Science of the Total Environment 566–567 (2016) 102–112

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

A quantitative risk assessment for metals in surface water following the application of biosolids to grassland

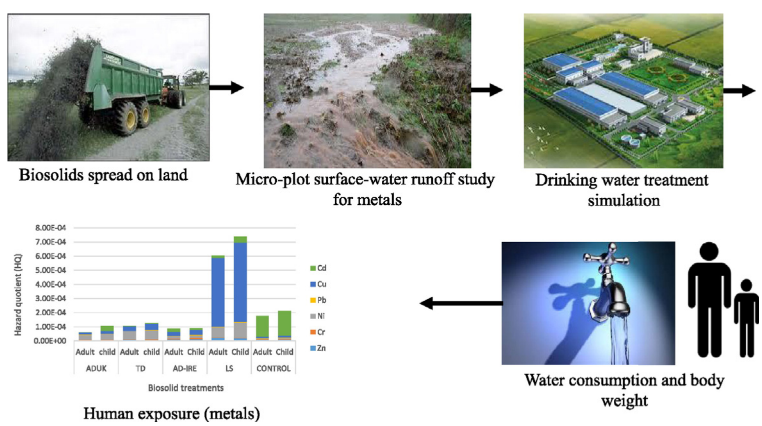
Rachel Clarke [a,*], Dara Peyton [b], Mark G. Healy [b], Owen Fenton [c], Enda Cummins [a]

[a] School of Biosystems and Food Engineering, Agriculture and Food Science Centre, University College Dublin, Belfield, Dublin 4, Ireland
[b] Civil Engineering, National University of Ireland, Galway, Co. Galway, Ireland
[c] Teagasc Environment Research Centre, Johnstown Castle, Co. Wexford, Ireland

HIGHLIGHTS

- The application of biosolids on agricultural land may lead to accumulation of metals in soil.
- Results show that child exposure was highest for copper and lime stabilised biosolids.
- Sensitivity analysis reveal tap water intake and filtration reduction as parameters of importance.
- Metal concentrations in the biosolids were not considered a risk to human health.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 January 2016
Received in revised form 10 May 2016
Accepted 13 May 2016
Available online xxxx

Editor: F.M. Tack

Keywords:
Biosolids
Drinking water
Metals
Risk
Water treatment

ABSTRACT

During episodic rainfall events, land application of treated municipal sludge ('biosolids') may give rise to surface runoff of metals, which may be potentially harmful to human health if not fully treated in a water treatment plant (WTP). This study used surface runoff water quality data generated from a field-scale study in which three types of biosolids (anaerobically digested (AD), lime stabilised (LS), and thermally dried (TD)) were spread on micro-plots of land and subjected to three rainfall events at time intervals of 24, 48 and 360 h following application. Making the assumption that this water directly entered abstraction waters for a WTP without any grassed buffer zone being present, accounting for stream dilution, and modelling various performance scenarios within the WTP, the aim of this research was to conduct a human health risk assessment of metals (Cu, Ni, Pb, Zn, Cd and Cr), which may still be present in drinking water after the WTP. Different dose-response relationships were characterised for the different metals with reference to the lifetime average daily dose (LADD) and the Hazard Quotient (HQ). The results for the LADD show that child exposure concentrations were highest for Cu when the measured surface runoff concentrations from the LS biosolids treatment were used as input into the model. The results for the HQ showed that of all the scenarios considered, Cu had the highest HQ for children. However, values were below the threshold value of risk (HQ < 0.01 - no existing risk). Under the conditions monitored, metal concentrations in the biosolids applied to grassland were not considered to result in a risk to human health in surface water systems.

* Corresponding author.
E-mail addresses: rachel.clarke.1@ucdconnect.ie (R. Clarke), enda.cummins@ucd.ie.ph (E. Cummins).

http://dx.doi.org/10.1016/j.scitotenv.2016.05.092
0048-9697/

1. Introduction

Long-term application of treated municipal sewage sludge ('biosolids') to agricultural land has led to concerns regarding the potential accumulation of metals in soil, their subsequent runoff into surface waters, and the potential risk to human health through drinking water consumption. While the environmental occurrence of these contaminants is usually low (μg kg^{-1} down to sub ng kg^{-1}), toxicologists, epidemiologists and risk assessment experts advise that there may still be significant and widespread adverse environmental and human health consequences (i.e. cancer risk and adverse reproductive development) at the detected levels (Clarke and Cummins, 2014). The metals of concern and those primarily linked to human poisoning are lead (Pb), iron (Fe), copper (Cu), cadmium (Cd), zinc (Zn), chromium (Cr), mercury (Hg) and arsenic (As) (Singh et al., 2011; Tchounwou et al., 2012). Essential metals such as Cu, Zn and Cr are required by the body in trace amounts, but can be toxic in large doses (Mohod and Dhote, 2013). A distinguishable feature of metals is that, unlike any other toxic substance, they are not biodegradable and can accumulate in the sludge to potentially toxic concentrations (Chen et al., 2008). The main cause of this toxic effect is due to the chemical binding of metals to enzymes and subsequent disruption to enzyme structure and function (Appels et al., 2008). Metal toxicity can result in brain damage or a reduction in mental processes (Fernández-Luqueño et al., 2013). Salem et al. (2000) reported that in some cities in Egypt, there was a strong correlation between consumption of water heavily contaminated with metals and chronic diseases such as renal failure, liver cirrhosis, chronic anaemia and hair loss. Excessive consumption of Cu can lead to gastrointestinal problems, kidney damage, anaemia and lung cancer (Mahiya et al., 2014). Children are more vulnerable to metal exposure, which can lead to several paediatric effects including neurodevelopment disorders (Oyoo-Okoth et al., 2013). Davis et al. (2014) reported that infants and children are more vulnerable to neurotoxic effects of metals due to more rapid bone growth and differences in physiology, even at low levels of exposure. Due to the adverse effects on the central nervous system, the US Centre for Disease Control and Prevention (CDC) introduced guidelines that identifies a blood level > 0.48 μmol Pb L^{-1} (100 μg L^{-1}) to be of concern in children, and it was recommended to lower the Pb level to 0.24 μmol Pb L^{-1} (50 μg L^{-1}), the amount that sometimes may occur as background levels in some countries (Nordberg et al., 2014).

Increasingly, there is evidence to show negative health effects from cumulative, lower level exposures to some metals (Tchounwou et al., 2012). The biological half-lives of metals vary and the amounts excreted can reflect a combination of recent and past exposures (Quandt et al., 2010). For instance, the half-life of Cd is one-to-four decades, and urinary excretion of Cd reveals long-term exposure to the metal (ATSDR, 2008). Liu et al. (2013) reported an increased life-time risk of death due to lung cancer resulting from occupational exposure to dusts and mists containing hexavalent Cr.

Soils represent a major sink for metal ions that can then enter the food chain (i.e. drinking water) *via* surface (e.g. in runoff after episodic rainfall events) and subsurface pathways (i.e. ground water) (Fernández-Luqueño et al., 2013; Clarke et al., 2015). In fact, groundwater and surface waters can be linked and thereby affect each other (Vero et al., 2014). Previous studies have shown that overland transport of metals from fields (with eventual runoff to the transfer continuum at delivery points) amended with biosolids can impact the quality of surface waters (Topp et al., 2008). These metals may be present in mobile forms in biosolids, which may migrate to the fertilised soil, or in immobile forms, which do not produce any toxicological effect (Gawdzik and Gawdzik, 2012). Chang et al. (1984) found that >90% of the Cd, Cr, Zn, Cu, Ni and Pb present in biosolids, which were land applied over a 6-year period in a field-scale experiment, remained in the cultivated layer (0–15 cm) in both sandy and loam soils. Similarly, Hinesly et al. (1972) reported the movement of Cd, Cr, Ni, Zn and Cu to a depth of 30–45 cm in arable agricultural soil (permeable silt loam texture) following biosolids application (applied at 13.6 t $acre^{-1}$) over a 4-year period. Therefore, greater concentrations of metals in biosolids, combined with long-term use on some soil types, may potentially be a hazard to the environment. Joshua et al. (1998) monitored the surface and subsurface movement of nutrients and metals in runoff and the soil profile following land application of biosolids over a 3-year period, and found that biosolids reduced runoff and increased surface retention of rainfall. The study concluded that there was a low potential for pollution of surface or groundwaters by metals.

With regards to the behaviour and fate of metals in soils and transfer along the food chain, the "plateau" and "time bomb" theories are opposite philosophies used to explain the behaviour of metals in soil and uptake by plants in response to biosolid application on agricultural land. The "plateau" hypothesis considers that metals are so tightly bound by the organic matter in biosolids and hydrous oxides of Fe and Mn and clays in the soil, that their bioavailability or toxicity is greatly reduced and that they are retained in the soil's surface horizon or in the plough layer instead of the being taken up by plants or leaching down the soil profile (Lu et al., 2012). The "time bomb" hypothesis considers that the slow mineralisation of the organic matter present in the biosolids could release metals in readily soluble form, which then may become available for plant up-take (Silveira et al., 2003). Chang et al. (1997) obtained experimental data from a 10-year field biosolids study on agricultural land to evaluate the hypothesis of the plateau and time bomb theories. They concluded that neither a plateau nor time bomb was evident despite an increasing rate of biosolid application (2880 mg ha^{-1}), which represented a "worst case scenario" in terms of contaminant loading.

1.1. Drinking water treatment process

Drinking water treatment may involve several stages such as pre-treatment or primary treatment (coarse screening, storage and neutralisation), secondary treatment (coagulation/flocculation/sedimentation, rapid and slow sand filtration) and tertiary treatments (disinfection, activated carbon and membrane processes). The pre-treatment process is defined depending on the closeness of the water source to the treatment plant and whether it is an upland or lowland water source. Storage is used primarily for water abstracted from lowland rivers to improve water quality before treatment and to ensure adequate supplies at periods of peak demand (Gray, 2010).

Secondary treatment involves the coagulation, flocculation, sedimentation and filtration of the influent. The commonest types of coagulants used are aluminium-based (e.g., aluminium sulphate (alum) or polyaluminium chloride (PAC)). Both aluminium (Al) and ferric salts, either in monomer or polymeric forms, have been reported to be effective coagulants in treating metals in wastewater (Kang et al., 2003; Pang et al., 2009). In Ireland, the most commonly used coagulant is alum, followed by a very small number of plants using Fe-based coagulants (ferric chloride or ferric sulphate) (Cummins et al., 2010). Fatoki and Ogunfowokan (2004) reported removal efficiencies of 90% for Cr, 68% for Zn, and 100% for Ni using ferric sulphate, compared to alum, which had removal efficiencies of 81%, 47% and 55%, for Cr, Zn and Ni, respectively. Jiménez (2005) reported 78, 39 and 36% removals of Cd, Ni and Cr, respectively, following 100 mg L^{-1} dose of alum on wastewater in Mexico. With the use of recycled alum sludge in the coagulation process, Chu (1999) reported that Pb removals increased from 79 to 98% with 100–180 mg L^{-1} of recycled alum sludge. Hannah et al. (1977) reported metal removals of between 25 and 100% using alum and incorporating chemical clarification and carbon adsorption.

The filtration process in a conventional WTP consists of slow or rapid sand filtration. The purpose of filtration is to remove suspended particles in the water by moving the water through a medium such as sand. Aulenbach and Chan (1988) reported the effect of rapid sand filtration on metal removal from mixed industrial and domestic wastewater. Cadmium and Cu were removed in the order of 20%, whereas Pb and Zn were removed in the order of 35–40%.

Detection of metals in drinking water and effects on human health has been widely reported (Muhammad et al., 2011; Mohod and Dhote, 2013). However, there is a knowledge gap regarding the environmental fate of metals in surface runoff waters from biosolids-amended grassland and their potential risk to human health following treatment of these waters in water treatment plants (WTPs). Using surface runoff data generated from field plots, onto which three types of biosolids (lime stabilised (LS), anaerobically digested (AD), and thermally dried (TD)) were applied and which were subject to three rainfall events shortly after their application, and making the assumptions that no buffer zones were present and that stream dilution took place, this study develops a quantitative risk assessment model for metals in drinking water following their treatment in a conventional WTP.

2. Materials and methods

2.1. Biosolids characterisation

Three types of biosolids were investigated in this study. They were: anaerobically digested biosolids from the UK (AD-UK) and Ireland (AD-IRE), and LS and TD biosolids. With the exception of AD-UK, all biosolids originated from the same wastewater treatment plant (WWTP) in Ireland. The AD-UK biosolids were sourced from United Utilities, Ellesmere Port, UK, and were used as part of an EU-funded FP7 project (END-O-SLUDG, 2014). These biosolids were land applied to small field plots at the maximum legal application rate in Ireland (Fehily Timoney and Company, 1999) and subjected to three successive rainfall events, applied using a rainfall simulator, at time intervals of 24 (RS1), 48 (RS2) and 360 (RS3) hour after application. The design of the field experiment, including application, rainfall intensity (mm h^{-1}), drop size (mm) etc. are detailed in Peyton et al. (2016). The mean and standard deviation of the surface runoff ($C_{surface\text{-}runoff}$) of Cd, Cr, Cu, Ni, Pb and Zn at each time interval are shown in Table 1 and based on Peyton et al. (2016).

Table 1
Metal concentrations in surface runoff (mean ± standard deviation, n = 15).

Metals (μg L^{-1})		Times of rainfall application (hr)		
		24	48	360
Cd	Control	0.18 ± 0.06	0.18 ± 0.12	0.15 ± 0.05
	AD-UK	0.13 ± 0.09	0.1 ± 0.03	0.11 ± 0.04
	TD	0.11 ± 0.05	0.13 ± 0.1	0.14 ± 0.09
	AD-IRE	0.08 ± 0.08	0.16 ± 0.07	0.14 ± 0.12
	LS	0.14 ± 0.1	0.14 ± 0.09	0.22 ± 0.02
Cr	Control	0.78 ± 0.41	0.40 ± 0.26	0.83 ± 0.78
	AD-UK	0.44 ± 0.5	0.25 ± 0.11	0.30 ± 0.31
	TD	0.57 ± 0.39	0.41 ± 0.23	0.78 ± 0.62
	AD-IRE	0.67 ± 0.68	0.66 ± 0.46	0.48 ± 0.32
	LS	0.38 ± 0.24	0.56 ± 0.49	1.10 ± 0.75
Cu	Control	5.4 ± 1.1	3.9 ± 1.8	6.0 ± 2.5
	AD-UK	6.0 ± 3.1	8.3 ± 1.9	19 ± 3.7
	TD	14 ± 2.9	10 ± 4.8	8.2 ± 2.5
	AD-IRE	13 ± 6.1	10 ± 5.9	7.5 ± 2
	LS	213 ± 74	156 ± 27	113 ± 99
Ni	Control	0.34 ± 0.10	0.43 ± 0.15	0.55 ± 0.39
	AD-UK	3.6 ± 2.5	3.0 ± 1.1	1.9 ± 0.8
	TD	6.2 ± 4.0	2.9 ± 1.8	0.9 ± 0.2
	AD-IRE	1.7 ± 1.8	1.4 ± 0.7	1.1 ± 0.6
	LS	8.0 ± 2.2	5.4 ± 1.7	4.7 ± 4.1
Pb	Control	1.0 ± 0.87	0.48 ± 0.33	0.72 ± 0.60
	AD-UK	0.72 ± 0.74	0.42 ± 0.37	0.92 ± 0.78
	TD	0.93 ± 0.40	0.32 ± 0.40	0.60 ± 0.84
	AD-IRE	1.2 ± 1.1	0.62 ± 0.67	0.65 ± 0.69
	LS	1.4 ± 1.5	0.74 ± 0.94	0.43 ± 0.32
Zn	Control	21 ± 14	3.4 ± 1.0	7.6 ± 7.6
	AD-UK	13 ± 17	7.9 ± 7.4	11 ± 9.1
	TD	20 ± 9.7	8.8 ± 6.8	13 ± 9.9
	AD-IRE	31 ± 16	9.8 ± 5.9	11 ± 8.0
	LS	56 ± 90	23 ± 21	27 ± 30

A normal distribution was assigned to account for uncertainty in the data. All runoff samples were below their respective drinking water standards intended for human consumption (S.I. No. 122 of 2014). However, it remains pertinent to evaluate final human exposure and risk, as treatment processes could result in an accumulation/increase (Renault et al., 2009; Ersoz and Barrott, 2012) as well as decrease in metal levels along the drinking water treatment chain, therefore potentially increasing exposure above the level found in runoff. In addition, drinking water standards relate to levels found at the point of the tap, hence processes that can affect this final level need to be evaluated, including the varying water treatment effects, varying levels of water drunk by different groups, while varying body weigh will affect final risk estimates and should also be considered. This is especially important when looking at susceptible groups (e.g. children). Failure to evaluate the final human exposure and risk may result in incorrect ordering of priority metals which may require vigilance. As drinking water treatment effects will be contaminant-specific, the final human exposure and risk may not be in the same order (i.e. going from higher to lower) as levels found in the runoff; hence failure to evaluate the final human exposure and risk may result in incorrect ordering of priority metals which may require vigilance. Hazard and risk characterisation are identified in European Union (EU) law (EC 178/2002) as important stages of risk assessment, and are important steps to consider.

2.2. Model development

The diagram of the model framework used in this study is shown in Fig. 1. Most drinking water in Ireland is sourced from surface waters. As a "worst case scenario" it was assumed that surface runoff following biosolid application to grassland entered an adjacent stream without any chance of attenuation along the transfer continuum before delivery to the surface water body. This is atypical in terms of grassland management. To account for metal concentrations in surface water being discharged into the stream, a dilution factor (DF) was used (Colman et al., 2011). When considering risk assessment for new chemicals entering the market within the EU, a DF of 10 is normally applied (ECB, 2003). This assumes a homogenous distribution of the chemical in the river, and does not account for dispersion or advection. Therefore, in the current study, a default DF of 10 was applied to the data to calculate the predicted environmental concentrations in surface water (Eq. (1)):

$$\text{TS-W}_M = \frac{C_{surface\text{-}runoff}}{DF}. \quad (1)$$

where:

TS-W_M is total metal in surface-water (μg L^{-1}).
DF is the dilution factor (dimensionless).
$C_{surface\text{-}runoff}$ is the initial concentration in runoff (μg L^{-1}).
This water was then assumed to represent influent into a WTP.

Three stages of drinking water treatment (Fig. 1) were used based on the Irish Environmental Protection Agency's (EPA) best practice guidelines for drinking water treatment manuals (Ireland EPA, 1995, 2003, 2011). The first stage (primary treatment) considers the screening, storage, pre-conditioning and pre-chlorination of the water. In the current study, primary treatment was assumed to have a negligible impact on metal removal, and is incorporated into this drinking water model merely to emulate real drinking water conditions.

Levels of coagulation/flocculation and sedimentation for metal removal efficiency are divided into three categories (optimal, sub-optimal and failure). Amuda and Alade (2006) reported that the chemical type and dose were the most influential parameters for the optimised treatment results. Thirty to 50% of known waterborne disease outbreaks are due to sub-optimum conditions in water treatment, and treatment barrier efficiency and stability are critically dependent on good operation performance (Techneau, 2010). As a "worst case scenario" the model assumed a 90% probability of coagulation and flocculation occurring at an

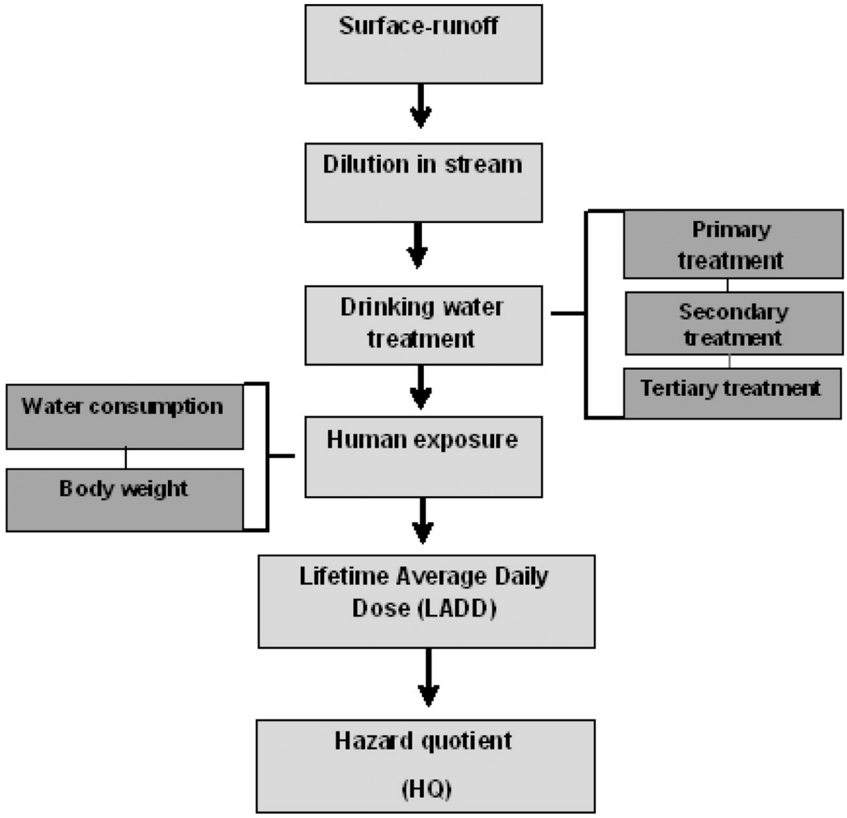


Fig. 1. Quantitative risk assessment model for metals in biosolids applied to grassland.

optimum stable run (Copt) and 5% probability for both sub-optimal (CS-opt) and failure (C-fail) (Table 2). When operating optimally, the model assumed a removal rate which was metal-specific (Table 3). When operating sub-optimally, the model assumed a removal of 50% at the optimal removal rate, and zero removal during failure events. It was assumed that the coagulant aluminium sulphate was used, keeping to the Irish EPA's best practice guideline.

In the current study, rapid gravity filtration (the most commonly used process in WTPs) was considered in the model. Filtration can be stable or unstable due to optimum, sub-optimum, or failure of the coagulation/flocculation process (Table 2). As a "worst case scenario" the model assumed a 90% probability of filtration operating at an optimum stable run (F-opt) and 10% probability for sub-optimal run (F-sub). When operating optimally, the model assumed a removal rate (F-rd)

Table 2
Parameter values and distributions for simulation model.

Stage	Symbol	Description	Model/distribution	Units
Application of biosolids to agricultural land				
	$C_{surface\text{-}runoff}$	Initial concentration in runoff	Lognormal	$\mu g\ L^{-1}$
Dilution	DF	Dilution in stream	Dilution factor (10)	–
	$TS\text{-}W_M$	Total metal in surface-water	$C_{surface\text{-}runoff}$ / Df	$\mu g\ L^{-1}$
Secondary treatment				
	C-opt	Coagulation/flocculation and sedimentation opt	0.90	Probability
	CS-opt	Coagulation/flocculation and sedimentation sub-optimum	0.05	Probability
	C-fail	Coagulation/flocculation and sedimentation fail	0.05	Probability
	C-rd	Coagulation/flocculation and sedimentation reduction	Uniform (metal specific, see Table 3)	Decimal reduction
	F-opt	Filter optimum	0.9	Probability
	F-sub	Filter sub-optimum	0.1	Probability
	F-run	Filter run	Discrete (stable, unstable), (Fopt, Fsub)	
	F-rd	Filtration reduction (RAPID sand)	Uniform (metal specific, see Table 3)	Decimal reduction
Tertiary treatment				
Output	D	Disinfection	0	Probability
	$C\text{-}_{PSTT}$	Post-secondary and tertiary treatment	$C_{PSTT} = TS\text{-}W_M \times (1\text{-Cr}) \times (1\text{-Frd}) \times (1\text{-D})$	μg/L
Human exposure				
Consumption	TWi	Tap water intake (adult)	Lognormal (mean 0.564, SD 0.617)	$L\ d^{-1}$
		Tap water intake (child)	Lognormal (mean 0.238, SD 0.208)	$L\ d^{-1}$
Body weight	BW_a	Body weight (adult)	Normal (adult) (mean 78, SD 16.5)	Kg
	BW_c	Body weight (child)	Normal (child) (mean 33, SD 11.3)	Kg
Dose response (metals)				
Output	LADD	Lifetime average daily dose	$C_{PSTT} \times$ TWi / BW	$\mu g\ kg^{-1}\ bw\ d^{-1}$
Output	HQ	Hazard quotient	LADD / Rfd (Reference dose see Table 4)	–

Table 3
Metal removal range rate for aluminium sulphate and rapid sand filtration processes.

Metal	Distribution	Min%	Max%	Reference
Coagulation/flocculation and sedimentation (aluminium sulphate)				
Cd	Uniform	45	98	Hannah et al. (1977)
Cr	Uniform	95	100	Jiménez (2005), Hannah et al. (1977)
Cu	Uniform	70	90	Jiménez (2005), Hannah et al. (1977)
Ni	Uniform	45	90	Jiménez (2005), Hannah et al. (1977)
Pb	Uniform	50	90	Jiménez (2005)
Zn	Uniform	50	90	Jiménez, (2005), Hannah et al. (1977)
Filtration (rapid sand)				
Cd	Uniform	20	50	Aulenbach and Chan (1988)
Cr	Uniform	64	96	Thapa (2009)
Cu	Uniform	20	98	Aulenbach and Chan (1988), Daneshi et al. (2009)
Ni	Uniform	20	50	Aulenbach and Chan, (1988)
Pb	Uniform	35	40	Aulenbach and Chan, (1988)
Zn	Uniform	35	40	Aulenbach and Chan, (1988)

Table 4
Threshold of risk limits for the HQ (Lemly, 1996).

<0.01	No existing risk
0.1–1.0	Risk is low
1.1–10	Risk is moderate
>10	Risk is high

which was metal-specific (Table 3). When operating sub-optimally, the model assumed a removal of 50% of the optimal removal rate.

Tertiary treatment – the third stage of drinking water treatment – is employed when specific drinking water constituents, not removed by secondary treatment, must be removed. Chlorination is the most popular tertiary treatment in Ireland. The disinfection process does not have an effect on metals, therefore no removal distribution was assigned.

In the model used in this paper, removal of metals is quantified in terms of a decimal reduction. The concentration of metals remaining after secondary and tertiary treatment in a WTP was calculated by multiplying the level present post primary treatment by the decimal reduction due to coagulation/flocculation, sedimentation, filtration and disinfection. The equation is:

$$C\text{-}_{PSTT} = TS\text{-}W_M \times (1\text{-Cr}) \times (1\text{-Frd}) \times (1\text{-D}) \quad (2)$$

where:

$C\text{-}_{PSTT}$ is the metal concentration post-secondary and tertiary treatment ($\mu g\ L^{-1}$).

C-rd is decimal reduction due to coagulation/flocculation and sedimentation.

F-rd is decimal reduction due to filtration.

D is the decimal reduction due to disinfection.

2.3. Human exposure

Human exposure is defined by the World Health Organisation (WHO) as the amount of a substance in contact over time and space, with the outer boundary of the body (WHO/IPCS, 2000). To evaluate how much drinking water a person needs to consume in order to be affected by a hazard, the water consumption of the individual needs to be examined. The water consumption for adults was modelled using a log-normal distribution with a mean and standard deviation of $0.564 \pm 0.617\ L\ d^{-1}$, and was based on a survey on adult nutrition of 1274 consumers in Ireland (IUNA, 2011). A similar study focusing on child nutrition, entitled, "The National Children Food Survey", found that children consume 0.238 L of water d^{-1} (IUNA, 2005). Based on this finding, a log-normal distribution with a mean and standard deviation value of $0.238 \pm 0.208\ L\ d^{-1}$ was used for children.

Table 5
The oral toxicity reference dose value, *Rfd*, of each metal in surface water (Muhammad et al., 2011).

Metal	*Rfd* mg kg^{-1} d^{-1}
Cd	5.0×10^{-04}
Cr	1.5
Cu	3.7×10^{-02}
Ni	2.0×10^{-02}
Pb	3.6×10^{-02}
Zn	3.0×10^{-01}

2.4. Dose response model

To evaluate the human health risk, the lifetime average daily dose (LADD) ($\mu g\ kg^{-1}$ bw d^{-1}) and the hazard quotient (HQ) were used as toxicity endpoints in the model, and were metal-specific. The LADD considers the concentration of metal in the water ($\mu g\ L^{-1}$), the average daily intake rate of water ($L\ d^{-1}$), and the body weights of adults and children (kg). A normal distribution with a mean and standard deviation value of 78 ± 16.5 kg was used to model the variation in body weight for adults (IUNA, 2011), and a normal distribution with a mean value and standard deviation of 33 ± 11.3 kg was used to model variation in body weight for children (IUNA, 2005). The Joint FAO/WHO Expert Committee on Food Additives (JECFA) has established provisional maximum tolerable daily intake (PMTDI) values for metals in food. The recommended daily intake values have been set for Cd, Ni, Zn and Cu (7, 5, 100 and 500 $\mu g\ kg^{-1}$ bw $d^{-1,}$ respectively). 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, 2011b). There may be bias with regards to the permissible limits set by different agencies (WHO, US EPA, European Union Commission, APHA). Kumar and Puri (2012) reported that there was "no uniformity" within parameter limits set by different agencies. The permissible limits may be based on physio-chemical parameters such as pH, alkalinity, temperature, dissolved oxygen, etc. The lack of uniformity of permissible limits between agencies may cause confusion for the researcher and public health officials who depend on the guidelines as a measure of risk. There is still insufficient scientific data on the health risks associated with metal exposure at low levels.

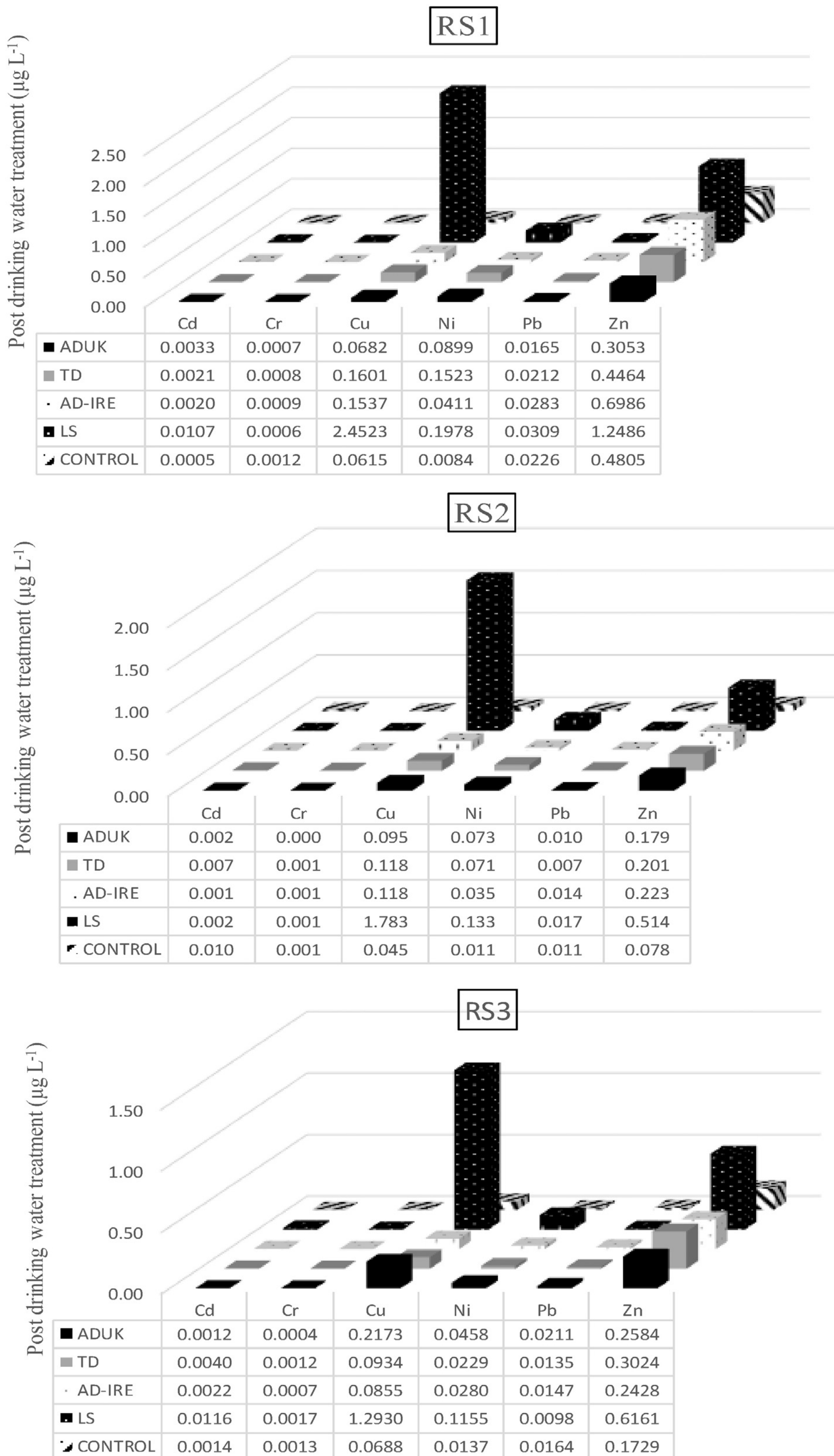
The LADD through water ingestion was calculated according to:

$$LADD = C\text{-}_{PSTT} \times TWi/BW_{a,c} \left(\mu g\ kg^{-1}\ bwd^{-1}\right) \quad (3)$$

where:

TWi is the tap water intake rate ($L\ d^{-1}$).

$BW_{a,c}$ is body weight (adult and child) (kg).



RS1

	Cd	Cr	Cu	Ni	Pb	Zn
ADUK	0.0033	0.0007	0.0682	0.0899	0.0165	0.3053
TD	0.0021	0.0008	0.1601	0.1523	0.0212	0.4464
AD-IRE	0.0020	0.0009	0.1537	0.0411	0.0283	0.6986
LS	0.0107	0.0006	2.4523	0.1978	0.0309	1.2486
CONTROL	0.0005	0.0012	0.0615	0.0084	0.0226	0.4805

RS2

	Cd	Cr	Cu	Ni	Pb	Zn
ADUK	0.002	0.000	0.095	0.073	0.010	0.179
TD	0.007	0.001	0.118	0.071	0.007	0.201
AD-IRE	0.001	0.001	0.118	0.035	0.014	0.223
LS	0.002	0.001	1.783	0.133	0.017	0.514
CONTROL	0.010	0.001	0.045	0.011	0.011	0.078

RS3

	Cd	Cr	Cu	Ni	Pb	Zn
ADUK	0.0012	0.0004	0.2173	0.0458	0.0211	0.2584
TD	0.0040	0.0012	0.0934	0.0229	0.0135	0.3024
AD-IRE	0.0022	0.0007	0.0855	0.0280	0.0147	0.2428
LS	0.0116	0.0017	1.2930	0.1155	0.0098	0.6161
CONTROL	0.0014	0.0013	0.0688	0.0137	0.0164	0.1729

Fig. 2. Metal concentration (µg L^{-1}) in effluent post drinking water treatment using surface runoff data from rainfall simulations on field scale plots occurring 24 (RS1), 48 (RS2) and 360 h (RS3) after land application.

Risk characterisation was quantified by potential non-carcinogenic risks, reflected by the hazard quotient (HQ) – the ratio of the potential exposure to a substance and the level at which no adverse effects are expected (the threshold toxicity reference value). If the HQ exceeds 1, there may be concern for non-carcinogenic risks (Lemly, 1996). Table 4 gives an overview of the HQ thresholds that indicate risk. Table 5 gives an overview of the oral toxicity reference dose values for all metals. The HQ for non-carcinogenic risk was calculated according to:

$$HQ = \frac{LADD}{Rfd} \tag{4}$$

where:

Rfd is the oral toxicity reference dose value (Table 5).

2.5. Model run and sensitivity analysis

A quantitative drinking water treatment model was developed to estimate likely human exposure and the resulting risk in drinking water based on a hypothetical scenario where surface runoff on land onto which biosolids were applied, transported metals (Cu, Cd, Cr, Pb, Ni and Zn) directly without the possibility for attenuation to waters used for WTPs. The authors acknowledge that, in reality, biosolids would not be spread to the edge of the field and that grassed buffer zones would be in place. The simulations were performed using data from the RS1, RS2 and RS3 rainfall simulations (Table 1). Distributions were used to account for uncertainty in the data. The input parameters were assembled in a spreadsheet in Microsoft Excel 2010 with the add-on package @Risk (version 6.0, Palisade Corporation, New York, USA), and the simulation was performed using Monte Carlo sampling.

A sensitivity analysis, based on rank order correlation, was carried out to assess how the model's predictions are dependent on variability and uncertainty in the model input parameters. Sensitivity analysis assesses how the model predictions are dependent on variability and uncertainty in the model's inputs. Monte Carlo simulation performs risk analysis by building models of possible results by substituting a range of values—a probability distribution—for any factor that has inherent uncertainty or variability (Kavcar et al., 2009). It then iterates the results using a different set of random values from the probability functions. Ten thousand iterations were performed for each simulation.

3. Results

The results for metals in runoff over three time periods (RS1, RS2 and RS3) are displayed in Table 1 and indicate that of all the metals analysed, Cu had the greatest concentration (mean value and standard deviation 213 ± 74 μg L^{-1}) in a rainfall event occurring 24 h following application of LS biosolids. The concentration of Cu decreased over the following two rainfall events at 48 and 360 h.

The drinking water model produced several output distributions (metal concentration in effluent post WTP, lifetime average daily dose, and hazard quotient) 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 after tertiary treatment (Fig. 2) was highest when the surface runoff concentrations from the LS biosolids at each rainfall simulation time (24, 48 and 360 h) were used as input into the model (mean concentration values 2.45, 1.78 and 1.2 μg L^{-1}, respectively). This was followed by Zn, which had mean concentrations of 1.25, 5.14×10^{-1} and 6.16×10^{-1} μg L^{-1} for each rainfall event. All metal concentrations were below the metal threshold values of the EU and the World Health Organisation (European statutory instrument (S.I. No. 122 of 2014; WHO, 2011a) (Table 6).

Table 6
Comparison of heavy metal threshold values in drinking water between the EU and the World Health Organisation (European statutory instrument (S.I. No. 122 of 2014); WHO, 2011a).

Heavy metal	EU (μg L^{-1})	WHO (μg L^{-1})
As	10	10
Cd	5	3
Co	50	50
Cr	50	50
Cu	2000	2000
Fe	200	NGL
Ni	20	70
Pb	10	10
Zn	NM	3000

NM = not mentioned, NGL = no guideline limit.

The modelled results for the exposure assessment (LADD) (Fig. 3) showed that surface runoff resulting from the land-spreading of LS biosolids produced the highest child exposure concentrations for Cu when the average concentrations from each rainfall simulation time (24, 48 and 360 h) were used as input in the model (mean values 2.07×10^{-2}, 2.07×10^{-2} and 1.18×10^{-2} μg kg^{-1} bw d^{-1}). This was followed by adult Cu exposure concentrations (mean value 1.80×10^{-2}, 1.31×10^{-3} and 9.21×10^{-3} μg kg^{-1} bw d^{-1}, for all three time frames). All LADD values were below the proposed PMTDI values for Cd, Cu, Ni and Zn proposed by JECFA (WHO, 2011b). Therefore, the results indicate that there is negligible risk to both adults and children, however the model provides a useful ranking of exposure and risk for the suite of metals assessed, highlight priority ones requiring vigilance from a human health perspective.

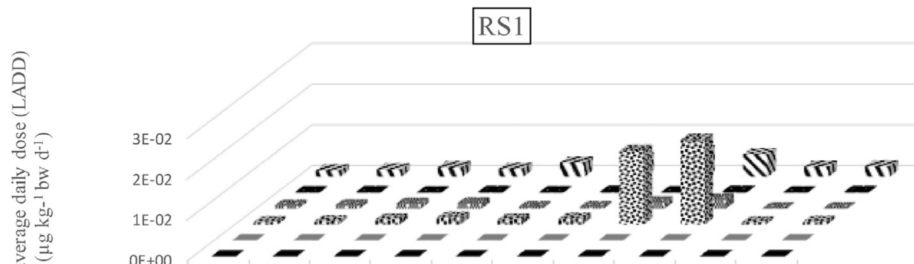
The results for the hazard quotient (Fig. 4) showed that of all the scenarios considered, Cu arising from LS biosolids was the highest for children for all three surface runoff events, with mean child HQ values of 5.59×10^{-4}, 4.09×10^{-4} and 3.18×10^{-4}, respectively, followed by adult Cu concentrations (mean adult HQ values of 4.87×10^{-4}, 3.54×10^{-4} and 2.49×10^{-4}). However, these were still below the threshold value of risk (HQ < 0.01).

As the LS biosolids produced the highest concentration in both toxicity endpoints (LADD and HQ), a sensitivity analysis was conducted for Cu. Results revealed that tap water intake (TWi) and filtration reduction were the most important parameters (correlation coefficient values 0.67 and −0.54, respectively) that affected the variance in model predictions (Fig. 5). This highlights, of all the inputs assessed, the efficiency of the filtration system as one of the 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 an important parameter as body weight is reduced; the risk is increased. The initial concentration in runoff was also an important parameter (correlation coefficient 0.12) highlighting the importance of having the initial concentration of metals in sludge as low as possible (Fig. 5).

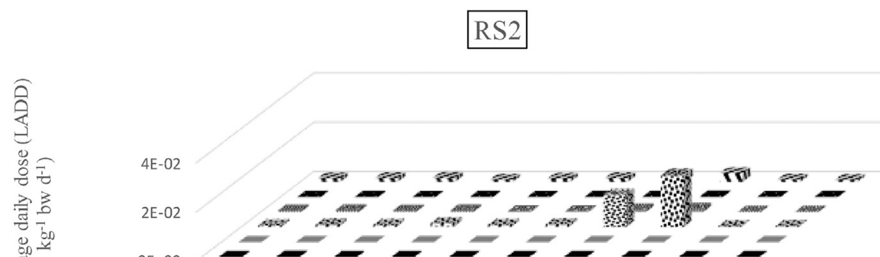
4. Discussion

The initial concentrations of metals in surface runoff over all three rainfall simulations were below their respective drinking water standards intended for human consumption (S.I. No. 122 of 2014). However, although the guidelines describe a quality of water that is acceptable for lifelong consumption, the guideline values do not imply that the quality of drinking water may be "degraded to the recommended level" (WHO, 2008). Drinking water standards do not guarantee that water below the threshold limit is risk-free nor do they indicate that higher levels of contaminants in water are unsafe. Standards are considered to be a conservative estimate of risk judged by scientists and regulatory bodies based on adverse health effects. Furthermore, the drinking water standards do not consider the drinking water habits (consumption), body weight, or vulnerability of the population. Among the metals, the extent of decrease in surface runoff was in the order of Cu < Zn < Ni < Pb < Cr < Cd, which were consistent with the levels of metals in the original biosolids (Peyton et al., 2016). This is similar to the results of Gove et al. (2001), who found that Cu and Zn, albeit in sandy soils as opposed to clay loam in this study, cumulatively leached after the first rainfall event, implying that an equilibrium exists between absorbed metal and solution metal and that steady-state hydrological conditions were maintained, which support assertions that there is a soluble or mobile fraction of metals in soil. Copper and Zn are considered to be more soluble metals (Joshua et al., 1998). McBride et al. (1997) reported high solubility values for Cu (ranges 0.06 to 0.27 mg L^{-1}) several decades after cessation of biosolid application to land. In the soil, Cu will adhere strongly to organic matter, therefore only a small fraction of Cu will be found in solution as ionic copper, Cu (II) (Wuana and Okieimen, 2011). Mamindy-Pajany et al. (2014) found that a single application of LS biosolids at a rate ranging from 15 to 30 t ha^{-1} tended to decrease the mobility of metals, whereas repeated applications (2 × 15 t ha^{-1}) increased metal leaching from the soil. The application of lime to biosolids will raise the pH and precipitate most metals, reducing their solubility and rendering them immobile. Nonetheless, dissolved organic carbon (DOM) will begin to dissociate at a higher pH and the metals complexed within these compounds will become mobile (Lasley, 2008).

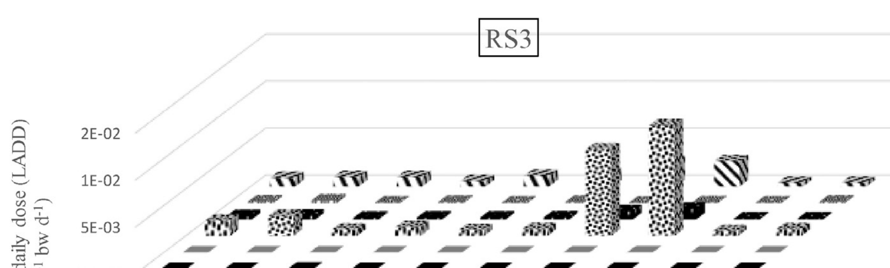
The mean metal concentration of Cu was highest in post-secondary treatment following incorporation of the surface runoff results from the LS biosolids. This was attributed to the initial concentrations of metals in the influent and the removal rates associated with secondary



	Adult	Child	Adult	Child	Adult	Child	Adult	Child	Adult	Child
Cd	8E-06	1E-05	1E-05	3E-05	6E-06	1E-05	2E-05	2E-05	1E-05	2E-05
Cr	5E-06	5E-06	6E-06	7E-06	8E-06	9E-06	4E-06	5E-06	9E-06	1E-05
Cu	5E-04	7E-04	1E-03	2E-03	1E-03	1E-03	2E-02	2E-02	4E-04	6E-04
Ni	7E-04	8E-04	1E-03	1E-03	3E-04	3E-04	1E-03	2E-03	6E-05	7E-05
Pb	1E-04	1E-04	7E-05	2E-04	1E-04	2E-04	1E-04	3E-04	8E-05	2E-04
Zn	2E-03	2E-03	2E-03	2E-03	3E-03	4E-03	6E-03	5E-03	2E-03	2E-03

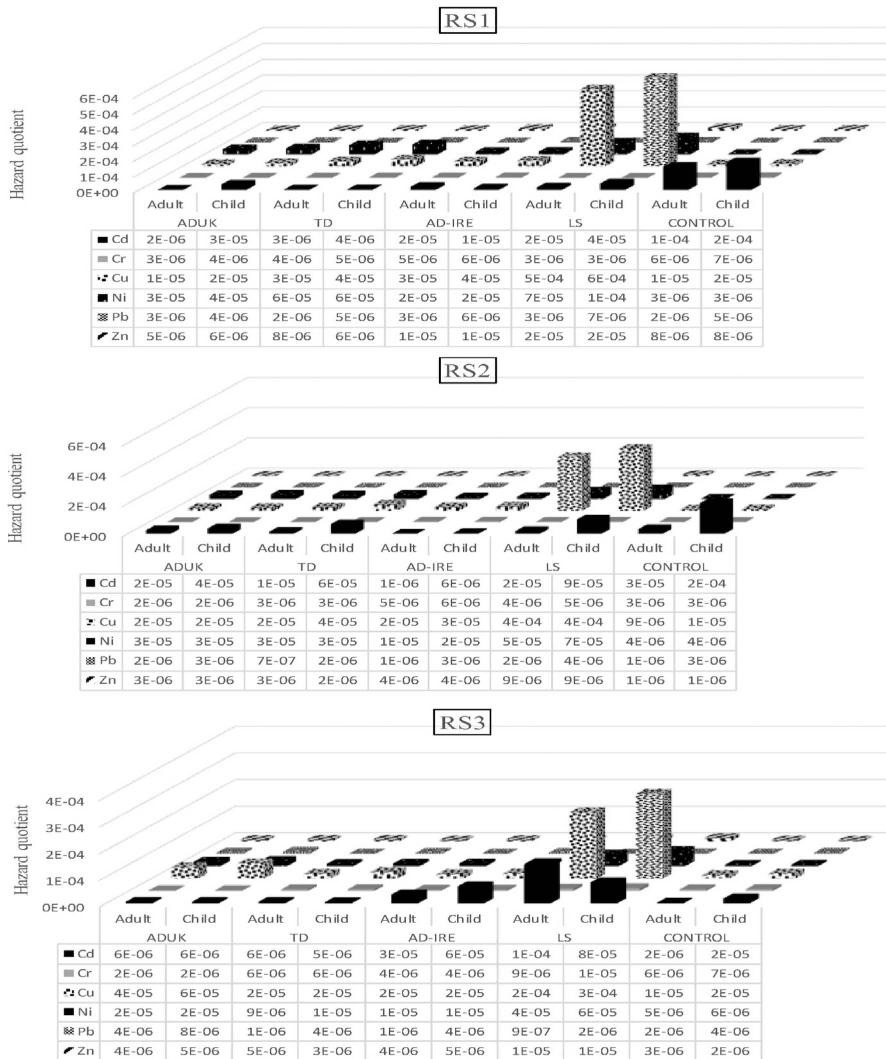


	Adult	Child	Adult	Child	Adult	Child	Adult	Child	Adult	Child
Cd	5E-05	1E-04	2E-06	2E-06	2E-07	2E-06	1E-05	5E-05	5E-06	3E-05
Cr	3E-06	3E-06	5E-06	5E-06	8E-06	9E-06	6E-06	8E-06	5E-06	5E-06
Cu	7E-04	1E-03	8E-04	2E-03	9E-04	1E-03	1E-02	2E-02	3E-04	4E-04
Ni	6E-04	6E-04	5E-04	6E-04	3E-04	3E-04	1E-03	1E-03	8E-05	8E-05
Pb	7E-05	9E-05	2E-05	7E-05	5E-05	1E-04	6E-05	2E-04	4E-05	9E-05
Zn	1E-03	1E-03	2E-03	8E-04	1E-03	1E-03	3E-03	3E-03	9E-04	7E-04



	Adult	Child	Adult	Child	Adult	Child	Adult	Child	Adult	Child
Cd	7E-06	8E-06	3E-05	4E-06	6E-06	3E-06	7E-06	2E-05	6E-07	2E-06
Cr	3E-06	4E-06	9E-06	1E-05	6E-06	6E-06	1E-05	2E-05	9E-06	1E-05
Cu	2E-03	2E-03	7E-04	9E-04	6E-04	7E-04	9E-03	1E-02	5E-04	7E-04
Ni	3E-04	4E-04	2E-04	2E-04	2E-04	2E-04	9E-04	1E-03	1E-04	1E-04
Pb	2E-04	3E-04	5E-05	1E-04	5E-05	1E-04	3E-05	8E-05	6E-05	1E-04
Zn	9E-04	1E-03	1E-03	6E-04	1E-03	1E-03	3E-03	3E-03	4E-04	4E-04

Fig. 3. Lifetime average daily dose (µg kg^{-1} bw d^{-1}) using surface runoff data from rainfall simulations on field scale plots occurring 24 (RS1), 48 (RS2) and 360 h (RS3) after land application.



RS1

	ADUK Adult	ADUK Child	TD Adult	TD Child	AD-IRE Adult	AD-IRE Child	LS Adult	LS Child	CONTROL Adult	CONTROL Child
Cd	2E-06	3E-05	3E-06	4E-06	2E-05	1E-05	2E-05	4E-05	1E-04	2E-04
Cr	3E-06	4E-06	4E-06	5E-06	5E-06	6E-06	3E-06	3E-06	6E-06	7E-06
Cu	1E-05	2E-05	3E-05	4E-05	3E-05	4E-05	5E-04	6E-04	1E-05	2E-05
Ni	3E-05	4E-05	6E-05	6E-05	2E-05	2E-05	7E-05	1E-04	3E-06	3E-06
Pb	3E-06	4E-06	2E-06	5E-06	3E-06	6E-06	3E-06	7E-06	2E-06	5E-06
Zn	5E-06	6E-06	8E-06	6E-06	1E-05	1E-05	2E-05	2E-05	8E-06	8E-06

RS2

	ADUK Adult	ADUK Child	TD Adult	TD Child	AD-IRE Adult	AD-IRE Child	LS Adult	LS Child	CONTROL Adult	CONTROL Child
Cd	2E-05	4E-05	1E-05	6E-05	1E-06	6E-06	2E-05	9E-05	3E-05	2E-04
Cr	2E-06	2E-06	3E-06	3E-06	5E-06	6E-06	4E-06	5E-06	3E-06	3E-06
Cu	2E-05	2E-05	2E-05	4E-05	2E-05	3E-05	4E-04	4E-04	9E-06	1E-05
Ni	3E-05	3E-05	3E-05	3E-05	1E-05	2E-05	5E-05	7E-05	4E-06	4E-06
Pb	2E-06	3E-06	7E-07	2E-06	1E-06	3E-06	2E-06	4E-06	1E-06	3E-06
Zn	3E-06	3E-06	3E-06	2E-06	4E-06	4E-06	9E-06	9E-06	1E-06	1E-06

RS3

	ADUK Adult	ADUK Child	TD Adult	TD Child	AD-IRE Adult	AD-IRE Child	LS Adult	LS Child	CONTROL Adult	CONTROL Child
Cd	6E-06	6E-06	6E-06	5E-06	3E-05	6E-05	1E-04	8E-05	2E-06	2E-05
Cr	2E-06	2E-06	6E-06	6E-06	4E-06	4E-06	9E-06	1E-05	6E-06	7E-06
Cu	4E-05	6E-05	2E-05	2E-05	2E-05	2E-05	2E-04	3E-04	1E-05	2E-05
Ni	2E-05	2E-05	9E-06	1E-05	1E-05	1E-05	4E-05	6E-05	5E-06	6E-06
Pb	4E-06	8E-06	1E-06	4E-06	1E-06	4E-06	9E-07	2E-06	2E-06	4E-06
Zn	4E-06	5E-06	5E-06	3E-06	4E-06	5E-06	1E-05	1E-05	3E-06	2E-06

Fig. 4. Hazard quotient for all biosolids treatment (adult and child) using surface runoff data from rainfall simulations on field scale plots occurring 24 (RS1), 48 (RS2) and 360 h (RS3) after land application.

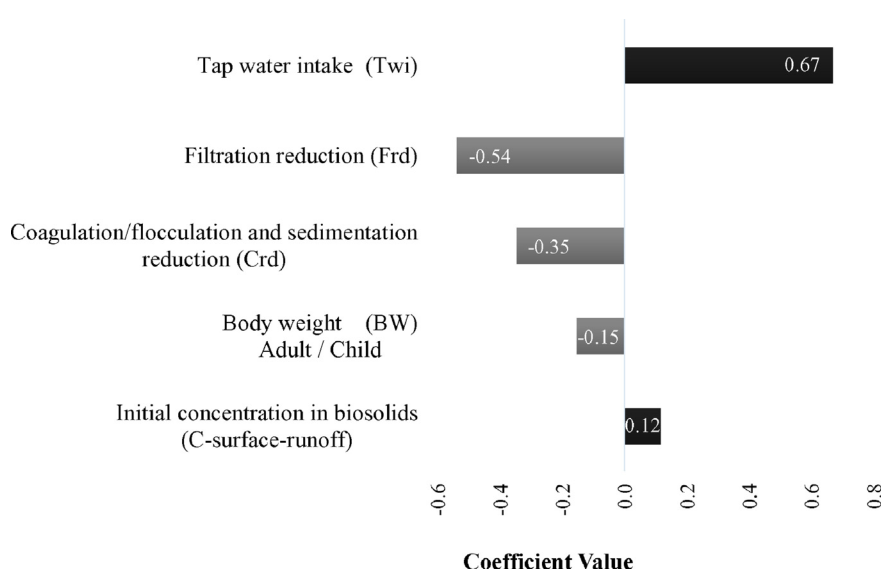


Fig. 5. Sensitivity analysis for Cu and LS biosolid treatment.

treatment (e.g. coagulation/flocculation and sedimentation and filtration).

The health risk assessment (LADD) incorporates the amount of contaminant (remaining metal) in drinking water post treatment, the drinking water rate, and body weights of adult and children. This showed that consumption by children, incorporating Cu and the LS biosolids, had the highest exposure over the three rainfall simulations. Although children consume less, they have a greater exposure due to their physiological make-up. Therefore, even small amounts of metals in the drinking water may be harmful depending on the size and weight of the individual. The LADD results were compared to the provisional maximum tolerable daily intake (PMTDI) values for metals in food as proposed by the Food and Agricultural Organisation/World Health Organisation (FAO/WHO) Joint Expert Committee on Food Additives (JECFA) (WHO, 2011b).

The results of the HQ indicate that the probability of risk is negligible, as the threshold value of risk (HQ < 0.01) was well below 1. This study highlights the differences in wastewater treatment and the efficacy of each treatment, along with the effect of mobility/solubility on the metals studied. Mean concentrations of metals in drinking water post WTPs are normally well below concentrations found in the literature (Kavcar et al., 2009; Muhammad et al., 2011; Lucid et al., 2013).

It is important to note that the results from the runoff experiment represent a single biosolid application. In general, biosolids are applied according to the phosphorus requirement of the crop; grassland etc., therefore the rate of biosolid application may have to be increased accordingly. Greater concentrations and long-term use of biosolids on some soil types may be potentially hazardous to the environment. Harrison et al., (2000) demonstrated how metals were strongly retained in the surface soil horizons after 15 years of biosolid spreading at a high rate (500 t ha^{-1}). Silva and Camilotti (2014) reported a linear increase in total concentrations of Cu and Zn in a clayey oxisol in the first year of application (single application rates) which reached maximum of 80 mg ha^{-1}. Four years later, the same linear increase was observed and concentrations were similar to the first year, indicating that metals persist in the soil for a long time.

5. Conclusion

A quantitative risk assessment model capable of estimating human health risk following land application of biosolids to agricultural grasslands was developed. It was assumed that surface runoff entered an adjacent stream without any chance of attenuation along the transfer continuum before delivery to the surface water body. It was then assumed that the water was abstracted for drinking water treatment. Metal concentrations in surface-runoff following land application of biosolids to agricultural grasslands were below their respective drinking water limits for human consumption. Following further risk assessment (based on LADD and HQ), the results indicated that there was no immediate risk from consumption of drinking water following treatment; however, there is a concern that consumption of lower levels of metals and long-term exposure may show potential chronic effects. It is important to consider body weight, as well as overall consumption, when evaluating potential hazard due to physiological differences as children may be more vulnerable. As this study only focused on metals, future studies are needed in order to assess other compounds of concern e.g. pharmaceutical contaminants that may be present in biosolids. Under the conditions monitored, metal concentrations in the four biosolids evaluated were not considered a risk to human health.

Acknowledgements

The authors acknowledge the Irish EPA for the funding of this project under the STRIVE Programme (2007-2013).

References

Amuda, O.S., Alade, A., 2006. Coagulation/flocculation process in the treatment of abattoir wastewater. Desalination 196, 22–31.

Appels, L., Baeyens, J., Degrève, J., Dewil, R., 2008. Principles and potential of the anaerobic digestion of waste-activated sludge. Prog. Energy Combust. Sci. 34, 755–781.

ATSDR, 2008. Public Health Statement. Cadmium (Available http://www.atsdr.cdc.gov/toxprofiles/phs5.html. Accessed September 18th 2015).

Aulenbach, D.B., Chan, Y.-Y., 1988. Heavy metals removal in a rapid infiltration sand column. Part. Sci. Technol. 6, 467–481.

Chang, A.C., Warneke, J.E., Page, A.L., Lund, L.J., 1984. Accumulation of heavy metals in sewage sludge-treated soils. J. Environ. Qual. 13, 87–91.

Chang, A., Page, A., Hyun, H.-N., 1997. Cadmium uptake for Swiss chard grown on composted sewage sludge treated field plots: plateau or time bomb? J. Environ. Qual. 26, 11–19.

Chen, Y., Cheng, J.J., creamer, K.S., 2008. Inhibition of anaerobic digestion process: a review. Bioresour. Technol. 99, 4044–4064.

Chu, W., 1999. Lead metal removal by recycled alum sludge. Water Res. 33, 3019–3025.

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. http://dx.doi.org/10.1080/10807039.2014.930295.

Clarke, R., Healy, M.G., Fenton, O., Cummins, E., 2015. A quantitative risk ranking model to evaluate emerging organic contaminants in biosolid amended land and potential transport to drinking water. Hum. Ecol. Risk Assess. http://dx.doi.org/10.1080/10807039.2015.1121376.

Colman, J.A., Massey, A.J., Levin, S.B., 2011. Determination of dilution factors for discharge of aluminum-containing wastes by public water-supply treatment facilities into lakes and reservoirs in Massachusetts. US Department of the Interior, US Geological Survey.

Cummins, E., Kennedy, R., Cormican, M., 2010. Quantitative risk assessment of cryptosporidium in tap water in Ireland. Sci. Total Environ. 408, 740–753.

Daneshi, N., Banejad, H., Pirtaj Pirtaj Hamedany, R., Faraji, H. & Rahimpour Golroubari, V. 2009. Removal of copper and zinc existing in water and wastewater in presence of phosphate by rapid sand filter. 33rd IAHR 2009 Congress-Water Engineering for a Sustainable-Vancouver-Canada, 2009.

Davis, M.A., Gilbert-Diamond, D., Karagas, M.R., Li, Z., Moore, J.H., Williams, S.M., Frost, H.R., 2014. A dietary-wide association study (DWAS) of environmental metal exposure in US children and adults.

ECB (European Chemical Bureau), 2003. Technical guidance document on risk assessment; part II. Environmental Exposure Assessment. EUR 20418 En/2 (Available at https://echa.europa.eu/documents/10162/16960216/tgdpart2_2ed_en.pdf. Accessed July 31st 2015).

END-O-SLUDG, 2014. Available at. http://www.end-o-sludg.eu. Accessed June 15th 2015.

Ersoz, M., Barrott, L., 2012. Best practice guide on metals removal from drinking water by treatment. IWA Publishing, London, UK, p. 17.

Fatoki, O., Ogunfowokan, A., 2004. Effect of coagulant treatment on the metal composition of raw water. Water SA 28, 293–298.

Fehily Timoney and Company, 1999. Codes of Good Practice for the Use of Biosolids in Agriculture (Available at http://www.environ.ie/en/Publications/Environment/Water/FileDownLoad,17228,en.pdf. Accessed June 5th 2015).

Fernández-Luqueño, F., López-Valdez, F., Gamero-Melo, P., Luna-Suárez, S., Aguilera-González, E., Martínez, A., García-Guillermo, M., Hernández-Martínez, G., Herrera-Mendoza, R., Álvarez-Garza, M., 2013. Heavy metal pollution in drinking water-a global risk for human health: a review. Afr. J. Environ. Sci. Technol. 7, 567–584.

Gawdzik, J., Gawdzik, B., 2012. Mobility of heavy metals in municipal sewage sludge from different throughput sewage treatment plant. Pol. J. Environ. Stud. 21, 1603–1611.

Gove, L., Cooke, C.M., Nicholson, F.A., Beck, A.J., 2001. Movement of water and heavy metals (Zn, Cu, Pb and Ni) through sand and sandy loam amended with biosolids under steady-state hydrological conditions. Bioresour. Technol. 78, 171–179.

Gray, N.F., 2010. Water Technology An Introduction for Environmental Scientists and Engineers, London, UK. Elsevier Ltd., p. 304.

Hannah, S., Jelus, M., Cohen, J., 1977. Removal of uncommon trace metals by physical and chemical treatment processes. J. Water Pollut. Control Fed. 2297–2309.

Harrison, R., Henry, C., Xue, D., Canary, J., Leonard, P., King, R., 2000. The fate of metals in land application systems. Digestion 3, 2.

Hinesly, T.D., Jones, R.L., Ziegler, E.L., 1972. Effects on corn by application of heated anaerobically digested sludge. Compost. Sci. 13, 26–30.

Ireland EPA, 1995. Water Treatment Manual-filtration (Available at https://www.epa.ie/pubs/advice/drinkingwater/EPA_water_treatment_manual_%20filtration1.pdf. Accessed 5th June 2015).

Ireland EPA, 2003. The Quality of Drinking Water in Ireland (Available at http://www.carlow.ie/SiteCollectionDocuments/All%20Services/Water%20Services/Publications/EPA-drinking-water-quality-2003.pdf. Accessed May 21st 2015).

Ireland EPA, 2011. Water Treatment Manual: Disinfection (Available at http://www.epa.ie/pubs/advice/drinkingwater/disinfection2_web.pdf. Accessed May 21st 2015).

IUNA (Irish Universities Nutrition Alliance), 2005. National Children's Food Survey. Main Report (Available at www.iuna.net. Accessed September 14th 2014).

IUNA (Irish Universities Nutrition Alliance), 2011. National Adult Nutrition Survey. Summary Report (Available at www.iuna.net. Accessed September 14th 2014).

Jiménez, B., 2005. Treatment technology and standards for agricultural wastewater reuse: a case study in Mexico. Irrig. Drain. 54, S23–S33.

Joshua, W.D., Michalk, D.L., Curtis, I.H., Salt, M., 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 (1), 135–156.

Kang, M., Kamei, T., Magara, Y., 2003. Comparing polyaluminum chloride and ferric chloride for antimony removal. Water Res. 37, 4171–4179.

Kavcar, P., Sofuoglu, A., Sofuoglu, S.C., 2009. A health risk assessment for exposure to trace metals via drinking water ingestion pathway. Int. J. Hyg. Environ. Health 212, 216–227.
Kumar, M., Puri, A., 2012. A review of permissible limits of drinking water. Indian J. Occup. Environ. Med. 16, 40.
Lasley, K.K., 2008. Chemistry and Transport of Metals from Entrenched Biosolids at a Reclaimed Mineral Sands Mining Site in Dinwiddie County. Virginia Polytechnic Institute and State University, Virginia.
Lemly, A.D., 1996. Evaluation of the hazard quotient method for risk assessment of selenium. Ecotoxicol. Environ. Saf. 35, 156–162.
Liu, X., Song, Q., Tang, Y., Li, W., Xu, J., Wu, J., Wang, F., Brookes, P.C., 2013. Human health risk assessment of heavy metals in soil–vegetable system: a multi-medium analysis. Sci. Total Environ. 463, 530–540.
Lu, Q., He, Z.L., Stoffella, P.J., 2012. Land application of biosolids in the USA: a review. Appl. Environ. Soil Sci. 2012, 11.
Lucid, J., Fenton, O., Healy, M., 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 Pollut. 224, 1–12.
Mamindy-Pajany, Y., Sayen, S., Guillon, E., 2014. Impact of lime-stabilized biosolid application on Cu, Ni, Pb and Zn mobility in an acidic soil. Environ. Sci. Pollut. Res. 21, 4473–4481.
Mahiya, S., L., G., Sharma, S.K., 2014. Heavy metals in water, their adverse health effects and biosorptive removal. Int. J. Chem. 3, 132–149.
McBride, M.B., Richards, B.K., Steenhuis, T., Russo, J.J., Sauvé, S., 1997. Mobility and solubility of toxic metals and nutrients in soil fifteen tears after sludge application. Soil Sci. 162, 487–500.
Mohod, C.V., Dhote, J., 2013. Review of heavy metals in drinking water and their effect on human health. Int. J. Innov. Res. Sci. Eng. Technol. 2, 2992–2996.
Muhammad, S., Shah, M.T., Khan, S., 2011. Health risk assessment of heavy metals and their source apportionment in drinking water of Kohistan region, northern Pakistan. Microchem. J. 98, 334–343.
Nordberg, G.F., Fowler, B.A., Nordberg, M., 2014. Handbook on the Toxicology of Metals. Academic Press, p. 8.
Oyoo-Okoth, E., Admiraal, W., Osano, O., Manguya-Lusega, D., Ngure, V., Kraak, M.H.S., Chepkirui-Boit, V., Makwali, J., 2013. Contribution of soil, water and food consumption to metal exposure of children from geological enriched environments in the coastal zone of Lake Victoria, Kenya. Int. J. Hyg. Environ. Health 216, 8–16.
Pang, F.M., Teng, S.P., Teng, T.T., 2009. Heavy metals removal by hydroxide precipitation and coagulation-flocculation methods from aqueous solutions. Water Qual. Res. J. Can. 44, 174–182.
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.
Quandt, S.A., Jones, B.T., Talton, J.W., Whalley, L.E., Galván, L., Vallejos, Q.M., Grzywacz, J.G., Chen, H., Pharr, K.E., Isom, S., 2010. Heavy metals exposures among Mexican farmworkers in eastern North Carolina. Environ. Res. 110, 83–88.
Renault, F., Sancey, B., Badot, P.-M., Crini, G., 2009. Chitosan for coagulation/flocculation processes–an eco-friendly approach. Eur. Polym. J. 45, 1337–1348.
Salem, H.M., Eweida, E.A., Farag, A., 2000. ICEHM2000. Cairo University, Egypt, pp. 542–556 (Available at http://www.virtualacademia.com/pdf/health542_556.pdf. Accessed October 10th 2015).
S.I. (Statutory Instrument) No.122 of, 2014. European Union (Drinking Water) Regulations 2014 Arrangement of Regulations. The Stationary Office, Dublin, Ireland (Available at: http://www.irishstatutebook.ie/pdf/2014/en.si.2014.0122.pdf. Accessed September 2nd 2015).
Silva, A.R.B., Camilotti, F., 2014. Risks of heavy metals contamination of soil-pant system by land application of sewage sludge: a review with data from Brazil. Embrapa Amazônia Oriental-Capítulo em livro técnico-científico (ALICE).
Silveira, M.L.A., Alleoni, L.R.F., Guilherme, L.R.G., 2003. Biosolids and heavy metals in soils. Sci. Agric. 60, 793–806.
Singh, R., Gautam, N., Mishra, A., Gupta, R., 2011. Heavy metals and living systems: an overview. Indian J. Pharmacol. 43, 246.
Tchounwou, P.B., Yedjou, C.G., Patlolla, A.K., Sutton, D.J., 2012. Heavy metal toxicity and the environment. Molecular, Clinical and Environmental Toxicology. Springer.
Techneau, W.A., 2010. Optimization of water treatment: Enhanced coagulation and ozonation-biofiltration. Summary Report on Performance Assessment Tools and Optimization (Available at http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.431.5558&rep=rep1&type=pdfAccessed May 5th 2015).
Thapa, K., 2009. Effect of Water Quality Matrix on Chromium Removal, MSc Thesis, UNESCO-IHE. Institute for Water Education, Delft, The Netherlands.
Topp, E., Monteiro, S.C., Beck, A., Coelho, B.B., Boxall, A., Duenk, P.W., Kleywegt, S., Lapen, D.R., Payne, M., Sabourin, L., 2008. Runoff of pharmaceuticals and personal care products following application of biosolids to an agricultural field. Sci. Total Environ. 396, 52–59.
VERO, S.E., ANTILLE, D.L., LALOR, S.T.J., HOLDEN, N.M., 2014. Field evaluation of soil moisture deficit thresholds for limits to trafficability with slurry spreading equipment on grassland. Soil Use Manag. 30, 69–77.
WHO/IPCS, 2000. Human Exposure Assessment, Environmental Health Criteria 214, WHO, Geneva (Available at http://www.who.int/ipcs/publications/ehc/en/. Accessed August 21st 2015).
WHO (World Health Organisation), 2008. Guidelines for Drinking-water Quality, F Edition (Available at http://www.who.int/water_sanitation_health/dwq/fulltext.pdf?ua=1. Accessed May 3rd 2015).
WHO (World Health Organisation), 2011a. Guidelines for Drinking-Water Quality. fourth ed. 1 ((Geneva). Available at http://apps.who.int/iris/bitstream/10665/44584/1/9789241548151_eng.pdf. Accessed May 3rd 2015).
WHO (World Health Organisation), 2011b. Joint FAO/WHO Food Standards Programme Codex Committee On Contaminants in Foods. Fifth Session. The Hague, The Netherlands (21–25 March 2011. Available at ftp://ftp.fao.org/codex/meetings/CCCF/cccf5/cf05_INF.pdf Accessed May 3rd 2015).
Wuana, R.A., Okieimen, F.E., 2011. Heavy metals in contaminated soils: a review of sources, chemistry, risks and best available strategies for remediation. ISRN Ecol. 2011, 20.