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Title: A review of selected microcontaminants and microorganisms in land runoff and tile drainage in treated sludge-amended soils.

Article Type: Review Article

Keywords: Surface runoff; tile drainage; microcontaminants; bacteria; sludge-amended soil; rainfall intensity

Corresponding Author: Professor Paola Verlicchi, Ph.D.

Corresponding Author's Institution: University of Ferrara

First Author: Andrea Ghirardini

Order of Authors: Andrea Ghirardini; Paola Verlicchi, Ph.D.

Abstract: The objective of this study is to provide a snapshot of the quality of surface runoff and tile drainage in sludge-amended soil in terms of 57 microcontaminants, including pharmaceuticals, hormones and fragrances, and 5 different species of bacteria. It also discusses the main factors affecting their occurrence (soil characteristics, applied sludge load and rate, sludge application method, rain intensity and frequency). It is based on 38 investigations carried out by different research groups in Canada, Australia, the USA and Ireland. The most frequently investigated compounds were hormones, the antiseptics triclosan and triclocarban, the analgesics and anti-inflammatories acetaminophen, ibuprofen and naproxen, the antibiotic sulphamethoxazole, the lipid regulator gemfibrozil and the psychiatric drug carbamazepine. Of all the bacteria, E. coli was the most monitored species. It was found that concentrations of the studied pollutants in surface runoff and tile drainage may vary, depending on many factors. They are generally lower than those observed in the secondary municipal effluent and in surface water, but their contribution to the deterioration of surface water quality might be relevant, mainly in wide rural areas. In this context, the reported data or their ranges represent an attempt to provide reference thresholds and bands of observed concentrations for a rough estimation of the contribution made by the release of the selected pollutants into surface water bodies via surface runoff and tile drainage.

Response to Reviewers: Replies to comments and suggestions by the reviewers

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Cover Letter

Ferrara, October, 12th 2018

Dear Editor
Prof. Damia Barcelò
Science of the Total Environment

referring to the manuscript we submit to your Journal:

A review of selected microcontaminants and microorganisms in land runoff and tile drainage in treated sludge-amended soils.

by

Andrea Ghirardini and Paola Verlicchi

I would like to make the following remarks:

- the work described in this paper has not been previously published and it is not under consideration for publication elsewhere,
- the *Corresponding Author* is PAOLA VERLICCHI
- Her address is:

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mail paola.verlicchi@unife.it

UNIQUE FEATURES OF THE STUDY

The paper we propose is an overview of the concentrations of micropollutants and 5 bacteria species in surface runoff and tile drainage in case of sludge-amended soil. The topic is new and original but a debate is ongoing among the scientific community. Not only secondary effluents or combined sewage overflows may contribute in deteriorating the quality of a receiving water body, but also land runoff in those areas where treated municipal sludge is disposed in soil for agricultural benefits. The manuscript presents and compares the concentrations of the investigated pharmaceuticals, hormones and fragrances as well as bacteria species found in land runoff and tile drainage in different investigations carried out in Europe, the USA and Canada. It also discusses the influence on their occurrence of the characteristics of the contaminants, the soil, the sludge treatment, way and rate of application and rainfall intensity and frequency,
It highlights the main lessons learned from these investigations and the areas requiring further research and perspectives.
I think that *Stoten* is a suitable journal for this kind of topic and the most interested readers are environmental and sanitary engineers, biologists, chemists, scientists, researchers working in sludge management sector.

Sincerely Yours

Paola Verlicchi

*Title Page

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Abstract

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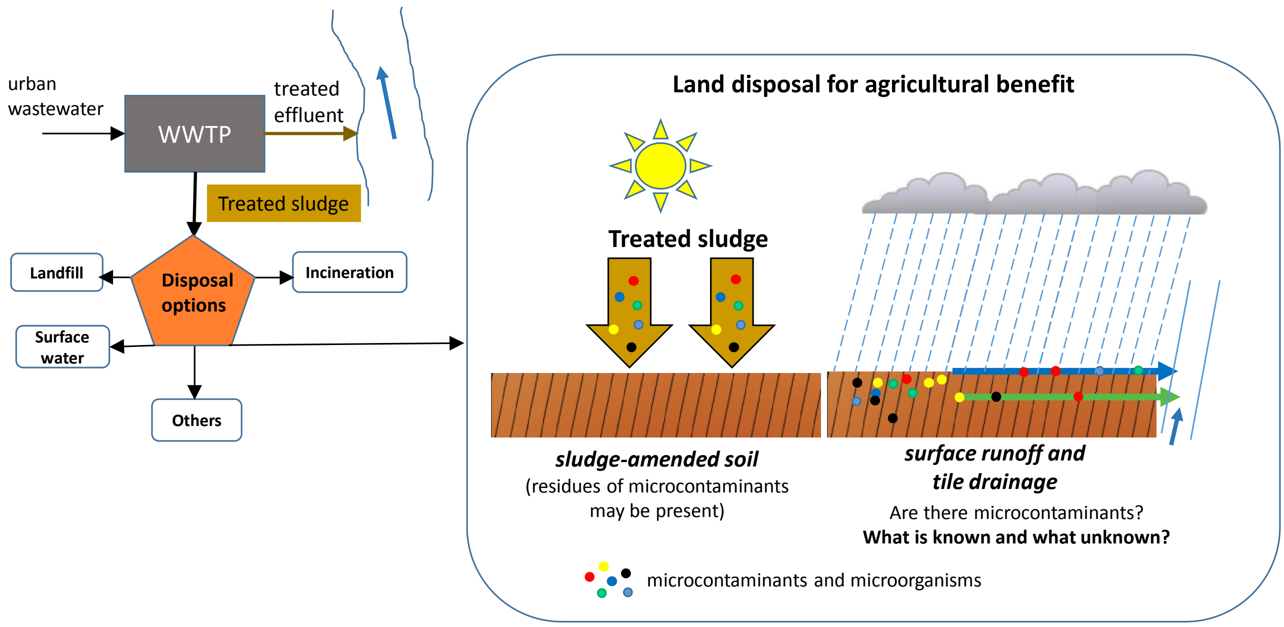
Graphical abstract



List of abbreviations:

AOX adsorbable organic halides;

AWI anthropogenic waste indicators;

~~BC Background concentration,~~

CEC Cation exchange capacity;

dm dry matter;

DMB dewatered municipal biosolids;

D_{ow} octanol-water distribution coefficient;

FC Fecal coliforms;

HM heavy metal;

K_{ow} octanol-water partition coefficient;

LAS Linear Alkylbenzene;

LMB liquid municipal biosolids;

LOD limit of detection;

LOQ limit of quantification;

MEC measured environmental concentration;

MW molecular weight;

PAH Polycyclic aromatic hydrocarbons;

PCB Polychlorinated biphenyl;

PCDD/F dioxins and furans;

pK_a dissociation constant

PPCPs pharmaceutical and personal care products;

RL reporting limit; SD standard deviation;

TC Total coliforms;

u.o.m. unit of measure

1 Introduction

Intense rainfall events detach and transport fine and low-density particles in land runoff, which may contain different kinds of pollutants. In addition, rain infiltrating dry soils can also leachate natural and anthropogenic substances (contaminants) retained and accumulated in the soil matrix and convey them to other environmental compartments, including groundwater and surface water bodies.

Contaminant accumulation in/on soil can be due to different routes. The most important contributions come from the disposal of treated sludge (Torri and Cabrera, 2017), the disposal of manure (Segat et al.,2015), land irrigation with reclaimed wastewater (Dodgen and Zheng 2016; Pedersen et al., 2003,2005, Xu et al., 2009), and land irrigation with surface water containing these contaminants (Calderon-Preciado et al., 2011).

Land disposal of treated municipal sludges is a common practice in many countries worldwide (Ingleziakis et al., 2014; Kelessidis and Stasinakis, 2012). In the following the term *biosolids* will be used as an alternative of treated sludges: the term biosolids was introduced in 1991 in the USA by the Water Environment Federation (WEF, 2005) to distinguish raw, untreated sewage sludge from treated and tested sewage sludge, which could legally be used for agricultural benefits.

This method of disposal can positively contribute to the improvement of soil properties and fertility (Clarke and Smith, 2011) due to the presence of nutrients and other substances in the sludges able to improve soil porosity or permeability (amendant effects), to favor aggregation of the main soil constituents (conditioning effects), to change chemical and physical soil properties (corrective effects) and/or to provide elements in assimilable or available form for plants (fertilizing effects).

Sewage sludge not only provides soil with organic matter, but it also increases infiltration, reduces the possibility of soil erosion (Lucid et al., 2014) and increases agronomic productivity (Samaras et al. 2008, Tsadilas et al. 2005, Zartman et al. 2012). Its use for agricultural benefits also addresses European Union policy on sustainability and the recycling of resources (COM, 2014).

In the case of intense rain events, surface runoff could seriously impact on near surface water bodies and affect their quality in terms of suspended solids, nutrients, and bacteria, as well as other emerging contaminants.

In addition, in those regions where natural field drainage can adversely affect crop production activities, it may interfere with the groundwater if the groundwater system is near the surface on a year round basis, as could be the case in any of the poorly drained soils in eastern Ontario (Lapen et al., 2008a,b,2018). There, tile drains are placed on agricultural areas within 1 m of the soil surface in order to collect draining water and short-circuit it to the adjacent surface water streams or rivers. This stream is then conveyed to a surface water body.

In the last few years, issues related to land runoff as well as tile drainage quali-quantitative characteristics have caused increasing concern. For the most part, attention has been paid to macro-pollutants (suspended solids, organic substances, nitrogen and phosphorus compounds) (Paule et al., 2014), heavy metals (Hosseini Koupaie and Eskicioglu 2015), and pesticides (Torri and Cabrera, 2017). Some investigations have strongly focused on the environmental risks posed by the presence of nutrients and heavy metals due to the land application of treated sludge, as well as-manure (Eldridge et al., 2009; Peyton et al., 2016; Jia et al.,2015; Bai et al., 2016). Some studies have also addressed mobilization in the runoff of bacteria applied to soil with the treated sludge. It has been highlighted that the soil environment is hostile for their development and that their survival time, following land application, is around 2-4 months (Brennan et al., 2012). As a consequence, bacteria are more likely to be transported into receiving water courses after rainfall events.

Recent studies have highlighted the occurrence of micro-contaminants, mainly pharmaceuticals and personal care products (PPCPs) in treated sludges and underlined the importance of more thorough investigations into the fate of these pollutants once spread on soil (Verlicchi and Zambello, 2015). In this way, contaminants could reach surface water bodies and in some cases they could pose a potentially acute and chronic risk for aquatic life (Clarke and Cummins, 2015), or ~~could~~ deteriorate the quality of freshwater reserves used for potable needs (Clarke et al., 2016).

From a legislative view point, different scenarios exist. The reuse of biosolids is not allowed in Belgium, Romania and Switzerland (Healy et al., 2017). In other countries it is possible (many European countries, New South Wales-Australia, Ontario-Canada, and the USA) and the current legal requirements regarding sludge disposal on soil commonly concern maximum sludge concentrations and/or maximum sludge loads for organic matter and nutrients, heavy metals, selected pesticides, and organic microcontaminants ~~pollutants~~ such as AOX, PCB, PCDD/F, as well as chemical-physical characteristics of the receiving soil, and the maximum quantity of sludge to be disposed on soil on a yearly basis (Mininni et al. 2015; Kelessidis and Stasinakis 2012; Le Blanc et al. 2008).

To date, no legal requirement has been set concerning the maximum permitted concentrations or loads for PPCPs ~~pharmaceuticals and personal care products~~ (Kelessidis and Stasinakis, 2012; Lu et al., 2012, Leblanc et al., 2008). With regard to microorganisms, only a few States have standards regarding the maximum concentrations in sewage sludge to be disposed of on soil, and these mainly concern *Salmonella* and *E. coli* (Lu et al., 2012; Minnini et al., 2015).

As reported above, reclaimed water reuse for irrigation purposes may also contribute to the introduction of residues of microcontaminants of emerging concern into the soil (Kinney et al., 2006; Martinez-Piernas et al., 2018). The benefits due to the reduced demand for fresh water and the supply of nutrients (occurring in reclaimed water) are counterbalanced by the potential contamination risk to water and plants by still unregulated pollutants (Christou et al. 2017; Wu et al. 2015). This reuse practice is of great interest, principally for regions characterized by water scarcity (among them Spain, Cyprus, Lybia, and Jordan) and/or frequent periods of drought (Morocco, Algeria, and Tunisia). The contribution may be relevant but also limited to specific case studies.

This review aims to provide a snapshot of the chemical characteristics of surface runoff and also the leachate in sludge-amended soil with regard to investigated PPCPs and bacteria species. A further objective is to investigate the main factors affecting them (compound properties, soil characteristics, applied sludge load and flow rate, sludge application method, rain intensity and frequency). The idea is to provide reliable data on the quality of surface runoff and tile drainage leading to an assessment of the potential contribution of these streams to the quality of the surface water body during intense rain events. This review also underlines the strengths and weaknesses of available studies, the gaps in current knowledge and the research fields requiring further investigation. The reported data or their ranges could represent reference thresholds or bands of observed concentrations for a rough estimation of the contribution made by the release of the selected pollutants into surface water bodies *via* surface runoff.

1.1 Framework of the study

This study provides an overview of chemical characteristics in terms of concentrations of a selection of microcontaminants ~~pollutants~~ and microorganisms (Table 1) in the water streams (surface runoff and tile drainage) which, due to rain events, leave agricultural soils where treated sludge (= biosolids) has previously been applied. The review is based on a collection of 16 papers, published between 1980 and 2017, referring to 38 investigations into the occurrence of 57 PPCPs and 5 species of microorganisms (*E. coli*, Fecal coliform, Total coliform, Fecal streptococcus, and *Clostridium perfringens)*, in land runoff or in tile drainage after the disposal of treated municipal sludge onto soil.

Selected investigations differ in at least one of the following issues: (i) soil type, (ii) municipal sludge type (depending on the treatment it was subjected to), (iii) sludge application method, (iv) sludge application rate, (v) investigated water stream (runoff or tile drainage), and (vi) rainfall frequency pattern. One study may include more than one investigation.

The 38 investigations were carried out in Ireland (8), the USA (15), Canada (11) and Australia (4) and most of the research groups belong to agricultural research centers. Investigations into land runoff in the case of manure applied on soil were not included, since manure disposal on rural land is subject to specific regulations from country to country and many types of manures are available depending on the animals (cattle, pigs, chickens, sheep, etc.). Table 2 reports the main characteristics of the studies included in the review with the number of investigations specified for each study. Their aims and scope and the principal issues addressed are also underlined.

Figure S1 shows how these studies are temporally and spatially correlated and whether they include common research groups; Table S1 details the main characteristics of the reviewed 38 investigations with regard to field/plots, soil, sludge, rainfall, sampling strategy and the main findings. Investigations referring to the spiking of soil with specific microcontaminants (among them Davis et al., 2006) were not included, as according to Al-Rajab et al., 2009, the effect of the presence of treated sludge (the matrix containing microcontaminants ~~pollutants~~) strongly influences the fate and behaviour of such contaminants in the soil.

Bearing in mind the definition sets in chemical engineering manuals, leachate is the liquid stream obtained from a leaching process, that is a unit operation consisting of a mass (and energy) transport from a solid phase (the soil) to a liquid one (the water leaving the soil) when they come into contact. With regard to Figure 1, once the rain starts, dry soil begins to retain water within its macro- and micro-pores. Water tends to percolate (generating the *leachate* or *percolate*) and in the case of prolonged rain events, when the soil becomes saturated, the water starts moving (flowing) on the soil surface, according to its slope, generating the so-called *surface runoff*. Sludge retained on the land surface is also subject to light exposure and phodegradation processes may occur, changing the characteristics of the sludge.

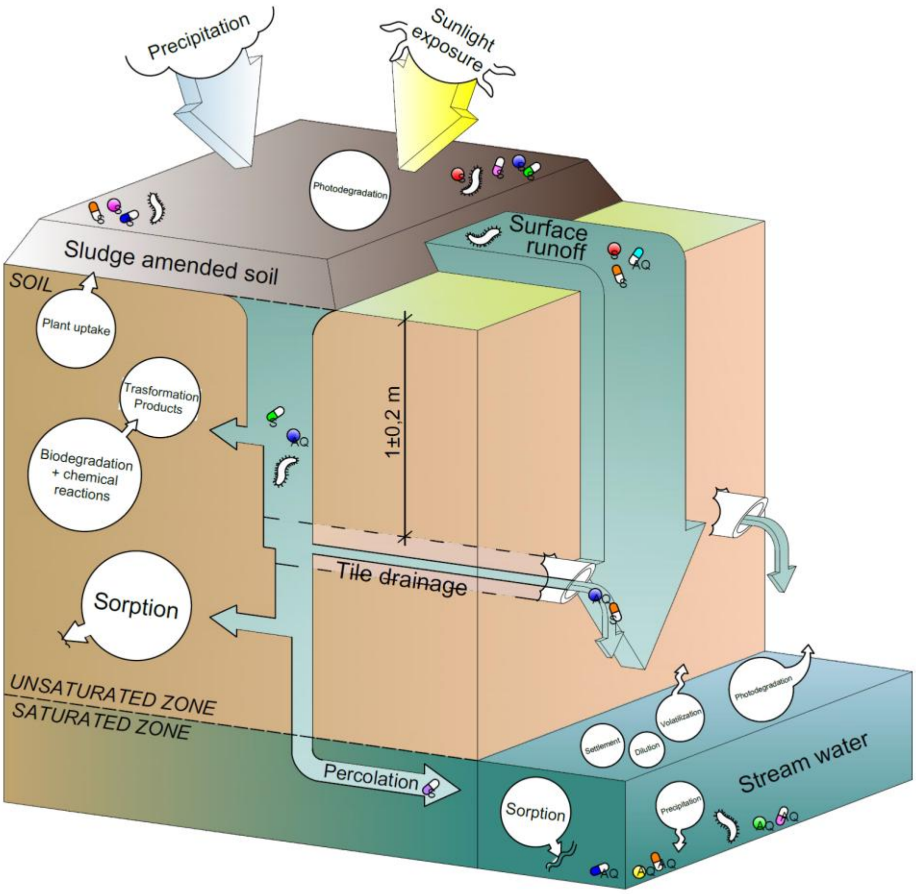
With regard to percolation of the water through the soil, if this stream is intercepted by pipes (drains), the water flow which spills out is called *tile drainage*. Figure 1 shows the different water flow paths on soil in the case of precipitation and it also shows the potential degradation/removal mechanisms pollutants and microorganisms occurring in the soil may undergo. Figure 1 is the conceptual scheme this study will refer to. In particular, it will investigate surface runoff and tile drainage characteristics in treated municipal sludge-amended soil: the two streams which can rapidly reach the receiving water stream, affecting its quality.

Section 2.2 deals with sludge application on soil in terms of sludge types based on the treatment before application, sludge application methods (compared in Table 3), the maximum loads allowed by the different regulations, and a brief overview of the legal requirements (standards for specific pollutants and in particular for microorganisms, section 2.2.3, with further details provided in Tables S3 and S4).

This study goes on to present the characteristics of the soil which can affect the runoff/tile drainage quality, the size of the plots and the characteristics of the rainfall events of the investigations. Special attention was also paid to data reliability and accuracy (section 2.5), and an analysis of the reviewed studies can be found in Table S1. The results are reported in graphs which show measured concentrations of selected PPCPs and bacteria in surface runoff and tile drainage as well as background concentrations in the absence of sludge application (when available). In the Supplementary Materials section, details are available in terms of a descriptive statistical analysis of the concentrations observed in surface runoff (Tab S5) and tile drainage (Tab S6).

Discussion of the results focuses mainly on the influence of the factors affecting runoff/tile drainage concentrations:

- compound characteristics;
- soil characteristics (matrix, pH, organic matter, organic carbon, cationic exchange capacity);
- sludge properties (CEC, moisture, pH, chemical composition) and its application rate;
- applied pollutant load;
- application method;
- application depth;
- applied water volume.



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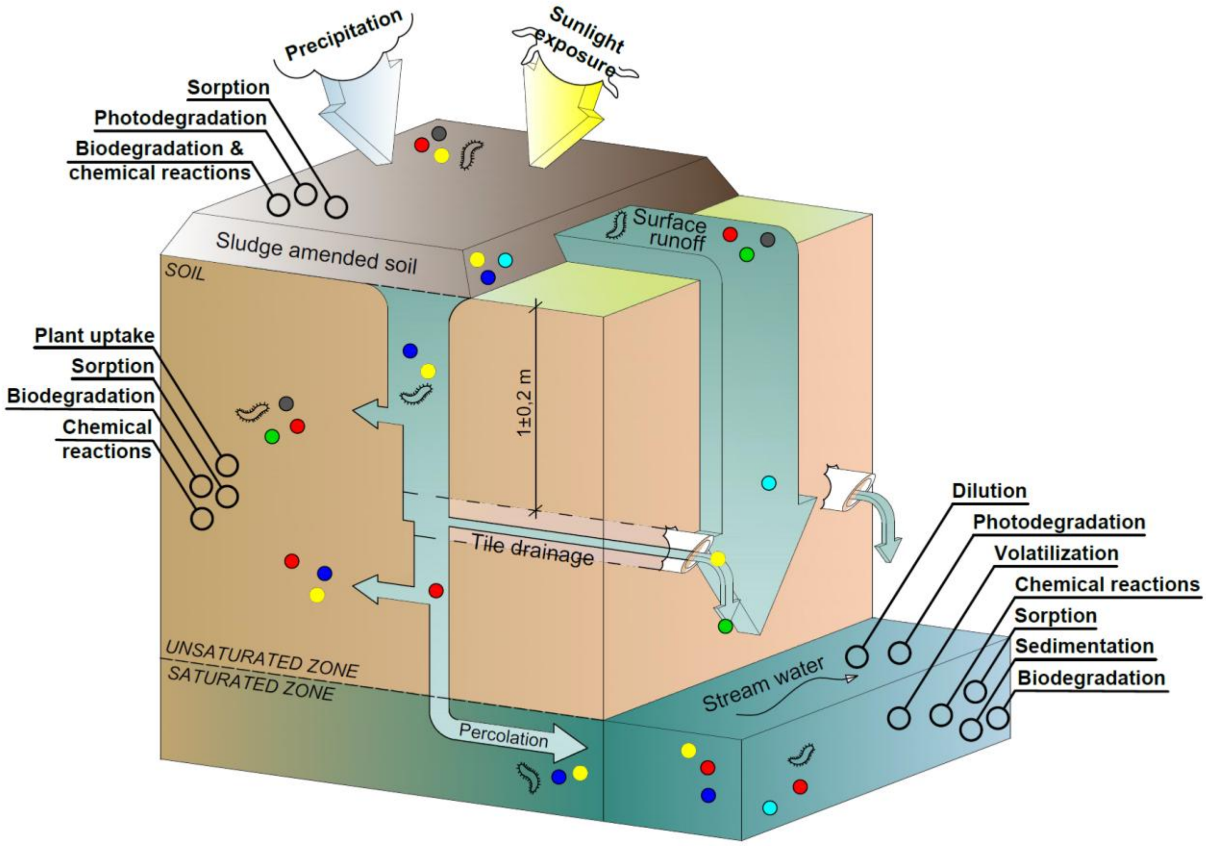


Figure 1. The two water streams leaving soil in the case of rain events (surface runoff and tile drainage) and the main removal mechanisms for microcontaminants (PPCPs and microorganisms) occurring within the soil.

Moreover, discussion of the collected results also refers to the ranges of measured concentrations of selected contaminants in secondary effluents, anaerobically digested sludges, runoff of rural soil irrigated with reclaimed water and surface water. The literature ranges to which the comparison refers are reported in Tables S2 and S5.

The study concludes with a list of the lessons learned from past investigations, the main gaps in the investigations and the issues requiring further study.

2 Materials and Methods

2.1 Compounds included in the review and main investigations

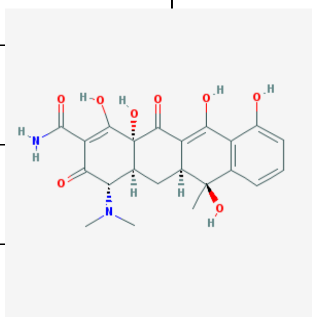
Investigated chemical compounds belong to 11 different therapeutic classes or groups: analgesics and anti-inflammatories (class A including 3 compounds); antibiotics (class B with 7 compounds); antifungals (class C, 1 compound); antihistamines (class D, 1 compound); antiseptics (class E, 2 compounds); beta-blockers (class F, 1 compound); fragrances (class G, 5 compounds), hormones (class H, 22 compounds), lipid regulators (class I, 1 compound); stimulants (class J, 2 compounds) and psychiatric drugs (class K, 12 compounds).

Table 1 compiles all of these with the main chemical characteristics (molecular weight MW, chemical formula, pK_a, LogK_{ow}), which are useful for analyzing or predicting their fate/behaviour once on the soil following sludge disposal, the number of related studies and corresponding references are also provided. The last group refers to bacteria commonly monitored in municipal wastewater treatments: *Clostridium perfringens*, *Escherichia coli*, Fecal coliforms, Fecal streptococci and Total coliforms.

Table 1 Pharmaceutical compounds, hormones, fragrances and microorganisms included in this study

Therapeutic class	**Pharmaceutical compound/ species**	**MW**	**Chemical formula**	**pK_a**	**LogK_{ow}**	**# papers**	**Reference**
Analgesics/ anti-inflammatories (A) (3)	Acetaminophen	151.2	$C_8H_9NO_2$	9.38	0.46 – 0.49	5	Edwards et al. 2009; Gottschall et al. 2012; Lapen et al. 2008b; Sabourin et al. 2009; Topp et al. 2008b
	Ibuprofen	206.3	$C_{13}H_{18}O_2$	4.94	3.97	5	Edwards et al. 2009; Gottschall et al. 2012; Lapen et al. 2008b; Sabourin et al. 2009; Topp et al. 2008b

Therapeutic class	**Pharmaceutical compound/ species**	**MW**	**Chemical formula**	**p*K*$_a$**	**Log*K*$_{ow}$**	**# papers**	**Reference**
	Naproxen	230.3	$C_{14}H_{14}O_3$	4.15	3.18	5	Edwards et al. 2009; Gottschall et al. 2012; Lapen et al. 2008b; Sabourin et al. 2009; Topp et al. 2008b
Antibiotics (B) (7)	4-Epitetracycline	444.4	$C_{22}H_{24}N_2O_8$	3.3	-1.37	1	Gottschall et al. 2012
	Ciprofloxacin	331.3	$C_{17}H_{18}FN_3O_3$	6.09	0.28	1	Gottschall et al. 2012
	Ofloxacin	3614.	$C_{18}H_{20}FN_3O_4$	pK_{a1}: 5.97 pK_{a2}: 9.28	-0.39	1	Gottschall et al. 2012
	Oxytetracycline	460.4	$C_{22}H_{24}N_2O_9$	3.27	-0.9	1	Gottschall et al. 2012
	Sulfamethoxazole	253.3	$C_{10}H_{11}N_3O_3S$	pK_{a1}: 1.60 pK_{a2}: 5.70	0.89	5	Edwards et al. 2009; Lapen et al. 2008b; Pedersen et al. 2005; Sabourin et al. 2009; Topp et al. 2008b
	Sulfapyridine	249.3	$C_{11}H_{11}N_3O_2S$	8.43	0.35 - 0.9	1	Lapen et al. 2008b;
	Tetracycline	444.4	$C_{22}H_{24}N_2O_8$			1	Gottschall et al. 2012
Antifungals (C) (1)	Miconazole	416.1	$C_{18}H_{14}Cl_4N_2O$			1	Gottschall et al. 2012
Antihistamines (D) (1)	Diphenhydramine	255.4	$C_{17}H_{21}NO$			1	Gottschall et al. 2012
Antiseptics (E) (2)	Triclocarban	345.6	$C_{13}H_9Cl_3N_2O$	12.7	4.9	5	Edwards et al. 2009; Giudice and Yang 2011; Gottschall et al. 2012; Healy et al.



Therapeutic class	**Pharmaceutical compound/ species**	**MW**	**Chemical formula**	**pK_a**	**LogK_{ow}**	**# papers**	**Reference**
							2017; Sabourin et al. 2009
	Triclosan	289.5	$C_{12}H_7Cl_3O_2$	7.9	4.76	8	Edwards et al. 2009; Giudice and Yang 2011; Gottschall et al. 2012; Gray et al. 2017; Healy et al. 2017; Lapen et al. 2008b; Sabourin et al. 2009; Topp et al. 2008b
Beta-blockers (F) (1)	Atenolol	266.3	$C_{14}H_{22}N_2O_3$	9.6	0.16	4	Edwards et al. 2009; Lapen et al. 2008b; Sabourin et al. 2009; Topp et al. 2008b
Fragrances and PCPs ingredients (G) (4)	Galaxolide (HHCB ~~AHTN~~)	258.4	$C_{18}H_{26}O$		5.9	1	Gray et al. 2017
	Indole	117.2	C_8H_7N	-2.4	2.14	1	Gray et al. 2017
	Menthol	156.3	$C_{10}H_{20}O$		3.2	1	Gray et al. 2017
	Skatole (3-Menthyl-1H-Indole)	131.2	C_9H_9N		2.6	1	Gray et al. 2017
	Tonalide (AHTN ~~HHCB~~)	258.4	$C_{18}H_{26}O$		5.7	1	Gray et al. 2017
Hormones (H) (22)	11-Ketotestosterone	302.4	$C_{19}H_{26}O_3$		1.92	1	Yang et al. 2012
	17-α-estradiol (Alfatradiol)	272.4	$C_{18}H_{24}O_2$		3.94 – 4.01	2	Gottschall et al. 2013; Yang et al. 2012
	17-beta-estradiol (or Estradiol)	272.4	$C_{18}H_{24}O_2$		3.94 – 4.01	2	Gottschall et al. 2013; Yang et al. 2012

Therapeutic class	**Pharmaceutical compound/ species**	**MW**	**Chemical formula**	**p*K_a***	**Log*K_{ow}***	**# papers**	**Reference**
	α-Dihydroequilin	270.4	$C_{18}H_{22}O_2$			1	Gotschall et al. 2013
	Androstenedione	286.4	$C_{19}H_{26}O_2$		2.75 – 2.76	2	Gottschall et al. 2013; Yang et al. 2012;
	Androsterone	290.4	$C_{19}H_{30}O_2$		3.69	1	Gotschall et al. 2013
	Cis-androsterone	290.4	$C_{19}H_{30}O_2$		3.07 – 3.69	1	Yang et al. 2012
	Desogestrel	310.5	$C_{22}H_{30}O$		5.65	1	Gotschall et al. 2013
	Diethylstilbestrol	268.4	$C_{18}H_{20}O_2$		5.07 – 5.64	1	Yang et al. 2012
	Dihydrotestosterone (Stanolone)	290.4	$C_{19}H_{30}O_2$		3.07 – 3.55	1	Yang et al. 2012
	Epitestosterone	288.4	$C_{19}H_{28}O_2$		3.27 – 3.32	1	Yang et al. 2012
	Equilenin	266.3	$C_{18}H_{18}O_2$		3.93	2	Gottschall et al. 2013; Yang et al. 2012
	Equilin	268.4	$C_{18}H_{20}O_2$		3.35	2	Gottschall et al. 2013; Yang et al. 2012
	Estradiol Benzoate	376.5	$C_{25}H_{28}O_3$			1	Gotschall et al. 2013
	Estriol	288.4	$C_{18}H_{24}O_3$	10.54	2.45 - 3.67	2	Gottschall et al. 2013; Yang et al. 2012
	Estrone	270.4	$C_{18}H_{22}O_2$		3.13 - 3.43	2	Gottschall et al. 2013; Yang et al. 2012
	Ethinyl Estradiol	296.4	$C_{20}H_{24}O_2$	10.4	3.67 – 4.15	3	Giudice and Yang 2011: Gottschall et al. 2013; Yang et al. 2012
	Mestranol	310.4	$C_{21}H_{26}O_2$		4.61 – 4.68	2	Gottschall et al. 2013; Yang et al.

Therapeutic class	**Pharmaceutical compound/ species**	**MW**	**Chemical formula**	**pK_a**	**LogK_{ow}**	**# papers**	**Reference**
							2012
	Norethindrone	298.4	$C_{20}H_{26}O_2$		2.97 – 2.99	2	Gottschall et al. 2013; Yang et al. 2012
	Norgestrel (Levonorgestrel)	312.5	$C_{21}H_{28}O_2$		3.48	1	Gottschall et al. 2013
	Progesterone	314.5	$C_{21}H_{30}O_2$		3.67 – 3.87	2	Gottschall et al. 2013; Yang et al. 2012
	Testosterone	288.4	$C_{19}H_{28}O_2$		3.27 – 3.32	2	Gottschall et al. 2013; Yang et al. 2012
Lipid regulators (I) (1)	Gemfibrozil	250.3	$C_{15}H_{22}O_3$	4.5	4.77	5	Edwards et al. 2009; Gottschall et al. 2012; Lapen et al. 2008b; Sabourin et al. 2009; Topp et al. 2008b
Stimulant (J) (2)	Caffeine	194,.	$C_8H_{10}N_4O_2$	10.4	-0.07	1	Sabourin et al. 2009
	Cotinine	176.2	$C_{10}H_{12}N_2O$		0.07	5	Edwards et al. 2009; Gottschall et al. 2012; Lapen et al. 2008b; Sabourin et al. 2009; Topp et al. 2008b
Psychiatric drugs (K) (12)	Bupropion	239.7	$C_{13}H_{18}ClNO$	8.22	3.85	1	Gottschall et al. 2012
	Carbamazepine	236.3	$C_{15}H_{12}N_2O$	13.9	2.45	5	Edwards et al. 2009; Gottschall et al. 2012; Lapen et al. 2008b; Sabourin

Therapeutic class	**Pharmaceutical compound/ species**	**MW**	**Chemical formula**	**pK_a**	**LogK_{ow}**	**# papers**	**Reference**
							et al. 2009; Topp et al. 2008b
	Citalopram	324.4	$C_{20}H_{21}FN_2O$		3.5	1	Gottschall et al. 2012
	Desmethyl Citalopram	310.4	$C_{19}H_{19}FN_2O$		2.8	1	Gottschall et al. 2012;
	Desmethyl Sertraline	320.2	$C_{17}H_{15}Cl_2NO$		4.5	1	Gottschall et al. 2012
	Desvenlafaxine	263.4	$C_{16}H_{25}NO_2$	pK_{a1}: 9.45 pK_{a2}: 10.66	2.72	1	Gottschall et al. 2012
	Fluoxetine	309.3	$C_{17}H_{18}F_3NO$	9.5	4.05	3	Edwards et al. 2009; Gottschall et al. 2012; Lapen et al. 2008b
	Norfluoxetine	295,.	$C_{16}H_{16}F_3NO$		3.5	1	Gottschall et al. 2012
	Norvenlafaxine	263.4	$C_{16}H_{25}NO_2$		3	1	Gottschall et al. 2012
	Paroxetine	329.4	$C_{19}H_{20}FNO_3$	9.6	1.23	1	Gottschall et al. 2012
	Sertraline	30.,2	$C_{17}H_{17}Cl_2N$		5.1	1	Gottschall et al. 2012
	Venlafaxine	277.4	$C_{17}H_{27}NO_2$	10.09	3.2	1	Gottschall et al. 2012
Group	**Species**					**# papers**	**Ref**
Bacteria (5)	*Clostridium perfringens*					2	Gottschall et al. 2013; Lapen et al. 2008a
	Escherichia coli					5	Atalay et al. 2007; Eldridge et al. 2009; Gottschall et al. 2013; Lapen et

Therapeutic class	Pharmaceutical compound/ species	MW	Chemical formula	pK_a	LogK_{ow}	# papers	Reference
							al. 2008a; Peyton et al. 2016
	Fecal Coliforms					2	Dunigand and Dick, 1980; Wallace et al. 2014
	Faecal Streptococcus					1	Gottschall et al. 2013
	Total Coliforms					3	Atalay et al. 2007; Gottschall et al. 2013; Peyton et al. 2016

Table 2. A brief presentation of the studies included in this review, in terms of their main characteristics, aims, scope of the investigations and number of investigations (see Table S1 for details).

Reference		**Main characteristics of the investigations**
Atalay et al. 2007	USA	Lab investigations were carried out into the occurrence of 2 microorganisms (*E. coli* and Total coliforms), nutrients and heavy metals in **surface runoff** after treated sludge applications. Air-dried sludge was applied at a rate of 2,240 kg/ha and mixed with the top 5 cm of the soil bed, on two different soils (a clay loam soil and a sandy loam soil called, respectively, Cullen and Bojac, see Table S1) to compare the influence of soil on runoff quality. Investigation fields consisted of 12 microplots (2 soils x 2 treatments x 3 replicates) - tilted aluminium beds (0.8 m x 1.9 m = 1.62 m^2 each) set up in an environmentally controlled greenhouse and used both for treatment and to control the investigation. Rainfall simulation (deionized water at a rate of 65 mm/h for 45 min) took place immediately before the sludge application (control investigation) and immediately after (treatment investigation), resulting in 2 samples (each with 3 replicates) per plot available for chemical and microbiological analyses. Number of investigations: 2
Dunigan and	USA	On-field investigations were carried out on the occurrence of nutrients and Fecal coliforms in

Dick, 1980		**surface runoff** in sludge-amended soil. Treated municipal sludge was applied at different rates (14.8, 16.2, and 28.9 tons/ha) and the concentrations of bacteria were monitored during the following weeks in order to evaluate their temporal variations. Investigation fields consisted of triplicate plots and a control one. Rainfall was simulated by applying deionized water at a rate of 1.11 cm/h for 2 hours. Number of investigations: 3
Edwards et al. 2009	Canada	On-field investigations were carried out on the occurrence (concentrations) and mass loads of 11 PPCPs in agricultural **tile drainage** systems following sludge application. Monitoring lasted approximately 162 d. Dewatered (centrifugated) anaerobically digested sludge was applied to loam soil at a rate of 8,000 kg/ha and mixed with the soil bed using two different methods (to compare the results): tilling with the top 10 cm of the soil and direct injections at a depth of 11 cm. The aim was to test the capacity to break DMB solid/aggregates apart and the effect of the atmosphere exposure and the soil environment on the PPCPs. Investigation fields consisted of 8 plots (100 m x 15 m= 1,500 m^2 each) in a field with tiles placed 0.8 m below the soil surface and spaced 15 m apart; 2 of them were hydraulically isolated and used for the control investigation (they never received DMB). Sampling occurred after a real rain event (in the case of a rainfall depth of 5 mm/h in summer and 7 mm/24 h in fall gathered in a rainwater collection vessel) which took place in the study period, with a total depth of 413 mm. Samples were collected with an automatic water sampler when a rainfall with a depth of 5 mm/h (summer) and 7 mm/d (fall) was gathered in a rain collection vessel. Samples were taken more frequently near the trigger followed by a gradual reduction (sample intervals were initially every 15 min, then every 30, 60, 90 and 120 mins) Number of investigations: 2
Eldridge et al. 2009	Australia	On-field investigations were carried out into the occurrence of *E. coli* and nutrients in **surface runoff** after surface spreading of 2 types of dewatered sludges (irradiated, non-irradiated and granulated biosolids) and a manure (poultry) on a silty clay loam soil covered by turf. Sludges and manure were spread on the surface. The applied sludges were a high temperature dried sludge (at a rate of 4,500 kg/ha, DMB1), a high temperature dried sludge that received gamma irradiation (pathogen free, at a rate of 4,500 kg/ha, DMB2), and a poultry litter (at a rate of 5,150 kg/ha). Investigation fields consisted of three replicate plots for four scenarios, resulting in 12 microplots (1 m x 2 m= 2 m^2 each) in a field with a slope of 10%. The four scenarios were an

		untreated control plot; poultry application, DMB1 application and DMB2 application. Rainfall simulation (potable water at a rate of 90 mm/h for 30 min) took place 7 days after application; 2 samples were collected for each plot - one for the first 3 L of runoff (first flush) and another for the total runoff volume. Number of investigations: 3
Giudice and Yang 2011	USA	Investigations were carried out into the occurrence of endocrine-disrupting compounds and heavy metals in **surface runoff** after sludge application for approximately 31 d. Dewatered (and thermally dried) anaerobically digested sludge was applied to sandy loam soil at a rate of 22,500 kg/ha and mixed with the top 7÷15 cm of the soil bed. The investigation fields consisted of 3 replicated plots (2m x 1m x 0.38m depth each) which were built in a field with a slope of 3,5÷4% and used for control (before sludge application) and for runoff analysis (after sludge application, for three different simulated rain events) as well as leachate analysis. Rainfall simulations (carbon filtrated well water at a rate of 60 mm/h until runoff occurred) took place 5 days before application (control) and 3, 9, and 24 days after application in the three plots. Six runoff samples (4 L) were collected after each rainfall simulation and their cumulative volume was investigated for the analytes of interest. A single 2.5-L leachate sample was withdrawn at the end of each simulation from the composite reservoir collecting the generated leachate (**tile drain** depth = 0.38 m; space between tiles = 0.025 m). Number of investigations: 2
Gottschall et al. 2012	Canada	An on-field investigation into the occurrence of 26 PPCPs in **tile drainage** (PPCPs in soil matrix, groundwater and wheat grain grown on the field) after sludge application was carried out for approximately 365 days. Dewatered (centrifugated) anaerobically digested sludge was applied to loam soil at a rate of 22,000 kg/ha and mixed with the top 20 cm of the soil bed. Investigation fields consisted of 2 macroplots (3 ha each) in an agricultural field located in Ontario, Canada, which was fallow the year before the investigation. Tiles were placed 1.1÷1.2 m below the soil surface and spaced 15 m apart. The first macroplot represents the control system and the second the treatment system (where sludge was applied). Real rainfall occurred in the study period with a total depth of 1,070 mm. Samples were time-proportionally collected at the bottom of the tiles when a trigger (adjusted depending on weather and soil water content) occurred. A total of 10 hydrograph event samples were selected for analysis. Number of investigations: 1

Gottschall et al. 2013	Canada	A commercial field-scale investigation was carried out into the occurrence of 17 PPCPs (hormones), 3 pathogens and 10 sterols in **tile drainage**, in the surface soil core, DMB aggregates mixed with soil, groundwater and wheat grain after sludge application in a real agricultural field (the same as that of Gottschall et al., 2012) for approximately 365 days. The aim was to study the long-term persistence of the selected compounds in the environmental matrices and to correlate the occurrence of fecal bacteria with sterols. Dewatered (centrifugated) anaerobically digested sludge was applied to loam soil at a rate of 22,000 kg/ha and mixed with the top 20 cm of the soil bed. Investigation fields consisted of the same 2 macroplots (3 ha each) as in the agricultural field described in Gottchall et al. (2012), with tiles positioned 1.1÷1.2 m below the soil surface and spaced 15 m apart. 1 of them was isolated and used for the control investigation. Real rainfall occurred in the study period with a total depth of 1,070 mm. Samples were time-proportionally collected at the bottom of the tiles when a trigger (adjusted depending on weather and soil water content) occurred. A total of 8 hydrograph event samples were selected for analysis. Number of investigations: 1
Gray et al. 2017	USA	On-field investigations were carried out into the occurrence of a wide spectrum of anthropogenic waste indicators (including 6 PPCPs) in **surface runoff** after sludge application on an agricultural field in Colorado for approximately 40 d. The site had not previously been treated with biosolids. Dewatered anaerobically digested sludge was applied on loamy sand soil at a rate of 3,500 kg/ha and mixed with the top 15 cm of the soil bed. The investigation fields consisted of 5 microplots (6 m^2 each) in a field with a slope of 2.1÷3%; each one was used both for treatment and control investigations. Rainfall simulations (application of hormone-free well water at a rate of 65 mm/h, corresponding to a 100-year simulated rain event) took place 5 days before (control plot) and 1, 8, and 35 days after application in the three plots. In the remaining two plots, rainfalls were conducted only on day 35 in order to evaluate the fate of compounds in the absence of repeated rainfall events. The same plots and similar operational conditions were used in a previous investigation by Yang et al., 2012 Number of investigations: 2
Healy et al. 2017	Ireland	Investigations were carried out into the occurrence of 2 PPCPs (TCS and TCC) in **surface runoff** after sludge application in a field experiment lasting approximately 15 d. In order to compare different types of behaviour, three differently treated sludges were spread on the surface of

		loam soil: an anaerobically digested sludge (at a rate of 6,727 kg/ha), a thermally dried sludge (at a rate of 2,683 kg/ha), and a lime stabilized sludge (at a rate of 29,536 kg/ha). The investigation fields consisted of replicated (n=3) hydraulically isolated microplots (0.4 mx 0.9 m= 0.36 m^2 each) in a field with a slope of 2.8÷3.7% (without controls). Each microplot was equipped with a channel collecting all the runoff during a rain event. Rainfall simulations (at a rate of 11 mm/h) took place 1, 2, and 15 days after sludge application in the same plots. Each rainfall lasted 30 minutes from the time of the first occurrence of surface runoff. Number of investigations: 3
Lapen et al. 2008b	Canada	On-field investigations carried out on the occurrence of 11 PPCPs in **tile drainage** after sludge application were performed in Ontario, Canada, for approximately 46 d. Liquid anaerobically digested sludge was applied on silty clay loam soil at a rate of 9,3500 L/ha and mixed with the soil bed with two different approaches (in order to compare the influence on tile drain quality): tilling with the top 10 cm of the soil (subsurface spreading) and one-pass aeration tilling with the top 11 cm (surface spreading). Most of the selected PPCPs were spiked in the sludge before soil application as their concentration was found to be below the detection limits. The investigation fields consisted of three plot replications for each application type with one control bed, giving a total of 8 plots (740 m^2 each) in a field with tiles positioned 0.8 m below the soil surface and placed 15 m apart. Real rainfall occurred in the study period with a total depth of 124 mm. Samples were time-proportionally collected at the bottom of the tiles when a trigger occurred. Number of investigations: 2
Lapen et al. 2008a	Canada	On-field investigations into the occurrence of *E. co*li and *C. perfringens* as well as nutrients in **tile drainage** after sludge application were carried out in Ontario, Canada, for approximately 46 d. Liquid anaerobically digested sludge was applied on silty clay loam soil at a rate of 93,500 L/ha and mixed with the soil bed using two different methods (in order to compare the influence on the loss of microorganisms): tilling with the top 10 cm of the soil and one-pass aeration tilling with the top 11 cm. The investigation fields consisted of three plot replications for each application type with one control bed, for a total of 8 plots (740 m^2 each) in a field with tiles positioned 0.8 m below the soil surface and placed 15 m apart. Real rainfall occurred in the study period with a total depth of 124 mm. Samples were time-proportionally collected at the bottom of the tiles when a trigger occurred.

		Number of investigations: 2
Peyton et al. 2016	Ireland	Investigations into the occurrence of 2 microorganisms, nutrients and metals in **surface runoff** after sludge application were carried out in Ireland, for approximately 15 d. Five different sludges were applied on the surface of loam soil and the resulting runoff was compared: an anaerobically digested sludge from the UK (at a rate of 6,775 kg/ha), an anaerobically digested sludge from EIRE (at a rate of 6,727 kg/ha), a thermally dried sludge (at a rate of 2,683 kg/ha), a lime stabilized sludge (at a rate of 29,536 kg/ha) and a dairy cattle slurry (at a rate of 80,000 kg/ha). The investigation fields consisted of 30 microplots (0.9mx0.4m=0.36 m^2 each) in a field with a slope of 2.8÷3.7% in order to compare six different scenarios (treatment with one sludge type + control). For this reason, 6 of them were isolated and used for the control investigation. Rainfall simulations (at a rate of 11 mm/h) took place 1, 2, and 15 days after application in the same plots. The first and the last 50 mL of runoff occurring on each plot were collected (2 samples per plot). Number of investigations: 5
Sabourin et al. 2009	Canada	An on-field investigation into the occurrence of 13 PPCPs in **surface runoff** after sludge application was carried out in Ontario, Canada, for approximately 36 d. Dewatered (centrifugated) anaerobically digested sludge was applied on silt loam soil at a rate of 8,000 kg/ha and mixed with the top 15 cm of the soil bed. The investigation fields consisted of 30 microplots (2 mx 3 m=6 m^2 each) in a field with a slope of 7 %. 5 of them were isolated and used for a control investigation (no sludge applied on them). A group of 5 (+1 control) microplots was considered for each rain event which took place 1, 3, 7, 21 and 36 d after sludge application. Rainfall simulations consisted of ozonated groundwater at a rate of 4.1 mm/min. One runoff sample was collected for each plot. Number of investigations: 1
Topp et al. 2008b	Canada	Investigations into the occurrence of 9 PPCPs in **surface runoff** after sludge application were carried out in Ontario in a real field for approximately 266 d. Liquid anaerobically digested sludge and ozonated groundwater spiked with pharmaceuticals were applied on silt loam soil (slope 5 %) at a rate of 93,500 L/ha and mixed with the soil bed. Sludge was amended to soil using two different approaches: by tilling with the top 15 cm of the soil and by subsurface injections at a depth of 10 cm. Spiked ozonated groundwater was added to the plots only by subsurface injection at a depth of 10 cm.

		The investigation fields consisted of 75 microplots (2 m x 1 m =2 m^2 each) in a field with a slope of 5%. The “control” plots were the 25 receiving spiked water but none of the plots were tested without PPCPs sources. Rainfall simulations (ozonated groundwater) took place 1, 3,7,21, 36 or 266 days after application in plots that had never received rainfall before to investigate the degradation/adsorption effects. Rainfall simulated events lasted until a minimum of 10 l of runoff had been collected in each microplot. Number of investigations: 3
Wallace et al. 2014	USA	Investigations into the occurrence of microorganisms and nutrients in **surface runoff** after dewatered anaerobically digested sludge application were carried out in Missouri for approximately 54 d. Sludge and mineral fertilizer were applied (to compare results) on silt loam soil and on the same soil but with a vegetation strip buffer (to compare the buffer ability in reducing key compound losses in runoff) with surface spreading applications. Four investigations occurred: untreated control plot; low rate (1,664 kg/ha) of biosolids with 1 m of vegetative filter; low rate (1,664 kg/ha) of biosolids without filter, and high rate of biosolids with 1 m of vegetative filter (3,328 kg/ka). The investigation fields consisted of operating and control plots (1.5mx2x=3 m^2 each) in a field of a slope of 3÷6%. For each experiment, four replicates were conducted. Rainfall simulations (deionized water at a rate of 70 mm/h) took place immediately after application. One sample per plot was collected. Number of investigations: 5
Yang et al. 2012	USA	An on-field investigation was carried out in Colorado into the occurrence of 17 PPCPs (hormones) and 2 sterols in **surface runoff** after sludge application for approximately 40 d. Dewatered anaerobically digested sludge was applied on loamy sand soil at a rate of 3,500 kg/ha and mixed with the top 15 cm of the soil bed. An analysis of the hormone partitioning between the dissolved phase and suspended-particle bond phase was reported. The investigation fields consisted of the microplots (6 m^2 each) in a field with a slope of 2.1÷3%; used both for treatment and control investigations. Rainfall simulations (hormone-free well water at a rate of 65 mm/h) took place 5 days before (control) and 1, 8, and 35 days after application in the same plots. 3 composite samples (early, middle and late rain events) were collected per plot for the control (5 days before sludge application) and on the first, 8^{th} and 35^{th} day. Since on day 35 only two plots were monitored, a total of 33 composite samples were

		available. Number of investigations: 1

2.2 Sludge application on soil – Sludge types, application methods, authorized loads, and legal requirements

2.2.1 Sludge types

Based on the studies under review, it was found that sludge intended for land disposal was generally anaerobically digested and, in many cases, dewatered. In a few cases it was subjected to further treatments: high temperature drying (Eldridge et al., 2009; Giudice and Young 2011, Healy et al., 2017, Peyton et al., 2016), gamma irradiation (Eldridge et al., 2009), centrifugal dewatering (Gottschall et al., 2012) or lime stabilization (Healy et al., 2017; Peyton et al., 2016). With regard to the selected micro-contaminants and bacteria, the concentrations in the applied sludge were included in the ranges reported in Table S2, even in the case of sludges spiked with micro-contaminants, with just two excpetions referring to acetaminophen and ibuprofen (in both cases final concentration was higher than the maximum literature value).

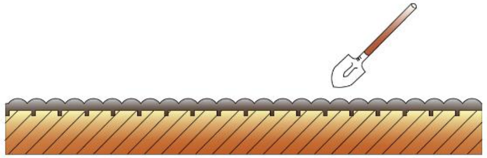
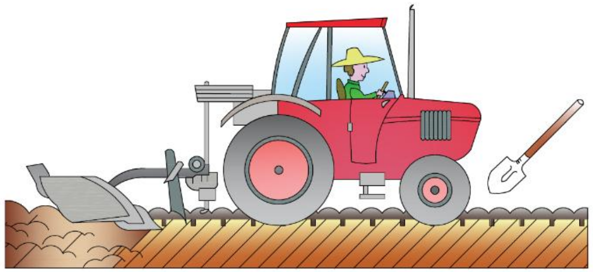
According to Sabourin et al. (2009) it was assumed that the sludge is considered liquid (often called liquid municipal biosolids LMB) if its solid content is less than 18 %, and dewatered (dewatered municipal biosolid DMB) if its solid content is higher than 18 %. In the different investigations, the sludge had a largely different solid content; on the basis of 11 of the 16 studies which reported sludge composition in detail, the solid content varied between < 18 % and 91.6 % (granulated high temperature dried sludge in Eldridge et al., 2009).

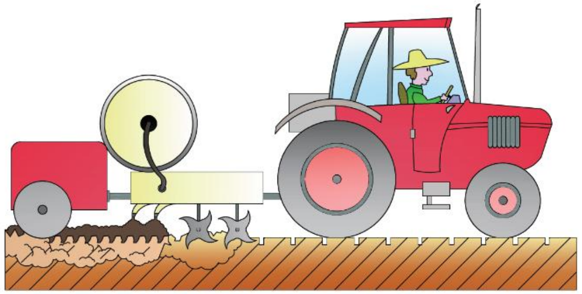
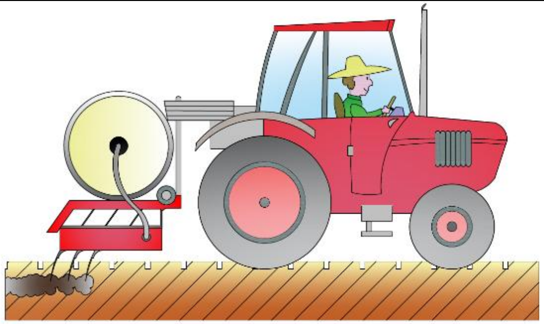
2.2.2 Application methods

Four different disposal methods were followed according to the collected studies. Table 3 shows the main sludge disposal strategies followed in the investigations under review, with a diagram and description for each of them, along with information regarding the papers dealing with them.

Table S1 includes many details referring to sludge application in the different investigations. In particular, as well as compiling sludge properties (pH, CEC, moisture/solid content) and treatment, it also details the application rate (dry matter kg/ha), application method and application depth.

Table 3. The application strategies for sludge disposal in agricultural soils considered in this review, the typical application depth, and relative references.

Application method	Graphical description	Application depth	Description	References
Land or Surface spreading		0 cm	With *land* or *surface spreading*, biosolids are deposited on the land surface without other operations.	Dunigan and Dick, 1980; Eldridge et al. 2009; Healy et al. 207; Peyton et al. 2016; Wallace et al. 2014
Tilling		5÷20 cm	In the case of *tilling*, sludge is spread on soil and then it is amended with the first 20 ÷ 30 cm of soil within 20-24 h.	Atalay et al. 2007; Edwards et al. 2009; Giudice and Young 2011; Gottschall et al. 2012; 2013 Gray et al. 2017; Lapen et al. 2008a,b Sabourin et al. 2009; Topp et al. 2008b; Yang et al. 2012

One-pass aeration tilling		13÷15 cm	In the case of *one-pass aeration tilling*, just before receiving the sludge, the soil is tilled. It is generally performed by a specific mechanical system that applies the sludge close to the ground, immediately following the passage of rolling tines which affect aerator-type tillage of the soil.	Lapen et al. 2008a;b
Subsurface injections		10÷13 cm (typical application depth, as reported in the cited studies)	*Subsurface injection* consists of the injection of biosolids within 50 cm of the top of the soil surface. Generally, injection can be used for LMB application or DMBs that have a low solid content and can be easily shovelled	Edwards et al. 2009; Topp et al. 2008b

2.2.3 Authorized concentrations and loads and other legal requirements

Regulations in force place great attention on the concentrations of heavy metals ~~(HMs)~~, microorganisms, some organic microcontaminants ~~pollutants~~ (including AOX, PAH, PCB, PCDD/F) and define limits of their concentrations in the treated sludge intended for land disposal.

In addition, they set maximum rates of sludge to be applied on soil (kg/ha year), maximum rate of nutrients (kg nutrient/ha year) and heavy metals (kg HM/ha year) in sludge. Some of them also set the maximum concentrations of heavy metals in soil (mg HM/kg dm).

Table S3 summarizes the main characteristics of the regulations in the European Community and in countries including those where most of the investigations under review took place (Ireland, Italy, New South Wales-Australia, Ontario-Canada, and the USA).

Table S4 compares the limits for the different microorganisms in treated sludge to be fulfilled in the case of land disposal in many European countries, as well as in New South Wales (Australia), Ontario (Canada) and the USA.

It is important to highlight that most of the current regulations clearly define spreading and tilling procedures, the maximum slope values, and pH and CEC in soil. In addition, some legislations require that a minimum distance from waterways and a minimum depth from the aquifer is respected with regard to the plot size where sludge is applied (Table S3).

Limits referring to new contaminants of emerging interest, including pharmaceuticals, hormones, and fragrances of interest in this review have not yet been set.

2.3 Characteristics of the soils in the investigations included in the review

The texture of the soils where investigations took place are reported in Figure 2 in the well-known texture triangle. A rapid glance shows the percentage of the main soil components (sand:silt:clay) in each case study. The legend on the right reports the studies shown in the diagram.

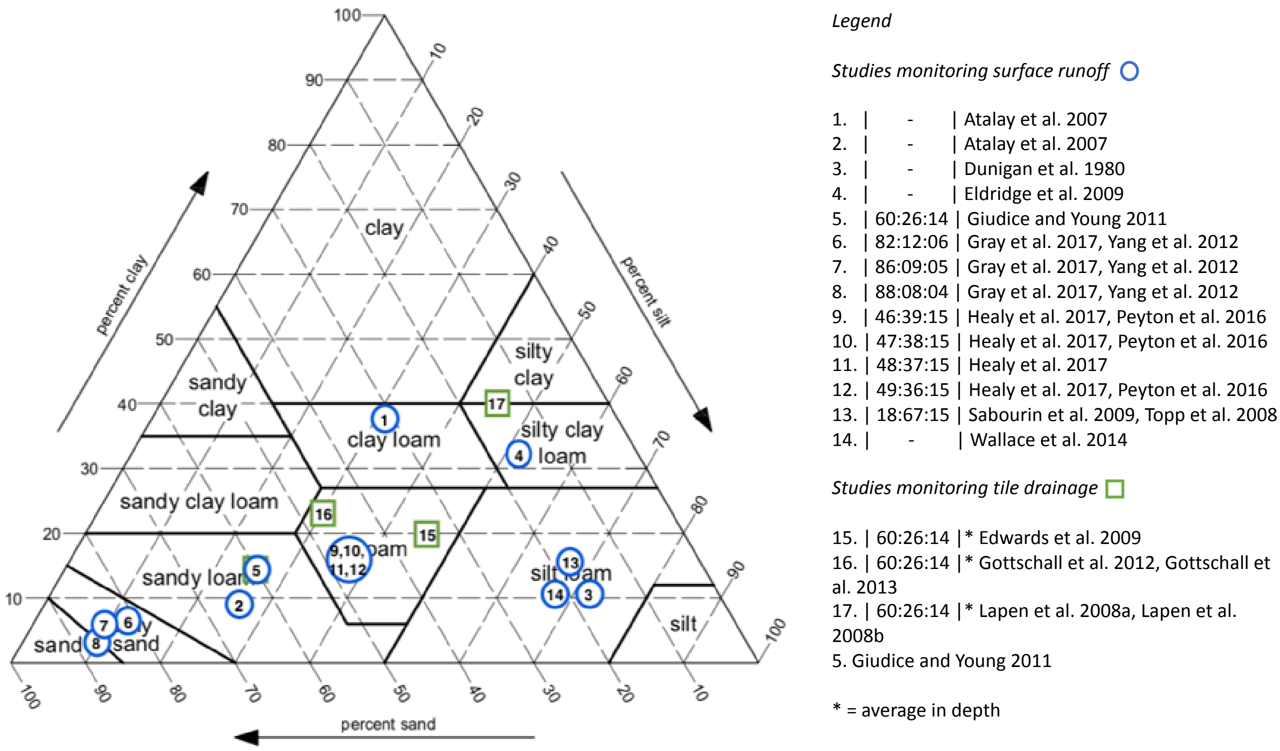


Figure 2 Characteristics of the soil texture in the investigations included in this review in the soil textural classification triangle.

2.4 Plot size, precipitation and sampling strategy

Plot size - Concerning land runoff, investigations took place in plots whose size was in the range 0.36-6 m^2 (0.36 m^2, 1.62 m^2, 2 m^2, 3 m^2, 4.5 m^2, and 6 m^2). Tile drainage experiments were carried out in wider surface plots: 740 m^2, 1,500 m^2 and 3 ha, with the only exception being the investigation carried out by Giudice and Young (2011), which was carried out in 3 plots of 2 m^2. 32 of the 38 investigations included a control plot where sludge was not amended in order to compare the quality of surface runoff/tile drainage without sludge application - only the investigations carried out by Healy et al. (2017) and Topp et al. (2008b) did not include such a plot.

Rainfall type, *intensity, duration and frequency* - In 30 of the 38 investigations, rainfall was artificial (ozonated groundwater, carbon filtrated groundwater, deionized water, or drinking water) and after the simulated rain event, runoff samples were collected. The rain intensity was in the range of 11-90 mm/h and the chosen intensity corresponded to ain with a specified return period, typical of the country where the investigation was being carried out - 2 years in Missouri (Wallace et al., 2014) and 100 years in Canada and in the USA (Sabourin et al., 2009, Gray et al., 2017).

The duration of the rain events was clearly defined in some studies (30 min by Eldridge et al., 2009; 45 min in Atalay et al., 2007), whereas in others it was a defined period from the first occurrence of runoff (for instance 30 min in Healy et al., 2017, Peyton et al., 2016) or related to the desired runoff volume to be collected during the investigation (Giudice and Young 2011; Topp et al., 2008b, Sabourin et al., 2009, Wallace et al., 2014).

With regard to frequency, artificial rainfall was applied on different days - : often some days before sludge application (control step) and then after sludge application with a different frequency pattern, covering a period ranging from a few days to one year. In the case of only one investigation was the interval as long as 266 days (Topp et al., 2008b), while in all the others it was < 54 d (Table S1).

Rain was applied in the same plot to assess pollutant mobilization following rain events (Atalay et al., 2007; Eldridge et al., 2009; Giudice and Young 2011; Gray et al., 2017; Healy et al., 2017; Peyton et al., 2016; Wallace et al., 2014, and Yang et al., 2012) or in different plots with different frequencies to evaluate the contribution of degradation and sequestration of the investigated compounds after different prolonged dry periods (Sabourin et al., 2009; Topp et al., 2008b).

In only 5 studies, all referring to tile drainage tests, (Edward et al., 2009; Gottschall et al., 2012, 2013, Lapen et al., 2008a,b), was the rainfall real, with its total depth varying between 124 mm (Lapen et al., 2008a,b) and 1,070 mm (Gottschall et al., 2012, 2013). Investigations lasted from 46 days (Lapen et al., 2008a,b) to 365 days (Gottschall et al., 2012, 2013).

Many other details for the different investigations are reported in Table S1.

Sampling mode and frequency

Different sampling strategies were applied in surface runoff and details are reported in table S1. Not all the studies clearly reported the description of the sampling mode and frequency,and analysis may refer to grab or composite samples.

In other studies, composite samples were collected and derived from the mixture of samples withdrawn from different plots (Sabourin et al., 2009; Giudice and Young, 2011). In Yang et al. (2012) analyses were performed on composite samples referring to different phases of the runoff (early, medium and late runoff).

Regarding tile drainage, analyses were on grab samples - water samples were collected during real rainfall events by means of in-line water flow control structures on the tile drain headers for each field section under study (Edward et al., 2009; Gottschall et al., 2012, 2013, Lapen et al., 2008a,b).

2.5 Accuracy and uncertainty of the collected data

The collected data reported in graphs and tables in the manuscript and in the supplementary material section come not only from tables, but also graphs and in this case, the uncertainties associated with the values add to the uncertainties due to sampling and analysis (as discussed in Verlicchi and Zambello 2016), even in cases where the reading of the data was quite accurate. If a value was reported below its limit of detection (LOD) or its reporting limit (RL) it was assumed equal to the LOD or the RL and if it was reported below its limit of quantification (LOQ), it was assumed to be half its LOQ value. Table S1 reports the details provided referring to the experimental campaigns and a rough estimation (good, modest or poor) of the accuracy/reliability of the reported data, the description of sampling strategies and the adopted equipment.

3 Results

3.1 Ranges of the concentration of selected compounds in land runoff and tile drainage samples

A rapid glance at Table S1 highlights that 29 of the 38 investigations refer to surface runoff monitoring, only 9 investigations monitored tile drainage, 21 investigations dealt with bacteria and 17 with pharmaceuticals, hormones and fragrances.

Figures 3 and 4 report the measured concentrations found for the selected pollutants in land runoff and in tile drainage samples in the case of sludge-amended soil. Where available, the background concentrations ~~BC~~ (control concentrations related to runoff or tile drainage from soil where sludge was not applied) of the compounds are also reported for comparison and analysis. Generally, these concentrations refer to water samples resulting from artificial rainfall applied some days before sludge application.

With regard to land runoff, it emerges that 33 compounds were monitored in the different investigations. The most studied compounds were hormones (class H), with ~~ethynil~~ ethinyl estradiol at the top with 37 measures, followed by all the other hormones with 33 values. The antiseptics triclosan and triclocarban and the analgesic ibuprofen were frequently monitored (values of 26 and 20, respectively), while fewer than 10 values were recorded for the remaining 14 compounds. MECs referring to hormones were collected in investigations tackling the application of dewatered anaerobically digested sludge on loamy sand and sandy loam soils. The data comes from the studies by Giudice and Young (2011) and Yang et al. (2012), which correspond to investigation numbers 4,5,6 and 7 in Figure 2. Table S5 reports the number of data for each compound, together with the minimum, maximum, average and standard deviation values for MECs and where possible, the minimum and maximum for background concentration ~~BC~~ values in case of surface runoff.

It emerges that variability ranges vary from 1 to 3 orders of magnitude and concentrations were found between <LOD to 1,477 ng/L (ibuprofen according to Topp et al., 2008b). Average values varied between < LOD and 707 ng/L (ibuprofen). The highest concentrations (ibuprofen, tonalide, and gemfibrozil) were found in the investigation by Topp et al. (2008b) in which a liquid anaerobically digested sludge was applied on silt loam soil (point 12 in Fig. 2).

The intervals emerging from Figure 3 also depend on the fact that some studies presented measured concentrations of PPCPs in different events after the sludge had been applied. As remarked by several authors (among them Topp et al., 2008b; and Sabourin et al., 2009), the temporal patterns of runoff exports (aqueous+particulate) were different from the investigated compounds. Concentrations varied, and for some compounds (triclosan, atenolol, acetaminophen, and sulphametoxazole) the highest values correspond to the first rainfall after sludge application, for others they may occur during subsequent events (for naproxen during the second event, on the third day following application; for triclocarban, carbamazepine and caffeine after seven days, during the third rain event).

With regard to background concentrations (the red stars in Figure 3), these were found to be < LOD for all compounds with the sole exceptions of estrone, androstenedione (with 2.2 ng/L and 1.54 ng/L respectively, Yang et al. 2012), caffeine and triclosan (21, 27, 49 ng/L and 35, 37, 47 ng/L respectively, Sabourin et al. 2009,). All studies reported that no previous sludge application on soil had occurred before their investigation. The occurrence of compounds in soil could thus be due to other sources, for instance irrigation with surface water containing residues of the compounds under study (Ma et al., 2018). In this context, Table S5 shows the measured concentrations for the selected compounds in surface water.

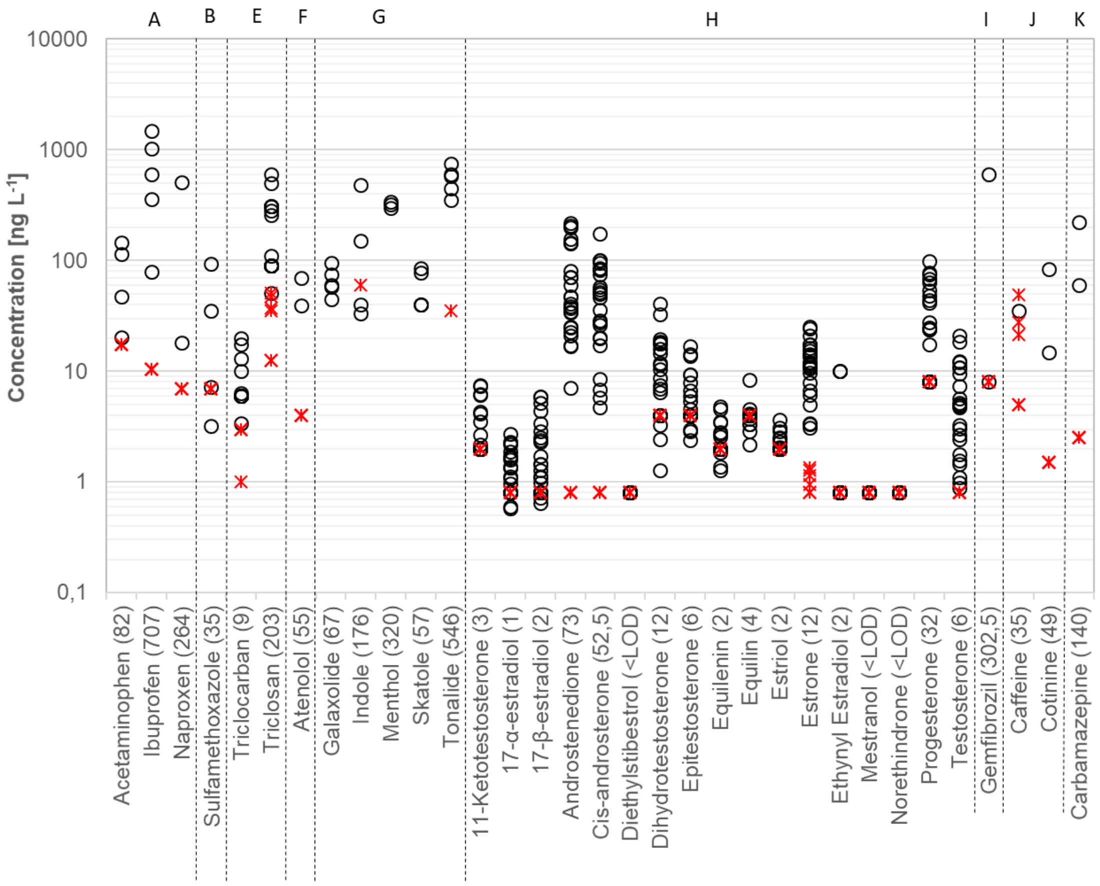


Figure 3. Measured concentrations of selected compounds in land runoff with (MEC, ○) or without (background concentration ~~BC~~,*) sludge application on soil.

Data from: Giudice and Young 2011, Gray et al. 2017, Healy et al. 2017, Peyton et al. 2016, Sabourin et al. 2009, Topp et al. 2008b, Yang et al. 2012

With regard to tile drainage samples, 46 compounds were analyzed, but for 13 hormones (17-α-estradiol, 17-β-estradiol, α-dihydroequilin, androstenedione, equilenin, equilin, estradiol benzoate, estriol, mestranol, norethindrone, norgestrel, progesterone and testosterone), Gottschall et al. (2013) only reported background concentrations (always below the corresponding LOD, as shown by the red stars in Fig. 4) and this is the reason why these are not included in Figure 4, which shows the remaining 33. Among all these PPCPs, the most studied belong to different classes: the antiseptic triclosan (90 values), the stimulant cotinine (85 values), and the psychiatric drug carbamazepine (80 values). For 8 compounds, the collected data vary between 33 and 75, and for the other compounds the available data are less than 5.

Measured concentrations varied between 1.5 and 4,117 ng/L and, for each compound, the range of variability was equal to 2 or 3 orders of magnitude, with the exception of sulfapyridine, estrone and fluoxetine whose range was of 1 order of magnitude.

The highest values (> 1,000 ng/L) are related to ibuprofen (4,117 ng/L), naproxen (1,045 ng/L), triclosan (3,676 ng/L), gemfibrozil (1,040 ng/L), and carbamazepine (1,136 ng/L). All these values were collected by Lapen et al. (2008b), whose investigation dealt with the application of liquid anaerobically digested sludge on silty clay loam (number 15 in Figure 2).

Average concentrations varied between 1.5 ng/L (ofloxacin and miconazole) and 551 ng/L (triclosan).

The background concentrations were investigated for all the compounds (Lapen et al., 2008b; Edwards et al., 2009, Giudice and Young, 2011; and Gottschall et al, 2013) and they resulted below LOD or below LOQ, with four exceptions. As reported in Figure 4, these refer to naproxen (35 ng/L), triclosan (95 ng/L), atenolol (135 ng/L) and cotinine (5 ng/L) and were reported by Edwards et al. (2009), who investigated the application of dewatered anaerobically digested sludge on loam soil (number 13 in Figure 2), which had previously received sludge.

Further details regarding these collected data are reported in Table S6, in particular the number of data for each compound, together with the minimum, maximum, and average values and standard deviation (SD) for MECs and, where possible, the minimum and maximum for background concentration ~~BC~~ values in the case of tile drainage.

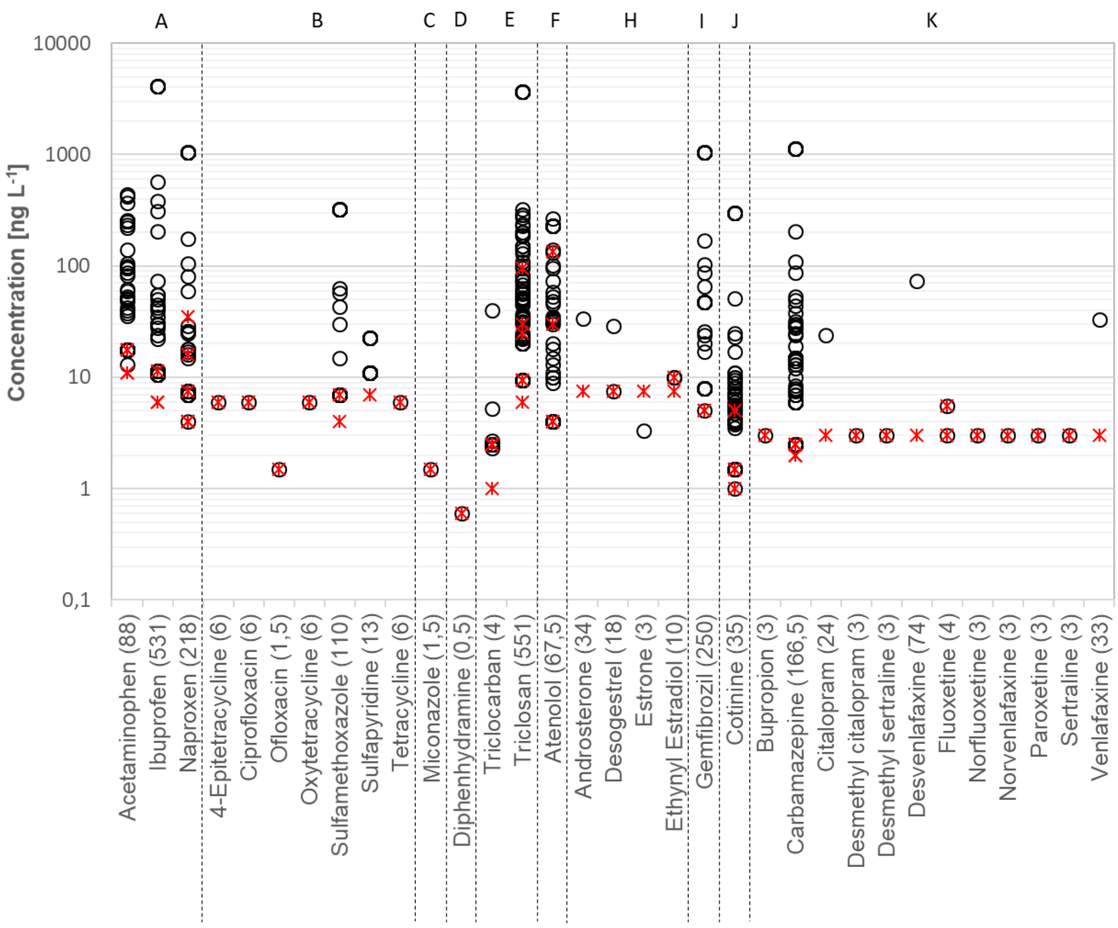


Figure 4. Range of concentrations for a selection of compounds in drainage samples with (MEC, ○) or without (background concentration ~~BC~~,*) sludge application on soil. Data from: Edwards et al. 2009, Giudice and Young 2011, Gottschall et al. 2012, Lapen et al. 2008a

Observed concentrations for the selected compounds in both runoff and tile drainage are generally lower than the values found both in the municipal WWTP secondary effluent, in surface water as well as in runoff in case of reclaimed water reuse. The corresponding range of concentrations found in literature (Verlicchi et al., 2012, Ben et al., 2018; Chalew and Halden 2009; Metcalfe et al., 2003; and Pedersen et al., 2005) are reported in Tables S5 and S6.

Moreover, the observed concentrations for hormones are unlikely to result in any significant pulse environmental exposure impact, from a pure tile effluent concentration perspective (Gottschall et al., 2013). In addition, once released into surface water, the dilution effect and photodegradation of microcontaminants pollutants due to UV exposure contribute to a further reduction of their concentrations. Sabourin et al. (2009) remarked that the runoff concentrations of the selected PPCPs were lower than the reported acute toxicological endpoints, and for most compounds a thousand times lower.

3.2 Range of concentrations for the bacteria included in the review

Few papers tackle the monitoring of bacteria in surface runoff and tile drainage after sludge disposal. Four studies have investigated surface runoff (Dunigan and Dick, 1980; Atalay et al., 2007; Eldridge et al., 2009; Peyton et al., 2016; Wallace et al., 2014) and two tile drainage (Gottschall et al., 2013; Lapen et al., 2008a). Moreover, different units of measures were sometimes used and thus analyses are not easy to perform. Figure 5 reports the collected concentrations and background concentration for bacteria species with more than 12 reported measures, with the exception of Fecal coliforms as they are in another unit of measurement. A descriptive statistical analysis was carried out for all of the bacteria (Table 4). Investigations by Peyton et al. (2016) with 5 differently treated sludges applied on rural land showed that there is no correlation between sludge treatment and runoff concentration of Fecal and Total coliforms.

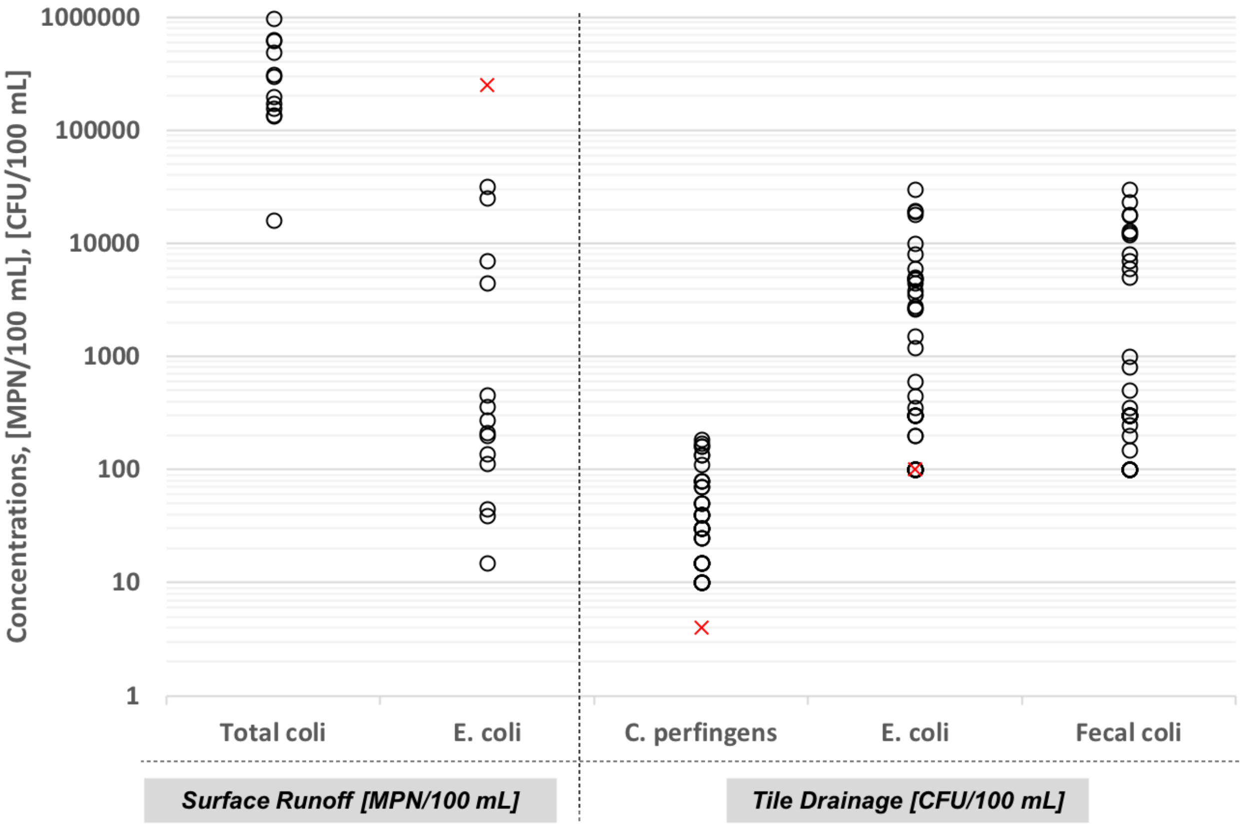


Figure 5. Collected data for bacteria in surface runoff and tile drainage

Data from Eldridge et al. 2009, Gottschall et al. 2013, Peyton et al. 2016;

The profile of bacteria content in runoff after three different simulated rain events (1 d, 2 d and 15 d after application; same rain intensity) strictly depends on the sludge type (differently treated) applied on the soil, (Peyton et al., 2016) and the maximum concentrations vary in different cases. This could be explained by the fact that once sludge is applied on the soil, UV light and desiccation are responsible for the decay of occurring bacteria (Lang et al., 2007), but in some cases, bacteria could also find soil conditions which favour their development.

A comparison with TC and FC concentrations in runoff in the case of dairy cattle slurry application shows that they were always 1 order of magnitude higher than in the case of treated sludge application (Peyton et al., 2016).

It emerges that investigations report a variable number of values - from 3 (Atalay et al., 2007) to 46 (Gottschall et al., 2013); background concentration was measured once in the studies by Atalay et al., (2007), Eldridge et al. (2009) and Wallace et al. (2014) for surface runoff and Gottschall et al. (2013) for tile drainage.

Table 4. Main findings in monitoring bacteria occurrence in surface runoff and tile drainage.

	Microorganism (u.o.m.)	**Background Conc.**	**min**	**max**	**mean**	**SD**	**# data**
Surface runoff	Total coliforms [CFU/ml]	0	63.1	79.4	71.3	11.5	3
	E. coli [CFU/ml]	0	1.8	2.4	2.1	0.4	3
	Fecal Coliforms [CFU/100ml]	100	5,000	36,000	16,167	17,222	4
	Fecal Coliforms [MPN/mL]	0-70	60	55,000			12
	Total coliforms [MPN/100ml]	--	15858	980,600	344,622	280,808	12
	E. coli [MPN/100ml]	251,188	15	31,622	5,009	10,191	15
Tile drainage	*C. perfringens* [cts/100 mL]	4.0	10	185	50	49	46
	E. coli, [cts/100 mL]	100	100	30000	3504	6363	46
	Fecal coliforms, [cts/100 mL]	--	100	30000	3568	6963	45

Wallace et al. (2014) highlighted the low content of FC in control plots (116 CFU/100 mL) and a wide variability in the case of sludge application on soil with or without a vegetative filter, from 4,880 to 35,720 CFU/100 mL. These values are higher than the maximum amount allowed in Missouri (where the investigation took place) for whole body contact recreation use (maximum of 206 CFU/100 mL).

Sludge disposal always led to an increment in the bacteria concentrations in surface runoff and tile drainage with concentration ranges as wide as 3-5 orders of magnitude depending on many factors, as will be discussed later.

The investigation by Eldridge et al. (2009) was the only scenario in which this phenomenon did not occur. They found a background concentration for *E. coli* equal to 251,188 MPN/100 mL and after sludge application, MECs in surface runoff were always lower, between 25,000 and 31,000 MPN/100 mL.

Measured concentrations are strictly correlated to the sampling procedure followed in the investigations. As reported in Table S1, water samples were instantaneous or (time or volume) composite, and in some cases (Yang et al., 2012) water samples were related to early, middle and late rain events corresponding to the mix of different collected samples. Lapen et al. (2008a) found that LMB application-induced contamination starts some minutes after sludge application. *E. coli* and *C. perfringens* were still high 24 h after application while over a study season basis, *E. coli* showed a significant decline in mass loads, whereas *C. perfringens* presented some peaks during the observation periods and did not follow a similar pattern of decay.

Unfortunately, it is not possible to compare the observed concentration ranges for surface runoff and tile drainage, as data are reported in different units of measurement.

3.3 Influence of the main factors affecting runoff and tile drainage quality – PPCPs

Once in the soil, a micropollutant may be subject to different phenomena: it may be sequestered, sorbed on the soil matrix (depending on its organic carbon content, CEC, pH, etc.), biodegraded (due to microorganisms present in the soil as well as in the applied sludge), photodegraded (due to light exposure), it may take part in chemical reactions with other compounds, or it may be transported away by a liquid phase. Prediction of its behaviour is complex, as environmental and matrix conditions may rapidly change, and intense rain events may enhance its vertical mobility through soil pores. The following sections will discuss the main factors affecting the occurrence of microcontaminants ~~pollutants~~ and bacteria in runoff and tile drainage in sludge-amended soil.

3.3.1 Influence of K_{ow}

The partitioning between solid and liquid phases was not always addressed by the authors, as it requires lengthy investigations, as shown in Yang et al. (2012). More frequently, coefficients derived from literature were used. In this context, the octanol-water partition coefficient K_{ow}, describing the distribution between the octanol and water of a compound, is commonly used to assess the sorption potential on a solid phase by a compound. As a rule of thumb, if Log $K_{ow} > 4$ it could be expected that the compound is highly adsorbed due to hydrophobic partitioning, while if Log $K_{ow} < 2.5$ the compound has a low level of sorption (Verlicchi and Zambello, 2015). The graphs shown in Figures 5 and 6 report MECs in runoff and tile drainage *vs.* Log K_{ow} for the investigated compounds. For quick reference, Table S7 compiles Log K_{ow} values for the compounds investigated in surface runoff or tile drainage analysis.

In Figures 5 and 6, values are dispersed in a wide cloud and it emerges that no clear correlation exists between the sorption potential of a compound and its measured concentration in runoff or in tile drainage. It is important to bear in mind that the reported data refer to different investigations, in terms of soil characteristics, rain fall intensity, sludge application rate, and concentration for the different compounds in the applied sludge and the MECs depend on these factors.

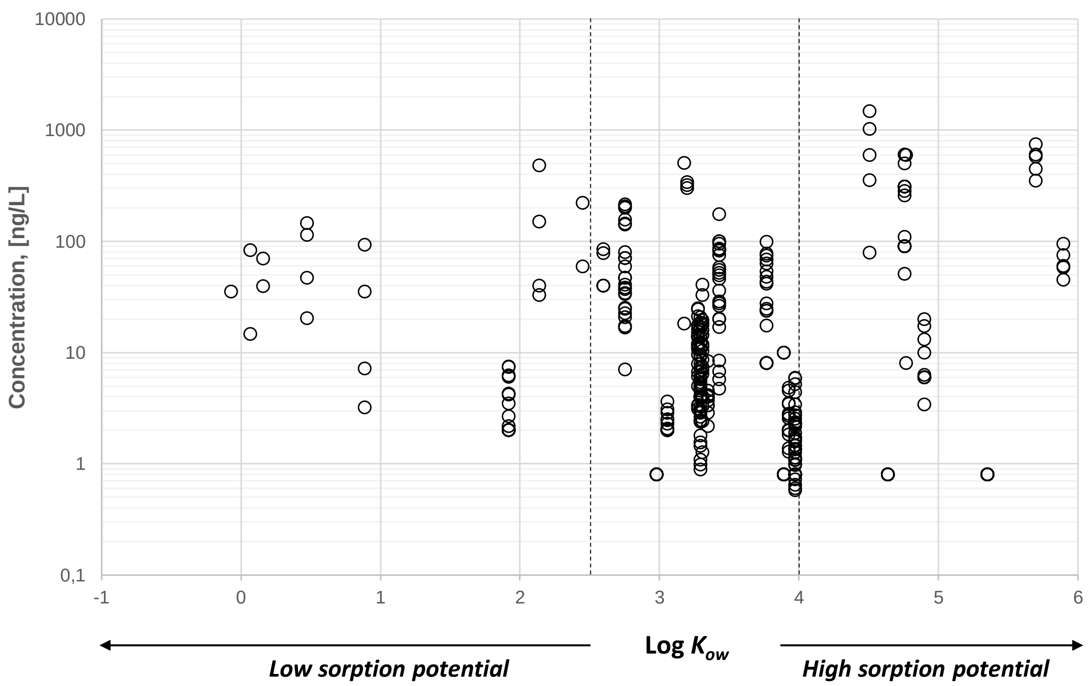


Figure 5 Runoff concentrations *versus* Log K_{ow} for the investigated compounds

Data from: Giudice and Young 2011, Gray et al. 2017, Healy et al. 2017, Peyton et al. 2016, Sabourin et al. 2009, Topp et al. 2008, Yang et al. 2012

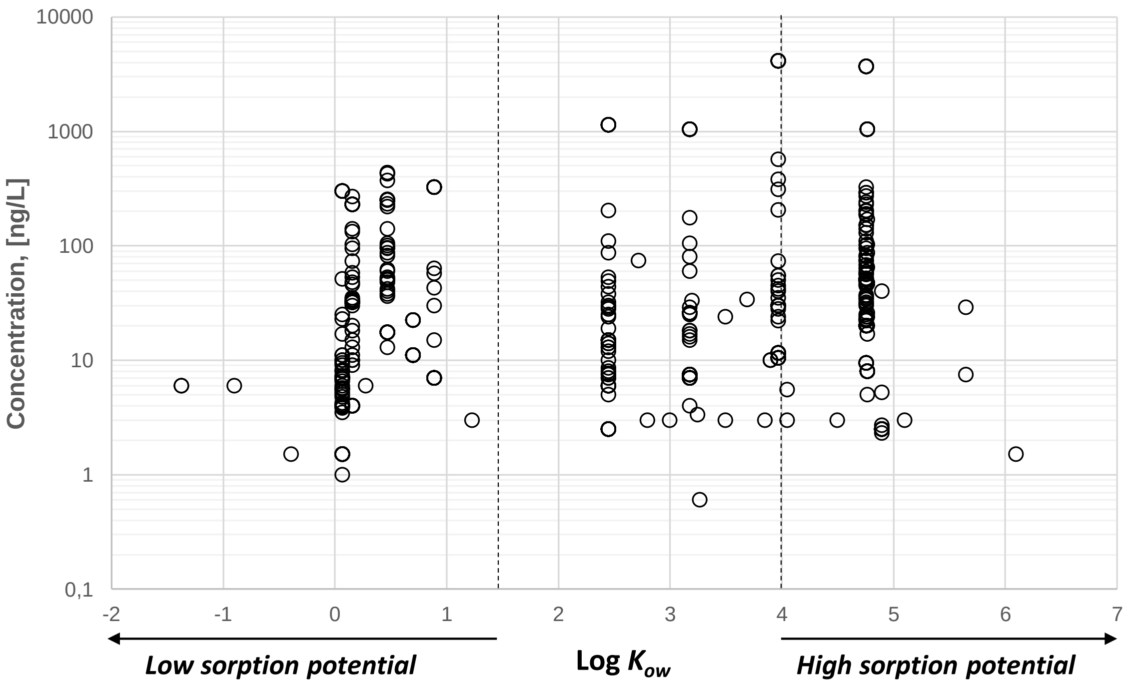


Figure 6 Tile drainage concentrations *versus* Log *K*ow for the investigated compounds

Data from: Edwards et al. 2009, Giudice and Young 2011, Gottschall et al. 2012, Lapen et al. 2008

Limiting attention to single investigations where soil characteristics, sludge properties and rainfall intensity are defined and are the same for all the compounds, it seems that Log K_{ow} may be correlated with the pharmaceutical mass load (or concentration) in the runoff. Sabourin et al. (2009) found that chemicals with Log K_{ow} less than 2.45 (atenolol, carbamazepine, cotinine, caffeine and acetaminophen) were rapidly transported in runoff and those with Log K_{ow} greater than 3.18 tended to be retained in the soil (gemfibrozil, naproxen and ibuprofen). The same behaviour is confirmed by the investigations and results obtained by Gottschall et al. (2012) referring to fluoxetine, miconazole, tetracyclines and fluoquinolones (with Log K_{ow} > 4). These compounds were not found in tile drainage and they may have been more strongly bound to DMB, which can also explain their long-term detection in incorporated DMB.

Sabourin et al. (2009) also found that although sulfametoxazole had a Log K_{ow} equal to 0.89, it was not largely exported in runoff (only 0.51 % was found on a mass basis). Triclosan and triclocarban have similar K_{ow}, but in the study by Sabourin et al. (2009), it was found that about 40-times more triclosan was exported than triclocarban, and that even their concentrations in the sludge applied on the soil were similar (around 7,000 and 8,000 ng/g dm, respectively). This different behaviour could be explained by the different values of pK_a (the dissociation constant, reported in Table 1) of the two antiseptics (8.1 for triclosan and 12.7 for triclocarban) and the ionic forms at the pH of the soil/runoff, as discussed in Giudice and Young (2011). They also remarked that in their study conditions (soil pH at 8 and runoff pH variable between 7.8 and 8) half of the triclosan present in the sludge is ionized and as a result, it is much more prone to leachate and to be exported in the runoff than the neutral molecules of triclocarban.

The study by Yang et al. (2012) thoroughly investigated the fractioning between dissolved and suspended-particle bound phases for a wide spectrum of steroid hormones and found that Log K_{ow} values were not correlated with estrogen sorption to colloids.

According to Cunningham (2008), the octanol-water *distribution* coefficient D_{ow} is more adequate in studying microcontaminants ~~pharmaceuticals~~, as it is pK_a-dependent at environmental pH.

D_{ow} is defined by Equation (1), and, according to Schwarzenbach et al. (2003), evaluated through Equation. (2) for acidic compounds and Equation (3) for basic ones:

$$D_{ow} \equiv \frac{\text{concentration in } n\text{−octanol}}{\text{concentration in water}} \qquad \text{Eqn. (1)}$$

$$Log\ D_{ow} = Log\ K_{ow} + Log\frac{1}{1+10^{pH-pK_a}} \qquad \text{(acidic compound)} \qquad \text{Eqn. (2)}$$

$$Log\ D_{ow} = Log\ K_{ow} + Log\frac{1}{1+10^{pK_a-pH}} \qquad \text{(basic compound)} \qquad \text{Eqn. (3)}$$

where $\mathrm{Log}D_{ow} = \log_{10} D_{ow}$.

In the case of neutral moieties, the two previous correlations result in Equation (4):

$$\mathrm{Log}D_{ow} = LogK_{ow} \qquad \text{Eqn. (4)}$$

The rule of thumb when using Log D_{ow} to predict ~~PhC~~ PPCP behaviour in aquatic compartments is good sorption if Log D_{ow} >3 and low sorption if Log D_{ow} < 1.

3.3.2 The influence of soil characteristics

On the basis of the lab investigations by Topp et al. (2008b), Cha and Cupples (2009), and Al-Rajab (2010a,b, 2015), soil characteristics (soil texture, pH, moisture content and temperature) seem to have a relevant influence on the quality of the runoff/tile drainage of studied microcontaminants ~~pollutants~~.

As expected, runoff and tile drainage flows depend on the level of soil saturation. In loose and uncompacted soil, percolation is higher than land runoff, whereas when the soil becomes compact, percolation is lower than surface runoff (Giudice and Young, 2011).

Moreover, all studies agree with the consideration that moisture content and temperature in the soil mostly influence the fate of microcontaminants ~~pollutants~~ (sorption, degradation, and mineralization) and soil texture does not seem to influence leaching (that is the passage in the liquid phase due to rain events).

In particular, Topp et al. (2008a), Cha and Cupples (2009), and Al-Rajab (2010a,b,2015) mainly refer to triclosan, triclocarban and naproxen, and in-depth investigations on the fate of all the compounds under review are not available for different soil characteristics.

Macropores, due to worm burrows, soil cracks and abandoned root channels, can favor the rapid gravity flow of contaminant-laden material in the vadose zone towards tile and shallow ground water depth (Lapen et al., 2008a). The pore size and distribution of the soil also affects the mobility of PPCPs within the medium. Hormones in a soil characterized by macropores rapidly move downwards (and may be collected in tile drainage), whereas in the case of soil with micropores, they move slowly and to a lesser extent (Gottschall et al., 2013).

It is important to highlight that at the modest slope of the investigations under review, surface runoff generally occurs when the soil is saturated, otherwise rain drops enter the sludge-amended soil and percolates. During their passage through the solid phase, rain drops meet compounds (including microcontaminants ~~pollutants~~) sorbed on the soil which may be transported to the liquid phase (leaching) according to the compound-specific equilibrium conditions at the occurring environmental conditions (temperature, pH, etc.).

From a microscopic view point, the soil environment is continuously changing and surface runoff/tile drainage following two different rain events may have different characteristics. This is confirmed by Gray et al. (2017), who analyzed and compared the surface runoff in the same plot 1, 8 and 35 days after sludge application and the surface runoff in another plot 1 and 35 days after sludge deposition, in order to evaluate the fate of a wide spectrum of microcontaminants ~~pollutants~~ (triclosan, menthole, indole, skatole, galaxolide and tonalide) under different rainfall patterns, and Sabourin et al. (2009) who analyzed the surface runoff quality in five different plot sets that received rainfall after 1, 3, 7, 21 and 36 days, respectively.

As already highlighted in section 3.3.1 for triclosan and triclocarban, soil pH influences the ionization of a compound and thus its partition between soil and liquid (runoff/leachate).

3.3.3 Influence of sludge treatment

Liquid or dewatered sludge has different behaviour once applied on a soil. Topp et al. (2008a,b) and Sabourin et al. (2009) thoroughly investigated these issues and found in particular that LMB applied to unsaturated (also called uncompacted) soil behaves as a liquid, filling the available pore space. In this way, the exposure of PPCPs to soil microorganisms is favored and their biodegradation promoted. In contrast, in the case of dewatered sludge, the diffusion of oxygen into DMB aggregates, as well as the diffusion of PPCPs out of the DMB aggregates into the surrounding soil matrix are limited, resulting in greater persistence of PPCPs.

If an LMB is applied on a soil, PPCPs have a greater potential to transport within and over the soil at the time of application. Dewatered biosolids require an external source (rainfall or irrigation water) to favor the mobilization of pollutants within the soil/biosolids.

The highest concentrations of PPCPs in tile drainage following the application of biosolid slurry (i.e. liquid municipal biosolids) were detected immediately after application (Lapen et al., 2008b). In contrast, large cohesive DMB aggregates remain at the point of deposition on the soil. The concentrations of PPCPs in tile drainage following the application of dewatered biosolids were generally lower than those following LMB application, and, in contrast to LMB applications, the highest concentrations were only measured some time after application (Edwards et al., 2009).

Presumably, the slower release of residues from the DMB aggregates, and drying and physical deterioration of the aggregates was extending the period of availability for transport in runoff, compared to LMB where the PPCPs were applied in a more uniform matrix.

It is important to highlight that in the case of tile drainage in LMB-amended soil, the time the LMB took to reach the tiles (around 80 cm below) ranged between 3 and 39 min in unsaturated soil (Lapen et al., 2008b), whereas in the case of DMB-amended soil, contaminants due to dewatered sludge application reached the tile at least 8 days after sludge application (Edwards et al., 2009).

The maximum concentrations of the selected PPCPs in tile drainage were higher in the case of application of LMB than that of DMB.

Anoxic conditions in soils (vadose zone) do not favor the degradation of contaminants, in particular persistent ones, and this could have contributed to the persistence of some LMB-derived PPCPs in the tile drainage in the soils investigated by Edwards et al. (2009) in 2006, which had previously been used for another investigation by Lapen et al. (2008b), who applied LMB on the same plots.

3.3.4 Influence of sludge application rate and of pharmaceutical load

In the different investigations, the applied sludge ranged between 2,683 kg/ha (Healy et al., 2017) and 29,536 kg/ha (Peyton et al., 2016) (see Tab. S1). Some investigations used extremely high quantities of sludge on soil in order to enhance the behaviour of the microcontaminants ~~pollutants~~ under study (Giudice and Young, 2011 and Gottschall et al., 2012). Current regulations allow a maximum rate which can be expressed in terms of kg/ha year or kg/ha over a longer period, for instance 3 years in Italy. Sometimes the maximum sludge rate to apply depends on the N and P maximum applied rate, as reported in Table S3.

Table 4 reports PPCPs ~~PhCs~~ concentrations in runoff after sludge application. Attempts to correlate the available data were carried out, but no clear correlation was found for the studied compounds between the applied load and resulting concentrations.

A factor which seems to affect runoff concentration is the solid content of the applied sludge. Sabourin et al. (2009) used dewatered sludge (the so-called solid sludge, with a solid content of > 18 %) on the same soil where Topp et al. (2008b) carried out their studies with liquid biosolids. They found that with dewatered sludge, the concentrations of microcontaminants ~~pollutants~~ were in general lower than in the case of liquid biosolid application and only some days after application they may be found. This delay in the release of PPCPs may be explained by the fact that in dewatered sludge, PPCPs are more retained in the aggregates.

Table 4 Runoff concentration as a function of the applied load of pharmaceuticals.

	Sludge concentration	Application rate	load [mg/ha]	Runoff concentration [ng/L]	Reference
Acetaminophen	28.6 ng/g	8,000 kg/ha	229	20,3	Sabourin et al. 2009
	100,000 ng/L	93.5 m^3/ha	9,350	47; 114; 146	Topp et al. 2008b
Naproxen	394 ng/g	8,000 kg/ha	3,152	18,1	Sabourin et al. 2009
	10,000 ng/L	93.5 m^3/ha	935	509	Topp et al. 2008b
Sulfamethoxazole	12.4 ng/g	8,000 kg/ha	99	3.2	Sabourin et al. 2009
	10,000 ng/L	93.5 m^3/ha	935	7,15[c]; 35,4; 93	Topp et al. 2008b
Triclocarban	50 ng/g	2,683.3 kg/ha	134	6[b]; 10	Healy et al. 2017
	8,194 ng/g	8,000 kg/ha	65,552	3,4	Sabourin et al. 2009
	17,600 ng/g	22,500 kg/ha	396,000	6,3; 13,1; 17,3	Giudice and Young 2011
Triclosan	270 ng/g	6751.4 kg/ha	1,823	90[b]	Healy et al. 2017
	4,900 ng/g	2683.3 kg/ha	13,148	90[b]	Healy et al. 2017
	7,066 ng/g	8,000 kg/ha	56,528	109.7	Sabourin et al. 2009
	9,140 ng/g	3,500 kg/ha	31,990	310[a, b]; 500[a]; 600[a]	Gray et al. 2017
	15,900 ng/g	22,500 kg/ha	357,750	51 [b]; 282.1; 309.6	Giudice and Young 2011
Atenolol	1.6 ng/g	8,000 kg/ha	13	39.6	Sabourin et al. 2009
	10,000 ng/L	93.5 m^3/ha	935	70	Topp et al. 2008b
Gemfibrozil	31 ng/g	8,000 kg/ha	248	8	Sabourin et al. 2009
	10,000 ng/L	93.5 m^3/ha	935	597	Topp et al. 2008b

[a] values graphically estimated; [b] < LOD; [c] < LOQ

Table 5 Tile drainage concentrations as a function of the applied load of pharmaceuticals (Num = graphically estimated; **Num** = below LOD; *Num* = below LOQ)

Compound	Concentration [ng/g]	Application rate [kg/ha]	Load [mg/ha]	Tile drainage concentration, [ng/L]	reference
Acetaminophen	18.7	22,000	411.4	13	Gottschall et al. 2012
	24	8,000	192	*17,5*[a]; 36[a], 38[a], 40[a], 42[a], 48[a], 5 [a], 53[a], 60[a], 62[a], 87[a], 105[a], 220[a], 233	Edwards et al. 2009
Ibuprofen	63.6	22,000	1399.2	24	Gottschall et al. 2012
	750	8,000	6,000	*11,5*[a]; 22[a]; 28[a]; 30[a]; 5 [a]; 73	Edwards et al. 2009
Naproxen	6	22,000	132	**4**	Gottschall et al. 2012
	470	8,000	3,760	*7,5*; 18; 29	Edwards et al. 2009
Triclocarban	4,940	22,000	108,680	40	Gottschall et al. 2012
	8,000	8,000	64,000	*2.5*	Edwards et al. 2009
Triclosan	10,900	22,000	239,800	73	Gottschall et al. 2012
	14,000	8,000	112,000	*9,5* [a]; 20 [a]; 22 [a]; 22,5 [a]; 23 [a]; 24 [a]; 25 [a]; 30 [a]; 31 [a]; 32 [a]; 34 [a]; 35 [a]; 36 [a]; 37 [a]; 45 [a]; 46 [a]; 48 [a]; 52 [a]; 56 [a]; 57 [a]; 59 [a]; 63[a]; 68 [a]; 75 [a]; 82 [a]; 95 [a]; 101 [a]; 140[a]; 185[a]; 190[a]; 230[a]; 240	Edwards et al. 2009

Gemfibrozil	24	8,000	192	*8*	Edwards et al. 2009
	57	22,000	1,254	**5**	Gottschall et al. 2012
Cotinine	1.3	8,000	10.4	*1,5;* 3,9; 4,8; 5,5; 5,7; 6,5; 8,2; 9,5; 11	Edwards et al. 2009
	9.4	22,000	206.8	**1**	Gottschall et al. 2012
Carbamazepine	9	8,000	72	*2,5;* 6; 7; 7,5; 7,6; 8,5; 13; 14; 19; 24; 30; 32; 38; 44; 49	Edwards et al. 2009
	183.6	22,000	4039.2	13; 5	Gottschall et al. 2012

[a] values graphically estimated; [b] < LOD; [c] < LOQ

3.3.5 Influence of the sludge application method

Edwards et al. (2009) remarked that the investigated application mode (direct injection, surface spreading and tilling) may influence the quality of tile drainage and surface runoff, due to the resulting different capacities of breaking dewatered sludge solids/aggregates apart and the fact that the microcontaminants and microorganisms have different types of exposure to the atmosphere (mainly UV and oxygen).

Moreover, the moisture content of the applied sludge may also greatly influence the behaviour of PPCPs, as remarked by Edwards et al. (2009). In the case of dewatered sludge, microcontaminants ~~pollutants~~ present a more modest level of mobility and potential to biodegrade than in the case of liquid sludge, and differences may be more likely to occur in PPCPs associated with aggregate interiors rather than exteriors. According to the cited study, there is no significant difference in the concentrations of PPCPs in tile drainage in the case of surface spreading and direct injection of dewatered sludge.

Surface spreading allows a faster degradation of the most degradable PPCPs.

Topp et al. (2008b) found that through the injection of liquid sludge into the soil, surface runoff presents a lower concentration of selected microcontaminants ~~pollutants~~ in a short time as direct injection promotes pollutant ~~contaminant~~ sequestration and reduces the surface mobility of pollutants ~~contaminants~~. Analysis of surface runoff after a prolonged period showed that the release of microcontaminants ~~pollutants~~ may occur later for the most persistent compounds retained within the soil, whereas for those which are more biodegradable, degradation processes take place and their concentration is low or they are not detected (Al-Rajab et al., 2015).

In their investigation comparing sludge application approaches (surface spreading and subsurface spreading) on the quality of tile drainage in terms of a selection of different PPCPs, Lapen et al. (2008b) remarked that microcontaminants ~~pollutants~~ rapidly move downwards, reaching the tile drains in a few minutes, regardless of the application method: the larger the soil macropores, the shorter their transport time. Applied sludge fluidity also influences the gravity-based flow of occurring pollutants: liquid municipal biosolids can be considered similar to diluted wastewaters and thus they rapidly move downwards. In this context, the sorption to the macropore walls is limited, as the rapid vertical motion of the leaching stream is the dominant process. The sludge is subsurface spread by means of an applicator which applies slurry close to the ground immediately following the passage of rolling tines that affect aerator-type tillage of the soil (Lapen et al., 2008a,b). This application method leads to the reduction of soil macropore size and fosters the sorption of microcontaminants ~~pollutants~~ and liquid biosolids in the tilled surface layers.

3.3.6 Influence of rainfall intensity, frequency and volume

Giudice et al. (2011) analyzed the composition of the surface runoff during three storm events of the same intensity occurring on the same plot (2 m^2) 3, 9 and 24 days after sludge application. Data reported on triclosan and triclocarban show that for each rain event, micropollutant concentration in surface runoff remains constant in the first 4, 8, 12, 16, 20 and 24 liters. They also found that in the three rain events, measured concentrations varied. This could be attributed to the sequestration of the compounds, and their scarce biodegradation within the soil rather than to the increasing water volume applied to the plot in the three events.

In Yang et al. (2012) and Gray et al. (2017) the concentration of a selection of anthropogenic waste indicators (fragrances and hormones) in runoff due to three replicated 100-year rainfall events was investigated. After 35 days the runoff concentration decreased with respect to previous rain events (1 and 8 days after sludge application) but remained at comparable values. This suggests that hormones may persist in the soil even if leaching and, possibly, onsite transformation may occur. That study compared the runoff quality in the case of frequent heavy rain events and after only one intense rainstorm, 35 days after sludge application. It was found that onsite attenuation was minimal and that natural weathering processes may make some compounds more easily leachable from the sludge amended soil even in the case of dry periods. In addition, they also found that once the soil becomes saturated, an increase in runoff rate leads to an increment in hormone load.

In tile drainage, the concentrations of investigated compounds decreased in the rain events occurring many days after sludge application on the soil (Lapen et al., 2008b) compared to the events nearly immediately after the application.

3.4 Influence of the main factors on the concentrations of microorganisms in runoff and tile drainage

Sludge treatment – No specific investigation compared the quality of runoff and tile drainage in terms of microorganisms in the case of LMB and DMB application. It can be expected that a “liquid” biosolid could lead to a higher concentration in tile drainage than a dewatered one, as it quickly crosses the layer through the macropores and reaches the tile drain (Lapen et al., 2008a,b).

Referring to surface runoff, similarly to PPCPs, there could be a slower release of microorganisms adherent to DMB aggregates, and they become available to the runoff over a longer period (Sabourin et al., 2009).

Thermal drying, gamma irradiation and disinfection greatly reduce microorganism content in sludge and thus, in the case of land reuse, the risk of microbial contamination of the receiving waters due to surface runoff or tile drainage is reduced.

Application methods – If the sludge is spread on the surface, the major removal mechanisms are due to desiccation and ultraviolet light (Lu et al., 2012; Gondim-Porto et al., 2016), whereas if the biosolid is incorporated into the soil, microorganism survival is strictly related to soil pH, organic matter content, texture, temperature, and competitive organisms developed in the soil.

In tile drainage, investigations by Lapen et al. (2008a) showed that one-pass aeration tilling mode (Table 3) enhances contaminant sorption/retention in the soil as it disrupts surface macropores and increases sorptivity. In their investigation, they reported that the average mass load ratios between tilling mode and one-pass aeration tilling application were 6 for *E. coli* and 12 for *C. perfringens*. Unlike the case of PPCPs investigated by Edwards et al. (2009) (see section 3.3.5), Gottschall et al. (2009) found differences in the concentrations of bacteria in tile drainage in the case of surface spreading and direct injection of dewatered sludge: concentrations of *E. coli,* Enterococci, *C. perfringens* were higher in the case of direct injection.

Soil characteristics: Interesting findings were reported by Atalay et al. (2007) in their investigation of the content of *E. coli* and Total coliform in runoff and percolate in two different sludge-amended soils - sandy loam and clay loam. They found that in the case of clay loamy soil the concentrations of *E. coli* were higher than in the sandy loam. With regard to the Total coliforms, no significant differences were found when the sludge was amended to the two soils. They also found that sludge incorporated into the first 5 cm of soil instead of the first 10 cm may lead to a higher occurrence of microbes in the surface runoff.

Rainfall – Unfortunately, little data is available for evaluating the effect of rainfall on microbial occurrence in surface runoff. According to Peyton et al. (2016), there could be a regrowth of Fecal coliform after a rain event on dry soil. Earlier studies (Dunigan and Dick, 1980) found that Fecal coliform indicator bacteria counts in surface runoff waters from sewage-treated plots were very high during the first days of sludge application, but they rapidly decreased as the soil became drier.

4 Lessons learned from past investigations

Importance of sludge type (liquid or dewatered) on the runoff and tile drainage quality and quantity - Soon after land application, liquid municipal sludge moves more rapidly through the available pores in unsaturated soil, ensuring a greater exposure of contaminants to soil microorganisms, which may accelerate degradation processes. On the other hand, in the case of application of dewatered sludge, the degradation of contaminants is hampered by the modest diffusion of oxygen into the aggregates and of microcontaminants out of the aggregates towards the soil environment. In addition, when liquid sludge is applied, microcontaminant concentrations in surface runoff and tile drainage are higher than in the case of DMB (Sabourin et al., 2009).

Phenomena occurring within the soil. They are quite complex and affected by many parameters (Gray et al. 2017; Gottschall et al. 2013; Topp et al. 2008a; Healy et al. 2017, Lapen et al., 2008a). Different scenarios have been highlighted:

- the mass of microcontaminants which leachates after biosolid application is small with regard to the quantity present in the soil due to sludge application, and runoff concentrations are generally low and similar after different rain events;
- the release of microcontaminants could be minimal and occur in many successive events;
- rain events tend to wash down biosolid particulates and the microcontaminants are associated with the suspended solids rather than being leached in the dissolved phase (and chemical analysis does not detect them);
- microcontaminants are not released in the dissolved phase but persist in the soil and their mass reduction is only due to soil erosion, washed out by heavy rain events via solid aggregates,
- natural weathering processes may make some compounds more easily leachable from the sludge-amended soil even in the case of prolonged dry periods.
- referring to microorganisms, due to the unfavorable soil conditions for microorganisms, in the sludge-amended soil, they are immediately subject to dessication, irradiation, competition with other species already present, etc. Their concentration in runoff and tile drainage is also affected by rain event characteristics: rain duration, intensity and frequency.

Persistence of microcontaminants in the soil - Some compounds persist in the soil environment within sludge aggregates for a long time: up to 1 year after sludge application. Their runoff concentrations generally decrease, following first order kinetics but, sometimes they may also remain constant. This means that even for long periods of time, these compounds do not seem to deplete within the soil. The reason could be due to the fact that sludge is the end product of a series of mechanical and above all biological treatments under different conditions (aerobic, anoxic, and anaerobic) within wastewater treatment plants. Macro- and micro-contaminants still present in the treated sludge are thus resistant to the different environments and for these reasons are still present even after many weeks or months.

Some hormones can interconvert via microbial activities within the soil. As a result, their runoff concentration may increase after multiple rainfall events and exposure to environmental conditions due to the biodegradation of a related compound.

Environmental risk posed by the release of microcontaminants via surface runoff and tile drainage - Based on current findings limited to specific compounds, it seems unlikely that a significant environmental risk could be due to the release of PPCPs by tile drainage and surface runoff. However, neither mixture effects nor the chronic effects on different aquatic species have as yet been investigated.

Good practices for sludge disposal - Correct sludge disposal on rural land should favor the retention of pollutants and microcontaminants in the rooting zone away from groundwater, artificial drainage and surface water sources. Bearing this in mind, good practices include (but are not limited to): (i) proper sludge rates of application, (ii) pre-application tillage of the soil to foster the disruption of continuous macropore networks and improve surface soil sorptivity, (iii) land application when soil macroporosity is reduced and when the soil sorption capacity is higher, (iv) controlling product placement and using application equipment that decreases the absolute amount of amendment available for local infiltration/surface runoff; (v) installation of a deeper tile drainage system, and application on soil characterized by a lighter texture, as it may enhance the sorption and sequestration of microcontaminants ~~pollutants~~ and finally, (vi) lowering temperatures, which may reduce the decomposition of DMB and the release of active ingredients of microcontaminants.

~~*Phenomena occurring within the soil.* They are quite complex and affected by many parameters. The analysis outlined by Gray et al. (2017) accurately describes the potential scenarios: (i) the mass of microcontaminants pollutants which leachates after biosolid application is small with regard to the quantity~~

present in the soil due to sludge application, and runoff concentrations are generally low and similar after different rain events; (ii) the release of microcontaminants pollutants could be minimal and occur in many successive events; (iii) rain events tend to wash down biosolid particulates and the microcontaminants pollutants are associated with the suspended solids rather than being leached in the dissolved phase (and chemical analysis does not detect them); (iv) attenuation within the soil is negligible, microcontaminants pollutants are not released in the dissolved phase but persist in the soil and their mass reduction is only due to soil erosion, washed out by heavy rain events via solid aggregates, (v) natural weathering processes may make some compounds more easily leachable from the sludge-amended soil even in the case of prolonged dry periods.

PPCP concentrations in surface runoff from a liquid sludge-amended soil decrease in sequential runoff events after the application with kinetics that approximated the first-order (Topp et al., 2008a).

Due to the unfavorable soil conditions for microorganisms, in the sludge-amended soil, microorganisms are immediately subject to different removal paths (dessication, irradiation, competition with other species already present, etc.). Their concentration in runoff and tile drainage is also affected by rain event characteristics - the duration of the dry period before the rain event (that is how many days after the spreading or injection of the sludge on the soil it starts), rain duration and intensity.

Mobility of the microcontaminants pollutants within the soil depends on many factors, and a high degree of vertical macroporosity seems to facilitate this mobility even though compounds could have a medium-high sorption potential as in the case of some hormones, as discussed in Gottschall et al. (2013).

Referring to rainfall, it was found that although intense events (65 mm/h, simulating a rain event with 100 years as a return period) were applied to the plots, compounds including triclosan, galaxolide, tonalide and indole were found in surface runoff 35 days after sludge application.

Some compounds persist in the soil environment for a long time – antibiotics and antifungals, for instance, persist within sludge aggregates for up to 1 year after their application. Their attenuation is not due to mobilization, as they were not found in tile drainage or in groundwater, and neither can it be attributed to plant uptake, since they were not detected in the crop grown on the investigated plots.

The persistence of microcontaminants pollutants seems to be correlated to the organic content of the soil, soil temperature, the physico-chemical properties of the compounds themselves and the occurrence of co-contaminants, making them potentially more susceptible to loss in surface runoff during rainfall events (Healy et al., 2017).

Medium term investigations, such as those by Gray et al. (2017), concerning hormones in runoff which cover a period of around 40 days after sludge application, showed that runoff concentrations for different sampling days (1, 8, and 35 days) generally decreased or remained constant for most compounds.

Longer investigations such as in Topp et al. (2008b), remarked that triclosan, gemfibrozil, cotinine and carbamazepine in surface runoff are present even 266 days after sludge application.

This means that even for long periods of time, these compounds do not seem to deplete within the soil. It should not be surprising, as sludge is the end product of a series of mechanical and above all biological treatments under different conditions (aerobic, anoxic, and anaerobic) within wastewater treatment plants. Pollutants still present in the treated sludge are thus resistant to the different environments and for these reasons are still present even after many weeks. Moreover, these findings suggest that investigations should cover longer observation periods, as the losses of microcontaminants may occur long after sludge application.

Finally, hormones are molecules which can interconvert via microbial activities within the soil. For some of them, runoff concentration may increase after multiple rainfall events and exposure to environmental conditions due to the biodegradation of a related compound (Yang et al., 2012; Gray et al., 2017).

The percentage of PPCP mass loads lost in all runoff events (in a dissolved phase as well as in sediments) considered in the experimental campaigns with regard to the applied biosolids was found to be compound-specific, ranging from very low values (0.001 % for triclocarban, 0.03 % for naproxen, 0.04 % for triclosan,

~~and 0.27 % for ibuprofen) to 14.58 % for cotinine, 19.06 % for carbamazepine and 29.06 % for atenolol (Sabourin et al., 2009).~~

~~Many authors have pointed out that data referring to lab or soil column investigations may lead to results which are not collected in field studies. Among these, Gottschall et al. (2013) found that estrogens showed greater downward mobility towards the water table than in the case of lab investigations.~~

~~Some investigations represent worse scenarios, for example those involving applied sludges spiked with PPCPs at higher concentrations, to better follow the fate of the key compounds (Lapen et al., 2009b). In addition, PPCP monitoring in runoff and tile drains could be conducted over a relatively short time interval and more persistent compounds retained or adsorbed in the soil may be released into runoff or tile drains at times surpassing the end of monitoring in the investigations considered here.~~

~~Based on current findings limited to specific compounds, it seems unlikely that a significant environmental risk could be due to the release of PPCPs by tile drainage and surface runoff. However, neither mixture effects nor the chronic effects on different aquatic species have as yet been investigated.~~

~~Correct sludge disposal on rural land should favor the retention of pollutants and microcontaminants pollutants s in the rooting zone away from groundwater, artificial drainage and surface water sources. Bearing this in mind, good practices include (but are not limited to): (i) proper sludge rates of application, (ii) pre-application tillage of the soil to foster the disruption of continuous macropore networks and improve surface soil sorptivity, (iii) land application when soil macroporosity is reduced and when the soil sorption capacity is higher, (iv) controlling product placement and using application equipment that decreases the absolute amount of amendment available for local infiltration/surface runoff; (v) installation of a deeper tile drainage system, and application on soil characterized by a lighter texture, as it may enhance the sorption and sequestration of microcontaminants pollutants and finally, (vi) lowering~~

~~temperatures, which may reduce the decomposition of DMB and the release of active ingredients of pharmaceuticals (Lapen et al., 2008a; Gottschall et al., 2012).~~

5 Main areas lacking in investigations, further research and perspectives

In many investigations, the main scope was the occurrence of target compounds in runoff or tile drainage, and data referring to rainfall events were often incomplete. In particular, the volume of rain entering and exiting the system is not always provided and thus, neither a water mass balance nor a pollutant mass balance is possible. A complete hydrologic description of the plot where the investigation takes place is necessary because the transport of PPCPs in soil is strongly influenced by the soil saturation ratio.

As remarked by Gray et al. (2017) and Yang et al. (2012), even if intense rain events are considered in the investigations, longer monitoring periods (greater than 40 days) should be adopted, as losses of microcontaminants may occur many days after application, especially in the case of dewatered sludge applied in the soil.

Sampling strategies adopted in the investigations are not always well reported and it is not clear exactly how and with what frequency the sampling occurred. In order to have reliable data and reproducible tests, all details should be provided and analyses should be performed according to standard methodologies. In addition, concentrations should be provided in tables, as in figures they are not easily readable. In any case, a descriptive statistical analysis of the collected data should be reported in terms of the minimum, maximum and standard deviations.

Environmental conditions are essential in defining the main removal mechanisms of pollutants. These parameters are rarely provided but soil temperature or at least ambient temperature should be made available.

Further research should address the effect of different soil compositions and different agricultural management practices (including application methods, sludge application rate and frequency, and irrigation application rate) on the quality of surface runoff and tile drainage.

Investigations should consist of a comparative analysis of the results achieved by applying different types of sludge, different application rates, different application methods, and different irrigation frequencies on different soils in order to evaluate the most influential parameters on surface runoff. A common observation is that PPCPs tend to accumulate in soil, mainly in the case of soil characterized by micropores which do not favor the downward mobility of contaminants. Long-term investigations should also address the probability of the release of these accumulated compounds in the case of intense rain events, or drought/wet periods which could greatly influence the mobility of the contaminants by creating preferential paths within the soil.

Further studies should focus on the occurrence of microbial indicators in surface runoff and in tile drainage during different rainfall events, in particular different frequencies and in different soil types. The occurrence of antibiotic-resistant genes and bacteria in sludge amended soil should also be addressed, as highlighted by Urra et al. (2019).

Supplementary Materials

In the Supplementary materials section, tables and figures provide further details of the reviewed studies (Table S1 in an Excel file and Figure 1 and Tables S2-S7 in a pdf file).

Conflict of interest

The authors declare that there are no conflicts of interest

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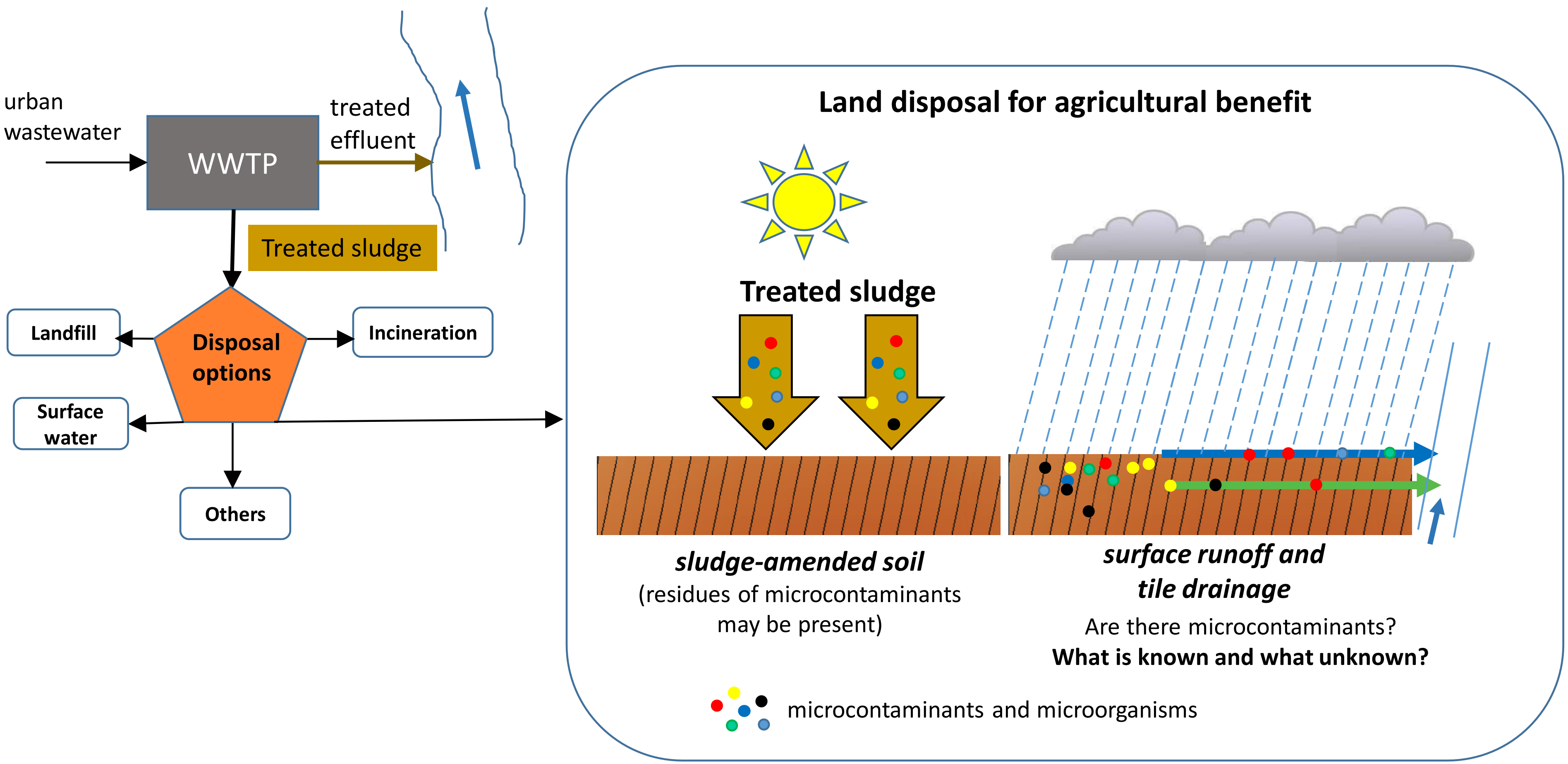
*Graphical Abstract

Graphical abstract



***Highlights (for review : 3 to 5 bullet points (maximum 85 characters including spaces per bullet point)**

Highlights

Runoff in sludge-amended soil is a source of pollutants in surface water

Occurrence of microcontaminants in sludge-amended soil runoff was reviewed

Ibuprofen, tonalide and gemfibrozil exhibited the highest concentrations.

Occurrence in runoff was found lower than in secondary effluent and in surface water

Sludge application strategy greatly influences land unoff quality.

A review of selected microcontaminants and microorganisms in land runoff and tile drainage in treated sludge-amended soils.

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Abstract

The objective of this study is to provide a snapshot of the quality of surface runoff and tile drainage in sludge-amended soil in terms of 57 microcontaminants, including pharmaceuticals, hormones and fragrances, and 5 different species of bacteria. It also discusses the main factors affecting their occurrence (soil characteristics, applied sludge load and rate, sludge application method, rain intensity and frequency). It is based on 38 investigations carried out by different research groups in Canada, Australia, the USA and Ireland. The most frequently investigated compounds were hormones, the antiseptics triclosan and triclocarban, the analgesics and anti-inflammatories acetaminophen, ibuprofen and naproxen, the antibiotic sulphamethoxazole, the lipid regulator gemfibrozil and the psychiatric drug carbamazepine. Of all the bacteria, *E. coli* was the most monitored species. It was found that concentrations of the studied pollutants in surface runoff and tile drainage may vary, depending on many factors. They are generally lower than those observed in the secondary municipal effluent and in surface water, but their contribution to the deterioration of surface water quality might be relevant, mainly in wide rural areas. In this context, the reported data or their ranges represent an attempt to provide reference thresholds and bands of

observed concentrations for a rough estimation of the contribution made by the release of the selected pollutants into surface water bodies *via* surface runoff and tile drainage.

Keywords:

Surface runoff, tile drainage, microcontaminants, bacteria, sludge-amended soil, rainfall intensity

Graphical abstract

List of abbreviations:

AOX adsorbable organic halides;

AWI anthropogenic waste indicators;

CEC Cation exchange capacity;

dm dry matter;

DMB dewatered municipal biosolids;

D_{ow} octanol-water distribution coefficient;

FC Fecal coliforms;

HM heavy metal;

K_{ow} octanol-water partition coefficient;

LAS Linear Alkylbenzene;

LMB liquid municipal biosolids;

LOD limit of detection;

LOQ limit of quantification;

MEC measured environmental concentration;

MW molecular weight;

PAH Polycyclic aromatic hydrocarbons;

PCB Polychlorinated biphenyl;

PCDD/F dioxins and furans;

pK_a dissociation constant

PPCPs pharmaceutical and personal care products;

RL reporting limit;

SD standard deviation;

TC Total coliforms;

u.o.m. unit of measure

1 Introduction

Intense rainfall events detach and transport fine and low-density particles in land runoff, which may contain different kinds of pollutants. In addition, rain infiltrating dry soils can also leachate natural and anthropogenic substances (contaminants) retained and accumulated in the soil matrix and convey them to other environmental compartments, including groundwater and surface water bodies.

Contaminant accumulation in/on soil can be due to different routes. The most important contributions come from the disposal of treated sludge (Torri and Cabrera, 2017), the disposal of manure (Segat et al.,2015), land irrigation with reclaimed wastewater (Dodgen and Zheng 2016; Pedersen et al., 2003,2005, Xu et al., 2009), and land irrigation with surface water containing these contaminants (Calderon-Preciado et al., 2011).

Land disposal of treated municipal sludges is a common practice in many countries worldwide (Ingleziakis et al., 2014; Kelessidis and Stasinakis, 2012). In the following the term *biosolids* will be used as an alternative of treated sludges: the term biosolids was introduced in 1991 in the USA by the Water Environment Federation (WEF, 2005) to distinguish raw, untreated sewage sludge from treated and tested sewage sludge, which could legally be used for agricultural benefits.

This method of disposal can positively contribute to the improvement of soil properties and fertility (Clarke and Smith, 2011) due to the presence of nutrients and other substances in the sludges able to improve soil porosity or permeability (amendant effects), to favor aggregation of the main soil constituents (conditioning effects), to change chemical and physical soil properties (corrective effects) and/or to provide elements in assimilable or available form for plants (fertilizing effects).

Sewage sludge not only provides soil with organic matter, but it also increases infiltration, reduces the possibility of soil erosion (Lucid et al., 2014) and increases agronomic productivity (Samaras et al. 2008, Tsadilas et al. 2005, Zartman et al. 2012). Its use for agricultural benefits also addresses European Union policy on sustainability and the recycling of resources (COM, 2014).

In the case of intense rain events, surface runoff could seriously impact on near surface water bodies and affect their quality in terms of suspended solids, nutrients, and bacteria, as well as other emerging contaminants.

In addition, in those regions where natural field drainage can adversely affect crop production activities, it may interfere with the groundwater if the groundwater system is near the surface on a year round basis, as could be the case in any of the poorly drained soils in eastern Ontario (Lapen et al., 2008a,b,2018). There, tile drains are placed on agricultural areas within 1 m of the soil surface in order to collect draining water and short-circuit it to the adjacent surface water streams or rivers. This stream is then conveyed to a surface water body.

In the last few years, issues related to land runoff as well as tile drainage quali-quantitative characteristics have caused increasing concern. For the most part, attention has been paid to macro-pollutants (suspended solids, organic substances, nitrogen and phosphorus compounds) (Paule et al., 2014), heavy metals (Hosseini Koupaie and Eskicioglu 2015), and pesticides (Torri and Cabrera, 2017). Some investigations have strongly focused on the environmental risks posed by the presence of nutrients and heavy metals due to the land application of treated sludge, as well as-manure (Eldridge et al., 2009; Peyton et al., 2016; Jia et al.,2015; Bai et al., 2016). Some studies have also addressed mobilization in the runoff of bacteria applied to soil with the treated sludge. It has been highlighted that the soil environment is hostile for their development and that their survival time, following land application, is around 2-4 months (Brennan et al., 2012). As a consequence, bacteria are more likely to be transported into receiving water courses after rainfall events.

Recent studies have highlighted the occurrence of micro-contaminants, mainly pharmaceuticals and personal care products (PPCPs) in treated sludges and underlined the importance of more thorough investigations into the fate of these pollutants once spread on soil (Verlicchi and Zambello, 2015). In this way, contaminants could reach surface water bodies and in some cases they could pose a potentially acute and chronic risk for aquatic life (Clarke and Cummins, 2015), or ~~could~~ deteriorate the quality of freshwater reserves used for potable needs (Clarke et al., 2016).

From a legislative view point, different scenarios exist. The reuse of biosolids is not allowed in Belgium, Romania and Switzerland (Healy et al., 2017). In other countries it is possible (many European countries, New South Wales-Australia, Ontario-Canada, and the USA) and the current legal requirements regarding sludge disposal on soil commonly concern maximum sludge concentrations and/or maximum sludge loads for organic matter and nutrients, heavy metals, selected pesticides, and organic microcontaminants such as AOX, PCB, PCDD/F, as well as chemical-physical characteristics of the receiving soil, and the maximum quantity of sludge to be disposed on soil on a yearly basis (Mininni et al. 2015; Kelessidis and Stasinakis 2012; Le Blanc et al. 2008).

To date, no legal requirement has been set concerning the maximum permitted concentrations or loads for PPCPs (Kelessidis and Stasinakis, 2012; Lu et al., 2012, Leblanc et al., 2008). With regard to microorganisms, only a few States have standards regarding the maximum concentrations in sewage sludge to be disposed of on soil, and these mainly concern *Salmonella* and *E. coli* (Lu et al., 2012; Minnini et al., 2015).

As reported above, reclaimed water reuse for irrigation purposes may also contribute to the introduction of residues of microcontaminants of emerging concern into the soil (Kinney et al., 2006; Martinez-Piernas et al., 2018). The benefits due to the reduced demand for fresh water and the supply of nutrients (occurring in reclaimed water) are counterbalanced by the potential contamination risk to water and plants by still unregulated pollutants (Christou et al. 2017; Wu et al. 2015). This reuse practice is of great interest, principally for regions characterized by water scarcity (among them Spain, Cyprus, Lybia, and Jordan) and/or frequent periods of drought (Morocco, Algeria, and Tunisia). The contribution may be relevant but also limited to specific case studies.

This review aims to provide a snapshot of the chemical characteristics of surface runoff and also the leachate in sludge-amended soil with regard to investigated PPCPs and bacteria species. A further objective is to investigate the main factors affecting them (compound properties, soil characteristics, applied sludge load and flow rate, sludge application method, rain intensity and frequency). The idea is to provide reliable data on the quality of surface runoff and tile drainage leading to an assessment of the potential contribution of these streams to the quality of the surface water body during intense rain events. This review also underlines the strengths and weaknesses of available studies, the gaps in current knowledge and the research fields requiring further investigation. The reported data or their ranges could represent reference thresholds or bands of observed concentrations for a rough estimation of the contribution made by the release of the selected pollutants into surface water bodies *via* surface runoff.

1.1 Framework of the study

This study provides an overview of chemical characteristics in terms of concentrations of a selection of microcontaminants and microorganisms (Table 1) in the water streams (surface runoff and tile drainage) which, due to rain events, leave agricultural soils where treated sludge (= biosolids) has previously been applied. The review is based on a collection of 16 papers, published between 1980 and 2017, referring to 38 investigations into the occurrence of 57 PPCPs and 5 species of microorganisms (*E. coli*, Fecal coliform, Total coliform, Fecal streptococcus, and *Clostridium perfringens)*, in land runoff or in tile drainage after the disposal of treated municipal sludge onto soil.

Selected investigations differ in at least one of the following issues: (i) soil type, (ii) municipal sludge type (depending on the treatment it was subjected to), (iii) sludge application method, (iv) sludge application rate, (v) investigated water stream (runoff or tile drainage), and (vi) rainfall frequency pattern. One study may include more than one investigation.

The 38 investigations were carried out in Ireland (8), the USA (15), Canada (11) and Australia (4) and most of the research groups belong to agricultural research centers. Investigations into land runoff in the case of manure applied on soil were not included, since manure disposal on rural land is subject to specific regulations from country to country and many types of manures are available depending on the animals (cattle, pigs, chickens, sheep, etc.). Table 2 reports the main characteristics of the studies included in the review with the number of investigations specified for each study. Their aims and scope and the principal issues addressed are also underlined.

Figure S1 shows how these studies are temporally and spatially correlated and whether they include common research groups; Table S1 details the main characteristics of the reviewed 38 investigations with regard to field/plots, soil, sludge, rainfall, sampling strategy and the main findings. Investigations referring to the spiking of soil with specific microcontaminants (among them Davis et al., 2006) were not included, as according to Al-Rajab et al., 2009, the effect of the presence of treated sludge (the matrix containing microcontaminants) strongly influences the fate and behaviour of such contaminants in the soil.

Bearing in mind the definition sets in chemical engineering manuals, leachate is the liquid stream obtained from a leaching process, that is a unit operation consisting of a mass (and energy) transport from a solid phase (the soil) to a liquid one (the water leaving the soil) when they come into contact. With regard to Figure 1, once the rain starts, dry soil begins to retain water within its macro- and micro-pores. Water tends to percolate (generating the *leachate* or *percolate*) and in the case of prolonged rain events, when the soil becomes saturated, the water starts moving (flowing) on the soil surface, according to its slope, generating the so-called *surface runoff*. Sludge retained on the land surface is also subject to light exposure and phodegradation processes may occur, changing the characteristics of the sludge.

With regard to percolation of the water through the soil, if this stream is intercepted by pipes (drains), the water flow which spills out is called *tile drainage*. Figure 1 shows the different water flow paths on soil in the case of precipitation and it also shows the potential degradation/removal mechanisms pollutants and microorganisms occurring in the soil may undergo. Figure 1 is the conceptual scheme this study will refer to. In particular, it will investigate surface runoff and tile drainage characteristics in treated municipal sludge-amended soil: the two streams which can rapidly reach the receiving water stream, affecting its quality.

Section 2.2 deals with sludge application on soil in terms of sludge types based on the treatment before application, sludge application methods (compared in Table 3), the maximum loads allowed by the different regulations, and a brief overview of the legal requirements (standards for specific pollutants and in particular for microorganisms, section 2.2.3, with further details provided in Tables S3 and S4).

This study goes on to present the characteristics of the soil which can affect the runoff/tile drainage quality, the size of the plots and the characteristics of the rainfall events of the investigations. Special attention was also paid to data reliability and accuracy (section 2.5), and an analysis of the reviewed studies can be found in Table S1. The results are reported in graphs which show measured concentrations of selected PPCPs and bacteria in surface runoff and tile drainage as well as background concentrations in the absence of sludge application (when available). In the Supplementary Materials section, details are available in terms of a descriptive statistical analysis of the concentrations observed in surface runoff (Tab S5) and tile drainage (Tab S6).

Discussion of the results focuses mainly on the influence of the factors affecting runoff/tile drainage concentrations:

- compound characteristics;
- soil characteristics (matrix, pH, organic matter, organic carbon, cationic exchange capacity);
- sludge properties (CEC, moisture, pH, chemical composition) and its application rate;
- applied pollutant load;

- application method;
- application depth;
- applied water volume.

Figure 1.

Moreover, discussion of the collected results also refers to the ranges of measured concentrations of selected contaminants in secondary effluents, anaerobically digested sludges, runoff of rural soil irrigated with reclaimed water and surface water. The literature ranges to which the comparison refers are reported in Tables S2 and S5.

The study concludes with a list of the lessons learned from past investigations, the main gaps in the investigations and the issues requiring further study.

2 Materials and Methods

2.1 Compounds included in the review and main investigations

Investigated chemical compounds belong to 11 different therapeutic classes or groups: analgesics and anti-inflammatories (class A including 3 compounds); antibiotics (class B with 7 compounds); antifungals (class C, 1 compound); antihistamines (class D, 1 compound); antiseptics (class E, 2 compounds); beta-blockers (class F, 1 compound); fragrances (class G, 5 compounds), hormones (class H, 22 compounds), lipid regulators (class I, 1 compound); stimulants (class J, 2 compounds) and psychiatric drugs (class K, 12 compounds).

Table 1 compiles all of these with the main chemical characteristics (molecular weight MW, chemical formula, pK_a, LogK_{ow}), which are useful for analyzing or predicting their fate/behaviour once on the soil following sludge disposal, the number of related studies and corresponding references are also provided.

The last group refers to bacteria commonly monitored in municipal wastewater treatments: *Clostridium perfringens*, *Escherichia coli*, Fecal coliforms, Fecal streptococci and Total coliforms.

Table 1

Table 2.

2.2 Sludge application on soil – Sludge types, application methods, authorized loads, and legal requirements

2.2.1 Sludge types

Based on the studies under review, it was found that sludge intended for land disposal was generally anaerobically digested and, in many cases, dewatered. In a few cases it was subjected to further treatments: high temperature drying (Eldridge et al., 2009; Giudice and Young 2011, Healy et al., 2017, Peyton et al., 2016), gamma irradiation (Eldridge et al., 2009), centrifugal dewatering (Gottschall et al., 2012) or lime stabilization (Healy et al., 2017; Peyton et al., 2016). With regard to the selected micro-contaminants and bacteria, the concentrations in the applied sludge were included in the ranges reported in Table S2, even in the case of sludges spiked with micro-contaminants, with just two excpetions referring to acetaminophen and ibuprofen (in both cases final concentration was higher than the maximum literature value).

According to Sabourin et al. (2009) it was assumed that the sludge is considered liquid (often called liquid municipal biosolids LMB) if its solid content is less than 18 %, and dewatered (dewatered municipal biosolid DMB) if its solid content is higher than 18 %. In the different investigations, the sludge had a largely different solid content; on the basis of 11 of the 16 studies which reported sludge composition in detail, the solid content varied between < 18 % and 91.6 % (granulated high temperature dried sludge in Eldridge et al., 2009).

2.2.2 Application methods

Four different disposal methods were followed according to the collected studies. Table 3 shows the main sludge disposal strategies followed in the investigations under review, with a diagram and description for each of them, along with information regarding the papers dealing with them.

Table S1 includes many details referring to sludge application in the different investigations. In particular, as well as compiling sludge properties (pH, CEC, moisture/solid content) and treatment, it also details the application rate (dry matter kg/ha), application method and application depth.

Table 3.

2.2.3 Authorized concentrations and loads and other legal requirements

Regulations in force place great attention on the concentrations of heavy metals ~~(HMs)~~, microorganisms, some organic microcontaminants (including AOX, PAH, PCB, PCDD/F) and define limits of their concentrations in the treated sludge intended for land disposal.

In addition, they set maximum rates of sludge to be applied on soil (kg/ha year), maximum rate of nutrients (kg nutrient/ha year) and heavy metals (kg HM/ha year) in sludge. Some of them also set the maximum concentrations of heavy metals in soil (mg HM/kg dm).

Table S3 summarizes the main characteristics of the regulations in the European Community and in countries including those where most of the investigations under review took place (Ireland, Italy, New South Wales-Australia, Ontario-Canada, and the USA).

Table S4 compares the limits for the different microorganisms in treated sludge to be fulfilled in the case of land disposal in many European countries, as well as in New South Wales (Australia), Ontario (Canada) and the USA.

It is important to highlight that most of the current regulations clearly define spreading and tilling procedures, the maximum slope values, and pH and CEC in soil. In addition, some legislations require that a minimum distance from waterways and a minimum depth from the aquifer is respected with regard to the plot size where sludge is applied (Table S3).

Limits referring to new contaminants of emerging interest, including pharmaceuticals, hormones, and fragrances of interest in this review have not yet been set.

2.3 Characteristics of the soils in the investigations included in the review

The texture of the soils where investigations took place are reported in Figure 2 in the well-known texture triangle. A rapid glance shows the percentage of the main soil components (sand:silt:clay) in each case study. The legend on the right reports the studies shown in the diagram.

Figure 2

2.4 Plot size, precipitation and sampling strategy

Plot size - Concerning land runoff, investigations took place in plots whose size was in the range 0.36-6 m^2 (0.36 m^2, 1.62 m^2, 2 m^2, 3 m^2, 4.5 m^2, and 6 m^2). Tile drainage experiments were carried out in wider surface plots: 740 m^2, 1,500 m^2 and 3 ha, with the only exception being the investigation carried out by Giudice and Young (2011), which was carried out in 3 plots of 2 m^2. 32 of the 38 investigations included a control plot where sludge was not amended in order to compare the quality of surface runoff/tile drainage without sludge application - only the investigations carried out by Healy et al. (2017) and Topp et al. (2008b) did not include such a plot.

Rainfall type, *intensity, duration and frequency* - In 30 of the 38 investigations, rainfall was artificial (ozonated groundwater, carbon filtrated groundwater, deionized water, or drinking water) and after the simulated rain event, runoff samples were collected. The rain intensity was in the range of 11-90 mm/h and the chosen intensity corresponded to ain with a specified return period, typical of the country where the investigation was being carried out - 2 years in Missouri (Wallace et al., 2014) and 100 years in Canada and in the USA (Sabourin et al., 2009, Gray et al., 2017).

The duration of the rain events was clearly defined in some studies (30 min by Eldridge et al., 2009; 45 min in Atalay et al., 2007), whereas in others it was a defined period from the first occurrence of runoff (for instance 30 min in Healy et al., 2017, Peyton et al., 2016) or related to the desired runoff volume to be collected during the investigation (Giudice and Young 2011; Topp et al., 2008b, Sabourin et al., 2009, Wallace et al., 2014).

With regard to frequency, artificial rainfall was applied on different days - : often some days before sludge application (control step) and then after sludge application with a different frequency pattern, covering a period ranging from a few days to one year. In the case of only one investigation was the interval as long as 266 days (Topp et al., 2008b), while in all the others it was < 54 d (Table S1).

Rain was applied in the same plot to assess pollutant mobilization following rain events (Atalay et al., 2007; Eldridge et al., 2009; Giudice and Young 2011; Gray et al., 2017; Healy et al., 2017; Peyton et al., 2016; Wallace et al., 2014, and Yang et al., 2012) or in different plots with different frequencies to evaluate the contribution of degradation and sequestration of the investigated compounds after different prolonged dry periods (Sabourin et al., 2009; Topp et al., 2008b).

In only 5 studies, all referring to tile drainage tests, (Edward et al., 2009; Gottschall et al., 2012, 2013, Lapen et al., 2008a,b), was the rainfall real, with its total depth varying between 124 mm (Lapen et al., 2008a,b) and 1,070 mm (Gottschall et al., 2012, 2013). Investigations lasted from 46 days (Lapen et al., 2008a,b) to 365 days (Gottschall et al., 2012, 2013).

Many other details for the different investigations are reported in Table S1.

Sampling mode and frequency

Different sampling strategies were applied in surface runoff and details are reported in Table S1. Not all the studies clearly reported the description of the sampling mode and frequency, and analysis may refer to grab or composite samples.

In other studies, composite samples were collected and derived from the mixture of samples withdrawn from different plots (Sabourin et al., 2009; Giudice and Young, 2011). In Yang et al. (2012) analyses were performed on composite samples referring to different phases of the runoff (early, medium and late runoff).

Regarding tile drainage, analyses were on grab samples - water samples were collected during real rainfall events by means of in-line water flow control structures on the tile drain headers for each field section under study (Edward et al., 2009; Gottschall et al., 2012, 2013, Lapen et al., 2008a,b).

2.5 Accuracy and uncertainty of the collected data

The collected data reported in graphs and tables in the manuscript and in the supplementary material section come not only from tables, but also graphs and in this case, the uncertainties associated with the values add to the uncertainties due to sampling and analysis (as discussed in Verlicchi and Zambello 2016), even in cases where the reading of the data was quite accurate. If a value was reported below its limit of detection (LOD) or its reporting limit (RL) it was assumed equal to the LOD or the RL and if it was reported below its limit of quantification (LOQ), it was assumed to be half its LOQ value. Table S1 reports the details provided referring to the experimental campaigns and a rough estimation (good, modest or poor) of the accuracy/reliability of the reported data, the description of sampling strategies and the adopted equipment.

3 Results

3.1 Ranges of the concentration of selected compounds in land runoff and tile drainage samples

A rapid glance at Table S1 highlights that 29 of the 38 investigations refer to surface runoff monitoring, only 9 investigations monitored tile drainage, 21 investigations dealt with bacteria and 17 with pharmaceuticals, hormones and fragrances.

Figures 3 and 4 report the measured concentrations found for the selected pollutants in land runoff and in tile drainage samples in the case of sludge-amended soil. Where available, the background concentrations ~~BC~~ (control concentrations related to runoff or tile drainage from soil where sludge was not applied) of the compounds are also reported for comparison and analysis. Generally, these concentrations refer to water samples resulting from artificial rainfall applied some days before sludge application.

With regard to land runoff, it emerges that 33 compounds were monitored in the different investigations. The most studied compounds were hormones (class H), with ethinyl estradiol at the top with 37 measures, followed by all the other hormones with 33 values. The antiseptics triclosan and triclocarban and the analgesic ibuprofen were frequently monitored (values of 26 and 20, respectively), while fewer than 10 values were recorded for the remaining 14 compounds. MECs referring to hormones were collected in investigations tackling the application of dewatered anaerobically digested sludge on loamy sand and sandy loam soils. The data comes from the studies by Giudice and Young (2011) and Yang et al. (2012), which correspond to investigation numbers 4,5,6 and 7 in Figure 2. Table S5 reports the number of data for each compound, together with the minimum, maximum, average and standard deviation values for MECs and where possible, the minimum and maximum for background concentration values in case of surface runoff. It emerges that variability ranges vary from 1 to 3 orders of magnitude and concentrations were found between <LOD to 1,477 ng/L (ibuprofen according to Topp et al., 2008b). Average values varied between < LOD and 707 ng/L (ibuprofen). The highest concentrations (ibuprofen, tonalide, and gemfibrozil) were found in the investigation by Topp et al. (2008b) in which a liquid anaerobically digested sludge was applied on silt loam soil (point 12 in Fig. 2).

The intervals emerging from Figure 3 also depend on the fact that some studies presented measured concentrations of PPCPs in different events after the sludge had been applied. As remarked by several authors (among them Topp et al., 2008b; and Sabourin et al., 2009), the temporal patterns of runoff exports (aqueous+particulate) were different from the investigated compounds. Concentrations varied, and for some compounds (triclosan, atenolol, acetaminophen, and sulphametoxazole) the highest values correspond to the first rainfall after sludge application, for others they may occur during subsequent events (for naproxen during the second event, on the third day following application; for triclocarban, carbamazepine and caffeine after seven days, during the third rain event).

With regard to background concentrations (the red stars in Figure 3), these were found to be < LOD for all compounds with the sole exceptions of estrone, androstenedione (with 2.2 ng/L and 1.54 ng/L respectively, Yang et al. 2012), caffeine and triclosan (21, 27, 49 ng/L and 35, 37, 47 ng/L respectively, Sabourin et al. 2009,). All studies reported that no previous sludge application on soil had occurred before their investigation. The occurrence of compounds in soil could thus be due to other sources, for instance irrigation with surface water containing residues of the compounds under study (Ma et al., 2018). In this context, Table S5 shows the measured concentrations for the selected compounds in surface water.

Figure 3.

With regard to tile drainage samples, 46 compounds were analyzed, but for 13 hormones (17-α-estradiol, 17-β-estradiol, α-dihydroequilin, androstenedione, equilenin, equilin, estradiol benzoate, estriol, mestranol, norethindrone, norgestrel, progesterone and testosterone), Gottschall et al. (2013) only reported background concentrations (always below the corresponding LOD, as shown by the red stars in Fig. 4) and this is the reason why these are not included in Figure 4, which shows the remaining 33.

Among all these PPCPs, the most studied belong to different classes: the antiseptic triclosan (90 values), the stimulant cotinine (85 values), and the psychiatric drug carbamazepine (80 values). For 8 compounds, the collected data vary between 33 and 75, and for the other compounds the available data are less than 5. Measured concentrations varied between 1.5 and 4,117 ng/L and, for each compound, the range of variability was equal to 2 or 3 orders of magnitude, with the exception of sulfapyridine, estrone and fluoxetine whose range was of 1 order of magnitude.

The highest values (> 1,000 ng/L) are related to ibuprofen (4,117 ng/L), naproxen (1,045 ng/L), triclosan (3,676 ng/L), gemfibrozil (1,040 ng/L), and carbamazepine (1,136 ng/L). All these values were collected by Lapen et al. (2008b), whose investigation dealt with the application of liquid anaerobically digested sludge on silty clay loam (number 15 in Figure 2).

Average concentrations varied between 1.5 ng/L (ofloxacin and miconazole) and 551 ng/L (triclosan).

The background concentrations were investigated for all the compounds (Lapen et al., 2008b; Edwards et al., 2009, Giudice and Young, 2011; and Gottschall et al, 2013) and they resulted below LOD or below LOQ, with four exceptions. As reported in Figure 4, these refer to naproxen (35 ng/L), triclosan (95 ng/L), atenolol (135 ng/L) and cotinine (5 ng/L) and were reported by Edwards et al. (2009), who investigated the application of dewatered anaerobically digested sludge on loam soil (number 13 in Figure 2), which had previously received sludge.

Further details regarding these collected data are reported in Table S6, in particular the number of data for each compound, together with the minimum, maximum, and average values and standard deviation (SD) for MECs and, where possible, the minimum and maximum for background concentration values in the case of tile drainage.

Figure 4.

Observed concentrations for the selected compounds in both runoff and tile drainage are generally lower than the values found both in the municipal WWTP secondary effluent, in surface water as well as in runoff in case of reclaimed water reuse. The corresponding range of concentrations found in literature (Verlicchi et al., 2012, Ben et al., 2018; Chalew and Halden 2009; Metcalfe et al., 2003; and Pedersen et al., 2005) are reported in Tables S5 and S6.

Moreover, the observed concentrations for hormones are unlikely to result in any significant pulse environmental exposure impact, from a pure tile effluent concentration perspective (Gottschall et al., 2013). In addition, once released into surface water, the dilution effect and photodegradation of microcontaminants due to UV exposure contribute to a further reduction of their concentrations. Sabourin et al. (2009) remarked that the runoff concentrations of the selected PPCPs were lower than the reported acute toxicological endpoints, and for most compounds a thousand times lower.

3.2 Range of concentrations for the bacteria included in the review

Few papers tackle the monitoring of bacteria in surface runoff and tile drainage after sludge disposal. Four studies have investigated surface runoff (Dunigan and Dick, 1980; Atalay et al., 2007; Eldridge et al., 2009; Peyton et al., 2016; Wallace et al., 2014) and two tile drainage (Gottschall et al., 2013; Lapen et al., 2008a). Moreover, different units of measures were sometimes used and thus analyses are not easy to perform. Figure 5 reports the collected concentrations and background concentration for bacteria species with more than 12 reported measures, with the exception of Fecal coliforms as they are in another unit of measurement. A descriptive statistical analysis was carried out for all of the bacteria (Table 4).

Investigations by Peyton et al. (2016) with 5 differently treated sludges applied on rural land showed that there is no correlation between sludge treatment and runoff concentration of Fecal and Total coliforms.

Figure 5

The profile of bacteria content in runoff after three different simulated rain events (1 d, 2 d and 15 d after application; same rain intensity) strictly depends on the sludge type (differently treated) applied on the soil, (Peyton et al., 2016) and the maximum concentrations vary in different cases. This could be explained by the fact that once sludge is applied on the soil, UV light and desiccation are responsible for the decay of occurring bacteria (Lang et al., 2007), but in some cases, bacteria could also find soil conditions which favour their development.

A comparison with TC and FC concentrations in runoff in the case of dairy cattle slurry application shows that they were always 1 order of magnitude higher than in the case of treated sludge application (Peyton et al., 2016).

It emerges that investigations report a variable number of values - from 3 (Atalay et al., 2007) to 46 (Gottschall et al., 2013); background concentration was measured once in the studies by Atalay et al., (2007), Eldridge et al. (2009) and Wallace et al. (2014) for surface runoff and Gottschall et al. (2013) for tile drainage.

Table 4.

Wallace et al. (2014) highlighted the low content of FC in control plots (116 CFU/100 mL) and a wide variability in the case of sludge application on soil with or without a vegetative filter, from 4,880 to 35,720 CFU/100 mL. These values are higher than the maximum amount allowed in Missouri (where the investigation took place) for whole body contact recreation use (maximum of 206 CFU/100 mL).

Sludge disposal always led to an increment in the bacteria concentrations in surface runoff and tile drainage with concentration ranges as wide as 3-5 orders of magnitude depending on many factors, as will be discussed later.

The investigation by Eldridge et al. (2009) was the only scenario in which this phenomenon did not occur. They found a background concentration for *E. coli* equal to 251,188 MPN/100 mL and after sludge application, MECs in surface runoff were always lower, between 25,000 and 31,000 MPN/100 mL. Measured concentrations are strictly correlated to the sampling procedure followed in the investigations. As reported in Table S1, water samples were instantaneous or (time or volume) composite, and in some cases (Yang et al., 2012) water samples were related to early, middle and late rain events corresponding to the mix of different collected samples. Lapen et al. (2008a) found that LMB application-induced contamination starts some minutes after sludge application. *E. coli* and *C. perfringens* were still high 24 h after application while over a study season basis, *E. coli* showed a significant decline in mass loads, whereas *C. perfringens* presented some peaks during the observation periods and did not follow a similar pattern of decay.

Unfortunately, it is not possible to compare the observed concentration ranges for surface runoff and tile drainage, as data are reported in different units of measurement.

3.3 Influence of the main factors affecting runoff and tile drainage quality – PPCPs

Once in the soil, a micropollutant may be subject to different phenomena: it may be sequestered, sorbed on the soil matrix (depending on its organic carbon content, CEC, pH, etc.), biodegraded (due to microorganisms present in the soil as well as in the applied sludge), photodegraded (due to light exposure), it may take part in chemical reactions with other compounds, or it may be transported away by a liquid phase. Prediction of its behaviour is complex, as environmental and matrix conditions may rapidly change, and intense rain events may enhance its vertical mobility through soil pores. The following sections will discuss the main factors affecting the occurrence of microcontaminants and bacteria in runoff and tile drainage in sludge-amended soil.

3.3.1 Influence of K_{ow}

The partitioning between solid and liquid phases was not always addressed by the authors, as it requires lengthy investigations, as shown in Yang et al. (2012). More frequently, coefficients derived from literature were used. In this context, the octanol-water partition coefficient K_{ow}, describing the distribution between the octanol and water of a compound, is commonly used to assess the sorption potential on a solid phase by a compound. As a rule of thumb, if Log $K_{ow} > 4$ it could be expected that the compound is highly adsorbed due to hydrophobic partitioning, while if Log $K_{ow} < 2.5$ the compound has a low level of sorption (Verlicchi and Zambello, 2015). The graphs shown in Figures 6 and 7 report MECs in runoff and tile drainage *vs.* Log K_{ow} for the investigated compounds. For quick reference, Table S7 compiles Log K_{ow} values for the compounds investigated in surface runoff or tile drainage analysis.

In Figures 6 and 7, values are dispersed in a wide cloud and it emerges that no clear correlation exists between the sorption potential of a compound and its measured concentration in runoff or in tile drainage. It is important to bear in mind that the reported data refer to different investigations, in terms of soil characteristics, rain fall intensity, sludge application rate, and concentration for the different compounds in the applied sludge and the MECs depend on these factors.

Figure 6

Figure 7

Limiting attention to single investigations where soil characteristics, sludge properties and rainfall intensity are defined and are the same for all the compounds, it seems that Log K_{ow} may be correlated with the pharmaceutical mass load (or concentration) in the runoff. Sabourin et al. (2009) found that chemicals with Log K_{ow} less than 2.45 (atenolol, carbamazepine, cotinine, caffeine and acetaminophen) were rapidly transported in runoff and those with Log K_{ow} greater than 3.18 tended to be retained in the soil (gemfibrozil, naproxen and ibuprofen). The same behaviour is confirmed by the investigations and results obtained by Gottschall et al. (2012) referring to fluoxetine, miconazole, tetracyclines and fluoquinolones (with Log K_{ow} > 4). These compounds were not found in tile drainage and they may have been more strongly bound to DMB, which can also explain their long-term detection in incorporated DMB.

Sabourin et al. (2009) also found that although sulfametoxazole had a Log K_{ow} equal to 0.89, it was not largely exported in runoff (only 0.51 % was found on a mass basis). Triclosan and triclocarban have similar K_{ow}, but in the study by Sabourin et al. (2009), it was found that about 40-times more triclosan was exported than triclocarban, and that even their concentrations in the sludge applied on the soil were similar (around 7,000 and 8,000 ng/g dm, respectively). This different behaviour could be explained by the different values of pK_a (the dissociation constant, reported in Table 1) of the two antiseptics (8.1 for triclosan and 12.7 for triclocarban) and the ionic forms at the pH of the soil/runoff, as discussed in Giudice and Young (2011). They also remarked that in their study conditions (soil pH at 8 and runoff pH variable between 7.8 and 8) half of the triclosan present in the sludge is ionized and as a result, it is much more prone to leachate and to be exported in the runoff than the neutral molecules of triclocarban.

The study by Yang et al. (2012) thoroughly investigated the fractioning between dissolved and suspended-particle bound phases for a wide spectrum of steroid hormones and found that Log K_{ow} values were not correlated with estrogen sorption to colloids.

According to Cunningham (2008), the octanol-water *distribution* coefficient D_{ow} is more adequate in studying microcontaminants, as it is pK_a-dependent at environmental pH.

D_{ow} is defined by Equation (1), and, according to Schwarzenbach et al. (2003), evaluated through Equation. (2) for acidic compounds and Equation (3) for basic ones:

$$D_{ow} \equiv \frac{\text{concentration in } n\text{−octanol}}{\text{concentration in water}} \qquad \text{Eqn. (1)}$$

$$Log\ D_{ow} = Log\ K_{ow} + Log \frac{1}{1 + 10^{pH - pKa}} \qquad \text{(acidic compound)} \qquad \text{Eqn. (2)}$$

$$Log\ D_{ow} = Log\ K_{ow} + Log \frac{1}{1 + 10^{pKa - pH}} \qquad \text{(basic compound)} \qquad \text{Eqn. (3)}$$

where $\mathrm{Log}D_{ow} = \log_{10} D_{ow}$.

In the case of neutral moieties, the two previous correlations result in Equation (4):

$$\text{Log}D_{ow} = LogK_{ow} \qquad \text{Eqn. (4)}$$

The rule of thumb when using Log D_{ow} to predict PPCP behaviour in aquatic compartments is good sorption if Log D_{ow} >3 and low sorption if Log D_{ow} < 1.

3.3.2 The influence of soil characteristics

On the basis of the lab investigations by Topp et al. (2008b), Cha and Cupples (2009), and Al-Rajab (2010a,b, 2015), soil characteristics (soil texture, pH, moisture content and temperature) seem to have a relevant influence on the quality of the runoff/tile drainage of studied microcontaminants.

As expected, runoff and tile drainage flows depend on the level of soil saturation. In loose and uncompacted soil, percolation is higher than land runoff, whereas when the soil becomes compact, percolation is lower than surface runoff (Giudice and Young, 2011).

Moreover, all studies agree with the consideration that moisture content and temperature in the soil mostly influence the fate of microcontaminants (sorption, degradation, and mineralization) and soil texture does not seem to influence leaching (that is the passage in the liquid phase due to rain events). In particular, Topp et al. (2008a), Cha and Cupples (2009), and Al-Rajab (2010a,b,2015) mainly refer to triclosan, triclocarban and naproxen, and in-depth investigations on the fate of all the compounds under review are not available for different soil characteristics.

Macropores, due to worm burrows, soil cracks and abandoned root channels, can favor the rapid gravity flow of contaminant-laden material in the vadose zone towards tile and shallow ground water depth (Lapen et al., 2008a). The pore size and distribution of the soil also affects the mobility of PPCPs within the medium. Hormones in a soil characterized by macropores rapidly move downwards (and may be collected in tile drainage), whereas in the case of soil with micropores, they move slowly and to a lesser extent (Gottschall et al., 2013).

It is important to highlight that at the modest slope of the investigations under review, surface runoff generally occurs when the soil is saturated, otherwise rain drops enter the sludge-amended soil and percolates. During their passage through the solid phase, rain drops meet compounds (including microcontaminants) sorbed on the soil which may be transported to the liquid phase (leaching) according to the compound-specific equilibrium conditions at the occurring environmental conditions (temperature, pH, etc.).

From a microscopic view point, the soil environment is continuously changing and surface runoff/tile drainage following two different rain events may have different characteristics. This is confirmed by Gray et al. (2017), who analyzed and compared the surface runoff in the same plot 1, 8 and 35 days after sludge application and the surface runoff in another plot 1 and 35 days after sludge deposition, in order to evaluate the fate of a wide spectrum of microcontaminants (triclosan, menthole, indole, skatole, galaxolide and tonalide) under different rainfall patterns, and Sabourin et al. (2009) who analyzed the surface runoff quality in five different plot sets that received rainfall after 1, 3, 7, 21 and 36 days, respectively.

As already highlighted in section 3.3.1 for triclosan and triclocarban, soil pH influences the ionization of a compound and thus its partition between soil and liquid (runoff/leachate).

3.3.3 Influence of sludge treatment

Liquid or dewatered sludge has different behaviour once applied on a soil. Topp et al. (2008a,b) and Sabourin et al. (2009) thoroughly investigated these issues and found in particular that LMB applied to unsaturated (also called uncompacted) soil behaves as a liquid, filling the available pore space. In this way, the exposure of PPCPs to soil microorganisms is favored and their biodegradation promoted. In contrast, in the case of dewatered sludge, the diffusion of oxygen into DMB aggregates, as well as the diffusion of PPCPs out of the DMB aggregates into the surrounding soil matrix are limited, resulting in greater persistence of PPCPs.

If an LMB is applied on a soil, PPCPs have a greater potential to transport within and over the soil at the time of application. Dewatered biosolids require an external source (rainfall or irrigation water) to favor the mobilization of pollutants within the soil/biosolids.

The highest concentrations of PPCPs in tile drainage following the application of biosolid slurry (i.e. liquid municipal biosolids) were detected immediately after application (Lapen et al., 2008b). In contrast, large cohesive DMB aggregates remain at the point of deposition on the soil. The concentrations of PPCPs in tile drainage following the application of dewatered biosolids were generally lower than those following LMB application, and, in contrast to LMB applications, the highest concentrations were only measured some time after application (Edwards et al., 2009).

Presumably, the slower release of residues from the DMB aggregates, and drying and physical deterioration of the aggregates was extending the period of availability for transport in runoff, compared to LMB where the PPCPs were applied in a more uniform matrix.

It is important to highlight that in the case of tile drainage in LMB-amended soil, the time the LMB took to reach the tiles (around 80 cm below) ranged between 3 and 39 min in unsaturated soil (Lapen et al., 2008b), whereas in the case of DMB-amended soil, contaminants due to dewatered sludge application reached the tile at least 8 days after sludge application (Edwards et al., 2009).

The maximum concentrations of the selected PPCPs in tile drainage were higher in the case of application of LMB than that of DMB.

Anoxic conditions in soils (vadose zone) do not favor the degradation of contaminants, in particular persistent ones, and this could have contributed to the persistence of some LMB-derived PPCPs in the tile drainage in the soils investigated by Edwards et al. (2009) in 2006, which had previously been used for another investigation by Lapen et al. (2008b), who applied LMB on the same plots.

3.3.4 Influence of sludge application rate and of pharmaceutical load

In the different investigations, the applied sludge ranged between 2,683 kg/ha (Healy et al., 2017) and 29,536 kg/ha (Peyton et al., 2016) (see Tab. S1). Some investigations used extremely high quantities of sludge on soil in order to enhance the behaviour of the microcontaminants under study (Giudice and Young, 2011 and Gottschall et al., 2012). Current regulations allow a maximum rate which can be expressed in terms of kg/ha year or kg/ha over a longer period, for instance 3 years in Italy. Sometimes the maximum sludge rate to apply depends on the N and P maximum applied rate, as reported in Table S3. Tables 5 and 6 reports PPCPs concentrations in runoff and tile drainage after sludge application. Attempts to correlate the available data were carried out, but no clear correlation was found for the studied compounds between the applied load and resulting concentrations.

A factor which seems to affect runoff concentration is the solid content of the applied sludge. Sabourin et al. (2009) used dewatered sludge (the so-called solid sludge, with a solid content of > 18 %) on the same soil where Topp et al. (2008b) carried out their studies with liquid biosolids. They found that with dewatered sludge, the concentrations of microcontaminants were in general lower than in the case of liquid biosolid application and only some days after application they may be found. This delay in the release of PPCPs may be explained by the fact that in dewatered sludge, PPCPs are more retained in the aggregates.

Table 5

Table 6

3.3.5 Influence of the sludge application method

Edwards et al. (2009) remarked that the investigated application mode (direct injection, surface spreading and tilling) may influence the quality of tile drainage and surface runoff, due to the resulting different capacities of breaking dewatered sludge solids/aggregates apart and the fact that the microcontaminants and microorganisms have different types of exposure to the atmosphere (mainly UV and oxygen). Moreover, the moisture content of the applied sludge may also greatly influence the behaviour of PPCPs, as remarked by Edwards et al. (2009). In the case of dewatered sludge, microcontaminants present a more modest level of mobility and potential to biodegrade than in the case of liquid sludge, and differences may be more likely to occur in PPCPs associated with aggregate interiors rather than exteriors. According to the cited study, there is no significant difference in the concentrations of PPCPs in tile drainage in the case of surface spreading and direct injection of dewatered sludge.

Surface spreading allows a faster degradation of the most degradable PPCPs.

Topp et al. (2008b) found that through the injection of liquid sludge into the soil, surface runoff presents a lower concentration of selected microcontaminants in a short time as direct injection promotes pollutant sequestration and reduces the surface mobility of pollutants. Analysis of surface runoff after a prolonged period showed that the release of microcontaminants may occur later for the most persistent compounds retained within the soil, whereas for those which are more biodegradable, degradation processes take place and their concentration is low or they are not detected (Al-Rajab et al., 2015).

In their investigation comparing sludge application approaches (surface spreading and subsurface spreading) on the quality of tile drainage in terms of a selection of different PPCPs, Lapen et al. (2008b) remarked that microcontaminants rapidly move downwards, reaching the tile drains in a few minutes, regardless of the application method: the larger the soil macropores, the shorter their transport time.

Applied sludge fluidity also influences the gravity-based flow of occurring pollutants: liquid municipal biosolids can be considered similar to diluted wastewaters and thus they rapidly move downwards. In this context, the sorption to the macropore walls is limited, as the rapid vertical motion of the leaching stream is the dominant process. The sludge is subsurface spread by means of an applicator which applies slurry close to the ground immediately following the passage of rolling tines that affect aerator-type tillage of the soil (Lapen et al., 2008a,b). This application method leads to the reduction of soil macropore size and fosters the sorption of microcontaminants and liquid biosolids in the tilled surface layers.

3.3.6 Influence of rainfall intensity, frequency and volume

Giudice et al. (2011) analyzed the composition of the surface runoff during three storm events of the same intensity occurring on the same plot (2 m^2) 3, 9 and 24 days after sludge application. Data reported on triclosan and triclocarban show that for each rain event, micropollutant concentration in surface runoff remains constant in the first 4, 8, 12, 16, 20 and 24 liters. They also found that in the three rain events, measured concentrations varied. This could be attributed to the sequestration of the compounds, and their scarce biodegradation within the soil rather than to the increasing water volume applied to the plot in the three events.

In Yang et al. (2012) and Gray et al. (2017) the concentration of a selection of anthropogenic waste indicators (fragrances and hormones) in runoff due to three replicated 100-year rainfall events was investigated. After 35 days the runoff concentration decreased with respect to previous rain events (1 and 8 days after sludge application) but remained at comparable values. This suggests that hormones may persist in the soil even if leaching and, possibly, onsite transformation may occur. That study compared the runoff quality in the case of frequent heavy rain events and after only one intense rainstorm, 35 days after sludge application. It was found that onsite attenuation was minimal and that natural weathering processes may make some compounds more easily leachable from the sludge amended soil even in the case of dry periods. In addition, they also found that once the soil becomes saturated, an increase in runoff rate leads to an increment in hormone load.

In tile drainage, the concentrations of investigated compounds decreased in the rain events occurring many days after sludge application on the soil (Lapen et al., 2008b) compared to the events nearly immediately after the application.

3.4 Influence of the main factors on the concentrations of microorganisms in runoff and tile drainage

Sludge treatment – No specific investigation compared the quality of runoff and tile drainage in terms of microorganisms in the case of LMB and DMB application. It can be expected that a “liquid” biosolid could lead to a higher concentration in tile drainage than a dewatered one, as it quickly crosses the layer through the macropores and reaches the tile drain (Lapen et al., 2008a,b).

Referring to surface runoff, similarly to PPCPs, there could be a slower release of microorganisms adherent to DMB aggregates, and they become available to the runoff over a longer period (Sabourin et al., 2009).

Thermal drying, gamma irradiation and disinfection greatly reduce microorganism content in sludge and thus, in the case of land reuse, the risk of microbial contamination of the receiving waters due to surface runoff or tile drainage is reduced.

Application methods – If the sludge is spread on the surface, the major removal mechanisms are due to desiccation and ultraviolet light (Lu et al., 2012; Gondim-Porto et al., 2016), whereas if the biosolid is incorporated into the soil, microorganism survival is strictly related to soil pH, organic matter content, texture, temperature, and competitive organisms developed in the soil.
In tile drainage, investigations by Lapen et al. (2008a) showed that one-pass aeration tilling mode (Table 3) enhances contaminant sorption/retention in the soil as it disrupts surface macropores and increases sorptivity. In their investigation, they reported that the average mass load ratios between tilling mode and one-pass aeration tilling application were 6 for *E. coli* and 12 for *C. perfringens*. Unlike the case of PPCPs investigated by Edwards et al. (2009) (see section 3.3.5), Gottschall et al. (2009) found differences in the concentrations of bacteria in tile drainage in the case of surface spreading and direct injection of dewatered sludge: concentrations of *E. coli,* Enterococci, *C. perfringens* were higher in the case of direct injection.

Soil characteristics: Interesting findings were reported by Atalay et al. (2007) in their investigation of the content of *E. coli* and Total coliform in runoff and percolate in two different sludge-amended soils - sandy loam and clay loam. They found that in the case of clay loamy soil the concentrations of *E. coli* were higher than in the sandy loam. With regard to the Total coliforms, no significant differences were found when the sludge was amended to the two soils. They also found that sludge incorporated into the first 5 cm of soil instead of the first 10 cm may lead to a higher occurrence of microbes in the surface runoff.

Rainfall – Unfortunately, little data is available for evaluating the effect of rainfall on microbial occurrence in surface runoff. According to Peyton et al. (2016), there could be a regrowth of Fecal coliform after a rain event on dry soil. Earlier studies (Dunigan and Dick, 1980) found that Fecal coliform indicator bacteria counts in surface runoff waters from sewage-treated plots were very high during the first days of sludge application, but they rapidly decreased as the soil became drier.

4 Lessons learned from past investigations

Importance of sludge type (liquid or dewatered) on the runoff and tile drainage quality and quantity - Soon after land application, liquid municipal sludge moves more rapidly through the available pores in unsaturated soil, ensuring a greater exposure of contaminants to soil microorganisms, which may accelerate degradation processes. On the other hand, in the case of application of dewatered sludge, the degradation of contaminants is hampered by the modest diffusion of oxygen into the aggregates and of microcontaminants out of the aggregates towards the soil environment. In addition, when liquid sludge is applied, microcontaminant concentrations in surface runoff and tile drainage are higher than in the case of DMB (Sabourin et al., 2009).

Phenomena occurring within the soil. They are quite complex and affected by many parameters (Gray et al. 2017; Gottschall et al. 2013; Topp et al. 2008a; Healy et al. 2017, Lapen et al., 2008a). Different scenarios have been highlighted:

- the mass of microcontaminants which leachates after biosolid application is small with regard to the quantity present in the soil due to sludge application, and runoff concentrations are generally low and similar after different rain events;
- the release of microcontaminants could be minimal and occur in many successive events;
- rain events tend to wash down biosolid particulates and the microcontaminants are associated with the suspended solids rather than being leached in the dissolved phase (and chemical analysis does not detect them);
- microcontaminants are not released in the dissolved phase but persist in the soil and their mass reduction is only due to soil erosion, washed out by heavy rain events via solid aggregates,

- natural weathering processes may make some compounds more easily leachable from the sludge-amended soil even in the case of prolonged dry periods.
- referring to microorganisms, due to the unfavorable soil conditions for microorganisms, in the sludge-amended soil, they are immediately subject to dessication, irradiation, competition with other species already present, etc. Their concentration in runoff and tile drainage is also affected by rain event characteristics: rain duration, intensity and frequency.

Persistence of microcontaminants in the soil - Some compounds persist in the soil environment within sludge aggregates for a long time: up to 1 year after sludge application. Their runoff concentrations generally decrease, following first order kinetics but, sometimes they may also remain constant. This means that even for long periods of time, these compounds do not seem to deplete within the soil. The reason could be due to the fact that sludge is the end product of a series of mechanical and above all biological treatments under different conditions (aerobic, anoxic, and anaerobic) within wastewater treatment plants. Macro- and micro-contaminants still present in the treated sludge are thus resistant to the different environments and for these reasons are still present even after many weeks or months.
Some hormones can interconvert via microbial activities within the soil. As a result, their runoff concentration may increase after multiple rainfall events and exposure to environmental conditions due to the biodegradation of a related compound.

Environmental risk posed by the release of microcontaminants via surface runoff and tile drainage - Based on current findings limited to specific compounds, it seems unlikely that a significant environmental risk could be due to the release of PPCPs by tile drainage and surface runoff. However, neither mixture effects nor the chronic effects on different aquatic species have as yet been investigated.

Good practices for sludge disposal - Correct sludge disposal on rural land should favor the retention of pollutants and microcontaminants in the rooting zone away from groundwater, artificial drainage and surface water sources. Bearing this in mind, good practices include (but are not limited to): (i) proper sludge rates of application, (ii) pre-application tillage of the soil to foster the disruption of continuous macropore networks and improve surface soil sorptivity, (iii) land application when soil macroporosity is reduced and when the soil sorption capacity is higher, (iv) controlling product placement and using application equipment that decreases the absolute amount of amendment available for local infiltration/surface runoff; (v) installation of a deeper tile drainage system, and application on soil characterized by a lighter texture, as it may enhance the sorption and sequestration of microcontaminants ~~pollutants~~ and finally, (vi) lowering temperatures, which may reduce the decomposition of DMB and the release of active ingredients of microcontaminants.

5 Main areas lacking in investigations, further research and perspectives

In many investigations, the main scope was the occurrence of target compounds in runoff or tile drainage, and data referring to rainfall events were often incomplete. In particular, the volume of rain entering and exiting the system is not always provided and thus, neither a water mass balance nor a pollutant mass balance is possible. A complete hydrologic description of the plot where the investigation takes place is necessary because the transport of PPCPs in soil is strongly influenced by the soil saturation ratio.

As remarked by Gray et al. (2017) and Yang et al. (2012), even if intense rain events are considered in the investigations, longer monitoring periods (greater than 40 days) should be adopted, as losses of microcontaminants may occur many days after application, especially in the case of dewatered sludge applied in the soil.

Sampling strategies adopted in the investigations are not always well reported and it is not clear exactly how and with what frequency the sampling occurred. In order to have reliable data and reproducible tests, all details should be provided and analyses should be performed according to standard methodologies. In addition, concentrations should be provided in tables, as in figures they are not easily readable. In any case, a descriptive statistical analysis of the collected data should be reported in terms of the minimum, maximum and standard deviations.

Environmental conditions are essential in defining the main removal mechanisms of pollutants. These parameters are rarely provided but soil temperature or at least ambient temperature should be made available.

Further research should address the effect of different soil compositions and different agricultural management practices (including application methods, sludge application rate and frequency, and irrigation application rate) on the quality of surface runoff and tile drainage.

Investigations should consist of a comparative analysis of the results achieved by applying different types of sludge, different application rates, different application methods, and different irrigation frequencies on different soils in order to evaluate the most influential parameters on surface runoff. A common observation is that PPCPs tend to accumulate in soil, mainly in the case of soil characterized by micropores which do not favor the downward mobility of contaminants. Long-term investigations should also address the probability of the release of these accumulated compounds in the case of intense rain events, or drought/wet periods which could greatly influence the mobility of the contaminants by creating preferential paths within the soil.

Further studies should focus on the occurrence of microbial indicators in surface runoff and in tile drainage during different rainfall events, in particular different frequencies and in different soil types. The occurrence of antibiotic-resistant genes and bacteria in sludge amended soil should also be addressed, as highlighted by Urra et al. (2019).

Supplementary Materials

In the Supplementary materials section, tables and figures provide further details of the reviewed studies (Table S1 in an Excel file and Figure S1 and Tables S2-S7 in a pdf file).

Conflict of interest

The authors declare that there are no conflicts of interest.

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Table
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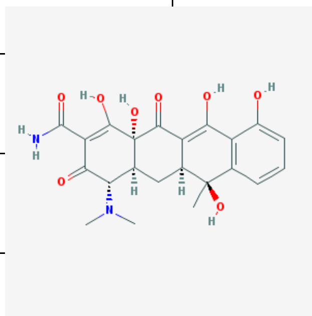
Tables

Table 1 Pharmaceutical compounds, hormones, fragrances and microorganisms included in this study

Therapeutic class	**Pharmaceutical compound/ species**	**MW**	**Chemical formula**	**p*K*$_a$**	**Log*K*$_{ow}$**	**# papers**	**Reference**
Analgesics/ anti-inflammatories (A) (3)	Acetaminophen	151.2	$C_8H_9NO_2$	9.38	0.46 – 0.49	5	Edwards et al. 2009; Gottschall et al. 2012; Lapen et al. 2008b; Sabourin et al. 2009; Topp et al. 2008b
	Ibuprofen	206.3	$C_{13}H_{18}O_2$	4.94	3.97	5	Edwards et al. 2009; Gottschall et al. 2012; Lapen et al. 2008b; Sabourin et al. 2009; Topp et al. 2008b
	Naproxen	230.3	$C_{14}H_{14}O_3$	4.15	3.18	5	Edwards et al. 2009; Gottschall et al. 2012; Lapen et al. 2008b; Sabourin et al. 2009; Topp et al. 2008b
Antibiotics (B) (7)	4-Epitetracycline	444.4	$C_{22}H_{24}N_2O_8$	3.3	-1.37	1	Gottschall et al. 2012
	Ciprofloxacin	331.3	$C_{17}H_{18}FN_3O_3$	6.09	0.28	1	Gottschall et al. 2012
	Ofloxacin	3614.	$C_{18}H_{20}FN_3O_4$	pK_{a1}: 5.97 pK_{a2}: 9.28	-0.39	1	Gottschall et al. 2012
	Oxytetracycline	460.4	$C_{22}H_{24}N_2O_9$	3.27	-0.9	1	Gottschall et al. 2012
	Sulfamethoxazole	253.3	$C_{10}H_{11}N_3O_3S$	pK_{a1}: 1.60 pK_{a2}: 5.70	0.89	5	Edwards et al. 2009; Lapen et

Therapeutic class	Pharmaceutical compound/ species	MW	Chemical formula	pK_a	LogK_{ow}	# papers	Reference
							al. 2008b; Pedersen et al. 2005; Sabourin et al. 2009; Topp et al. 2008b
	Sulfapyridine	249.3	$C_{11}H_{11}N_3O_2S$	8.43	0.35 - 0.9	1	Lapen et al. 2008b;
	Tetracycline	444.4	$C_{22}H_{24}N_2O_8$			1	Gottschall et al. 2012
Antifungals (C) (1)	Miconazole	416.1	$C_{18}H_{14}Cl_4N_2O$			1	Gottschall et al. 2012
Antihistamines (D) (1)	Diphenhydramine	255.4	$C_{17}H_{21}NO$			1	Gottschall et al. 2012
Antiseptics (E) (2)	Triclocarban	345.6	$C_{13}H_9Cl_3N_2O$	12.7	4.9	5	Edwards et al. 2009; Giudice and Yang 2011; Gottschall et al. 2012; Healy et al. 2017; Sabourin et al. 2009
	Triclosan	289.5	$C_{12}H_7Cl_3O_2$	7.9	4.76	8	Edwards et al. 2009; Giudice and Yang 2011; Gottschall et al. 2012; Gray et al. 2017; Healy et al. 2017; Lapen et al. 2008b; Sabourin et al. 2009; Topp et al. 2008b
Beta-blockers (F) (1)	Atenolol	266.3	$C_{14}H_{22}N_2O_3$	9.6	0.16	4	Edwards et al. 2009; Lapen et al. 2008b; Sabourin et al.

Therapeutic class	**Pharmaceutical compound/ species**	**MW**	**Chemical formula**	**p*K*$_a$**	**Log*K*$_{ow}$**	**# papers**	**Reference**
							2009; Topp et al. 2008b
Fragrances and PCPs ingredients (G) (4)	Galaxolide (HHCB ~~AHTN~~)	258.4	$C_{18}H_{26}O$		5.9	1	Gray et al. 2017
	Indole	117.2	C_8H_7N	-2.4	2.14	1	Gray et al. 2017
	Menthol	156.3	$C_{10}H_{20}O$		3.2	1	Gray et al. 2017
	Skatole (3-Menthyl-1H-Indole)	131.2	C_9H_9N		2.6	1	Gray et al. 2017
	Tonalide (AHTN ~~HHCB~~)	258.4	$C_{18}H_{26}O$		5.7	1	Gray et al. 2017
Hormones (H) (22)	11-Ketotestosterone	302.4	$C_{19}H_{26}O_3$		1.92	1	Yang et al. 2012
	17-α-estradiol (Alfatradiol)	272.4	$C_{18}H_{24}O_2$		3.94 – 4.01	2	Gottschall et al. 2013; Yang et al. 2012
	17-beta-estradiol (or Estradiol)	272.4	$C_{18}H_{24}O_2$		3.94 – 4.01	2	Gottschall et al. 2013; Yang et al. 2012
	α-Dihydroequilin	270.4	$C_{18}H_{22}O_2$			1	Gotschall et al. 2013
	Androstenedione	286.4	$C_{19}H_{26}O_2$		2.75 – 2.76	2	Gottschall et al. 2013; Yang et al. 2012;
	Androsterone	290.4	$C_{19}H_{30}O_2$		3.69	1	Gotschall et al. 2013
	Cis-androsterone	290.4	$C_{19}H_{30}O_2$		3.07 – 3.69	1	Yang et al. 2012
	Desogestrel	310.5	$C_{22}H_{30}O$		5.65	1	Gotschall et al. 2013
	Diethylstilbestrol	268.4	$C_{18}H_{20}O_2$		5.07 – 5.64	1	Yang et al. 2012
	Dihydrotestosterone (Stanolone)	290.4	$C_{19}H_{30}O_2$		3.07 – 3.55	1	Yang et al. 2012
	Epitestosterone	288.4	$C_{19}H_{28}O_2$		3.27 – 3.32	1	Yang et al. 2012
	Equilenin	266.3	$C_{18}H_{18}O_2$		3.93	2	Gottschall et al. 2013; Yang et al. 2012

Therapeutic class	Pharmaceutical compound/ species	MW	Chemical formula	pK_a	LogK_{ow}	# papers	Reference
	Equilin	268.4	$C_{18}H_{20}O_2$		3.35	2	Gottschall et al. 2013; Yang et al. 2012
	Estradiol Benzoate	376.5	$C_{25}H_{28}O_3$			1	Gotschall et al. 2013
	Estriol	288.4	$C_{18}H_{24}O_3$	10.54	2.45 - 3.67	2	Gottschall et al. 2013; Yang et al. 2012
	Estrone	270.4	$C_{18}H_{22}O_2$		3.13 - 3.43	2	Gottschall et al. 2013; Yang et al. 2012
	Ethinyl Estradiol	296.4	$C_{20}H_{24}O_2$	10.4	3.67 – 4.15	3	Giudice and Yang 2011: Gottschall et al. 2013; Yang et al. 2012
	Mestranol	310.4	$C_{21}H_{26}O_2$		4.61 – 4.68	2	Gottschall et al. 2013; Yang et al. 2012
	Norethindrone	298.4	$C_{20}H_{26}O_2$		2.97 – 2.99	2	Gottschall et al. 2013; Yang et al. 2012
	Norgestrel (Levonorgestrel)	312.5	$C_{21}H_{28}O_2$		3.48	1	Gottschall et al. 2013
	Progesterone	314.5	$C_{21}H_{30}O_2$		3.67 – 3.87	2	Gottschall et al. 2013; Yang et al. 2012
	Testosterone	288.4	$C_{19}H_{28}O_2$		3.27 – 3.32	2	Gottschall et al. 2013; Yang et al. 2012
Lipid regulators (I) (1)	Gemfibrozil	250.3	$C_{15}H_{22}O_3$	4.5	4.77	5	Edwards et al. 2009; Gottschall et al. 2012; Lapen et al. 2008b; Sabourin

Therapeutic class	**Pharmaceutical compound/ species**	**MW**	**Chemical formula**	**p*K*a**	**Log*K*ow**	**# papers**	**Reference**
							et al. 2009; Topp et al. 2008b
Stimulant (J) (2)	Caffeine	194,.	$C_8H_{10}N_4O_2$	10.4	-0.07	1	Sabourin et al. 2009
	Cotinine	176.2	$C_{10}H_{12}N_2O$		0.07	5	Edwards et al. 2009; Gottschall et al. 2012; Lapen et al. 2008b; Sabourin et al. 2009; Topp et al. 2008b
Psychiatric drugs (K) (12)	Bupropion	239.7	$C_{13}H_{18}ClNO$	8.22	3.85	1	Gottschall et al. 2012
	Carbamazepine	236.3	$C_{15}H_{12}N_2O$	13.9	2.45	5	Edwards et al. 2009; Gottschall et al. 2012; Lapen et al. 2008b; Sabourin et al. 2009; Topp et al. 2008b
	Citalopram	324.4	$C_{20}H_{21}FN_2O$		3.5	1	Gottschall et al. 2012
	Desmethyl Citalopram	310.4	$C_{19}H_{19}FN_2O$		2.8	1	Gottschall et al. 2012;
	Desmethyl Sertraline	320.2	$C_{17}H_{15}Cl_2NO$		4.5	1	Gottschall et al. 2012
	Desvenlafaxine	263.4	$C_{16}H_{25}NO_2$	pK_{a1}: 9.45 pK_{a2}: 10.66	2.72	1	Gottschall et al. 2012
	Fluoxetine	309.3	$C_{17}H_{18}F_3NO$	9.5	4.05	3	Edwards et al. 2009; Gottschall et al. 2012; Lapen et al. 2008b
	Norfluoxetine	295,.	$C_{16}H_{16}F_3NO$		3.5	1	Gottschall et al. 2012

Therapeutic class	**Pharmaceutical compound/ species**	**MW**	**Chemical formula**	**p*K*$_a$**	**Log*K*$_{ow}$**	**# papers**	**Reference**
	Norvenlafaxine	263.4	$C_{16}H_{25}NO_2$		3	1	Gottschall et al. 2012
	Paroxetine	329.4	$C_{19}H_{20}FNO_3$	9.6	1.23	1	Gottschall et al. 2012
	Sertraline	30.,2	$C_{17}H_{17}Cl_2N$		5.1	1	Gottschall et al. 2012
	Venlafaxine	277.4	$C_{17}H_{27}NO_2$	10.09	3.2	1	Gottschall et al. 2012
Group	**Species**					**# papers**	**Ref**
Bacteria (5)	*Clostridium perfringens*					2	Gottschall et al. 2013; Lapen et al. 2008a
	Escherichia coli					5	Atalay et al. 2007; Eldridge et al. 2009; Gottschall et al. 2013; Lapen et al. 2008a; Peyton et al. 2016
	Fecal Coliforms					2	Dunigand and Dick, 1980; Wallace et al. 2014
	Faecal Streptococcus					1	Gottschall et al. 2013
	Total Coliforms					3	Atalay et al. 2007; Gottschall et al. 2013; Peyton et al. 2016

Table 2. A brief presentation of the studies included in this review, in terms of their main characteristics, aims, scope of the investigations and number of investigations (see Table S1 for details).

Reference		**Main characteristics of the investigations**
Atalay et al. 2007	USA	Lab investigations were carried out into the occurrence of 2 microorganisms (*E. coli* and Total coliforms), nutrients and heavy metals in **surface runoff** after treated sludge applications. Air-dried sludge was applied at a rate of 2,240 kg/ha and mixed with the top 5 cm of the soil bed, on two different soils (a clay loam soil and a sandy loam soil called, respectively, Cullen and Bojac, see Table S1) to compare the influence of soil on runoff quality. Investigation fields consisted of 12 microplots (2 soils x 2 treatments x 3 replicates) - tilted aluminium beds (0.8 m x 1.9 m = 1.62 m^2 each) set up in an environmentally controlled greenhouse and used both for treatment and to control the investigation. Rainfall simulation (deionized water at a rate of 65 mm/h for 45 min) took place immediately before the sludge application (control investigation) and immediately after (treatment investigation), resulting in 2 samples (each with 3 replicates) per plot available for chemical and microbiological analyses. Number of investigations: 2
Dunigan and Dick, 1980	USA	On-field investigations were carried out on the occurrence of nutrients and Fecal coliforms in **surface runoff** in sludge-amended soil. Treated municipal sludge was applied at different rates (14.8, 16.2, and 28.9 tons/ha) and the concentrations of bacteria were monitored during the following weeks in order to evaluate their temporal variations. Investigation fields consisted of triplicate plots and a control one. Rainfall was simulated by applying deionized water at a rate of 1.11 cm/h for 2 hours. Number of investigations: 3
Edwards et al. 2009	Canada	On-field investigations were carried out on the occurrence (concentrations) and mass loads of 11 PPCPs in agricultural **tile drainage** systems following sludge application. Monitoring lasted approximately 162 d. Dewatered (centrifugated) anaerobically digested sludge was applied to loam soil at a rate of 8,000 kg/ha and mixed with the soil bed using two different methods (to compare the results): tilling with the top 10 cm of the soil and direct injections at a depth of 11 cm. The aim was to test the capacity to break DMB solid/aggregates apart and the effect of the atmosphere exposure and the soil environment on the PPCPs. Investigation fields consisted of 8 plots (100 m x 15 m= 1,500 m^2 each) in a field with tiles placed 0.8 m below the soil surface and spaced 15 m apart; 2 of them were hydraulically isolated and

		used for the control investigation (they never received DMB). Sampling occurred after a real rain event (in the case of a rainfall depth of 5 mm/h in summer and 7 mm/24 h in fall gathered in a rainwater collection vessel) which took place in the study period, with a total depth of 413 mm. Samples were collected with an automatic water sampler when a rainfall with a depth of 5 mm/h (summer) and 7 mm/d (fall) was gathered in a rain collection vessel. Samples were taken more frequently near the trigger followed by a gradual reduction (sample intervals were initially every 15 min, then every 30, 60, 90 and 120 mins) Number of investigations: 2
Eldridge et al. 2009	Australia	On-field investigations were carried out into the occurrence of *E. coli* and nutrients in **surface runoff** after surface spreading of 2 types of dewatered sludges (irradiated, non-irradiated and granulated biosolids) and a manure (poultry) on a silty clay loam soil covered by turf. Sludges and manure were spread on the surface. The applied sludges were a high temperature dried sludge (at a rate of 4,500 kg/ha, DMB1), a high temperature dried sludge that received gamma irradiation (pathogen free, at a rate of 4,500 kg/ha, DMB2), and a poultry litter (at a rate of 5,150 kg/ha). Investigation fields consisted of three replicate plots for four scenarios, resulting in 12 microplots (1 m x 2 m= 2 m^2 each) in a field with a slope of 10%. The four scenarios were an untreated control plot; poultry application, DMB1 application and DMB2 application. Rainfall simulation (potable water at a rate of 90 mm/h for 30 min) took place 7 days after application; 2 samples were collected for each plot - one for the first 3 L of runoff (first flush) and another for the total runoff volume. Number of investigations: 3
Giudice and Yang 2011	USA	Investigations were carried out into the occurrence of endocrine-disrupting compounds and heavy metals in **surface runoff** after sludge application for approximately 31 d. Dewatered (and thermally dried) anaerobically digested sludge was applied to sandy loam soil at a rate of 22,500 kg/ha and mixed with the top 7÷15 cm of the soil bed. The investigation fields consisted of 3 replicated plots (2m x 1m x 0.38m depth each) which were built in a field with a slope of 3,5÷4% and used for control (before sludge application) and for runoff analysis (after sludge application, for three different simulated rain events) as well as leachate analysis. Rainfall simulations (carbon filtrated well water at a rate of 60 mm/h until runoff occurred) took place 5 days before application (control) and 3, 9, and 24 days after application in the three plots. Six runoff samples (4 L) were collected after each rainfall

		simulation and their cumulative volume was investigated for the analytes of interest. A single 2.5-L leachate sample was withdrawn at the end of each simulation from the composite reservoir collecting the generated leachate (**tile drain** depth = 0.38 m; space between tiles = 0.025 m). Number of investigations: 2
Gottschall et al. 2012	Canada	An on-field investigation into the occurrence of 26 PPCPs in **tile drainage** (PPCPs in soil matrix, groundwater and wheat grain grown on the field) after sludge application was carried out for approximately 365 days. Dewatered (centrifugated) anaerobically digested sludge was applied to loam soil at a rate of 22,000 kg/ha and mixed with the top 20 cm of the soil bed. Investigation fields consisted of 2 macroplots (3 ha each) in an agricultural field located in Ontario, Canada, which was fallow the year before the investigation. Tiles were placed 1.1÷1.2 m below the soil surface and spaced 15 m apart. The first macroplot represents the control system and the second the treatment system (where sludge was applied). Real rainfall occurred in the study period with a total depth of 1,070 mm. Samples were time-proportionally collected at the bottom of the tiles when a trigger (adjusted depending on weather and soil water content) occurred. A total of 10 hydrograph event samples were selected for analysis. Number of investigations: 1
Gottschall et al. 2013	Canada	A commercial field-scale investigation was carried out into the occurrence of 17 PPCPs (hormones), 3 pathogens and 10 sterols in **tile drainage**, in the surface soil core, DMB aggregates mixed with soil, groundwater and wheat grain after sludge application in a real agricultural field (the same as that of Gottschall et al., 2012) for approximately 365 days. The aim was to study the long-term persistence of the selected compounds in the environmental matrices and to correlate the occurrence of fecal bacteria with sterols. Dewatered (centrifugated) anaerobically digested sludge was applied to loam soil at a rate of 22,000 kg/ha and mixed with the top 20 cm of the soil bed. Investigation fields consisted of the same 2 macroplots (3 ha each) as in the agricultural field described in Gottchall et al. (2012), with tiles positioned 1.1÷1.2 m below the soil surface and spaced 15 m apart. 1 of them was isolated and used for the control investigation. Real rainfall occurred in the study period with a total depth of 1,070 mm. Samples were time-proportionally collected at the bottom of the tiles when a trigger (adjusted depending on weather and soil water content) occurred. A total of 8 hydrograph event samples were selected for analysis. Number of investigations: 1

Gray et al. 2017	USA	On-field investigations were carried out into the occurrence of a wide spectrum of anthropogenic waste indicators (including 6 PPCPs) in **surface runoff** after sludge application on an agricultural field in Colorado for approximately 40 d. The site had not previously been treated with biosolids. Dewatered anaerobically digested sludge was applied on loamy sand soil at a rate of 3,500 kg/ha and mixed with the top 15 cm of the soil bed. The investigation fields consisted of 5 microplots (6 m^2 each) in a field with a slope of 2.1÷3%; each one was used both for treatment and control investigations. Rainfall simulations (application of hormone-free well water at a rate of 65 mm/h, corresponding to a 100-year simulated rain event) took place 5 days before (control plot) and 1, 8, and 35 days after application in the three plots. In the remaining two plots, rainfalls were conducted only on day 35 in order to evaluate the fate of compounds in the absence of repeated rainfall events. The same plots and similar operational conditions were used in a previous investigation by Yang et al., 2012 Number of investigations: 2
Healy et al. 2017	Ireland	Investigations were carried out into the occurrence of 2 PPCPs (TCS and TCC) in **surface runoff** after sludge application in a field experiment lasting approximately 15 d. In order to compare different types of behaviour, three differently treated sludges were spread on the surface of loam soil: an anaerobically digested sludge (at a rate of 6,727 kg/ha), a thermally dried sludge (at a rate of 2,683 kg/ha), and a lime stabilized sludge (at a rate of 29,536 kg/ha). The investigation fields consisted of replicated (n=3) hydraulically isolated microplots (0.4 mx 0.9 m= 0.36 m^2 each) in a field with a slope of 2.8÷3.7% (without controls). Each microplot was equipped with a channel collecting all the runoff during a rain event. Rainfall simulations (at a rate of 11 mm/h) took place 1, 2, and 15 days after sludge application in the same plots. Each rainfall lasted 30 minutes from the time of the first occurrence of surface runoff. Number of investigations: 3
Lapen et al. 2008b	Canada	On-field investigations carried out on the occurrence of 11 PPCPs in **tile drainage** after sludge application were performed in Ontario, Canada, for approximately 46 d. Liquid anaerobically digested sludge was applied on silty clay loam soil at a rate of 9,3500 L/ha and mixed with the soil bed with two different approaches (in order to compare the influence on tile drain quality): tilling with the top 10 cm of the soil (subsurface spreading) and one-pass aeration tilling with the top 11 cm (surface spreading). Most of the selected PPCPs were spiked in the sludge before soil application as their concentration was found to be below the detection limits.

		The investigation fields consisted of three plot replications for each application type with one control bed, giving a total of 8 plots (740 m^2 each) in a field with tiles positioned 0.8 m below the soil surface and placed 15 m apart. Real rainfall occurred in the study period with a total depth of 124 mm. Samples were time-proportionally collected at the bottom of the tiles when a trigger occurred. Number of investigations: 2
Lapen et al. 2008a	Canada	On-field investigations into the occurrence of *E. co*li and *C. perfringens* as well as nutrients in **tile drainage** after sludge application were carried out in Ontario, Canada, for approximately 46 d. Liquid anaerobically digested sludge was applied on silty clay loam soil at a rate of 93,500 L/ha and mixed with the soil bed using two different methods (in order to compare the influence on the loss of microorganisms): tilling with the top 10 cm of the soil and one-pass aeration tilling with the top 11 cm. The investigation fields consisted of three plot replications for each application type with one control bed, for a total of 8 plots (740 m^2 each) in a field with tiles positioned 0.8 m below the soil surface and placed 15 m apart. Real rainfall occurred in the study period with a total depth of 124 mm. Samples were time-proportionally collected at the bottom of the tiles when a trigger occurred. Number of investigations: 2
Peyton et al. 2016	Ireland	Investigations into the occurrence of 2 microorganisms, nutrients and metals in **surface runoff** after sludge application were carried out in Ireland, for approximately 15 d. Five different sludges were applied on the surface of loam soil and the resulting runoff was compared: an anaerobically digested sludge from the UK (at a rate of 6,775 kg/ha), an anaerobically digested sludge from EIRE (at a rate of 6,727 kg/ha), a thermally dried sludge (at a rate of 2,683 kg/ha), a lime stabilized sludge (at a rate of 29,536 kg/ha) and a dairy cattle slurry (at a rate of 80,000 kg/ha). The investigation fields consisted of 30 microplots (0.9mx0.4m=0.36 m^2 each) in a field with a slope of 2.8÷3.7% in order to compare six different scenarios (treatment with one sludge type + control). For this reason, 6 of them were isolated and used for the control investigation. Rainfall simulations (at a rate of 11 mm/h) took place 1, 2, and 15 days after application in the same plots. The first and the last 50 mL of runoff occurring on each plot were collected (2 samples per plot). Number of investigations: 5

Sabourin et al. 2009	Canada	An on-field investigation into the occurrence of 13 PPCPs in **surface runoff** after sludge application was carried out in Ontario, Canada, for approximately 36 d. Dewatered (centrifugated) anaerobically digested sludge was applied on silt loam soil at a rate of 8,000 kg/ha and mixed with the top 15 cm of the soil bed. The investigation fields consisted of 30 microplots (2 mx 3 m=6 m^2 each) in a field with a slope of 7 %. 5 of them were isolated and used for a control investigation (no sludge applied on them). A group of 5 (+1 control) microplots was considered for each rain event which took place 1, 3, 7, 21 and 36 d after sludge application. Rainfall simulations consisted of ozonated groundwater at a rate of 4.1 mm/min. One runoff sample was collected for each plot. Number of investigations: 1
Topp et al. 2008b	Canada	Investigations into the occurrence of 9 PPCPs in **surface runoff** after sludge application were carried out in Ontario in a real field for approximately 266 d. Liquid anaerobically digested sludge and ozonated groundwater spiked with pharmaceuticals were applied on silt loam soil (slope 5 %) at a rate of 93,500 L/ha and mixed with the soil bed. Sludge was amended to soil using two different approaches: by tilling with the top 15 cm of the soil and by subsurface injections at a depth of 10 cm. Spiked ozonated groundwater was added to the plots only by subsurface injection at a depth of 10 cm. The investigation fields consisted of 75 microplots (2 m x 1 m =2 m^2 each) in a field with a slope of 5%. The "control" plots were the 25 receiving spiked water but none of the plots were tested without PPCPs sources. Rainfall simulations (ozonated groundwater) took place 1, 3,7,21, 36 or 266 days after application in plots that had never received rainfall before to investigate the degradation/adsorption effects. Rainfall simulated events lasted until a minimum of 10 l of runoff had been collected in each microplot. Number of investigations: 3
Wallace et al. 2014	USA	Investigations into the occurrence of microorganisms and nutrients in **surface runoff** after dewatered anaerobically digested sludge application were carried out in Missouri for approximately 54 d. Sludge and mineral fertilizer were applied (to compare results) on silt loam soil and on the same soil but with a vegetation strip buffer (to compare the buffer ability in reducing key compound losses in runoff) with surface spreading applications. Four investigations occurred: untreated control plot; low rate (1,664 kg/ha) of biosolids with 1 m of vegetative filter; low rate (1,664 kg/ha) of biosolids without filter, and high rate of biosolids with 1 m of

		vegetative filter (3,328 kg/ka). The investigation fields consisted of operating and control plots (1.5mx2x=3 m^2 each) in a field of a slope of 3÷6%. For each experiment, four replicates were conducted. Rainfall simulations (deionized water at a rate of 70 mm/h) took place immediately after application. One sample per plot was collected. Number of investigations: 5
Yang et al. 2012	USA	An on-field investigation was carried out in Colorado into the occurrence of 17 PPCPs (hormones) and 2 sterols in **surface runoff** after sludge application for approximately 40 d. Dewatered anaerobically digested sludge was applied on loamy sand soil at a rate of 3,500 kg/ha and mixed with the top 15 cm of the soil bed. An analysis of the hormone partitioning between the dissolved phase and suspended-particle bond phase was reported. The investigation fields consisted of the microplots (6 m^2 each) in a field with a slope of 2.1÷3%; used both for treatment and control investigations. Rainfall simulations (hormone-free well water at a rate of 65 mm/h) took place 5 days before (control) and 1, 8, and 35 days after application in the same plots. 3 composite samples (early, middle and late rain events) were collected per plot for the control (5 days before sludge application) and on the first, 8^{th} and 35^{th} day. Since on day 35 only two plots were monitored, a total of 33 composite samples were available. Number of investigations: 1

Table 3. The application strategies for sludge disposal in agricultural soils considered in this review, the typical application depth, and relative references

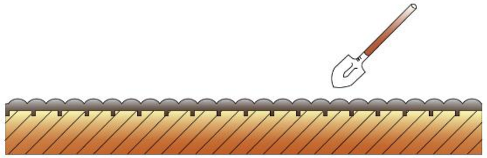
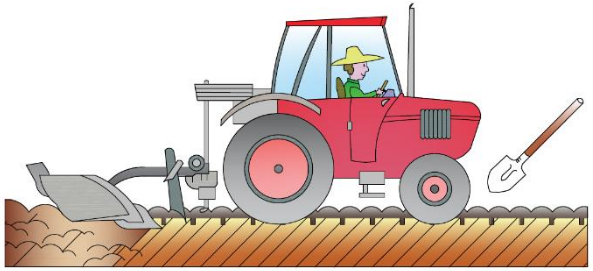
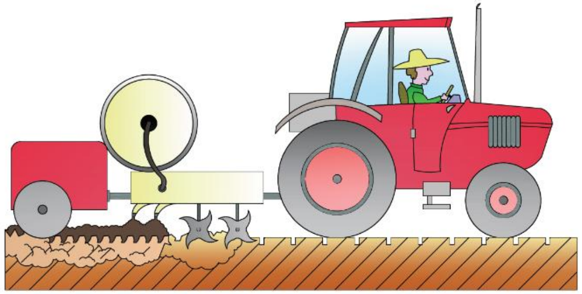
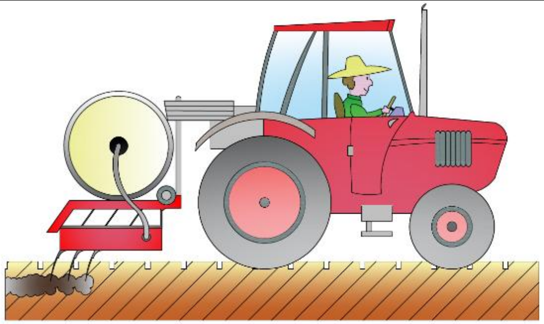
Application method	Graphical description	Application depth	Description	References
Land or Surface spreading		0 cm	With *land* or *surface spreading*, biosolids are deposited on the land surface without other operations.	Dunigan and Dick, 1980; Eldridge et al. 2009; Healy et al. 207; Peyton et al. 2016; Wallace et al. 2014
Tilling		5÷20 cm	In the case of *tilling*, sludge is spread on soil and then it is amended with the first 20 ÷ 30 cm of soil within 20-24 h.	Atalay et al. 2007; Edwards et al. 2009; Giudice and Young 2011; Gottschall et al. 2012; 2013 Gray et al. 2017; Lapen et al. 2008a,b Sabourin et al. 2009; Topp et al. 2008b; Yang et al. 2012
One-pass aeration tilling		13÷15 cm	In the case of *one-pass aeration tilling*, just before receiving the sludge, the soil is tilled. It is generally performed by a specific mechanical system that applies the sludge close to the ground, immediately following the passage of rolling tines which affect aerator-type tillage of the soil.	Lapen et al. 2008a;b
Subsurface injections		10÷13 cm (typical application depth, as reported in the cited studies)	*Subsurface injection* consists of the injection of biosolids within 50 cm of the top of the soil surface. Generally, injection can be used for LMB application or DMBs that have a low solid content and can be easily shovelled	Edwards et al. 2009; Topp et al. 2008b

Table 4. Main findings in monitoring bacteria occurrence in surface runoff and tile drainage.

	Microorganism (u.o.m.)	**Background Concentr.**	**min**	**max**	**mean**	**SD**	**# data**
Surface runoff	Total coliforms [CFU/ml]	0	63.1	79.4	71.3	11.5	3
	E. coli [CFU/ml]	0	1.8	2.4	2.1	0.4	3
	Fecal Coliforms [CFU/100ml]	100	5,000	36,000	16,167	17,222	4
	Fecal Coliforms [MPN/mL]	0-70	60	55,000			12
	Total coliforms [MPN/100ml]	--	15858	980,600	344,622	280,808	12
	E. coli [MPN/100ml]	251,188	15	31,622	5,009	10,191	15
Tile drainage	*C. perfringens* [cts/100 mL]	4.0	10	185	50	49	46
	E. coli, [cts/100 mL]	100	100	30000	3504	6363	46
	Fecal coliforms, [cts/100 mL]	--	100	30000	3568	6963	45

Table 5 Runoff concentration as a function of the applied load of pharmaceuticals.

	Sludge concentration	Application rate	load [mg/ha]	Runoff concentration [ng/L]	Reference
Acetaminophen	28.6 ng/g	8,000 kg/ha	229	20,3	Sabourin et al. 2009
	100,000 ng/L	93.5 m^3/ha	9,350	47; 114; 146	Topp et al. 2008b
Naproxen	394 ng/g	8,000 kg/ha	3,152	18,1	Sabourin et al. 2009
	10,000 ng/L	93.5 m^3/ha	935	509	Topp et al. 2008b
Sulfamethoxazole	12.4 ng/g	8,000 kg/ha	99	3.2	Sabourin et al. 2009
	10,000 ng/L	93.5 m^3/ha	935	7,15[c]; 35,4; 93	Topp et al. 2008b
Triclocarban	50 ng/g	2,683.3 kg/ha	134	6[b]; 10	Healy et al. 2017
	8,194 ng/g	8,000 kg/ha	65,552	3,4	Sabourin et al. 2009
	17,600 ng/g	22,500 kg/ha	396,000	6,3; 13,1; 17,3	Giudice and Young 2011
Triclosan	270 ng/g	6751.4 kg/ha	1,823	90[b]	Healy et al. 2017
	4,900 ng/g	2683.3 kg/ha	13,148	90[b]	Healy et al. 2017
	7,066 ng/g	8,000 kg/ha	56,528	109.7	Sabourin et al. 2009
	9,140 ng/g	3,500 kg/ha	31,990	310[a, b]; 500[a]; 600[a]	Gray et al. 2017
	15,900 ng/g	22,500 kg/ha	357,750	51 [b]; 282.1; 309.6	Giudice and Young 2011
Atenolol	1.6 ng/g	8,000 kg/ha	13	39.6	Sabourin et al. 2009
	10,000 ng/L	93.5 m^3/ha	935	70	Topp et al. 2008b
Gemfibrozil	31 ng/g	8,000 kg/ha	248	8	Sabourin et al. 2009
	10,000 ng/L	93.5 m^3/ha	935	597	Topp et al. 2008b

[a] values graphically estimated; [b] < LOD; [c] < LOQ

Table 6 Tile drainage concentrations as a function of the applied load of pharmaceuticals

Compound	Concentration [ng/g]	Application rate [kg/ha]	Load [mg/ha]	Tile drainage concentration, [ng/L]	reference
Acetaminophen	18.7	22,000	411.4	13	Gottschall et al. 2012
	24	8,000	192	*17,5*[a]; 36[a], 38[a], 40[a], 42[a], 48[a], 5[a], 53[a], 60[a], 62[a], 87[a], 105[a], 220[a], 233	Edwards et al. 2009
Ibuprofen	63.6	22,000	1399.2	24	Gottschall et al. 2012
	750	8,000	6,000	*11,5*[a]; 22[a]; 28[a]; 30[a]; 5[a]; 73	Edwards et al. 2009
Naproxen	6	22,000	132	**4**	Gottschall et al. 2012
	470	8,000	3,760	*7,5*; 18; 29	Edwards et al. 2009
Triclocarban	4,940	22,000	108,680	40	Gottschall et al. 2012
	8,000	8,000	64,000	*2.5*	Edwards et al. 2009
Triclosan	10,900	22,000	239,800	73	Gottschall et al. 2012
	14,000	8,000	112,000	*9,5*[a]; 20[a]; 22[a]; 22,5[a]; 23[a]; 24[a]; 25[a]; 30[a]; 31[a]; 32[a]; 34[a]; 35[a]; 36[a]; 37[a]; 45[a]; 46[a]; 48[a]; 52[a]; 56[a]; 57[a]; 59[a]; 63[a]; 68[a]; 75[a]; 82[a]; 95[a]; 101[a]; 140[a]; 185[a]; 190[a]; 230[a]; 240	Edwards et al. 2009
Gemfibrozil	24	8,000	192	*8*	Edwards et al. 2009
	57	22,000	1,254	**5**	Gottschall et al. 2012
Cotinine	1.3	8,000	10.4	*1,5;* 3,9; 4,8; 5,5; 5,7; 6,5; 8,2; 9,5; 11	Edwards et al. 2009
	9.4	22,000	206.8	**1**	Gottschall et al. 2012
Carbamazepine	9	8,000	72	*2,5;* 6; 7; 7,5; 7,6; 8,5; 13; 14; 19; 24; 30; 32; 38; 44; 49	Edwards et al. 2009
	183.6	22,000	4039.2	13; 5	Gottschall et al. 2012

[a] values graphically estimated; [b] < LOD; [c] < LOQ

FIGURES – CAPTIONS

Figure 1. The two water streams leaving soil in the case of rain events (surface runoff and tile drainage) and the main removal mechanisms for microcontaminants (PPCPs and microorganisms) occurring within the soil.

Figure 2. Characteristics of the soil texture in the investigations included in this review in the soil textural classification triangle

Figure 3. Measured concentrations of selected compounds in land runoff with (MEC, ○) or without (background concentration,*) sludge application on soil. Data from: Giudice and Young 2011, Gray et al. 2017, Healy et al. 2017, Peyton et al. 2016, Sabourin et al. 2009, Topp et al. 2008b, Yang et al. 2012.

Figure 4. Range of concentrations for a selection of compounds in drainage samples with (MEC, ○) or without (background concentration,*) sludge application on soil. Data from: Edwards et al. 2009, Giudice and Young 2011, Gottschall et al. 2012, Lapen et al. 2008a.

Figure 5. Collected data for bacteria in surface runoff and tile drainage. Data from Eldridge et al. 2009, Gottschall et al. 2013, Peyton et al. 2016.

Figure 6 Runoff concentrations *versus* Log K_{ow} for the investigated compounds. Data from: Giudice and Young 2011, Gray et al. 2017, Healy et al. 2017, Peyton et al. 2016, Sabourin et al. 2009, Topp et al. 2008, Yang et al. 2012

Figure 7 Tile drainage concentrations *versus* Log K_{ow} for the investigated compounds. Data from: Edwards et al. 2009, Giudice and Young 2011, Gottschall et al. 2012, Lapen et al. 2008.

Figures
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FIGURES

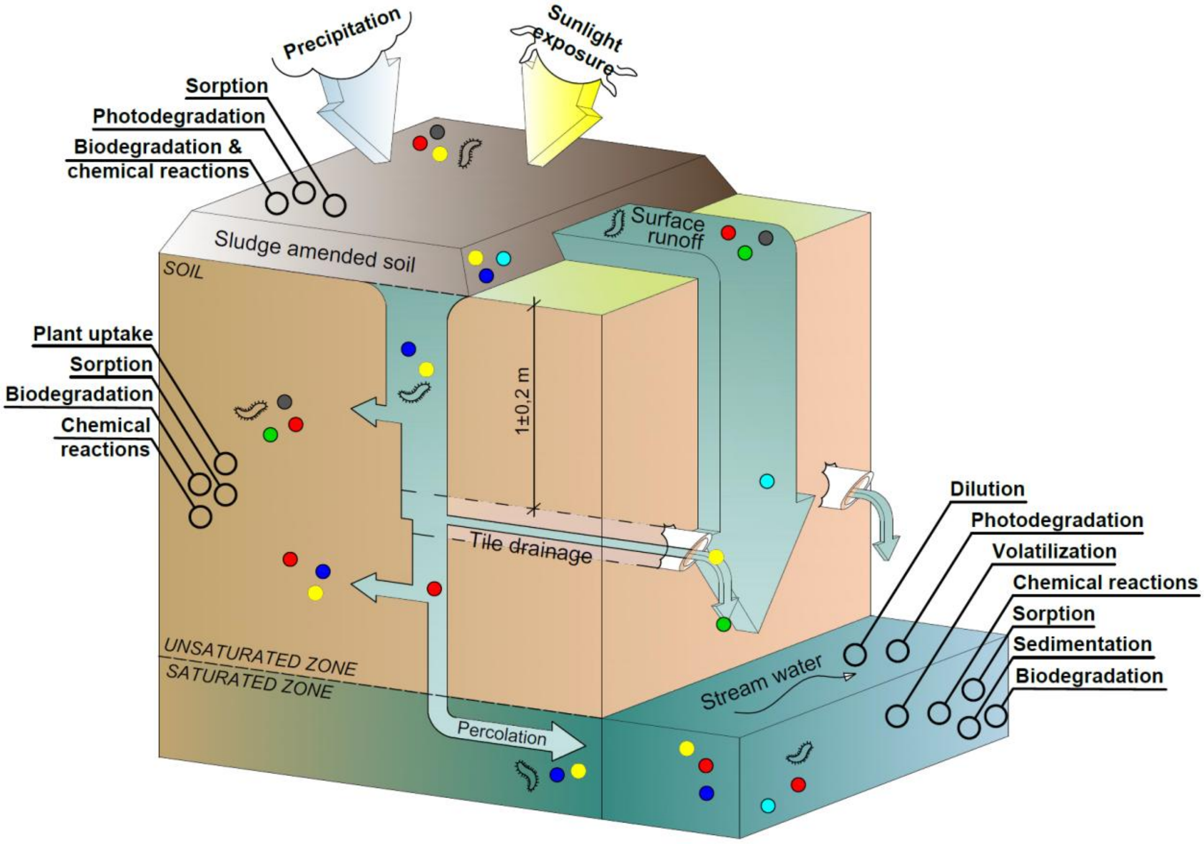
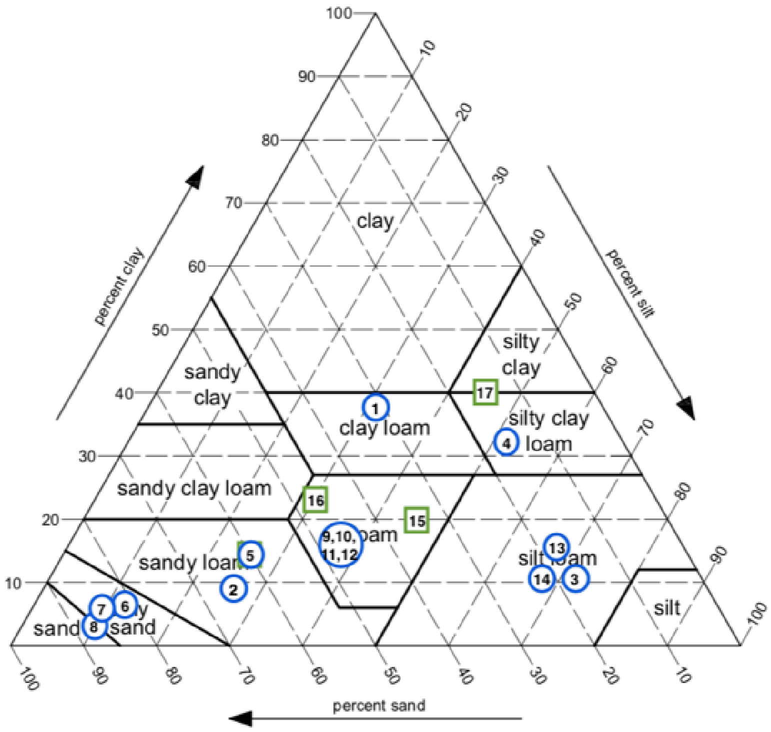


Fig 1



Legend

Studies monitoring surface runoff ○

1. | - | Atalay et al. 2007
2. | - | Atalay et al. 2007
3. | - | Dunigan et al. 1980
4. | - | Eldridge et al. 2009
5. | 60:26:14 | Giudice and Young 2011
6. | 82:12:06 | Gray et al. 2017, Yang et al. 2012
7. | 86:09:05 | Gray et al. 2017, Yang et al. 2012
8. | 88:08:04 | Gray et al. 2017, Yang et al. 2012
9. | 46:39:15 | Healy et al. 2017, Peyton et al. 2016
10. | 47:38:15 | Healy et al. 2017, Peyton et al. 2016
11. | 48:37:15 | Healy et al. 2017
12. | 49:36:15 | Healy et al. 2017, Peyton et al. 2016
13. | 18:67:15 | Sabourin et al. 2009, Topp et al. 2008
14. | - | Wallace et al. 2014

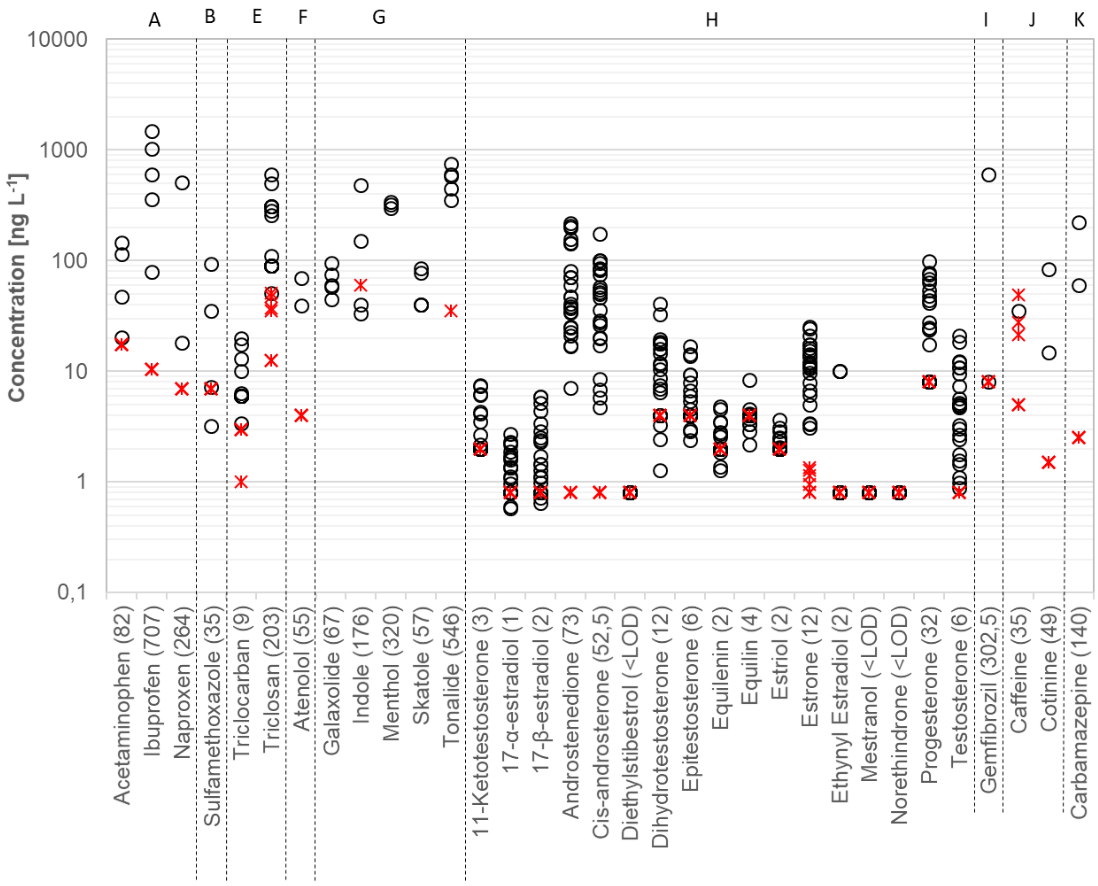
Studies monitoring tile drainage □

15. | 60:26:14 |* Edwards et al. 2009
16. | 60:26:14 |* Gottschall et al. 2012, Gottschall et al. 2013
17. | 60:26:14 |* Lapen et al. 2008a, Lapen et al. 2008b

5. Giudice and Young 2011

* = average in depth

Fig. 2



A
B
E
F
G
H
I
J
K
10000
1000
100
10
1
0,1
Concentration [ng L-1]
Acetaminophen (82)
Ibuprofen (707)
Naproxen (264)
Sulfamethoxazole (35)
Triclocarban (9)
Triclosan (203)
Atenolol (55)
Galaxolide (67)
Indole (176)
Menthol (320)
Skatole (57)
Tonalide (546)
11-Ketotestosterone (3)
17-α-estradiol (1)
17-β-estradiol (2)
Androstenedione (73)
Cis-androsterone (52,5)
Diethylstibestrol (<LOD)
Dihydrotestosterone (12)
Epitestosterone (6)
Equilenin (2)
Equilin (4)
Estriol (2)
Estrone (12)
Ethynyl Estradiol (2)
Mestranol (<LOD)
Norethindrone (<LOD)
Progesterone (32)
Testosterone (6)
Gemfibrozil (302,5)
Caffeine (35)
Cotinine (49)
Carbamazepine (140)

Fig. 3

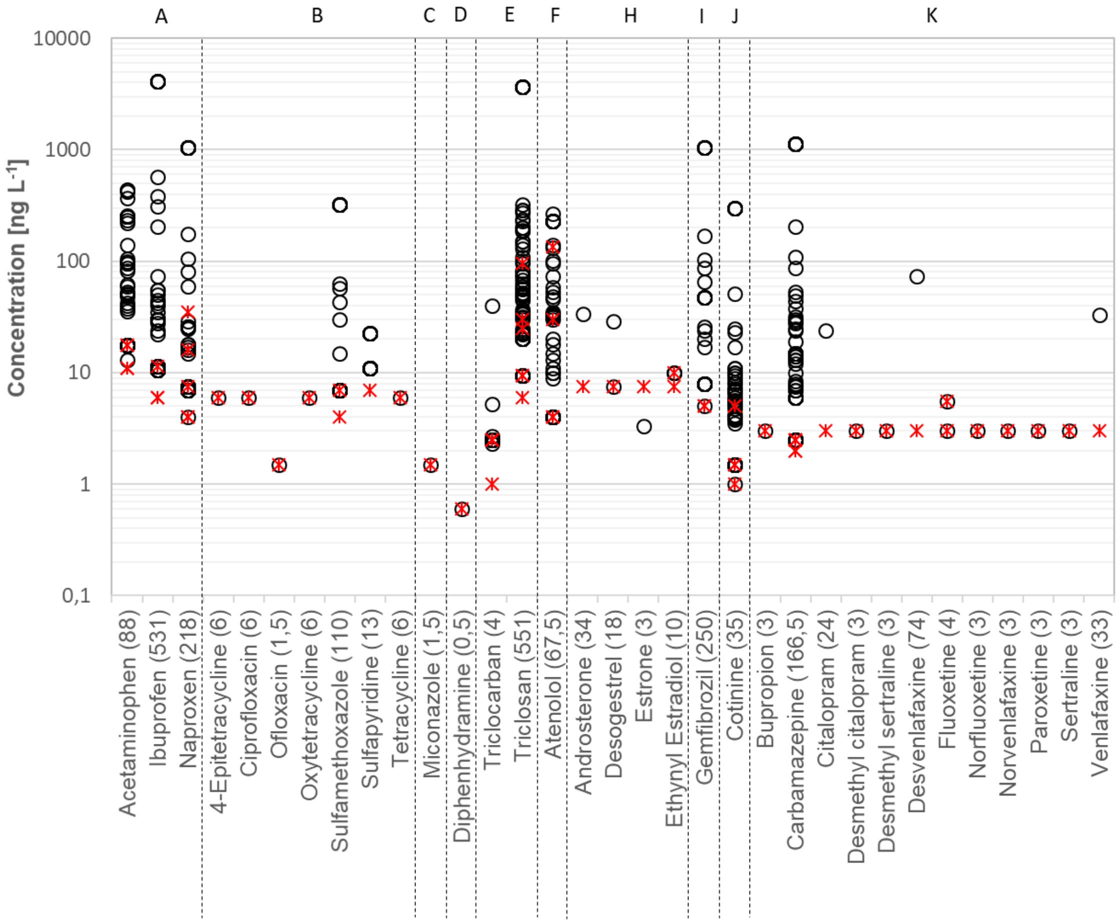
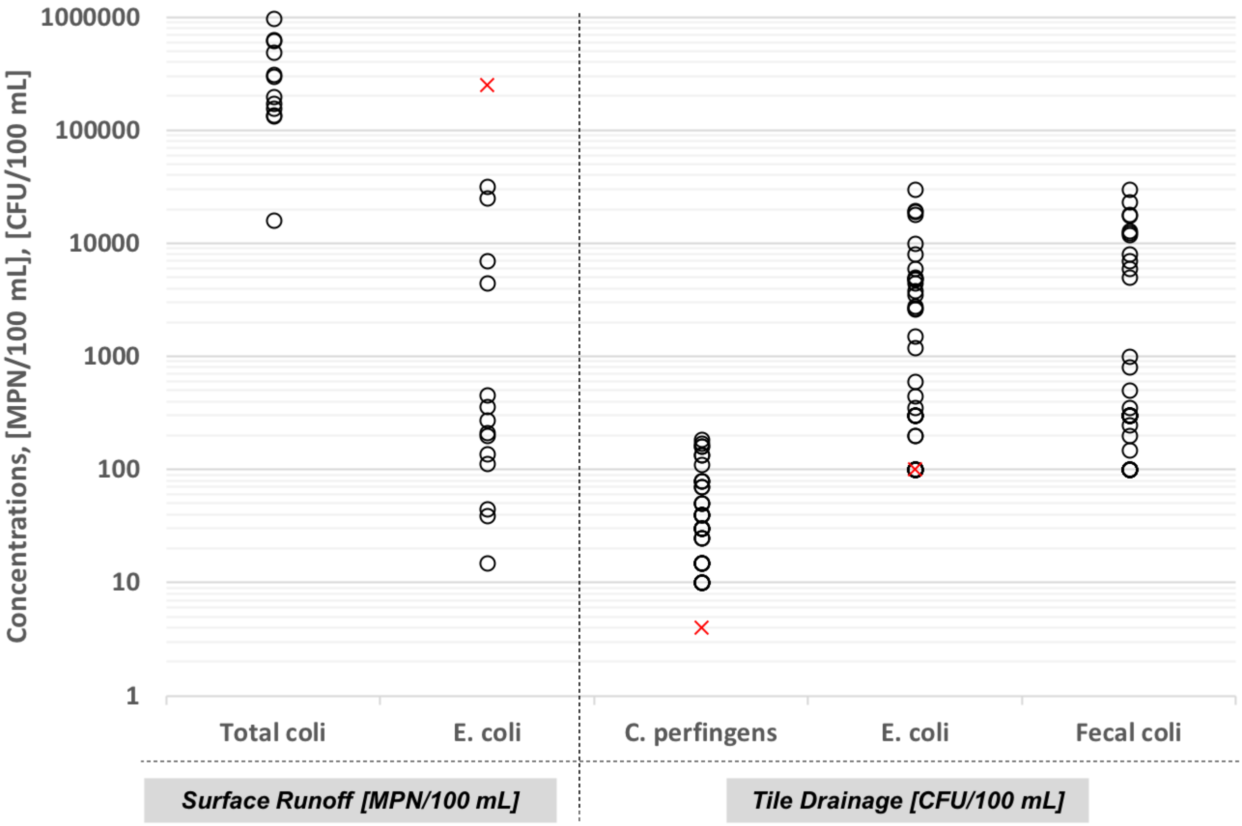

A
B
C
D
E
F
H
I
J
K
10000
1000
100
10
1
0,1
Concentration [ng L-1]
Acetaminophen (88)
Ibuprofen (531)
Naproxen (218)
4-Epitetracycline (6)
Ciprofloxacin (6)
Ofloxacin (1,5)
Oxytetracycline (6)
Sulfamethoxazole (110)
Sulfapyridine (13)
Tetracycline (6)
Miconazole (1,5)
Diphenhydramine (0,5)
Triclocarban (4)
Triclosan (551)
Atenolol (67,5)
Androsterone (34)
Desogestrel (18)
Estrone (3)
Ethynyl Estradiol (10)
Gemfibrozil (250)
Cotinine (35)
Bupropion (3)
Carbamazepine (166,5)
Citalopram (24)
Desmethyl citalopram (3)
Desmethyl sertraline (3)
Desvenlafaxine (74)
Fluoxetine (4)
Norfluoxetine (3)
Norvenlafaxine (3)
Paroxetine (3)
Sertraline (3)
Venlafaxine (33)

Fig. 4



1000000
100000
10000
1000
100
10
1
Concentrations, [MPN/100 mL], [CFU/100 mL]
Total coli
E. coli
C. perfingens
E. coli
Fecal coli
Surface Runoff [MPN/100 mL]
Tile Drainage [CFU/100 mL]

Fig. 5

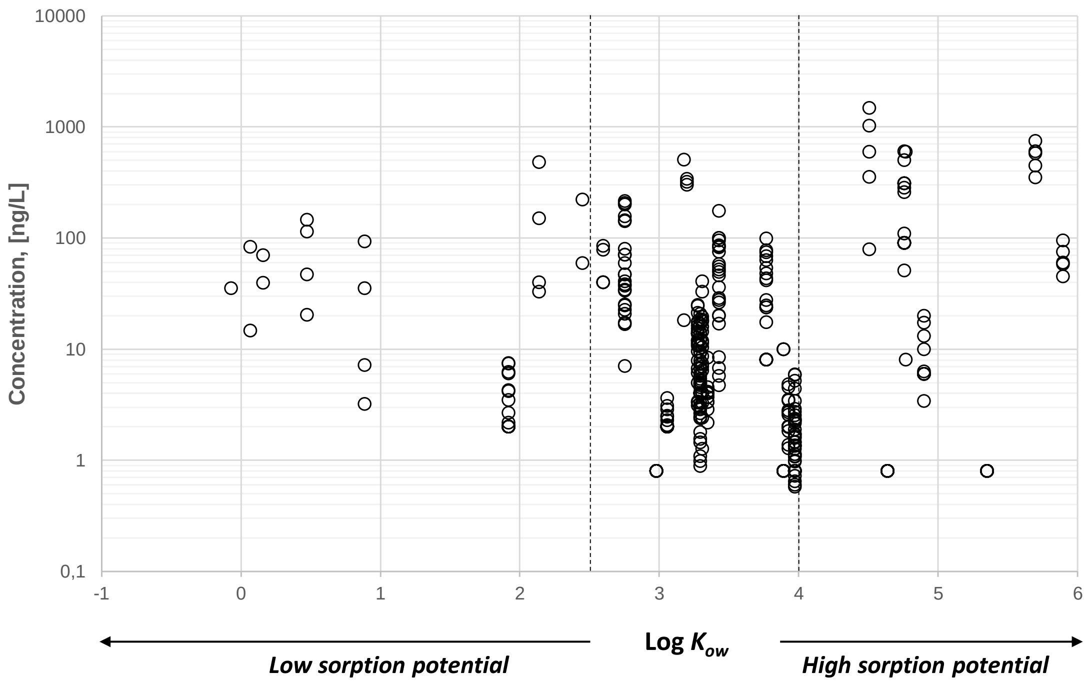

10000
1000
100
10
1
0,1
Concentration, [ng/L]
-1
0
1
2
3
4
5
6
Log K_{ow}
Low sorption potential
High sorption potential

Fig. 6

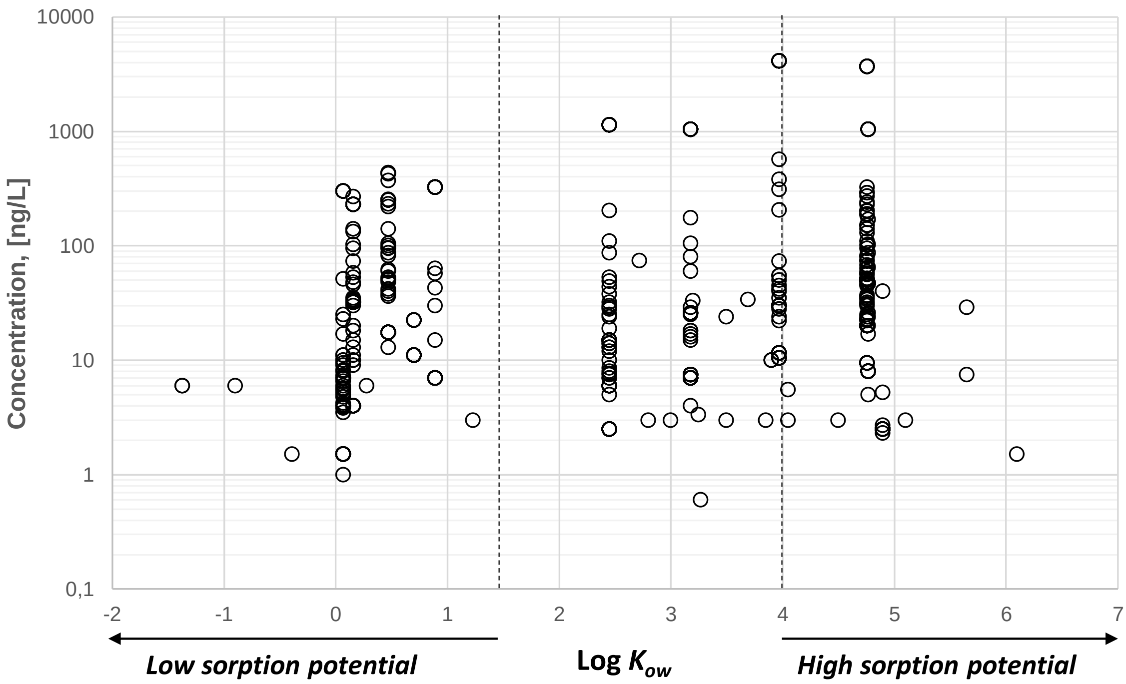

10000
1000
100
10
1
0,1
Concentration, [ng/L]
-2
-1
0
1
2
3
4
5
6
7
Low sorption potential
Log K_{ow}
High sorption potential

Fig. 7