

Health and Water Quality Impacts Arising from Land Spreading of Biosolids

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Contents

Acknowledgements	ii
Disclaimer	ii
Project Partners	iii
List of Figures	ix
List of Tables	x
Executive Summary	xi
1 Introduction	1
1.1 Overview	1
1.2 Objectives	1
2 Literature Review on Risks Arising from Biosolids Application to Land	3
2.1 Overview	3
2.2 Introduction	3
2.3 Trends in Municipal Sewage Sludge Treatment	3
2.4 Legislation Covering Disposal of Sewage Sludge on Land	4
2.5 Existing and Emerging Issues Concerning the Reuse of Sludge on Land	5
2.5.1 Nutrient and metal losses	5
2.5.2 Pathogens	5
2.5.3 Persistent organic pollutants, pharmaceutical and personal care products	6
2.6 Conclusions	6
3 Metal and PPCP Concentrations in Lime Stabilised, Thermally Dried and Anaerobically Digested Sewage Sludges	7
3.1 Overview	7
3.2 Introduction	7
3.3 Materials and Methods	7
3.3.1 Sample collection and preparation	7
3.3.2 Elemental determination	7
3.3.3 Triclosan and triclocarban determination	8
3.4 Results and Discussion	8
3.4.1 Metal concentrations	8

3.4.2	Triclosan and triclocarban concentrations	8
3.4.3	Environmental policy and management implications	10
3.5	Conclusions	10
4	Nutrient, Metal, Microbial, Triclosan and Triclocarban Loss in Surface Runoff Following Application to Grassland Soil	11
4.1	Overview	11
4.2	Study Site Description	11
4.3	Micro-plot Installation and Characterisation	11
4.4	Biosolids Characterisation	11
4.5	Slurry Characterisation	12
4.6	Rainfall Event Simulation and Application	12
4.7	Runoff Sample Collection	13
4.8	Nutrient and Metal Runoff Analysis	13
4.9	Total and Faecal Coliform Analysis	14
4.10	Data Analysis	14
4.11	Results	14
4.11.1	Nutrient losses in surface runoff	14
4.11.2	Metal losses in surface runoff	14
4.11.3	Microbial losses in surface runoff	15
4.11.4	Triclosan and triclocarban losses in surface runoff	17
4.12	Discussion	17
4.12.1	Incidental nutrient losses	17
4.12.2	Incidental metal losses	18
4.12.3	Incidental triclosan and triclocarban losses	19
4.12.4	Incidental losses of indicator microorganisms	19
4.13	Conclusions	20
5	Metal Concentrations in Ryegrass Following a Single Application of Lime Stabilised, Thermally Dried and Anaerobically Digested Sludge	21
5.1	Overview	21
5.2	Introduction	21
5.3	Materials and Methods	21
5.3.1	Study site and instrumentation of micro-plots	21

5.3.2	Biosolids application to plots	21
5.3.3	Rainfall event simulation and application	21
5.3.4	Collection of grass samples	22
5.3.5	Preparation and analysis of ryegrass samples	22
5.3.6	Statistical analysis	22
5.4	Results and Discussion	23
5.5	Conclusions	24
6	Hazard Identification	25
6.1	Overview	25
6.2	Contaminants of Concern	25
6.3	Multimedia Risk Assessment Model Tools	25
6.4	Probabilistic Model	26
6.5	Results and Discussion	26
6.6	Sensitivity Analysis	28
6.7	Conclusion	28
7	Exposure Assessment and Characterisation for Metals	30
7.1	Overview	30
7.2	Metal Accumulation in Soil	30
7.3	Quantitative Drinking Water Treatment Model	30
7.4	Water Treatment Effects	30
7.5	Human Exposure	31
7.6	Results and Discussion	31
7.7	Sensitivity Analysis	32
7.8	Conclusions	32
8	Exposure Assessment and Characterisation for <i>E. coli</i>	34
8.1	Faecal Coliforms and the Sewage Sludge Directive (86/278/EC)	34
8.2	Quantitative Drinking Water Treatment Model (<i>E. coli</i>)	34
8.3	Water Treatment Effects	34
8.4	Human Exposure	35
8.5	Results and Discussion	35
8.6	Sensitivity Analysis	35
8.7	Conclusions	37

9	Conclusions and Recommendations	38
9.1	Overview	38
9.2	Conclusions	38
9.2.1	Land application	38
9.2.2	Health issues	38
9.3	Recommendations	39
	References	40
	Abbreviations	49

List of Figures

Figure ES1.	Graphical abstract of project	xiii
Figure 3.1.	Triclosan and triclocarban concentrations in treated sludge from 16 wastewater treatment plants in Ireland, ranging (numerically in ascending order) from a PE of 2.3 million to 6500	9
Figure 4.1.	Experimental plots used in this study	11
Figure 4.2.	Amsterdam drip-type rainfall simulators used in this study	13
Figure 4.3.	Flow-weighted mean concentrations of P and N in the runoff over three successive rainfall events at 24 hours (RS1), 48 hours (RS2) and 360 hours (RS3) after application to grassland	15
Figure 4.4.	Flow-weighted mean concentrations of Cd, Cr, Cu, Ni, Pb and Zn in the runoff over three successive rainfall events at 24 hours (RS1), 48 hours (RS2) and 360 hours (RS3) after application to grassland	16
Figure 4.5.	Total coliforms and faecal coliforms in the runoff per 100 mL over three successive rainfall events at 24 hours (RS1), 48 hours (RS2) and 360 hours (RS3) after application to grassland	17
Figure 5.1.	Measured metal content of legislated metals in Ireland (Ni, Zn, Cr, Pb Cu) in ryegrass up to 3120 hours (130 days) after a single application of either ADUK or AD originating from Ireland (AD), LS or TD biosolids	23
Figure 6.1.	Sensitivity analysis for input parameters and the contaminant NP	28
Figure 7.1.	Metal concentration in the outflow post-drinking water treatment using surface runoff data from rainfall simulations on field scale plots occurring 24 hours (RS1), 48 hours (RS2) and 360 hours (RS3) after land application	31
Figure 7.2.	HQ for all biosolids treatments (RS1, RS2 and RS3, and both adult and child)	32
Figure 7.3.	Sensitivity analysis for HQ of Cu in LS biosolids	33
Figure 8.1.	Viable <i>E. coli</i> consumed vs biosolids treatments	36
Figure 8.2.	Probability of illness/day (healthy and IC)	36
Figure 8.3.	Sensitivity analysis for input parameters and ADUK biosolids treatment	37

List of Tables

Table 2.1.	Impacts of biosolids application on soil fertility and plant productivity	4
Table 3.1.	Mean metal concentration in sludge following anaerobic digestion, lime stabilisation, or thermal drying	9
Table 4.1.	Concentrations of triclosan and triclocarban in applied biosolids to field plots (“Influent”) and average concentrations of triclosan and triclocarban in surface runoff ($\mu\text{g L}^{-1}$) from field plots	18
Table 6.1.	Ranking according to human health-based risk. Results are based on mean $\text{PEC}_{\text{runoff}}$ and $\text{PEC}_{\text{groundwater}}$ combined with LC_{50} (RR)	27

Executive Summary

Treated sewage sludge, commonly referred to as “biosolids”, is the organic by-product of urban wastewater treatment. If appropriate treatment is applied, it may be reused as an agricultural fertiliser. Despite this benefit, several issues are associated with the reuse of municipal sewage sludge in agriculture. Although many of these are issues of perception, there is considerable concern over the presence of metals, nutrients, pathogens, pharmaceutical and personal care products (PPCPs), and other endocrine-disrupting and synthetic compounds in biosolids, which may cause environmental and human health problems.

The main aims of this research were to (1) quantify the range of concentrations of metals and two of the most abundant PPCPs in the world, the antimicrobials triclosan (TCS) and triclocarban (TCC), in biosolids from a range of wastewater treatment plants (WWTPs) in Ireland; (2) undertake a field-scale experiment to assess losses of nutrients (nitrogen and phosphorus), metals, TCS, TCC and microbial matter (total and faecal coliforms) after successive rainfall events on grassland onto which biosolids had been applied, and to compare the results with another commonly spread organic fertiliser, dairy cattle slurry (DCS); (3) measure the uptake of metals by ryegrass for a period of time after the application of biosolids; and (4) conduct a risk assessment of potential hazards to human health based on the experimental data.

Three types of biosolids commonly used in Ireland were examined as part of this study: anaerobically digested (AD), lime stabilised (LS) and thermally dried (TD) biosolids. Biosolids and DCS were surface applied in accordance with the legislation in Ireland. A rainfall simulator was used to generate surface runoff over three successive events (24 hours, 48 hours and 360 hours) after a single application.

The metals in the biosolids from the WWTPs examined were below the maximum allowable concentrations for use in agriculture in the European Union (EU). Some priority metals, such as antimony and tin, which are potentially harmful to human health, were identified in some of the samples analysed. As these parameters are not currently regulated, this means that a number of toxic metals, which are at concentrations of up to

40-times higher than their baseline concentrations in soils, are being applied to land without regulation. In the WWTPs examined, the concentrations of TCS and TCC were 0.61 and 0.08 $\mu\text{g g}^{-1}$, which are below the concentrations for these parameters measured in other countries. Similar to the findings for metals, the possibility exists that these potentially harmful, unregulated contaminants, for which no international standards currently exist for recycling in agriculture, may accumulate in the soil upon repeated application.

When losses of nutrients, metals and indicator micro-organisms arising from biosolid-amended plots were compared with slurry treatments, biosolids did not pose a greater risk in terms of losses along the surface runoff pathway. The concentrations of TCS and TCC in surface runoff were also mainly below the limits of detection (90 ng L^{-1} for TCS, 6 ng L^{-1} for TCC). Furthermore, there was no significant difference in metal bioaccumulation for the ryegrass between plots that received biosolids and those that did not over the course of the study.

A literature review identified contaminants of concern based on relevant risk factors, persistence, bioaccumulation and toxicity (PBT). The contaminants identified were persistent organic pollutants (POPs), pharmaceuticals and PPCPs. A suite of 16 contaminants identified in the literature was further analysed in a risk-ranking model to include health-based risk endpoints. A probabilistic model was constructed in Excel 2010 (incorporating @Risk 6.0) to estimate human exposure to the organic contaminants that are contained within biosolids destined for land application. Nonylphenols ranked highest across all environmental compartments. The use of these contaminants is heavily restricted in the EU; however, because of their persistence, the bioaccumulation and toxicity of these compounds in the environment remains a concern. TCC and TCS also ranked highly, and may be considered potentially greater risks, as their use is not restricted and they are known to cause adverse health effects.

An exposure assessment model was further developed both for metals and for *Escherichia coli* (*E. coli*). The model considered exposure to metals and *E. coli* through surface water abstracted for drinking, taking account of surface runoff, dilution and water treatment

effects. The likelihood of illness arising from exposure, and the severity of the resulting illness, were evaluated. Different dose–response relationships were characterised for the different pollutants with reference to the lifetime average daily dose (LADD) and hazard quotient (HQ) for metals, while a worst-case negative exponential dose–response model was used for *E. coli*. Of the three biosolids treatment scenarios considered, and with regard to LADD, the results showed that mean copper exposure concentrations for children were highest in all three rainfall events corresponding to the LS treatment (mean values of 2.07×10^{-2} , 2.07×10^{-2} and $1.18 \times 10^{-2} \mu\text{g kg}^{-1} \text{bw d}^{-1}$). This was followed by adult copper exposure concentrations (mean values of 1.80×10^{-2} , 1.31×10^{-3} and $9.21 \times 10^{-3} \mu\text{g kg}^{-1} \text{bw d}^{-1}$, for all three rainfall events). The results for the HQ showed that, of all the scenarios considered, the metal, copper, and biosolid treatment, LS, had the highest HQ for children for all three rainfall events, with mean child HQ values of 5.59×10^{-4} , 4.09×10^{-4} and $3.18 \times 10^{-4} \mu\text{g kg}^{-1} \text{bw d}^{-1}$, respectively, followed by mean adult HQ values of 4.87×10^{-4} , 3.54×10^{-4} and $2.49 \times 10^{-4} \mu\text{g kg}^{-1} \text{bw d}^{-1}$, respectively. However, these were still below the threshold value of risk ($\text{HQ} < 0.01$, no existing risk).

The results for viable *E. coli* consumed show that one of the sludges examined [an anaerobically digested sludge originating from a WWTP in the UK (ADUK)]

was highest for the first and second rainfall events, with mean exposure values of $5.20 \times 10^{-1} \text{MPN}/100 \text{mL}$ and $2.34 \times 10^{-1} \text{MPN}/100 \text{mL}$, respectively. The results for the probability of illness for healthy and immunocompromised populations showed that among immunocompromised populations the biosolids treatment ADUK (first and second rainfall events) had the greatest probability of illness/day, with mean probability values of 3.68×10^{-3} and 2.1×10^{-3} illnesses/day, respectively. The results indicate that the risk of illness was negligible for healthy individuals; however, care is required with immunocompromised individuals if the annual risk is greater than the threshold risk of illness (10^{-4}), as set by the US Environmental Protection Agency.

The overall conclusion from this study is that, although, in general, land applied biosolids pose no greater threat to water quality than DCS, cattle exclusion times from biosolid-amended fields may be overly strict (within the context of current exclusion criteria). A matter of concern is that unlegislated metals and PPCPs, which were found to be present in biosolids originating from a selection of the WWTPs examined in this study, may be inadvertently applied to land. With multiple applications over several years, these may build up in the soil and may enter the food chain; this gives rise to concerns over the continued application of biosolids to land in Ireland.

1 Introduction

1.1 Overview

In the European Union (EU), implementation of directives and other legislative measures in recent decades concerning the collection, treatment and discharge of wastewater, as well as technological advances in the upgrading and development of wastewater treatment plants (WWTPs) (Robinson *et al.*, 2012), has resulted in a rise in the number of households connected to sewers, which has increased the loadings on WWTPs. Production of untreated sewage sludge (the by-product of wastewater treatment plants) across the EU has increased from 5.5 million tonnes of dry matter (DM) in 1992 to an estimated 10 million tonnes in 2010 (Eurostat, 2014), with production expected to increase further to 13 million tonnes in all EU Member States by 2020 (EC, 2010).

Recycling to land is currently considered the most economical and beneficial method of municipal sewage sludge management (Haynes *et al.*, 2009; Peters and Rowley, 2009; Healy *et al.*, 2015). However, before this can occur, it must be treated to prevent harmful effects on soil, vegetation, animals and humans (EC, 2016). Chemical, thermal or biological treatments, which may include composting (USEPA, 2002), aerobic and anaerobic digestion (USEPA, 2006a), thermal drying (USEPA, 2006b), or lime stabilisation (USEPA, 2000), produce a stabilised organic material frequently referred to as “biosolids”.

Recycling biosolids provides many benefits to grassland: (1) their use completes the urban–rural cycle (Fehily Timoney and Company, 1999); (2) they may be used as a soil conditioner, improving its physical, chemical and biological properties, and reducing the possibility of soil erosion (Lucid *et al.*, 2014); and, most importantly, (3) they are a cheap organic alternative to commercial fertiliser (Lu *et al.*, 2012).

Many potential problems are associated with the land application of biosolids and these were reviewed by, among others, Lu *et al.* (2012) and Singh and Agrawa (2008). Among the main concerns are nutrient, metal, microbial and emerging contaminant losses in runoff (Dowdy *et al.*, 1991; Eldridge *et al.*, 2009; Wallace *et al.*, 2014) and the accumulation of metals in both soil and

crops after repeated applications of biosolids (McBride, 2003; Bai *et al.*, 2010). For example, micro-plastics, which have been found in high concentrations in sewage sludge and have been detected on soils 15 years post-application (Zubris and Richards, 2005; Magnusson and Norén, 2014), may leach organic contaminants and/or endocrine disruptors and can be translocated to the human lymph and circulatory system upon ingestion (Hussain *et al.*, 2001; Cole *et al.*, 2011). Of particular concern is the content of the pharmaceutical and personal care products (PPCPs), in particular the antimicrobials triclosan (TCS) and triclocarban (TCC), in biosolids. Both compounds are commonly found to be the most abundant contaminants in biosolids (McClellan and Halden, 2010) and both are listed among the top contaminants of concern worldwide (Verlicchi and Zambello, 2015). Even though their use has been restricted in the US (USFDA, 2015) and EU (EC, 2016), there may still be legacy issues in municipal sewage sludge and wastewater for some time to come.

Biosolids may provide an excellent opportunity to improve crop profit margins and reduce potential environmental impact by means of reducing the input costs of production, use and distribution of chemical fertilisers. However, there is a need for continued research into land spreading practices to ensure that environmental losses and associated concerns are minimised.

1.2 Objectives

The following were the specific objectives of this project:

- To characterise the metal, TCS and TCC content of biosolids originating from a number of WWTPs in Ireland.
- To quantify losses of nutrients [nitrogen (N), phosphorus (P)], metals [copper (Cu), nickel (Ni), lead (Pb), zinc (Zn), cadmium (Cd), chromium (Cr)], TCS and TCC, and microbes [total coliforms (TC) and faecal coliforms (FC)], in surface runoff from experimental micro-plots at time intervals of 24, 48 and 360 hours, following application of three types of biosolids at the legal application rate based on current EU legislation. The losses arising from no application (the study control) and the application

- of the biosolids to grassland were compared to losses on similar micro-plots following application of another organic fertiliser that is commonly spread in Ireland, dairy cattle slurry (DCS).
- To measure the bioaccumulation of metals in ryegrass for a period of up to 130 days after the land application of biosolids.
 - To develop a risk assessment model of human exposure to pathogens and emerging pollutants resulting from the application of urban wastewater biosolids to agricultural land.

2 Literature Review on Risks Arising from Application of Biosolids to Land

2.1 Overview

The aim of this chapter is to examine the recovery of nutrients and other compounds, such as volatile fatty acids, polymers and proteins, from municipal sewage sludge. Due to the increasing awareness regarding risks to the environment and human health, the application of sewage sludge to land, following treatment, as a fertiliser in agricultural systems has come under increased scrutiny. Therefore, any potential benefits accruing from the reuse of sewage sludge are considered after having been compared with possible adverse impacts associated with its use. This chapter is an abridged version of Healy *et al.* (2015).

2.2 Introduction

“Sludge” is residual-treated or untreated sludge from urban WWTPs (S.I. 254 of 2001). Due to the treatment processes employed in WWTPs, metals, trace organic compounds and pathogenic organisms are concentrated in sludge. However, it is also rich in nutrients and contains valuable organic matter (OM). European policy promotes a “circular economy” (EC, 2014) and emphasises a hierarchy of waste management, including prevention, preparing for reuse, recycling, other recovery and disposal (EU, 2008). This has prompted efforts within municipal sewage sludge management to utilise sewage sludge as a commodity. The terminology “biosolids” reflects the effort to consider these materials as potential resources (Isaac and Boothroyd, 1996).

The use of biosolids in agriculture provides the necessary nutrients and micronutrients necessary for plant and crop growth. They may be used as a soil conditioner, improving its physical and chemical properties (Hargreaves *et al.*, 2008) and reducing the possibility of soil erosion (Lucid *et al.*, 2014). Their use also addresses EU policy on sustainability and reuse of resources (EC, 2014). Numerous studies have documented their efficacy in increasing crop yields and their use in biofuel cropping systems, and in general, biosolids applications to land have been found to have a statistically significant impact on crop yields (e.g. Latare *et al.*, 2014; Liu *et al.*, 2015) and soil phosphorus (Shu

et al., 2016), while having negligible adverse ecological impacts (Xue *et al.*, 2015). A selection of recent studies that report impacts of biosolids application on crop growth, soil fertility and water holding capacity, is shown in Table 2.1.

Despite these benefits, however, there are several issues associated with the reuse of municipal sewage sludge in agriculture, which deserve particular attention. While many of these are issues of perception (Robinson *et al.*, 2012), there is considerable concern about the presence of persistent and emerging contaminants in biosolids, the risk of contamination of soil and water (Fu *et al.*, 2016), and the presence of toxic metals and pharmaceuticals in the sludge. The latter may build up in the soil and enter the food chain following continuous applications of biosolids to land (Latare *et al.*, 2014).

2.3 Trends in Municipal Sewage Sludge Treatment

In Ireland, more than 53,000 tonnes of sewage sludge was produced in 2014, of which 79% was used on agricultural land as a fertiliser or soil enhancer (EPA, 2015). The amount of sewage sludge produced in Europe has generally increased, which is mainly attributable to the implementation of the Urban Waste Water Treatment Directive 91/271/EC (EU, 1991) and other legislative measures. The treatment and disposal of municipal sewage sludge presents a major challenge in wastewater management. As seen over the last decade, the upgrading and development of effective treatment plants has facilitated efforts to improve the quality of the effluent (i.e. removal of microorganisms, viruses, pollutants). Subsequently, legislation regarding municipal sewage sludge in the EU (Sewage Sludge Directive 86/278/EEC; EEC, 1986) and the USA (40 CFR Part 503; USEPA, 1995) has focused on effluent quality and potential contamination. Within the EU, treated municipal sewage sludge is defined as having undergone biological, chemical or heat treatment, long-term storage, or any other appropriate process so as to significantly reduce fermentability and any health hazards

Table 2.1. Impacts of biosolids application on soil fertility and plant productivity

Country	Research focus	Application rate	% increase of parameter measured vs no biosolids application				Reference
			Biomass yield	Mehlich P	Organic matter	Water holding capacity	
USA	Switchgrass growth	0 kg N ha ⁻¹	0				Liu <i>et al.</i> (2015)
		153 kg N ha ⁻¹	25				
		306 kg N ha ⁻¹	37				
		459 kg N ha ⁻¹	46				
Canada	Soil test phosphorus	0 Mg ha ⁻¹		0			Shu <i>et al.</i> (2016)
		28 Mg ha ⁻¹		30			
South Africa	Organic matter, water holding capacity	0 t ha ⁻¹			0	0	Cele and Maboeta (2016)
		25 t ha ⁻¹			157	3	
		100 t ha ⁻¹			576	5	

ha, hectare.

resulting from its use (EC, 2016). Physical-chemical treatment of wastewater has been widely practised, introducing biodegradation and chemical advanced oxidation for biological treatment (Mouri *et al.*, 2013). In the treatment of wastewater, biological treatments, such as aerobic and anaerobic digestion, appear to be the more favoured option. Aerobic treatment has a high degree of treatment efficiency, while anaerobic biotechnology has significantly progressed, offering resource recovery and utilisation while still achieving the objective of waste control (Chan *et al.*, 2009). With regard to sludge stabilisation, aerobic and anaerobic treatments are the most widely used methods of sewage sludge treatment. Within the EU, anaerobic and aerobic wastewater treatments appear to be the most common methods, with 24 out of 27 countries applying this method (Kelessidis and Stasinakis, 2012).

2.4 Legislation Covering Disposal of Sewage Sludge on Land

The drive to reuse sewage sludge has been accelerated by, among other legislation, the Landfill Directive, 1999/31/EC (EU, 1999), the Urban Wastewater Treatment Directive, 91/271/EEC (EU, 1991), the Waste Framework Directive, 2008/98/EC (EU, 2008) and the Renewable Energy Directive, 2009/28/EC (EU,

2009), the last of which places an increased emphasis on the production of biomass-derived energy.

In the EU, the application of treated municipal sewage sludge to agricultural land is governed by EU Directive 86/278/EEC (EU, 1986), which requires that sewage sludge undergoes biological, chemical or heat treatment, long-term storage, or any other process to reduce the potential for health hazards associated with its use. In the EU, land application of treated municipal sewage sludge is typically based on its nutrient and metal content, although individual Member States often have more stringent limits than the directive (EC, 2010; Milieu Ltd *et al.*, 2013a,b,c). Generally, when applying treated sewage sludge based on these guidelines and depending on the nutrient and metal content of the treated sewage sludge, P becomes the limiting factor for application.

In Ireland, the use of sewage sludge in agriculture is regulated by the Waste Management (Use of Sewage Sludge in Agriculture) Regulations (S.I. 148 of 1998 and S.I. 267 of 2001), which prescribe standards and limits on sludge used in agriculture subject to the carrying out of nutrient management plans. In addition, the “Code of Good Practice for the Use of Biosolids in Agriculture” sets out mandatory guidelines for producers, end-users and local authority regulators of sewage sludge used

in agriculture. The use of sewage sludge in agriculture must also comply with the provisions of the EU (Good Agricultural Practice for Protection of Waters) Regulations, 2014, as amended (S.I. 31 of 2014), which specify the periods when land application of fertilisers is prohibited and limits application of fertilisers on the land.

2.5 Existing and Emerging Issues Concerning the Reuse of Sludge on Land

2.5.1 Nutrient and metal losses

Phosphorus and reactive N losses to a surface water body originate from either the soil (chronic) or in runoff where episodic rainfall events follow land application of fertiliser (incidental sources) (Brennan *et al.*, 2012). Such losses to a surface water body occur via primary drainage systems, runoff and/or groundwater discharges. Application of treated sewage sludge to soils may also contribute to soil test P build-up in soils, thereby contributing to chronic losses of P in runoff (Gerba and Smith, 2005). Dissolved reactive P losses may also be leached from an agricultural system to shallow groundwater (Galbally *et al.*, 2013) and, where a connectivity exists, may affect surface water quality for long periods of time (Schulte *et al.*, 2010; Fenton *et al.*, 2011).

The metal content of treated sludge, and of the soil onto which it can be spread, is also regulated by legislation in Europe (86/278/EEC; EU, 1986). However, guidelines governing the application of treated sewage sludge to land (e.g. Fehily Timoney and Company, 1999) mean that it is frequently the case that application rates are determined by the nutrient content of the sludge and not its metal content (Lucid *et al.*, 2013). Regardless, concerns have been raised about the potential for transfer of metals into water bodies, soil structures and, consequently, the food chain (Navas *et al.*, 1999).

2.5.2 Pathogens

During wastewater treatment, the sludge component of the waste becomes separated from the water component. As the survival of many microorganisms and viruses in wastewater is linked to the solid fraction of the waste, the numbers of pathogens present in sludge may be much higher than the water component (Straub

et al., 1992). Although treatment of municipal sewage sludge using lime, anaerobic digestion or temperature may substantially reduce pathogens, complete sterilisation is difficult to achieve (Sidhu and Toze, 2009) and some pathogens, particularly enteric viruses, may persist. Persistence may be related to factors such as temperature, pH, water content (of treated sludge) and sunlight exposure (Sidhu and Toze, 2009). Also, there is often resurgence in pathogen numbers post-treatment, known as the “regrowth” phenomenon. This may be linked to contamination within the centrifuge, reactivation of viable, but non-culturable, organisms (Higgins *et al.*, 2007), storage conditions post-centrifugation (Zaleski *et al.*, 2005) and proliferation of a resistant sub-population due to newly available niche space associated with reduction in biomass and activity (McKinley and Vestal, 1985).

The risk associated with sludge-derived pathogens is largely determined by their ability to survive and maintain viability in the soil environment after landspreading. Survival is determined by both soil and sludge characteristics. The major physico-chemical factors that influence the survival of microorganisms in soil are currently considered to be soil texture and structure, pH, moisture levels, temperature, UV radiation, nutrient and oxygen availability, and land management regimes [reviewed in van Elsas *et al.* (2011)]. In contrast, survival in sludge is primarily related to temperature, pH, water content (of treated sewage sludge), and sunlight exposure (Sidhu and Toze, 2009). Pertinent biotic interactions include antagonism from indigenous microorganisms and viruses, competition for resources, predation and occupation of niche space (van Elsas *et al.*, 2002). Pathogen-specific biotic factors that influence survival include physiological status and initial inoculum concentration (van Veen *et al.*, 1997).

Following landspreading, there are two main scenarios that can lead to human infection. First, pathogens may be transported via overland or sub-surface flow to surface and groundwaters, and infection may arise via (accidental) ingestion of contaminated water (recreational) (Tyrrel and Quinton, 2003). Second, it is possible that viable pathogens could be present on the crop surface following biosolids application, or may become internalised within the crop tissue where they are protected from conventional sanitisation (Solomon *et al.*, 2002). In this case, a person may become infected if they consume the contaminated produce.

2.5.3 Persistent organic pollutants, pharmaceutical and personal care products

The United Nations Environment Programme (UNEP) defines persistent organic pollutants (POPs) as organic compounds that, to a varying degree, resist photolytic, biological and chemical degradation (UNEP, 2013). They are characterised by low water solubility and high lipid solubility, which gives them high potential for bioaccumulation; they also have a long half-life in soil, sediment, air or biota. The lipophilic nature of POPs means that they appear at higher concentrations in fat-containing foods, including fish, meat, eggs and milk, and so traces of POPs are found in the human body (UNEP, 2013). Therefore, food consumption is considered the main pathway of human exposure to POPs for the majority of the population. High lipophilicity results in the substance bio-concentrating from the surrounding medium into the organism; combined with environmental persistence and a resistance to biological degradation, lipophilicity also results in biomagnification through the food chain (Smith and Riddell-Black, 2007). Some cancers, birth defects, dysfunctional immune and reproductive systems, and even some diminished intelligence, are suspected to be related to exposure to these chemicals (UNEP, 2013).

Pharmaceuticals and personal care products refer to any product used by individuals for personal health or cosmetic reasons, or those that are used in agriculture to enhance growth or health of livestock. PPCPs comprise a diverse collection of thousands of chemical substances, including prescription and over-the-counter therapeutic drugs, veterinary drugs, fragrances and cosmetics (Yang *et al.*, 2011). Pharmaceuticals are specifically designed to alter both biochemical and physiological functions of biological systems in humans and animals. However, these features can unintentionally affect soil or aquatic organisms should their habitats become contaminated with these chemicals. Unlike pharmaceuticals, personal care products are directly washed into wastewater during showering and bathing, and thus enter WWTPs and, subsequently, the environment (Richardson *et al.*, 2005). PPCPs are referred to as “pseudo persistent” contaminants (i.e. high transformation/removal rates are counteracted by their continuous introduction into the environment)

(Cooper *et al.*, 2008). PPCPs are likely to be found in any body of water influenced by raw or treated wastewater, including rivers, lakes, streams and groundwater, many of which are used as a source of drinking water (Yang *et al.*, 2011), as well as in agricultural soils. In addition, PPCPs with antimicrobial activity may contribute to antimicrobial resistance formation and persistence of antimicrobial bacteria.

2.6 Conclusions

The application of biosolids to agricultural soils can be sustainable and economical on the basis of the recycling of nutrients and the waste disposal of sewage sludge. However, it also has potential risks with respect to the potential for the build-up of contaminants in the soil and the runoff of contaminants. There are also growing concerns that POPs and PPCPs may accumulate in the soil, which can then be taken up by plants and grazing animals and transferred to humans via the food chain. PPCPs are generally more water soluble in nature and tend to have shorter half-lives in soil compared to POPs. However, PPCPs are considered to be “pseudo persistent”, as their supply to the environment via biosolids is continually replenished. The risk of indirect exposure can occur through several pathways (consumption of food-crops, animal uptake of meat or milk, etc.). Risk assessment approaches have been adopted to assess the environmental fate of contaminants in biosolids, with quantitative structure–activity relationship (QSAR) model approaches dominating. Judicious selection of suitable modelling approaches is required to ensure accurate representation of human/environmental risks from emerging contaminants.

While the majority of sewage sludge is reused in agriculture, there are still public perception issues surrounding its use. For example, raw or treated sewage sludges are prohibited from being used on Bord Bia-certified farms (Bord Bia, 2010). In addition, before the publication of this report, no empirical information had been produced regarding the surface runoff of contaminants from land-applied treated sludge in Ireland. Moreover, fears regarding the uptake of metals by grass following land application, and potential incorporation into the food chain, still exist. These factors all have contributed to a general unease regarding the reuse of sewage sludge in agriculture.

3 Metal and PPCP Concentrations in Lime Stabilised, Thermally Dried and Anaerobically Digested Sewage Sludges

3.1 Overview

There is considerable debate and public sentiment about the land application of treated sewage sludges (biosolids). Concerns may be warranted, as many priority metal and PPCP pollutants may be present in biosolids. In this study, metal content and two of the most abundant PPCP components in sewage sludge, the anti-microbials TCS and TCC, were examined in biosolids from 16 WWTPs in Ireland.

For more technical detail on the metal analysis component of this study, the reader is referred to Healy *et al.* (2016a).

3.2 Introduction

In the EU, land application of biosolids is typically based on its nutrient and metal content, although individual Member States often have more stringent limits than governing directives (LeBlanc *et al.*, 2008; EC, 2010; Milieu *et al.*, 2013a,b,c). Guidelines govern the maximum allowable levels of nutrients and metals (e.g. Fehily Timoney and Company, 1999), although, as the metal content is normally low relative to the nutrient content of biosolids, application rates are frequently determined by the nutrient content of the biosolids and not by their metal content (Lucid *et al.*, 2013). There is a potential risk of metal accumulation in the soil (Mamindy-Pajany *et al.*, 2014), in plants (Latare *et al.*, 2014), or in transport to groundwater, particularly if biosolids are applied in excess (McBride *et al.*, 1999). Parameters that are also of concern are the PPCPs, which cannot be fully removed from WWTPs (Narumiya *et al.*, 2013). Two PPCPs of particular interest are TCS, a broadspectrum bacteriostat and fungicide, and TCC, also a bacteriostat and fungicide, which are known toxins for humans and which are listed among the top contaminants of concern worldwide (Verlicchi and Zambello, 2015).

Due to the increasing awareness regarding potential risks to the environment and human health, the application of sewage sludge, following treatment, to land as a fertiliser in agricultural systems has come under

increased scrutiny. As metals and PPCPs probably remain in the soil indefinitely, the characterisation of biosolids for these parameters prior to land application is important. The aim of this study was to: (1) examine if the metal content of biosolids from high population equivalent (PE) WWTPs in Ireland exceeded permitted limit values; (2) to establish a baseline for unregulated metals and potential pollutants of which little is known and from which other global studies may be compared; and (3) characterise the TCS and TCC content of the biosolids.

3.3 Materials and Methods

3.3.1 Sample collection and preparation

Biosolids were collected from 16 WWTPs or agglomerations, with PEs of up to approximately 2.3 million. Selection of the WWTPs was based on willingness to participate in this monitoring study, PE (large PEs were desirable) and geographical location (a good geographical spread was also desirable). Of the WWTPs examined, most received landfill leachate in low quantities [no greater than 2% of the total biological oxygen demand (BOD) loading on the WWTP], while others received industrial, commercial and domestic/septic tank sludge comprising up to 30% of the total influent BOD loading on the WWTP. Eight discrete samples of 100g were collected in clean low-density polyethylene containers (Fisher, UK) from each WWTP and stored at -20°C prior to analysis. The biosolid samples were freeze-dried at -50°C and pulverised in an agate ball mill with a rotational speed of 500rpm for 5 minutes (repeated three times) using an 80 mL agate vial and balls (\varnothing 10mm).

3.3.2 Elemental determination

A handheld X-ray fluorescence (XRF) analyser was employed to determine metal concentrations [Cd, Cr, Cu, iron (Fe), mercury (Hg), molybdenum (Mo), Ni, Pb, antimony (Sb), selenium (Se), tin (Sn), and Zn]. This

portable XRF system consists of a powerful X-ray tube [4W, gold anode] and a 30 cm² Silicon Drift Detector. An internal instrument standardisation was performed using an alloy chip, and sewage sludge certified reference materials (CRMs) were used for calibration/verification. Quality control included the use of instrumental blanks and analysis of duplicate samples. The performance of the method and stability of the instrument was evaluated by using CRMs for sewage sludge.

3.3.3 *Triclosan and triclocarban determination*

The method of analysis for TCS and TCC in the biosolids was in accordance with US Environmental Protection Agency (USEPA) method 1694 (USEPA, 2007). The analysis was conducted in three stages: (1) proof of limit of detection (LOD) and limits of quantification (LOQ); (2) proof of concept, method implementation and linearity/recovery; and (3) sample analysis. In stage 1, a mixed standard of TCS and TCC was prepared at a level of 0.5 ppm for each analyte and was analysed by LC-MS-MS using reversed phase chromatography, to determine extraction efficiency, demonstrate linearity and determine probable LOD/LOQ in samples. In stage 2, triplicate extractions of spiked biosolids were performed to determine the accuracy and precision of the method. In stage 3, biosolids and surface runoff water samples were extracted using the established method. Quality control monitoring of the analysis was performed using a spiked reference material, which was analysed every 10 samples.

3.4 Results and Discussion

3.4.1 *Metal concentrations*

The mean concentrations of the metals in the sewage sludge following treatment in the 16 WWTPs are given in Table 3.1. The concentrations of the metals that are regulated in the EU [expressed as mg kg⁻¹ DS (dried solids)] ranged from 11 mg kg⁻¹ (Cd, anaerobically digested (AD) biosolids) to 1273 mg kg⁻¹ [Zn, AD biosolids] and were well below EU regulatory limits. Of the parameters not regulated in the EU, As (arsenic), Se, Mo and Cr were well below the upper limits of 75, 100, 75 and 1000 mg kg⁻¹, respectively. Of the elements considered bioessential micro-nutrients measured in this study (Se, Fe, Cu and Zn), all were within either EU or international limits (no limits govern Fe).

The biosolids from one WWTP, in which anaerobic digestion was carried out, had an average Pb concentration of 3696 mg kg⁻¹, which is well in excess of the threshold value of 1200 mg kg⁻¹. The average concentrations (across all treatments) of Cu, Pb and Zn were also well above the median values of internationally published results. Lead is among the most hazardous metals that are potentially harmful to human health (Johnson and Bretsch, 2002). Other metals measured in this study, which are also potentially harmful, were Cr, Cd, Sn and Sb. Of these parameters, no international standards exist, to date, for Sb or Sn in biosolids for reuse in agriculture. In the current study, the average concentration of Sb ranged from 17 to 20 mg kg⁻¹, which was substantially higher than recorded elsewhere, e.g. <0.01 to 0.06 mg kg⁻¹ (LeBlanc *et al.*, 2008) and 3.4 mg kg⁻¹ (Eriksson, 2001). As the average concentration of Sb in non-polluted soils is around 0.53 mg kg⁻¹ (Fay *et al.*, 2007) and elevated concentrations in the soil inhibit the early growth of crop plants (Fjällborg and Dave, 2004; Baek *et al.*, 2014), the possibility exists that large quantities of this metal are being applied to land without regulation. Tin, in its inorganic form, is non-toxic; however, a significant portion of sewage sludges may be in a highly toxic, organic form and include compounds such as tributyltin (McBride, 2003). The concentrations of Sn measured in this study ranged from 23 to 55 mg kg⁻¹, which was of the same order as other studies (26 mg kg⁻¹; Eriksson, 2001). Normal ranges of Sn in non-polluted Irish soils are around 1.68 mg kg⁻¹ (Fay *et al.*, 2007). Both metals, Sb and Sn, however, are not considered to be of risk to animals or humans (USEPA, 1995).

3.4.2 *Triclosan and triclocarban concentrations*

The TCS and TCC concentrations in the biosolids samples are shown in Figure 3.1. There was no trend between the type of treatment carried out and the concentrations measured, nor was there any trend with PE served or geographical location of the WWTP. One of the WWTPs examined (1 and 2 in Figure 3.1) had a history of high concentrations of TCS, with concentrations of 25 µg g⁻¹ being previously reported (EPA, 2013), but the concentrations in this study were below this. Of the previous studies that have carried out testing of TCS and TCC across a number of WWTPs in a given region, the concentrations of both compounds measured in this study rank the lowest. There are currently no limits

Table 3.1. Mean [\pm standard deviation (SD)] metal concentration (mg kg^{-1} dry weight) in sludge following anaerobic digestion, lime stabilisation, or thermal drying. *n* refers to the number of treatments^a

Metal	Anaerobic digestion (<i>n</i> =5)		Lime stabilisation (<i>n</i> =4)		Thermal drying (<i>n</i> =8)		EU regularity upper limits (EU, 1986)
	Mean	SD	Mean	SD	Mean	SD	
<i>Regulated parameters in EU</i>							
Cu	640	411	491	452	464	205	1750
Ni	25	5	13	2.5	15	7	400
Pb	791	1625	33	25	54	30	1200
Cd	11	1	13	1	10	3	40
Zn	1273	749	526	388	869	400	4000
Hg ^b	<LOD		<LOD		<LOD		25
<i>Non-regulated parameters in EU</i>							
As ^c	<LOD		<LOD		<LOD		
Se	3	2	3	1	2	1	
Sr	162	61	183	75	114	36	
Mo	5	2	4	1	5	1	
Ag	11	2	11	3	8	3	
Sn	55	57	23	4	23	5	
Sb	20	5	17	3	17	4	
Cr	51	43	25	15	16	12	
Fe	32,135	41,717	9654	7264	33,087	43,373	

^aBoth anaerobic digestion and thermal drying were carried out in one wastewater treatment plant.

^bLOD = 10 ppm.

^cLOD = 100 ppm.

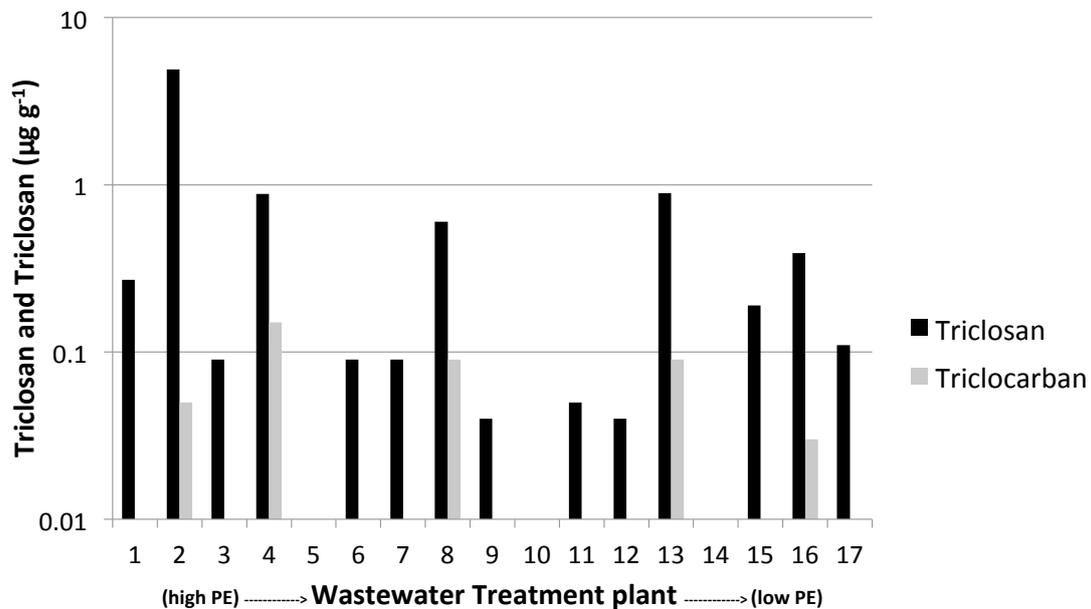


Figure 3.1. Triclosan and triclocarban concentrations ($\mu\text{g g}^{-1}$) in treated sludge from 16 wastewater treatment plants in Ireland, ranging (numerically in ascending order) from a PE of 2.3 million to 6500. Note that two forms of treatment of sludge are carried out in one WWTP: AD (WWTP 1) and thermal drying (WWTP 2). WWTPs with no concentrations shown are WWTPs in which triclosan or triclocarban were below the LOD (TCS, $0.006 \mu\text{g g}^{-1}$; TCC, $0.0024 \mu\text{g g}^{-1}$).

set for PPCPs in sludge or biosolids (Verlicchi and Zambello, 2015), so the concentrations measured in the current study may only be compared with similar studies. The biosolid samples used in this study were collected in January and February of 2015, so there may be seasonal variation in the concentrations of TCS and TCC that were measured in other studies (Martin *et al.*, 2012).

3.4.3 Environmental policy and management implications

Land application of biosolids is, in the main, determined by the nutrient content of biosolids and not by the metal or PPCP content. Therefore, accumulation of metals and PPCPs in soil following repeated applications of biosolids may be problematic, particularly for those elements that are not regulated and are harmful to human health. Guidelines should aim to govern the maximum allowable concentrations of these elements in biosolids, as well as the land to which they are applied. Handheld XRF analysis is a useful, quick and relatively inexpensive method for determining the metal content of biosolids and should be used frequently to characterise it. In contrast, PPCP testing is extremely expensive, so the costs of routinely testing sludge for all possible contaminants would be prohibitive.

3.5 Conclusions

The concentration of metals detected in 16 WWTPs in Ireland were below the maximum allowable concentrations of metals for use in agriculture in the EU. In addition, they were also within the median levels for biosolids globally. While current EU and international regulations govern certain priority metal pollutants and bioessential elements, other metals that are potentially harmful to human health, such as Se and Sn (both of

which were present in the treated sewage sludge in this study), are omitted from the regulations. This means that a number of toxic metals, at levels much higher than their baseline concentrations in soils, are being applied without regulation.

While the metal, TCS and TCC contents of the biosolids in the WWTPs examined were below the concentrations measured elsewhere, there is a possibility that this may increase from one season to the next. In addition, until threshold values, based on human or ecological risk, are set, there is a possibility that the concentrations of TCS and TCC, even at the relatively low concentrations measured in the current study, may be considered to be a risk. Furthermore, the current study only examined two types of PPCPs (albeit the ones that are the most abundant and problematic of the PPCPs worldwide), which are only a small fraction of the total number of contaminants that may be present in biosolids.

To fully characterise all existing known contaminants, as well as emerging contaminants, is cost prohibitive. Therefore, any potential economic and practical gains arising from the recycling of sewage sludge in agriculture need to be considered alongside cost and public health issues. A significant component of the cost of performing such analyses is related to the development and validation of approaches for analyte extraction, detection and quantification. Differences in methodology and lack of data on inter-laboratory comparability also limit confidence in assessing the significance of reported differences in levels of contaminants. Harmonisation/standardisation of methods and development of standards may help to reduce costs and enhance comparability.

It is recommended that, in the first instance, priority elements and TCS and TCC are assessed in sewage sludge in Ireland. Following this, regulations may be extended to cover these parameters.

4 Nutrient, Metal, Microbial, Triclosan and Triclocarban Loss in Surface Runoff Following Application to Grassland Soil

4.1 Overview

Treated municipal sewage sludge (biosolids) may be applied to agricultural land as an organic fertiliser. This study investigates losses of nutrients (N and P), metals (Cu, Ni, Pb, Zn, Cd, Cr), two selected PPCPs (TCC and TCS) and microbial indicators of pollution (total and faecal coliforms) arising from the land application of four types of treated biosolids to field micro-plots. This was done during 60-minute simulated rainfall events at three time intervals (24, 48, 360 hours) after application. To contextualise the results, the plots were also treated with DCS, which was applied at the same rate as the biosolids.

For more technical details on this study, the reader is referred to Peyton *et al.* (2016).

4.2 Study Site Description

The study site was a 0.6-ha grassland plot located at Teagasc, Johnstown Castle Environment Research Centre, Co. Wexford, Ireland (latitude 52.293415, longitude -6.518497). The area has a cool maritime climate, with an average temperature of 10°C and a mean annual precipitation of 1002mm. The site has been used as a grassland sward for over 20 years, with nutrient inputs (organic and inorganic) applied based on routine soil testing. The site has undulating topography with average slopes of 6.7% along the length of the site and 3.6% across the width. Overall, the site is moderately drained with a soil texture gradient of clay loam to sand silt loam, as classified by Brennan *et al.* (2012). Physico-chemical characterisation of the site is detailed in Peyton *et al.* (2016).

4.3 Micro-plot Installation and Characterisation

Thirty grassland micro-plots (Figure 4.1), each 0.9 m in length and 0.4 m in width (0.36 m²), were isolated using continuous 2.2-m-long, 100 mm-wide rigid polythene plastic strips, which were pushed to a depth of 50 mm

into the soil to isolate three sides of the plot. A 0.6-m polypropylene plastic runoff collection channel was fitted at the end of each plot. Micro-plots were orientated with the longest dimension in the direction of the slope. Once installed, plots were left uncovered to allow natural rainfall to wash away any soil that had been disturbed during their construction. Physico-chemical characterisation of the micro-plots, including textural analysis, soil nutrient status, metal and microbial content, is detailed in Peyton *et al.* (2016).

4.4 Biosolids Characterisation

Three types of biosolids were examined in this study: two types of AD sludge, one sourced from a WWTP in Ireland [anaerobically digested biosolids sourced in Ireland (ADIRE)] and another used in an EU-funded FP7 (Seventh Framework Programme) project (END-O-SLUDG, 2014) [anaerobically digested biosolids sourced in the UK (ADUK)]; thermally dried (TD) biosolids; and lime stabilised (LS) biosolids. With the



Figure 4.1. Experimental plots used in this study.

exception of ADUK, all biosolids were sourced from the same WWTP in Ireland. As the Irish WWTP only employed two methods to treat sludge (AD and TD), an untreated, dewatered sewage sludge cake was also collected from the same WWTP, so that it could be manually lime treated. The treated sludge and the dewatered sludge cake were collected in sealed, 50L capacity plastic storage boxes and transported to the Teagasc Environment Research Centre, where they were labelled and stored at 4°C. In accordance with standard methods in Ireland (Fehily Timoney and Company, 1999), lime (calcium oxide) was added to the raw dewatered sewage sludge to raise the pH to greater than 12 and to generate heat. If this had not been done, the sludge would not have been adequately treated and would have carried greater risk. The treated sludge samples (each at $n=3$) were tested for DM, total Kjeldahl nitrogen, nitrite-N ($\text{NO}_2\text{-N}$), ammonium-N ($\text{NH}_4\text{-N}$), organic-N, total P (TP), P as phosphorus pentoxide (P_2O_5), potassium (K), K as potassium oxide (K_2O), pH, TCS, TCC and metal content (Cu, Ni, Pb, Zn, Cd, Cr, Hg) (Peyton *et al.*, 2016). Water extractable P was tested after Kleinman *et al.* (2007). In addition, the biosolids samples (each at $n=3$) were tested for TC and FC immediately after collection, using the same methods as for soil (Peyton *et al.*, 2016).

4.5 Slurry Characterisation

Dairy cattle slurry was collected from the dairy farm unit at Teagasc, Johnstown Castle Environmental Research Centre. The storage tanks were agitated and slurry samples were transported to the laboratory in 25-L drums. Slurry samples were stored at 4°C prior to land application. Slurry pH was determined using a pH probe and a 2:1 ratio of deionised water to soil. The DCS was tested for: DM, N (Kjeldahl, 1883), P, K and metal content (Cu, Ni, Pb, Zn, Cd and Cr) (Peyton *et al.*, 2016). In addition, the DCS samples (each at $n=3$) were also tested for TC and FC immediately after collection using the same methods as for soil (Peyton *et al.*, 2016).

4.6 Rainfall Event Simulation and Application

Amsterdam drip-type rainfall simulators, as described by Bowyer-Bower and Burt (1989), were used to provide rainfall in this study (Figure 4.2). It was designed to form droplets with a median diameter of 2.3 mm, spaced 30 mm apart in a 1000 mm × 500 mm × 8 mm Perspex

plate over a 0.5 m² simulator area. The simulator was calibrated to deliver a rainfall intensity of 11 mm h⁻¹. A video of the operation of the rainfall simulator (“Rainfall simulator”) is available online (<https://youtube.com/watch?v=JYhsmE8SHvU>). Water samples used in the rainfall simulations, were collected over the duration of the three rainfall events; the average concentrations are detailed in Peyton *et al.* (2016).

The six treatments (four biosolids, one DCS and one soil-only study control) used in this study were assigned to 30 micro-plots by dividing the plots in five blocks (five blocks each containing six micro-plots, so that each treatment was replicated $n=5$ times). As metal content was not limited in soil, DCS or biosolids application to the micro-plots was governed by the P content of the biosolids, and DCS and the P by the index of the soil. For comparable results, all micro-plots were classified into Index 2P soil, which meant that all biosolids and DCS treatments were applied to all plots at a rate of 40 kg P ha⁻¹ (Coulter and Lalor, 2008). As a result of the P content and the DM of each individual biosolid, application rates per designated, individual plot were 96.6 g of TD, 242.2 g of ADIRE, 1063.3 g of LS, 243.9 g of ADUK. The DCS was spread at 2880 g per individual plot.

Prior to application, grass on all plots was cut to 50 mm 48 hours before the first rainfall simulation (RS1). For better control of rainfall simulations and to prevent runoff losses caused by natural rainfall events, individual micro-plots were covered from the time of grass cutting to the end of the last rainfall event by “rainout” shelters (Hoekstra *et al.*, 2014). Surfaces of biosolids were applied to each micro-plot by hand. To ensure even distribution, each micro-plot was divided into four quadrants (each 0.09 m² in area) and a proportionate amount of biosolids was applied in each quadrant. The DCS was applied in rows using a watering can to replicate normal trailing shoe application. The biosolids and DCS were then left for 24 hours on the soil before RS1. The RS1 occurred 24 hours after biosolids and DCS application, so as to demonstrate losses representative of a worst case scenario. The second rainfall simulation event (RS2) was 2 days (48 hours) after initial biosolids/DCS application, which was representative of current legislation, and the third rainfall simulation event (RS3) took place 15 days (360 hours) after initial application.

Volumetric water content of the soil in each plot ($n=3$) was measured immediately prior to each rainfall event

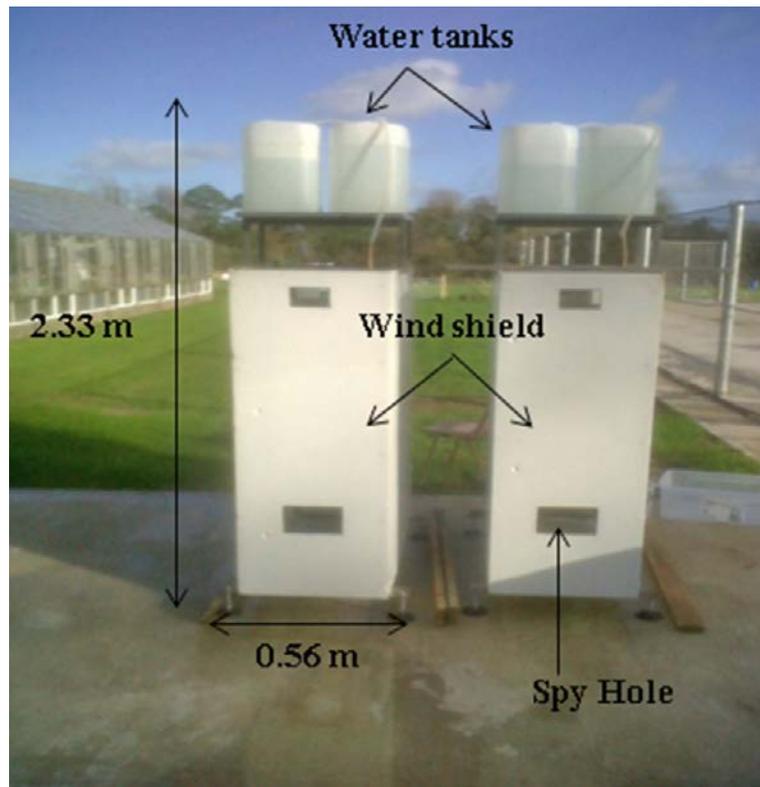


Figure 4.2. Amsterdam drip-type rainfall simulators used in this study.

using a time domain reflectometry device (Delta-T Devices Ltd., Cambridge, UK), which was calibrated to measure resistivity in the upper 50 mm of the soil in each plot. Prior to each rainfall event, collection channels from the micro-plots were also rinsed with boiling hot water to decontaminate them.

4.7 Runoff Sample Collection

Surface runoff was judged to occur once 50 mL of water was collected from the runoff collection channel from the start of simulated rainfall to runoff. The collection of the first 50 L ($t=0$) was used to indicate time to runoff (TR) and was used as part of the microbial analysis. Samples for nutrient and metal analysis were collected every 10 minutes ($t=10$, $t=20$, $t=30$) from TR to allow for the flow-weighted mean concentration (FWMC) to be calculated (Brennan *et al.*, 2012). After this time, another 50 mL of surface runoff water was collected for microbial analysis, so that it could be bulked with the first 50 mL of runoff to create a 100 mL sample for microbial analysis. Immediately after collection, all samples were stored in cool boxes with ice until they were returned to the laboratory for analysis. For TCS and TCC analyses, runoff water samples (from the TD, ADIRE and LS plots) were collected in solvent washed

amber glass Pyrex bottles with PTFE-lined lids and were decanted into clean amber bottles to remove any sediment that was present in the samples on returning to the laboratory. Immediately after decanting, 4 mol L^{-1} of sulfuric acid was added to adjust the water to pH 3 to prevent biodegradation by microorganisms. Samples were then frozen and stored at -20°C until analysis.

4.8 Nutrient and Metal Runoff Analysis

Runoff water samples were filtered through $0.45 \mu\text{m}$ filters (Sarstedt-Filtropur S 0.45) and a sub-sample was analysed calorimetrically for dissolved reactive phosphorus (DRP), $\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{NH}_4\text{-N}$ using a nutrient analyser (Aquachem Labmedics Analytics, Thermo Clinical Labsystems, Finland). A second filtered sub-sample was analysed for total dissolved phosphorus (TDP) using acid persulfate. Unfiltered runoff water samples were analysed for TP with an acid persulfate digestion and total reactive phosphorus using the Aquachem Analyser. Metal analysis was tested on the filtered samples using inductively coupled plasma optical emission spectroscopy. Particulate phosphorus (PP) was calculated by subtracting TDP from TP. The DRP was subtracted from the TDP to give the dissolved

unreactive phosphorus (DUP). All samples were tested for P, N and suspended sediment in accordance with the Standard Methods (APHA, 2005) and TCS and TCC were tested in accordance with USEPA Method 1694 (USEPA, 2007).

4.9 Total and Faecal Coliform Analysis

Samples (2×50mL aliquots) of runoff water were collected at the start and towards the end of rainfall simulation experiments, and were stored in cool boxes (4°C) filled with ice until they were returned to the laboratory for analysis. The time interval between the first collection and analysis was always less than 9 hours. Samples were appropriately diluted using sterile isotonic phosphate buffered saline (Osoid, UK) made with water from a Millipore automatic sanitisation module and 100-mL aliquots were apportioned for analysis in accordance with standard methods (APHA, 2005). Total and faecal coliforms were enumerated using the IDEXX Coilsure Quanti Tray/2000 method (IDEXX Laboratories, Westbrook, ME) after incubation at 37±0.5°C degrees for 24 hours. Results were expressed as the most probable number (MPN) of TC and FC per 100 mL.

4.10 Data Analysis

The structure of the data set was a blocked one-way classification (treatments) with repeated measures over time (RS1–RS3). The analysis was conducted using Proc Mixed in SAS software (SAS, 2013) with the inclusion of a covariance model to estimate the correlation between rainfall events. Details of the statistical treatments employed are in Peyton *et al.* (2016).

4.11 Results

4.11.1 Nutrient losses in surface runoff

the average FWMC of TP, comprising DUP, PP and DRP, for all treatments and rainfall events is shown in Figure 4.3. The application of TD and ADIRE biosolids and DCS significantly increased the average FWMC of DRP in RS1 and RS2 compared to the study control, but this highly mobile P fraction was low for the other biosolids treatments. The highest median FWMC of DRP in the biosolids treatments (0.86 mg L⁻¹) was measured during RS1 for TD-amended plots and this decreased

significantly ($p=0.02$) over subsequent rainfall events to 0.14 mg L⁻¹ for RS3. In comparison, the median FWMC of DRP from the ADIRE treatment was highest for RS2 (0.78 mg L⁻¹), although results for the three events were not significantly different. However, losses for DRP from biosolids treatments were low compared to the DCS. Dissolved reactive phosphorus loss for DCS during RS1 was 7.0 mg L⁻¹ and this remained higher than any of the biosolids treatment losses during all simulation events.

Losses of PP were detected across all treatments, including the study control. Particulate P comprised >45% of TP losses for ADUK, ADIRE and LS biosolids, and the study control. PP losses comprised only 14% of TD biosolids, due to the high proportion of DRP losses, and were much lower than the losses from the DCS plots.

The average FWMC of total nitrogen (TN) across all treatments is shown in Figure 4.3. There was a significant interaction between treatment and the rainfall simulation for NH₄-N. The application of all biosolids treatments increased the average FWMC of NH₄-N for RS1, compared to the study control, and while there was a downwards trend between RS1 and RS3 for all treatments except the control, the decrease was not significant for LS. The ADUK-amended plots had the highest FWMC of surface runoff of NH₄-N for all biosolids treatments in RS1 (15.3 mg L⁻¹). TD and ADIRE treatments had the next highest FWMCs of NH₄-N, but these were not significantly different from each other or from the LS runoff during RS1.

4.11.2 Metal losses in surface runoff

The average FWMC of metals (Cu, Ni, Pb, Zn, Cd, Cr) in runoff are shown in Figure 4.4. All runoff samples, except the surface runoff of Cu from the LS plots, were below their respective surface water standards intended for human consumption (S.L.549.21). With the exception of Cu, the surface runoff of all the parameters measured was of the same order, or much less than, the DCS. For Cu, the LS-amended plots had significantly higher FWMCs than all other treatments ($p<0.001$), with the highest median concentration of 202 µg L⁻¹ measured during RS1. There was a decreasing trend in Ni concentrations across all treatments from RS1 to RS3, except for the study control, but there were no significant differences within treatments. All Ni concentrations were elevated in comparison to the study

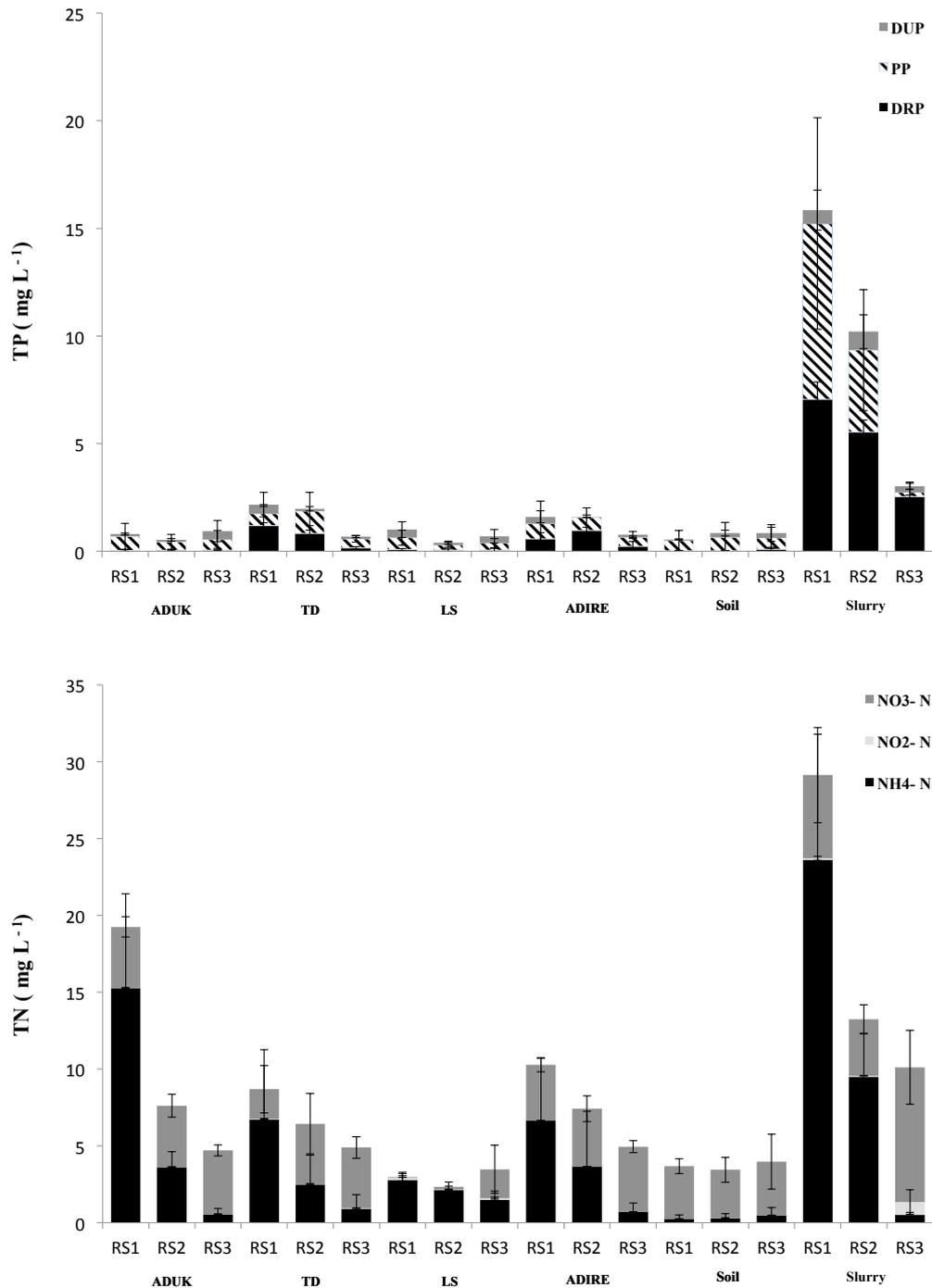


Figure 4.3. Flow-weighted mean concentrations of P (top) and N (bottom) in the runoff over three successive rainfall events at 24 hours (RS1), 48 hours (RS2) and 360 hours (RS3) after application to grassland (standard deviation error bars).

control. The highest median FWMC for Pb ($1.5\mu\text{g L}^{-1}$) was measured during RS3 for the DCS and the second highest was $0.82\mu\text{g L}^{-1}$ during RS1 for TD-amended plots. However, there was no significant difference between the treatments and the study control. The highest median FWMC of Zn ($30.8\mu\text{g L}^{-1}$) was during RS1 for DCS-amended plots, but there were no significant differences across treatments or events.

4.11.3 Microbial losses in surface runoff

The average losses of TC and FC are shown in Figure 4.5. The ADUK-amended plots produced runoff with the lowest number of TC (averaged over the three rainfall simulations), but produced the highest average number of FC: 7.1×10^3 MPN per 100 mL during RS1 and RS2. While median losses from the TD-amended

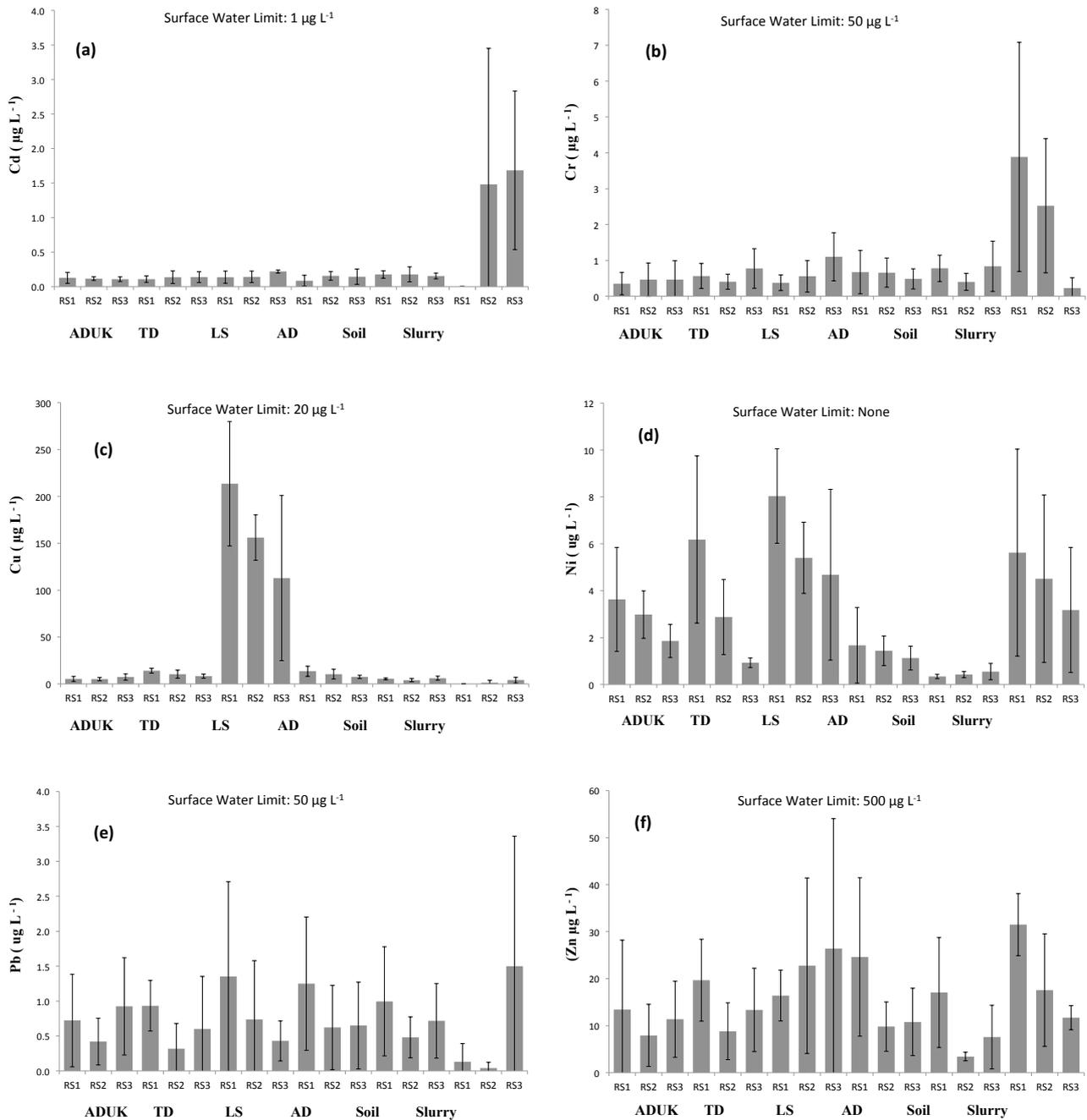


Figure 4.4. Flow-weighted mean concentrations of (a) Cd, (b) Cr, (c) Cu, (d) Ni, (e) Pb and (f) Zn in the runoff over three successive rainfall events at 24 hours (RS1), 48 hours (RS2) and 360 hours (RS3) after application to grassland.

plots increased with successive rainfall events from 1.9×10^5 MPN per 100 mL during RS1 to 1.0×10^6 MPN per 100 mL during RS3, there were no significant differences within treatments. Overall losses from DCS (3.1×10^2 MPN) were greatest and significantly greater than LS, ADIRE and the study control. ADUK losses (1.7×10^2 MPN) were not statistically different from

DCS, but they were significantly greater than the control ($p=0.009$). The highest median count of TC and FC measured in LS biosolid-amended plots was 5.6×10^5 and 1.5×10^1 MPN per 100 mL, respectively. The highest median loss of TC for DCS-amended plots was 1.5×10^5 MPN per 100 mL.

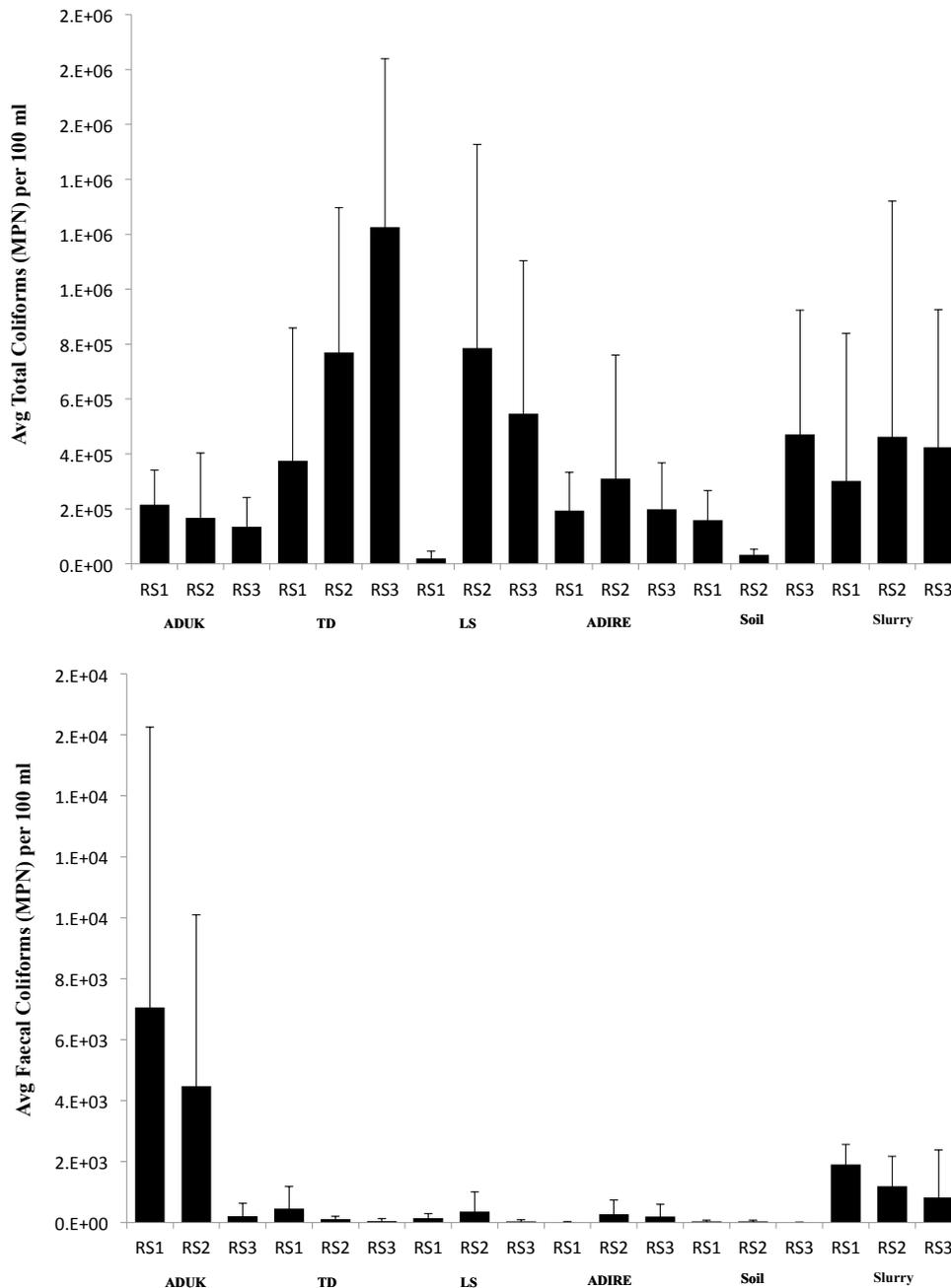


Figure 4.5. Total coliforms (top) and faecal coliforms (bottom) in the runoff per 100 mL over three successive rainfall events at 24 hours (RS1), 48 hours (RS2) and 360 hours (RS3) after application to grassland (standard deviations error bars).

4.11.4 Triclosan and triclocarban losses in surface runoff

The surface runoff concentrations of TCS and TCC were below the LOD in all cases, with the exception of TD biosolids at 360 hours ($0.01 \mu\text{g L}^{-1}$) and LS biosolids ($0.02 \mu\text{g L}^{-1}$) one day after application (Table 4.1). These TCS and TCC concentrations in the surface runoff were lower than values observed in similar studies and below the concentrations at which biota are considered to probably be or are known to be potentially impacted.

4.12 Discussion

4.12.1 Incidental nutrient losses

With the exception of LS biosolids, FWMCs of TP and DRP across all treatments were significantly higher than the study control and, in some cases, were in breach of maximum admissible concentrations for surface water. The volumetric water content of all study micro-plots was approximately 40% and the runoff ratio (the volume of runoff as a percentage of the volume of water applied

Table 4.1. Concentrations of triclosan and triclocarban in applied biosolids to field plots (“Influent”) and average concentrations of triclosan and triclocarban in surface runoff ($\mu\text{g L}^{-1}$) from field plots. LOD=0.09 $\mu\text{g L}^{-1}$ (TCS) and LOD=0.006 $\mu\text{g L}^{-1}$ (TCC) in this study

	Triclosan				Triclocarban			
	Influent	24 hour	48 hour	360 hour	Influent	24 hour	48 hour	360 hour
TD	4.9	<LOD	<LOD	<LOD	0.05	<LOD	<LOD	0.01
LS		<LOD	<LOD	<LOD		0.02	<LOD	<LOD
ADIRE	0.27	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

to each micro-plot) was broadly similar across treatments (data not shown). Therefore, the nutrient load from each micro-plot was proportional to the FWMCs.

The FWMCs of TP and TN generally decreased across successive rainfall events. This trend was similar to several studies that have examined runoff of nutrients resulting from the land application of different types of biosolids and DCS (Rostagno and Sosebee, 2001; Penn and Sims, 2002; Ojeda *et al.*, 2006; Eldridge *et al.*, 2009; Lucid *et al.*, 2014). The DRP losses measured in the current study were proportional to the water-extractable phosphorus (WEP) of the biosolids. Several studies have shown that WEP is an effective quantitative indicator of dissolved P losses from surface applied biosolids (Kleinman *et al.*, 2002, 2007; Elliot *et al.*, 2005). Thermally dried and ADIRE biosolids, which also had high WEPs, had the highest losses of dissolved P from their respective plots.

All biosolids treatments had elevated FWMCs of $\text{NH}_4\text{-N}$ in runoff compared to the study control across all rainfall simulations, whereas the study control and biosolid-amended plots had the same $\text{NO}_3\text{-N}$ concentrations. Ammonium can be volatilised (or rapidly mobilised by runoff and leaching) after OM spreading (Quilbé *et al.*, 2005). ADUK biosolids, which had the highest initial $\text{NH}_4\text{-N}$ concentration of the biosolids at the time of application ($3846 \text{ mg kg}^{-1} \text{ DM}$; Peyton *et al.*, 2016), also had the highest FWMC of $\text{NH}_4\text{-N}$ in runoff compared to biosolids treatments during RS1. Similar trends were noted for the ADIRE and LS biosolids. However, the initial concentration of $\text{NH}_4\text{-N}$ in TD biosolids before application (573 mg kg^{-1}) was lower than the ADIRE biosolids (3428 mg kg^{-1}), but had similar losses of $\text{NH}_4\text{-N}$ in surface runoff during RS1. These types of anomalies may be due to the consistency of the biosolids, which means that different types of biosolids will have varying surface area exposure to rainfall. Therefore, TD biosolids could possibly be more

easily diluted and transported in the runoff compared to the ADIRE, ADUK and LS biosolids, due to their finer particle granulated consistency. This is also the reason for the high proportion of runoff measured for the DCS; it had the highest FWMC of $\text{NH}_4\text{-N}$ and DRP. A possible reason for this is that the DCS had a DM composition of 8% and was highly mobile following an episodic rainfall event. This study showed that biosolids, although having a higher DM than DCS, are not as easily mobilised.

4.12.2 Incidental metal losses

The concentrations of metals, excluding Cu for LS biosolids, in runoff were below surface water standards intended for human consumption (S.L. 549.21, 2002). Similar results have been reported for several runoff studies using different types of biosolids at higher application rates than the current study (Dowdy *et al.*, 1991; Joshua *et al.*, 1998; Eldridge *et al.*, 2009; Lucid *et al.*, 2013). This shows that the codes of good practice for the use of biosolids in agriculture (Fehily Timoney and Company, 1999) are appropriate in limiting metal application and, therefore, losses to water bodies. The metal content in the biosolids was not the limiting factor for the spreading rate and the soil metal content was also below maximum permissible guidelines (Fehily Timoney and Company, 1999). The soil pH and clay content were within the recommended guidelines set out in the code of good practice (Fehily Timoney and Company, 1999).

While there was generally low FWMC of metals across all rainfall simulations, the LS biosolid-amended plots released the highest quantity of Cu, Ni and Zn compared to other plots. One possible explanation for this is that Cu, Ni and Zn are more soluble metals (Joshua *et al.*, 1998), and as LS biosolids consist of larger sized particles of a more compact consistency, time to runoff increased (results not shown). This gave these metals more contact time to dissolve and to subsequently be

released compared to the other biosolids treatments. Metal concentration was low in DCS in comparison to the biosolids before application and, as a result, did not cause excessive losses of metals in runoff. However, the FWMCs of Cd and Cr in DCS-amended plots were higher than any of the biosolids plots, with peak concentrations of $1.68 \mu\text{gL}^{-1}$ during RS3 for Cd and $3.89 \mu\text{gL}^{-1}$ during RS1 for Cr.

4.12.3 *Incidental triclosan and triclocarban losses*

The low concentrations of TCS and TCC in surface runoff may have been a function of the low TCS and TCC concentrations in the biosolids applied to land relative to similar studies, but were probably either due to their degradation or transformation to other compounds or due to the soil characteristics at the study site. This suggests that TCS and TCC may build up in the soil over continuous applications and may be incorporated into crop biomass (Mathews *et al.*, 2014). The relationship between persistence of PPCPs and the composition and physico-chemical properties of soil is well established in the literature (Verlicchi and Zambello, 2015). As reported in other studies (e.g. Wu *et al.*, 2009), the high soil OM content in the micro-plots of the current study (8.1–9.0%) may have adsorbed some of the TCS and TCC.

4.12.4 *Incidental losses of indicator microorganisms*

Understanding the environmental persistence and fate of the introduction of enteric microorganisms following land application of biosolids and organic amendments is necessary, as it provides a sound scientific basis for management practices designed to mitigate the potential microbiological health risks associated with spreading on agricultural land (Lang *et al.*, 2007). The risk associated with biosolid-derived microorganisms and other organic-amendment microorganisms is largely determined by their ability to survive and maintain viability in the soil environment after land spreading. In general, enteric pathogens are poorly adapted for survival in a soil environment and pathogens that are land applied from biosolids are influenced by climatic and agronomic variables (Lang *et al.*, 2003). Others have reported the persistence of enteric microorganisms in soils (Brennan *et al.* 2010). When biosolids are incorporated into the soil, microorganism survival is affected by factors such

as pH, OM, soil texture, temperature, moisture content and competition with other microorganisms (Lang *et al.*, 2007). These factors were reviewed by Erickson *et al.* (2014). However, when biosolids are surface applied, as in the current study, desiccation and UV light are the key factors in the decay of pathogens (Lu *et al.*, 2012). Desiccation of pathogens is influenced by the soil and biosolids moisture content. In the current study, soil moisture remained constant at approximately 40%, which was unlikely to affect pathogen survival or regrowth. However, as the rainfall simulator provided moisture to the biosolids, there may have been regrowth of the FC in the ADIRE and LS biosolids between RS1 and RS2. Similar FC regrowth in AD biosolids was also reported by Zaleski *et al.* (2005). All TC and FC in biosolids had decayed by RS3, which was most likely due to the desiccation of microorganisms rather than the influence of UV, as all plots were covered by the rainout shelter, which prevented natural rainfall between RS2 and RS3.

ADUK biosolids had significantly higher concentrations of FC in runoff during RS1 and RS2 compared to other treatments. At the start of the experiment, the ADUK biosolids were above the recommended standards of $1 \times 10^3 \text{MPNg}^{-1}$ (Fehily Timoney and Company, 1999), and, as a result, were equivalent to Class B microbial matter under the USEPA Part 503 Regulations (USEPA, 1993), which allows detectable levels of FC up to $2 \times 10^6 \text{MPNg}^{-1} \text{DS}$. All the Irish biosolids were some 10-fold below the Class A Irish standard (Peyton *et al.*, 2016).

It is important to evaluate the risks arising from the application of biosolids to land in relation to other common agricultural practices, such as the application of animal waste on land (Vinten *et al.*, 2004), which is commonly spread as an organic fertiliser. Hubbs (2002) reported that land application of DCS as a fertiliser had FC concentrations in surface runoff of up to $1.2 \times 10^5 \text{cfu}$ (colony-forming units) per 100 mL 2 days after application. Furthermore, after five rainfall events over 30 days, the mean FC concentrations in runoff, although decreasing, remained at high levels compared to the biosolids in the same study ($4.0 \times 10^3 \text{cfu}$ per 100 mL). This was also observed in the current study, as the DCS had the second highest FC during RS1 and RS2; however, it was the highest by RS3, showing that FC survive for a longer period in DCS compared to biosolids. This may result in loss of microorganisms to water bodies for a longer period following application. Moreover, Payment

et al. (2001) found that the pathogen concentration was lower in untreated sludge (3×10^2 to 6×10^2 cfug⁻¹) compared to fresh and stored cattle slurries (7.5×10^4 to 2.6×10^8 cfug⁻¹) (Hutchison *et al.*, 2004). When considered within this context, the risk of infectious diseases arising from the land application of biosolids appears to be low in magnitude. This study also did not provide buffering capacity to the runoff samples and overland flow was not sampled at delivery end of the transfer continuum; therefore, the bacterial results represent a worst case scenario.

While this and many other studies focus on the TC group as an indicator of the presence of pathogens, relying on them does have the drawback that they are a poor indicator of the presence of viruses and parasitic protozoa, which may survive for much longer periods (NHMRC, 2003).

4.13 Conclusions

The results of this plot-scale study show that there were elevated losses of nutrients, TC and FC from biosolid-amended plots compared to unamended plots.

However, nutrient and microbial losses were higher from DCS-amended plots. The metal concentrations in surface runoff of Cr, Ni, Pb and Zn were below their respective surface water limits for both biosolids and DCS, and TCS and TCC concentrations were below the limits of detection (90 ng L^{-1} for TCS, 6 ng L^{-1} for TCC). The surface runoff concentrations measured in this study represented a worst case scenario for potential losses, as further buffering (e.g. in open ditch networks with high P sequestration capacity) may be possible further down the transfer continuum. This study was conducted at a micro-plot scale, but the results should be verified at field-scale. In addition, future work should also be carried out to assess other emerging contaminants that may be present in biosolids and to assess the comparative impact of biosolids and cattle slurry on environmental levels of specific associated pathogens, such as verotoxigenic *Escherichia coli* (*E. coli*), *Cryptosporidium parvum* and *Norovirus*. Notwithstanding these caveats, these results are significant as they show that fears over elevated losses of nutrients, TCS, TCC, metals and microorganisms may be unfounded.

5 Metal Concentrations in Ryegrass Following a Single Application of Lime Stabilised, Thermally Dried and Anaerobically Digested Sludge

5.1 Overview

This chapter measures the uptake of metals by ryegrass following land application of biosolids. For more technical details on this study, the reader is referred to Healy *et al.* (2016b).

5.2 Introduction

While numerous studies have examined issues surrounding surface runoff water quality following biosolids application to land (Quilbé *et al.*, 2005; Ojeda *et al.*, 2006; Eldridge *et al.*, 2009; Lucid *et al.*, 2014) and the subsequent uptake of metals by plants (Dijkshoorn *et al.*, 1981; Antoniadis *et al.*, 2008), to our knowledge no study has examined the relative impact of the land application of various types of biosolids (originating from the same WWTP) on metal uptake by *Lolium perenne* (ryegrass), a common grass species generally used for cattle grazing. As different types of treatments are used prior to land application, such a study may inform policy on land spreading and on appropriate crop harvesting and cattle grazing exclusion times.

Regulations governing the land application of biosolids frequently place constraints on crop harvesting and cattle grazing subsequent to land application of biosolids. In Ireland, for example, no animal fodder, including kale, fodder beet or silage, may be harvested until at least 3 weeks after application of biosolids and cattle should not be turned out onto a pasture that has been fertilised with biosolids for 3 to 6 weeks after the date of application (Fehily Timoney and Company, 1999).

The aims of this study were to examine (1) if biosolids application to ryegrass at the legal rate in Ireland increases the metal content of the plant biomass; (2) if the method used to generate the biosolids results in different metal bioavailability and subsequent uptake and bioaccumulation rates in ryegrass; and (3) if the metal content of the ryegrass following the application of biosolids reduces as the ryegrass plants grow. To address these aims, biosolids were applied to ryegrass at the

legal permissible rate in Ireland and ryegrass samples were collected and tested for metal content at time intervals of up to 18 weeks from the time of application.

5.3 Materials and Methods

5.3.1 Study site and instrumentation of micro-plots

Twenty-five grassland micro-plots, each 0.9m in length and 0.4m in width (0.36m²), were isolated using continuous 2.2m-long, 100 mm-wide rigid polythene plastic strips, which were pushed to a depth of 50mm into the soil to isolate three sides of each micro-plot. A 0.6-m polypropylene plastic runoff collection channel was fitted at the end of each micro-plot to facilitate surface runoff. Micro-plots were orientated with the longest dimension in the direction of the slope.

5.3.2 Biosolids application to plots

Three types of biosolids were examined in this study: two types of AD sludge, one sourced from a WWTP in Ireland (AD) and another used in an EU-funded FP7 project (ADUK) (END-O-SLUDG, 2014), and TD and LS biosolids. With the exception of ADUK, all biosolids were sourced from the same WWTP in Ireland.

5.3.3 Rainfall event simulation and application

Legislation governing the application of any type of organic or inorganic waste in Ireland states that there should be a period of 48 hours between the land application and the first rainfall event (S.I. 610 of 2010). As the greatest amount of organic, nutrient, metal and microbial matter is released from the soil surface in rainfall events close to the time of waste application, an Amsterdam drip-type rainfall simulator (as discussed in Chapter 4) was used in this experiment. This way the rainfall events, intensity and durations could be controlled for the first 360 hours after biosolids application.

The five treatments (four biosolids and one soil-only study control) used in this study were assigned to 25 micro-plots by dividing the plots in five blocks (each block containing five micro-plots on which each of the five treatments were examined). Biosolids application to the micro-plots commenced in January 2014 (winter time in Ireland). The biosolids were applied to each micro-plot at a rate of 40kg P ha^{-1} ($0.04\text{ tonne P ha}^{-1}$) and the rate of application was governed by the P content of the biosolids and the P concentration (agronomic soil P index) of the soil.

Prior to application, grass on all micro-plots was cut uniformly to 50mm using plastic hand shears, 48 hours before the first rainfall simulation. Biosolids were applied to the surface of each micro-plot by hand and to ensure even distribution, each micro-plot was divided into four quadrants (each 0.09m^2 in area) and a proportionate amount of biosolids was applied in each quadrant. The biosolids were then left on the soil for 24 hours before the first rainfall simulation. The first rainfall simulation event occurred 24 hours after the application of biosolids, which was less than the 48 hours legal limit; however, this allowed a worst case surface runoff scenario to be evaluated. The second rainfall event took place 2 days (48 hours) after initial biosolids application, which was representative of current legislation, and the third took place 15 days (360 hours) after initial application. During the period between these three rainfall applications, a “rainout” shelter was used (Hoekstra *et al.*, 2014). A rainout shelter is a large, plastic shelter on a steel frame that protects the soil from direct rainfall, while allowing air to circulate over the soil surface. After 360 hours (the time of the third rainfall simulation), the micro-plots were exposed to normal weather conditions.

5.3.4 Collection of grass samples

Three grass samples, each comprising a composite of six to eight blades or shoots of ryegrass, were cut at the soil surface in each of the 25 micro-plots immediately prior to the second (at 48 hours after application) and third (at 360 hours after application) rainfall simulations, and finally at a time varying between 55 and 130 days from the time of the application of biosolids. This variation was due to the staggered nature of the initial application of biosolids to the micro-plots and the fact that the final collection of grass blades occurred on the same day in June 2014. Nitrile gloves were

used to collect the grass samples and the gloves were changed between plots to avoid cross-contamination. Each grass sample was thoroughly washed with ultra-pure water ($18.3\text{ m}\Omega$, Milli-Q Element System, Merck Millipore, Cork, Ireland) to remove any particulate or adhered material, before being placed into separate, clean, sealed bags and frozen at -20°C , after which they were transported to the laboratory.

5.3.5 Preparation and analysis of ryegrass samples

The ryegrass was freeze-dried at -52°C (Freezone 12, Labconco, Kansas City, MO, USA). Approximately 0.1g of the sample was digested with an optimised microwave digestion procedure (Anton Paar Multiwave 3000, Graz, Austria) using 3L of trace metal grade 67–69% HNO_3 (ROMIL-SpA™, USA) and 3L of 30% H_2O_2 (TraceSELECT® Ultra $\geq 30\%$, SIGMA-ALDRICH, USA) (Morrison *et al.*, 2008). The digested samples were transferred into trace metal-free centrifuge tubes (Labcon, Petaluma, CA, USA). The determination of Cr, Cu, Pb, Ni, Zn, Cd, B (boron), Co (cobalt), Fe, Mn (manganese), Mo, Al (aluminium), V (vanadium), As, Nb (niobium), Sb, Ba (barium), and W (tungsten) in the ryegrass digests were performed on a PerkinElmer ELAN DRCe (Perkin Elmer, Waltham, USA) inductively coupled plasma mass spectrometer using both standard and dynamic reaction cell mode (Staunton *et al.*, 2014; Ratcliff *et al.*, 2016) in a class1000 (ISO class 6) clean room. A CRM of ryegrass (ERM® – CD281 RYE GRASS, European Commission, Joint Research Centre, Institute for Reference Materials and Measurements, Belgium) was used with method blanks and duplicate samples for method validation and quality assurance purposes.

5.3.6 Statistical analysis

The data were assessed using analysis of variance (ANOVA). Minitab statistical software (Pennsylvania, USA) was used for the analysis, with a two-sided confidence interval level set at 95%. Variances were not assumed to be equal across treatments and control, and consequently the Welch’s ANOVA test was utilised in the Minitab software. The same approach was used to test the statistical significance of the observed reduction in metal content with test program duration across all treatments and control.

5.4 Results and Discussion

The average concentrations of metals that are subject to legislation in Ireland in the ryegrass for each treatment over the duration of the study are displayed in Figure 5.1. The reader is referred to Healy *et al.* (2016b) for graphs of unlegislated metal concentrations. For most metals examined, there was no statistically significant difference between the biosolids treatments and the study control except for Cu (ADUK biosolids; from 360 hours onwards) and Ni (LS biosolids; at 360 hours).

As the application rate of the biosolids to each micro-plot was determined by their P content, and not by their metal content, application of metals was different between treatments. As a result, for example, the application rate of Cu was much higher for LS and AD biosolid-amended micro-plots (119 and 183 mg per micro-plot, respectively) than the other micro-plots (70 mg for ADUK-amended micro-plots and 49 mg for TD-amended micro-plots). Over the 18-week duration of the study, and with the exception of Ni, Cu and Al,

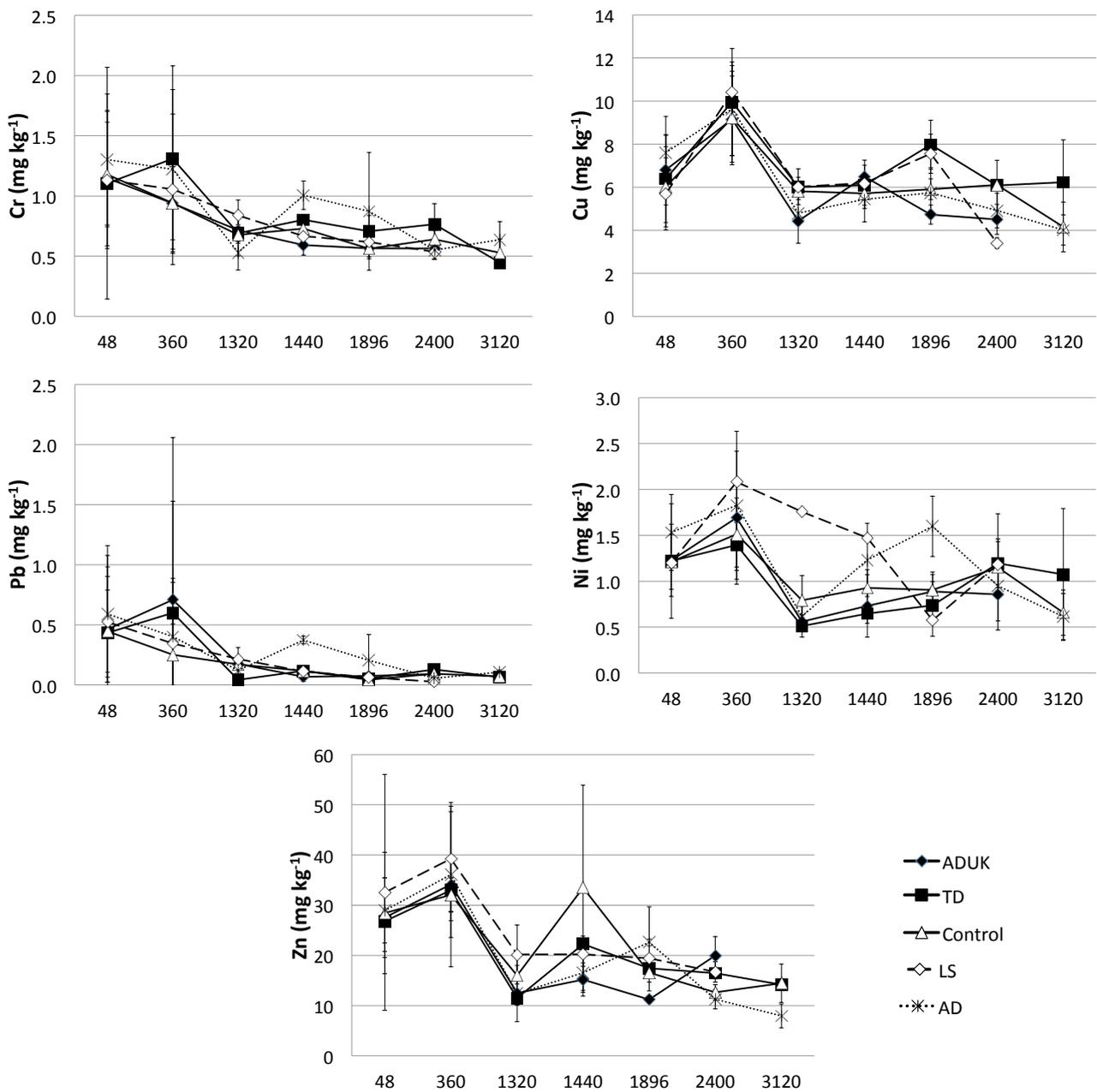


Figure 5.1. Measured metal content of legislated metals in Ireland (Ni, Zn, Cr, Pb, Cu) in ryegrass up to 3120 hours (130 days) after a single application of either ADUK or AD originating from Ireland (AD), LS or TD biosolids. Cadmium is not displayed as it was below the LOD. Control refers to ryegrass that did not receive any biosolids application.

there was no statistically significant difference in metal uptake by the ryegrass between treatments.

In general, the element concentration of the ryegrass followed the temporal fluctuation of the study control. On the basis of these findings, biosolids application at the legal rate in Ireland (which is currently based on the metal content of biosolids and the available P content of the soil) did not increase the metal content of the plant biomass. Moreover, the method used to generate the biosolids (AD, LS, TD) did not result in different metal bioavailability and subsequent uptake and bioaccumulation rates in ryegrass. While the maximum average concentrations of As, Cr, Fe and V were at, or above, the ranges of trace elements in Irish pastures, no measured metals were within or above the concentration at which phytotoxicity of ryegrass occurs. The metals were also below the maximum levels specified for animal feeds (EU, 2002).

There was a statistically significant downwards trend with time from around 360 hours onwards in the concentration of all metals in all treatments, including the study control. Concentration of some metals such as As, Nb and Sb, reduced from low initial concentrations (average initial concentrations for each were 0.2, 0.07 and 0.01 mg kg⁻¹, respectively) to below the LOD of the instrumental technique over the duration of the study, indicating the impact of metal dilution by shoot growth. There was a residual metal concentration in

the ryegrass (prior to biosolids application) at the start of the growing season, but this became more diluted as the growing season progressed. When the metal uptake in the biosolid-amended micro-plots were taken away from the metal uptake in the control micro-plots at each of the time intervals sampled, the metal content of the shoots reduced from the time of the first sampling (at 48 hours) through all subsequent sampling times.

5.5 Conclusions

This study found that, in general, there was no statistically significant difference in the shoot metal concentration of ryegrass cultivated on biosolid-amended plots and unamended plots when the biosolids were spread at the maximum permissible rate in Ireland. Over a period of 18 weeks after land application of biosolids, a downwards trend in the concentration of metals in the shoots of ryegrass was observed, which was attributed to a dilution effect as the ryegrass grew. On the basis of the parameters measured in this study, it would appear that the legislation governing livestock exclusion rates from land after biosolids application are overly strict. However, a short period of withdrawal (e.g. 3 weeks) seems reasonable to reduce the risk of biosolids ingestion by the animals; this is also the case with cattle slurries. Any further restrictions may be overly strict for a single application to land at compliant application rates.

6 Hazard Identification

6.1 Overview

The aim of this chapter is to identify potential chemical and biological hazards present in biosolids that are capable of causing adverse human health effects through surface water. A suite of 16 contaminants identified in the literature review were further analysed in a risk-ranking model to include a health-based risk endpoint. A probabilistic model was constructed in Microsoft Excel (incorporating @Risk 6.0) to estimate human exposure to organic contaminants that are contained within biosolids destined for land application. Probability density distributions were used to take account of uncertainty and variability in the model inputs. A database of inputs was collated from international and European peer-reviewed journals, online chemical databases (Chemfinder, CAS and, ECHA, ESIS), regulatory agency data and internet search engines

6.2 Contaminants of Concern

The contaminants analysed in this study comprise a group of organic contaminants belonging to various categories and were chosen based on the following risk factors: persistence, bioaccumulation and toxicity (PBT). The selected contaminants include: POPs [polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxin furans (PCDD/Fs) and polybrominated diphenyl ethers (PBDEs)]; PPCPs (carbamazepine, triclosan, triclocarban, propranolol and metoprolol); perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) substances; natural hormones (estrone and estradiol); surfactants [nonylphenol (NP), its short ethoxy chain precursors nonylphenol mono-(NP1EO) and di-ethoxylate (NP2EO)]; and bisphenol A (BPA).

The aforementioned contaminants show that the compounds that are expected to remain in the soil at the origin of application [Log K_{oc} (soil adsorption coefficient) > 3.5] are of exceptional concern, given the effectively longer organism exposure periods and the potential for increasing soil concentrations with repeated applications (Snyder *et al.*, 2011). Recent toxicological reports have shown that TCC has the potential to disrupt excitation–contraction coupling in skeletal and cardiac muscles in humans (Gautam *et al.*, 2014). Emerging

persistent organic pollutants, such as PFOS and PFOA, have frequently been detected in drinking water and have become a significant concern to human health at a concentration of 40 ng L⁻¹ or higher (Xiao *et al.*, 2013). The widespread use of the surfactant NP, and its short ethoxy chain precursors, NP1EO and NP2EO, has led to the detection of these contaminants in many environmental matrices such as water, sediment, air and soil (Mao *et al.*, 2012). Due to their physical–chemical characteristics, such as high hydrophobicity and low solubility, NP, NP1EO and NP2EO accumulate in the environmental compartments that are considered high in organic content, such as sewage sludge (Soares *et al.*, 2008).

6.3 Multimedia Risk Assessment Model Tools

Environmental exposure modelling has been developed in an effort to quantify human exposure to chemicals via contact with the surrounding natural environment and to evaluate the safe use of biosolids (Morais *et al.*, 2013). Biosolids risk assessment has mainly focused on risks from microbials and infectious diseases in biosolids (Cummins and Adkin, 2007; Gottschall *et al.*, 2013). However, with an increasing number of reports in the literature regarding identification of contaminants in biosolids, risk assessment models have been devised to assess the chemical fate from sewage treatment to biosolids application. The identification of emerging contaminants in biosolids has provoked academics and policymakers alike to evaluate the risks associated with land spreading of biosolids and contaminant exposure by humans through the food chain. This has spawned the development of environmental risk assessment models.

The evaluation of the removal efficiency and emission of a chemical from a WWTP requires an effective model. SimpleTreat 3.1 was developed for use under the Dutch Chemical Substances Act as a spreadsheet model for use as a tool for undertaking chemical risk assessment. SimpleTreat 3.1 is now a recommended model in the EU for environmental risk assessment. The SimpleTreat computational model is widely used to quickly calculate the relevant fate of a substance and

the exposure concentrations in the effluent, sludge and air directly surrounding the plant (van Egmond *et al.*, 2013).

The European Union System for the Evaluation of Substances (EUSES) is a decision support instrument that enables government authorities, research institutes and chemical companies to carry out rapid and efficient assessments of the general risks posed by chemical substances to people and the environment (EC, 2016). As an assessment tool to calculate the predicted environmental concentration (PEC), EUSES has been applied as the standard risk assessment model in the EU for several years. The system is based on the EU Technical Guidance Document on Risk Assessment for new notified substances, existing substances and biocides. It represents a level III-type multimedia fate model that works with numerous QSARs, regression and default parameters in order to make predictions of steady state exposure concentrations based on a minimum set of input parameters (Wind, 2004).

The Risk Assessment Identification and Ranking (RAIDAR) model is a screening level risk assessment model that brings together information on chemical partitioning, reactivity, environmental fate and transport, bioaccumulation, exposure, critical objective or effect levels, and emission rates in a coherent system for assessing risk (CCEMC, 2007). The RAIDAR and EUSES models are conceptually similar in many respects: however, there are differences in the treatment of key processes. For example, the food web bioaccumulation models in RAIDAR allow for biotransformation rate estimates to be included, whereas the default food web bioaccumulation models in EUSES do not allow for this (Arnot *et al.*, 2010).

Quantitative structure–activity relationship models are mathematical models that approximate the, often complex, link between chemical properties and biological activities of a compound (de Tillegem and Govaerts, 2007). QSAR models enable prediction of physical, chemical and biological properties of non-assessed compounds by comparing structurally and/or quantitatively similar assessed compounds based on the structure and composition of the molecule (Sanderson *et al.*, 2003). With regard to toxicity, QSARs have been successful in predicting well defined endpoints with a similar mode of action, e.g. baseline toxicity (narcosis) (Öberg and Iqbal, 2012).

The Pharmaceutical Assessment and Transport Evaluation (*PhATE*) model was developed by the Pharmaceutical Research and Manufacturers of America. This model was designed to offer a PEC of pharmaceuticals discharged into surface waters through WWTP (Anderson *et al.*, 2012). Implementation of *PhATE* provides the advantage of evaluating the potential effect on human health associated with an active pharmaceutical ingredient (API) concentration that is below detection limits in surface waters. Predicted environmental concentrations generated by *PhATE* are based on average per capita human use of an API in the US. This assumption would cause *PhATE* to underestimate exposure in areas where per capita use is higher than the national average (Schwab *et al.*, 2005).

6.4 Probabilistic Model

A probabilistic model was constructed to estimate and rank human exposure to organic contaminants that are contained within biosolids destined for land application. The model includes four major compartments: concentration in soil (PEC_{soil}), surface runoff (PEC_{runoff}), groundwater ($PEC_{\text{groundwater}}$), and final human risk [consisting of the level of chemical intake or human exposure (HE) and the chemical intake toxicity ratio (RR)]. The risk of organic contaminants leaching into surface water, groundwater or lakes from land spreading of biosolids can be estimated by the PEC_{soil} , PEC_{runoff} and $PEC_{\text{groundwater}}$ model adopted from Trevisan *et al.* (2009), which was designed for the PECs of pesticides in ground and surface water. The model has been modified for use in Irish conditions. Toxicological indicator LC_{50} (median lethal concentration) was used to assess the effect of the contaminants on human health. The 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 it was run for 10,000 iterations.

6.5 Results and Discussion

The results of the PEC_{soil} indicate that from the contaminants analysed, the contaminants NP, NP1EO and NP2EO ranked the highest with mean PEC_{soil} values of 5.69 mg kg^{-1} , 1.72 mg kg^{-1} and 1.44 mg kg^{-1} (95th percentiles 13.69 mg kg^{-1} , 5.14 mg kg^{-1} and 2.88 mg kg^{-1} , respectively). This was attributed to the initial high concentrations of NP, NP1EO and NP2EO in the biosolids

(mean values 103.8, 83.3 and 25.7 mg kg⁻¹, respectively), with NP and NP1EO exceeding the critical levels of 50 mg kg⁻¹ DM as suggested by the EU Working Document on Sludge 3rd Draft (Ömeroğlu *et al.*, 2015). NPs are also restricted under the 2003/53/EC Directive, which restricts the use and marketing of products and product formulations that contain more than 0.1% NP or NPE in Europe (EC, 2002).

The results for PEC_{runoff} revealed that the highest values obtained were from NP, NP1EO and NP2EO with mean values of 1.17 × 10⁻² µg L⁻¹, 4.13 × 10⁻³ µg L⁻¹ and 3.36 × 10⁻³ µg L⁻¹ (95th percentiles 4.08 × 10⁻² µg L⁻¹, 1.36 × 10⁻² µg L⁻¹ and 9.99 × 10⁻³ µg L⁻¹, respectively). NP, NP1EO and NP2EO ranked highest for PEC_{groundwater} with mean values of 2.22 × 10⁻¹ µg L⁻¹, 1.84 × 10⁻¹ µg L⁻¹ and 9.11 × 10⁻² µg L⁻¹ (95th percentiles 1.27 µg L⁻¹, 5.5 × 10⁻¹ µg L⁻¹ and 3.8 × 10⁻¹ µg L⁻¹, respectively). The contaminants that follow NP, NP1EO and NP2EO in the risk ranking are the microbials, TCC and TCS. These microbials have only recently been regulated by the EU. Recent toxicological reports have shown that TCC has the potential to disrupt excitation–contraction coupling in skeletal and cardiac muscles in humans (Gautam *et al.*, 2014). TCC has been linked to endocrine disruption by amplifying androgen receptor-mediated activity in rats; furthermore, TCC has also caused methemoglobinemia in humans who were exposed to boiled water containing 1.1% TCC, which formed a primary aromatic

amine (Palenske, 2009). Recent reports have revealed that TCS is capable of interfering with various hormones as a weak endocrine disruptor in multiple species and it can also impair muscle contraction (Yeuh *et al.*, 2014). Therefore, emerging contaminants such as TCS and TCC may rank higher as contaminants such as NP are phased out over time.

The results of this study suggest that the spreading of biosolids on agricultural land can result in moderate concentrations in the environment. Although the predicted concentrations in runoff and groundwater are low, it is imperative to note that these contaminants are continuously released into the environment. The top ranking contaminants for PEC_{runoff} (NP, NP1EO and NP2EO) are below the Water Framework Directive (WFD) threshold value (0.3 µg L⁻¹) for annual average and the maximum allowable concentrations (2 µg L⁻¹), for surface waters (Lepom *et al.*, 2009).

Human exposure through consumption of drinking water (combined with body weight and PEC_{runoff}) showed that the contaminants that ranked the highest for adult and child consumption were NP, NP1EO and NP2EO, with mean values of 8.5 × 10⁻⁵, 3.0 × 10⁻⁵ and 2.8 × 10⁻⁵ µg kg⁻¹ bw d⁻¹, respectively, for adult consumption, and 9.7 × 10⁻⁵, 3.4 × 10⁻⁵ and 2.2 × 10⁻⁵ µg kg⁻¹ bw d⁻¹, respectively, for child consumption. HE and PEC_{groundwater} showed that NP, NP1EO, and NP2EO ranked the highest

Table 6.1. Ranking according to human health-based risk. Results are based on mean PEC_{runoff} and PEC_{groundwater} combined with LC₅₀ (RR)

Contaminant	(RR) PEC _{runoff}	Rank	(RR) PEC _{groundwater}	Rank
NP	1.10 × 10 ⁻⁴	1	2.40 × 10 ⁻³	1
NP1EO	3.94 × 10 ⁻⁵	2	1.64 × 10 ⁻³	2
NP2EO	1.35 × 10 ⁻⁵	3	3.66 × 10 ⁻⁴	3
TCC	1.20 × 10 ⁻⁵	4	1.80 × 10 ⁻⁴	4
TCS	4.45 × 10 ⁻⁶	5	7.40 × 10 ⁻⁶	5
PCBs	4.45 × 10 ⁻⁶	6	1.26 × 10 ⁻⁶	6
BPA	2.92 × 10 ⁻⁸	7	1.77 × 10 ⁻⁷	7
PBDE	7.42 × 10 ⁻⁹	8	9.68 × 10 ⁻⁸	8
Carbamazepine	1.48 × 10 ⁻⁹	9	3.79 × 10 ⁻⁸	9
17β Estradiol	1.29 × 10 ⁻⁹	10	2.40 × 10 ⁻¹⁴	15
Estrone	1.61 × 10 ⁻¹⁰	11	1.21 × 10 ⁻¹⁰	11
PFOS	1.36 × 10 ⁻¹⁰	12	1.76 × 10 ⁻⁹	10
PFOA	1.23 × 10 ⁻¹¹	13	5.65 × 10 ⁻¹⁴	14
PCDD/Fs	6.10 × 10 ⁻¹²	14	1.56 × 10 ⁻¹⁶	16
Propranolol	3.19 × 10 ⁻¹²	15	6.95 × 10 ⁻¹²	12
Metoprolol	2.11 × 10 ⁻¹³	16	4.44 × 10 ⁻¹²	13

for adult and child consumption, with mean values of 1.5×10^{-3} , 1.4×10^{-3} and $7.2 \times 10^{-4} \mu\text{g kg}^{-1} \text{bw d}^{-1}$, respectively, for adult consumption, and 2.2×10^{-3} , 1.6×10^{-3} and $5.1 \times 10^{-4} \mu\text{g kg}^{-1} \text{bw d}^{-1}$, respectively, for child consumption. The daily intake values of NP are much lower than the tolerable daily intake value of $5 \mu\text{g kg}^{-1} \text{bw d}^{-1}$ of NP proposed by the Danish Institute of Safety and Toxicity (Ademollo *et al.*, 2008). No European tolerable daily intake value has yet been established.

According to the LC_{50} risk-ranking results for human exposure (LC_{50} RR; PEC_{runoff}), the top ranked contaminants considered to be a risk to human health include NP, NP1EO and NP2EO, with mean LC_{50} RR values of 1.10×10^{-4} , 3.94×10^{-5} and 1.35×10^{-5} , respectively. Similarly, the results of the $PEC_{\text{groundwater}}$ also included NP, NP1EO and NP2EO. Mean RR values for $PEC_{\text{groundwater}}$ were 2.40×10^{-3} , 1.64×10^{-3} and 3.66×10^{-4} for NP1EO, NP and triclocarban, respectively (Table 6.1).

6.6 Sensitivity Analysis

A sensitivity analysis based on rank order correlation coefficient was conducted for NP as this contaminant ranked the highest across all of the environmental compartments. Results revealed that the Koc and soil organic carbon (SOC) were the most important parameters (correlation values of -0.89 and -0.30 , respectively) that affected the variance in model predictions (Figure 6.1). This highlights the importance of the soil and site conditions [SOC, DT_{50} -soil (degradation time for 50% of

a compound)] that influence the runoff and leaching of the contaminants through the soil matrix and the importance of contaminant properties (Koc) in influencing risk estimates. Furthermore, the sensitivity analysis results also showed that precipitation amount and water table level are other parameters of importance in the human health risk model.

6.7 Conclusion

A probabilistic model was developed to rank “classic” and emerging contaminants according to PEC_{soil} , PEC_{runoff} , $PEC_{\text{groundwater}}$ and resulting human health risk (RR). The highest rank obtained for PEC_{soil} , PEC_{runoff} and $PEC_{\text{groundwater}}$ was the surfactant NP. To compare toxicity endpoints, the LC_{50} was combined with PEC_{runoff} and $PEC_{\text{groundwater}}$. The LC_{50} combined with PEC_{runoff} and $PEC_{\text{groundwater}}$ revealed that NP and NP1EO ranked the highest. A sensitivity analysis revealed that Koc and SOC were the most important parameters that affected model variance. This indicates that the type of soil that biosolids are spread on and its chemical properties are critical in controlling human health risk. Although the NPs ranked highest in this study, it is important to note that these contaminants have either been restricted or banned in Europe since 2005; therefore, these contaminants will reduce in risk. However, they still persist in the environment. The contaminants that ranked lower than the NPs, such as TCC and TCS, can be considered of greater interest as these contaminants are emerging

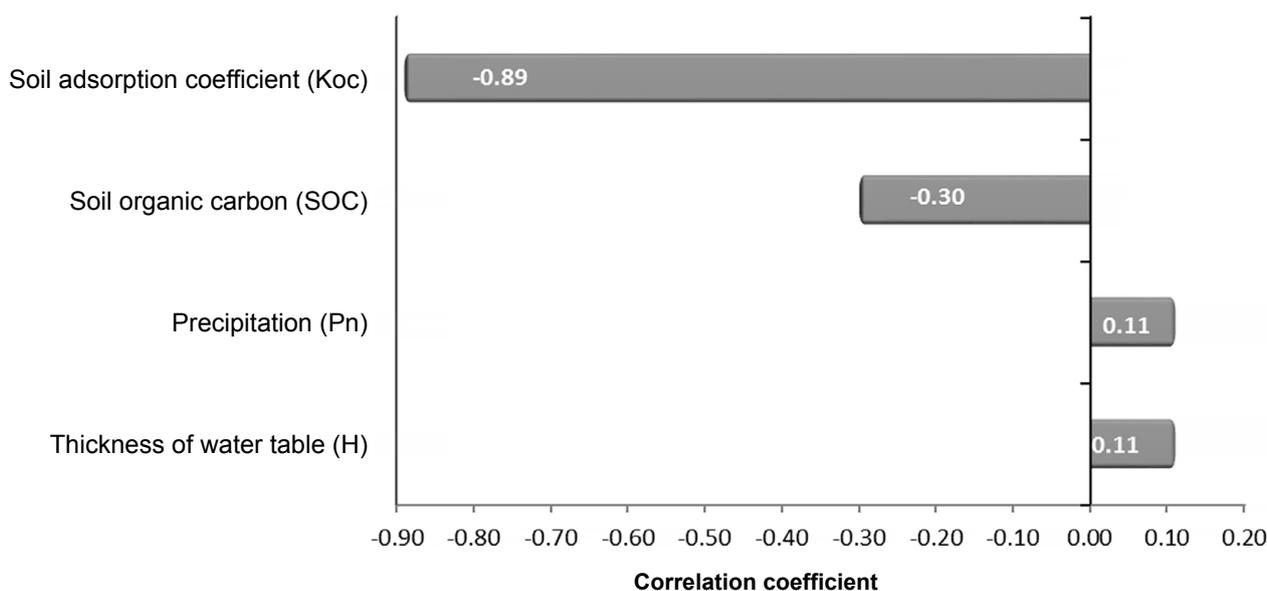


Figure 6.1. Sensitivity analysis for input parameters and the contaminant NP.

and have only recently been restricted within the EU, despite ongoing toxicological reports. The model developed in this study is of importance for risk managers as it provides a ranking of potential chemical hazards

resulting from the spreading of biosolids on agricultural land, while it also highlights some emerging contaminants that will require vigilance in the future.

7 Exposure Assessment and Characterisation for Metals

7.1 Overview

An exposure assessment model was developed for metals. The model considered exposure to metals through surface water that was abstracted for drinking; it takes account of surface runoff amount, dilution and water treatment effects. Data from the field trials (Chapter 3) were used to model the initial level of metals in surface runoff.

7.2 Metal Accumulation in Soil

Long-term application of biosolids to agricultural land has led to concerns regarding the potential accumulation of metals in soil, the subsequent runoff into surface waters and the potential risk to human health through drinking water consumption. Previous studies have shown that overland transport from fields amended with biosolids can impact the quality of surface waters through runoff of heavy metals (Topp *et al.*, 2008). The long-term use of biosolids can cause heavy metal accumulation in the soil (Elkhatib and Moharem, 2015). Furthermore, accumulation of these metals in the soils can have toxic effects on microorganisms and plants, and ultimately also on animals and human health via the food chain (Wang *et al.*, 2005). Severe effects include reduced growth and development, cancer, organ damage, nervous system damage and, in extreme cases, death (Akpor and Muchie, 2010).

7.3 Quantitative Drinking Water Treatment Model

A quantitative drinking water treatment model that is capable of predicting probable human exposure and resulting risk from six metals (Cu, Cd, Cr, Pb, Ni and Zn) present in treated drinking water was developed. The model was created in Microsoft Excel 2010 with the add-on package @Risk. Data from peer-reviewed scientific literature was incorporated at various steps of the drinking water treatment (i.e. coagulation, flocculation, sedimentation and disinfection). Distributions were used to account for uncertainty in the data. The data for biosolids runoff post-application were generated by project partners (NUI Galway, Teagasc). Four types of biosolids (ADUK, ADIRE, LS and TD) were investigated.

The mean and standard deviation were calculated for all surface runoff results and a normal distribution was assigned to account for uncertainty in the data. Most drinking water in Ireland is sourced from surface waters. When there is a lack of data, a standard dilution factor of 10 was used, as proposed by the EU Technical Guidance Document on Risk Assessment Part II (EC, 2003), and applied to the data to take account of dilution effects in the predicted environmental concentrations.

7.4 Water Treatment Effects

Three stages of drinking water treatment were used based on the Irish Environmental Protection Agency's (EPA) best practice guidelines for drinking water treatment manuals (EPA, 1995, 2002, 2011). The first stage, primary treatment, considers the screening, storage, pre-conditioning and pre-chlorination of the water. Primary treatment is typically used to screen out large objects such as sticks, stones and other debris that may restrict flow. In this instance the effect of primary treatment was deemed negligible in terms of contaminant removal.

As a worst case scenario, the model assumes a 90% probability of coagulation and flocculation operating at an optimum stable run (Copt) and a 5% probability for both sub-optimal (CS-opt) and failure (C-fail). When operating optimally, the model assumes a removal rate (metal specific). When operating sub-optimally, the model assumes a removal of 50% of the optimal removal rate and zero removal during failure events.

The filtration process in a conventional drinking water treatment plant consists of slow or rapid sand filtration. The filter run time is not only an indicator of the effectiveness of prior treatment (i.e. the ability of the coagulation and sedimentation steps to remove suspended solids), but it also plays a role in the effectiveness of the filter itself (WHO, 2004). In keeping with the EPA's filtration manual guidelines, the filtration process of rapid gravity filtration was considered in the model. As a worst case scenario the model assumes a 90% probability of filtration operating at an optimum stable run (Fopt) and a 10% probability for sub-optimal run (Fsub). When operating optimally, the model assumes a removal rate

that is metal specific. When operating sub-optimally, the model assumes a removal of 50% of the optimal removal rate.

Worldwide, chlorine is the most commonly used disinfection in drinking water treatment, although other alternatives are being increasingly introduced such as ozonation, UV irradiation, ultrasonic vibration, ultra-filtration, silver, bromide and iodine, membrane filtration and granular activated carbon. Chlorination does not remove metals (O'Connor and O'Connor, 2001) and therefore no removal distribution was assigned.

7.5 Human Exposure

The water consumption in Ireland was modelled using a log-normal distribution with a mean daily consumption of 0.564 L and a standard deviation of 0.617 L according to a survey on adult nutrition conducted by the Irish Universities Nutrition Alliance (IUNA), which was based on 1274 consumers (IUNA, 2011). A normal distribution with a mean value of 78 kg and standard deviation of 16.5 kg was used to model the variation in body weight for adults. A normal distribution with a mean value of 33 kg and standard deviation of 11.3 kg was used to model variation in body weight for children (IUNA, 2005). To evaluate the human health risk exposure, the lifetime average daily dose (LADD) (mg kg^{-1}) and the hazard quotient (HQ) were used as toxicity endpoints in the model and were metal specific. A Monte Carlo simulation technique was applied to sample from the input

distributions to create an output distribution for metal concentration in drinking water, LADD and the HQ.

7.6 Results and Discussion

The environmental fate of selected metals (Cd, Cr, Cu, Ni, Pb, Zn) was modelled from biosolids application at three different time periods, 24 hours (RS1), 48 hours (RS2) and 360 hours (RS3), to drinking water treatment and subsequent human exposure. The model resulted in several output distributions post-drinking water treatments (P_{dw}), LADDs and HQs that can be used to compare the concentration of metals that were detected in surface runoff and their potential risk to human health. The model predicted that surface runoff arising from the land spreading of LS biosolids produced the highest concentrations of Cu and Zn in drinking water. The modelled mean Cu concentration in drinking water (Figure 7.1) was highest when the surface runoff concentrations from the LS biosolids at each rainfall simulation time (24, 48 and 360 hours) were used as input into the model (mean concentration values of 2.45, 1.78 and $1.2 \mu\text{g L}^{-1}$, respectively). This was followed by Zn, which had mean concentrations of 1.25, 5.14×10^{-1} and $6.16 \times 10^{-1} \mu\text{g L}^{-1}$ for each rainfall event. All metal concentrations were below the metal threshold values of the EU and the World Health Organization (WHO, 2011a; S.I. No. 122 of 2014).

The results for the exposure assessment (LADD) show that child exposure concentrations were highest for

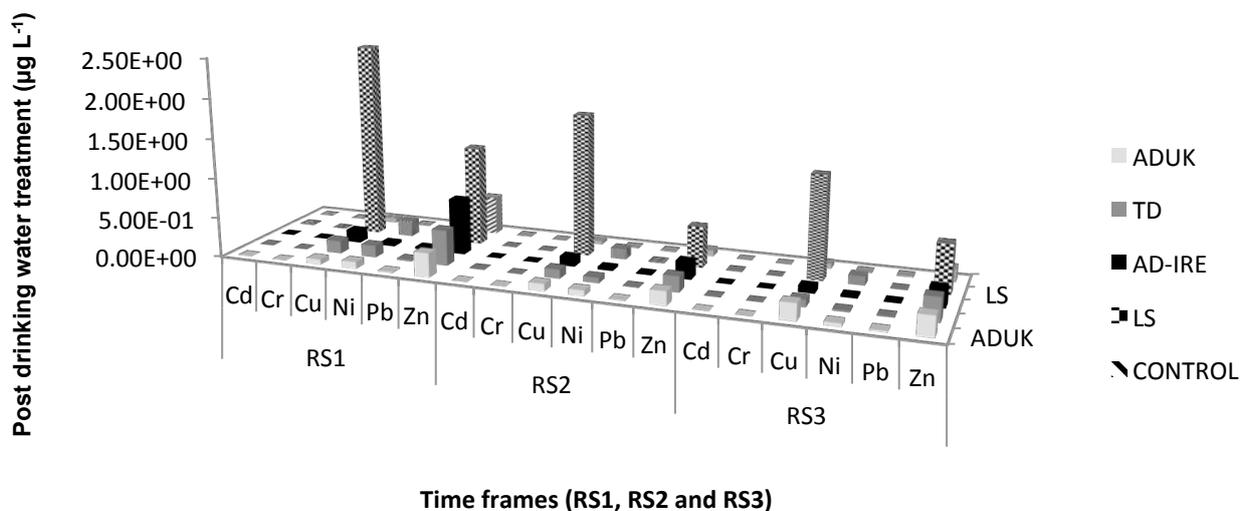


Figure 7.1. Metal concentration ($\mu\text{g L}^{-1}$) in the outflow post-drinking water treatment using surface runoff data from rainfall simulations on field scale plots occurring 24 hours (RS1), 48 hours (RS2) and 360 hours (RS3) after land application.

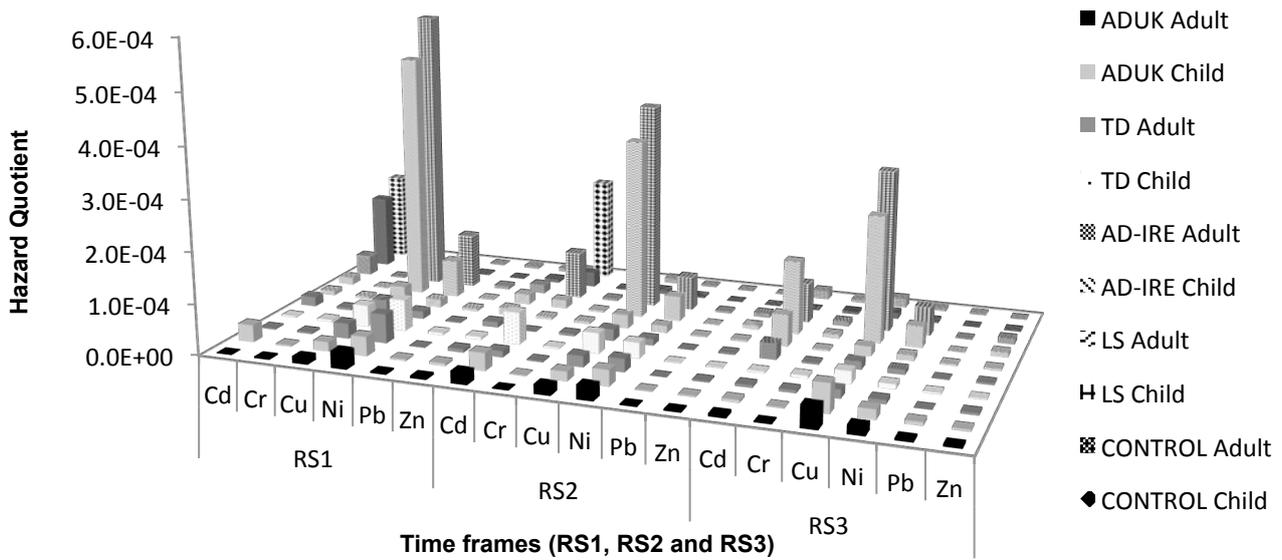


Figure 7.2. HQ for all biosolids treatments (RS1, RS2 and RS3, and both adult and child).

the metal Cu and for all three time frames RS1, RS2 and RS3 (mean values 2.07×10^{-2} , 2.07×10^{-2} and $1.18 \times 10^{-2} \mu\text{g kg}^{-1} \text{bw d}^{-1}$) and LS treatment. This was followed by adult Cu exposure concentrations (mean value 1.80×10^{-2} , 1.31×10^{-3} and $9.21 \times 10^{-3} \mu\text{g kg}^{-1} \text{bw d}^{-1}$, for all three time frames RS1, RS2 and RS3, respectively). All LADD values were below the recommended provisional maximum tolerable daily intake (PMTDI) values for Cd, Cu, Ni and Zn (7, 500, 5 and $100 \mu\text{g kg}^{-1} \text{bw d}^{-1}$, respectively) as proposed by the Joint FAO/WHO Expert Committee on Food Additives (JECFA). A PMTDI has not been established for Cr and the PMTDI for Pb was withdrawn in 2010 as it could no longer be considered health protective (WHO, 2011a).

The HQ is calculated by dividing an estimate of an exposure concentration by the threshold toxicity reference value such as a reference dose. A HQ value of <0.01 indicates no existing risk. The risk is low for HQ 0.1–1.0 and moderate for HQ 1.1–10; a HQ value of >10 indicates a high risk (Lemly, 1996). The results for the HQ showed that of all the scenarios considered, the metal Cu and the biosolids treatment LS were the highest for children for all three time frames (RS1, RS2 and RS3) with mean child HQ values of 5.59×10^{-4} , 4.09×10^{-4} and 3.18×10^{-4} , respectively, followed by adult Cu concentrations (mean adult HQ values of 4.87×10^{-4} , 3.54×10^{-4} and 2.49×10^{-4} , respectively). However, these were still below the threshold value of risk (HQ <0.01 ; no existing risk) (Figure 7.2).

7.7 Sensitivity Analysis

A sensitivity analysis based on rank order correlation was carried out to assess the ways in which the model's predictions are dependent on variability and uncertainty in the model input parameters. A sensitivity analysis was conducted for Cu corresponding with the LS biosolids treatment, as this metal and treatment had the highest concentration in both risk endpoints (LADD and HQ). Results revealed that tap water intake and filtration reduction were the most important parameters (correlation coefficient values of 0.67 and -0.54 , respectively) that affected the variance in model predictions. This highlights, of all the inputs assessed, the efficiency of the filtration system as one of the most important parameters influencing the final risk assessment. The effectiveness of the filtration is reliant on the efficiency of the coagulation/flocculation and sedimentation (correlation coefficient -0.35) stage of the process, as this stage can help to remove a majority of the metals in the water. Body weight (correlation coefficient -0.15) was also an important parameter, as when the body weight is reduced, the risk increases. The initial concentration in runoff was also an important parameter (correlation coefficient 0.12), which highlighted the importance of having the initial concentration of metals in sludge as low as possible (Figure 7.3).

7.8 Conclusions

Six metals were assessed to estimate the total concentration in surface runoff following land application of four

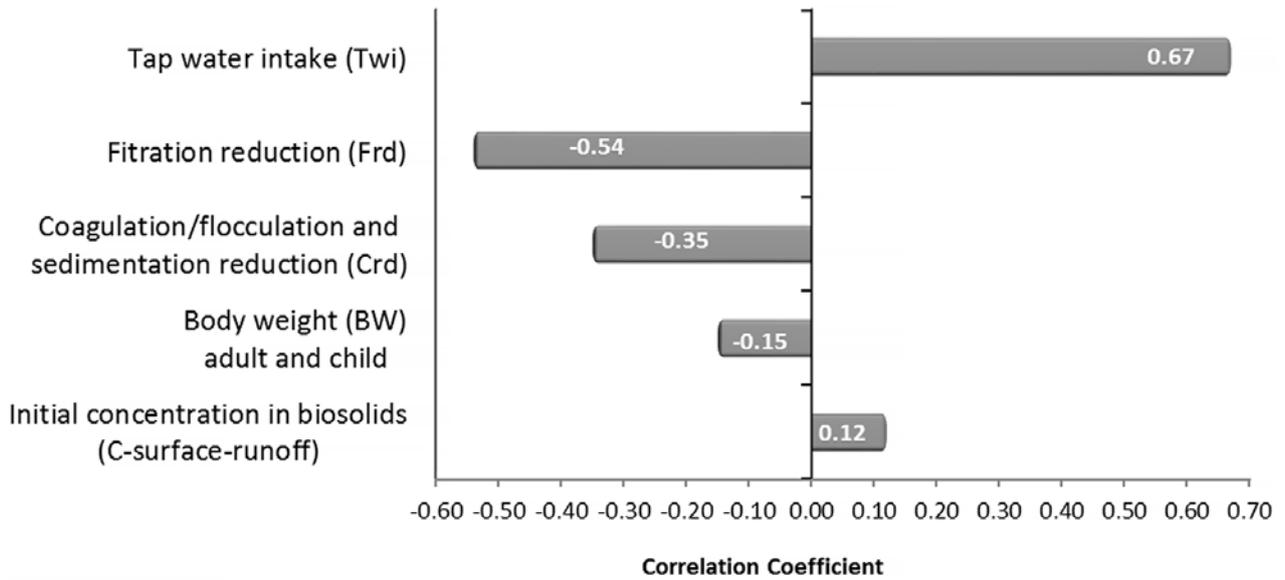


Figure 7.3. Sensitivity analysis for HQ of Cu in LS biosolids.

types of biosolids with a soil only control, following drinking water treatment and subsequent HE. A quantitative model was developed in Excel, using the @Risk add-on software, to follow the fate of all six metals. The model incorporated dilution of the runoff concentrations in a stream and it was assumed that water was extracted for drinking water treatment. Drinking water treatment included the primary, secondary and tertiary stages. The outputs of the model included metal concentration in drinking water post-treatment (P_{dw}) and exposure endpoints, LADD and the HQ. Results showed that the heavy metal Cu had the greatest concentration in drinking water post-secondary and tertiary treatments. The

results for HE (LADD) showed that Cu had the greatest concentration, especially for child consumption; however, it was still below the World Health Organization (WHO) tolerable daily dose. The results for the HQ showed that of all the scenarios considered, the metal Cu was the highest risk, particularly for children, and those corresponding to the lime treated biosolids. However, these were still below the threshold value of risk ($HQ < 0.01$: no existing risk). Under the conditions monitored, metal concentrations in the four biosolids were not considered a risk to human health. Although metal accumulation in soil was not considered in this study, it is worth considering for future research.

8 Exposure Assessment and Characterisation for *E. coli*

8.1 Faecal Coliforms and the Sewage Sludge Directive (86/278/EC)

Faecal coliforms are used as indicator organisms; high levels of these bacteria indicate the potential presence of pathogens that cause waterborne diseases (Selvaratnam and Kunberger, 2004). Faecal coliforms include *E. coli*, among other coliforms. In the EU, sewage sludge production is regulated by the Sewage Sludge Directive 86/287/EC. It does not specify limits for pathogen populations but specifies general land use and harvesting and grazing limits to provide protection against the risk of infection (Sobrados-Bernardos and Smith, 2012). A revision of the Sewage Sludge Directive (Working Document 3rd Draft) states that “the use of microbial indicators to evaluate the hygienisation of treated sludge is based on fulfilling the limits of *E. coli* to achieve a 99.9% reduction and to less than 1×10^3 cfu/g dry weight, produce a sludge containing $< 3 \times 10^3$ spores of *Clostridium perfringens*/g (dry weight) and absence of *Salmonella. spp* in 50 g (wet weight)” (EEC, 2000). Furthermore, the Working Document also states that sludge produced by conventional treatment shall achieve at least a $2 \log_{10}$ reduction of *E. coli* (Mininni *et al.*, 2014). In their Guidelines for Drinking Water Quality, the WHO have developed a risk classification to prioritise interventions, as higher levels of indicator organisms are generally indicative of greater levels of faecal contamination. The risk classification is based on the number of indicator organisms in a 100-mL sample, which includes < 1 “very low risk”, 1–10 “low risk”, 10–100 “medium risk”, > 100 “high risk” or “very high risk” (WHO, 2011b).

8.2 Quantitative Drinking Water Treatment Model (*E. coli*)

A quantitative drinking water treatment model that is capable of predicting probable human exposure and resulting risk from *E. coli* present in drinking water was developed. The model was created in Microsoft Excel 2010 with the add-on package @Risk. Data from peer-reviewed scientific literature were incorporated at various steps of the drinking water treatment (i.e. coagulation, flocculation, sedimentation and disinfection). Distributions were used to account for uncertainty in the

data. The data for biosolids runoff post-application were generated by project partners (NUI Galway, Teagasc).

The mean and standard deviation were calculated for all surface runoff levels and a log-normal distribution was assigned to account for uncertainty in the data. Most drinking water in Ireland is sourced from surface waters and therefore a standard dilution factor of 10 (EC, 2003) was applied to the data to take dilution effects into account. The model simulates the surface water die-off rate using Chick’s law first-order decay equation $N_t = N_0 e^{(-Kt)}$, where N_t is the number of organisms at time (t), N_0 is the initial number of organisms, K is the first-order inactivation constant (day^{-1}) and t is the time in the stream (day^{-1}). To account for the uncertainty in the data, a uniform distribution using K values (minimum 0.7, maximum 1.5) (Schueler, 2000) was assigned. “ K ” values in this range mean that about 90% of the bacteria present will disappear from the water within 2 to 5 days. Therefore, it was assumed that water was abstracted from the stream to a nearby water treatment plant between 0 and 5 days. To account for uncertainty, the time in stream “ t ” was fitted with a uniform distribution (minimum 0, maximum 5 days).

8.3 Water Treatment Effects

Three stages of drinking water treatment were used based on the EPA’s best practice guidelines for drinking water treatment manual (EPA, 2011). The first stage (primary treatment) considers the screening, storage, pre-conditioning and pre-chlorination of the water. The second stage (secondary treatment) considers coagulation, flocculation and sedimentation. Flocculation, sedimentation and removal of *E. coli* were reported by Pritchard *et al.* (2010); the authors compared the efficacy of aluminium sulfate to more natural coagulants and reported *E. coli* reductions of 89% using $30\text{--}50 \text{ mg L}^{-1}$ of aluminium sulfate. Bulson *et al.* (1984) reported removal rates of *E. coli* of 99.99% following a dose of 15 mg L^{-1} of aluminium sulfate. Rapid mixing for a few seconds is important once a coagulant is added to ensure uniform dispersion. Subsequent and prolonged mixing aids in the formation of flocs. The flocs settle by gravity and can be removed via filtration. Therefore, a uniform distribution was assigned to the

percentage reduction in bacteria during a stable optimal run (minimum 0.89, maximum 0.99 reduction). As a worst case scenario, the model assumes a 90% probability of coagulation/flocculation and sedimentation at an optimum stable run (Copt), a 5% probability for sub optimal (CS-opt) and a 5% probability for failure (Cfail). The model assumes a bacterial reduction at a rate of 50% of the optimal removal rate during a suboptimal run and a rate of 0% reduction during a failed run.

Rapid sand filtration provides fast and efficient removal of relatively large suspended particles. It is a relatively erudite process, which usually requires power-operated pumps, regular backwashing or cleaning and flow control of the filter outlet. In keeping with the EPA's filtration manual guidelines, the process of rapid gravity filtration was considered in the model. As a worst case scenario, the model assumes a 90% probability of filtration operating at an optimum stable run (Fopt) and a 10% probability for sub-optimal run (Fsub). When operating optimally, the model assumes a uniform log removal rate (minimum 74%, maximum 99%). When operating sub-optimally, the model assumes a removal of 50% of the optimal removal rate.

The third stage (tertiary) involves the disinfection of the effluent. Chlorination is the most popular tertiary treatment in Ireland; it has been found to remove between 97% and 99% of *E. coli* (O'Connor and O'Connor, 2001). To account for uncertainty in the data, a uniform distribution (minimum 0.97, maximum 0.99) was assigned to the disinfection process of the model.

8.4 Human Exposure

Two dose response models were considered for *E. coli* exposure [healthy population and immunocompromised (IC) populations]. The probability for illness was calculated using a negative exponential model for *E. coli* O157 as proposed by Gale (2005): $P_N = 1 - e^{-rN}$, where r is the risk of illness from ingestion of a single bacterial cell. To account for susceptibility in IC populations an “ r ” value of 0.01 was used, while for healthy populations an “ r ” value of 0.0000005 was used. As a worst case scenario, the illness model was parameterised with the assumption that the virulence of the pathogen is similar to *E. coli* O157:H7. The *E. coli* O157:H7 strain is a particular serotype of the group referred to as verocytotoxigenic *E. coli* (VTEC). VTEC produces verotoxins or shiga-like toxins that are closely related to the toxin produced by *Shigella dysenteriae* (Cassin et al., 1998).

The USEPA have proposed a drinking water limit of 10^{-4} per person per year for *Shigella* (Grant et al., 2012). The entire model was constructed in Microsoft Excel 2010 with the @Risk add-on using Monte Carlo simulation techniques and it was run for 10,000 iterations.

8.5 Results and Discussion

The environmental fate of *E. coli* was modelled from biosolids application at three different time periods, 24 hours (RS1), 48 hours (RS2) and 360 hours (RS3), to drinking water treatment and subsequent drinking water consumption. The model resulted in several output distributions that can be used to compare the coliforms that were detected in surface runoff and their potential risk to human health. Outputs from the model include viable *E. coli* consumption and the probability of illness (both for healthy and IC individuals). The results for viable *E. coli* consumed show that the biosolids treatment ADUK was highest for RS1 and RS2, with exposure mean values of 5.20×10^{-1} and 2.34×10^{-1} MPN d⁻¹, respectively (Figure 8.1). The WHO states that any treated water should have no *E. coli* detection per 100 mL. A consequence of variable susceptibility to pathogens is that exposure to drinking water of a particular quality may lead to health problems in different populations (WHO, 2011b), particularly in the very young and IC individuals.

The results for the probability of illness for healthy and IC populations show that, among IC populations, the biosolid treatment ADUK (RS1 and RS2) had the greatest probability of illness/day with mean probability values of 3.68×10^{-3} and 2.1×10^{-3} , respectively (Figure 8.2). The probability of illness over a period of a year was also analysed and this showed that the biosolids treatment ADUK combined with IC populations had the greatest probability of illness in time frames RS1 and RS2, with mean values of 2.0×10^{-1} and 1.7×10^{-1} , respectively.

8.6 Sensitivity Analysis

A sensitivity analysis based on rank order correlation was carried out to assess the ways in which the model's predictions are dependent on variability and uncertainty in the model input parameters. A sensitivity analysis was conducted for ADUK biosolids treatment as this treatment had the highest concentration in both dose-response models. Results revealed that from all the inputs considered, the time in stream, concentration in

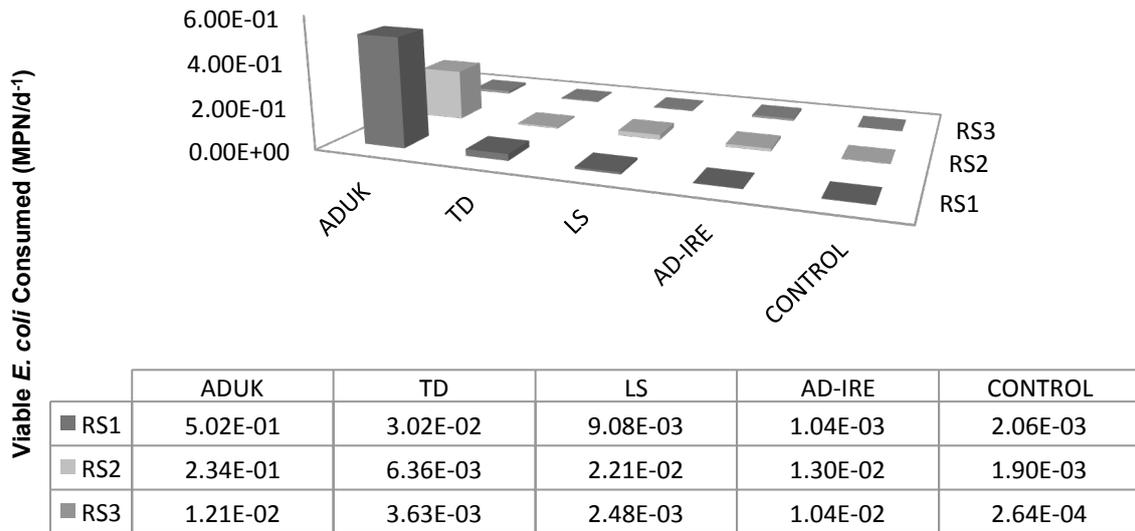


Figure 8.1. Viable *E. coli* consumed vs biosolid treatments.

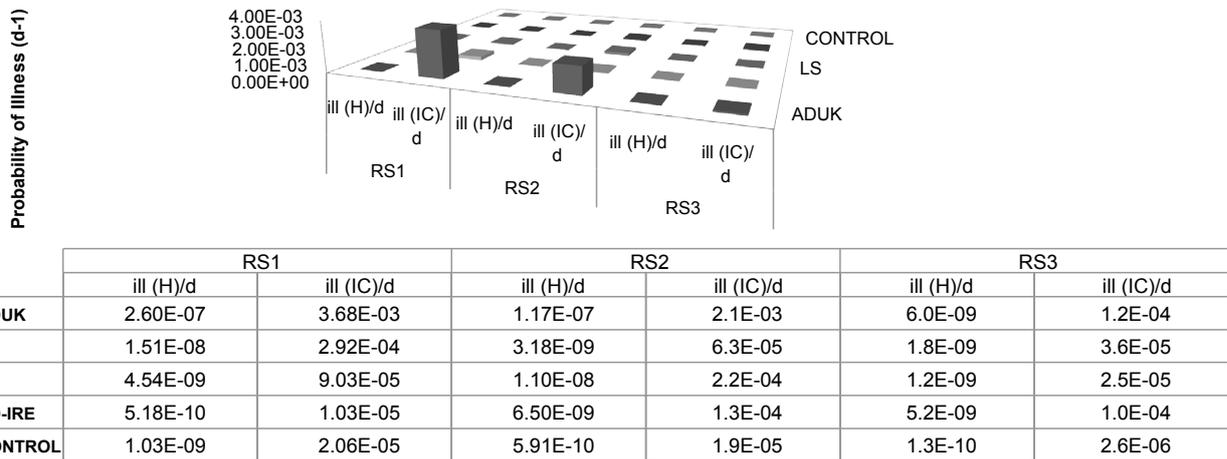


Figure 8.2. Probability of illness/day (healthy and IC).

surface runoff, tap water intake and *E. coli* inactivation were the most important parameters that affected the variance in model predictions (correlation coefficient values of -0.55, 0.42, 0.30 and -0.20, respectively) (Figure 8.3).

Ideally, water intended for human consumption should be pathogen free; however, this is an unachievable goal in practice. The risk of illness for IC individuals was greater than the acceptable level of risk of illness per year (1×10^{-4}), as set by the USEPA. It is noted in such cases that vulnerable groups may take specific precautions with respect to the intake of food and water, which, as a result, controls the vulnerable nature of this sub-population. The biosolids treatment ADUK was persistently high throughout the model [VCC and probability of illness/day (RS1 and RS2)]. Anaerobic digestion

is the most popular method of stabilisation of sewage waste in Europe. A key factor in pathogen removal is the sludge retention time, as was reported by Chen *et al.* (2012). It is unknown how long the ADUK sludge was digested for, but it may explain the consistency of *E. coli* throughout the model. The disinfection process used (i.e. chlorination) is in line with the recommended disinfection treatment commonly used in Ireland. The efficacy of chlorine in relation to inactivation of bacteria such as *E. coli* is high (between 97% and 99%). Other factors, such as die-off in stream, also reduced the colony counts by a factor of 2. Under the conditions monitored, *E. coli* concentrations in the four biosolids were not considered a risk to healthy individuals but, as always, caution is required with IC individuals.

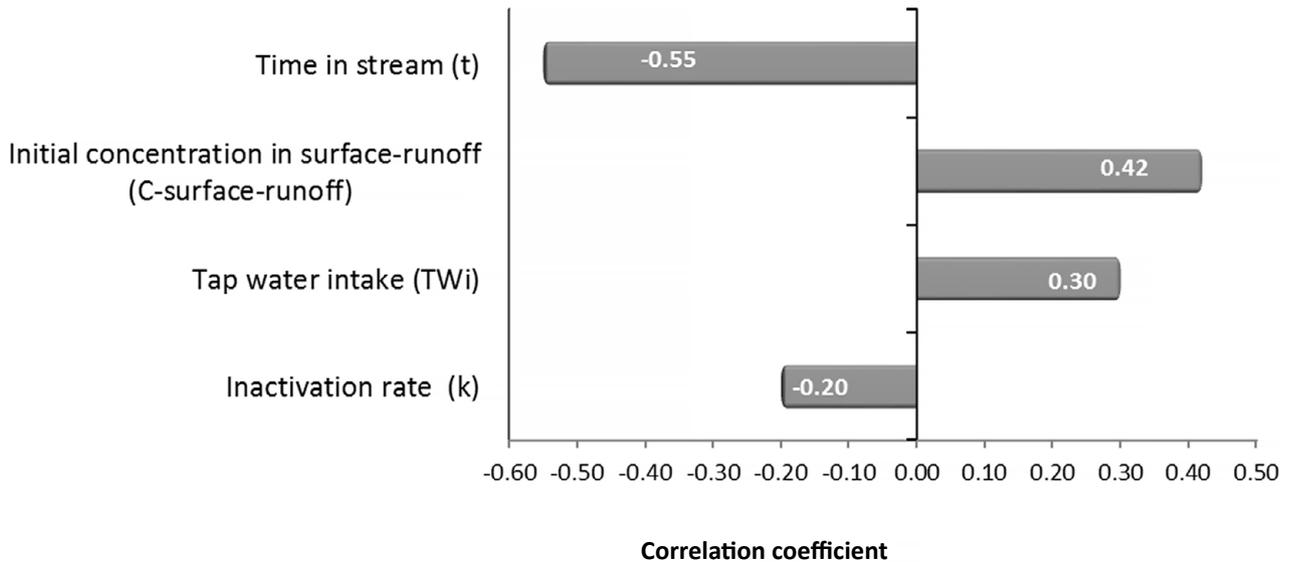


Figure 8.3. Sensitivity analysis for input parameters and ADUK biosolids treatment.

8.7 Conclusions

A quantitative risk assessment model was developed to assess the probability of human exposure to *E. coli* following land application of various biosolids treatments to agricultural land. The model inputs included application to agricultural land, dilution in stream, die-off in stream, drinking water treatment processes (coagulation, flocculation, sedimentation and disinfection) and a dose–response model to calculate human health risk. Outputs from the model include viable *E. coli* consumed and probability of illness for healthy and IC populations. Results from the model looking at viable *E. coli* consumed show that the biosolids treatment ADUK had the highest concentration of *E. coli* for RS1 and RS2 time frames, while biosolids treatment ADIRE showed the greatest concentration of *E. coli* for RS3 time frame.

Results for HE via a pessimistic dose–response model (i.e. *E. coli* O157:H7) for the probability of illness/day showed that the biosolids treatment ADUK had the greatest probability of illness risk for all time frames except RS3. ADUK was also greater for the probability of illness/year (RS1 and RS2). The risk of illness for IC individuals was greater than the acceptable level of risk of illness/year (1×10^{-4}), as set by the USEPA, which highlights the vulnerable nature of this sub-population. A sensitivity analysis revealed that the inputs that influenced the model's variance were: the time in stream, concentration in surface runoff, tap water intake and *E. coli* inactivation. The results of the model showed that the concentrations of *E. coli* in the final effluent could be a hazard for IC populations when assuming a worst case scenario.

9 Conclusions and Recommendations

9.1 Overview

The objective of this study was to (1) characterise the concentrations of metal, TCS and TCC in biosolids from a selection of wastewater treatment plants in Ireland; (2) determine the impact on surface runoff following land application of three types of biosolids (AD, LS and TD) and compare them to another commonly spread organic fertiliser, DCS; (3) measure the uptake of metals by ryegrass for a period of time after the application of biosolids; and (4) model and conduct a risk assessment of potential hazards of human health concern based on the experimental data. To achieve this, a simple, novel, field-scale micro-plot study was designed and conducted, which examined the possible impacts arising from the land application of these treatments on surface runoff water and soil properties. Sections 9.2 and 9.3 present the main conclusions and recommendations arising from this study.

9.2 Conclusions

9.2.1 Land application

1. The impact of biosolids spread at the maximum application rate on grassland had no adverse impact on surface water quality compared to DCS in terms of nutrients and metal losses in surface runoff. The concentrations of TCS and TCC were not compared to DCS as they were below the LOD of the instrumentation used in this analysis.
2. With the exception of Cu in runoff from LS biosolids plots, all runoff samples from the biosolid-amended field plots were below their respective surface water standards.
3. Surface runoff losses of the water quality parameters analysed from biosolid-amended plots were higher than the study control (soil only) plots, and followed a general trend of highest losses occurring during RS1 and reduced losses in the subsequent events.
4. With the exception of total coliforms and some metal parameters, the greatest losses were from

the DCS-amended plots over the time studied (15 days). This means that with respect to the parameters studied, biosolids do not pose a greater risk in terms of runoff losses following land application over a 15-day period from the time of first application.

5. The concentrations of metal of the treated sludge from the WWTPs examined as part of this study were below the maximum allowable concentrations of metals for use in agriculture in the EU.
6. TCS and TCC, for which no regulatory standards for sewage sludge exist, were present in the treated sludge from the WWTPs examined. They were below the concentrations measured in other studies; the concentrations of these parameters may, however, vary throughout the year.
7. This study found that, in general, there was no statistically significant difference in the shoot metal concentration of ryegrass cultivated on biosolid-amended plots and those cultivated on unamended plots, when the biosolids were spread at the maximum permissible rate in Ireland.

9.2.2 Health issues

1. Under the conditions and for the parameters monitored, there was no measurable risk to human health. However, further testing in a larger field-scale experiment is needed to verify the findings of this study.
2. A risk-ranking model highlighted the importance of soil type (viz. SOC) and chemical properties (viz. Koc) in influencing the human health risk.
3. For both the metal and *E. coli* models, the initial concentration in the biosolids and filter reduction were the key parameters influencing the final risk estimates.

Under the conditions monitored, metal and *E. coli* concentrations in the four biosolids were not considered to pose a measurable risk to human health when spread on land, although caution is warranted when it comes to

IC individuals. However, such individuals would follow strict food and water intake guidelines, thus reducing the risk of illness.

9.3 Recommendations

1. While current EU and international regulations govern certain priority metal pollutants and bio-essential elements, other emerging contaminants that are potentially harmful to human health are omitted from the regulations. This means that, potentially, a number of emerging contaminants are being applied to land without regulation. As metals are relatively easy to measure using the techniques detailed in this study, it is recommended that the regulations governing the values for metal concentrations in biosolids for recycling in agriculture are extended to cover more metals. The measurement of pharmaceuticals is more problematic as it is very costly to measure these numerous parameters. In the first instance, it is recommended to test biosolids for TCS and TCC, as these parameters are of the greatest concern

internationally. WWTPs may also be upgraded or retrofitted to include treatment of these emerging contaminants, thereby negating the issue of their potential land application.

2. On the basis of the parameters measured in this study, it would appear that the legislation governing livestock exclusion rates from land after biosolids application are overly strict. However, a short period of withdrawal (e.g. 3 weeks) seems reasonable to reduce the risk of biosolids ingestion by the animals (as would be the case with cattle slurries). Any further restrictions may be overly strict for a single application to land at compliant application rates.
3. Currently, there is a knowledge gap concerning the effectiveness of LS in adhering to the pH and temperature requirements of the Codes of Good Practice. There is a need for research into the LS process and its effectiveness to minimise food safety concerns. This research should result in the introduction of mandatory standards governing LS methodologies.

References

- Ademollo, N., Ferrara, F., Delise, M., Fabietti, F. and Funari, E., 2008. Nonylphenol and octylphenol in human breast milk. *Environment International* 34: 984–987.
- Akpor, O. and Muchie, M., 2010. Remediation of heavy metals in drinking water and wastewater treatment systems: processes and applications. *International Journal of Physical Sciences* 5: 1807–1817.
- Anderson P.D., Johnson, A.C. and Pfeiffer, D., 2012. Endocrine disruption due to estrogens derived from humans predicted to be low in the majority of US surface waters. *Environmental Toxicology and Chemistry* 31: 1407–1415.
- Antoniadis, V., Robinson, J.S. and Alloway, B.J., 2008. Effects of short-term pH fluctuations on cadmium, nickel, lead, and zinc availability to ryegrass in a sewage-amended field. *Chemosphere* 71: 759–764.
- APHA (American Public Health Association), 2005. Standard Methods for the Examination of Water and Wastewater. APHA, Washington, DC.
- Arnot J.A., Mackay, D. and Parkerton, T.F., 2010. Multimedia modeling of human exposure to chemical substances: the roles of food web biomagnification and biotransformation. *Environmental Toxicology and Chemistry* 29: 45–55.
- Baek, Y.W., Lee, W.M., Jeong, S.W. and An, Y.J., 2014. Ecological effects of soil antimony on the crop plant growth and earthworm activity. *Environmental Earth Science* 71: 895–900.
- Bai, Y., Chen, W., Chang, A.C. and Page, A.L., 2010. Uptake of metals by food plants grown on soils 10 years after biosolids application. *Journal of Environmental Science and Health Part B* 45: 531–539.
- Bord Bia, 2010. Beef and Lamb Quality Assurance Scheme. Producer Standard Revision 01. Available online: <http://www.bordbia.ie/industry/farmers/quality/BeefSchemeStandards/Beef%20and%20Lamb%20QAS%20Producer%20Manual.pdf>
- Bowyer-Bower, T.A.S. and Burt, T.P., 1989. Rainfall simulators for investigating soil response to rainfall. *Soil Technology* 2: 1–16.
- Brennan, F.P., O'Flaherty, V., Kramers, G., Grant, J. and Richards, K.G., 2010. Long-term persistence and leaching of *Escherichia coli* in temperate maritime soils. *Applied and Environmental Microbiology* 76: 1449–1455.
- Brennan, R.B., Healy, M.G., Grant, J., Ibrahim, T.G. and Fenton, O., 2012. Incidental phosphorus and nitrogen loss from grassland plots receiving chemically amended dairy cattle slurry. *Science of the Total Environment* 441: 132–140.
- Bulson, P.C., Johnstone, D.L., Gibbons, H.L. and Funk, W.H., 1984. Removal and inactivation of bacteria during alum treatment of a lake. *Applied and Environmental Microbiology* 48: 425–430.
- Cassin, M.H., Lammerding, A.M., Todd, E.C., Ross, W. and McColl, R.S., 1998. Quantitative risk assessment for *Escherichia coli* O157:H7 in ground beef hamburgers. *International Journal of Food Microbiology* 41: 21–44.
- CCEMC (Canadian Centre for Environmental Modelling and Chemistry), 2007. RAIDAR Model. Available online: <http://www.trentu.ca/academic/aminss/envmodel/models/RAIDAR100.html>
- Cele, E.N. and Maboeta, M., 2016. A greenhouse trial to investigate the ameliorative properties of biosolids and plants on physiochemical conditions of iron ore tailings: implications for an iron ore mine site remediation. *Journal of Environment Management* 165: 167–174.
- Chan Y.J., Chong M.F., Law C.L., Hassell D.G., 2009. A review on anaerobic–aerobic treatment of industrial and municipal wastewater. *Chemical Engineering Journal* 155: 1–18.658.
- Chen, Y., Fu, B., Wang, Y., Jiang, Q. and Liu, H., 2012. Reactor performance and bacterial pathogen removal in response to sludge retention time in a mesophilic anaerobic digester treating sewage sludge. *Bioresource Technology* 106: 20–26.
- Cole, M., Lindeque, P., Halsband, C. and Galloway, T.S., 2011. Microplastics as contaminants in the marine environment: a review. *Marine Pollution Bulletin* 62: 2588–2597
- Cooper, E.R., Siewicki, T.C., Phillips, K., 2008. Preliminary risk assessment database and risk ranking of pharmaceuticals in the environment. *Science of the Total Environment* 398: 26–33.
- Coulter, B.S. and Lalor, S., 2008. Major and Micro Nutrient Advice for Productive Agricultural Crops. Third edition. Teagasc, Johnstown Castle, Ireland, p. 116.
- Cummins, E. and Adkin, A., 2007. Exposure assessment of TSEs from the landspreading of meat and bone meal. *Risk Analysis* 27: 1179–202.

- de Tilleghem, C.L.B. and Govaerts, B., 2007. A review of quantitative structure–activity relationship (QSAR) models. *Environmental Health Perspectives* 111: 1358–1360
- Dijkshoorn, W., Lampe, J.E.M. and van Broekhoven, L.W., 1981. Influence of soil pH on heavy metals in ryegrass from sludge-amended soil. *Plant Soil* 61: 277–284.
- Dowdy, R.H., Page, A.L. and Chang, A.C., 1991. Management of agricultural land receiving wastewater sludges. In Lal, R. and Pierce, F.J. (eds), *Soil Management for Sustainability*. Soil and Water Conservation Society, Ankeny, IA, pp. 85–101.
- EC (European Commission), 2000. Working document on sludge, 3rd draft, DG-Environnement. Available online: http://www.ewa-online.eu/comments.html?file=tl_files/_media/content/documents_pdf/European%20Water%20Policy/Comments/Sewage%20Sludge/EWA_WD_sludge_en.pdf
- EC (European Commission), 2002. Proposal for a Directive of the European Parliament and of the Council relating to restrictions on the marketing and use of nonylphenol, nonylphenol ethoxylate and cement (twenty-sixth amendment of Council Directive 76/769/EEC. COM(2002) 459 final. Available online: <http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:52003AE0399&from=EN>
- EC (European Commission), 2003. Technical Guidance Document on Risk Assessment, part II. Available online: https://echa.europa.eu/documents/10162/16960216/tgdpart2_2ed_en.pdf
- EC (European Commission), 2010. Environmental, economic and social impacts of the use of sewage sludge on land. Final Report Part I: Overview Report. Available online: http://ec.europa.eu/environment/archives/waste/sludge/pdf/part_i_report.pdf
- EC (European Commission), 2014. Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions “Towards a circular economy: a zero waste programme for Europe”. COM(2014) 398 final 2, 2 July 2014, Brussels. Available online: <http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A52014DC0398>
- EC (European Commission), 2016. Sewage sludge. Available online: <http://ec.europa.eu/environment/waste/sludge/index.htm>
- Eldridge, S.M., Chan, K.Y., Barchia, I., Pengelly, P.K., Katupitiya, S. and Davis, J.M., 2009. A comparison of surface applied granulated biosolids and poultry litter in terms of risk to runoff water quality on turf farms in Western Sydney, Australia. *Agriculture, Ecosystems & Environment* 134: 243–250.
- Elkhatib, E., Moharem, M., 2015. Immobilization of copper, lead, and nickel in two arid soils amended with biosolids: effect of drinking water treatment residuals. *Journal of Soils and Sediments* 15: 1937–1946. DOI: 10.1007/s11368-015-1127-1.
- Elliott, H.A., Brandt, R.C. and O’Connor, G.A., 2005. Runoff phosphorus losses from surface-applied biosolids. *Journal of Environmental Quality* 34: 1632–1639.
- END-O-SLUDG, 2014. Available online: <http://www.eip-water.eu/projects/end-o-sludg-marketable-sludge-derivatives-sustainable-processing-wastewater-highly>
- EPA (Environmental Protection Agency), 1995. *Water Treatment Manuals: Filtration*. EPA, Johnstown Castle, Ireland. Available online: https://www.epa.ie/pubs/advice/drinkingwater/EPA_water_treatment_manual_%20filtration1.pdf
- EPA (Environmental Protection Agency), 2002. *The Quality of Drinking Water in Ireland*. EPA, Johnstown Castle, Ireland. Available online: http://www.kilkenny-coco.ie/resources/eng/Services/Sanitary_Services/waterquality/WS%20-%20Water%20Quality%20-%20DW%20-%20Report%20-%20EPA%20-%20Drinking%20Water%20Report%202002.pdf
- EPA (Environmental Protection Agency), 2011. *Water Treatment Manual: Disinfection*. EPA, Johnstown Castle, Ireland. Available online: http://www.epa.ie/pubs/advice/drinkingwater/disinfection2_web.pdf
- EPA (Environmental Protection Agency), 2013. Occurrence and fate of pharmaceuticals and personal care products within sewage sludge and sludge-enriched soils. STRIVE Report Series No. 34. EPA, Johnstown Castle, Ireland. Available online at https://www.epa.ie/pubs/reports/research/waste/STRIVE_34_Barron_PCPs_web.pdf
- EPA (Environmental Protection Agency), 2015. *Urban Waste Water Treatment in 2014*. EPA, Johnstown Castle, Ireland. Available online: http://www.epa.ie/pubs/reports/water/wastewater/2014%20waste%20water%20report_web.pdf
- Erickson, M.C., Habteselassie, M.Y., Liao, J., Webb, C.C., Mantripragada, V., Davey, L.E. and Doyle, M.P., 2014. Examination of factors for use as potential predictors of human enteric pathogen survival in soil. *Journal of Applied Microbiology* 116: 335–349.
- Eriksson, J., 2001. Concentration of 61 trace elements in sewage sludge, farmyard manure, mineral fertiliser, precipitation and in soil and crops. Swedish Environmental Protection Agency, Stockholm.

- EU (European Union), 1986. Council Directive 86/278/EEC of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. OJ L 181, 4.7.1986, p. 6–12. Available online: <http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A31986L0278>
- EU (European Union), 1991. Council Directive of 21 May 1991 concerning urban waste water treatment. Available online: <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:1991:135:0040:0052:EN:PDF>
- EU (European Union), 1999. Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste. Available online: <http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:31999L0031&from=GA>
- EU (European Union), 2002. Directive 2002/32/EC of the European Parliament and of the Council of 7 May 2002 on undesirable substances in animal feed. OJ L 140, 30.5.2002, p. 10. Available online: <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CONSLEG:2002L0032:20061020:EN:PDF>
- EU (European Union), 2008. Waste Framework Directive. Available online: <http://ec.europa.eu/environment/waste/legislation/a.htm> (accessed 18 September 2013).
- EU (European Union), 2009. Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC. OJ L 140, 5.6.2009, p. 16–63.
- Eurostat, 2014. Sewage Sludge Production and Disposal. Available online: http://appsso.eurostat.ec.europa.eu/nui/show.do?dataset=env_ww_spd&lang=en
- Fay, D., McGrath, D., Zhang, C., Carrigg, C., O'Flaherty, V., Kramers, G., Carton, O.T. and Grennan, E., 2007. National Soils Database. End of Project Report—RMIS 5192. Teagasc, Johnstown Castle, Ireland.
- Fehily Timoney And Company, 1999. Codes of Good Practice for the Use of Biosolids in Agriculture. Available online: <http://www.environ.ie/en/Publications/Environment/Water/FileDownload,17228,en.pdf>
- Fenton O., Schulte R.P.O., Jordan P., Lalor S.T.J. and Richards K.G., 2011. Time lag: a methodology for the estimation of vertical and horizontal travel and flushing timescales to nitrate threshold concentrations in Irish aquifers. *Environmental Science and Policy* 14: 419–431.
- Fjällborg, B. and Dave, G. 2004. Toxicity of Sb and Cu in sewage sludge to terrestrial plants (lettuce, oat, radish) and of sewage sludge elutriate to aquatic organisms (daphnia and lemna) and its interaction. *Water, Air and Soil Pollution* 155: 3–20.
- Fu, Q., Sanganyado, E., Ye, Q. and Gan, J., 2016. Meta-analysis of biosolid effects on persistence of triclosan and triclocarban in soil. *Environmental Pollution* 210: 137–144.
- Galbally, P., Ryan, D., Fagan, C.C., Finnan, J., Grant, J. and McDonnell, K., 2013. Biosolid and distillery effluent amendments to Irish short rotation coppiced willow plantations: impacts on groundwater quality and soil. *Agricultural Water Management* 116: 193–203.
- Gale, P., 2005. Matrix effects, non-uniform reduction and dispersion in risk assessment for *Escherichia coli* O157. *Journal of Applied Microbiology* 99: 259–270
- Gautam, P., Carsella, J.S. and Kinney, C.A., 2014. Presence and transport of the antimicrobials triclocarban and triclosan in a wastewater-dominated stream and freshwater environment. *Water Research* 48: 247–256.
- Gerba C.P. and Smith J.E., 2005. Sources of pathogenic microorganisms and their fate during land application of wastes. *Journal of Environmental Quality* 34: 42–48.
- Gottshall, N., Topp E. and Edwards M., 2013. Hormones, sterols, and fecal indicator bacteria in groundwater, soil, and subsurface drainage following a high single application of municipal biosolids to a field. *Chemosphere* 91: 275–286.
- Grant, E., Rouch, D., Deighton, M. and Smith, S., 2012. Pathogen risks in land-applied biosolids. Evaluating risks of biosolids. Evaluating risks of biosolids produced by conventional treatment. *Water* 391: 72–78.
- Hargreaves, J.C., Adl, M.S. and Warman, P.R., 2008. A review of the use of composted municipal solid waste in agriculture. *Agriculture, Ecosystems and Environment* 123: 1–14.
- Haynes, R.J., Murtaza, G. and Naidu, R., 2009. Inorganic and organic constituents and contaminants of biosolids: implications for land application. *Advances in Agronomy* 104: 165–267.
- Healy, M.G., Clarke, R., Peyton, D., Cummins, E., Moynihan, E.L., Martins, A., Beraud, P. and Fenton, O., 2015. Resource Recovery from sludge. In Konstantinos, K. (ed), *Sewage Treatment Plants: Economic Evaluation of Innovative Technologies for Energy Efficiency*. IWA, London.
- Healy, M.G., Fenton, O., Forrestal, P.J., Danaher, M., Brennan, R.B. and Morrison, O., 2016a. Metal concentrations in lime stabilised, thermally dried and anaerobically digested sewage sludges. *Waste Management* 48: 404–408.
- Healy, M.G., Ryan, P.C., Fenton, O., Peyton, D.P., Wall, D. and Morrison, L., 2016b. Bioaccumulation of metals in ryegrass (*Lolium perenne* L.) following the application of lime stabilised, thermally dried and anaerobically digested sewage sludge. *Ecotoxicology and Environmental Safety* 130: 303–309.

- Higgins M.J., Chen, Y.-C., Murthy, S.N., Hendrickson, D., Farrel, J. and Schafer, P., 2007. Reactivation and growth of non-culturable indicator bacteria in anaerobically digested biosolids after centrifuge dewatering. *Water Research* 41: 665–673.
- Hoekstra, N.J., Finn, J.A., Hofer, D. and Lüscher, A., 2014. The effect of drought and interspecific interactions on depth of water uptake in deep- and shallow-rooting grassland species as determined by $\delta^{18}\text{O}$ natural abundance. *Biogeosciences* 11: 4493–4506.
- Hubbs, A.K.B., 2002. Fecal coliform concentration in surface runoff from pastures with applied dairy manure. Doctoral dissertation. Louisiana State University, Baton Rouge, LA.
- Hussain, N., Jaitley, V. and Florence, A.T., 2001. Recent advances in the understanding in the uptake of micro-particulates across the gastrointestinal lymphatics. *Advanced Drug Delivery Reviews* 50: 107–142.
- Hutchison, M.L., Walters, L.D., Avery, S.M., Syngé, B.A. and Moore, A., 2004. Levels of zoonotic agents in British livestock manures. *Letters in Applied Microbiology* 39: 207–214.
- Isaac R.A. and Boothroyd, Y., 1996. Beneficial use of biosolids: progress in controlling metals. *Water Science and Technology* 34: 493–497.
- IUNA (Irish Universities Nutrition Alliance), 2005–2006. Chapter 2 – Food Consumption. Available online: <http://www.iuna.net/wp-content/uploads/2011/04/Food-Consumption-Tables-2.1-to-2.16.pdf>
- IUNA (Irish Universities Nutrition Alliance), 2011. National Adult Nutrition Survey. Available online: <http://www.iuna.net/wp-content/uploads/2010/12/National-Adult-Nutrition-Survey-Summary-Report-March-2011.pdf>
- Johnson, D.L. and Bretsch, J.K., 2002. Soil lead and children's blood lead levels in Syracuse, N.Y., USA. *Environmental Geochemistry and Health* 24: 375–385.
- Joshua, W.D., Michalk, D.L., Curtis, I.H., Salt, M. and Osborne, G.J., 1998. The potential for contamination of soil and surface waters from sewage sludge (biosolids) in a sheep grazing study, Australia. *Geoderma* 84: 135–156.
- Kelessidis, A. and Stasinakis, A.S., 2012. Comparative study of the methods used for treatment and final disposal of sewage sludge in European countries. *Waste Management* 32: 1186–1195.
- Kjeldahl, J., 1883. A new method for the estimation of nitrogen in organic compounds. *Zeitschrift für Analytische Chemie* 22: 366–383.
- Kleinman, P.J., Sharpley, A.N., Wolf, A.M., Beegle, D.B. and Moore, P.A., 2002. Measuring water-extractable phosphorus in manure as an indicator of phosphorus in runoff. *Soil Science Society of America Journal* 66: 2009–2015.
- Kleinman, P.J.A., Sullivan, D., Wolf, A., Brandt, R., Dou, Z., Elliott, H., Kovar, J., Leytem, A., Maguire, R., Moore, P., Saporito, L., Sharpley, A., Shober, A., Sims, T., Toth, J., Toor, G., Zhang, H. and Zhang, T., 2007. Selection of a water-extractable phosphorus test for manures and biosolids as an indicator of runoff loss potential. *Journal of Environmental Quality* 36: 1357–1367.
- Lang, N.L., Smith, S.R., Bellett-Travers, D.M. and Rowlands, C.L., 2003. Decay of *Escherichia coli* in soil following the application of biosolids to agricultural land. *Water and Environment Journal* 17: 23–28.
- Lang, N.L., Bellett-Travers, M.D. and Smith, S.R., 2007. Field investigations on the survival of *Escherichia coli* and presence of other enteric micro-organisms in biosolids-amended agricultural soil. *Journal of Applied Microbiology* 103: 1868–1882.
- Latore, A.M., Kumar, O., Singh, S.K. and Gupta, A., 2014. Direct and residual effect of sewage sludge on yield, heavy metals content and soil fertility under rice-wheat system. *Ecological Engineering* 69: 17–24.
- LeBlanc, R.J., Matthews, P. and Richard, R.P., 2008. Global atlas of excreta, wastewater sludge, and biosolids management: moving forward the sustainable and welcome uses of a global resource. United Nations Human Settlements Programme (UN-HABITAT), Kenya. Available online: http://esa.un.org/iys/docs/san_lib_docs/habitat2008.pdf
- Lemly, A.D., 1996. Evaluation of the hazard quotient method for risk assessment of selenium. *Ecotoxicology and Environmental Safety* 35: 156–62.
- Lepom, P., Brown, B., Hanke, G. Loos, R., Quevauviller, P. and Wollgast, J., 2009. Needs for reliable analytical methods for monitoring chemical pollutants in surface water under the European Water Framework Directive. *Journal of Chromatography A* 1216: 302–315.
- Liu, X.A., Fike, J.H., Galbraith, J.M. Fike, W.B., Parrish, D.J., Evanylo, G.K. and Strahm, B.D., 2015. Effects of harvest frequency and biosolids application on switch-grass yield, feedstock quality, and theoretical ethanol yield. *Global Change Biology* 7: 112–121.
- Lu, Q., He, Z.L. and Stoffella, P.J., 2012. Land application of biosolids in the USA: a review. *Applied and Environmental Soil Science*. DOI: 10.1155/2012/201462.
- Lucid, J.D., Fenton, O. and Healy, M.G., 2013. Estimation of maximum biosolids and meat and bone meal application to a low P index soil and a method to test for nutrient and metal losses. *Water, Air, & Soil Pollution* 224: 1–12.

- Lucid, J.D., Fenton, O., Grant, J. and Healy, M.G., 2014. Effect of rainfall time interval on runoff losses of biosolids and meat and bone meal when applied to a grassland soil. *Water, Air, & Soil Pollution* 225: 1–11.
- McBride, M.B., 2003. Toxic metals in sewage sludge-amended soils: has promotion of beneficial use discounted the risks? *Advances in Environmental Research* 8: 5–19.
- McBride, M.B., Richards, B.K., Steenhuis, T. and Spiers, G., 1999. Long-term leaching of trace elements in a heavily sludge-amended sily clay loam soil. *Soil Science* 164: 613–623.
- McClellan, K. and Halden, R.U., 2010. Pharmaceuticals and personal care products in archived U.S. biosolids from the 2001 EPA national sewage sludge survey. *Water Research* 44: 658–668.
- McKinley, V.L. and Vestal, J.R., 1985. Physical and chemical correlates of microbial activity and biomass in composting municipal sewage sludge. *Applied and Environmental Microbiology* 50: 1395–1403.
- Magnusson, K. and Noren, F., 2014. Screening of microplastic particles in and downstream a wastewater treatment plant. IVL Swedish Environmental Research Institute, Stockholm.
- Mamindy-Pajany, Y., Sayen, S., Mosselmans, J.F., Guillon and Guillon, E., 2014. Copper, nickel and zinc speciation in a biosolid-amended soil: pH adsorption edge, μ -XRF and μ -XANES investigations. *Environmental Science and Technology* 48: 7237–7244.
- Mao, Z., Zheng, X.-F., Zhang, Y.-Q., Tao, X.-X., Li, Y. and Wang, W., 2012. Occurrence and biodegradation of nonylphenol in the environment. *International Journal of Molecular Sciences* 13: 491–505.
- Martin, J., Camacho-Muñoz, D., Santos, J.L., Aparicio, I. and Alonso, E., 2012. Distribution and temporal evolution of pharmaceutically active compounds alongside sewage sludge treatment. Risk assessment of sludge application onto soils. *Journal of Environmental Management* 102: 18–25.
- Mathews, S., Henderson, S. and Reinhold, D., 2014. Uptake and accumulation of antimicrobials, triclocarban and triclosan, by food crops in a hydroponic system. *Environmental Science and Pollution Research* 21: 6025–6033.
- Milieu Ltd, WRc and RPA, 2013a. Environmental, economic and social impacts of the use of sewage sludge on land. Final Report – Part I: Overview Report. Service contract No. 070307/2008/517358/ETU/G4. Milieu Ltd, Brussels.
- Milieu Ltd, WRc and RPA, 2013b. Environmental, economic and social impacts of the use of sewage sludge on land. Final Report – Part II: Report on Options and Impacts. Service contract No. 070307/2008/517358/ETU/G4. Milieu Ltd, Brussels.
- Milieu Ltd, WRc and RPA, 2013c. Environmental, economic and social impacts of the use of sewage sludge on land. Final Report – Part III: Project Interim Reports. Service contract No. 070307/2008/517358/ETU/G4. Milieu Ltd, Brussels.
- Mininni, G., Blanch, A., Lucena, F. and Berselli, S., 2014. EU policy on sewage sludge utilization and perspectives on new approaches of sludge management. *Environmental Science and Pollution Research* 22: 7361–7374.
- Morais, S. A., Delerue-Matos, C. and Gabarrell, X., 2013. Accounting for the dissociating properties of organic chemicals in LCIA: An uncertainty analysis applied to micropollutants in the assessment of freshwater ecotoxicity. *Journal of Hazardous Materials* 248: 461–468.
- Morrison, L., Baumann, H.A. and Stengel, D.B., 2008. An assessment of metal contamination along the Irish coast using the seaweed *Ascophyllum nodosum* (Fucales, Phaeophyceae), *Environmental Pollution* 152: 293–303.
- Mouri, G., Takizawa, S., Fukushi, K. and Oki, T., 2013. Estimation of the effects of chemically-enhanced treatment of urban sewage system based on life-cycle management. *Sustainable Cities and Society* 9: 23–31.
- Narumiya, M., Nakada, N., Yamashita, N. and Tanaka, H., 2013. Phase distribution and removal of pharmaceuticals and personal care products during anaerobic sludge digestion. *Journal of Hazardous Materials* 260: 305–312.
- Navas, A., Machn, J. and Navas, B., 1999. Use of biosolids to restore the natural vegetation cover on degraded soils in the badlands of Zaragoza (NE Spain). *Bioresource Technology* 69: 199–205.
- NHMRC (National Health and Medical Research Council), 2003. Review of Coliforms as Microbial Indicators of Drinking Water Quality. Available online: http://www.nhmrc.gov.au/_files_nhmrc/publications/attachments/eh32.pdf
- Öberg, T. and Iqbal, M.S., 2012. The chemical and environmental property space of REACH chemicals. *Chemosphere* 87: 975–981.
- O'Connor, J.T. and O'Connor, T., 2001. Water Quality Deterioration in Distribution Systems Part 4: Microbiologically-Mediated Deterioration in Surface Water Supplies. *Water Engineering & Management*. Available online: http://www.wqpmag.com/sites/default/files/WQDET_Part_IV_2_01.pdf

- Ojeda, G., Tarrasón, D., Ortiz, O. and Alcaniz, J., 2006. Nitrogen losses in runoff waters from a loamy soil treated with sewage sludge. *Agriculture, Ecosystems & Environment* 117: 49–56.
- Ömeroglu, S., Murdoch, F.K. and Sanin, F.D., 2015. Investigation of nonylphenol and nonylphenol ethoxylates in sewage sludge samples from a metropolitan wastewater treatment plant in Turkey. *Talanta* 131: 650–655.
- Palenske, N.M., 2009. Effects of triclosan, triclocarban, and caffeine exposure on the development of amphibian larvae. PhD Thesis. University of North Texas, Denton, TX.
- Payment, P., Plante, R. and Cejka, P., 2001. Removal of indicator bacteria, human enteric viruses, Giardia cysts, and Cryptosporidium oocysts at a large wastewater primary treatment facility. *Canadian Journal of Microbiology* 47: 188–193.
- Penn, C.J. and Sims, J.T., 2002. Phosphorus forms in biosolids-amended soils and losses in runoff. *Journal of Environmental Quality* 31: 1349–1361.
- Peters, G.M. and Rowley, H.V., 2009. Environmental comparison of biosolids management systems using life cycle assessment. *Environmental Science & Technology* 43: 2674–2679.
- Peyton, D.P., Healy, M.G., Fleming, G.T.A., Grant, J., Wall, D., Morrison, L., Cormican, M. and Fenton, O., 2016. Nutrient, metal and microbial loss in surface runoff following treated sludge and dairy cattle slurry application to an Irish grassland soil. *Science of the Total Environment* 541: 218–229.
- Pritchard, M., Craven, T., Mkandawire, T., Edmondson, A.S. and O'Neill, J.G., 2010. A comparison between Moringa oleifera and chemical coagulants in the purification of drinking water – an alternative sustainable solution for developing countries. *Physics and Chemistry of the Earth, Parts A/B/C* 35: 798–805.
- Quilbe, R., Serreau, C., Wicherek, S., Bernard, C., Thomas, Y. and Oudinet, J.P., 2005. Nutrient transfer by runoff from sewage sludge amended soil under simulated rainfall. *Environmental Monitoring and Assessment* 100: 177–190.
- Ratcliff, J.J., Wan, A.H.L., Edwards, A., Soler-Vila, A., Johnson, M.P., Abreu, M.H. and Morrison, L., 2016. Metal content of kelp (*Laminaria digitata*) co-cultivated with Atlantic salmon in an Integrated Multi-Trophic Aquaculture System. *Aquaculture* 450: 234–243.
- Richardson, B.J., Lam, P.K.S. and Martin, M., 2005. Emerging chemicals of concern: Pharmaceuticals and personal care products (PPCPs) in Asia, with particular reference to Southern China. *Marine Pollution Bulletin* 50: 913–920.
- Robinson, K.G., Robinson, C.H., Raup, L.A. and Markum, T.R., 2012. Public attitudes and risk perception toward land application of biosolids within the south-eastern United States. *Journal of Environmental Management* 98: 29.
- Rostagno, C.M. and Sosebee, R.E., 2001. Biosolids application in the Chihuahuan Desert. *Journal of Environmental Quality* 30: 160–170.
- Sanderson, H., Johnson, D.J., Wilson, C.J., Brain, R.A. and Solomon, K.R., 2003. Probabilistic hazard assessment of environmentally occurring pharmaceuticals toxicity to fish, daphnids and algae by ECOSAR screening. *Toxicology Letters* 144: 383–395.
- SAS (Statistical Analysis System). SAS for windows. Version 9.4. SAS/STAT® User's Guide. SAS Institute Inc, Cary, NC.
- Schueler, T., 2000. Microbes and Urban Watersheds: Ways to Kill 'Em. The Practice of Watershed Protection. Center for Watershed Protection, Ellicott City, MD, pp. 392–400.
- Schulte, R., Melland, A., Fenton, O., Herlihy, M., Richards, K. and Jordan, P., 2010. Modelling soil phosphorus decline: Expectations of Water Framework Directive policies. *Environmental Science & Policy* 13(6): 472–484.
- Schwab, B.W., Hayes, E.P., Fiori J.M., Mastrocco, F.J., Roden, N.M., Cragin, D., Meyerhoff, R.D., D'Aco, V.J. and Anderson, P.D., 2005. Human pharmaceuticals in US surface waters: a human health risk assessment. *Regulatory Toxicology and Pharmacology* 42: 296–312.
- Selvaratnam, S. and Kunberger, J.D., 2004. Increased frequency of drug-resistant bacteria and fecal coliforms in an Indiana Creek adjacent to farmland amended with treated sludge. *Canadian Journal of Microbiology* 50: 653–656.
- Shu, W., Price, G.W., Sharifi, M. and Cade-Menun, B.J., 2016. Impact of annual and single application of alkaline treated biosolids on soil extractable phosphorus and total phosphorus. *Agriculture, Ecosystems and Environment* 219: 111–118.
- Sidhu, J.P. and Toze, S.G., 2009. Human pathogens and their indicators in biosolids: a literature review. *Environment International* 35: 187–201.
- Singh, R.P. and Agrawal, M., 2008. Potential benefits and risks of land application of sewage sludge. *Waste Management* 28: 347–358.
- S.I. No. 122 of 2014, European Union (Drinking Water) Regulations 2014 Arrangement of Regulations. The Stationery Office. Available online at: <http://www.irishstatutebook.ie/pdf/2014/en.si.2014.0122.pdf>

- S.I. No. 148 of 1998. Waste Management (Use of Sewage Sludge in Agriculture Regulations). The Stationery Office. Available online: <http://www.irishstatutebook.ie/eli/1998/si/148/made/en/print>
- S.I. No. 267 of 2001. Waste Management (Use of Sewage Sludge in Agriculture) (Amendment) Regulations, 2001. The Stationery Office. Available online: <http://www.irishstatutebook.ie/eli/2001/si/267/made/en/print>
- S.I. No. 254 of 2001. Urban Waste Water Treatment Regulations, 2001. The Stationery Office. Available online: <http://www.irishstatutebook.ie/eli/2001/si/254/made/en/print>
- S.I. No. 610 of 2010. European Communities (Good Agricultural Practice for Protection of Waters) Regulations, 2010. Available online: <http://www.irishstatutebook.ie/eli/2010/si/610/made/en/pdf>
- S.I. No. 31 of 2014. European Union (Good Agricultural Practice for Protection of Waters) Regulations 2014. The Stationery Office. Available online: <http://www.irishstatutebook.ie/eli/2014/si/31/made/en/pdf>
- S.L. 549.21., 2002. Subsidiary Legislation 549.21. Quality required of surface water intended for the abstraction of drinking water regulations. Government of Malta. Available online: <http://www.justiceservices.gov.mt/DownloadDocument.aspx?app=lom&itemid=11516&l=1>
- Smith, S.R., and Riddell-Black, D., 2007. *Sources and Impacts of Past, Current and Future Contamination of Soil*. Appendix 2: Organic contaminants. Final report to DEFRA. Department for Food, Environment and Rural Affairs, London.
- Snyder, E.H., O'Connor, G.A. and McAvoy, D.C., 2011. Toxicity and bioaccumulation of biosolids-borne triclocarban (TCC) in terrestrial organisms. *Chemosphere* 82: 460–467.
- Soares, A., Guieysse, B., Jefferson, B., Cartmell, E. and Lester, J.N., 2008. Nonylphenol in the environment: a critical review on occurrence, fate, toxicity and treatment in wastewaters. *Environment International* 34: 1033–1049.
- Sobrados-Bernardos, L. and Smith, J.E., 2012. Controlling pathogens and stabilizing sludge/biosolids: a global perspective of where we are today and where we need to go. *Proceedings of the Water Environment Federation* 2012: 56–70.
- Solomon E.B., Yaron S. and Matthews, K.R., 2002. Transmission of *Escherichia coli* O157:H7 from contaminated manure and irrigation water to lettuce plant tissue and its subsequent internalization. *Applied and Environmental Microbiology* 68: 397–400.
- Staunton, J., Mc Donnell, R.J., Gormally, M.J., Williams, C.D., Henry, T. and Morrison, L., 2014. Assessing metal contamination from construction and demolition (C&D) waste used to infill wetlands: using *Deroceras reticulatum* (Mollusca: Gastropoda). *Environmental Science: Processes and Impacts* 16: 2463–2668.
- Straub, T.M., Pepper, I.L. and Gerba, C.P., 1992. Persistence of viruses in desert soils amended with anaerobically digested sewage sludge. *Applied Environmental Microbiology* 58: 636–641.
- Topp, E., Monteiro, S.C., Beck, A., Coelho, B.B., Boxall, A., Duenk, P.W. and Sabourin, L., 2008. Runoff of pharmaceuticals and personal care products following application of biosolids to an agricultural field. *Science of the Total Environment* 396: 52–59.
- Trevisan, M., Di Guardo, A. and Balderacchi, M., 2009. An environmental indicator to drive sustainable pest management practices. *Environmental Modelling and Software* 24: 994–1002.
- Tyrrel S.F. and Quinton J.N., 2003. Overland flow transport of pathogens from agricultural land receiving faecal wastes. *Journal of Applied Microbiology* 94: 87–93.
- UNEP, 2013. Stockholm convention on persistent organic pollutants. Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants. Geneva, 28 April – 10 May. Available online: <http://www.unep.org/chemicalsandwaste/portals/9/POPs/docs/UNEP-POPS-COP.6-INF-33.English.pdf>
- USEPA (US Environmental Protection Agency), 1993. 40 CFR Part 503. Standards for use or disposal of sewage sludge; final rules. Federal Reg 1993; 58(32): 9248.
- USEPA (US Environmental Protection Agency), 1995. *A Guide to the Biosolids Risk Assessments for the EPA Part 503 Rule. Chapter 2*. EPA/832-B-93-005. USEPA, Washington, DC. Available online: http://water.epa.gov/scitech/wastetech/biosolids/upload/2002_06_28_mtb_biosolids_503rule_503g_ch2.pdf
- USEPA (US Environmental Protection Agency), 2000. *Biosolids Technology Fact Sheet*. Alkaline Stabilisation of Biosolids. Available online: <http://bit.ly/2gntvez>
- USEPA (US Environmental Protection Agency), 2002. *Biosolids Technology Fact Sheet*. Use of Composting for Biosolid Management. Available online: https://www.epa.gov/sites/production/files/2015-06/documents/use_of_composting_for_biosolids_management.pdf
- USEPA (US Environmental Protection Agency), 2006a. *Biosolids Technology Fact Sheet*. Multi-Stage Anaerobic Digestion. Available online: <http://bit.ly/2gdZnHM>
- USEPA (US Environmental Protection Agency), 2006b. *Biosolids Technology Fact Sheet*. Heat Drying. Available online: http://water.epa.gov/scitech/wastetech/upload/2006_10_16_mtb_heat-drying.pdf

- USEPA (US Environmental Protection Agency), 2007. *Method 1694: Pharmaceuticals and Personal Care Products in Water, Soil, Sediment, and Biosolids by HPLC/MS/MS*. USEPA, Washington, DC.
- USFDA (United States Food and Drug Authority), 2015. FDA taking closer look at “antibacterial” soap. Available online: <http://www.fda.gov/ForConsumers/ConsumerUpdates/ucm378393.htm>
- van Egmond, R., Sparham, C., Hastie, C. Gore, D. and Chowdhury, N., 2013. Monitoring and modelling of siloxanes in a sewage treatment plant in the UK. *Chemosphere* 93: 757–765.
- van Elsas, J.D., Garbeva, P. and Salles, J., 2002. Effects of agronomical measures on the microbial diversity of soils as related to the suppression of soil-borne plant pathogens. *Biodegradation* 13: 29–40.
- van Elsas, J.D., Semenov, A.V., Costa, R. and Trevors, J.T., 2011. Survival of *Escherichia coli* in the environment: fundamental and public health aspects. *The ISME Journal* 5: 173–183.
- van Veen, J.A., van Overbeek, L.S. and van Elsas, J.D., 1997. Fate and activity of microorganisms introduced into soil. *Microbiology and Molecular Biology Reviews* 61: 121–135.
- Verlicchi, P. and Zambello, E., 2015. Pharmaceuticals and personal care products in untreated and treated sewage sludge: occurrence and environmental risk in the case of application to soil – a review. *Science of the Total Environment* 538: 750–767.
- Vinten, A.J.A., Douglas, J.T., Lewis, D.R., Aitken, M.N. and Fenlon, D.R., 2004. Relative risk of surface water pollution by *E. coli* derived from faeces of grazing animals compared to slurry application. *Soil Use and Management* 20: 13–22.
- Wallace, C.B., Burton, M.G., Hefner, S.G. and DeWitt, T.A., 2014. Sediment, nutrient, and bacterial runoff from biosolids and mineral fertilizer applied to a mixed cool-and native warm-season grassland in the Ozark mountains. *Applied and Environmental Soil Science*
- Wang, X., Sato, T., Xing, B. and Tao, S., 2005. Health risks of heavy metals to the general public in Tianjin, China via consumption of vegetables and fish. *Science of the Total Environment* 350, 28–37.
- WHO (World Health Organization), 2004. *Copper in Drinking-water. Background Document for Development of WHO Guidelines for Drinking-water Quality*. Available online: http://www.who.int/water_sanitation_health/dwq/chemicals/copper.pdf
- WHO (World Health Organization), 2011a. Joint FAO/WHO Food Standards Programme Codex Committee on contaminants in foods, fifth session, The Hague, the Netherlands, 21–25 March 2011. Available online: ftp://ftp.fao.org/codex/meetings/CCCCF/coccf5/cf05_INF.pdf
- WHO (World Health Organization), 2011b. *Guidelines for Drinking-water Quality*. Fourth edition. Available online: http://www.who.int/water_sanitation_health/publications/2011/dwq_guidelines/en/
- Wind, T., 2004. Prognosis of environmental concentrations by geo-referenced and generic models: a comparison of GREAT-ER and EUSES exposure simulations for some consumer-product ingredients in the litter. *Chemosphere*, 54: 1135–1143.
- Wu, C., Spongberg, A.L. and Witter, J.D., 2009. Adsorption and degradation of triclosan and triclocarban in soils and biosolids-amended soils. *Journal of Agricultural and Food Chemistry* 57: 4900–4905.
- Xiao, F., Simcik, M.F. and Gulliver, J.S., 2013. Mechanisms for removal of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) from drinking water by conventional and enhanced coagulation. *Water Research* 47: 49–56.
- Xue, J., Kimberley, M.O., Ross, C., Gielen, G., Tremblay, L.A., Champeau, O., Horswell, J. and Wang, H., 2015. Ecological impacts of long-term application of biosolids to a radiate pine plantation. *Science of the Total Environment* 530–531: 233–240.
- Yang, X., Flowers, R.C., Weinberg, H.S. and Singer, P.C., 2011. Occurrence and removal of pharmaceuticals and personal care products (PPCPs) in an advanced wastewater reclamation plant. *Water Research* 45: 5218–5228.
- Yueh, M.-F., Taniguchi, K., Chen, S., Evans, R.M., Hammock, B.D., Karin, M. and Tukey, R.H., 2014. The commonly used antimicrobial additive triclosan is a liver tumor promoter. *Proceedings of the National Academy of Sciences* 111: 17200–17205.
- Zaleski, K.J., Josephson, K.L., Gerba, C.P. and Pepper, I.L., 2005. Potential regrowth and recolonization of salmonellae and indicators in biosolids and biosolid-amended soil. *Applied and Environmental Microbiology* 71: 3701–3708.
- Zubris, K.A.V. and Richards, B.K., 2005. Synthetic fibers as an indicator of land application of sludge. *Environmental Pollution* 138: 201–11.

Abbreviations

AD	Anaerobically digested	Mo	Molybdenum
ADIRE	Anaerobically digested biosolids sourced in Ireland	MPN	Most probable number
ADUK	Anaerobically digested biosolids sourced in the United Kingdom	NH₄-N	Ammonium-nitrogen
Al	Aluminium	N	Nitrogen
ANOVA	Analysis of variance	Nb	Niobium
API	Active pharmaceutical ingredient	Ni	Nickel
As	Arsenic	NO₂-N	Nitrate-nitrogen
BOD	Biological oxygen demand	NP	Nonylphenol
BPA	Bisphenol A	NP1EO	Nonylphenol mono
Ca	Calcium	NP2EO	Di-ethoxylate
Cd	Cadmium	OM	Organic matter
cfu	Colony-forming units	P	Phosphorus
Cr	Chromium	P₂O₅	Phosphorus pentoxide
CRM	Certified reference material	PBDEs	Polybrominated diphenyl ethers
Cu	Copper	PBT	Persistence, bioaccumulation and toxicity
DCS	Dairy cattle slurry	PCBs	Polychlorinated biphenyls
DM	Dry matter	PCDD/Fs	Polychlorinated dibenzo- <i>p</i> -dioxin furans
DRP	Dissolved reactive phosphorus	PCPs	Personal care products
DS	Dried solids	PE	Population equivalent
DUP	Dissolved unreactive phosphorus	PEC	Predicted environmental concentration
<i>E. coli</i>	<i>Escherichia coli</i>	PFOA	Perfluorooctanoate
EPA	Environmental Protection Agency	PFOS	Perfluorooctane sulfonate
EU	European Union	PhATE	Pharmaceutical Assessment and Transport Evaluation (model)
EUSES	European Union Systems for the Evaluation of Substances	PMTDI	Provisional maximum tolerable daily intake
FC	Faecal coliforms	POPs	Persistent organic pollutants
Fe	Iron	PP	Particulate phosphorus
FP7	Seventh Framework Programme	PPCP	Pharmaceuticals and personal care product
FWMC	Flow-weighted mean concentration	QSAR	Quantitative structure–activity relationship
ha	Hectare	RAIDAR	Risk Assessment Identification and Ranking (model)
HE	Human exposure	RR	Chemical intake toxicity ratio
Hg	Mercury	RS1	Rainfall simulation event 1
HQ	Hazard quotient	RS2	Rainfall simulation event 2
IC	Immunocompromised	RS3	Rainfall simulation event 3
IUNA	Irish Universities Nutritional Alliance	Sb	Antimony
K	Potassium	Se	Selenium
Koc	Soil adsorption coefficient	Sn	Tin
LADD	Lifetime average daily dose	SOC	Soil organic carbon
LC₅₀	Median lethal concentration		
LOD	Limit of detection		
LOQ	Limits of quantification		
LS	Lime stabilised/Lime stabilisation		
Mg	Magnesium		

TC	Total coliforms	USEPA	United States Environmental Protection Agency
TCC	Triclocarban		
TCS	Triclosan	V	Vanadium
TD	Thermally dried	VTEX	Verocytotoxigenic <i>E. coli</i>
TDP	Total dissolved phosphorus	WEP	Water-extractable phosphorus
TN	Total nitrogen	WFD	Water Framework Directive
TP	Total phosphorus	WHO	World Health Organization
TR	Time to runoff	WWTP	Wastewater treatment plant
UNEP	United Nations Environment Programme	XRF	X-ray fluorescence
		Zn	Zinc

AN GHNÍOMHAIREACHT UM CHAOMHNÚ COMHSHAOIL

Tá an Gníomhaireacht um Chaomhnú Comhshaoil (GCC) freagrach as an gcomhshaoil a chaomhnú agus a fheabhsú mar shócmhainn luachmhar do mhuintir na hÉireann. Táimid tiomanta do dhaoine agus don chomhshaoil a chosaint ó éifeachtaí díobhálacha na radaíochta agus an truaillithe.

Is féidir obair na Gníomhaireachta a roinnt ina trí phríomhréimse:

Rialú: Déanaimid córais éifeachtacha rialaithe agus comhlionta comhshaoil a chur i bhfeidhm chun torthaí maithe comhshaoil a sholáthar agus chun díriú orthu siúd nach gcleoíonn leis na córais sin.

Eolas: Soláthraimid sonraí, faisnéis agus measúnú comhshaoil atá ar ardchaighdeán, spriocdhírthe agus tráthúil chun bonn eolais a chur faoin gcinnteoireacht ar gach leibhéal.

Tacaíocht: Bimid ag saothrú i gcomhar le grúpaí eile chun tacú le comhshaoil atá glan, táirgiúil agus cosanta go maith, agus le hiompar a chuirfidh le comhshaoil inbhuanaithe.

Ár bhFreagrachtaí

Ceadúnú

Déanaimid na gníomhaíochtaí seo a leanas a rialú ionas nach ndéanann siad dochar do shláinte an phobail ná don chomhshaoil:

- saoráidí dramhaíola (*m.sh. láithreáin líonta talún, loisceoirí, stáisiúin aistrithe dramhaíola*);
- gníomhaíochtaí tionsclaíocha ar scála mór (*m.sh. déantúsaíocht cógaisíochta, déantúsaíocht stroighne, stáisiúin chumhachta*);
- an diantalmhaíocht (*m.sh. muca, éanlaith*);
- úsáid shrianta agus scaoileadh rialaithe Orgánach Géimhódhnaíthe (*OGM*);
- foinsí radaíochta ianúcháin (*m.sh. trealamh x-gha agus radaiteiripe, foinsí tionsclaíocha*);
- áiseanna móra stórála peitрил;
- scardadh dramhuise; agus
- gníomhaíochtaí dumpála ar farraige.

Forfheidhmiú Náisiúnta i leith Cúrsaí Comhshaoil

- Clár náisiúnta iniúchtaí agus cigireachtaí a dhéanamh gach bliain ar shaoráidí a bhfuil ceadúnas ón nGníomhaireacht acu.
- Maoirseacht a dhéanamh ar fhreagrachtaí cosanta comhshaoil na n-údarás áitiúil.
- Caighdeán an uisce óil, arna sholáthar ag soláthraithe uisce phoiblí, a mhaoirsiú.
- Obair le húdarás áitiúla agus le gníomhaireachtaí eile chun dul i ngleic le coireanna comhshaoil trí chomhordú a dhéanamh ar líonra forfheidhmiúcháin náisiúnta, trí dhírú ar chiontóirí, agus trí mhaoirsiú a dhéanamh ar leasúchán.
- Cur i bhfeidhm rialachán ar nós na Rialachán um Dhramhthrealamh Leictreach agus Leictreonach (DTLL), um Shrian ar Shubstaintí Guaiseacha agus na Rialachán um rialú ar shubstaintí a ídiú an ciseal ózóin.
- An dlí a chur orthu siúd a bhriseann dlí an chomhshaoil agus a dhéanann dochar don chomhshaoil.

Bainistíocht Uisce

- Monatóireacht agus tuairisciú a dhéanamh ar cháilíocht aibhneacha, lochanna, uisce idirchríosacha agus cósta na hÉireann, agus screamhuise; leibhéal uisce agus sruthanna aibhneacha a thomhas.
- Comhordú náisiúnta agus maoirsiú a dhéanamh ar an gCreat-Treoir Uisce.
- Monatóireacht agus tuairisciú a dhéanamh ar Cháilíocht an Uisce Snámha.

Monatóireacht, Anailís agus Tuairisciú ar an gComhshaoil

- Monatóireacht a dhéanamh ar cháilíocht an aeir agus Treoir an AE maidir le hAer Glan don Eoraip (CAFÉ) a chur chun feidhme.
- Tuairisciú neamhspleách le cabhrú le cinnteoireacht an rialtais náisiúnta agus na n-údarás áitiúil (*m.sh. tuairisciú tréimhsúil ar staid Chomhshaoil na hÉireann agus Tuarascálacha ar Tháscairí*).

Rialú Astaíochtaí na nGás Ceaptha Teasa in Éirinn

- Fardail agus réamh-mheastacháin na hÉireann maidir le gás ceaptha teasa a ullmhú.
- An Treoir maidir le Trádáil Astaíochtaí a chur chun feidhme i gcomhair breis agus 100 de na táirgeoirí dé-ocsaíde carbóin is mó in Éirinn.

Taighde agus Forbairt Comhshaoil

- Taighde comhshaoil a chistiú chun brúnna a shainiú, bonn eolais a chur faoi bheartais, agus réitigh a sholáthar i réimsí na haeráide, an uisce agus na hinbhuanaitheachta.

Measúnacht Straitéiseach Timpeallachta

- Measúnacht a dhéanamh ar thionchar pleananna agus clár beartaithe ar an gcomhshaoil in Éirinn (*m.sh. mórfheleananna forbartha*).

Cosaint Raideolaíoch

- Monatóireacht a dhéanamh ar leibhéal radaíochta, measúnacht a dhéanamh ar nochtadh mhuintir na hÉireann don radaíocht ianúcháin.
- Cabhrú le pleananna náisiúnta a fhorbairt le haghaidh éigeandálaí ag eascairt as taismí núicléacha.
- Monatóireacht a dhéanamh ar fhorbairtí thar lear a bhaineann le saoráidí núicléacha agus leis an tsábháilteacht raideolaíochta.
- Sainseirbhísí cosanta ar an radaíocht a sholáthar, nó maoirsiú a dhéanamh ar sholáthar na seirbhísí sin.

Treoir, Faisnéis Inrochtana agus Oideachas

- Comhairle agus treoir a chur ar fáil d'earnáil na tionsclaíochta agus don phobal maidir le hábhair a bhaineann le caomhnú an chomhshaoil agus leis an gcosaint raideolaíoch.
- Faisnéis thráthúil ar an gcomhshaoil ar a bhfuil fáil éasca a chur ar fáil chun rannpháirtíocht an phobail a spreagadh sa chinnteoireacht i ndáil leis an gcomhshaoil (*m.sh. Timpeall an Tí, léarscáileanna radóin*).
- Comhairle a chur ar fáil don Rialtas maidir le hábhair a bhaineann leis an tsábháilteacht raideolaíoch agus le cúrsaí práinnfhreagartha.
- Plean Náisiúnta Bainistíochta Dramhaíola Guaisí a fhorbairt chun dramhail ghuaiseach a chosc agus a bhainistiú.

Múscailt Feasachta agus Athrú Iompraíochta

- Feasacht chomhshaoil níos fearr a ghiniúint agus dul i bhfeidhm ar athrú iompraíochta dearfach trí thacú le gnóthais, le pobail agus le teaghlaigh a bheith níos éifeachtúla ar acmhainní.
- Tástáil le haghaidh radóin a chur chun cinn i dtithe agus in ionaid oibre, agus gníomhartha leasúcháin a spreagadh nuair is gá.

Bainistíocht agus struchtúr na Gníomhaireachta um Chaomhnú Comhshaoil

Tá an ghníomhaíocht á bainistiú ag Bord Iánamseartha, ar a bhfuil Ard-Stiúrthóir agus cúigear Stiúrthóirí. Déantar an obair ar fud cúig cinn d'Oifigí:

- An Oifig um Inmharthanacht Comhshaoil
- An Oifig Forfheidhmithe i leith cúrsaí Comhshaoil
- An Oifig um Fianaise is Measúnú
- An Oifig um Cosaint Raideolaíoch
- An Oifig Cumarsáide agus Seirbhísí Corparáideacha

Tá Coiste Comhairleach ag an nGníomhaireacht le cabhrú léi. Tá dáréag comhaltaí air agus tagann siad le chéile go rialta le plé a dhéanamh ar ábhair inní agus le comhairle a chur ar an mBord.

Health and Water Quality Impacts Arising from Land Spreading of Biosolids



Authors: Mark G. Healy, Owen Fenton, Enda Cummins, Rachel Clarke, Dara Peyton, Ger Fleming, David Wall, Liam Morrison and Martin Cormican

The aims of this study were to: (1) undertake a thorough literature review of the spreading of treated sewage sludge (biosolids) on land to include analysis of potential impacts on environmental and human health; (2) examine, under controlled conditions in the laboratory and field, the impact of the landspreading of biosolids (on grassland) on surface runoff/subsurface drainage/shallow groundwater of nutrients, solids, metals, pathogens and some specified emerging contaminants identified in the literature review, when spread based on N and P application rates; and (3) to model and conduct a risk assessment of potential hazards of human health concern.

Identifying Risks

Implementation of European Union Directives in recent decades concerning the collection, treatment and discharge of wastewater, as well as technological advances in the upgrading and development of wastewater treatment plants, has resulted in an increase in the number of households connected to sewers and an increase in the production of sewage sludge (the by-product of wastewater treatment plants). Recycling to land is currently considered the most economical and beneficial way for municipal sewage sludge management. However, despite the many potential benefits of recycling municipal sewage sludge to land, there are many risks, which include the presence of emerging contaminants in the sewage sludge that may enter the food chain, and the potential for surface runoff of contaminants into receiving waters. This project found that although the application of biosolids poses no greater threat to surface water quality than the land application of dairy cattle slurry, there is a possibility that many non-priority elements and emerging contaminants, for which no legislation currently exists, may be applied to land without regulation, and may accumulate in the soils and enter the food chain.

Informing Policy

Current legislation governing the land application of municipal sewage sludge to land considers certain priority pollutants and bio-essential elements. However, other emerging contaminants may be inadvertently applied to land. Regulations should be extended to cover non-priority elements, pharmaceuticals and personal care products (PPCPs). Non-priority elements are relatively inexpensive to measure, but PPCPs are prohibitively expensive as well as being continuously evolving. Wastewater treatment plants may be upgraded to include treatment of emerging contaminants, but the potential presence of known, as well as currently unknown parameters, raises concerns over the continued application of biosolids to land in Ireland.