



Antimicrobial compounds (triclosan and triclocarban) in sewage sludges, and their presence in runoff following land application

M.G. Healy^a, O. Fenton^b, M. Cormican^c, D.P. Peyton^{a,b}, N. Ordsmith^{d,e}, K. Kimber^{d,e}, L. Morrison^{f,*}

^a Civil Engineering, National University of Ireland, Galway, Ireland

^b Teagasc Johnstown Castle Environment Research Centre, Co., Wexford, Ireland

^c School of Medicine, National University of Ireland, Galway, Ireland

^d Crawford Scientific Ltd., Holm Street, Strathaven, South Lanarkshire, ML10 6NB, Scotland, United Kingdom

^e Hall Analytical Laboratories Ltd., Unit A, Millbrook Business Centre, Floats Road, Manchester M23 9YJ, England, United Kingdom

^f Earth and Ocean Sciences, School of Natural Sciences and Ryan Institute, National University of Ireland, Galway, Ireland

ARTICLE INFO

Keywords:

Triclosan
Triclocarban
Biosolids
Wastewater treatment plants
Surface runoff

ABSTRACT

The reuse of treated municipal sewage (“biosolids”) on land is an effective method to divert waste away from landfill and to use an alternative, low cost method of fertilisation. While legislation has mainly focused on the control of nutrient and metal application rates to land, other potentially harmful emerging contaminants (ECs) may be present in biosolids. Up to 80% of municipal sewage sludge is reused in agriculture in Ireland, which is currently the highest rate of reuse in Europe. However, unlike other countries, no study has been conducted on the presence of ECs across a range of wastewater treatment plants (WWTPs) in this country. This study evaluated the concentrations of two ECs in sewage sludge, the antimicrobials triclosan (TCS) and triclocarban (TCC), and their presence in surface runoff following land application in controlled rainfall simulation studies. In 16 WWTPs, concentrations of TCS and TCC were 0.61 and 0.08 $\mu\text{g g}^{-1}$, which is at the lower end of concentrations measured in other countries. The concentrations in runoff post land application were also mainly below the limits of detection (90 ng L^{-1} for TCS, 6 ng L^{-1} for TCC), indicating that runoff is not a significant pathway of entry into the environment.

1. Introduction

The reuse of treated municipal sewage sludge (“biosolids”) in agriculture provides the necessary nutrients and micronutrients essential for plant and crop growth (Latare et al., 2014; Liu et al., 2015). Biosolids may be used as a soil conditioner, improving its physical (e.g. water holding capacity; Cele and Maboeta, 2016) and chemical properties (e.g. soil test phosphorus; Shu et al., 2016). Their use also addresses European Union (EU) policy on sustainability and recycling of resources (COM, 2014a).

There are several issues associated with the reuse of municipal sewage sludge in agriculture (Peyton et al., 2016). While many of these are issues of perception (Robinson et al., 2012), there is considerable concern, which is scientifically based, regarding a number of substances that may be present in biosolids. There are concerns regarding pharmaceutical and personal care products (PPCPs), antimicrobial compounds, and other endocrine-disrupting compounds and synthetic compounds in biosolids (Clarke and Cummins, 2014) and the associated

risk of contamination of soil, and surface and groundwater (Hanief et al., 2015; Fu et al., 2016). Toxic metals in sludge may accumulate in the soil and crops and enter the food chain following continuous applications to land (Stietiya and Wang, 2011; Latare et al., 2014; García-Santiago et al., 2016). Organic and inorganic contaminants may be lost along surface runoff and leaching pathways following land application (Gottschall et al., 2012; Peyton et al., 2016). Furthermore, there is a risk of emission and transport of bioaerosols containing manure pathogens following land application of biosolids (Brooks et al., 2005; Jahne et al., 2015). These concerns are confounded by the fact that although EU legislation controls the application of biosolids to land by setting limit values for nutrients and metals (EEC, 1986), no safety guidelines currently exist for PPCPs or many emerging contaminants (ECs).

Wastewater treatment plants (WWTPs) cannot fully remove PPCPs or other organic or synthetic compounds from wastewater, the removal of which is affected by treatment technique and operating conditions (Narumiya et al., 2013). Removal pathways include sorption onto

* Corresponding author.

E-mail address: liam.morrison@nuigalway.ie (L. Morrison).

sludge (Ternes et al., 2004) and biodegradation/biotransformation (Verlicchi et al., 2012). Despite this, several compounds have been measured in digested sewage sludge (Walters et al., 2010; Verlicchi and Zambello, 2015). Therefore, when biosolids are spread on land, there is a risk of indirect exposure to humans through several pathways, including the food chain (consumption of crops, meat, dairy products and drinking water), surface runoff, and leaching to land drainage systems or groundwater used for abstraction by water treatment plants. Clarke et al. (2016) developed a quantitative risk ranking model for human exposure to 16 organic contaminants following biosolids application to land. They found that while nonylphenols had the highest risk, the antimicrobials, triclosan (TCS) and triclocarban (TCC), were considered more of an evolving risk, as these contaminants are emerging and have only recently been restricted within the US (US-FDA, 2015a, 2015b) and EU (COM, 2014b). In addition, both compounds are commonly the most abundant contaminants in biosolids (McClellan and Halden, 2010) and both are listed in the top contaminants of concern worldwide (von der Ohe, 2012; Verlicchi and Zambello, 2015). Triclosan, a broad-spectrum bacteriostat and fungicide, and TCC, a fungicide and bacteriostat, are known toxins for humans and have been linked to inhibition of muscle function (Cherednichenko et al., 2012), resistance to antibiotics used in human medicine (Yazdankhah et al., 2006), and ecotoxicity in the environment such as the inhibition and killing of algae, crustaceans and fish (Chalew and Halden, 2009). On account of this, these compounds are the main focus of the current study.

In the EU there are considerable differences in national policy regarding the reuse of biosolids in agriculture. In some countries, such as Belgium (Brussels and Flanders), Switzerland and Romania, the reuse of biosolids in agriculture is prohibited (Milieu et al., 2013a, 2013b, 2013c), whereas in other countries, such as Ireland, up to 80% of municipal wastewater sludge is reused in agriculture (EPA, 2014; Eurostat, 2016). However, despite this, as the country with the greatest reuse of biosolids on land, no study has examined the concentrations of TCS or TCC in biosolids from WWTPs in Ireland. Such national studies of TCS and TCC have been conducted in the USA, Canada, India and South Korea (Table 1), but currently no extensive study across a range of WWTPs exists in the EU.

Once applied to land, TCS and TCC in biosolids may either accumulate in plants (Mathews et al., 2014); accumulate, biodegrade or biotransform in soil (Wu et al., 2009), or be released in surface runoff during rainfall-runoff or leaching events (Sabourin et al., 2009). The potential for loss via surface runoff or leaching depends on their availability in soil, which is a function of their persistence or half-life (Fu et al., 2016). It has been speculated that the persistence of TCS or TCC in the soil may be enhanced by the organic content of the soil (Fu et al., 2016), soil temperature (which is positively correlated to half-life), the physicochemical properties of the compounds (Wu et al., 2009), and the presence of co-contaminants (Walters et al., 2010), making them potentially more available for loss in surface runoff during rainfall events. Many studies have investigated losses of TCS and TCC in surface runoff from agricultural lands (Table 2), but few, if any, studies have investigated the surface losses from lands which have received

sludge applications from the same WWTP having undergone different treatments. Such an experiment may allow the potential for surface water contamination from different sludge treatment methods to be evaluated.

Therefore, the aim of this study was to (1) characterise, for the first time, the TCS and TCC in biosolids from a range of WWTPs in Ireland, and (2) measure the surface runoff of TCS and TCC under successive rainfall simulations at 1, 2 and 15 days after application of two types of biosolids, originating from the same WWTP.

2. Methodology

2.1. WWTP identification and sample collection

In January and February 2015 (Winter in Ireland), biosolids were collected from 16 WWTPs, which had population equivalents (PEs, i.e. the amount of oxygen demanding substances in wastewater equivalent to the demand of the wastewater produced by a single person) ranging from 2.3 million to 6500. Details of the PE and influent wastewater characteristics of each WWTP are given in Healy et al. (2016a). Most WWTPs received quantities of landfill leachate in low quantities (less than 2% of the influent biochemical oxygen demand (BOD) load), whilst others received industrial, commercial and domestic septic tank sludge comprising up to 30% of the influent BOD load. Anaerobic digestion of sewage sludge was carried out in five WWTPs, thermal drying in eight WWTPs, and lime stabilisation in four WWTPs (one WWTP carried out both anaerobic digestion and thermal drying). Discrete samples (n=8) of biosolids were collected in clean LDPE containers from each WWTP, and were pulverised in an agate ball mill (Fritsch™ Pulverisette 6 Panetary Mono Mill) with a rotational speed of 500 rpm for 5 min (repeated three times). The metal content of the biosolids are reported in Healy et al. (2016a).

2.2. Field study site description and runoff simulations

Treated municipal sewage sludge from the WWTP in which anaerobic digestion and thermal drying was carried out, was used in this study. Raw, untreated sludge from the same WWTP was modified by the authors with calcium oxide following the method outlined by Fehily Timoney and Company (1999). Therefore, the anaerobically digested (AD), thermally dried (TD) and lime stabilised (LS) biosolids used in this study originated from the same WWTP. The biosolids were applied to replicated (n=3), hydraulically isolated, field-scale micro-plots, each measuring 0.4 m-wide by 0.9 m-long. The slope of each micro-plot ranged from 2.9% to 3.7% and each micro-plot was instrumented with a runoff collection channel, which allowed all surface runoff to be collected over the duration of a rainfall event (Peyton et al., 2016). The site was planted with ryegrass for over twenty years and the soil pH ranged from 5.9 to 6. The soil in all micro-plots was classified as loam and the soil organic matter ranged from 8.1% to 9.0%. Full classification of the plots is detailed in Peyton et al. (2016).

Anaerobically digested, TD and LS biosolids were applied by hand to the surface of each micro-plot at the maximum legal application rate in

Table 1
Triclosan and triclocarban concentrations ($\mu\text{g g}^{-1}$ dry weight) in national studies of biosolids produced in municipal wastewater treatment plants.

Reference	Country	# WWTPs examined	Mean concentration ($\mu\text{g g}^{-1}$)		Maximum concentration ($\mu\text{g g}^{-1}$)	
			Triclosan	Triclocarban	Triclosan	Triclocarban
McClellan and Halden (2010)	USA	94	12.6	36	19.7	48.1
Subedi et al. (2015)	India	5	1.2	7.0		
Chu and Metcalfe (2007)	Canada	4	4.2	4.3		
Guerra et al. (2014)	Canada	6	6.8	2.9	11.0	8.9
Subedi et al. (2014)	S. Korea	40		3.1		6.9
This study	Ireland	16	0.61	0.08	4.9	0.15

Table 2
Studies examining the surface losses of triclosan and triclocarban from land applied biosolids.

Reference	Type of sludge used	Compound in biosolids ($\mu\text{g g}^{-1}$)		Application rate (expressed as dry matter)	Concentration in surface water (ng L^{-1})		Time of detection (days post application)
		Triclosan	Triclocarban		Triclosan	Triclocarban	
Edwards et al. (2009)	Anaerobically digested	14	8	$\sim 8 \text{ Mt ha}^{-1}$	240	< LOQ	
Gottschall et al. (2012)	Anaerobically digested	10.9	4.9	$\sim 22 \text{ t ha}^{-1}$	73	40	22
Topp et al. (2008)	Not stated			$92,500 \text{ L ha}^{-1}$	258		1
This study ^a	Anaerobically digested	0.27	< 2.4	6.7 t ha^{-1}	< 90	< 6	15
	Thermally dried	4.9	0.05	2.6 t ha^{-1}	< 90	< 6	15

^a Values in this study were below the limits of detection (90 ng L^{-1} for triclosan and 6 ng L^{-1} for triclocarban). First row refers to anaerobically digested sludge, second row refers to thermally dried sludge.

Ireland (Statutory Instrument 610 of 2010), which is currently $40 \text{ kg phosphorus (P) ha}^{-1}$. As the P content and the dry matter (DM) of the biosolids varied, the application rates were equivalent to 2.6 t DM ha^{-1} for TD biosolids (97 g per plot), 6.7 t DM ha^{-1} for AD biosolids (242 g per plot), and $29.5 \text{ t DM ha}^{-1}$ for LS biosolids (1063 g per plot). The biosolids used in this experiment were natural and were not spiked with either triclosan or triclocarban. As the experiment was designed to compare the surface runoff from plots amended with three types of biosolids, no study control (grass only) plots were used in this experiment.

A rainfall simulator was used to apply rainfall to each micro-plot at intensity of approximately 11 mm h^{-1} (corresponding to a 3 year return period in Ireland; Met Éireann, 2016) in time intervals of 1, 2 and 15 d after the time of biosolids application. Each rainfall simulation lasted 30 min from the time of first occurrence of surface runoff. Runoff water samples were collected in solvent washed amber glass Pyrex® bottles with PTFE lined lids and upon returning the laboratory, 4 mol L^{-1} of sulphuric acid (H_2SO_4) was added to adjust the water to pH 3 to prevent biodegradation by microorganisms. Samples were then stored and frozen at $-20 \text{ }^\circ\text{C}$ until analysis.

2.3. Analysis of triclosan and triclocarban in biosolids and surface runoff

The method of analysis for TCS and TCC in the biosolids and surface runoff was conducted in accordance with USEPA Method 1694 (USEPA, 2007) for the determination of pharmaceuticals and personal care products in water, soil, sediment, and biosolids by liquid chromatography tandem-mass spectrometry (HPLC-MS/MS) analyses (McClellan and Halden, 2010; Walters et al., 2010; Klosterhaus et al., 2013).

LC-MS-MS analyses was performed using a Waters Xevo™ TQ MS triple-quadrupole mass spectrometer (Waters Corp., Milford, MA, USA) coupled with a Waters Acquity UPLC™ system (Waters Corp., Milford, MA, USA) using reverse phase chromatography. Experimentation was based upon the conditions specified in the USEPA Method 1694, and summarised in Table S1 of the Supplementary material. Details on the methodology employed may also be found in the Supplementary material.

3. Results and discussion

3.1. Triclosan and triclocarban content of biosolids from WWTPs

The TCS and TCC concentrations in the biosolids samples are shown in the Fig. 1. The concentrations of compounds in sewage sludge are dependent on the influent wastewater characteristics, and up to 50% of the mass of TCS entering a WWTP may remain in the sludge (Heidler and Halden, 2007). Studies have examined the effectiveness of various sludge treatment methods (e.g. Carballa et al., 2007), but there is no indication that one form of treatment is more efficient in TCS or TCC

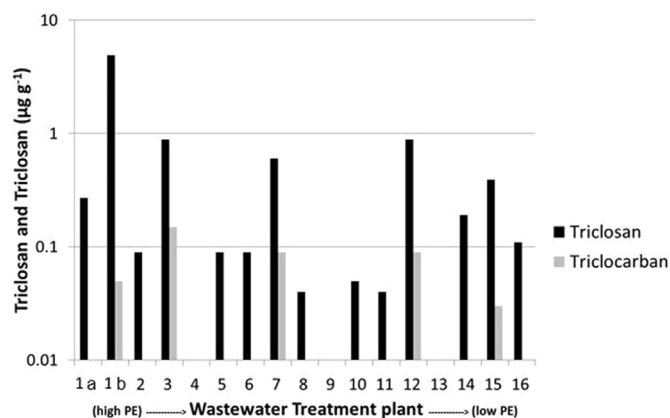


Fig. 1. Triclosan and triclocarban concentrations ($\mu\text{g g}^{-1}$) in treated sludge from 16 wastewater treatment plants in Ireland, ranging (numerically in ascending order) from a population equivalent (PE) of 2.3 million to 6500. Two forms of treatment of sludge are carried out in one WWTP: anaerobic digestion (1a) and thermal drying (1b). WWTPs with no concentrations shown are WWTPs in which triclosan or triclocarban were below the limits of detection (TCS, $0.006 \mu\text{g g}^{-1}$ and TCC, $0.0024 \mu\text{g g}^{-1}$).

removal.

One of the WWTPs examined (1a and 1b in Fig. 1) had a history of high concentrations of TCS, with concentrations of $25 \mu\text{g g}^{-1}$ previously being reported (EPA, 2009), 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 parameters measured in this study ranked the lowest (Table 1). This may be due to the fact that TCS has been restricted in the EU since 2014 (COM, 2014b), whereas its use in ‘consumer antiseptic wash products’ will only be restricted in the USA from September 2017 (US-FDA, 2015b). The use of TCC has been phased out by pharmaceutical companies in the last number of years (Westervelt, 2014). The biosolids 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 as have been measured in other studies (Martin et al., 2012).

3.2. Triclosan and triclocarban content of surface runoff

The surface runoff concentrations of TCS and TCC were below the LOD in all cases, with the exception of TD biosolids at 15 days ($0.01 \mu\text{g L}^{-1}$) and LS biosolids ($0.02 \mu\text{g L}^{-1}$) one day after application (Table 3). 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 likely to be potentially impacted (120 ng L^{-1} for TCS, Wilson et al. (2003); 101 ng L^{-1} for TCC, McClellan and Halden (2010)). The low concentrations in surface

Table 3

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

	Triclosan			Triclocarban				
	TCS in applied sludge dose $\mu\text{g g}^{-1}$	1 d $\mu\text{g L}^{-1}$	2 d	15 d	TCC in applied sludge dose $\mu\text{g g}^{-1}$	1 d $\mu\text{g L}^{-1}$	2 d	15 d
TD	4.9	< LOD	< LOD	< LOD	0.05	< LOD	< LOD	0.01
LS	Not measured	< LOD	< LOD	< LOD	Not measured	0.02	< LOD	< LOD
AD	0.27	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

runoff may have been a function of the low TCS and TCC concentrations in the biosolids applied to land relative to similar studies (Table 2), but more likely were either due to their degradation or transformation to other compounds, or due to the soil characteristics at the study site. Less than 0.5% of the mass of TCS and TCC applied to each plot was lost in each rainfall event (Table 3). Similar results (expressed as a % of mass released versus mass of compound applied) were obtained in a runoff study by Sabourin et al. (2009), who speculated that they remained sequestered in the soil or were leached to groundwater. The relationship between persistence of organic or synthetic compounds and the composition and physico-chemical properties of soil is well established in the literature (Verlicchi and Zambello, 2015). As reported in other studies (Wu et al., 2009), the high soil organic matter content in the micro-plots of the current study (8.1–9.0%) may have adsorbed some of the TCS and TCC. Unlike other studies which had durations ranging from 46 days (Wu et al., 2009) to 60 days (Fu et al., 2016), it was impossible to determine if the addition of the biosolids altered the soil's physicochemical properties, as soil analysis was only conducted before the experiment commenced and at the end of the experiment (15 days after application of biosolids) (Peyton et al., 2016), which is too short a period to determine if such changes occur.

Another factor influencing the persistence of organic and synthetic compounds is the manner in which they are applied to the soil. Al-Rajab et al. (2015) reported that dissipation of PPCPs and antimicrobials, including TCS and TCC, increase over a duration of several months if they are placed below the soil surface (i.e. through ground injection systems). Therefore, the surface runoff of TCS and TCC in the current study may have been further reduced if the biosolids were applied in the soil subsurface.

3.3. Impact of the experiment results on reuse of biosolids in agriculture

The current study forms part of a larger study in which the metal content of biosolids from a selection of WWTPs were evaluated (Healy et al., 2016a), and the loss of nutrients, metals and pathogens in surface runoff (Peyton et al., 2016) and the uptake of metals by ryegrass following their land application was quantified (Healy et al., 2016b). For the water quality parameters analysed in these studies, the environmental impacts on receiving waters arising from the land-spreading of biosolids are no different to those arising from the land-spreading of, for example, dairy cattle slurry (Brennan et al., 2012). It was also found that the metal content of ryegrass in biosolids-amended plots and control plots were similar (Healy et al., 2016b).

While the metal, TCS and TCC contents of the biosolids in the WWTPs examined in our studies were below the concentrations measured elsewhere, there may be 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 no clear basis for determining if the concentrations of TCS and TCC, as measured in the current study, are safe. Furthermore, the current study only examined two types of antimicrobials, which is only a small fraction of the total number of contaminants that may be present in biosolids. Parameter testing of this type is extremely expensive, so the costs of routinely

testing sludge for all possible contaminants would be prohibitive. While most commentators have stated that the risk to human health following dietary intake of organic contaminants from crops grown on biosolids-amended lands is minimal (Verslycke et al., 2016), they acknowledge that a certain amount of uncertainty still exists (Smith, 2009; Oun et al., 2014). On account of these issues, and public perception issues in particular, many countries have prohibited the use of biosolids in agriculture, and even in those countries that permit their use, local restrictions exist (e.g. Bord Bia, 2013). This conservative ethos has a substantial 'buy-in' from major industries, who use products sourced from agricultural land, as there would be reputational damage to a brand if it emerged that biosolids, which could potentially contain ECs, were used in the production of their feedstock.

Although legislation has attempted to address public concern by regulating the amount of biosolids applied to land, there are considerable differences in national policy regarding the reuse of biosolids in agriculture. In Europe, the application of biosolids to land is governed by EU Directive 86/278/EEC (EEC, 1986), which is based on the nutrient and metal content of the biosolids (although more stringent guidelines are enforced in some member states). In comparison, in the majority of states of the USA, biosolids are applied to land based on the nitrogen requirement of the crop being grown and not on a soil-based test (McDonald and Wall, 2011). It would be impossible to fully regulate the application rates of all potential contaminants in biosolids, so while legislation has mainly focused on nutrient and metal content of biosolids, the possibility exists that other potentially harmful, unregulated ECs, for which no international standards exist for reuse in agriculture, may accumulate in the soil upon repeated application.

4. Conclusions

There were low concentrations of triclosan and triclocarban in treated sewage sludge across a number of WWTPs of varying PE. In addition, measurements of triclosan and triclocarban in surface runoff following land application were at or below the limits of detection, which indicates that there appears to be no risk of acute biological effects as a result of runoff.

There is a need to fully quantify the concentration of pharmaceuticals and other emerging contaminants in treated municipal wastewater, particularly in countries that recycle a high percentage of sludge produced in municipal sewage treatment plants in agriculture. To fully characterise all existing known, 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.

Acknowledgements

The authors wish to acknowledge funding from the Irish EPA (Project reference number 2012-EH-MS-13).

Appendix A. Supporting material

Supplementary data associated with this article can be found in the

online version at <http://dx.doi.org/10.1016/j.ecoenv.2017.04.046>.

References

- Al-Rajab, A.J., Sabourin, L., Lapen, D.R., Topp, E., 2015. Dissipation of triclosan, triclocarban, carbamazepine and naproxen in agricultural soil following surface or sub-surface application of dewatered municipal biosolids. *Sci. Total Environ.* 512–513, 480–488.
- Bord Bia, 2013. Sustainable dairy assurance scheme – producer Standard. <<http://www.bordbia.ie/industry/farmers/quality/SQASDocuments/SustainableDairyAssuranceScheme-ProducerStandard.pdf>> (Accessed January 2017).
- Brennan, R.B., Healy, M.G., Grant, J., Ibrahim, T.G., Fenton, O., 2012. Incidental phosphorus and nitrogen loss from grassland plots receiving chemically amended dairy cattle slurry. *Sci. Total Environ.* 441, 132–140.
- Brooks, J.P., Tanner, B.D., Josephson, K.L., Gerba, C.P., Haas, C.N., Pepper, I.L., 2005. A national study on the residential impact of biological aerosols from the land application of biosolids. *J. Appl. Microbiol.* 99, 310–322.
- Carballa, M., Manterola, G., Larrea, L., Ternes, T., Omil, F., Lema, J.M., 2007. Influence of ozone pre-treatment on sludge anaerobic digestion: removal of pharmaceutical and personal care products. *Chemosphere* 67, 144–1452.
- Cele, E.N., Maboeta, M., 2016. A greenhouse trial to investigate the ameliorative properties of biosolids and plants on physicochemical conditions of iron ore tailings: implications for an iron ore mine site remediation. *J. Environ. Manag.* 165, 167–174.
- Chalew, T.E.A., Halden, R.U., 2009. Environmental exposure of aquatic and terrestrial biota to triclosan and triclocarban. *J. Am. Water Resour. Assoc.* 45, 4–13.
- Cherednichenko, G., Zhang, R., Bannister, R.A., Timofeyev, V., Li, N., Fritsch, E.B., Feng, W., Barrientos, G.C., Schebb, N.H., 2012. Triclosan impairs excitation-contraction coupling and Ca²⁺ dynamics in striated muscle. *Proc. Natl. Acad. Sci. USA* 109, 14158–14163.
- Chu, S., Metcalfe, C.D., 2007. Simultaneous determination of triclocarban and triclosan in municipal biosolids by liquid chromatography tandem mass spectrometry. *J. Chromatogr. A* 1164, 212–218.
- Clarke, R.M., Cummins, E., 2014. Evaluation of ‘classic’ and emerging contaminants resulting from the application of biosolids to agricultural lands: a review. *Hum. Ecol. Risk Assess.* 21, 492–513.
- Clarke, R.M., Healy, M.G., Fenton, O., Cummins, E., 2016. A quantitative risk ranking model to evaluate emerging contaminants in biosolid amended land and potential transport to drinking water. *Hum. Ecol. Risk Assess.* 22, 958–990.
- Commission of the European Communities (COM), 2014a. Towards a circular economy: a zero waste programme for Europe. <http://eur-lex.europa.eu/resource.html?uri=cellar:aa88c66d-4553-11e4-a0cb-01aa75ed71a1.0022.03/DOC_1&format=PDF> (Accessed January 2017).
- Commission of the European Communities (COM), 2014b. Commission regulation (EU) no. 358/2014 of 9 April 2014 amending annexes II and V to regulation (EC) No 1223/2009 of the European Parliament and of the Council on cosmetic products. *Official Journal of the European Union* L107/5. <<http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=OJ:L:2014:107:FULL&from=EN>> (Accessed January 2017).
- Edwards, M., Topp, E., Metcalfe, C.D., Li, H., Gottschall, N., Bolton, P., Curoe, W., Payne, M., Beck, A., Kleywegt, S., Lapen, D.R., 2009. Pharmaceutical and personal care products in tile drainage following surface spreading and injection of dewatered municipal biosolids to an agricultural field. *Sci. Total Environ.* 407, 4220–4230.
- EEC, 1986. Council Directive of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture (86/278/EEC). <<http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:31986L0278&from=EN>> (Accessed January 2017).
- EPA, 2009. Occurrence and fate of pharmaceuticals and personal care products within sewage sludge and sludge-enriched soils. EPA Strive Report Series No. 34. <https://www.epa.ie/pubs/reports/research/waste/STRIVE_34_Barron_PCPs_web.pdf.pdf> (Accessed January 2017).
- EPA, 2014. Urban waste water treatment in 2014. <http://www.epa.ie/pubs/reports/water/wastewater/2014%20waste%20water%20report_web.pdf> (Accessed January 2017).
- Eurostat, 2016. Sewage sludge production and disposal from urban wastewater (in dry substance (d.s.)). <<http://ec.europa.eu/eurostat/web/products-datasets/-/ten00030>> (Accessed January 2017).
- Fehily Timoney and Company, 1999. Codes of good practice for the use of biosolids in agriculture – guidelines for farmers. <<http://www.environ.ie/en/Publications/Environment/Water/FileDownload,17228,en.pdf>>.
- Fu, Q., Sanganyado, E., Ye, Q., Gan, J., 2016. Meta-analysis of biosolid effects on persistence of triclosan and triclocarban in soil. *Environ. Poll.* 210, 137–144.
- García-Santiago, X., Franco-Uría, A., Omil, F., Lema, J.M., 2016. Risk assessment of persistent pharmaceuticals in biosolids: dealing with uncertainty. *J. Hazard. Mater.* 302, 72–81.
- Gottschall, N., Topp, E., Metcalfe, C., Edwards, M., Payne, M., Kleywegt, S., Russell, P., Lapen, D.R., 2012. Pharmaceutical and personal care products in groundwater, subsurface drainage, soil, and wheat grain, following a high single application of municipal biosolids to a field. *Chemosphere* 87, 194–203.
- Guerra, P., Kim, M., Shah, A., Alae, M., Smyth, S.A., 2014. Occurrence and fate of antibiatic, analgesic/anti-inflammatory, and antifungal compounds in five wastewater treatment processes. *Sci. Total Environ.* 473–474, 235–243.
- Hanief, A., Mattichine, D., Laursen, A.E., Bostan, I.V., McCarthy, L.H., 2015. Nitrogen and phosphorus loss potential from biosolids-amended soils and biotic response in the receiving water. *J. Environ. Qual.* 44, 1293–1303.
- Healy, M.G., Fenton, O., Forrestal, P.J., Danaher, M., Brennan, R.B., Morrison, O., 2016a. Metal concentrations in lime stabilised, thermally dried and anaerobically digested sewage sludges. *Waste Manag.* 48, 404–408.
- Healy, M.G., Ryan, P.C., Fenton, O., Peyton, D.P., Wall, D.P., Morrison, L., 2016b. Bioaccumulation of metals in ryegrass (*Lolium perenne* L.) following the application of lime stabilised, thermally dried and anaerobically digested sewage sludge. *Ecotoxicol. Environ. Saf.* 130, 303–309.
- Heidler, J., Halden, R.U., 2007. Mass balance assessment of triclosan removal during conventional sewage treatment. *Chemosphere* 66, 362–369.
- Jahne, M.A., Rogers, S.W., Holsen, T.M., Grimberg, S.J., Ramler, I.P., 2015. Emission and dispersion of bioaerosols from dairy manure application sites: human health risk assessment. *Environ. Sci. Technol.* 49, 9842–9849.
- Klosterhaus, S.L., Grace, R., Hamilton, M.C., Yee, D., 2013. Method validation and reconnaissance of pharmaceuticals, personal care products, and alkylphenols in surface waters, sediments and mussels in an urban estuary. *Environ. Int.* 54, 92–99.
- Latere, A.M., Kumar, O., Singh, S.K., Gupta, A., 2014. Direct and residual effect of sewage sludge on yield, heavy metals content and soil fertility under rice-wheat system. *Ecol. Eng.* 69, 17–24.
- Liu, X.A., Fike, J.H., Galbraith, J.M., Fike, W.B., Parrish, D.J., Evanylo, G.K., Strahm, B.D., 2015. Effects of harvest frequency and biosolids application on switchgrass yield, feedstock quality, and theoretical ethanol yield. *Glob. Change Biol.* 7, 112–121.
- Martin, J., Camacho-Muñoz, D., Santos, J.L., Aparicio, I., Alonso, E., 2012. Distribution and temporal evolution of pharmaceutically active compounds alongside sewage sludge treatment. risk assessment of sludge application onto soils. *J. Environ. Manag.* 102, 18–25.
- Mathews, S., Henderson, S., Reinhold, D., 2014. Uptake and accumulation of antimicrobials, triclocarban and triclosan, by food crops in a hydroponic system. *Environ. Sci. Pollut. Res.* 21, 6025–6033.
- McClellan, K., Halden, R.U., 2010. Pharmaceuticals and personal care products in archived U.S. biosolids from the 2001 EPA national sewage sludge survey. *Water Res.* 44, 658–668.
- McDonald, N., Wall, D., 2011. Soil specific N advice – utilising our soil nitrogen resources. National Agri-environment Conference 2011 10 November 2011, Athlone. <http://www.teagasc.ie/publications/2011/1050/Agrienvironment_Proceedings.pdf> (Accessed January 2017).
- Met Éireann, 2016. Rainfall return periods table. <<http://www.met.ie/climate/products03.asp>> (Accessed January 2017).
- Milieu, WRC, 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, WRC, 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, WRC, 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.
- Narumiya, M., Nakada, N., Yamashita, N., Tanaka, H., 2013. Phase distribution and removal of pharmaceuticals and personal care products during anaerobic sludge digestion. *J. Hazard. Mater.* 260, 305–312.
- Oun, A., Kumar, A., Harrigan, T., Angelakis, A., Xagorarakis, I., 2014. Effects of biosolids and manure application on microbial water quality in rural areas in the US. *Water* 6, 3701–3723.
- Peyton, D.P., Healy, M.G., Fleming, G.T.A., Grant, J., Wall, D., Morrison, L., Cormican, M., Fenton, O., 2016. Nutrient, metal and microbial loss in surface runoff following treated sludge and dairy cattle slurry application to an Irish grassland soil. *Sci. Total Environ.* 541, 218–229.
- Robinson, K.G., Robinson, C.H., Raup, L.A., Markum, T.R., 2012. Public attitudes and risk perception toward land application of biosolids within the south-eastern United States. *J. Environ. Manag.* 98, 29–36.
- Sabourin, L., Beck, A., Duenk, P.W., Kleywegt, S., Lapen, D.R., Li, H., Metcalfe, C.D., Payne, M., Topp, E., 2009. Runoff of pharmaceuticals and personal care products following application of dewatered municipal biosolids to an agricultural field. *Sci. Total Environ.* 407, 4596–4604.
- Shu, W., Price, G.W., Sharifi, M., Cade-Menun, B.J., 2016. Impact of annual and single application of alkaline treated biosolids on soil extractable phosphorus and total phosphorus. *Agric. Ecosyst. Environ.* 219, 111–118.
- Smith, S.R., 2009. Organic contaminants in sewage sludge (biosolids) and their significance for agricultural recycling. *Philos. Trans. Roy. Soc. A* 367, 4005–4041.
- Statutory Instrument (SI) 610 of 2010. European Communities (Good Agricultural Practice for Protection of Waters) Regulations 2010. <<http://www.teagasc.ie/pigs/advisory/docs/NitratesDirectiveS.I.610.pdf>> (Accessed January 2017).
- Stietiya, M.H., Wang, J.J., 2011. Effect of organic matter oxidation on the fractionation of copper, zinc, lead, and arsenic in sewage sludge and amended soils. *J. Environ. Qual.* 40, 1162–1171.
- Subedi, B., Lee, S., Moon, H.-B., Kannan, K., 2014. Emission of artificial sweeteners, select pharmaceuticals, and personal care products through sewage sludge from wastewater treatment plants in Korea. *Environ. Int.* 68, 33–40.
- Subedi, B., Balakrishna, K., Sinha, R.K., Yamashita, N., Balasubramanian, V.G., Kannan, K., 2015. Mass loading and removal of pharmaceuticals and personal care products, including psychoactive and illicit drugs and artificial sweeteners, in five sewage treatment plants in India. *J. Environ. Chem. Eng.* 3, 2882–2891.
- Ternes, T.A., Joss, A., Siegrist, H., 2004. Peer reviewed: scrutinizing pharmaceuticals and personal care products in wastewater treatment. *Environ. Sci. Technol.* 38, 392A–399A.
- Topp, E., Monteiro, S.C., Beck, A., Ball Coelho, B., Boxall, A.B.A., Duenk, P.W., Kleywegt, S., Lapen, D.R., Payne, M., Sabourin, L., Li, H., Metcalfe, C.D., 2008. Runoff of pharmaceuticals and personal care products following application of biosolids to an agricultural field. *Sci. Total Environ.* 396, 52–59.

- United States Food and Drug Authority (USFDA), 2015a. FDA taking closer look at 'antibacterial' soap. <<http://www.fda.gov/ForConsumers/ConsumerUpdates/ucm378393.htm>> (Accessed January 2017).
- United States Food and Drug Authority (USFDA), 2015b. Safety and effectiveness of consumer antiseptics; topical antimicrobial drug products for over-the-counter human use. <<https://www.federalregister.gov/documents/2016/09/06/2016-21337/safety-and-effectiveness-of-consumer-antiseptics-topical-antimicrobial-drug-products-for>> (Accessed January 2017).
- USEPA, 2007. Method 1694: Pharmaceuticals and personal care products in water, soil, sediment, and biosolids by HPLC/MS/MS. Washington, D.C.
- Verlicchi, P., 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. *Sci. Total Environ.* 538, 750–767.
- Verlicchi, P., Al Aukidy, M., Zambello, E., 2012. Occurrence of pharmaceutical compounds in urban wastewater: removal, mass load and environmental risk after a secondary treatment – a review. *Sci. Total Environ.* 429, 123–155.
- Verslycke, T., Mayfield, D.B., Tabony, J.A., Capdevielle, M., Slezak, B., 2016. Human health risk assessment of triclosan in land-applied biosolids. *Environ. Toxicol. Chem.* <http://dx.doi.org/10.1002/etc.3370>.
- Von der Ohe, P.C., Schmitt-Jansen, M., Slobodnik, J., Brack, W., 2012. Triclosan – the forgotten priority substance? *Environ. Sci. Pollut. Res.* 19, 585–591.
- Walters, E., McClellan, K., Halden, R.U., 2010. Occurrence and loss over three years of 72 pharmaceuticals and personal care products from biosolids-soil mixtures in outdoor mesocosms. *Water Res.* 44, 6011–6020.
- Westervelt, A., 2014. Avon plans to remove triclosan from products, but what will replace it? <<https://www.theguardian.com/sustainable-business/avon-remove-triclosan-product-cosmetic-chemicals>> (Accessed January 2017).
- Wilson, B.A., Smith, V.H., Denoyelles, F., Larive, G.K., 2003. Effects of three pharmaceutical and personal care products on natural freshwater algal assemblages. *Environ. Sci. Technol.* 37, 1713–1719.
- Wu, C., Spongberg, A.L., Witter, J.D., 2009. Adsorption and degradation of triclosan and triclocarban in soils and biosolids-amended soils. *J. Agric. Food Chem.* 57, 4900–4905.
- Yazdankhah, S.P., Scheie, A.A., Hoiby, E.A., Lunestad, B.T., Heir, E., Fotland, T.O., Natersted, K., Kruse, H., 2006. Triclosan and antimicrobial resistance in bacteria: an overview. *Microb. Drug Resist.* 12, 83–90.