, their contributions must be considered as part of a cumulative assessment. The cumulative impact of multiple unmapped farms in addition to those which exceed the licensing threshold could have potentially significant impacts.

This investigation will be done on a local basis and hence the effect of ammonia in the local zones will be assessed. The critical levels of ammonia are 1 µg/m³ and 3 µg/m³, for sensitive species (lichen and moss) and higher plants. Since pigs and poultry are raised in enclosed units, they are hence considered hotspot sources of ammonia. The mapping of ambient ammonia concentrations for Ireland was carried out in 1999-2000 by the EPA; these maps are currently being updated by the AmmoniaN2K Project.

This paper summarises the work that will be done in order to locate broiler units in County Limerick which are under the EPA licensing threshold. This county was chosen due to the relatively large number of poultry farms which are below the licensing threshold. The ammonia emissions from such units will then be assessed. This project creates scope for further study in the mapping and assessment of integrated farms for pigs and also assesses their ammonia emissions at a local level.

The objective of this study is to locate and assess the ammonia emissions from broilers units in Limerick which are below the EPA licensing threshold by using Geographical Information Systems.

Materials and Methods

Study area

County Limerick will be assessed in this project, as it has the highest difference between licensed and unlicensed broiler birds in the Republic of Ireland (Table 1). The assessment was carried on the basis of the counties with the highest number of IPPC (Integrated Pollution...
Prevention Control) broiler farms relative to the counties with the lowest number of IPPC broiler farms.

Table 1. EPA licensed and unlicensed broiler farms in selected counties in Ireland.

<table>
<thead>
<tr>
<th></th>
<th>CSO Farms</th>
<th>IPPC Farms</th>
<th>CSO 2010 Birds</th>
<th>IPPC 2014 Birds</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limerick</td>
<td>60</td>
<td>8</td>
<td>1,180,443</td>
<td>578,500</td>
<td>601943</td>
</tr>
<tr>
<td>Cavan</td>
<td>20</td>
<td>3</td>
<td>815,537</td>
<td>332,000</td>
<td>483537</td>
</tr>
<tr>
<td>Waterford</td>
<td>20</td>
<td>7</td>
<td>747,122</td>
<td>519,000</td>
<td>228122</td>
</tr>
<tr>
<td>Cork</td>
<td>60</td>
<td>6</td>
<td>360,523</td>
<td>136,000</td>
<td>224523</td>
</tr>
<tr>
<td>Monaghan</td>
<td>30</td>
<td>45</td>
<td>4,459,667</td>
<td>4,513,017</td>
<td>-53350</td>
</tr>
</tbody>
</table>

Input data
The manual survey of farms below the threshold is being carried out using satellite imagery available in ArcGIS. County Limerick is surveyed with the help of ArcGIS and it is divided into a network of 1 km$^2$ grids. Each grid is selected individually and the area is assessed. Locations of licensed farms are being mapped, and are included in the ArcGIS workspace as a shapefile. The unlicensed farms are surveyed in every grid and each building in that area is surveyed for the presences of structures such as silos and vents in addition to assessing the shape and structure of the building. This information reflects the possibility of an intensive agricultural unit. Once all units are mapped, the local planning authority website can be searched to view the type of farm present at each identified location.

Results and Discussion

Figure 1. Locating an unlicensed broiler unit in Limerick along with close-up.

Figure 1 shows the view of an unlicensed intensive agricultural unit in County Limerick; the area within the red square depicts an area of 1 km$^2$ which was manually located and assessed with the use of ArcGIS software.

Further scope of study
The next step is to model and map the local level impact of ammonia from identified poultry houses, while in the future, the same methodology can be used to carry out the local level impacts from pig farms.
Conclusions

At this point in the study, a limited number of 1 km\(^2\) grids have been surveyed. Further assessment will be carried out to find other unlicensed broiler houses in County Limerick. This will allow the identification of the unlicensed broiler houses and assess the ammonia emission from these units. A full report will be available at the end of this project.

All unlicensed farms will be identified and located via ArcMap. The data obtained will be combined in ArcGIS to estimate the cumulative impact of unlicensed broiler units in County Limerick, by assigning distance thresholds to each farm and identifying nearby Natura 2000 sites. Thus, critical levels of ammonia in sensitive ecosystems will be determined and exposure of habitats and species will be evaluated.

This study is part of the AmmoniaN2K Project, which aims to quantify and assess the impact of ammonia emissions from intensive pig and poultry units on Natura 2000 sites in Ireland.

Acknowledgements

The authors acknowledge funding for this project by STRIVE as administered by the Environmental Protection Agency. Further details of the project are available at [http://ssu.ie/research/ammonian2k/](http://ssu.ie/research/ammonian2k/) and on [https://twitter.com/AmmoniaN2K/](https://twitter.com/AmmoniaN2K/).

References


PRELIMINARY HUMAN EXPOSURE ASSESSMENT TO PHARMACEUTICALS AND PERSONAL CARE PRODUCTS IN PLANTS FOLLOWING THE APPLICATION OF BIOSOLIDS TO AGRICULTURAL LAND

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Abstract

There are many benefits to spreading biosolids on agricultural land as biosolids condition the land and is an economical way for a country to dispose of treated human waste. However, pharmaceuticals and personal care products (PPCPs) may persist in the biosolids post wastewater treatment. This study investigated if one application of biosolids on agricultural land could result in chemical up-taken by carrots used for human consumption and assess the potential significance of this exposure route in terms of human health. Simulated model results show that all PPCPs (carbamazepine, triclocarban and triclosan) were up taken in carrots. Predicted environmental concentrations (PEC) in carrots were used to assess potential human exposure for five human categories (infant, child, teen, adult and >65’s). All PPCPs in carrots were below the acceptable daily intake (ADI). This exposure route may be important when PPCPs have a lower ADI at which they cause subtle effects over long periods.

Introduction

The application of biosolids to agricultural land has many benefits including use as a soil conditioner, which helps improve its physical, chemical and biological properties, reduce the possibility of soil erosion (Lucid et al. 2013) and they are an inexpensive organic alternative to commercial fertilizer (Lu et al., 2012). However, there are also hazards associated with biosolid spreading and they include the detection of persistent environmental contaminants that remain in the biosolids post wastewater treatment and the subsequent introduction to different environmental media. There are concerns that contaminants may move from the biosolids/soil matrix and into plants grown for human consumption. The uptake of PPCPs into plants has been well documented (Herklotz et al. 2010, Calderón-Preciado et al. 2012). Wu et al. (2012) reported the uptake of carbamazepine diphenhydramine and triclocarban by 5 vegetable crop plants following land spreading of biosolids. At the time of harvest, 3 compounds were detected in all 5 plants. Similarly, Sabourin et al. (2012) reported detected concentrations of pharmaceuticals and transformation products in 8 out of 141 analytes in one or two crop replicates at concentrations ranging from 0.33 to 6.35 ng g\(^{-1}\) dry weight. It is generally accepted that the greatest route of contaminants to humans is through the diet. The consumption of contaminated crop plants may increase human exposure to those contaminants (Clarke and Cummins 2014).

Therefore the objective of this study is to develop a quantitative risk assessment model to estimate the transfer of PPCPs from biosolids applied to soil and subsequent uptake by plants (carrots).

Material and methods

The risk of plant up-take of PPCPs from land spreading of biosolids can be estimated by the predicted environmental concentration in soil (PEC\(_{\text{soil}}\)), concentration of contaminant in pore water (C\(_w\)) and the concentration in the plant (C\(_{\text{pt}}\)) using models adopted from Chitescu et al., (2014), which was designed for soil-to-plants. It has been modified for use in Irish conditions. The PEC\(_{\text{soil}}\) was estimated by
developing a distribution of contaminant exposure based on the variability and uncertainty of the predicted environmental concentrations in biosolids.

\[
\text{PEC}_{\text{soil}} \text{ (mg kg}^{-1}\text{)} = \frac{(C_{\text{biosolids}} \times \text{APPL})}{(100 \times D \times \text{BD})} \quad \text{Eq. 1}
\]

\(C_{\text{biosolids}}\) is the concentration of the contaminant of interest in biosolids (g/m\(^2\)), \(\text{APPL}\) is the application rate of biosolids on agricultural land for one application (g/m\(^2\)). Typical application rates of biosolids were retrieved from Lucid et al (2013). \(D\) is the depth (m) and was obtained from Padovani et al (2004) and \(\text{BD}\) is the soil bulk density (kg/m\(^3\)) which was obtained from Vero et al (2014).

The concentration of contaminant in pore-water (\(C_w\)) was calculated according to equation 2;

\[
C_w \text{ (mg kg}^{-1}\text{)} = \frac{(\text{PEC}_{\text{soil}} / F_{\text{oc soil}} \times K_{\text{oc}})}{\text{Eq. 2}}
\]

Where \(C_w\) is the contaminant concentration in the soil, \(F_{\text{oc soil}}\) is the fraction of organic matter content (\(F_{\text{oc}}\)) in the soil and \(K_{\text{oc}}\) is the soil organic-soil-water partition coefficient.

To calculate the concentration of contaminant in the whole plant, the contributions of water, carbohydrates and lipids are considered in quasi-equilibrium with the contaminant concentration in external water (\(C_w\)) (Eq. 3).

\[
\text{Cpt (mg kg}^{-1}\text{)} = \alpha_{\text{pt}} \times C_w \times [f_{\text{pw}} + f_{\text{ch}} \times K_{\text{ch}} + f_{\text{lip}} \times K_{\text{lip}}] \quad \text{Eq. 3}
\]

Where \(\text{Cpt}\) is the concentration of the contaminant in the plant on a fresh weight bases, \(\alpha_{\text{pt}}\) is the quasi-equilibrium factor, defined as the ratio of the respective concentration of the contaminant in plant water and external water, \(f_{\text{pw}}, f_{\text{ch}}\) and \(f_{\text{lip}}\) are the weight fractions of water, lipids and sum of carbohydrates, cellulose and proteins in the plant, respectively, \(K_{\text{lip}}\) is the partition coefficient for the lipids fraction of the plant (assumed to be equal to the octanol-water partition coefficient (Kow)) and \(K_{\text{ch}}\) is the partition coefficient for the carbohydrate fraction of the plant, available according to Kow.

Peer reviewed literature sources were examined for all input values for selected contaminants as each input is contaminant specific.

**Human exposure**

According to the Irish Phytochemical Food Network (IPFN) (2015), Ireland produces over 20,000 tonnes of carrots annually. To get a national overview of carrot consumption, the amount of carrots consumed was based on 4 different surveys (National pre-school Nutrition Survey, The National Children’s Food Survey, The National Teens Food Survey and The National Adult Food Survey, 2011) conducted by the Irish Universities Nutrition Alliance (IUNA) . The surveys assessed the consumption rates and body weights of infants (1-4 yrs), children (5-12 yrs), Teens (13-17 yrs), adults (18-64 yrs) and >65 yrs (Table 1).

**Table 1. Human exposure categories for human consumption of carrots and body weight**

<table>
<thead>
<tr>
<th>Age groups (yrs)</th>
<th>Infant (1-4)</th>
<th>Child (5-12)</th>
<th>Teens (13-17)</th>
<th>Adults (18-64)</th>
<th>&gt;65’s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Body weight (kg)</td>
<td>15.2</td>
<td>33</td>
<td>59.8</td>
<td>78</td>
<td>74.6</td>
</tr>
<tr>
<td>Carrot consumption (kg/d)</td>
<td>0.0067</td>
<td>0.009</td>
<td>0.01</td>
<td>0.013</td>
<td>0.017</td>
</tr>
</tbody>
</table>

The amount of contaminant that may be ingested by humans through carrot consumption was estimated by;

\[
\text{HE (µg kg}^{-1}\text{)} = \frac{\text{Cpt} \times \text{CI}}{\text{bw}} \quad \text{Eq. 4}
\]
Where HE is human exposure, CI is carrot consumption (kg d\(^{-1}\)) and bw is body weight (kg). A sensitivity analysis based on rank order correlation was carried out to assess how the model’s predictions are dependent on variability and uncertainty in the model input parameters. The simulation was performed using the parameters and calculations presented. The entire model was constructed in Microsoft Excel 2010 (with the @Risk 6.0 add-on) (V4.5, Palisade Corporation, Newfield, NY) using Monte Carlo simulation techniques and run for 10,000 iterations.

**Results and discussion**

The results for PEC\(_{\text{soil}}\) show that the contaminant triclocarban (mean value 1.02 mg kg\(^{-1}\)) had the greatest predicted concentration; this was followed by triclosan (mean value 0.50 mg kg\(^{-1}\)) and carbamazepine (mean value 6.99 × 10\(^{-3}\) mg kg\(^{-1}\)). Initial concentrations in biosolids as reported in peer-reviewed literature were greater for triclocarban and triclosan. The results for C\(_{\text{w}}\) show that triclocarban and triclosan had the greatest concentration (mean values 3.03 × 10\(^{-3}\), and 2.29 × 10\(^{-3}\) mg kg\(^{-1}\), respectively). However, results for C\(_{\text{pt}}\) show that carbamazepine had the greatest concentration in carrots (mean value 0.59 mg kg\(^{-1}\)). This was followed by triclocarban and triclosan (mean values 0.48 and 0.34 mg kg\(^{-1}\), respectively).

The results for human exposure show that carbamazepine had the greatest concentration combined with infant and child consumption (mean values 2.74 × 10\(^{-4}\), 1.22 × 10\(^{-4}\) µg kg\(^{-1}\), respectively), closely followed by triclocarban and triclosan and infant consumption (mean values 2.24 × 10\(^{-4}\) and 1.61 × 10\(^{-4}\), µg kg\(^{-1}\) respectively). All results were below the acceptable daily intake rate of 2.9 µg kg\(^{-1}\) d\(^{-1}\) for carbamazepine and 83 µg kg\(^{-1}\) d\(^{-1}\) for both triclocarban and triclosan (Prosser and Sibley, 2015).

Sensitivity analysis assesses how the model predictions are dependent on variability and uncertainty in the model’s inputs. Results revealed that Koc and F\(_{\text{oc}}\) soil were the parameters of importance (correlation coefficient values -0.53 and -0.50). This highlights the importance of soil conditions in influencing mobility of the contaminant into the plant as well as the chemical-physical properties of the contaminant. Other parameters of importance were carrot consumption for teens and the initial concentration in biosolids (correlation coefficient values 0.45 and 0.40) (Figure 1).

![Figure 1. Sensitivity analysis of input parameters for triclocarban](image-url)
Conclusions

The spreading of biosolids on agricultural land is the preferred options for human waste in Ireland. There is potential for hazards to translocate through soil, transfer to plants (carrots) and subsequent human exposure. Results show that concentrations of carbamazepine were greater in the plants (carrots). The sensitivity analysis show that Koc and Foc soil as parameters of importance. Human exposure was greater for infant and child for triclocarban and carbamazepine. All Human exposure values were below the acceptable daily intake rate.

References


doi:http://dx.doi.org/10.1016/j.chemosphere.2009.12.048


doi:http://dx.doi.org/10.1016/j.scitotenv.2012.05.017


doi:http://dx.doi.org/10.1016/j.ecoenv.2012.08.007
SOIL QUALITY OF LYONS RESEARCH FARM

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Abstract

Soil is a fundamental resource for human survival. The concept of soil quality can be used to describe the ability of soil to support a desired function, such as agricultural productivity. Soil quality can also be used as the basis of an evaluation tool to evaluate the influence of environmental change, land management and soil use. The land in arable rotation at UCD Lyons Research Farm was used to evaluate the impact of management on soil quality using a range of indicator methods. Physical and chemical properties were quantified and analysed to define indices of soil quality.

Introduction

Soil is the basic requirement for most terrestrial ecosystem to function. Its quality status is an important factor for the global biosphere sustainability. Soil quality is usually thought of in terms of a defined function, such as production, carbon management, water management or biodiversity support. Land use and management can change the status of land cover and also affect many ecological processes, including physical, chemical and biological processes in soils. Rational land use can improve soil structure and soil quality. Soil quality is a comprehensive reflection of characteristics of soil and it is also an indicator that reveals change of soil condition reflecting the impact of natural factors and human activities on soil (Pramod et al 2010). In the literatures there are many definitions of soil quality, but the most common is to regard soil quality as the capacity of the soil to function (Karlen et al 1997) in terms of fertility, soil environment and soil health, which reflect an ability to maintain biological production capacity, protect environmental quality and promoting the health of animals and plants. Soil quality is one of the most important factor to maintain the global biosphere, which can be defined by productivity, sustainability, environmental quality and effects on human nutrition and health (Smith et al 1993). Soil fertility quality is the ability to provide nutrients to plants and the produce biological substances, which is the fundamental guarantee of food production. Soil environmental quality is the ability to accommodate, absorb and degrade various environmental pollutants. And soil health quality is the ability that soil affect or promote the health of human beings, plants and animals (Doran et al 1994). Soil quality mainly depends on natural components of soil, but is also related to the changes caused by use and management by human. As a complex functional entity, soil quality cannot be measured directly, but it can be defined by soil quality indicators. Determining soil quality indicators is a very complex matter and soil quality indicators differ widely for different soil systems. So there are physical, chemical and biological indices to assess soil quality.

The objective of this work was to determine the soil quality of different areas of UCD Lyons Research Farm using physical, chemical and biological properties.

Materials and Methods

This work is focused on UCD Lyons Research Farm located near Newcastle, 17 km southwest of Dublin, Ireland. The main geographic information is shown in Table 1 (James 2003; James 2004). UCD Lyons Research Farm is used for arable crops and animal production. About half the farm is permanent pasture and arable rotations are carried out on the other half (James 2004). There are nine areas with different crops, including grassland, wheat, barley, oats, maize, beet and potatoes (Figure 1).
### Table 1. Geographic information of Lyons Research Farm

<table>
<thead>
<tr>
<th>Factor</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Topography</td>
<td>A flattish to gently rolling topography</td>
</tr>
<tr>
<td>Climate</td>
<td>Maritime climate</td>
</tr>
<tr>
<td>Annual rainfall</td>
<td>750 mm</td>
</tr>
<tr>
<td>Annual temperature</td>
<td>10 °C</td>
</tr>
<tr>
<td>Humidity</td>
<td>75%-85%</td>
</tr>
</tbody>
</table>

![Figure 1. Map of UCD Lyons Research Farm](image)

**Soil Samples**

Surface soils (0-20 cm) were collected in each area (3 replicates) using a spade or a trowel. After removing plant roots and clods, the soils were mixed and dried at room temperature. A 1 kg sub-sample was sieved through a 2 mm round-hole sieve. Soil samples were stored in labelled plastic bags at room temperature.

**Physical Properties**

Stone content was the weight of stone which cannot pass through the 2 mm sieve as a percentage of the weight of the sub-sample (equation 1).

\[
\text{Stone Content} = \frac{\text{The weight of which the material cannot pass through the 2 mm sieve} (g)}{\text{The weight of the original sample} (g)}
\]  

(1)

Soil moisture content was calculated on a gravimetric wet weight basis (equation 2).
Soil Moisture Content = \( \frac{\text{The weight of sample that was oven dried (g)}}{\text{The weight of the original sample (g)}} \) \hspace{1cm} (2)

Loss on Ignition (LOI) was calculated from the weight of the soil burnt at 400°C for four hours in a muffle furnace as a percentage of the weight of soil which was oven dried (equation 3)

\[ \text{LOI} = \frac{\text{The weight of burnt soil (g)}}{\text{The weight of the oven-dry soil (g)}} \] \hspace{1cm} (3)

**Chemical Properties**

Total Carbon (TC), inorganic carbon (IC) and Organic Carbon (OC) were assessed by SLC Analyser. Available nutrients (P, K, Mg and Ca) were assessed by first extracting with Morgan’s solution (sodium acetate and acetic acid buffered to pH 4.8), and then shaking for thirty minutes. Available P was tested by ammonium molybdate, potassium tartrate and ascorbic acid. And available K, Mg and Ca determined by Inductively-coupled plasma emission (ICP) spectrophotometry. (James 2004). Fe and Al were extracted by ammonium oxalate by shaking in the dark for two hours and determined using ICP spectrophotometry. (McKeague and Day 1966)

**Calculation of Soil Quality Index (SQI) Method**

A large diversity of cultivated soils necessitates development of an appropriate soil quality index (SQI) based on relative soil properties and crop yield (Atanu and Rattan 2014). A soil quality index was calculated using equation (4) (Fu et al. 2004) and principal component analysis (PCA) in SPSS software (Atanu and Rattan. 2014).

\[ \text{SQI} = \sum W_i \times Q(x_i) \] \hspace{1cm} (4)

Where \( W_i \) is the weight vector of \( i \) soil quality factor and \( Q(x_i) \) is the membership value of each soil quality factor. The membership values \( Q(x_i) \) were calculated by the ascending and descending functions. The equation was shown below (Fu B J et al. 2004).

\[ Q(x_i) = \frac{(x_{ij} - x_{imin})}{(x_{imax} - x_{imin})} \] \hspace{1cm} (5)

\[ Q(x_i) = \frac{(x_{imax} - x_{ij})}{(x_{imax} - x_{imin})} \] \hspace{1cm} (6)

\( x_{ij} \) is the value of the physical and chemical properties of soil and \( x_{imax} \) and \( x_{imin} \) are the maximum and minimum value of the i soil property (Fu et al. 2004).

**Results and Discussion**

Data are not yet available so the discussion considers why each of the indicators was selected for the SQI:

(i) **Stone content** influences implements interaction with soil and crop growth. High stone contents are harmful for the root crop harvesting and the stone content in Dangan and Skeagh (shallow phase) series will be greater than other areas on the farm.

(ii) **LOI**, reflects the amount of organic matter in the soil. Interaction with pH can reduce biotic activity and earthworm activity and it also impacts of soil structure. LOI is expected to be greater in the Lack series.

(iii) **Organic carbon (OC)** is closely related to LOI because both are controlled by organic matter.

(iv) **pH** values from 5.5-7.2, subacidic to neutral, indicate soils that are most suitable for plant growth. The Skeagh and Kearneystown series appear to have the most suitable pH.
Available nutrients, including soil phosphorus, potassium, magnesium and calcium are critical to plant growth. Available nutrients also influence soil pH. Too much or too little nutrient can inhibit the growth of crops and grass.

A SQI for each soil series will be determined, as well as a universal SQI for the whole area. These will be assessed by reference to yield data to identify their utility for describing the productive function of arable soils at UCD Lyons Research Farm, and to identify soils that are perhaps limiting productivity.

Conclusions

Soil quality is a tool to assess the soil but it is affected by land management, land utilization and natural conditions. Soil quality is too abstract to be measured directly. However, using physical, chemical and biological indices can translate soil quality from abstract an abstract idea into a usable tool.

Acknowledgements

The authors would like to thank UCD staff for their help and useful guidance.

References


HYPERSPECTRAL IMAGING OF PET, PLLA, P3HB AND P3HB/PLLA 50:50

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Abstract

Poly-3-hydroxybutyrate (P3HB) and Poly-L-Lactic Acid (PLLA) polymer samples were prepared. Spin-coating and solvent casting procedures were used to cast the blend to form thin homogeneous films. Methods for preparation of the thin films were optimized. The effect of degradation on Polyethylene Terephthalate (PET), PLLA, P3HB and P3HB/PLLA 50:50 blend using an alkaline solution (NaOH) for a hydrolysis reaction with respect to time. Hyperspectral imaging was used to evaluate the distribution of the polymer blend. The effect of degradation on spectra and spatial distribution is also investigated.

Introduction

A polymer is a chain of single unit carbohydrates, lipids, proteins or nucleic acids. A biopolymer is any polymer which can be naturally synthesised in nature (Wool and Sun 2005). P3HB and PLLA are useful in the renewable energy industry as competitors against PP, PET, polystyrene and PVC for applications in packaging and medical equipment (Mbeh and do Nascimento 2015).

These polymers are bio-based, biodegradable plastics, meaning they are synthesised from biological materials and are degraded by biological means. In contrast, an oil based polymer may only degrade, whereby it breaks down into smaller components via tearing, weathering and sunlight (Huang et al 1990). P3HB and PLLA are compostable polymers, meaning they biodegrade without the use of chemical additives, at a faster rate and always result in simple, stable compounds which can be assimilated into an ecosystem (Huang et al 1990). P3HB and PLLA polymers are thermoplastic polyesters. PLLA is derived from corn starch or sugarcane, while P3HB is extracted from micro-organisms when faced with a nutrient limited environment.

‘Hyperspectral imaging’ collects and analyses spectra across the electromagnetic spectrum. It combines image sensing with spectroscopy, where an image (of a set resolution) of a sample is obtained. At each point of that image spectra are superimposed along the z axis of the image. Different modes for data acquisition such as spatial scanning and spatio-spectral scanning, allow for different ways in which the data can analysed (ElMasry and Sun 2010). HSI is non-destructive technique. No prior knowledge of the sample is needed. It provides a vast array of data which allows for advanced spectral-spatial models for a more accurate classification of the image (Niaounakis 2015). Multivariate analysis works well with hyperspectral imaging (Roggo et al 2005).

The objective of this project is to determine the composition, hydrophilicity, distribution and degradation of PET, P3HB, PLLA and P3HB/PLLA using hyperspectral imaging.

Materials & Methods

Sample Preparation
P3HB (molecular weight (Mw) = 650,000 g/mol) and PLLA (Mw =24000 g/mol) were purchased from Sigma Aldrich (3050 Spruce Street, Saint Louis, MO 63103, USA). Chloroform density is 1.489 g/ml at 20 C and 1.394 g/ml at 60 C.

Using weighing scales, 30 mg of P3HB and 30 mg of PLLA were taken and put in a 50 ml beaker with 8 ml of Chloroform solvent to create a 0.5% m/v concentration 50:50 blend for subsequent spin coating and solvent casting. Cling film was put on the top of the beaker to prevent volatilisation when transporting to
spin coating lab. This procedure is altered depending on the number of samples and concentration required.

Solvent casting was done in a fume hood, where a water basin heated by an electromagnetic stirrer contains a flask with the polymer solution prepared. Aluminium foils with punctured holes cover the flask. The water basin temperature is set between 50-55 degrees Celsius for 3 hours. Spin coating takes the blend prepared after heating and mixing in the fume hood and pipettes it onto a glass slide being spun at ~700 rpm for 2 min. The solution was cast at the centre of the slide at a 45 degree angle.

**Optimization of procedure: Effect of mixing, heating**
The first preliminary experiment investigated the effect of solvent casting and spin coating samples without heating and mixing the polymer solutions in the fume hood. This first experiment used 3 samples of a 0.5% concentration 50:50 blend polymer solution for solvent casting and 3 samples for spin coating. Experiment 2 mirrors experiment 1 with the inclusion of heating and mixing in the fume hood with the electromagnetic stirrer outlined under sample preparation.

**Optimization of procedure: Effect of concentration**
Experiment 3 follows the procedure for experiment 2 for a 1% polymer blend solution. The Fourier Transform-IR results for this experiment will be compared to experiment 2 to verify if increasing the concentration of the polymer blend is necessary for detecting spectra.

**Optimization of procedure: Effect of drying method**
The effect of drying will be investigated testing the effect of drying in the fume hood versus oven drying and the effect of having a cover versus without a cover on the petri-dish.

**Future experiments**
Once optimization experiments are done for 50:50 P3HB/PLLA samples, degradation experiments using an alkaline solution will commence. A sodium hydroxide medium in a beaker will be used to hydrolyze PET, PLLA, P3HB and P3HB/PLLA samples (0.2 mm²). This is done three times for each time step, where six different time steps are used to assess degradation as a function of time. This will create 72 samples. See Figure 1.

![Figure 1. Hydrolytic reactions](image)

When removing samples from the NaOH solution, they should be washed with distilled water to remove residual NaOH and dried. Contact analysis will be used to determine hydrophilicity (polarity). The degradation of each polymer will be determined by weight loss or gain at room temperature over time (Škvarla et al 2010).

**Hyperspectral imaging system**
A Thermo Scientific™ Nicolet™ iN™10 Infrared Microscope offering a fixed 10x magnification, fitted with a nitrogen cooled Mercury-Cadmium-Tellurium (MCT) optical detector, capable of imaging in the 7800–650 cm⁻¹ range, with LED illuminators, was employed to image the thin film samples. See Figure 2 for visualisation of output.
Data analysis

Fourier-Transform Infrared spectroscopy is an analytical technique for identification of the presence of certain functional groups in a molecule (Griffiths and De Haseth 2007). Transmission mode FT-IR will be used for collection of spectra, as better baseline corrections can be made for samples created via spin coating. The thinness of a spin coated sample will mean glass spectra will be picked up by reflection mode IR. By using transmission mode the glass background can be cancelled out (Sato et al. 2010). A sample resolution of about 4 cm⁻¹ should be used.

Multivariate analysis is designed to extract useful information from the spectra that would correlate with an independent variable (i.e. degradation rate) so that a model can be created to predict the dependent variable in the future (Bansal et al 2010). Methods are employed to remove unnecessary information (spectral noise) without losing important information. This is known as data pre-processing. This is followed by model development, which is a series of mathematical functions which aim to create a model for prediction (Gosselin et al 2008). Partial least squares is a method frequently employed in this area of research (Rumondor and Taylor 2010). It will be used to predict the effect of degradation on the polymers using spectra from the most informative region of the spectra (Geladi and Kowalski 1986). The software Unscrambler or Matlab with a downloadable toolbox, are two options for which this analysis can be facilitated.

Expected Results and Discussion

No results have yet been obtained. The effect of mixing and heating should improve distribution of the polymers. Covered petri-dishes dried in the oven are expected to dry the polymer at the fastest rate while minimizing volatilization of chloroform from the thin films. It is unknown whether using a 0.5% concentration or a 1% concentration will have any effect on being better detectable by the FT-IR spectrometer.

Škvarla et al (2010) found that the surface of PET immersed in a NaOH solution heated for a short time period at atmospheric pressure, resulted in the suppression of PET flotation. A polymer's ability to degrade is determined by many physical factors such as diffusion, crystallinity, chain mobility, permeability. A polymer has a slower rate of degradation below its melting temperature and even lower below its glass transition temperature. Škvarla et al (2010) has however reported PET’s ability to float was suppressed (increased hydrophilicity) below its glass transition temperature (~85°C).

It is expected that the degradation experiments will cause biodegradable polymers to degrade at a faster rate compared to polyethylene terephthalate.

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References


INTELLIGENT SYSTEMS APPLIED TO CROP ASSESSMENT AND PRODUCTION

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Abstract

This project is designed to directly address common crop diseases and decision making across crop trials via state of the art fully automated crop monitoring system based on a combination of soil sensors, weather sensors, vision system and GPS geo-referencing. The project will develop predictive algorithms of disease profiles which will be development using artificial intelligence techniques based on sensor data collected in the crop fields. This technology solution is designed to function across crop trials supporting decision making and disease control, thus addressing critical global food security and sustainability issues.

Introduction

Studies suggest that the world will need twice as much food by 2050 (Alexandratos et al 2012). Yet, while farmers must squeeze more out of the land, they must also reduce their impact on the environment. All this means rethinking how agriculture is practised and taking automation to a whole new level. On the new model farms, precision will be key. Why dose a whole field with chemicals if you can spray only where they are needed? If each plant could get exactly the right amount of everything, no more or less, this approach could significantly reduce chemical use and improve yields in one move (Crow 2012). But this is easier said than done; the largest farms can cover thousands of hectares. And that is why sensing and automation are key factors to precision farming.

To meet this potential, the Irish agri-food industry must put smart thinking at the core on both its strategy and action. Precision agriculture is based on the management of agricultural systems, using resources such as mapping of factors of production, decision support tools, localized application of fertilizers and disease control through the use of sensing and actuation technologies.

In the current scenario, computer science based applications have been proposed to address some crop issues such as computer vision to disease detection, weed decriminalization and feature extraction (Ye et al 2015; Sankaran et al 2010); Remote sensing (Phillips et al 2014); Decision support systems (Kerselaers et al 2015) and Farm management (Voulodimos et al 2010).

The objectives of this study are: build a low-cost solution to acquire crops data using a multi-sensorial approach; develop a system to assess crop evolution in a geo-referenced basis, suggest farm actions, predict crop yield and quality; build a diseases detection module using computer vision and artificial intelligence algorithms.

Materials and Methods

Sensor Suite

The sensor suite will be established using a range of devices in order to extract data from the multiple factors that influence the crop development process. In order to capture the soil,
canopy, weather and visual properties during the season, the following suite is planned to be deployed:

Soil sensors: Moisture, soil compaction, pH, electric conductivity, nitrogen, calcium, sodium and potassium.

Canopy sensors: Chlorophyll, NDVI (Normalized Difference Vegetation Index), LAI (Leaf Area Index) and PAR (Photosynthetically Active Radiation).

Weather sensors: Temperature, relative humidity, barometric pressure, rain precipitation and solar radiation.

Vision sensors: Aerial vision using a drone with high definition camera and local images using a common camera.

Global positioning system: The gathered data will be geo-referenced so that is possible to generate local specific data analysis.

Pre-Processing: Before upload the data for a cloud database, the data will be fused in accordance to a region and date time. Mining algorithms must be applied to eliminate unnecessary data and compress images.

The Figure 1 depicts the described methodology in a high level vision of the inputs, processing phases and expected outputs of the proposed system. The sensorial suite is designed to operate in adverse climate conditions.

![Figure 1. High level vision of the proposed methodology.](image)

**Data Gathering**
The in-field data acquisition on crop trials will happen during the season using the proposed suite of sensors.
Data Analysis and Processing
For the cloud integration, first of all an evaluation of advantages and disadvantages of cloud computing storage and warehousing are planned. After that, the design of the interfaces and database model for storage data will take place. Finally, the development of a service to upload data to a remote database using secure connection. For the computer vision module, a feature extraction algorithm for disease detection will be developed as an algorithm for vegetation index calculation. Moreover, machine learning techniques will be employed for disease detection using supervised and unsupervised learning. In addition, an artificial intelligence based algorithm is designed to predict yield and quality using the data gathered by the sensors. Lastly, a decision support module is projected to support decision making using benchmark figures, rules and fuzzy logic based on an expert database, built on specialized documentation and personal professional knowledge.

Expected Results
After the data collection from different sources, is expected, a system that provides the following modules:

Sensing Module
During the developing stages of crops in the field, distinct sensorial data from the soil and canopy will be taken, such as moisture, nitrogen, chlorophyll, leaf reflectance and canopy size. As an outcome of this module, a complete data capture system is planned using the equipment described earlier and software to collect and transmit the information to a cloud database.

Disease Detection Module
Processing of the vision data by computer vision algorithms in order to extract features and use of Artificial Intelligence techniques such as neural networks to match visual features with known diseases.

Decision Support Module
Given the gathered data by the sensors, meteorological, soil, and seed information associated with pre-known conditions and benchmarks, this module, specified with a modelling language, such as fuzzy nets, will offer a recommendation action if a predefined condition is fulfilled. Crop assessment based on benchmark data will also be available in an organized way to offer to the farmer information about soil (nitrogen, moisture), crop status (vegetation indexes, crop stress, leaf reflectance), and yield projection (shoots/m$^2$, tillers/m$^2$, ears/m$^2$).

Conclusions
Given the future projections of global growth and food consumption, the research and development of new technologies for agriculture is currently a fundamental requirement for improvement of yield production and at the same time, reduction in the environment impacts. This paper presented a project that is directed to the automation of data collection for future farming systems, by means of an autonomous system for diseases detection and to support decision making using multi-sensorial data. The expected results are projected to support the autonomous use of precision agriculture technologies, where particular inputs and management decision are seized to attend the needs of a particular area, providing ways for a more productive, economic and sustainable practises of crop cultivation.

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References

A PRELIMINARY REVIEW OF WHOLE FARM N FLOW MODELS AND THEIR SUITABILITY FOR TEMPERATE PASTURE-BASED LIVESTOCK SYSTEMS

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Abstract

In pasture-based systems, only a small quantity (20-40%) of nitrogen (N) inputs that enter the system are converted into agricultural products (milk and meat). A large proportion of this surplus N is lost in the form of nitrous oxide (N₂O), ammonia (NH₃) and nitrate (NO₃) which are known to be detrimental to the environment. While there are many different types of N flow models available, there is no review of these models to assess the strengths and limitations of the respective approaches. This review focuses on whole farm N models and highlights key parameters such as the emission factors used, boundary of each model, its strengths and drawbacks. The study highlights the significance of modelling farm N flow for pasture-based systems and the importance that various data inputs and farm components have for an efficient whole farm N flow model.

Introduction

At present pasture-based and other agri-systems result in loss of nitrogen (N) in various forms which tend to be detrimental to the environment. Major pathways for N loss from agriculture include nitrous oxide (N₂O), which is a greenhouse gas, N losses to water and the trans-boundary gas ammonia (NH₃). In order to reduce and limit these N losses legislations such as Nitrates Directive, the National Emissions Ceiling Directive and the EU Climate and Energy Package are in place.

In a pasture-based system, N flows through the various components of a farm, with nitrogen entering the system as feed or fertiliser, for example. The feed is consumed by cattle wherein, 20%-30% is converted into animal protein. Excess N is excreted either directly onto grazing land (dung or urine) or accumulated in livestock housing and stored as solid or liquid manure. The manure deposited at housing is normally collected in a storage tanks and eventually spread on land. During these different stages N is lost via the pathways mentioned above, which reduces nitrogen use efficiency (NUE) in livestock systems. This makes pasture-based livestock systems a huge concern for N loss. Nitrogen flow models can be used to stimulate these N losses and can help to improve our management of N. At present there are numerous whole farm greenhouse gas (GHG) models which focus on N loss in the environment from livestock systems (Del Prado et al 2011). Despite the useful nature of such N flow models little is known on how these different N flow models compare to each other in terms of data inputs, boundaries & emission factors used and also their suitability for temperate pasture-based livestock systems. For temperate based pasture systems losses through grazing and land spreading form a major part with N loss being affected by rainfall, temperature and wind speed. Further, N losses tend to differ amongst various regions due to different farm management, climate and soil conditions. Therefore this study reviews N flow models available in the literature which assessed their appropriateness for use on pasture-based systems such as those in Ireland, the UK and New Zealand. This study is a preliminary investigation of these models and forms the basis of a more comprehensive evaluation of N flow models.

The objective of the study is to review whole farm approaches for modelling N flows and losses in temperate pasture-based livestock systems.
Material and methods

The literature review was conducted based on the publications obtained in key scientific search engines including Science Direct and Web of Knowledge by searching key words such as ‘whole farm N model’, ‘Nitrogen flow’ and ‘pasture-based livestock systems’. The N flow models were evaluated and compared with respect to the data inputs, emission factors used, system boundaries, the farm components that are included in each model and type of N losses that are accounted for. The models were also evaluated based on their strengths and shortcomings. The review looked at dealing with models of the N cycle on a farm, right from its entry as inputs of N into the farm as feed and fertilizers to its eventual output as dairy products (milk), meat (beef and sheep meat) and emissions such as N₂O, NH₃ and NO₃. The review looked at key papers looking at modelling N flow through these key components to determine losses of N in the various components and the biotic & abiotic factors that affect N loss.

Results and Discussion

Currently there are numerous studies modelling farm N flows with studies being carried out at both national and individual farm level. The study reviewed seven N flow models as seen in Table 1.

Model structure

The reviewed models were either empirical in nature, focusing on experimental data collection over a period of time, mechanistic which looked at emissions though a component in the system or dynamic which looked at flexible datasets over time. For instance the NARSES model is a national scale model making use of empirically derived factors which gives an insight into N loss through the manure management chain while the ALFAM is a mechanistic model dealing with emissions from field plots. At present the majority of the available models use IPCC (1997, 2006) emission factors. For instance (Del Prado et al., 2011) made use of constant emission factors. However these typically require modification (Reidy et al. 2008) as they would then be better able to evaluate the effects of changing levels of N loss in a farm during different environmental scenarios. The dynamic model of Hutchings et al. (1996) makes use of empirically based factors to simulate N flow on a day to day basis from inputs of N in the feed right up to loss as NH₃ during manure land application.

Data inputs and boundaries

The reviewed models showed similarities and variations in terms of farm components studied, period of data input and type of N losses studied. For instance as seen in Table 1, a dynamic model developed by (Hutchings et al., 1996) requires a description of inputs of N in the feed right up to loss as NH₃ during manure land application. The sub-components of the model include- losses from animal housing, slurry storage, losses during application of slurry, ground surface losses from applied manure and urine patch losses. The findings of the model highlight higher losses of N as ammonia from dairy systems as compared to beef systems perhaps due to the complex interactions between the various farm components and emphasis on the need to improve modelling of losses from housing and dealing with the fate of excreta at the farm level. Dairy-wise and SIMS_Dairy model looked at N loss as NO₃ and NH₃ from housing, storage, grazing and manure application. Dairy-wise, a whole-farm model developed for dairy systems by (Schils et al. 2007) adopted already existing crop and animal production, feed supply, nutrient cycling, GHG and energy use component models. The SIMS_Dairy model (Del Prado et al. 2011) looks at studying the effects of farm management, soil characteristics and climate conditions on losses of N, P and C. Both dairy models required data on a monthly bases and provide N output in unit of kg/ha as seen in Table 1. Rotz et al. (2014) looked at using the Integrated Farm Systems Model (IFSM) for dairy and beef production systems for determining N loss as NH₃ during housing, manure storage and field application. It used a mechanistic approach. Measured data was comprehensively evaluated with the simulated model data to show similarities in the findings for each component. The model was applied to a dairy farm which showed the various manure management strategies and abatement techniques on farm level N flows.
<table>
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<th>Reference</th>
<th>Model name</th>
<th>Model type</th>
<th>Model description</th>
<th>Model Boundaries</th>
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<th>N losses included</th>
<th>Data input</th>
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<td>(Del Prado et al 2011)</td>
<td>SIMS&lt;sub&gt;dairy&lt;/sub&gt;</td>
<td>Dynamic</td>
<td>Simulates monthly interactions between climate, farm management, soil type and genetics to determine effects on N flow</td>
<td>Direct on farm, N loss from farm management, soil &amp; climate characteristics</td>
<td>Soil, crop and animal components including Housing, manure storage, land spreading, grazing</td>
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<td>Livestock, climate, soil, diet (Monthly)</td>
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<td>*IPCC 2000</td>
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<td>(Hutchings et al 1996)</td>
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<td>Diet, climate (Daily)</td>
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<td>Integrated farm systems model - IFSM1</td>
<td>Mechanistic</td>
<td>Simulated processes of NH&lt;sub&gt;3&lt;/sub&gt; formation, speciation, aqueous-gas partitioning, mass transfer</td>
<td>Direct on farm, N loss from crop production, feed use &amp; manure management</td>
<td>Housing, manure storage, land spreading of manure, grazing</td>
<td>NH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Diet, livestock, climate (Daily)</td>
<td>N losses in (g/day/cow)</td>
<td>*USEPA</td>
<td>USA</td>
</tr>
<tr>
<td>(Schils et al 2007)</td>
<td>Dairy-wise</td>
<td>Empirical</td>
<td>Simulates technical, environmental &amp; economic processes on a dairy farm</td>
<td>Direct on farm, N loss from feed supply, livestock management, soil</td>
<td>crop &amp; animal production, feed supply, nutrient cycling and energy use components</td>
<td>NO&lt;sub&gt;x&lt;/sub&gt;, NH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Feed, diet, livestock, farm management (monthly)</td>
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<td>(Waldrup et al 2014)</td>
<td>Integrated farm systems model - IFSM2</td>
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<td>Simulation of daily NH&lt;sub&gt;3&lt;/sub&gt; emission rates &amp; comparison with pre-existing data</td>
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<td>N losses in (g/head/d)</td>
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<td>USA</td>
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<td>(Søgaard et al 2002)</td>
<td>ALFAM</td>
<td>Mechanistic</td>
<td>Simulating NH&lt;sub&gt;3&lt;/sub&gt; emission from field applied slurry with respect to climate, soil &amp; farm management</td>
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<td>(Webb &amp; Missetbrook, 2004)</td>
<td>NARSES</td>
<td>Empirical</td>
<td>Simulating NH&lt;sub&gt;3&lt;/sub&gt; emission from UK agriculture to determine cost-effective abatement solutions</td>
<td>Direct on farm, N loss from manure management</td>
<td>Housing, manure storage, land spreading of manure, grazing</td>
<td>NH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Livestock, manure characteristics (Yearly)</td>
<td>N losses kg/head/yr</td>
<td>*IAEUK</td>
<td>UK</td>
</tr>
</tbody>
</table>

** IPCC- Intergovernmental panel on climate change
*b* USEPA- United States Environmental Protection Agency
*c* IAEUK- Inventory of ammonia emissions for the UK
The IFSM was also used by (Waldrip et al 2014) to simulate N dynamics in a beef system to aid in improving farm nutrient balances and evaluating abatement potentials of NH3 reducing strategies. Overall the study found that there was a shortage of models focusing only on N flow at a farm level.

**Suitability for modelling temperate grass-based systems**

The list of reviewed models showed a range of strengths and drawbacks. However with respect to pasture-based systems, key areas of emissions would be from grazing and land spreading of manure. Thus models with these components such as NARSES, IFSM, NH3 volatilization model and SIMS\textsubscript{DAIRY} will make for an effective N flow model for pasture-based systems

**Conclusion**

This review conducted a study on whole farm approaches to model N flow from temperate pasture-based livestock systems. The study found that the majority of the research was focused on whole farm greenhouse gas models having an N flow component and there was a lack of research focusing solely on N flow models, thus highlighting the need for the development of more whole farm N flow modelling.

**Acknowledgement**

This work is part of the RSF ‘Low-Ammo’ project which is funded by the Irish Department of Agriculture, Food and the Marine (Project no. 13/S/430). The first author is also in receipt of a Teagasc Walsh Fellow scholarship.

**References**


DESIGN AND USE OF LOW COST CO₂ ANALYSER AND DATA LOGGER

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²University of the West of England, Bristol, United Kingdom.

Abstract

Rates of ammonia dispersion into the atmosphere from intensive agricultural units are highly dependent on the ventilation rate of each individual building. These rates can vary depending on the type of ventilation used in each individual house, including both natural and mechanical ventilation. A common method to calculate the ventilation rate of an intensive agricultural unit uses the carbon dioxide mass balance technique, which uses CO₂ as a target gas. For this project, gas concentrations at three different heights were measured in the layer house using the Senseair CO₂ Engine® K30 which was linked with an Arduino Uno board. Measurements taken by the Senseair monitor gave CO₂ concentration averages of 1267, 1270, and 1346 ppm at 0, 1 and 2.5 m heights respectively.

Introduction

The emission of ammonia into the atmosphere from intensive agriculture is a serious threat to biodiversity at a local level, considering it can often exceed the critical level of 3 µg/m³. In order to calculate this emission rate a number of options are possible. The current AmmoniaN2K project uses a carbon dioxide mass balance technique in order to calculate the ventilation rate of these buildings. Off-axis integrated cavity output spectroscopy, in the form of a Los Gatos Research (LGR) ammonia analyser was used to monitor the concentrations of ammonia in house. The LGR analyser pumps air from different locations in the house; the outlet air from this machine is sampled for CO₂ using the Non Dispersive Infrared (NDIR) Laser discussed throughout this paper.

A study across Europe used the concentration of a tracer gas, carbon dioxide to calculate ventilation rates of these houses (Seedorf et al 1998). This project generally used an infra-red analyser, these and similar methods of recording CO₂ concentrations in the air can be expensive, and have been known to exceed €7000. This project investigated the potential for a low cost analyser which fulfilled the requirements of measurements needed to calculate the ventilation rate in an intensive agricultural unit.

In order to use the CO₂ mass balance technique, a CO₂ sensor and data logger is required. This project sought to develop a low cost solution to CO₂ monitoring. An Arduino board and data logger were used in addition to a CO₂ Engine® K30, a NDIR laser. The total cost of this sensor was €170, significantly lower than alternative options. With a range of 0 -10000 ppm it has thus far been successfully used to monitor CO₂ concentrations in broiler and layer houses. Once a ventilation rate is calculated the ammonia concentration inside the house can be applied in order to calculate the ammonia emission rate.

The aim of this research was to construct a carbon dioxide monitor and data logger for use in calculating ventilation rates from intensive agriculture.

Materials and Methods

An Arduino Uno board was combined with an Adafruit data logger shield, wires were subsequently soldered onto the CO₂ Engine®K30 and inserted into the data logger shield as represented in Figure 1.
Figure 1. Combining Arduino Uno with Adafruit Datalogger Shield.

Figure 2. Wiring required to connect CO₂ Engine®K30 to Adafruit data logger shield with Arduino Uno. Note the Adafruit data logger shield is designed to fit directly onto the Arduino Uno.

Once the CO₂ Engine®K30 is connected to the Adafruit data logger and Arduino Uno, the Arduino Uno can be connected to a PC with Arduino software installed (Arduino, 2016a). Codes for this project were combined and modified from three publicly available sources to form a code which logged CO₂ measurements with a date and time stamp to an SD card (Paul McWhorter, 2014; Schwartz, 2013; Arduino 2016b). Based on the code (Table 1) below, data can be viewed on the built-in serial monitor of Arduino’s software by modifying “CO2sensordata” to “Serial”. This can be included in addition to the code below rather than instead of it; this can be useful for immediately viewing records as they are recorded.
Table 1. Code used to programme CO$_2$ data logger

```cpp
// Date and time functions using a DS1307 RTC connected via I2C and Wire lib
#include <Wire.h>
#include "RTClib.h"
#include <KSeries.h>
#include <SD.h>
#include <SPI.h> //load the SPI communication library

// Create K30 instance on pin 6 & 7
KSeries K_30(6, 7);
RTC_DS1307 RTC;

// for the data logging shield, we use digital pin 10 for the SD cs line
const int chipSelect = 4;

// the logging file
File CO2sensordata; //variable for working with sensor;

void setup () {
  Serial.begin(9600);
  Wire.begin();
  RTC.begin();
  pinMode(10, OUTPUT); //reserve pin10 as output
  SD.begin(chipSelect); //initialize sd card with chip select
  RTC.adjust(DateTime(__DATE__, __TIME__));
}

void loop () {
  DateTime now = RTC.now();
  // Get CO2 value from sensor
  double co2 = K_30.getCO2('p');
  CO2sensordata = SD.open("CO2data.txt", FILE_WRITE); //open file to append
  if (CO2sensordata) //only do these things if file is opened
  {
    CO2sensordata.print(now.year(), DEC);
    CO2sensordata.print(' ');
    CO2sensordata.print(now.month(), DEC);
    CO2sensordata.print(' ');
    CO2sensordata.print(now.day(), DEC);
    CO2sensordata.print(' ');
    CO2sensordata.print(now.hour(), DEC);
    CO2sensordata.print(':');
    CO2sensordata.print(now.minute(), DEC);
    CO2sensordata.print(':');
    CO2sensordata.print(now.second(), DEC);
    // Print the value on Serial
    CO2sensordata.print(' ');
    CO2sensordata.println(co2);
    CO2sensordata.close(); //close file
    delay(500);
  }
}
```
Results and Discussion

CO$_2$ concentrations from three different heights within a layer house gave averages of 1267, 1270, and 1346 ppm for 0 m, 1 m and 2.5 m high respectively. The slight increase in CO$_2$ from 1 – 2.5 m corresponds to the increase in the number of chickens at higher levels, with the rising warm air higher areas should generally have higher CO$_2$ concentrations. This is based on the layout of the farm, as chickens are raised in cages stacked three high. The combination of this CO$_2$ logger with a LGR ammonia analyzer allows for CO$_2$ sampling in multiple locations within each house, as the LGR samples multiple locations in sequence. In addition to concentrations inside the house, the CO$_2$ concentration outside also needs to be considered for the CO$_2$ mass balance technique, in this case upwind measurements at the farm showed concentrations of 420 ppm which is close to the expected ambient concentration in the area.

Conclusion

The constructed CO$_2$ monitor and datalogger is suitable when used in combination with the LGR ammonia analyzer, which samples different locations in the farm using a vacuum pump through tubing. Obtaining a unique CO$_2$ concentration for each ammonia sampling point allows for better estimation of ventilation and emission rates compared to sampling one location in a house. When deployed it was noted that loose connections after soldering wires to the CO$_2$ Engine®K30 can cause issues when logging data. It is also recommended that the datalogger be reprogrammed after each time the SD card is removed to download data.

Acknowledgements

The authors acknowledge funding for this project by STRIVE as administered by the Environmental Protection Agency. The authors would also like to thank both the EPA and the National Parks and Wildlife Service for information and support provided. Further details of the project are available at http://ssu.ie/research/ammonian2k/ and on our twitter page https://twitter.com/AmmoniaN2K/.

References

PULSED ELECTRIC FIELD TECHNOLOGY FOR THE PRE-TREATMENT OF ORGANIC MATERIAL TO INCREASE BIOGAS YIELDS IN ANAEROBIC DIGESTION

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Abstract

The need for renewable sources of energy in Ireland has never been higher. As a member of the European Union, Ireland is required to comply with various directives and targets set out by Europe and non-compliance can lead to fines. The requirement for energy security is always strong, especially on an island nation as this reduces reliance on external potentially more expensive fuels. Furthermore, environmentally friendly methods of producing energy are very popular, with sales of solar panels and wind turbines currently high, illustrating a desire for cleaner energy. Anaerobic digestion has become a popular option in recent years for renewable energy production based on the relatively high amount of energy that can be produced, the availability of the feedstock and the fact that the technology is reasonably common. The fact that it is a waste management system also adds to the appeal. However, the biogas produced can be limited by some material, such as high lignocellulosic organic matter and the use of pre-treatments have been investigated to establish if they are a solution to this problem. This study aims to investigate if pulsed-electric field technology can breakdown cells sufficiently to provide more material for biogas production in an anaerobic digester.

Introduction

Anaerobic digestion is the hydrolysis of organic material, then the fermentation of the solubilized organic materials which produce fatty acids and H₂, and methanogenesis of the fatty acids and H₂ (Lee and Rittmann 2011). This process encompasses the 4 stages which are hydrolysis, acidogenesis, acetogenesis and methanogenesis.

To improve the efficiency of anaerobic digestion and to reduce the retention time within the digester many pre-treatments have been considered. Pre-treatments are wide-ranging and can include mechanical, thermal, chemical, biological or combinations of these (Ariunbaatar et al 2014; Zhou et al 2015; López Torres and Espinosa Lloréns 2008; Cesaro and Belgiorno 2013; Yeneneh et al 2015). The pre-treatment that this project will examine is pulsed electric fields. Pulsed electric field technology (PEF) has various different uses. The technology is used in the medical sector as a way of inserting DNA or plasmids into cells through electroporation, which is the reversible expanding of the cell pores (Brambach et al. 2016). The technology is also commonly used in food preservation as an alternative pasteurisation technology and to prolong the shelf life of food products (Rittmann et al 2008). Finally pulsed electric fields are used as a pre-treatment for biogas increase in anaerobic digestion. The application of an electric pulse (usually with a strength between 10-30 kV/cm) causes the cells pores to open, this in turn causes a transmembrane potential difference which can lead to the membranes breakdown. The cells can recover from this, however if the pulse is strong enough complete cell destruction occurs (Ravishankar et al 2008). This aids in the biogas production of anaerobic digestion due to the fact that it creates more material which can then be broken down by the bacteria within the digester, thus creating the biogas. This pre-treatment also shortens the retention time within the digester as the membranes are already broken down for the bacteria.

The objective of this study is to investigate the application of pulsed electric fields on organic matter of varying structural properties, to observe the destruction of cells, which provides more material for anaerobic digestion biogas production and investigate potential pre-treatment combinations.
Materials and Methods

Organic Material
Materials of varying composition and lignin content will be analysed throughout this study in order to
gauge the effectiveness of the PEF on the cells and also evaluate the potential benefits of pre-
treatment combinations. Therefore, ‘soft’, ‘medium’ and ‘strong’ cell wall composition materials will
be used, which are outlined in Table 1.

<table>
<thead>
<tr>
<th>Soft Material</th>
<th>Medium Material</th>
<th>Strong Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apple</td>
<td>Straw</td>
<td>Miscanthus</td>
</tr>
<tr>
<td></td>
<td>Grass</td>
<td>Maize</td>
</tr>
</tbody>
</table>

Table 1. Materials to be used for analysis

The varying material strength is to ensure that a comprehensive study on the effectiveness of the PEF
treatment on various materials is conducted. These materials were also selected based on the fact that
they are relatively common and therefore would be practical and realistic examples of the types of
material which would undergo anaerobic digestion, especially in an Irish context.

Cell Staining
This study will use visual assessment to observe the effect that the pulsed electric fields have on the
cells of the material and therefore illustrate the cell membrane breakdown and ultimate destruction of
the cell. In order to do this the cells will be stained and visually assessed under an optical microscope,
with images being taken to document in the final report.

Staining the cells will be undertaken in the lab using a method yet to be finalised however it will be
similar to other plant material cell staining examples in the literature (Žárský and Cvrčková n.d.). The
objective for the staining of the cells is to observe the process outlined in Figure 1.

Figure 1. Pore formation and eventual destruction of the cell due to exposure to an external electrical
field (Verma 2012).

Pulsed-Electric field
The pulsed-electric field experiments will be conducted using a pilot scale PEF machine, ELCRACK
HVP-5, located in the Food Science building on the UCD campus. Samples will be cut to a uniform
size and prepared in order to flow through the machine. The PEF machine works generally in the
range of 10 to 30 kV. Parameters such as the pulse voltage, pulse width and length of treatment time
will all be varied in order to establish the optimum conditions for each materials cell breakdown.
Figure 2 illustrates the electric field treatment zone of a PEF machine.
Pre-treatment combinations

PEF treatment may be considered expensive or to require specialised equipment which may not be attractive to potential anaerobic digestion operators. This study aims to use the information gathered during the PEF treatment part of the study, outlined above, to create potential pre-treatment combinations which could be established to make PEF more effective or less expensive.

The pre-treatments which will be combined with the PEF are yet to be fully established however hot water and NaOH are likely pre-treatments for this analysis.

Expected results

This study is on-going and therefore there are no actual results to report however, results can be speculated based on assumptions and relevant literature.

It is expected that the effect that the PEF treatment has on the cells will be clearly visible after the staining process has been perfected. This is due to the wide range of papers and manuals associated with the PEF machines and technique which repeat the systems targeted approach at cell wall breakdown and therefore cell destruction (Schoenbach et al 1997).

Furthermore, it is expected that the varying strength materials (outlined in Table 1) will also vary in what their optimum combination of PEF parameters such as pulse voltage, width and treatment time. This is based on the differing lignin content within the materials cell walls. It should be expected that the material with the higher lignin content should require the strongest and longest electric field pulses in order for comprehensive cell breakdown.

Therefore, it is also expected that these same high lignin content materials will be the ones to benefit most, in terms of cell breakdown, from the combinations of pre-treatments outlined above. Another result which is expected in relation to these combinations is that the combinations of pre-treatments on these stronger substances will enable the decrease in the voltage or number of pulses required for comprehensive cell breakdown and therefore lower the potential cost of using the PEF treatment. This could have the outcome of making the technology a more attractive propositions for potential buyers.
Conclusion

In conclusion this study aims to investigate the effect that PEF pre-treatment has on organic material of varying properties in order to best establish a method of effectively and comprehensively facilitating cell wall breakdown.

The study will be lab based and will focus on materials such as apple, straw and miscanthus, which are both common and regularly used in anaerobic digesters. Staining of the cells and the visual assessment of this stain using microscopes will confirm the PEF treatment and will be used to analyse various parameters. Combinations of pre-treatments and the effect of the combinations on the PEF parameters will be studied and concluded upon. Ultimately the study will produce an optimal pre-treatment plan for each of the material studied.

References


Kinetics of Microbial Inactivation for Alternative Food Processing Technologies -- Pulsed Electric Fields [online] (2016) [online], Fda.gov.


APPLICATION OF LIFE CYCLE ASSESSMENT TO CONSTRUCTION MATERIALS: A CASE STUDY OF FARM BUILDINGS

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Abstract

The materials used to construct farm buildings cause impacts to the environment. In this study a numerical model of a farm building was developed to calculate the bill of materials required for Life Cycle Assessment (LCA). LCA is widely used to evaluate emissions and consumptions and to find out hotspots, yet many livestock system LCAs make a starting ‘exclusion assumption’ of not including farm buildings. Few studies have evaluated this assumption. The influence of seasonal changes, type of building material (steel and timber) is presented. This approach during the design stage of a building will ensure compliance with the legislation and is the first step towards a net zero building concept compatible with the exclusion assumption.

Introduction

According to the Department of Agriculture, Food and the Marine (DAFM) the agriculture and food sector in Ireland contributes about €24 billion to the national economy and a farm building represent about 30 to 45% of the overall project cost for farm development. Worldwide, more than 40% of all energy use is linked to buildings and they produce one third of greenhouse gas emissions during their entire life cycle (Koesling et al 2015). Despite this, many LCA studies of livestock systems omit farm buildings from the system. The methodology of the overall study was based inter-linking IPPC legislation, numerical modelling, thermal transmittance and model validation and finally the application of LCA to quantity impacts (emissions and energy consumption). This paper focuses on numerical modelling of the farm building.

A numerical model is a description of a system using mathematical concepts and language. Here numerical models are used because the model may help to explain a system, to study the effects of different components and to make predictions about behaviour. Experimentation with real farm buildings is very costly and time-consuming. A numerical model can be used to quantify each of the major materials to be used in construction of the building. Impact on heating and cooling, durability, type of animal and the distance from the source to the construction site have a major influence when selecting a specific type of building material. For example, timber is a good thermal insulator. Hence during winter, we need to provide less amounts of heat inside the building compared to a building made of metal and concrete. At the same time durability may be a concern for choice of materials, because they all do not have a same life span when in contact with urine and faeces, containing the aggressive ions Cl⁻, SO₄²⁻, Mg²⁺, NH₄⁺ with high concentration of H₂S, CO₂ and NH₃ (De Belie et al 2000b). Monahan and Powell (2011) provided a system diagram for construction materials: Extraction of raw material or recycled material > Transportation > Manufacturing of components and products > Transportation to site > Construction > Occupation > Maintenance and renovation > Deconstruction > Removal from site (Transport) > Disposal. LCA is a tool that can be used for assessing the global emissions for the materials used in the building. Some material choices are made due to technology, economy and purpose limitations such as concrete for slated floors in a farm building for cattle (De Belie et al 2000a). On the other hand, roof material can be flexible as it may be corrugated GI sheet, glass fibre or wooden. This study considers IPPC legislations and the flexible areas for a material choice.

The objective of this study was to model a farm building based on farm building legislation in order to quantify the bill of materials and to select an equation for heating as well as cooling which are key inputs for the subsequent LCA study.
Materials and Methods

**IPPC legislation and dimensions**

A simple steel frame (Figure 1) was assumed. This consisted of a framework of steel stanchions, rafters, and bracing. It is used for most animal houses with feeding passages, and also for sloped-roof ‘single-sided’ houses. It can easily accommodate feed barriers, pens, and facilitate good ventilation, and is therefore recommended for slatted or scraped floor houses for cattle, cows or sheep.

![Diagram of a steel frame house](image)

**Figure 1.** Single-sided simple steel frame (4 bay) house published by DAFM – S. 101: “Minimum specifications for the structure of Agricultural Buildings”

This study focuses on rafters and purlins, columns / stanchions, roof sheeting, claddings, sliding doors. Other components like foundations, mats, concrete floors, slurry tank, concrete apron, external walls, cubicles & cubic beds, path, metal trough, feeding barriers, automatic scrapers, water trough are not considered as they are common for scenarios whether steel or timber. The steel structure was designed in accordance with IS EN 1993 and expected to serve 30 years with a steel corrosion rate of 200 µm thickness loss per year (De Belie et al. 2000c). Whereas for timber-design IS 444 was adopted. All timber should have a minimum service life of 20 years (mostly pine or cedar) to satisfy hazard class 4 requirements, as defined in IS EN 335-1:1992. Hence the LCA comparison requires 2 steel buildings and 3 wooden building to provide 60 years of service.

<table>
<thead>
<tr>
<th>Feature</th>
<th>Steel (S)</th>
<th>Timber (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eve height</td>
<td>4m</td>
<td>4m</td>
</tr>
<tr>
<td>Bay width (max for timber)</td>
<td>4.8m</td>
<td>4.8m</td>
</tr>
<tr>
<td>Max purlin spacing</td>
<td>1.12 m</td>
<td>1.12 m</td>
</tr>
<tr>
<td>Cladding &amp; roof</td>
<td>(S) 0.5mm GI (T) 12mm ply. (with PVC)</td>
<td>Sliding door (S) 1mm steel (T) 12mm plywood</td>
</tr>
<tr>
<td>Angle brace (&gt;1.5m length)</td>
<td>(S) UA 60x60x6 (T) 75x175</td>
<td>Over hanging rafter and supporting member (S) IPE 180 (T) 75x175</td>
</tr>
<tr>
<td>Stanchions</td>
<td>(S) UB 203x102x23 (T) 150x225 (10 nos.)</td>
<td>Main purlin (S) UA 50x50x6 (T) 50x75</td>
</tr>
<tr>
<td>External column</td>
<td>(S) 50x50x6 (T) 75x175</td>
<td>Supporting purlin (S) UA 25x25x3 (T) 50x75</td>
</tr>
</tbody>
</table>

**Table 1.** Some features of the building according to legislation S. 101. (S) for steel, (T) for timber

**Numerical modelling to quantify the bill of materials**

The main elements of a numerical model are in the sequence of observation of the physical system > numerical model > simulation > prediction. Using finite element methods, the model was split into n
(number of) nodes each with relevant properties. Modelling software (STAAD pro) was used to solve differential equations to maintain equilibrium condition for each differential sub system.

**Figure 2.** Numerical model of the farm building: dimensioning and 3D view

**Thermal transmittance and model validation**

Mass balance of relative humidity, CO\(_2\) and heat balance can be estimated using equations:

\[
m^i = \frac{(1.5 \times W_a)}{W_i - W_o} \quad (1)
\]

\[
m^{ii} = \frac{CO_2a}{CO_{2i} - CO_{2o}} \quad (2)
\]

\[
S = [(A \times U + M_{min} \times C) \times \Delta T] - H_s \quad (3)
\]

\[
M_{max} = (H_s - A \times U) \times \Delta T / (C \times \Delta T) \quad (4)
\]

As a rule of thumb, \(M_{max}\) should be limited to ten times of \(M_{min}\). All the abbreviations are explained in Figure 3. Further work will validate the model and find ‘U’ for real conditions. With a set of known data ‘U’ an unknown scenario can then be assessed. Furthermore, depending on the supplement heating and maximum air flow rate the energy consumption can be calculated for comparison in the LCA stage of the work.

**Figure 3.** Model for mass balance of HVAC system in an animal farm

**Life Cycle Assessment**

After quantification of materials, LCA models for both the scenarios will be built. The functional unit of the study requires further consideration, but could be: per m\(^2\) of building, per m\(^3\) of building or per animal housed, assuming a building 19m x 4.8m x 4.6m providing animal shelter.
Results and Discussion

The numerical analysis with STAAD pro indicated the major quantities for each structure (Table 2).

**Table 2.** Final quantity of materials obtained from numerical model

<table>
<thead>
<tr>
<th>Scenarios</th>
<th>Major component</th>
<th>Quantity (ton)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel Structure</td>
<td>Structural steel</td>
<td>2.665</td>
<td>LCA to be performed for these materials in accordance with the energy required to produce supplementary heat</td>
</tr>
<tr>
<td></td>
<td>GI sheet</td>
<td>1.203</td>
<td></td>
</tr>
<tr>
<td>Timber Structure</td>
<td>Timber frame</td>
<td>2.429</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12mm Plywood</td>
<td>1.403</td>
<td></td>
</tr>
</tbody>
</table>

Limitations and future work

The gusset plate quantity and nuts-bolts were not considered. Also, the architectural aspects (Fuentes 2010) of farm buildings were not considered in the initial stage of the study. A survey of farms in Ireland will be undertaken to collect data for stepwise validation with SPSS statistical software. A set of random variables that could influence ‘U’ will be defined for the analysis and the regression will be used to eliminate variables and to establish a co-relation between the input variables and the dependant variable, ‘U’. LCA for the two scenarios will be used to assess environmental impact.

Conclusions

This study successfully calculated the quantities for the bill of materials of the flexible portion of a standard farm building for animal housing. This is the first step required to model the thermal properties and to use LCA for comparing building materials from an environmental perspective. This will provide a basis for eliminating materials prior to further design steps. This analysis will be the first step towards the optimization of energy for a net zero building concept. Estimation of total carbon balance may be possible after completion of an analysis with LCA.

References


META-ANALYSIS OF THE EFFECT OF UV WATER TREATMENT ON ESCHERICHIA COLI

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Abstract

It is important that harmful strains of Escherichia coli are eliminated from water ecosystems as when they are consumed by humans it can lead to severe illness. Ultraviolet water treatment is a disinfection method that can eliminate harmful bacteria from water and in turn this will reduce the risk to human health. A meta-analysis model was created to investigate the log reduction of Escherichia coli due to ultraviolet treatment. Over 250 data points were collected on the log reduction of Escherichia coli by ultraviolet treatment and a meta-analysis model was built using the Winbugs software. Preliminary results calculated from the meta-analysis model showed the average predicted log reduction due to ultraviolet level using all the data collected. The average predicted results calculated a 6 log reduction from an ultraviolet level of ~13mJ/cm². Initial results from the data collected showed different strains of Escherichia coli had different log reduction patterns due to ultraviolet level. Further investigation into the different Escherichia coli strains is required to establish a log reduction pattern for each type of strain due to ultraviolet treatment.

Introduction

It is a necessity for human life that water is safe and free from harmful bacteria for human consumption. Pathogenic strains of Escherichia coli (E. coli) can be of risk to human health when consumed through water. Infection from harmful E. coli bacteria can result in diarrhoeal disease, urinary tract infections or sepsis/meningitis (Sommer et al 2000; Kaper et al 2004). Some of the main disease causing E. coli strains transmitted through water are O148, O157 and O124 (Cabral, 2010). There are a number of pathways where harmful E. coli can be transmitted to humans they include drinking water, recreational water, wastewater, water used for irrigation and water used in food production (Sommer et al 2000). It is vital that harmful bacteria are eliminated through drinking and wastewater treatments to prevent them from coming into contact with humans.

Disinfection methods such as ozone, chlorination, chloramination, chlorine dioxide and ultraviolet (UV) treatment processes can be used to reduce the risk from harmful E. coli strains (Environmental Protection Agency, 2011). UV water treatment is growing in popularity as a water disinfection method because it does not use chemicals, a short contact time is required for treatment, no harmful by products are formed from the process, a small amount of space is required to add it to a water treatment system and capital costs are less compared to ozonation treatment (Quek and Hu, 2008; Environmental Protection Agency, 2011). UV treatment kills harmful bacteria in water by disrupting the structure of the DNA and destroying the nucleic acids in the bacterial cell, this then leads to the bacteria being unable to reproduce and this causes it to die off (Quek and Hu, 2008). It is important to use the correct UV level when treating water in order to kill off harmful bacteria. It is recommended that a level of 40 mJ/cm² UV level is used in order to achieve a 6 log reduction of water transmittable bacteria and a 4 log reduction for water transmittable viruses (Environmental Protection Agency, 2011).

The objective of this study is to create a meta-analysis model to examine the effect of UV treatment on the log reduction of Escherichia coli.

Materials and Methods

Meta-analysis
Meta-analysis is a statistical based method of combining data from comparable scientific research papers. When data from numerous studies are combined this can strengthen a study by giving a weighted average compared to relying on the results of just one study.

**Data collection**

In order to find the data required for the meta-analysis study a literature search was performed examining current, past, national, international scientific research papers and web sources to compile the data required for this study. Over 250 data points were collected from 21 scientific studies on *E. coli* log reduction due to UV treatment (Figure 1). Data was collected only if the results showed a clear log reduction of *E. coli* bacteria by UV treatment level (mJ/cm²).

**Software**

The *Winbugs* software was used to create the meta-analysis model. *Winbugs* is a statistical based modelling software for Bayesian analysis using Markov chain Monte Carlo methods.

**Meta-analysis model design**

There are two types of meta-analysis methods for incorporating study effects, they are called fixed effect and random effect. Fixed effect assumes there is one true effect size which is shared by all the included studies and random effect takes into consideration that the true effect could vary from study to study (Borenstein et al 2007). Log reduction was examined in a mixed-effect linear model as shown in equation 1. A mixed effect model is a combination of both fixed effect and random effect variables (Membré et al 2007). In this study the dependent variable was the log reduction of *E. coli*, the independent variable was the UV level and covariables were type of *E. coli* strain and the study from which the data was collected.

\[
\text{LogR} = \bar{R} + \alpha + \beta + \lambda + \Sigma
\]

Equation 1

LogR is the log reduction, \(\bar{R}\) is the log reduction at the average UV treatment, \(\alpha\) is the UV treatment effect, \(\beta\) is bacteria strain effect, \(\lambda\) is the study effect and \(\Sigma\) is the error.

![Figure 1](image_url). Distribution of data collected on *Escherichia coli* log reduction from UV treatment level

**Results and Discussion**

Preliminary results calculated by the meta-analysis model created on *Winbugs* show the average predicted log reduction pattern of *E. coli* from UV treatment level (Figure 2). The results predicted by the model showed a 6 log reduction was reached at a UV level of ~13 mJ/cm². In comparison to the recommended UV level of 40 mJ/cm² for a 6 log reduction of harmful bacteria (Environmental Protection Agency, 2011). The predicted average results show a lower UV level is required for a 6 log reduction of *E. coli*. However, the recommended UV level errs on the side of caution and ensures that *E.coli* is eliminated from the water following UV treatment.
From examining the data points collected from the 21 scientific studies (Figure 1), the raw data suggests different strains of *E. coli* have different log reduction patterns due to UV treatment level. An investigation into each *E. coli* strains log reduction pattern due to UV treatment would be interesting to examine further as future work. It would be of interest to establish an average predicted log reduction for each *E. coli* strain and this could show which strains of *E. coli* are more or less resistant to UV treatment.

![Figure 2. Preliminary results of average predicted log reduction of *Escherichia coli* from UV treatment level](image)

**Conclusion**

UV treatment is a good choice for a water treatment method due to its ability to eliminate harmful *E. coli* from water, it has a quick treatment time, no chemicals required and a small amount of space required to add it to a water treatment system. Preliminary results calculated from the meta-analysis model showed the average predicted log reduction due to UV level and a 6 log reduction from a UV treatment level of 13 mJ/cm² was calculated from the model. The UV level recommended is 40 mJ/cm² for a 6 log reduction therefore the predicted results illustrate the very conservative nature of recommended current UV treatment levels appear to show *E. coli* bacteria do not require as much UV level as what is recommended (Environmental Protection Agency, 2011). Given the health implications it is understandable to err on the side of caution. Also the log reduction patterns of *E. coli* due to UV treatment in the data collected from the scientific literature show different *E. coli* strains have different log reduction patterns due to UV level. Further investigation into the log reduction pattern of each strain of *E. coli* may show which strains are more/less resistant to UV treatment.

**Acknowledgements**

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**References**


LEAD IN WATER - ANALYSIS AND HUMAN EXPOSURE

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Abstract

Lead in drinking water has a negative effect on human health. Lead (Pb) is the most abundant heavy metal in the Earth’s crust which means that it is the heavy metal most likely to infiltrate groundwater. Lead has also been used for centuries to transport water and it is only in the last 40 years that the negative health impacts of lead has been realised. The World Health Organization guidelines advises that drinking water lead content must be below the limit of 10 µg/L. The use of spectrophotometry will be used to analyse the lead content of samples of water from three water supplies ranging from low to high risk. A first draw and full flush water at the point-of-use sampling method will be employed in the study. The results of the lead testing will be used in a quantitative risk assessment model with a Monte-Carlo simulation approach in order to analyse the risk to the consumer.

Introduction

Access to clean, good quality drinking water is a basic human right. High levels of lead present in our drinking water can have detrimental effects to our health. For humans lead in drinking water is the most bioavailable source of soluble lead as it is more easily absorbed in the intestine when compared to lead exposure from other dietary sources (Postawa 2015).

One of the biggest concerns from lead in drinking water is the negative neurodevelopmental effects it can have: poor attention span, hallucinations, headaches, irritability, ADHD, violent behaviour and restlessness (Postawa 2015; Pfadenhauer et al 2014). Infants and foetuses are the most sensitive to lead exposure as they can absorb up to five times more lead than adults and lead can have an negative effect on their cognitive development (Payne 2008; Kahn et al 2006; Getaneh et al 2014).

Worryingly the average pre-industrial human (pre-1800s) had blood lead levels of 0.16 µg/L compared to today’s average of between 8 and 32 µg/L (Getaneh et al 2014). Other health risks of of lead poisoning include: muscular exaustibility, coma, death, encephalopathy, weight loss, vomiting, tremors, kidney damage, gastrointestinal irritation, chronic renal failure and gonad dysfunction.

The main risk factors for lead contamination of drinking water are lead pipes. Lead service pipes were used for water supply in many countries up until the early 1980s (Postawa 2015). The Irish government claims to have replaced all public water supply pipes with non-lead replacements, however, many homes connecting pipes (from public pipe boundary with private property to tap) have not been replaced unless the owner has done so post 1980.

The WHO most recent guidelines for safe levels of lead in drinking water state that it should not exceed 10 µg/L as of 25th December 2013 (WHO 2011). This should be only viewed as a provisional value as the dose response analysis does not indicate a threshold for the principal negative effects of lead according to, especially for children and foetuses. The guideline before 2013 was 25 µg/L so it is clear that the World Health Organization is slowly lowering the limit so that countries can adapt, but the evidence points that the lead content for drinking water should be as close to 0 µg/L as possible in order to minimize the risk completely. This study will develop a risk assessment model to test the human exposure to lead through drinking water in Dublin using the WHO guidelines of 10 µg/L as the minimum level acceptable for the consumer.

The objective of this study was to test the hypothesis of whether human exposure to lead through drinking water is below any regulatory and toxicity level and poses negligible risk to the consumer in Dublin.
Materials and Methods

Sampling
Samples will be taken from a low, medium and high risk water supply. Homes built before the 1980s that are far away from the water source will be considered as high risk water supplies while newly built homes closer to the water source will be considered as low risk water supplies. These considerations are made as the closer the household is to the water source then the less time the water spends in different pipes which reduces the risk of lead contamination.

After an analysis of various sampling methods, the following sampling method was selected: 1 litre samples will be collected twice a day for a week from the point-of-use (tap). First draw samples will be taken in the morning after water has a residence time of 6 hours in the pipe and after full flushing of the system in the evening. This two part sampling method ensures that the supplies highest and lowest lead concentration is sampled and taken into account to produce and average over the day. Each 1 litre sample will be preserved with 10 ml of pPb-1 Acid Preservative, this preservative can be used to rinse apparatus and sampling bottles to minimize sample contamination. Lead free bottled water will be used as a control.

Testing
Water samples will be tested for lead contamination using the LeadTrak fast column extraction method. This method is accurate for readings of between 5 to 150 µg/L (ppb). This range is ideal for the study as the regulatory level for drinking water according to the World Health Organization is 10 µg/L. 100 ml from each 1 litre sample will be taken for testing.

The following experimental procedure will be used to calculate the lead content of each sample:

- Add 2 ml of fixer (Hach pPb-2 Fixer Solution) and swirl to mix.
- Pass sample through Hach Fast Column Extractor column to retain Pb.
- Elute Pb from column using Hach pPb-3 Eluant Solution.
- Adjust pH of eluent using Hach pPb-4 Neutralizer Solution.
- Add colour agent (Hach pPb-5 Indicator Powder Pillow).
- Pour 10ml of solution into a sample cell and add pPb-6 Decolourizer Solution.
- Insert sample cell into the Hach Lange DR3900 spectrophotometer which will analyse the sample and show the lead content in µg/L Pb.

Deionized water will be used instead of the sample in the test for each new lot of reagent as a reagent blank in order to get more accurate results.

Model Development
A quantitative modelling risk assessment approach will be used to evaluate the likely level of human exposure to lead based on the results from the sampling plan. The likely water consumption pattern for different groups will be considered as well as the likely absorbance of each subset of the population. A Monte-Carlo simulation approach will be adopted. Uncertainty and variability will be considered using probability density distributions where possible.

A daily chemical intake calculation will be used in the model to assess the risk of adverse health impacts of lead to the consumer. The hazard quotient (HQ) will be calculated using the equation:

\[ HQ = \frac{DI}{RfD} \]

Where:
- \( DI \) is the daily intake (µg/kg/day).
- \( RfD \) the reference dose (µg/kg/day).
When HI values are greater than 1 there is a likelihood of adverse health effects and therefore a risk to the consumer. Averages to be used in the exposure assessment are listed in the table below:

<table>
<thead>
<tr>
<th>Weight (kg)</th>
<th>Children (&lt;7 years)</th>
<th>Children (7-15 years)</th>
<th>Adults (&gt;15 years)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15</td>
<td>40</td>
<td>70</td>
</tr>
<tr>
<td>Water intake (L/day)</td>
<td>1</td>
<td>1.5</td>
<td>2</td>
</tr>
</tbody>
</table>

Absorption of lead from drinking water was found to be 50% for adults and 10% for children in the study done by (Bois et al 1989). These values will be used for the exposure assessment.

**Results and Discussion**

The testing of this study and hypothesis is only beginning and there are no definitive results as of yet. It is anticipated that there will be negligible risk to the consumer in Dublin as most public water supply pipes have been replaced. The authors will also analyse the results with respect to possible limitations of the sampling approach taken.

**Conclusions**

Lead exposure through drinking water is dangerous to human health, there are a range of mental and physical ailments associated with lead poisoning. The main cause of lead contamination of drinking water can be attributed to an ageing water distribution network and connecting pipes which still use lead as a main component of the infrastructure. This can be fixed by complete replacement of the existing networks or fixing a filter at the point of use. Continuous monitoring of lead in drinking water must be maintained in order to completely eliminate the risk of lead poisoning. Further research is needed on what minimum level of lead in water is considered to have an impact on human health or whether it is unsafe to drink water containing any lead at all.

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**References**


DISPERSION MODELLING OF AMMONIA EMISSIONS FROM LICENSED BROILER UNITS IN IRELAND

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Abstract

Emission of ammonia ($\text{NH}_3$) and its deposition can result in eutrophication and acidification which can impact sensitive vegetation. Agriculture is the most significant contributor to ammonia emission in Ireland, therefore, finding ways to minimise and control ammonia emissions is important. This paper presents an ammonia dispersion output model from a licenced broiler farm using AERMOD. The model run uses the closest meteorological station data, maximum birds allowed by EPA licence, the EPA ammonia emission factor for broiler units in Ireland and ventilation rates observed in the UK. Preliminary results show that the 1 $\mu\text{g/m}^3$ critical level for sensitive vegetation such as lichens and bryophytes is within 200 m from the point source. It is necessary to run AERMOD dispersion model scenarios for all the licenced broilers units in Ireland and to combine them in ArcGIS, in order to estimate the cumulative impact and define areas that could be affected by critical ammonia levels.

Introduction

The concerns about ammonia ($\text{NH}_3$) emissions have been come increasingly important over the last number years. Since 1980, a growing effort has been made to understand and quantify the levels of ammonia in the environment in order to minimise its environmental impacts (Sutton et al. 2008). Ammonia is the primary basic gas in the atmosphere and, after $\text{N}_2$ and $\text{N}_2\text{O}$, is the most abundant nitrogen-containing compound (Seinfeld and Pandis 2006). In the 80’s it was recognized that deposition of atmospheric ammonia to sensitive terrestrial ecosystems leads to both soil acidification and eutrophication, resulting in losses of certain plant species (Sutton et al. 2008).

In the EEA (European Economic Area), the agricultural sector remains the major source of NH$_3$ emissions, contributing 94% in 2010 (European Environmental Agency 2016). In Ireland, ammonia emissions were 107.8 Kilotonnes in 2013, or 0.4 % less than emissions in 1990. Animal manure produces about 87 per cent of ammonia emissions in agriculture (Environmental Protection Agency 2015). Therefore, research to control and minimise ammonia from agriculture is vital in preserving areas and conserving Ireland’s biodiversity.

In order to conserve areas that could be affected by the ammonia deposition, it is necessary to determine critical levels for atmospheric NH$_3$ (Cape et al. 2009), i.e. Critical levels of 1 $\mu\text{g/m}^3$ for sensitive vegetation such as lichens and bryophytes and 3 $\mu\text{g/m}^3$ for higher plants. This paper summarises a dispersion model output of a broiler unit in Ireland. This can be used to determine the distance where the ammonia concentration exceeds the 1 $\mu\text{g/m}^3$ critical level.

The objective of this study is to determine the cumulative impact of ammonia emissions from licensed broilers units in Ireland by using the AERMOD dispersion model and ArcGIS.

Materials and Methods

Study area

This project is investigating the ecological impact of ammonia emissions from broiler units in the Republic of Ireland. The location of broiler houses is not evenly distributed throughout Ireland, as some counties have significantly higher numbers than others (Table 1).
Broiler farms to be inputted into the model were selected based on the highest number of farms, i.e. Monaghan. The model was run by starting in the areas with the highest number of IPPC (Integrated Pollution Prevention Control) licensed broiler farms to the areas with the lowest number of IPPC broiler farms.

Description of dispersion model
The most common models encountered by the Irish Environmental Protection Agency are ISC, ADMS, AERMOD and associated screening models, and modelling assessments based on these models have been accepted by the Agency. The preference of the Agency in most situations would be for the newer generation Gaussian models, such as ADMS or AERMOD (Porter et al. 2010). Using one of the EPA’s preferred models, AERMOD was the dispersion model chosen in this project.

Input data
The data required by AERMOD in order to model air quality impacts of pollution sources are: source data, meteorological data and geographical data.

Source characteristics
A total of 73 licensed broiler farms will be modelled. The first scenario to be modelled was a broiler house with a maximum of 86,000 birds. Each broiler house is considered a point source. An ammonia emission factor 0.22 g NH$_3$-N per bird place per day (European Environmental Agency 2016) was used to calculate the ammonia emission and, an overall 0.00042 m$^3$/s per bird air flow rate (Hill et al 2014) was applied in order to run the dispersion model.

Meteorological data
AERMET is a meteorological data pre-processor for AERMOD. The dispersion process is dependent on the meteorological conditions, therefore, it is crucial to ensure representative meteorological data by including five years of meteorology data (Mokhtar et al 2014) and using data from the closest meteorological station to the source.

The meteorological data used for modelling a broiler house in Monaghan was five years of continuous hourly data (2011 – 2015) from the Ballyhaise meteorological station, with coordinates $54^\circ03'05''$ N, $07^\circ18'35''$ W, 78 m above sea level. It is located within the grounds of Teagasc, Ballyhaise, Co. Cavan and was installed in 2003 (Met Éireann 2016).

Geographical Data
AERMAP is a terrain pre-processor and is used to prepare the terrain information required by AERMOD for complex terrain scenarios. The accurate determination of terrain elevations in air dispersion models is vital (Porter et al 2010). Terrain characteristic for this project was taken from STRM3 global dataset, which is presented in a form of a Digital Elevation Model (DEM) format required for AERMAP.
Results and Discussion

Figure 1 shows the dispersion model for a broiler house in Monaghan. The 1 µg/m³ critical level for sensitive vegetation is within 200 metres - a distance where vegetation such as lichens and bryophytes can be affected.

![Image of dispersion model](image)

**Figure 1.** Ammonia dispersion model scenario for a licensed broiler unit in Monaghan.

Conclusions

As one model dispersion scenario has been carried out, further dispersion scenarios for the remaining 72 licenced broiler houses in the Republic of Ireland is required. This will allow the identification of the distances from the point sources where ammonia concentration exceeds the critical levels of 1 µg/m³ and 3 µg/m³.

All 73 AERMOD modelled scenarios will be combined using ArcGIS to estimate the cumulative impact, in order to assess critical levels in the ecosystem exposure which are of international conservation importance.

Acknowledgements

This study is part of the AmmoniaN2K Project, which aims to quantify and assess the impact of ammonia emissions from intensive pig and poultry units on Natura 2000 sites in Ireland. The authors acknowledge funding for this project by STRIVE as administered by the EPA. The project details are available at [http://ssu.ie/research/ammonian2k/](http://ssu.ie/research/ammonian2k/) and on the twitter page [https://twitter.com/AmmoniaN2K/](https://twitter.com/AmmoniaN2K/).

References


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Abstract  
Engineered nano silver (nAg) is incorporated in a diverse range of products and processes. Subsequent use and disposal can result in nAg entering the aquatic environment through wastewater pathways. Silver is known to have toxic effects on biotic organisms and may therefore pose a risk to both animal and human health. In complex and variable aquatic environments, inputs of nAg are subjected to natural attenuation processes likely to reduce/retain or transform concentrations of this material within the aquatic compartment. Mathematical modelling approaches presented here allows predictions of likely endpoints and estimation of likely concentrations of nAg while uncertainly and variability can be accounted for through the use of risk analysis simulation and modelling. Exposure model development could aid in the assessment of nAg exposure to aquatic habitats and overall risk to biotic species.

Introduction  
Engineered nano materials (ENMs) are defined as being in the 1-100nm size range in at least one dimension and offer a wide range of functions due to their large surface area to mass ratio (Moreno-Garrido et al 2015). They have a diverse application throughout industry and in medical applications (Moreno-Garrido et al 2015). Increased use and disposal of materials incorporating ENMs will expose the environment to as yet unknown loads of ENMs and their inherent risk. Silver is known to have beneficial antimicrobial properties and is incorporated in textiles, food packaging and medical applications etc. (Brunetti et al 2015). The presence of Ag in textiles raises concerns about the potential release of fractional concentrations of silver during washing processes. Silver can be transported through wastewater pathways and released to the various environmental compartments (air, soil and water) (Brunetti et al 2015). Waste water treatment plants (WWTPs) are likely be the primary recipient of waste containing fractions of nAg. Removal efficiency of WWTP processes and containment in sludge will determine the levels of nAg that maybe released through effluent discharges to aquatic systems (Brunetti et al 2015).

Aquatic habitats are particularly sensitive to Ag because of its toxic effects on aquatic organisms. Natural waters comprise of a complex combination of organic and inorganic colloids which have the potential to alter and transform nAg influencing bioavailability, toxicity and eventual fate (Wang et al 2015). Natural colloids such as natural organic matter (NOM) are likely to influence nAg transport and fate. Dissolution of silver results in the release of Ag⁺ which are toxic to biotic organisms as they can interfere with cellular functions through the generation of reactive oxygen species (ROS) (Schaumann et al 2015). Aggregation is influenced by attractive forces on the particle surfaces, resulting in large clusters with reduced surface area which settle to the sediment under gravitational force. Sedimentation can act as a final sink for nAg where it can be sequestered or further transformed to insoluble silver sulphide (Ag₂S). Natural attenuation processes are complex and subject to considerable variability. Therefore, we have employed mathematical descriptions of these processes and risk analysis modelling to assess the fate of nAg in the aquatic environment.

The objective of this study is to review the effects of natural attenuation processes on fate and behaviour of nano silver in aquatic media.
Materials and Methods

A literature review was performed to identify primary sources (products and processes of nAg, major usage and disposal pathways). As part of this review, current scientific literature was critically analysed and data relevant for application within the model extracted. Main processes which influence particle fate and behaviour can be seen in Figure 1. Each process can be characterised using empirical relationships. Mathematical equations describing physical processes likely to impact on fate and behaviour of particles in aqueous media were identified through literature review. These include:

**Particle dissolution**
Quik et al. (2011) used a mathematical approach for determining the particle dissolution kinetics within aqueous media. The calculation is bases on pristine particles in filtered water. Considerable variability can be assumed as this does not account for the effect of colloidal interactions with NOM or other geo colloids which can reduce the available surface area for dissolution.

\[
\frac{dM}{dT} = -kSA
\]

Where:
- \( dM \) = Amount of substance that dissolves (kg)
- \( dT \) = Unit of time (s)
- \( k \) = Dissolution rate constant (m\(^{-1}\)s\(^{-1}\))
- \( S \) = Substance’s water solubility (kg m\(^{-3}\))
- \( A \) = Area (m\(^2\))
(Quik et al. 2011)

**Aggregation**
Colloids of both geo and bio origin will significantly impact on the accuracy of this mathematical approach. Attractive and repulsive forces between particles can be suppressed or enhanced by the presence of particle surface modifications. Aggregation of nAg in natural waters is expected to be in the form of hetero-aggregates comprising of multiple complex colloids. The rate of aggregation is influenced by ionic strength, pH and the concentration of bio and geo colloids. Figure 2. Indicates the relationship between zeta potential and pH for suppressing the barrier to aggregation.
Aggregation rate constant: \[ k_{11} = \propto \frac{1}{N_0} \frac{dr}{dt} \]

Where \( r \) is the hydrodynamic diameter, \( t \) is time, and \( N_0 \) is initial nAg concentration @ 25°C (Chen and Zhang 2012)

Attachment efficiency: \[ \alpha = \frac{k_{11}}{(k_{11})_{fast}} \]

Where \( k_{11} \) is rate constant and \( (k_{11})_{fast} \) is fast (diffusion – limited) aggregation (Chen and Zhang 2012)

**Sedimentation**

The Stokes equation is based on the velocity of a sphere through aqueous media. While the Stokes equation can be used to calculate the settling velocity of a particle through a fluid, its application is somewhat limited/incompatible with the complexities of natural media.

\[ \frac{dC}{dT} = -\frac{W_s}{H} C \]

Where:
- \( W_s \) is the sedimentation velocity (m/d)
- \( H \) is depth of the water column (m)
- \( C \) is the concentration of the nanoparticles adsorbed to the suspended solids (two different fractions actually: organic and inorganic) or the concentration of the clusters of nanoparticles (μg/L) (Markus et al. 2015).

**Results and Discussion**

Great uncertainty remains surrounding behaviour of nano silver in aquatic systems. Behaviour can be characterised using empirical/theoretical relationships which in turn can be used in evaluating risk to environmental health and potential risks to human health.

The rate of dissolution is dependent on the available surface area of the particle and thus dissolution is expected to increase as the particle size decreases although knowledge gaps still remain on dissolution kinetics (Quik et al. 2011). Liu and Hurt (2010), found that almost 100% dissolution of 2 mg L\(^{-1}\) silver occurred after 125 days.

Aggregation increases in the presence of monovalent and divalent cations, increasing electrolyte concentrations lead to critical coagulation concentration (CCC) resulting in rapid aggregation. Therefore, aggregation is expected to be favourable in seawater conditions in comparison to freshwater systems (Chen and Zhang 2012). Nano silver can be expected to form bonds with sulphur transforming the nAg to Ag\(_2\)S which is highly stable indicating that sediments could potentially sequester inputs of nAg (Dale et al. 2013).
Risk analysis modelling can be employed to account for the variability and uncertainty that is inherent when dealing with natural systems. Simulation of nAg exposure and the subsequent physical, chemical and biological processes that nAg is likely to undergo will result in confidence intervals for environmental concentrations and estimation of resultant risk to biota and the environment as a whole.

Conclusions

Waste water effluent containing fractions of nAg are likely to be a primary source of nAg emissions to aquatic systems. Aquatic sediments are likely to be the primary environmental sink for nAg entering surface waters. Contact and interaction with sulphur in sewage sludge is likely to sequester a large fraction of nAg. While particle mobility and degradation have been described mathematically these models are difficult to adapt for complex and variable environments. Environmentally relevant data on nAg fate and behaviour studies (where available) was collated to adequately describe fate and behaviour within a suitable model framework. Risk analysis modelling techniques such as Monte Carlo simulation can be employed to account for uncertainty and variability inherent in both the input data and the model system.

Acknowledgements

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References


FAT, OIL AND GREASE (FOG) UTILISATION TRENDS IN DUBLIN

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Abstract

Fat, oil and grease (FOG) is a by-product from food processing sites (meat plants, etc.), food service outlets (restaurants, etc.) and domestic dwellings. Management and control of FOG is essential to reduce sewer blockages. Food service outlets (FSOs) are one of the primary FOG producers. To divert FOG from the Dublin City Council sewer system grease trapping systems (GTS) are required. The function of GTS is to retain FOG, however the GTS must be maintained and the grease trap waste (GTW) recovered must be collected by a permitted waste haulier. The current FOG disposal trends vary from landfill disposal to use as a feedstock in biodiesel production. With FOG management there is no incentive to utilise the FOG produced by sites. According to the waste hierarchy it is preferred that the production of waste is reduced or prevented. When this cannot be done the production of a product or energy are preferred. This paper will review GTW patterns in an area with FOG management in place. By understanding the type of FOG diverted from the sewers the most effective utilisation trends can be determined.

Introduction

Fat, oil and grease (FOG) management is a requirement for food service outlets (FSOs) in the Dublin City Council catchment to diminish blockages in the sewer system. Awareness and education are the primary tools to reduce FOG related sewer blockages. The issues caused by FOG blockages can range from domestic flooding with sewage at a local level to city wide problems which are caused by sewer fatberg formation and sanitary sewer overflow. FOG blockages require road closures for mechanical sewer maintenance and can potentially release high concentrations of pathogens, nutrients, and solids to water bodies that impose a risk to public health and the environment (He et al 2013).

The Dublin FOG Programme, in place since 2008, requires the 2200 FSOs in Dublin City Council to install properly sized grease trapping systems (GTS) and increase best management practices on site. The GTS must be maintained regularly to meet the required standards. Collection of GTW must be by permitted waste hauliers. GTW can be designated as edible oil, biodegradable kitchen & canteen waste or as grease and oil mixture from oil/waste separation containing only edible oil and fats (Wallace et al 2015). There is no incentive for sites to upcycle FOG for bioenergy or biodiesel production. The choice of disposal route is primarily cost based.

In a previous study, it was determined that in a Dublin study area of 159 sites 110,000 litres of grease trap waste (GTW) were redirected from the sewer (Gibbons et al 2015). Diverting the FOG waste is step one in the management approach. The FOG streams must then be collected and utilised. FOG is not a uniform substance. Impurities vary depending on the cooking application and washing procedures on site. The quantity of lipids in GTW varies depending on the source with GTW generation ranges from 1,406-11,000 kg/yr/restaurant with a range of 0.1-40% lipid content (Hums et al 2016).

The objective of this study is to determine the current Dublin trends for FOG utilisation subject to the type of grease trapping systems in place.
Materials & Methods

Classification of grease trap waste (GTW) / grease trapping systems (GTS) categories

Grease traps are units through which the effluent from FSOs are plumbed prior to discharging to the sewer system. Gravitational separation (passive) grease traps are baffled tanks which allow less dense lipid rich FOG waste to form at the top and food waste to form at the bottom of the tank (Wang et al. 2013). Figure 1 details the basic design of a passive grease trap. Local authority operational experience has determined that GTS should be pumped out by a permitted haulier when 25% capacity of the unit is reached as FOG retention decreases after this (25% rule). The pump out involves removing all waste from the unit. Hydro-mechanical (automatic) grease traps remove the FOG layer into a receptacle by skimming and sometimes heating the contents. These automatic grease traps are smaller in size but remove the FOG layer daily and require additional maintenance.

![Figure 1. Passive grease trap (Aziz et al. 2010)](image)

Grease trap waste (GTW) is a low-quality waste material with variable lipid content, depending on the producing site. The recovered GTW can be divided into three sub-categories/grades.

GTW Grade 1: Automatic GTS separated FOG layer. With an efficient unit the water content of this stream should be minimal. This lipid rich FOG layer is the most similar to used cooking oil (UCO) and has less impurities than the other GTW streams detailed below. Often collected with the UCO for biodiesel feedstock with a potential 95% conversion rate.

GTW Grade 2: Content of a passive gravitational separation grease trap. The emptying of these grease traps includes removing all contents of the unit. Contents include the lipid rich layer, the aqueous phase and the solids waste layer. Gallimore et al (2011) have referred to these units as Passive Flow Based Grease Interceptor – PFGI and Retention Based Grease Interceptor (large outdoor GT) – RGI. The contents of this GTW are variable depending on the site that produces it and the frequency of the grease trap pump out. Based on the 25% rule when these units are pumped out 75% of the contents is waste water, 12.5% lipid rich FOG layer and 12.5% food waste layer. This GTW is commonly dewatered and used in anaerobic co-digestion where it can increase the biogas production by 27% with a 30% addition (Davidsson et al 2008).

GTW Grade 3: This is the remaining contents of the automatic grease traps after the FOG layer is separated. This waste stream should have the majority of the lipid rich FOG layer removed through the daily skimming and heating of the GTW. This is dependent on the performance of the unit and the maintenance carried out by staff. This stream should consist of an aqueous phase and a solids waste layer but FOG will still be present.
GTW utilisation trends data acquisition
Following on from research carried out by Gibbons et al (2015) it was determined that in a study area of 159 FSOs in Dublin city $110 \times 10^3$ Litres of grease trap waste (GTW) were redirected from the sewer system in 2014. In Dublin City Council all FSOs are required to install and maintain properly sized grease trapping systems. There is currently no incentive for the stakeholder to upcycle the diverted GTW. The trade effluent discharge licence dictates that the waste must be collected by a permitted haulier but does not dictate a preferred utilisation route. The permitted hauliers for the aforementioned Dublin Study area were determined through site visits and the utilisation trends were based on the disposal docket and permit data acquired from the National Waste Collection Permit Office. All GTW was collected by permitted waste hauliers; this is not representative of the national trend as the study area is within an area with a well-established FOG programme.

Results and Discussion
The DCC study area of 159 FSOs demonstrated a cross section of the entire DCC area of 2200 FSOs as it involves various types of FSO and GTS. Based on the data collected the type of GTS in place per FSE was recorded (Figure 2). In the study area of 159 FSOs, 110,000 litres of GTW were redirected from the sewer in 2014, the volumes of GTW diverted and its final utilisation based on its grade are detailed in Figure 3.

Figure 2. Food Service Outlet GTS type in Dublin Study Area in 2014

Figure 3. Dublin GTW utilisation routes in 2014

Figure 2 and 3 detail the type of GTS on site and the utilisation trend currently in place. It is evident that automatic GTS are more common in this study area but due to the larger capacity of the passive units, there is a larger volume of this GTW diverted from the sewer. Utilisation as a feedstock in
anaerobic co-digestion is the most recorded route. However, it should be acknowledged that approximately 75% of the Grade 2 GTW is waste water whereas Grade 1 is a higher quality FOG and requires less pre-treatment and has lower water content. With 110,000 L of GTW recorded in the study area it can be estimated that 1.9 million L of GTW are potentially available in a catchment area the size of DCC. This is based on a similar trend of FSO and GTS type.

Conclusion

The classification of GTS and GTW is essential to develop the most effective FOG management programme. This project is due for completion at the end of 2016 with the aim to develop a national strategy for the utilisation of FOG waste. FOG and GTW are not uniform and vary depending on the site that produces it. Further analysis to produce a FOG profile database would allow the upcycling of diverted GTW to a resource.

Acknowledgements

This project is funded by the Irish Research Council and Noonan Services Group in partnership with Evolution Environmental Services as part of the Employment Based Postgraduate Research Programme. The authors would like to thank all parties for their support. Further details regarding this project and a parallel project being carried out by David Gibbons are available at: http://ssu.ie/research/fog/.

References


EVALUATING THE IMPACT OF IRISH DAIRY FARMING ON HUMAN HEALTH: A CASE STUDY

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Abstract

Milk production on dairy farms can lead to significant environmental impacts. These impacts not only jeopardize ecosystem services and reduce resource availability, but also affect human health. The effect of environmental impacts on human health remains uncertain. The objective of this study was to quantify the effect of environmental impacts of a typical Irish dairy farm on human health. The farm system is grass-based rotational grazing, and life cycle assessment was used to model the environmental impacts from cradle to farm gate. It was found that 95% of the environmental burden on human health was from respiratory effects. The process of manure storage and application accounted for nearly 50% of the total environmental impacts on human health. In order to reduce these impacts, better manure storage and application technique should be introduced to reduce NH$_3$ and N$_2$O emissions.

Introduction

Due to the increasing global demand for dairy products and abolishment of EU milk quota (Kempen et al 2011), the output of the Irish dairy sector is expected to increase by 50% by 2020 (Department of Agriculture 2010). Milk production on dairy farm leads to significant environmental impacts (IDF 2009). These environmental burdens not only jeopardise the sustainability of the dairy sector, but also cause a negative impact on human health (Weidema 2009). The expansion of the Irish dairy sector could potentially increase its impact on human health. However, the effect of environmental impacts of dairy farms on human health remains unknown. Farmers and policy makers should understand this impact and make corresponding management changes to improve the environmental and social sustainability of Irish dairy farms as the dairy industry expands. In order to evaluate all environmental impacts on human health with the same criteria, different impacts need to be weighted into one scoring system. Monetarization has been used as a weighting method in many environmental evaluation studies (Nguyen et al 2012). The environmental impact can cause negative effect on ecosystem service, resource productivity and human health (Weidema 2009). Currently, in the LCA community, most available methodologies are used for total environmental costing evaluation (Pizzol et al 2015). Excluding the effects of environmental impact on ecosystem service and resource productivity in order to evaluate the environmental impact on human health is a key issue for this study.

The objective of this study was to evaluate the environmental impacts of a typical Irish dairy farm on human health, to identify the hotspot processes and to provide management recommendations for improvement.
Materials and Methods

Life cycle analysis

The environmental impacts of dairy farms can be characterized by life-cycle assessment (LCA) (ISO 2006a). The functional unit used in this study was 1 kg ECM (energy corrected milk) calculated by equation 1.

\[ ECM = \text{milk delivered} \times (0.25 + 0.122 \times \text{fat\%} + 0.077 \times \text{protein\%}) \]  

(1)

The system was low-cost, grass-based rotational gazing milk production operating over one year. The system boundary was from cradle to farm gate, including land preparation, cultivation processes and nutrient management for grass production, production and transportation of synthetic fertilizers, silage and concentrated feed, production and use of electricity and diesel on farm (Figure 1). The LCIA methodology was based on Stepwise 2006. In Stepwise 2006, the environmental impacts on ecosystem services, resource productivity and human health are evaluated in monetary units. This study only used the value for human health (Table 1). The allocation between milk and its co-product meat from dairy cows was based on the energy and protein requirement of the herd. The proportion of the total energy and protein requirements of the herd for meat production in an Irish pasture based system was taken as 12% (Shalloo et al 2004). The model was developed in LCA software Gabi 6.0 and majority of background data were from the Gabi database and the Eco-invent database. The activity data for characterizing a typical Irish dairy farm were taken from a survey by (Yan et al 2013).

Figure 1. “Cradle to farm-gate” system diagram of modelled Irish dairy farm
Table 1. Monetarization factors for human health impact category in Stepwise2006

<table>
<thead>
<tr>
<th>Impact category</th>
<th>Unit of characterized values at midpoint</th>
<th>Human well-being EUR/characterized unit at midpoint</th>
</tr>
</thead>
<tbody>
<tr>
<td>Global warming</td>
<td>kg CO2-eq.</td>
<td>0.0016</td>
</tr>
<tr>
<td>Respiratory, organics</td>
<td>person<em>ppm</em>h</td>
<td>0.2</td>
</tr>
<tr>
<td>Respiratory, inorganics</td>
<td>kg PM 2.5-eq.</td>
<td>52</td>
</tr>
<tr>
<td>Ozone layer depletion</td>
<td>kg CFC-11-eq.</td>
<td>78</td>
</tr>
<tr>
<td>Ionizing radiation</td>
<td>Bq C-14-eq.</td>
<td>1.55E^-05</td>
</tr>
<tr>
<td>Human toxicity, non-carcinogens</td>
<td>kg C2H3Cl-eq.</td>
<td>0.21</td>
</tr>
<tr>
<td>Human toxicity, carcinogens</td>
<td>kg C2H3Cl-eq.</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Results and Discussion

The results indicated that for every 1 kg ECM produced the environmental impacts generated from the life cycle of the production chain could cause an impact on human health costed as €0.0472. Table 2 shows the contribution of each environmental impact to the total cost of environmental burdens on human health and the share of each impacts from on-farm processes. The main impact on human health came from inorganic respiratory effects (90.85%), organic respiratory effects (4.47%) and global warming (4.18%). Other environmental burdens from Irish dairy farm only had minor effects on human health. From a supply chain perspective, on-farm activities (including milk production by animals, manure storage and application, animal excretion, fertilizer spreading) account for more than 77% of the total impact on human health. The biggest impact was from respiratory effects by inorganic pollution. This was mainly caused by the NH₃ and N₂O generated from manure storage/spreading process (49.27%) and cow excretion process (14.77%).

Table 2. Contribution analysis of environmental impact on human health

<table>
<thead>
<tr>
<th>Item</th>
<th>Contribution to total cost (%)</th>
<th>On farm impacts (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Global warming</td>
<td>4.18%</td>
<td>3.70%</td>
</tr>
<tr>
<td>Respiratory, organics</td>
<td>4.47%</td>
<td>3.82%</td>
</tr>
<tr>
<td>Respiratory, inorganics</td>
<td>90.85%</td>
<td>69.85%</td>
</tr>
<tr>
<td>Ozone layer depletion</td>
<td>0.00%</td>
<td>0.00%</td>
</tr>
<tr>
<td>Ionizing radiation</td>
<td>0.02%</td>
<td>0.00%</td>
</tr>
<tr>
<td>Human toxicity, non-carcinogens</td>
<td>0.45%</td>
<td>0.08%</td>
</tr>
<tr>
<td>Human toxicity, carcinogens</td>
<td>0.03%</td>
<td>0.00%</td>
</tr>
</tbody>
</table>

The 95% of impact due to respiratory effects suggested that most impact on human health was local to the farm. It could cause damage to the social sustainability of local community. Expansion of the dairy sector could increase this negative effect on local communities around
the farm. In order to reduce the impact on human health, more advanced manure storage and application technology could be introduced to reduce the NH$_3$ and N$_2$O emission. This approach means that within the sustainability triangle (environmental-economy-society), environmental performance can be linked to the social performance. Reducing the environmental impact of Irish dairy farms could minimize their impact on human health.

**Conclusions**

This study evaluated the environmental impact of dairy farm on human health. It was found the respiratory effect caused by the emission from manure has the biggest impact on human health. In order to achieve sustainable development and reduce the impact on human health, Irish dairy farms should introduce more advanced technology to reduce emission (NH$_3$, N$_2$O) from manure.

**Acknowledgements**

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**References**

Department of Agriculture (2010) '2020 Food Harvest-a vision for agri-food and fisheries'.
THE APPLICATION OF MID INFRARED (MIR) SPECTROSCOPY FOR THE PREDICTION OF PHOSPHORUS DYNAMICS IN AGRICULTURAL SOILS

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²Environment, Soils and Land Use Department, Teagasc, Johnstown Castle, Co. Wexford, Ireland.

Abstract

Dairy, beef, pig and sheep farming is becoming more intensive in Ireland in order to meet the challenging growth projections set by Food Wise 2025. Optimum soil quality and fertility will be required in order to achieve this intensification. Soil quality and fertility are monitored by testing for parameters such as: Morgan’s phosphorus (P), cation exchange capacity (CEC), aluminium (Al) and iron (Fe). Soil testing for P is also required for the national implementation of the Nitrates Directive, which protects water quality. However, there are disadvantages associated with traditional soil testing methods; they are time-consuming, costly and produce chemical waste. This project explores the application of infrared diffuse reflectance spectroscopy (DRIFT), in combination with chemometrics, to predict indicators of soil quality and fertility, specifically, P buffering capacity and P binding energy. This new technique will be less time-consuming, inexpensive and will hopefully act as a surrogate for extractive and digestive techniques traditionally used to analyse soil. To date, this project has generated preliminary results, using archived soil samples, from the Irish Soil Information System. Preliminary mid infrared (MIR) calibrations have been achieved for; CEC, Al and Fe. These soil properties are correlated with P buffering capacity and P binding energy in soil.

Introduction

Phosphorus can be one of the most limiting elements in crop production, so, mineral P fertilisers often need to be applied to agricultural soils to achieve optimal crop yield, however if amounts exceed crop requirements, this can have a negative environmental effect (Abdi et al. 2012). For this reason, P dynamics in agricultural soils must be monitored. In recent years, a large number of soil properties have been predicted using multivariate chemometric regression modeling, derived from reference soil data and UV, Vis, NIR and MIR spectra (Soriano-Disla et al. 2014). Soil analysis in this project focused on properties such as: oxalate extractable aluminium, oxalate extractable iron and cation exchange capacity (CEC). This is because P dynamics can be inferred from the analysis of these parameters (Herlihy and McGrath 2007). However, in this field of research, it is unclear if pre-processing of the spectral data is necessary prior to calibration (e.g. Cubist model in R). It is also unclear exactly how much pre-processing is necessary to eliminate physical effects such as light scattering, which can be caused by particles of different sizes and shapes (Forrester et al. 2015).

The experiment described in this paper aimed to determine the minimum amount of spectral pre-processing necessary to give successful predictions of parameters related to phosphorus buffering capacity and phosphorus binding energy.
Materials and Methods

Data acquisition
Two hundred and twenty five, first horizon, soil samples were taken from the Irish Soil Information System archive at Johnstown Castle, Wexford, Ireland. These samples were already dried at a temperature of 40 °C and ball-milled. The samples were scanned in duplicate, in the mid infrared (MIR) region of the spectrum, using a Perkin-Elmer Spectrum 400 FT-IR instrument with a DRIFT accessory. Instrument settings were as follows; 16 scans were taken of each replicate, resolution was set at 4 cm\(^{-1}\), data interval was set to 2, y-axis was set to absorbance (rather than transmittance), and the wavenumber range was set to between, 4000 cm\(^{-1}\) and 450 cm\(^{-1}\). Once absorbance \[\log (1/R), \text{ where } R \text{ is reflectance}\] of each sample was read in duplicate, spectra were exported as ‘.csv’ files and read into R Studio. The Irish Soil Information System project also provided reference data for this experiment. The parameters calibrated for were, oxalate extractable Al (n = 148), oxalate extractable Fe (n = 148) and CEC (n = 225), as these parameters are highly correlated with P buffering capacity and P binding energy (Daly et al. 2015). The reference data were also read into R Studio as ‘.csv’ files.

Modeling
The spectral data and reference data were both split, 75 % for calibration and 25 % for validation. The Cubist package in R Studio was used for modeling. Seven different pre-processing treatments were trialed on the spectral data. These were: 1. None (which was the use of raw spectra), 2. Trimming, 3. Trimming and Savitzky-Golay filter, 4. Trim, filter and standard normal variate (SNV), 5. Trim, filter and multiplicative scatter correction (MSC), 6. Trim, filter and first derivative of the spectra and 7. Trim, filter and second derivative of the spectra. The seven pre-processing treatments were ranked according to Cubist model outputs for oxalate extractable Al, oxalate extractable Fe and CEC. This was in order to easily identify the pre-processing treatment which gave the best calibration or validation result.

Results and Discussion

Preliminary results have been obtained for the calibration (Table 1) and validation (Table 2) of oxalate extractable aluminium using 7 different spectral pre-processing treatments.

Table 1. Ranking of spectral pre-processing treatments according to Cubist model outputs for the calibration of oxalate extractable Al

<table>
<thead>
<tr>
<th>Preprocessing</th>
<th>R2</th>
<th>Concordance</th>
<th>MSE</th>
<th>RMSE</th>
<th>Bias</th>
<th>RPIQ</th>
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<td>None</td>
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<td>3</td>
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<td>7</td>
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<td>3</td>
<td>7</td>
</tr>
</tbody>
</table>

Trim, trimming of noisy parts of the spectrum; SG, Savitzky-Golay filter; SNV, standard normal variate; MSC, multiplicative scatter correction; R2, coefficient of determination; MSE, mean square error; RMSE, root mean square error; RPIQ, ratio of performance to interquartile range.

According to model outputs, ‘trim, filter and multiplicative scatter correction’, is the best spectral pre-processing approach for the calibration of oxalate extractable Al.
Table 2. Ranking of spectral pre-processing treatments according to Cubist model outputs for the validation of oxalate extractable Al

<table>
<thead>
<tr>
<th>Preprocessing</th>
<th>R2</th>
<th>concordance</th>
<th>MSE</th>
<th>RMSE</th>
<th>bias</th>
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<tr>
<td>SNV</td>
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</tr>
</tbody>
</table>

According to model outputs, ‘trim, filter and first derivative of spectra’ is the best spectral pre-processing approach for the validation of oxalate extractable Al. Preliminary results have been obtained for the calibration (Table 3) and validation (Table 4) of oxalate extractable iron using 7 different spectral pre-processing treatments.

Table 3. Ranking of spectral pre-processing treatments according to Cubist model outputs for the calibration of oxalate extractable Fe

<table>
<thead>
<tr>
<th>Preprocessing</th>
<th>R2</th>
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</tbody>
</table>

According to model outputs, ‘trim, filter and multiplicative scatter correction’ is the best spectral pre-processing approach for the calibration of oxalate extractable Fe.

Table 4. Ranking of spectral pre-processing treatments according to Cubist model outputs for the validation of oxalate extractable Fe

<table>
<thead>
<tr>
<th>Preprocessing</th>
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</tbody>
</table>

According to model outputs, ‘trim, filter and standard normal variate’ is the best spectral pre-processing approach for the validation of oxalate extractable Fe. Preliminary results have been obtained for the calibration (Table 5) and validation (Table 6) of cation exchange capacity using 7 different spectral pre-processing treatments.

Table 5. Ranking of spectral pre-processing treatments according to Cubist model outputs for the calibration of cation exchange capacity

<table>
<thead>
<tr>
<th>Preprocessing</th>
<th>R2</th>
<th>concordance</th>
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<td>4</td>
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</table>
According to model outputs, ‘trim, filter and multiplicative scatter correction’, is the best spectral pre-processing approach for the calibration of cation exchange capacity.

Table 6. Ranking of spectral pre-processing treatments according to Cubist model outputs for the validation of cation exchange capacity

<table>
<thead>
<tr>
<th>Preprocessing</th>
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</table>

According to model outputs, ‘trim, filter and first derivative’, is the best spectral pre-processing approach for the validation of cation exchange capacity.

Conclusions

There seems to be a trade-off between the spectral pre-processing technique which gives the best calibration (usually mathematically complex), with the minimum amount necessary to give a sufficiently good calibration (look at the number 2 rankings, these are, on average, more simple to carry out, e.g. the use of raw spectra or simply trimming noise). It is also noted that these results are quite variable between calibration and validation, but it is suspected that this is due to them being preliminary results. There was a small problem with infrared beam centering at the time of scanning, which has since been rectified and these samples are going to be scanned again now that the instrument has been fixed.

Acknowledgements

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References


THE VISUAL EVALUATION OF SOIL STRUCTURE AT VARYING SOIL MOISTURE CONTENTS AT LYONS ESTATE

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Abstract

Visual Soil Evaluation (VSE) techniques are increasingly recognised as useful and robust methods for soil quality assessment. For example, the Visual Evaluation of Soil Structure (VESS) has been widely and successfully deployed and tested. However, one area that has not received attention is the influence of soil moisture content on VESS. This study aimed to identify the potential impact of soil moisture content on VESS results and ease of deployment. Two sites were selected at the UCD Lyons Research Farm, Co. Kildare at which VESS was periodically conducted. Four assessments took place between August 2014 and January 2015 at different moisture contents indicated by the Hybrid Soil Moisture Deficit (HSMD) Model. SMD values ranged from 54 mm to 1 mm during the period. Non-parametric statistics revealed a significant positive correlation between VESS “Sq” scores and SMD (P < 0.01). Additionally, key VESS diagnostic properties such as rupture resistance and visible intra-aggregate porosity were observed to change while the procedures ease of deployment was noticeably more difficult in drier conditions. This preliminary study clearly suggests soil moisture content does impact VESS results and further work is required.

Introduction

Soil degradation is of significant concern (Koch et al, 2013) and there is a clear need for tools to aid the sustainable management of soils. Visual Soil Evaluation (VSE) techniques, centred on the assessment of soil structure, are receiving increasing attention (Ball and Munkholm 2015). They require the visual and tactile assessment of soil properties within the field, often with reference to score sheets (McKenzie 1998, Shepherd 2009), providing useful and robust indicators of soil physical and biochemical quality (Mueller et al 2009; Askari et al 2015). Their ease of deployment and requirement for basic equipment make them accessible to a range of users, notably farmers and advisors (Boizard et al., 2005). One such VSE technique, and perhaps the simplest (Guimarães et al 2013), is the Visual Evaluation of Soil Structure (VESS) (Ball et al 2007; Guimarães et al 2011). This method requires the extraction of an intact soil sample block to 20 cm depth and the identification to structural layers within the block. Layers are assessed separately involving the manual exposure of aggregate which are examined in terms of size, shape and rupture resistance. Additional properties such as porosity, rooting and redox-morphology are assessed with the application of a final numeric “Sq” score, summarising structural state according to guided observations. Scores range from Sq 1 to Sq 5 indicating good and poor structural quality respectively. VESS has been widely deployed on both temperate (Ball et al 2007; Cui et al 2014) and tropical (Pulido Moncada et al 2014) soils and thus thoroughly tested in terms, relationships with quantitative measures of soil quality (Pulido Moncada et al 2014), soil texture limitations (Askari et al 2013) and reproducibility between operators (Ball et al 2007, Cui et al 2014). One area not been explored is the effect of moisture content on the procedure. McKenzie (1998) outlines differences in rupture resistance with moisture contents, a diagnostic property which could potentially influence results. VESS is recommended to be conducted on moist but not saturated soils (Ball et al 2007) but no research has been conducted on its application on the same soil over a range of moisture contents.

The objective of this study was to conduct a preliminary trial to identify potential impacts of soil moisture content on VESS Sq scores and ease of deployment.
**Materials and Methods**

The trial was conducted at the UCD Lyons Research Farm, Co. Kildare (Latitude: 53.295 N, Longitude: 06.530 W). Two sites were purposely selected representing different water transmitting zones (Kerebel *et al.*, 2013) and soil characteristics (Collins and Brickley, 1970). Site A. – a silty clay loam situated on a slight slope (water transmitting) and Site B. – a silty loam, on flat land (water receiving). At each site the VESS method (Guimarães *et al.*, 2011) was deployed and replicated twice, approximately six meters apart, located by handheld GPS devices. Relative moisture content was determined with reference to the Hybrid Soil Moisture Deficit (HSMD) model (Schulte *et al* 2005) available from the national meteorological service / Met Éireann website (www.met.ie). SMD indicates the water required to bring a soil to the arbitrary state of Field Capacity, the point at which drainage ceases (Collins *et al* 2004) and is predicted in real time by the HSMD model, accounting for three land drainage classes. Both Sites A. and B. were classified as “Moderately Drained” and assessments were conducted over a range of SMD values between August 2014 and January 2015. For each assessment, $Sq$ scores were obtained and recorded, along with observations on the ease of deployment. Mean values were calculated for each site and non-parametric correlations (Spearman rank ($r_s$) correlation coefficient) were determined using IBM SPSS Version 20.

**Results and Discussion**

Assessments took place at a maximum and minimum SMD of 54 mm and 1 mm respectively. For the entire study period, Site A. obtained a mean VESS score of $Sq$ 2.3. This ranged from $Sq$ 3.0, indicating moderate quality to $Sq$ 1.7, indicating good quality. Similarly Site B. obtained a means score of $Sq$ 2.8, ranging from $Sq$ 3.5 indicating moderate to poor quality to $Sq$ 2.1 indicating good quality. The relationship between $Sq$ scores and SMD values are illustrated (Figures 1 and 2) and showed a clear trend towards increasing $Sq$ scores with an increasing SMD.

![Figure 1](image1.png) **Figure 1.** The relationship between Site A. mean $Sq$ scores and SMD values

![Figure 2](image2.png) **Figure 2.** The relationship between Site B. mean $Sq$ scores and SMD values

When exploring statistical significance, $r_s$ indicated a highly significant ($P < 0.01$) positive and complete relationship between Site B. $Sq$ scores and SMD (Table 1). It must be remembered that $Sq$ values are in rank order and so a complete correlation ($r_s = 1$) is possible. Despite the limited number of assessments conducted, a clear indication that moisture content does impact $Sq$ scores was obtained.
Table 1. Relationships between Sites A and B and SMD values using Spearman’s rank ($r_s$) correlation coefficient

<table>
<thead>
<tr>
<th></th>
<th>Site A. Mean $S_q$</th>
<th>Site B. Mean $S_q$</th>
<th>SMD (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site A. Mean $S_q$ Scores</td>
<td>Correlation Coefficient</td>
<td>1.000</td>
<td>0.800</td>
</tr>
<tr>
<td>Sig. (2-tailed)</td>
<td>0.800</td>
<td>0.200</td>
<td>0.200</td>
</tr>
<tr>
<td>N</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Site B. Mean $S_q$ Scores</td>
<td>Correlation Coefficient</td>
<td>0.800</td>
<td>1.000</td>
</tr>
<tr>
<td>Sig. (2-tailed)</td>
<td>0.200</td>
<td>1.000**</td>
<td>1.000</td>
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<tr>
<td>N</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>SMD (mm)</td>
<td>Correlation Coefficient</td>
<td>0.800</td>
<td>1.000**</td>
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<tr>
<td>Sig. (2-tailed)</td>
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<tr>
<td>N</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

**. Correlation is significant at the 0.01 level (2-tailed).

When considering diagnostic properties, changes in rupture resistance with increasing SMD was observed. For example, at Site A and Site B at SMD 54 mm, significant force was required to break aggregates, in one case requiring two hands while at SMD 1 mm, aggregates were easy to break between fingers. This corresponded to the ease of sample block extraction with spade insertion ranging from “difficult” to “easy” with decreasing SMD. Indeed, Ball et al. (2007) originally identified the potential difficulty of sample block extraction when done in dry conditions. It was expected that significant changes in aggregate size distribution would be observed during the study. In some cases, differences were observed with a tendency for a greater incidence of large ($\approx 10$ cm) clods at the greater SMD value. However overall, these observations were inconclusive and similar size distributions were described. Interestingly, visible intra-aggregate porosity was found to increase with decreasing SMD with porosity described as “limited” at greater SMD values compared with “visible” at smaller SMD values.

**Conclusion**

This study suggests that soil moisture content affects both VESS results and the ease of its deployment. According to VESS structural classification, both Site A and B ranged from moderate to good structural quality depending on SMD. Key diagnostic soil properties were found to vary over the study period, notably rupture resistance and intra-aggregate porosity. It was concluded from this preliminary study that the influence of soil moisture content on VESS is worthy of further and more thorough research.

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References


GREENHOUSE GAS EMISSIONS FROM HOMOGENIZATION FOR LIQUID MILK PRODUCTION

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Abstract

When milk is homogenized, its fat is separated to produce a layer of cream and the diameter of fat globules decrease from 1-10 microns to less than 1 micron. The process ensures that milk-fat globules, various solids and nutrients stay in solution. Homogenization is one of the most important unit operations in the production of liquid milk. This research used LCA as a tool to analysis the greenhouse gas emissions to the air when using different methods of homogenization. It was found that for optimum greenhouse gas emissions temperature of homogenization should be 55-70°C, the first stage pressure should be around 2000 psi and the second stage pressure around 500 psi.

Introduction

Dairy products are rich sources of protein, dairy fat, vitamins, calcium and trace elements. According to Kryserlingk et al (2012) the growing requirement of dairy production will cause significant environmental problems, such as water pollution and greater GHG emissions. There are three key processes during dairy processing: homogenization, which determines the quality and flavour, sterilization and packaging, which determine the shelf-life of the final products. These are all energy demanding processes, which means they must contribute to the GHG emissions of the final product. This paper will focus on the global warming potential of homogenization during liquid milk processing. The main function of homogenization is to make the dairy fat globules split into smaller fat globules with a diameter around 1µm (Edgar Spreer 1995), which helps prevent fat rising in the bottled product. This is because the effects of the Persian Brownian motion can overcome the trend of fat accumulation. The advantages of using homogenization for dairy processing are: 1. The homogeneous process can make fat globules into tiny balls of uniform size, increase light reflection, colour and lustre making the milk look whiter and brighter (Miller et al 2007); 2. It reduced butter fat adherence making cleaning of equipment much easier; 3. The flavour and taste of products is better; 4. The homogeneous milk is easier to digestion and absorption by the human body (Miler et al., 2007); 5. In some fermented dairy products homogenization can make safer products. The disadvantages are: 1. Dairy products will have greater light sensitivity acceleration oxidation of fat; 2. The thermal stability of dairy protein will decline; 3. The milk is less suitable for production of semi-hard or hard cheese, because the coagulum will be too soft and difficult to dewater (Edgar Spreer, 1995). To homogenize liquid milk, it is forced through a narrow slit. The slit is just a little larger than the diameter of the milk fat globules. The velocity while passing through the slit can be 100 to 250 m/s, which can cause high shearing stresses, cavitation and micro-turbulenc. The globules will be deformed, wavy and then be broken up (Ahmad, 2012) (Figure 1). Homogenizers can be classified by working principle and efficiency: plunger pump high pressure, ultrasonic, high shear and jet. Normally for dairy the homogenization temperature is 55-70°C and the pressure is 200-2500 psi (Edgar Spreer 1995). Homogenizers generally have two stages with preheating to 60-65°C to break the dairy fat globules at higher pressure (normally 2000 psi) followed by lower pressure (500 psi) to spread the broken fat globules to prevent adhesions (De 2001). Life Cycle Assessment (LCA) (based on the ISO14040) is a suitable tool to analysis global warming impacts.

The objective of this work was to use LCA to quantify GHG emissions to the air caused by homogenization of liquid milk.
Materials and methods

A Life Cycle Assessment in compliance with the ISO 14040 was used focusing on gate-to-gate impact during processing and considering homogenizer technology scenarios. There are three key stages in dairy product life cycles: pre-farm gate (production), post-farm gate (processing) and retail and consumption (Sarkar et al. 2014). Homogenization is a key process in the post-farm gate stage. Typically the preheated milk is treated in the homogenizer for the homogenization purpose. Electricity is required as the main source of energy. Waste heat, GHGs and homogenized milk are the main outputs of the system. The functional unit of the whole processing system will be 1 t of packaged full fat (4%) liquid milk. The system boundary is shown in Figure 2. GaBi was used to build the processing model.
Table 1. The basic parameters of chosen homogenizers

<table>
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<tr>
<th>Model type</th>
<th>Flowing rate (L/h)</th>
<th>Max. pressure (MPa)</th>
<th>Rated pressure (MPa)</th>
<th>Motor power (kW)</th>
<th>Size (m³)</th>
<th>Model type</th>
<th>Flowing rate (L/h)</th>
<th>Max. pressure (MPa)</th>
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<th>Size (m³)</th>
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<td>0.56</td>
<td>2</td>
<td>0.7<em>0.4</em>1.3</td>
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<td>-30</td>
<td>3500</td>
<td>50</td>
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<td>1.8<em>1.35</em>1.4</td>
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<td>4/5.5</td>
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<td>18/24</td>
<td>30/37</td>
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<td>40</td>
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<td>4000</td>
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<td>48/56</td>
<td>90/110</td>
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<td>28/36</td>
<td>11/15</td>
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<td>22</td>
<td>SRH8000</td>
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<td>8000</td>
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<td>2000</td>
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<td>0.24</td>
<td>200</td>
<td>2.2<em>1.8</em>1.4</td>
</tr>
</tbody>
</table>

Results and discussion

When producing 1 MJ of electricity power there will be around 0.083 MJ heat lost. All GHG emissions to the air are scaled relative to one tonne of full fat homogenized, packaged liquid milk. Using CM 2001 from April 2013, the GHG emissions to air were expressed as global warming potential over 100 years (Figure 3).

A higher pressure generates a greater velocity of liquid milk, which gives a stronger force to the fat globules. The size of the final fat globules will be decreased by the increase of force, but this is also associated with an increase in GHG emissions, therefore there is greater global warming impact with higher-pressure homogenization to produce the same liquid milk. As the higher pressure results in greater kinetic energy and thus velocity of the milk, this also effects...
the nature of the process (e.g. less eddies and greater processing temperature). If the temperature is too high, the thermostability of protein will be decreased, and the casein can also be influenced to cause flocculation, precipitation and sterilization.

**Figure 3.** The GHG emissions (kg CO₂-Equiv.) for type of homogenizer working pressure

**Conclusion**

The application of LCA systems inventory methods has permitted the comparison of homogenizer with different rated pressures. All the chosen types of homogenizer in this study can satisfy the lowest requirement of liquid milk homogenization (the rated pressure greater than 2000 psi). When producing the same amount of full fat liquid milk, a greater working pressure leads to greater CO₂ equivalent emissions.

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**References**


Lalita Oraon http://www.dairyknowledge.in/


THE CARBON FOOTPRINT OF BIOSOLARIZATION

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Abstract

Environmentally sustainable alternatives to chemical fumigants and other pesticides must be found and investigated to ensure continued pest management and control in agriculture. Biosolarization using tomato pomace as a substrate is one alternative. Its carbon footprint was assessed using life cycle assessment methodology. The process of plastic production was found to contribute most to the system (36%), and resulted in an overall carbon footprint of 155 kg CO$_2$-e per tonne of tomato pomace applied to soil. CO$_2$ emitted during biosolarization is biogenic and can be discounted depending on how the study is approached. Carbon reduction strategies for the system should focus on the transportation of pomace, the production of the plastic and fuel consumed during irrigation. The results are useful as a baseline study to compare other alternatives to chemical herbicide and fumigant application strategies.

Introduction

The widespread use of pesticide in agricultural systems is critical in order to manage pests that cause economic and aesthetic damage to crops and the environment. Approximately 2.5 million tonnes of pesticide are used globally, with over 450 thousand tonnes used in the United States of America (USA) each year (Alavanja 2009). Until recently Methyl Bromide (MeBr) was the most commonly used chemical fumigant, however in accordance with the Clean Air Act, MeBr has now been phased out (except for critical use exemptions) due to its harmful effect on human health and the depletion of the ozone layer (United Nations Environmental Programme (UNEP) 1992). The ban on MeBr has prompted innovative new formulations of pesticides by manufacturer’s pesticide alternatives by and researchers to meet the worldwide demand for pest management in agriculture. Alternative and sustainable integrated pest management approaches need to have a low environmental impact and be cost effective (Lightfouse et al 2009), and ideally, they should only be toxic to the target organisms (Ros et al 2008). One alternative approach is solarization, a natural hydrothermal process of disinfecting soil of plant pests. Solarization is accomplished through passive solar heating and occurs through a combination of physical, chemical, and biological mechanisms (Stapleton 2000). The addition of an organic amendment to solarization, known as biosolarization, has been shown to produce additional benefits (Achmon et al 2016).

Life cycle assessment (LCA) is a technique that quantifies the potential environmental impact and resource consumption of a product, system or service from cradle to grave (ISO 2006a/b). LCA methodology can be employed to assess the environmental impact of utilising tomato pomace for biosolarization.

The objective of this study was to calculate the carbon footprint of utilising tomato pomace as a substrate for biosolarization in order to replace fumigation and herbicide as soil treatments prior to crop (eggplant/aubergine) establishment.
Materials and Methods

Goal and Scope
The LCA study used observed field and laboratory data from experiments carried out in UC Davis, California. The LCA followed the four stage LCA methodology (ISO, 2006a,b), (1) goal and scope definition; (2) inventory analysis; (3) impact assessment; and, (4) interpretation. GaBi v.6 software (thinkstep 2016) was used for modelling. The goal was to calculate the carbon footprint when utilising tomato pomace as a substrate for biosolarization in order to replace fumigation and herbicide as soil treatments prior to crop establishment. The functional unit was 1 tonne of tomato pomace, this was chosen as this study will be further expanded to investigate alternate uses for tomato pomace utilisation.

The midpoint methodology CML (Guinee et al 2002) was used.

Figure 1. System diagram of Biosolarization

Life Cycle Inventory
Tomato pomace was transported from Tulare County to Fresno County in the central California valley, approximately 180 km. The eggplant establishment area, Fresno County, was assumed to be 1 m row width, with a 1 m spacing (50% land utilization). Field applications included spreading, ploughing, roller, list and shape, tarping, irrigation and plastic film removal. It was assumed that for all agricultural processes a 100 horse power tractor was used with fuel consumption estimated using the Flash Environmental Assessment Tool (FEAT) (2016). Tomato pomace application ranged from 37.4 to 63 t/ha (fresh weight). Pomace is only applied to the beds (1 m) and not the margins (1 m), therefore the application rate ranges from 18.7 to 31.5 t/ha (fresh weight). The average, 25.1 t of pomace per ha\(^{-1}\) was modelled. Biosolarization emissions were calculated as 23.8 mg CO\(_2\) per g of pomace applied.

The plastic film (polyethylene) was assumed to be produced in Point Comfort, Texas, and transported to Fresno County via rail (2787 km). During biosolarization plastic sheeting would be in situ for four weeks, after which, plastic sheeting was rendered ‘waste’ and sent to landfill. The closest waste facility (landfill) to Fresno County is located in Brea (oilandfills 2016), approximately 406 km.

For the transport of pomace, a diesel driven, US, semi-truck with a payload of 12.7-14.5 t was assumed, with data taken from GaBi 6 (thinkStep 2015). The transport processes were modelled to have full capacity and travel on motorway 90% and rural (10%) roads. For the transport of plastic prior to use, diesel rail transportation was assumed, and data taken from GaBi 6 (thinkStep 2015). LCI data for energy (US specific, average grid mix) and fuel (diesel) was taken from the GaBi 6 database (thinkStep 2015).

Results and Discussion
For biosolarization (Figure 2) the process that contributed most was plastic production (36.4%), this was because for every tonne of tomato pomace utilised approximately 27 kg of plastic was used. There were three other process that contributed to over 10% of the total impact, these were pomace transportation (12%) irrigation (21%) and biosolarization process (15%).
For biosolarization (Figure 3) it was found that per tonne of pomace utilised the carbon footprint was 155 kg CO$_2$-e.

The results showed that the most significant process was the production of plastic. Soil emissions during the biosolarization process resulted in an emission of 23.8 kg CO$_2$-e per tonne, however as these emissions are biogenic there is an argument that they should be excluded. If the biogenic emissions were excluded the carbon footprint would be 131 kg CO$_2$-e per tonne of pomace, a reduction of 15%.
In order to reduce the carbon footprint of this alternative to chemical fumigation and herbicide treatments, carbon reduction strategies need to be devised and implemented. As shown in this study the three areas where the greatest reduction is possible would be the transportation of pomace, the production of the plastic and fuel consumed during irrigation. Potential carbon reduction alternatives include the use of renewable energy (for example solar pumps for irrigation), the transportation via lower carbon alternatives (such as rail), and the use of a bioplastic. In order to ensure such initiatives result in a beneficial result further LCA’s should be carried out, including other environmental impacts and comparing against alternatives such as solarization and herbicide/fumigant application.

Conclusions

The results of this study were achieved using LCA methodology and showed that the carbon footprint of biosolarization is approximately 155 kg CO$_2$e per tonne of tomato pomace utilised, using California as a case study. The results are useful as a baseline study to compare other alternatives to chemical herbicide and fumigant application strategies.

Acknowledgements

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References

LONG-TERM PERFORMANCE EVALUATION OF ARTIFICIAL LAND DRAINAGE SYSTEMS IN HIGH RAINFALL AREAS IN THE SOUTH-WEST OF IRELAND

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Abstract

Artificial land drainage is used to improve the productivity and trafficability of poorly drained soils throughout the country. If the benefits of artificial land drainage are to be established, the effectiveness, consistency and long term usefulness of different drainage systems needs to be quantified. Site-specific artificial land drainage systems were installed on seven dairy farms in the south west of Ireland that suffer from impeded drainage. Performance of the different drainage systems was investigated in terms on-site meteorological conditions and drain discharge response parameters. Preliminary results show there is wide variation in drainage system performance and response.

Introduction

Meteorological records show that excess rainfall is a dominant feature of Irish agriculture (Galvin 1983). In Ireland, precipitation ranges from 750 to 1800 mm/year (excluding mountainous areas) (Met Eireann 2016). In addition, approximately 49.5% (3.4 M ha) of the total land area of Ireland is classified as “marginal land”. As a result, grassland farms on poorly drained soils in the wetter regions of Ireland suffer a dual handicap and experience significant difficulties in producing and utilising grass. Studies undertaken by Ryan (1974) and Thomasson (1979) observed that dry matter (DM) production is reduced by up to 25% on poorly drained soils, whereas Shalloo et al (2004) estimates that the average farm profitability on such soils ranged from 38% to 58% of that achievable on the drier soils in Ireland. The viability of grassland farms is dependent on good grass production and high grass utilisation. On poorly drained lands, one method by which this is achievable is the installation of artificial land drainage. The objective of land drainage is the removal of excess water from the soil, resulting in an improvement in trafficability and the development of a favourable root zone for plant growth (Robinson et al 1987; Morris 1992; Rasasamy et al 1997). Artificial drainage significantly alters field hydrology by increasing the hydrological connectivity of the landscape, allowing flows to bypass much of the complexity of the landscape (Guan et al 2011). Compared to natural drainage conditions, artificial drainage lowers water tables, increases sub-surface water movement and reduces surface runoff at the field edge (Radcliffe et al 2015). However, the effect of artificial drainage on field hydrology depends on the drainage system installed, management, soil type and climatic conditions. As of now, the understanding of the hydrological response of drainage systems is largely unknown (Tuohy et al 2016). Therefore, if the benefits of drainage to the landowner are to be established, the effectiveness, consistency and long term usefulness of different drainage systems needs to be established.

The objective of this study was to compare the effectiveness of various artificial land drainage systems on several soil types by investigating drain discharge over several episodic rainfall events.

Materials and Methods

Site Description
Seven dairy farms in the south west of Ireland using permanent grassland for livestock grazing and silage production were selected for this study. In consultation with each farmer an area of the farm that suffering impeded drainage was selected for the installation of a new drainage system. Following a visual drainage assessment undertaken by (Tuohy 2015) each site was characterised and prescribed an appropriate drainage system. A range of drainage system types was installed in terms of depth, spacing and supplementary measures. However for this paper, preliminary data from only a selection of sites are reported. The study sites selected are located at Doonbeg, Co. Clare, Athea, Co. Limerick and Castleisland Co. Kerry. All sites included have a shallow drainage system (0.9 m drain depth) installed which is supplemented by sub-soiling (Castleisland: Site A), mole drainage (Doonbeg) or gravel mole drainage (Athea and Castleisland: Site B). A full description of each site can be obtained from (Tuohy 2015).

Meteorological Data
An automatic meteorological weather station (Campbell Scientific BSW-200 weather station) was installed on all farm sites to record air temperature (°C) relative humidity (%), solar radiation (W m\(^{-2}\)), wind speed (m s\(^{-1}\)), wind direction, rainfall (mm) and soil temperature (°C) every 15 minutes.

Flow measurement data
Flow measurement data is measured either by end-of-pipe flowmeters (Water Technology Limited, Togher, Cork) attached to one sub-surface drain per site or by calibrated in-stream flumes (Corbett Concrete, Cahir, Tipperary) in tandem with mini-divers (Eijkelkamp Agrisearch Equipment, Giesbeek, Netherlands) which monitor water-head passing through the flume, which can then be converted to an open channel flow rate. In the latter case total flow from the sites was calculated by subtracting flow rate immediately upstream of the site from flow rate immediately downstream of the site. The flow measuring system selected for each site was dependent on the practicalities of equipment installation particular in relation to relative invert levels of subsurface and open drains and the geometry of the open drain. Flow rate was recorded automatically every 15 minutes.

Flow event delineation and antecedent conditions
A period of 12 hours without rainfall was used to separate one rainfall event from another (Tuohy et al 2015; Ibrahim et al 2013). A “perceptible rise in discharge” signalled the start of the flow event, while the end of the event was defined as flow returning to pre-event flow levels (Vidon et al 2010).

Results and Discussion
Daily precipitation and daily discharge rates for the four sites selected during the storm event “Desmond” are shown in Figure 1. The storm event started on the 3rd December 2015 and heavy rainfall persisted over a 10 day period with little stoppage. Total rainfall during this period, across all sites, ranged from 125.8 to 134.8 mm, with the highest in Castleisland and the lowest in Athea respectively. During the 10 day period, each site had several rainfall events with the most significant on each site dating from the 4th December to the 6th December 2015. For Castleisland 47 mm of rainfall was recorded over a 35 hr period. The rainfall event is illustrated in figure 1A and figure 1B. The peak discharge rate for Castleisland Site A occurred 2.8 hrs into the event with a peak discharge rate of 13210 Litres (L)/Hectare (Ha) / hr. Peak discharge rate of Castleisland Site B occurred 20.66 hrs into the event with a peak discharge of 36432 L/Ha/hr. In Athea 65 mm of rainfall was recorded over a 71.5 hr period. Peak discharge rate during this period was 10176 L/Ha/hr and occurred 42.2 hrs into the rainfall event. In Doonbeg, Co. Clare, the rainfall for this period was 59.4 mm of rainfall was recorded over a 35 hr period. The rainfall event is illustrated in figure 1A and figure 1B. The peak discharge rate for Castleisland Site A occurred 2.8 hrs into the event with a peak discharge rate of 13210 Litres (L)/Hectare (Ha) / hr. Peak discharge rate of Castleisland Site B occurred 20.66 hrs into the event with a peak discharge of 36432 L/Ha/hr. In Athea 65 mm of rainfall was recorded over a 71.5 hr period. Peak discharge rate during this period was 10176 L/Ha/hr and occurred 42.2 hrs into the rainfall event. In Doonbeg, Co. Clare, the rainfall for this period was 59.4 mm of rainfall was recorded over a 35.25 hr period. Peak discharge rate for this event was 33214 L/Ha/hr, and occurred 14 hrs into the event. The overall discharge rate and performance from each site is shown in Table 1.0. Removal rate of total precipitation ranged from 33% to 86% with Castleisland Site B having the highest removal rate and Athea having the lowest with 33%. The project is still at an early stage but the initial results indicate a range of performance efficiencies both between drainage systems and
temporally within specific sites. A further time frame with the inclusion of other key data such as groundwater levels and soil moisture content will give a better indication as to the performance of the drainage systems employed with respect to time.

**Figure 1.** Daily precipitation (gray lines) and daily discharge rates (black line) from A) Castleisland, Co. Kerry – Ripped, B); Castleisland, Co. Kerry - Gravel Mole, C); Athea, Co. Limerick D) Doonbeg, Co. Clare.

**Table 1.** Overall performance of the water removed by drains installed during the 10 day “Storm Sesmond” interval

<table>
<thead>
<tr>
<th>Sites</th>
<th>Rainfall (Litres/Ha)</th>
<th>Flow (Litres/Ha)</th>
<th>% of Rainfall Removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Castleisland (Ripped)</td>
<td>1348000</td>
<td>953586</td>
<td>71%</td>
</tr>
<tr>
<td>Castleisland (Gravel Mole)</td>
<td>1348000</td>
<td>1159743</td>
<td>86%</td>
</tr>
<tr>
<td>Athea</td>
<td>1252000</td>
<td>411875</td>
<td>33%</td>
</tr>
<tr>
<td>Doonbeg</td>
<td>1302000</td>
<td>758494</td>
<td>58%</td>
</tr>
</tbody>
</table>

**Conclusions**

From the preliminary data shown, there is a wide variation in drainage system performance and response. A long term assessment of these systems over several seasons, will allow for the effectiveness and economic benefit of land drainage to be appraised and assessed.

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**References**


DATA QUALITY AS A MEANS OF EVALUATING ALLOCATION METHODS FOR LCA

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Abstract

Allocation is a major methodological issue for life cycle assessment (LCA), which is commonly used to quantify greenhouse gas (GHG) emissions from livestock systems. When a process produces multiple outputs, the environmental burden has to be shared between the outputs, such as milk and liveweight from a dairy herd. Standards and Guidelines provide different recommendations but there is no objective function for choosing the best method. This study evaluated 7 allocation methods to calculate the carbon footprint (CF) of the economically average dairy farm in Ireland considering both milk and liveweight. The allocation methods were: economic, energy, protein, emergy, mass (liveweight), mass (carcass) and physical causality. System expansion was also assessed using an ‘avoided burden’ approach. The data quality for each method was determined using a pedigree matrix of reliability, completeness, temporal applicability, geographical alignment and technological appropriateness. For the average farm, GWP / FU ranged from 0.75 to 1.22 kg CO\textsubscript{2}-eq/kg FPC milk, with pedigree scores ranging from 6.0 to 15.9. Economic allocation and protein content had the best pedigree. The choice of allocation method should be based on the quality of the data available, but a range of allocation methods should be used to understand the uncertainty of the outcome.

Introduction

With the global human population predicted to increase to over 9 billion by 2050 there will be a rise in consumption of bovine milk and meat products (FAO, 2009). Increasing primary production from large ruminant systems to meet greater demand is expected to increase greenhouse gas (GHG) emissions. To tackle this problem, EU nations have legally agreed as part of the 2020 climate and energy bill to reduce GHG emissions from the non-emission trading sector, which includes agriculture. The EU aims to reduce these emissions by 10% (20% in an Irish context) by 2020 relative to 2005 levels.

Life cycle assessment (LCA), an internationally standardized methodology (ISO14040), is the preferred method to estimate GHG emissions from agricultural systems (IDF 2010; Thomassen and De Boer 2005). A single impact LCA focused on GHG emissions is commonly referred to as a carbon footprint (CF). A major methodological issue of LCA is allocation between multiple outputs of a process. When a system such as a dairy farm or a process produces more than one output, the environmental burden such as GHG emission, has to be allocated between these outputs, e.g. milk and meat. LCA guidelines (BSI 2011; IDF 2013) recommend where achievable, allocation should be avoided, but where this is not possible guidelines differ on how to allocate, e.g. PAS2050 recommends using economic relationships while IDF (2013) recommend using physical relationships. (Henriksson et al 2011; Rice et al forthcoming). While ISO standards recommend that data quality be reported, this is not that common in LCA studies. Consequently, it is typically necessary for LCA practitioners to make judgement with respect to the accuracy of LCA outcomes. While a data quality scoring/judgement matrix has been developed (Weidema and Wesnaes 1996), the concept has never been applied in the context of allocation and the choice of method.

The objective of this study was to evaluate and assess the suitability of seven different allocation methods (and system expansion) applied to grass based dairy production in terms of data quality.
Materials and methods

The methods of allocation assessed were: economic, energy, emergy (novel application), protein, mass of liveweight (LW), mass of carcass weight (CW) and physical causality. The data quality (pedigree) was assessed using (1) reliability of the source and completeness; (2) temporal correlation; (3) geographical correlation; and (4) technological correlation, which is in keeping with the data quality requirement stipulations set out by the ISO (2006).

The data used for completing the LCA of grass based milk production were derived from the 2012 Irish National Farm Survey (NFS, Hennessey et al. 2013) as previously described by O’Brien et al., (2015). The survey was carried out on 256 dairy farms in 2012 and was weighted according to farm area to represent the national population of specialized dairy farms (15,600). All the dairy farms in the NFS used grass-based spring calving with seasonal the milk supply matched to grass growth patterns, in order to maximise grazed grass intake (Kennedy et al. 2005).

The LCA methodology was applied according to the ISO (2006) guidelines. The goal was to evaluate seven methods of allocation using an economically average Irish dairy (€ / ha) farm between milk and meat. The system boundary was ‘cradle to farm gate’, including foreground processes of milk production and background processes for production and transportation of mineral fertilizer, cultivation, processing and transportation of concentrate feed. Infrastructure (animal housing, slurry storage facilities, and roads), machinery (tractor, milk cooling system) were not included, as these have a small influence on the GHG’s from milk production (O’Brien et al. 2014). The functional unit was kg of fat and protein corrected milk (FPCM) calculated as to 4% fat and 3.3% protein using (Clark et al., 2001) where FPCM (kg/yr) = Production (kg/yr) × (0.1226 × Fat % + 0.0776 × True Protein % + 0.2534).

The GHG emissions, methane (CH\(_4\)), nitrous oxide (N\(_2\)O), carbon dioxide (CO\(_2\)) and halocarbons (F-gases) were calculated using the cradle to farm-gate LCA model of O’Brien et al (2014) that was certified by the Carbon Trust. The model used previously published algorithms and data from the NFS to calculate on and off-farm GHG emissions using Intergovernmental Panel on Climate Change (IPCC) guidelines (IPCC, 2006) and Irish GHG national inventory methods (O’Brien et al. 2014). Within the model, the various GHG emissions were converted to CO\(_2\)-equivalents (CO\(_2\)-eq) using the IPCC (2007; O’Brien et al 2014) revised guidelines for GWP and summed to establish the farm CO\(_2\)-eq emissions. The GWP conversion factors for the key GHG emissions in the model were 1 for CO\(_2\), 25 for CH\(_4\) and 298 for N\(_2\)O, assuming a 100 year time horizon. The CF of both milk and meat were estimated by allocating the GHG emissions between milk and meat.

Emergy allocation is based on the ‘embodied energy’ in milk and meat from culled cows and surplus calves and quantified in solar energy equivalents (seJ). Allocation by physical causality was based on the IDF (2010) guidelines and reflected the underlying use of feed energy by the dairy animals to produce milk and meat. Economic allocation was based on sales receipts for milk and animals from culled cows and surplus calves at the farm gate. Mass allocation was based on the weight of milk and weight of culled dairy cows and surplus calves. The mass of animals was calculated in terms of LW and CW. Allocation by protein was expressed in kg of protein and based on the edible protein in milk and meat from culled cows and surplus calves. Energy allocation was expressed in joules (J) of energy and based on edible energy in milk and meat from culled cows and surplus calves.

The quality of the data was assessed by the pedigree matrix of Weidema and Wesnaes (1996) for each allocation method. The overall pedigree score was calculated for each allocation method based on the sum of the component scores, weighted by proportional contribution to the calculation where this could be assessed (e.g. proportional mass of milk and meat). The methods were then ranked based on pedigree score. For each allocation method the highest possible score was 25 and the lowest was 5 and a lower score represents a better pedigree of data.
Results and discussion

The results of this study have shown significant differences in CF for dairy products (and associated meat co-products)(Table 1). For the ‘Average’ farm, the allocation factors ranged from 54% (system expansion) to 89% (mass of carcass weight), which in turn resulted in a 63% difference in the CF values, i.e. 0.75 – 1.22 kgCO2-eq/kgFPCM, depending on which allocation method was used. This range in allocation of emissions to milk also resulted in over an 11-fold difference in the CF values, i.e. 0.61 – 7.49 kgCO2-eq/kg meat (Table 1). Regarding both FPCM and meat, physical causality resulted in the smallest difference i.e. 2.5% less for FPCM and 15% more for meat, compared to when economic allocation was applied. Moreover, the application of allocation by way of mass of carcass weight (CW) resulted in the greatest difference i.e. 15% more for FPCM and 90% less for meat, compared to when economic allocation was applied. The ranking order of the CF of milk and meat for the different allocation methods was the same for all three scenarios (Table 1). Energy content, followed by energy appeared to have an amplifying effect by widening the range across scenarios (Table 1). The other allocation methods had a similar effect on the range over scenarios. The CF’s were achieved with data of widely varying pedigree, from the simpler allocation methods (mass LW, mass CW), to the more complex methods (energy, energy, physical causality and system expansion) (Table 1).

Table 1. The effect of method of allocating greenhouse gas (GHG) emissions between milk and meat on the carbon footprint of both products for the mean and of Irish dairy farms in terms of gross margin/ha

<table>
<thead>
<tr>
<th>Method of allocation</th>
<th>GHG allocated to milk</th>
<th>Mass of Liveweight</th>
<th>Mass of carcass weight</th>
<th>Protein content</th>
<th>Energy content</th>
<th>Emergy</th>
<th>Economic</th>
<th>Physical causality</th>
<th>System expansion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>88%</td>
<td>89%</td>
<td>83%</td>
<td>83%</td>
<td>81%</td>
<td>84%</td>
<td>77%</td>
<td>75%</td>
</tr>
<tr>
<td>Carbon footprint of milk (kg CO2-eq/kg FPCM)</td>
<td>1.21</td>
<td>1.22</td>
<td>1.15</td>
<td>1.11</td>
<td>1.15</td>
<td>1.06</td>
<td>1.04</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>Carbon footprint of meat (kg CO2-eq/kg meat)</td>
<td>1.21</td>
<td>0.61</td>
<td>3.28</td>
<td>4.60</td>
<td>4.18</td>
<td>6.52</td>
<td>7.49</td>
<td>5.73</td>
<td></td>
</tr>
<tr>
<td>Pedigree matrix score FPCM</td>
<td>6.10</td>
<td>6.10</td>
<td>6.00</td>
<td>17.10</td>
<td>16.90</td>
<td>6.00</td>
<td>9.50</td>
<td>6.10</td>
<td></td>
</tr>
<tr>
<td>Pedigree matrix score meat</td>
<td>6.60</td>
<td>6.60</td>
<td>6.50</td>
<td>19.40</td>
<td>19.40</td>
<td>8.40</td>
<td>9.50</td>
<td>7.01</td>
<td></td>
</tr>
</tbody>
</table>

1Carbon footprint of products was calculated according to cradle to farm gate life cycle assessment using the model of O’Brien et al. (2014).

2 kg CO2-eq/kg FPCM = kg CO2 equivalent/kg of fat and protein corrected milk

Conclusion

Allocation method has a large effect on the CF result, > 12 fold difference in the case of meat. Based on pedigree score, protein content followed by the simple mass allocation methods by LW or CW were best for milk. Emergy and energy were of poorest pedigree and the others fitted in between. In most cases it was only the scores for one or two indicators that dominated the final pedigree score for each method. If a particular method is to be used for theoretical reasons, then focused effort will be required to ensure the best possible data are available in order to justify its use from a data pedigree perspective. A further reason to be careful with the more complex methods is that they are built on a foundation of the simple methods with a cascade of additional data. This study showed the importance of using country, technology and temporally specific data so the goal and scope specification for the study should be consistent with the time that can be committed to the allocation calculations. It was also noted that when assessing meat co-products the method chosen can be used to bias the study. From the data presented here it seems that physical causality will be biased in favour of milk, and in the case of physical causality, obtaining good pedigree data to justify such an approach is difficult. A range of methods should be deployed to understand the uncertainty associated with the decision.

References

SENSITIVITY ANALYSIS OF EUTROPHICATION IMPACT OF A TYPICAL IRISH DAIRY FARM

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Abstract

This study first quantified the eutrophication impact of a typical Irish dairy farm. Life cycle assessment methodology was developed to calculate eutrophication. Later, important parameters were selected to evaluate the sensitivity. The eutrophication was calculated as 9.02 g phosphate (PO₄) equiv. per kg of energy corrected milk (ECM). Sensitivity analysis revealed that the calcium ammonium nitrate (CAN) and phosphorous (P) surplus were the most important parameters that affect the eutrophication impact.

Introduction

Eutrophication is a widespread problem around the world. It includes emission of gases and substrates to water and air that affect the growth pattern of ecosystems (de Boer 2003). Due to high discharge of N and P from agriculture the ecological status of surface water is deteriorating. The European Union, Water Framework Directive (2000/60/EC), was launched in 2000, required all the EU members to reach good ecological status of all inland and coastal by 2015. The Nitrate Directive (91/676/EEC) aims to protect water quality from pollution by agricultural sources and promote good farming practices.

Nutrient pollution can come from agricultural, industrial and municipal sources. Agricultural nutrient is a non-point source load generally comes from field and farm runoff (Matlock et al 2013). The N and P loss, from the application of organic and inorganic fertiliser to grassland and nitrate leaching from manure on pasture were found to be the main contributors of on farm eutrophication for grass based dairy system (O’Brien et al 2012). A high level of nitrate in food and water causes deficiency of oxygen in blood, especially in small children (de Boer 2003). Phosphorous is an important component of nonpoint-source pollution and can accelerate eutrophication of lakes and streams (Daniel et al 1998). Runoff will depend on soil properties, rainfall intensity and duration and soil moisture conditions. Vadas et al (2015), suggested that at whole-farm level, average annual P loss from grazing based dairy farms was between 0.5 to 1.8 kg P ha⁻¹. Animal housing contributes from about 5% to almost 30% of total farm P loss, depending on the management and land use (Vadas et al 2015).

Life cycle assessment (LCA) is the preferred analysis to understand the environmental impact of milk production (Yan et al 2013a). The analysis indicated the environmental burden throughout the life cycle of a product (ISO 2006b). LCA studies of agricultural systems typically evaluate up to the point when the product is sold from the farm instead of a complete life cycle (O’Brien et al 2012). LCA is been widely used to evaluate eutrophication from dairy farms (O’Brien et al 2012, Chen et al 2016). According to the European Commission 2009, sensitivity analysis can be used to explore how the outcome would change in response to variations in key parameters. It is mostly used for checking the robustness of the results, uncertainty reduction, errors in the models and parametrising models.

The objective of this study was to estimate the eutrophication potential of a typical dairy farm in Ireland and its sensitivity to the parameters and assumptions made in LCA.
Materials and Methods

To estimate eutrophication from a dairy farm LCA was used. The four stages of LCA methodology (goal and scope, life cycle inventory, life cycle impact assessment and interpretation) was implemented according to ISO (2006a). The goal of the study was to quantify eutrophication and assess its sensitivity to the significant parameters of a grass-based dairy farm. The LCA model was developed using GaBi 6 software (thinkstep 2014). The functional unit was defined as 1kg of ECM delivered at the farm gate in 1 year, where ECM= milk delivered* (0.25 + 0.122 * %fat + 0.077 * %protein) (Yan et al. 2013b). The system boundary was cradle-to-farm gate. Background processes of production and transportation of fertiliser and concentrate feed, production and use of electricity were included. Infrastructure, machinery, medicines were not included due to lack of data. Eutrophication potential was the only environmental impact category chosen for the study. All the inputs and outputs were defined and quantified in life cycle inventory phase (ISO 2006a). The work of Yan et al. (2013b) was used to develop the inventory of all the processes of dairy farm.

Ammonia (NH₃), nitrate (NO₃⁻) and nitrous oxide (N₂O) were the main nitrogen emissions quantified. NH₃ volatilise during grazing, housing, manure storage, application of organic and inorganic fertiliser. N₂O emissions generates directly from manure storage and application, manure deposited by grazing cattle on pasture, spreading of inorganic fertilisers and indirectly as NO₃⁻ leaching and run-off. The P imported to the farm in concentrate feed was assumed to be 5kg per tonne (Ruane et al. 2014). The P content in milk was assumed to be 0.0009 kg P per kg of milk and P content of livestock sold was assumed to be 0.01 kg P per kg of live weight (Ruane et al 2014).

The parameters used to predict the environmental impacts and assumptions made during the modelling process affects the results of LCA studies (ISO 2006a). Sensitivity analysis was used to analyse the parameters and assumptions that strongly influence EP. The fertiliser inputs are important contributors to EP and the quantity of the fertilisers can vary among farms. Scenario analysis was investigated to test the sensitivity of EP as shown in Table 1. The sensitivity of P surplus loss to waterways was also done. The three surplus scenarios considered were 0.5 kg P ha⁻¹ per year when P surplus ha⁻¹ was between 1 and 10kg, 1.5kg P ha⁻¹ per year when P surplus was between 10 and 20kg, and 2.5kg P ha⁻¹ per year when P surplus ha⁻¹ was > 20kg (Schulte et al 2010, O’Brien et al 2014).

<table>
<thead>
<tr>
<th>Table 1. Variations in parameters for sensitivity analysis</th>
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<tr>
<td>Parameter</td>
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<tr>
<td>Calcium ammonium nitrate (kg CAN)</td>
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<tr>
<td>NPK fertiliser 27-2.5-10 (kg)</td>
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<tr>
<td>NPK fertiliser 24-2.5-5 (kg)</td>
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<tr>
<td>Stocking rate (no. of cows)</td>
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<td>Housing days (no.)</td>
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</table>

Results and Discussion

It was estimated that the eutrophication from a typical Irish dairy farm was 9.09 g PO₄₃⁻ equiv. per kg of ECM. The EP value was in the range of values mentioned in Guerci et al (2013) and Chen et al (2016). The sensitivity of EP per kg of ECM to key parameters is shown in Fig 1. Eutrophication was most sensitive to the CAN input and least sensitive to the stocking rate. EP is sensitive to housing time and NPK fertiliser 24-2.5-5 in same ratio. EP increased and
decreased by about 10% when CAN was increased and decreased by 50%. EP only increased by 1% when the stocking rate was increased by 50%. EP increased by 5% and 9% when P surplus increased from 1.5 kg P/ha and 2.5 kg P/ha, respectively.

Figure 1. Sensitivity of eutrophication potential (g PO₄ eq. per kg of ECM) to variation in parameters (a) calcium ammonium nitrate (kg CAN); (b) NPK fertiliser 27-2.5-10 (kg); (c) NPK fertiliser 24-2.5-5 (kg); (d) stocking rate (no. of cows); (e) housing days; (f) P surplus (kg ha⁻¹)
Conclusions

Eutrophication has a significant negative impact on the water bodies, its minimisation would improve water quality. LCA modelling of a typical Irish dairy farm quantified the eutrophication potential from the farm and sensitivity analysis revealed the most important contributors. The sensitivity analysis revealed that the CAN input and P surplus were the important parameters affecting the outcome of EP. Reduced and efficient use of N and P fertiliser will reduce eutrophication.

References


Guerci, M., Knudsen, M. T., Bava, L., Zucali, M., Schönbach, P. and Kristensen, T. (2013) 'Parameters affecting the environmental impact of a range of dairy farming systems in Denmark, Germany and Italy', *Journal of Cleaner Production*, 54, 133-141.


thinkstep (2014) 'GaBi 7.0 Life Cycle Engineering Software'.


The development of an *E.coli* whole cell based biological sensor capable of detecting the concentrations of the individual acetate and propionate volatile fatty acids (VFAs) within anaerobic digester leachate samples, is with a view to being able to fully automate and remotely control deployed Anaerobic Digester (AD) systems.

Introduction

The efficiency of 2 phase ADs with regards their methane outputs per substrate inputs, depends entirely on their respective monitoring and control implementations. It has been extensively documented that if the AD generated Volatile Fatty Acids’ (VFA) concentrations are known in conjunction with other well established monitoring techniques (biogas, methane yield, and pH) then a novel performance indicator profile can be established and the necessary adjustments to optimise AD’s operational parameters made (Miyamoto 1997; Andersson and Björnsson 2002; Pind et al. 2004; Ahring et al 1995). The equipment cost and time constraints required to perform such measurements has made such a performance indicator profile infeasible to date.

The volatile fatty acids; acetate and propionate are the indicator chemicals that the proposed biological sensor attempts to identify. To date only the acetate detecting component of the proposed biological sensor has been identified, the sensor comprises of an engineered acetate detecting *E.coli* strain (IMD Wldgy) which by means of a dissolved oxygen (DO) probe allows the respiration rate for a given acetate concentration to be measured (Sweeney et al. 2015). It is envisaged that acetate concentrations within biological leachate samples, will be identifiable by means of mapping the *E.coli* suspension’s respiration response for an unknown biological leachate sample to that of known acetate concentration respiration rates (fig 1a-d). A propionate detecting *E.coli* strain which is capable of detecting propionate concentrations within unknown biological leachate samples is currently being screened for and it is envisaged that by correlating the results obtained from the proposed propionate detecting biosensor with that of the IMD Wldgy acetate detecting biosensor both the acetate and propionate concentrations of the unknown biological leachate sample will be identifiable. Overall VFA concentrations within an AD leachate sample can be identified by titration (Dr Lange Cuvette Test®) or by an enzymatic assay (Zeravik et al 2010; Rajashekhara et al 2006) but both methods require extensive sample pre-treatments, are expensive and do not identify the individual VFA concentrations required. Pind et al (2003) proposed an automated method for identifying an AD leachate sample’s individual VFA concentrations which comprised of an expansive sample extraction and pre-treatment array coupled to GC enabled individual VFA component identification. Although accurate measurements of the individual VFAs were made, the expense of the proposed system coupled with the extensive sample pre-processing requirements, make this an unsuitable automated monitoring and control system for anything other than large scale AD deployments. The acetate detecting IMD Wldgy biosensor which can detect acetate in the presence of an acetate, propionate, butyrate, ethanol, D- and L- lactate synthetic leachate is discussed in detail in the paper below. Towards an effective biosensor for monitoring AD leachate: a knockout E. coli mutant that cannot catabolise lactate (Sweeney et al. 2015).

The objective of this study is the development of a long lasting *E.coli* based biological sensor capable of detecting acetate and propionate concentrations within leachate samples exiting the hydrolytic phase of a two-phase anaerobic digester.
Materials and Methods

Production of the E.coli IMD Wldgy quadruple mutant
A series of knockout mutations were performed to achieve the quadruple E.coli IMD Wldgy knockout mutant. The Sauer:P1vir phage lysate protocol (Sauer 2010) was used to generate the ∆lldD, ∆ldl, ∆glcD and ∆ykgF phage lysates from which the four knockouts could be generated. The initial W3110 (IMD W) strain was transduced by the ∆lldD phage lysate and the respective ∆lldD::Kan containing IMD WI strain produced (Sauer, 2010). IMD WI’s ∆lldD Kanamycin cassette was removed using a transformed pcp20 plasmid’s FLPase enzyme (Cherepanov and Wackernagel 1995) and the resulting IMD Wl (-Kan) strain produced. IMD Wl(-Kan) was transduced with the ∆ldl lysate and the transduction-FLPase procedure repeated. IMD Wld(-Kan) was transduced with ∆glcD and when the resulting IMD Wldg(-kan) was transduced with ∆ykgF the IMD Wldgy was produced.

Construction of the E.coli based biological sensor
E.coli cells which were grown in minimal media supplemented with either acetate or propionate were extracted and re-suspended in Tris-buffer at a concentration of 400 mg cell wet weight per 20 ml. A cell response curve was performed when a 20 ml cell suspension was placed into a 25 ml beaker into which a Dissolved Oxygen (DO) probe was submerged. A stirrer bar was added to the beaker and the cell suspension was vigorously stirred by a magnetic stirrer for in excess of 1 hour before an organic acid sample was added. The agitated organic acid - cell suspension’s rate and total O₂ consumption was logged at 5 second intervals for a three minute period and the respective response curves depicted in figure 1a-d produced.

Results and Discussion
To allow full deployment of the Biological Sensor, the sensor had to be capable of determining acetate and propionate concentrations within biological leachate (BL) which principally consisted of acetate, propionate, DL-lactate, ethanol and butyrate in a 1:0.5:20:5:1 ratio (Cirne et al. 2006). No appreciable response curve was evident for butyrate or ethanol at x10 and x50 the respective concentration of acetate but the D and L lactate isomers proved to be particularly problematic. The wild type E.coli strain W3110 (IMD W) had an incredibly strong response curve for both D and L lactate when supplied at only x10 the concentration of acetate and the combined acetate (0.1mM) and D (1mM) or L (1mM) lactate response curves indicated that it would be impossible to identify acetate or propionate concentrations within BL, unless IMD W’s D and L lactate utilisation capabilities were fully removed.

E.coli possesses two lactate dehydrogenases Dld and LldD. Dld is more specific for D-lactate than it is for L-lactate, possessing 20% the activity for L-lactate as it does for D-lactate (Futai 1973). LldD is L-lactate specific, possessing only 0.1% D-lactate activity (Futai and Kimura 1977). It was hoped that the creation of the double dld and lldD knockout mutant strain IMD Wld (fig. 1b) would produce an E.coli strain incapable of aerobically respiring either D- or L-lactate. It was apparent when the acetate (0.1mM) only response curve was compared to the combined acetate (0.1mM) and L-lactate (1mM) or L (1mM) lactate response curves indicated that it would be impossible to identify acetate or propionate concentrations within BL, unless IMD W’s D and L lactate utilisation capabilities were fully removed.

Lord (1972) described an E.coli glycolate oxidoreductase that oxidised D and L lactate to pyruvate at 114% and 16% the respective rate at which it oxidised glycolate to glyoxylate. Pellicer et al. (1999) reported that not only was E.coli’s glycolate oxidase (Glc) expressed when it was grown on glycolate but also when it was grown on either acetate- or propionate-supplemented minimal medium. Thus, the creation of an E.coli dld,lldD and glc (IMD Wldg) knockout mutant was expected to remove the D- and L- lactate activity observed in IMD Wld. It was evident from IMD Wldg’s L-lactate(5mM) only’s response curve depicted in Figure 1c that the removal of the Glc had caused the expression of an unknown enzyme which possessed stereospecific L-lactate dehydrogenase activity to be upregulated.
Pinchuk et al (2009) and Chai et al (2009) described previously unknown L-lactate dehydrogenases (L-LDH) LldEFG and LutABC, belonging to Shewanella oneidensis and Bacillus subtilis, respectively. They strongly suggested that E.coli’s ykgEFG gene which shared homology with LutABC was in fact a previously uncharacterised lactate dehydrogenase. Therefore, a quadruple knockout, IMD Wldgy (∆lldD∆dld∆glcD∆ykgF), was created which even when supplied with synthetic leachate with x50 the lactate concentration of acetate had no discernible impact on the response curve when compared to acetate (0.1mM) only samples (Fig. 1d).

Experiments were performed to identify the newly created IMD Wldgy’s ability to differentiate between the acetate and propionate components of combined acetate and propionate samples but it appeared that although IMD Wldgy’s gltA possessed a high acetate stereospecificity it seemed that its prpC’s 2 methyl-citrate synthase activity was severely reduced when compared to what had been reported in the literature (Man et al 1995).

Conclusions
To date there does not exist affordable robust sensory equipment capable of providing automated real time analysis of AD Leachate samples’ VFA compositions. The provision of such a sensor coupled with other well established monitoring techniques (Biogas, Methane yield, and pH) would allow for the implementation of an automated maintenance and control system capable of provisioning for continuous optimal operational parameter to remotely deployed AD units thus maximising methane yields.

Acknowledgements

This publication has emanated from research conducted with the financial support of the Charles Parsons Energy Research Programme.

References

Appendix 1
(Research projects in progress which have not been included in the Research Review)

**Walsh J** and Ward S. Carbon trading and management (PhD). Science Foundation Ireland under Grant Number 6C/CP/E001.

**Tuffy** K and Holden N. Impact of artificial sub-surface drainage on pasture production, the length of the grazing season and the profitability of milk production on a heavy wet soil (PhD). Research Stimulus Fund as administered by the Department of Agriculture, Food and the Marine and Teagasc Walsh Fellowship.


**Keena G** and O’Donnell C. Improving the efficiency and sustainability of cheese ripening processes (MEngSc). Teagasc Walsh Fellowship Scheme.

**Murphy E**, Curran T, Holden N, Upton J. Improving sustainability through water conservation on dairy farms (PhD). Teagasc Walsh Fellowship Scheme.

**Stanley S** and Curran T. An integrated systems approach to analyse and design wastewater treatment plans for minimising energy consumption, capital and operational costs (MEngSc). Irish Research Council.

**Su W** and Sun DW. Application of visible and near infrared Hyperspectral Imaging for Non Invasively Measuring potato quality (PhD)

**Charoux C** and O’Donnell C. Control of Biofilms in dried food ingredients (PhD)

**Henihan L** and O’Donnell C. Development of PAT tools for quality and safety improvement in dairy ingredient manufacture for infant formula (PhD). Food Institutional Research Measure (FIRM) administered by the Irish Department of Agriculture, Food and the Marine.
Appendix 2
Profiles of Postdoctoral Research Scholars only includes: Drs, Esquerre, Martínez-González, O’Brien

Carlos Alberto Esquerre Fernandez, BSc, MSc, PhD

Project title: Development of optical imaging technologies to rapidly assess safety and quality of cereals (CerealScan)

Project Leader: Professor Colm P. O’Donnell and Shane Ward

Abstract
The overall goal of this project is to develop and validate on-line, non-destructive optical imaging technologies to rapidly assess safety and quality of cereals at critical processing stages post-harvest. This will reduce food safety risks and result in economic benefit to the cereal industry.

Background, Qualifications and Skills
My main research interests are application of sensor technology and chemometric analysis. The objective of my PhD at UCD was to develop spectroscopy and hyperspectral methods for early detection of physical damage in mushrooms. During this study I developed skills and knowledge in the areas of NIR spectroscopy, NIR hyperspectral imaging and chemometrics. Following the successful completion of my PhD I took up a position as Postdoctoral Researcher at UCD Biosystems Engineering (2010) where I focused on chemometric and sensor development for (i) seaweed characterisation and (ii) to facilitate the transfer of my PhD findings to the Irish mushroom industry. My current research is funded by the EC FP7 Marie Curie International Outgoing Fellowship programme. My outgoing host was the Food Quality Laboratory, U.S. Department of Agriculture, Beltsville Agricultural Research Center, MD, USA. I also assisted in the supervision of PhD and MSc students. I was previously a lecturer in universities in Peru and Chile.

Recent Publications


José Ángel Martínez-González, BSc, MSc, PhD

Project Title: BIOWATER PROJECT: Molecular dynamics simulation for unraveling water structure at biomaterial interfaces

Project Leader: Dr. Aoife Gowen

Abstract
Molecular Dynamics (MD) is a theoretical methodology for studying atoms and molecules along a fixed period of time giving a view of the dynamical evolution of the system. MD simulations have many applications, for example it can be used to refine three-dimensional experimental structures from X-ray or NMR of biological systems (such as proteins or macromolecules) or to understand the growth of thin films, a dynamical atomic-level phenomenon. This project evaluates the use of MD simulations to provide a deeper understanding of the molecular structure of water at biomaterial interfaces and how this structure is conditioned according to the properties of the biomaterial. Additionally, nonequilibrium MD simulations help us to elucidate the key role that water adopts in protein adsorption from the atomic level perspective. This would allow a better understanding about the processes that occur in the interfacial zones, complementing the experimental research developed at Dr. Gowen’s group.

Background, Skills & Qualifications
I obtained my degree in Chemistry from University of La Rioja in 2006. I completed my PhD at the same university in 2013, with a study of the reaction mechanism and kinetics of hepatitis C virus NS3/NS4A protease. In this study I applied several theoretical approaches (QM/MM, EA-VTST, MMPBSA, SCC-DFTB) to simulate the enzymatic reaction mechanism. From January 2014 to January 2015, I was working in the soft matter field, focusing on the amorphization of silica family derivatives and electronic characterization of these materials at the University Autònoma de Barcelona under Dr A Rimola supervision.

Recent publications
Niall O’Brien, BE, M.EngSc., PhD

Project Title: Integrating engineered nanomaterial (ENM) kinetics with environmental exposure modelling

Project Leader: Dr. Enda Cummins

Abstract
The “nanoADJUST” project aims to develop expertise in the application of techniques and tools used to characterise and analyse the behaviour of metallic engineered nanomaterials (ENMs) in natural aquatic media and integrate this expertise with environmental exposure modelling and risk management data requirements and processes. Partitioning experiments in natural aquatic environmental matrices will be undertaken, generating data for use in exposure modelling and RA. Fit-for-purpose analytical methodology shall be developed for quantification of nanoparticle related elemental concentrations in model experiments and natural aquatic environmental matrices. Behavioural indicators or descriptors (i.e. partitioning likelihood distributions) shall also be developed for use in metallic ENM experimental analysis, exposure monitoring and risk assessment, and identification of organisms at risk of metallic ENM toxicity.

Background, Skills & Qualifications
My PhD thesis, concerning the development of development of a risk assessment methodology for evaluating ecological dispersion and human health risks from nanoparticles through environmental pathways, was completed in 2010 under the supervision of Dr. Enda Cummins. This involved developing techniques in environmental modelling, environmental risk assessment and bench mark dose modelling. I obtained a Masters in Engineering Science in the area of renewable fuel production in 2006 and a BE in Biosystems Engineering in 2004, both from UCD. I am currently funded as an EU FP7 Marie Curie International Outgoing Fellow and was based at the Centre for the Environmental Implications of Nanotechnology (CEINT), based in the Civil and Environmental Engineering Department, Duke University, NC, USA from Dec 2013-Dec 2015.

Selected Recent Publications
Appendix 3

UCD School of Biosystems and Food Engineering: Taught Postgraduate Students 2015/16 as photographed by David Kelleghan

O’ Meara Daniel  Murphy Michael  Idrees Absuleelah  Khan Atif  Du Chen

Kenny Finn  Browne Jack  Luo Jiani  Zhang Kexin  Arce Liliana Marcella Osorio

Fitzgerald Louis  Bhattacharjee Mayukh  Satir Mert  Rajat Nag  Menager Raphael
Appendix 4

UCD School of Biosystems and Food Engineering: Postgraduate Research Students 2015/16 as photographed by David Kelleghan

Kale Aneesh
Peyton Dara
Gonzales Eva
Maria Achata
Li Fang
Panikuttira
Kuttappa Bhavya

Guth Felipe
Tiwari Malika
Von Westerholt
Friedrich
Emmet-Booth
Jeremy
Dunne Kathleen

Hannon Joseph
Henihan Lisa
Rice Paul
Clarke Rachel
Oldfield Thomas
Appendix 5

UCD School of Biosystems and Food Engineering: Staff and Post Docs 2015/16 as photographed by Sean Kennedy

Butler Francis  Cummins Enda  Curran Thomas  Murphy Fionnuala  Fitzpatrick Tony

Esquerre Carlos  Grace Pat  Holden Nicholas  Gowen Aoife  McDonnell Kevin

Sun Da Wen  Ward Shane  O’Donnell Colm  O’Brien Niall
Appendix 6

Links to Postgrad Research Activities with YouTube Videos

Taught Masters
Daniel O'Meara (ME Biosystems and Food Eng)
Interview: https://www.youtube.com/watch?v=sVp6CDf8qWo
Presentation: https://www.youtube.com/watch?v=BGKnoNhR75I

Raphaël Menager (MSc Sustainable Energy and Green Technologies)
Interview: https://www.youtube.com/watch?v=l6nDt2aP22c
Presentation: https://www.youtube.com/watch?v=A-K4rXqpgB8

Research Masters
Ronan Dorrepaal
Interview: https://www.youtube.com/watch?v=bRCi_OyDxT4
Presentation: https://www.youtube.com/watch?v=MdcmAlWwJcA

Thomas Wallace
Interview: https://www.youtube.com/watch?v=vNhKpDazAYw
Presentation: https://www.youtube.com/watch?v=6OlmZisw43U

Junior PhD
Sindhuraj Mukherjee
Interview: https://www.youtube.com/watch?v=PcNWyKTOMQs
Presentation: https://www.youtube.com/watch?v=m6pLFQ2SK1c

Felipe Guth
Interview: https://www.youtube.com/watch?v=FnOl0U6ZQWI
Presentation: https://www.youtube.com/watch?v=eefOza2ScoM

Senior PhD
Rachel Clarke
Interview: https://www.youtube.com/watch?v=Qzu3kJc2GA
Presentation: https://www.youtube.com/watch?v=I5Q8Vfc-Fjl

David Kelleghan
Interview: https://www.youtube.com/watch?v=2Uj6TspGZH3k
Presentation: https://www.youtube.com/watch?v=y6bqPdqZnlQ