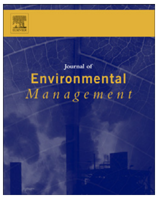
Journal of Environmental Management 147 (2015) 140–151

Contents lists available at ScienceDirect

Journal of Environmental Management

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



Ex-ante fate assessment of trace organic contaminants for decision making: A post-normal estimation for sludge recycling in Reunion

Tom Wassenaar [a, *], Matthieu N. Bravin [a], François Dumoulin [a], Emmanuel Doelsch [b]

[a] CIRAD, UPR Recyclage et risque, F-97743 Saint Denis, Reunion
[b] CIRAD, UPR Recyclage et risque, F-34398 Montpellier, France

ARTICLE INFO

Article history:
Received 24 April 2014
Received in revised form
22 August 2014
Accepted 9 September 2014
Available online 29 September 2014

Keywords:
Trace organic contaminants
PPCP
Organic waste recycling
Fate assessment
Soil
Sugarcane

ABSTRACT

The environmental fate of organic waste-derived trace organic contaminants is a recent focus of research. Public awareness of this issue and concern about the potential risks are increasing, partly as a result of this research. Knowledge remains sparse but, due to growing waste volumes and contaminant concentrations, situations are arising where decisions are urgently needed and the stakes are high. We present an approach to provide stakeholders with the soundest possible information on relevant risks in specific situations where local experimental data are scarce or inexistent. With accuracy taking precedence over precision in such situations, the quantitative fate assessment aspect of the approach considers uncertainty at all levels in order to estimate best-to-worst-case (cumulative uncertainty) fuzzy fate ranges. The approach was applied to conditions that prevail on the island of Réunion. Contrasting possible organic residue recycling scenarios are considered in which trace organic contaminants originate either from pig slurry or sewage sludge. The stakeholders' concerns targeted are leaching, soil persistence and crop (sugarcane) shoot translocation. The fate assessment results in soil removal dynamics that vary over a wide range, even for a particular chemical in a particular scenario. For 3 out of 27 chemicals residual soil concentrations after one sugarcane crop cycle could possibly exceed the 100 ng/g dry weight mass fraction range, only in a worst case situation. Substances predicted to be of the highest mobility (erythromycin, ofloxacin, ciprofloxacin) might produce appreciable leaching only in the event of substantial rainfall shortly after a high rate decadal application. And only the higher bound sugarcane shoot concentration estimates of 17 α-ethinylestradiol and tris(chloropropyl)phosphate are significant.

1. Introduction

Humanity is not outstanding in its respect of the precautionary principle when adopting innovations. The chemical industry is one sector where environmental concerns are traditionally (the European Union REACH regulation, which entered into force in 2007, represents a landmark change) only voiced when adverse effects on the environment, and on humanity itself, become apparent or when technological progress enables their monitoring. It is believed that some 50,000–100,000 chemicals are currently being produced commercially in a range of quantities, with approximately 1000 chemicals (mostly organic) being added each year (Mackay et al., 2006). The fact is that we know very little about the vast majority of the chemicals we use. In the EU, more than 100,000 chemicals were reported to be on the market in 1981, which was the first and only time that chemicals used in the EU were listed. Information on the properties, uses and risks related to 99% of chemicals (by volume) is sketchy (Smital, 2008).

In the late 1990s, Daughton and Ternes (1999) pointed out that, since its advent in the 1970s, environmental chemistry has focused almost exclusively on persistent organic pollutants, and they denounced the "paucity of information on the fate … of pharmaceuticals and personal care products". At the same time, Halling-Sorensen et al. (1998) noted that "very little is known about the environmental fate of medical substances. Only a few investigations have reported findings on medical substances in field samples other than sediment or treated waste water samples." Bibliometrics (Fig. 1) indicate that since the turn of the century there has been a boom in scientific interest in this field, although

---

* Corresponding author. CIRAD, UPR Recyclage et risque, Station de la Bretagne, 40, Chemin de Grand Canal, CS 12014, 97743 Saint Denis Cedex 9, Reunion. Tel.: +262 262528201; fax: +262 262528021.

E-mail addresses: tom.wassenaar@cirad.fr (T. Wassenaar), matthieu.bravin@cirad.fr (M.N. Bravin), francois.dumoulin@cirad.fr (F. Dumoulin), emmanuel.doelsch@cirad.fr (E. Doelsch).

http://dx.doi.org/10.1016/j.jenvman.2014.09.015

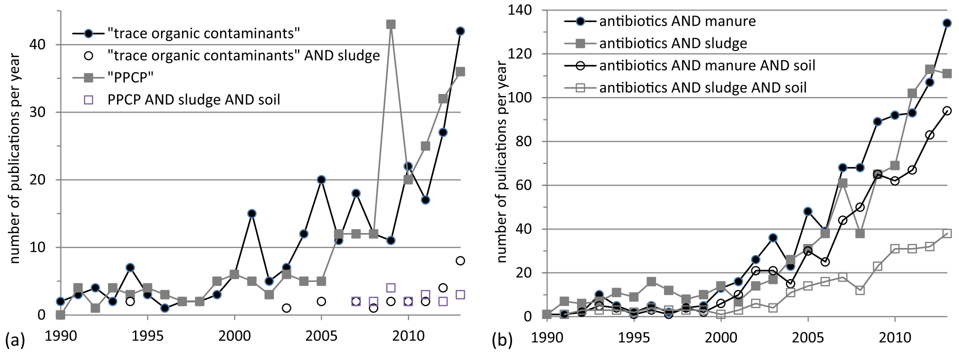


Fig. 1. Number of publications per year with the indicated keywords in their topic.
Extracted from Thomson Reuters' *Science Citation Index Expanded*. Web of Knowledge, accessed on 31/01/2014.

few studies have been focused to date on complex matrices like sewage treatment plant (STP) sludge and soil (Fig. 1a).

Sewage sludge application in crop fields is an important pathway via which chemicals enter the environment. Trace organic contaminants (TOC) contained in municipal STP sludge nearly all belong to the category generally designated as pharmaceuticals and personal care products (PPCP), broadly defined as “products used to improve the quality of daily life” (Boxall et al., 2012). Within these categories, there is currently a strong biased focus on antibiotics, with a steady increase in contributions concerning antibiotics that reach the soil through manure and sludge applications (although less marked for sludge, see Fig. 1b). Municipal sewage antibiotics are mainly studied at the STP level. There has been a substantial rise in the number of studies on antibiotics in field-applied sludge over the last 10 years, including the emergence of the first few studies more broadly looking at PPCPs in such situations (Fig. 1a).

The sudden increase in attention illustrated in Fig. 1 gives rise to significant concerns by society. Science so far remains insufficiently equipped to respond to the many emerging, but pressing, concerns (Smital, 2008). Only a limited number of substances have been studied in a few situations. Although models that enable robust prediction in unstudied environments are being developed (i.e. validated level IV fugacity models, Mackay and Webster, 2006), there is generally very little information on the required parameters. As normal science proceeds, a post-normal (Funtowicz and Ravetz, 1991) approach is required to generate information for society in such situations where “facts are uncertain, values in dispute, stakes high and decisions urgent”. In Section 2 we present such an approach, while considering problem-solving aspects like uncertainty, value loading, and a plurality of legitimate perspectives (Funtowicz et al., 1999).

The goal of this paper is to present a quantitative fate assessment method, constituting an integral part of the approach, and its application to a situation where stakes and uncertainties around sludge spreading are high. The situation selected for application is one where sludge spreading has yet to be introduced: the island of Réunion is a tropical French overseas territory with volcanic soils, a system where the little information obtained so far on the fate of sludge-derived TOCs in soil cannot easily be transposed and where, due to the absence of land spreading, the environmental fate cannot be studied experimentally. Given the rise in sludge production due to STP rehabilitation and construction, science urgently needs to “translate” its sparse knowledge into information for society. While landfilling is prohibited, the acceptance of land spreading plans by regional authorities and the production of sludge-containing fertilizer are impeded by the information void around possible TOC-induced risks. We report fate assessment results that aim at filling this void as accurately as is currently possible.

2. Material and methods of the Reunion post-normal assessment

The inquiry methodology proposed is part of a larger theoretical framework described in Wassenaar et al. (2014): Hard science is involved from an ‘involved actor’ stance (Alrøe and Kristensen, 2002) in a social science facilitated participatory research effort based on negotiation theory, thus providing that facilitator with credibility, insight and the capacity to fill knowledge gaps (Leeuwis, 2000). It is within this participatory research setting that the group of participating stakeholders is taken through a sequence consisting of the following five steps (see Supplementary information A for a succinct description of all steps): (step 1) creating awareness, in order to make sure that the discussion will differentiate contamination from pollution; (step 2) identifying areas of concern, to assure the provision of information most suited to unlocking the local decision-making process; (step 3) selecting indicator chemicals; (step 4) assessing their fate; and (step 5) interpreting and communicating results, with the aim to focus discussion on the acceptability of concentrations and on adaptive management. This sequence—more than an information production and provision process—is a necessary and inseparable whole that allows stakeholders to: (a) agree on objectively addressing a polemic issue; (b) agree on the assessment end-points; and (c) draw common conclusions. This paper is mainly concerned with the fate assessment results (step 4). PPCP fate is addressed through an as good as currently possible (AGAP) assessment, using simple existing models and data on aspects known to influence them. Such simple methods all have marked limitations. An important characteristic of post-normal appraisals is that accuracy matters more than precision for decision making. Uncertainty is therefore considered at all levels in order to estimate best-to-worst-case (cumulative uncertainty) fuzzy fate ranges. Although the accuracy is unknown, it is reasonable to suppose that the precision reduction of the range method curbs possible systemic errors. Lastly, for each fate, such baseline calculation results are then put into perspective by comparison with reported findings.

2.1. *Target substances and fates following from steps 2 and 3*

In the case of Réunion, for both situations described in Section 1 (land spreading and fertilizer production), the only crop to consider as a possible receptor is sugarcane, i.e. the island's geographically and economically dominant crop, which is grown on permeable land with deep lying aquifers. Local authorities are concerned about drinking water quality. Two other stakeholders have different concerns with high stakes. As voiced by the Agricultural Board, sugarcane farmers are concerned about soil contamination—are there substances that could, under the scenarios concerned, become chronically present and could they affect soil quality? The sugar industry has marketing concerns related to plant uptake—under the present scenarios, what are the chances of uptake of the substances into above-ground sugarcane stalks? These three midpoint fates thus constitute the assessment targets more than human and ecological health effects. It was also agreed that organic contaminants in livestock manure should be assessed in parallel with STP sludge (subsequently designated as ‘sludge’) and following a similar procedure. Pig slurry (subsequently designated as ‘slurry’) was selected as a ‘livestock effluent indicator’ material, since veterinary product use is common, farming practices are homogeneous and slurry is widely applied on sugarcane fields, while also being included in one of the scenarios of the prospective study. For both matrices, the indicator chemicals selected for analysis in Step 3 are classified according to their industrial purpose (Table 1). They can thus be linked to their usage, which in turn facilitates communication to the general public.

Samples were taken from the three activated sludge STPs on the western side of the island of Réunion, the study area of the participatory study, and sent for analysis following lyophilisation. Routine analytical capacities of any research laboratory, be they well equipped, rarely exactly fit the result of the substance selection. The few substances not covered are taken along in the subsequent appraisal on the basis of a literature and expert based estimation of concentration. Pig slurry was sampled from concrete storage pits on three farms in western Réunion. Following lyophilisation, they were sent for analysis of veterinary antibiotics based on knowledge of local veterinary practices. The basic characteristics of all samples were analytically determined. Dry matter, organic matter and major nutrient contents (see Supplementary information B) proved to be homogeneous and within a common range for both types of material.

Sludge samples were analyzed using pressurized liquid extraction and offline solid-phase extraction followed by ultra-performance liquid chromatography tandem mass spectrometry using a hybrid triple quadrupole-linear ion trap mass spectrometer (Jelić et al., 2009). Pig slurry samples were analyzed by accelerated solvent extraction and solid-phase extraction using an OASIS HLB cartridge followed by liquid chromatography-tandem mass spectrometry.

2.2. Substance flows from source to fate

Substance trajectories differ significantly according to the envisaged use (Fig. 2). The conditions of land spreading of raw sludge or pig slurry are specified in waste management regulations. Participatory research designed scenarios concerning pig slurry or activated sludge are geared towards the production of commercial fertilizer products based on co-composting with poultry litter and green waste (for pig slurry) and on co-composting with vinasse (from sugarcane molasses) and green waste followed by complementing and pelletizing before conditioning (for activated sludge). Allowed or recommended application rates are known for all situations. The amount of sludge/slurry that ends up in a sugarcane field soil can thus be estimated for each scenario (see Supplementary information C).

The substance flows presented in Fig. 2 indicate the chain of biophysical processes that may influence the fate of individual PPCPs, through degradation or by partitioning them away from their sludge/slurry matrix. Sludge/slurry adsorbed PPCPs are known to be of low volatility (Daughton and Ternes, 1999). Soil volatilization is only considered in our appraisal for the “A” scenarios: In the “B” scenarios, all possible volatilization is supposed to have taken place during composting as an effect of high temperature during its thermophilic phase and compost turning. AGAP assessment of these and other processes, i.e. degradation, soil sorption, plant uptake and leaching, is based on simple existing models and data on aspects known to be of major influence (Beck et al., 1996): physicochemical characteristics of soil and sludge/slurry, environmental conditions, and the specific properties of the chemicals.

2.3. Degradation during processing

In commercial fertilizer scenarios, most compounds will be affected by the aerobic digestion based nutrient concentrating and product stabilizing process. According to the scant literature concerning PPCP degradation during composting (see Supplementary information B), relatively broad degradation rate ranges are proposed (Table 2) that account for the combined effect of biotic degradation (i.e. biodegradation), abiotic degradation and volatilization. In the *Sludge B* scenario, additional pelletizing heat related abatement is applied to compounds where degradation has been shown to be partly the effect of abiotic, temperature induced hydrolysis (see Supplementary information B). PPCP doses applied to soil can be estimated while assuming that no further degradation takes place during storage of the dried (80% dry weight) product.

2.4. Soil concentration

As proposed by ECB (2003) and Eriksen et al. (2009), expected PPCP residual soil concentrations are estimated at fixed time horizons. Assuming that the background concentrations are negligible, the initial soil concentration ($w_{\mathrm{c,\ Soil,}\ t0}$) range is calculated from the sludge concentration extremes, composting degradation rate range, application rates, known soil bulk density variation in the area and mixing depth. Starting from $w_{\mathrm{c,\ Soil,}\ t0}$, $w_{\mathrm{c,\ Soil,}\ t1}$ is estimated as a residual in a balance calculation based on first-order kinetics that consider first-order rate constants for volatilization (scenarios “A” only), plant uptake, leaching and biodegradation. These simple calculations (see Supplementary information C) are based on the assumption that the compounds are neutral while it is well known that a significant proportion of PPCPs are ionizable substances. No models are currently available for estimating ionizable chemical partitioning in soil (Boxall et al., 2012; Boxall and Ericson, 2012). Our calculations assume a crisp ‘dominantly neutral’ to ‘dominantly ionized’ transition. For the latter state, neutrality-based parameter value ranges are tentatively adjusted (see Supplementary information C).

2.5. Soil volatilization

The purely physical process of volatilization after application to soil (scenarios “A” only) is estimated using the classical two-film resistance model, as recommended by the European Chemicals Bureau (ECB, 2003). See Supplementary information C for details on parameter estimation and resulting value ranges.

2.6. Soil biodegradation

In addition to chemical partitioning and the resulting possible removal pathways from soil, degradation within soil itself is a major ‘removal’ process. When organic fertiliser is added to soil, the contained chemicals are readily accessible to soil organisms. The rate of biodegradation in soil is influenced by a wide range of

Table 1
Selected compounds and product categories they belong to.

Selected class	Selected compounds	Information communicated to stakeholders on …	
		Usage/origin (in the EU if different from elsewhere)	Possible agricultural and water background contamination
Pharmaceuticals			
Analgesics/anti-inflammatories	Diclofenac, piroxicam, ketoprofen	Generic drugs	Possible water contamination from STP effluents and septic systems
Lipid regulators and cholesterol lowering drug	Pravastatin	Prescribed and generic drugs	Possible water contamination from STP effluents and septic systems
Histamine antagonist	Loratadine	Generic drugs	Possible water contamination from STP effluents and septic systems
Diuretic	Furosemide	Prescribed drugs	Possible water contamination from STP effluents and septic systems
Antibiotics	Erythromycin, ofloxacin, ciprofloxacin, sulfamethoxazole, trimethoprim, doxycycline	Prescribed curative drugs	Possible water contamination from STP effluents and septic systems
Veterinary antibiotics	Spiramycin, lincomycin, tetracycline, oxytetracycline, sulfadiazine, marbofloxacin	Curative or prophylactic/ metabolism enhancing use	Probable contamination of OM-rich soils receiving regular applications of raw monogastric manure (e.g. pig slurry on pasture)
Personal care products			
Oestrogenic compounds/ xenoestrogen	β-Estradiol	Natural human oestrogen also used in pharmaceutical preparations	Possible water contamination from STP effluents and septic systems
	17 α-Ethinylestradiol (EE2)	Contraceptive pills	
Preservatives/antibacterial and antifungal agents	Methylparaben	Widely and heavily used in cosmetics, toiletries, pharmaceuticals. Also used as a food preservative.	Possible water contamination from STP effluents and septic systems
	Triclosan	Common in household liquid hand soap, toothpaste, plastics, footwear	
Corrosion inhibitor/polisher	Tolyltriazole	Originates to a large extent from dishwasher formulations	Strong background pollution in water downstream of STP and septic systems (present in a vast majority of EU rivers). Agricultural contamination possible from triazole fungicides, but insignificant use in Réunion (INERIS-ONEMA, 2011).
Surfactants/plasticiser	Alkylphenols: octylphenol, nonylphenol	Degradation product of non-ionic industrial and laboratory detergents and some pesticides (limited to less than 0.1% by mass since 2003: EU directive 2003/53/EC)	Although being phased out in the EU, the use of nonylphenol ethoxylates in pesticide formulations can constitute a direct release of nonylphenols into the terrestrial compartment. Ground- and surface water contamination from STP effluents and septic systems is possible.
Flame retardant	Tris(chloropropyl)phosphate (TCPP)	Widely present in a large range of consumer products and construction materials	Ubiquitous presence in the environment. Highest background pollution in domestic and aquatic environment. Humans ingest and inhale flame retardants and their presence in our tissue has been demonstrated. Significant presence in protein-rich food.
Water and oil repellant	*Perfluorinated compounds:* *Perfluorooctane sulfonate (PFOS)* *Perfluorooctanoic acid (PFOA)*	Broad range of domestic products and packaging	Ubiquitous in humans, environment and wildlife worldwide. Virtually all people living in the industrialized world have many PFCs in their blood serum in the ng/mL range.
Fragrances	*Nitro-/polycyclic musks: galaxolide tonalide*	Widely used in cosmetics, perfume, soap, detergents. Also used as food additive.	Freshwater and fish are commonly contaminated
Other			
Polycyclic aromatic hydrocarbons	Benzo[a]pyrene[a], benzo[b] fluoranthene[a]	No intentional manufacturing, natural occurrence and by-products of fuel burning	Atmospheric deposition induced background contamination in the environment is common.

Compounds in italics were not part of the chemical analysis and are considered on the basis of recent and relevant literature findings (see Section 3). Columns on the right summarize qualitative, literature based information on usage and background pollution communicated to stakeholders.

[a] Denotes regulated chemicals, thus routinely analyzed by local STPs (PCBs, the regular analysis of which is imposed by law, are not identified in local sludge and thus excluded).

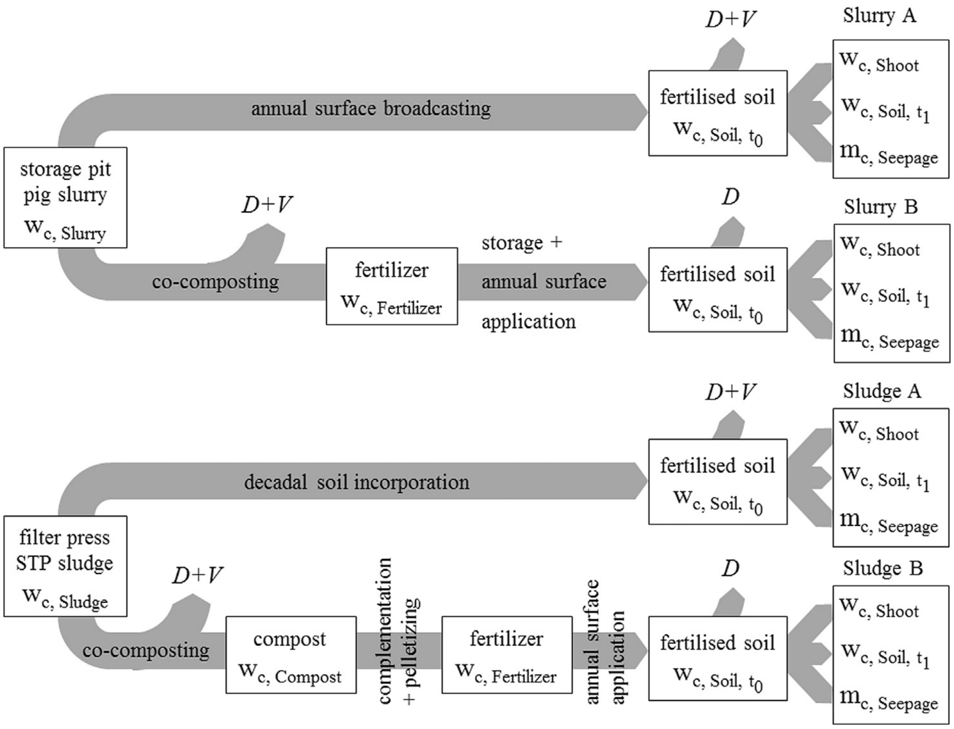


Fig. 2. Pathways from source to target fates under the four scenarios *Slurry A and B and Sludge A and B*, indicated on the right. $w_{c,\,X}$ indicates the mass fraction of contaminant c in compartment *X*. *D* indicates degradation and *V* volatilisation of a given fraction of the contaminant. t_0 indicates w_c right after application and t_1 w_c at the target time horizon. m_c indicates the mass of a contaminant (in a non-dimensionable compartment).

factors, with the most well-known being the chemical structure of substances, microbial activity, organic carbon content, and temperature. The bioavailable fraction of a substance in soil depends on the partitioning of the substance between the soil particles and the pore-water. Bioavailability of ionic substances is therefore surely influenced by soil parameters other than the carbon content. These parameters may be of particular importance in Réunion tropical soils (high oxide mineral content). These properties spatially vary and an accurate estimate of the biodegradation rate is very difficult even when laboratory or field data are available (which for the vast majority of the compounds considered is not the case). Fate and exposure models normally assume that the biodegradation kinetics are pseudo-first order. Converting soil half-life estimates (see Supplementary information C) to rate constants is the only proxy that can currently be used.

Hydrolysis and particularly photolysis (given the high insolation rate affecting the soil surface of the Réunion sugarcane fields at the time of fertilization) may be important for some chemicals contained in surface applied fertilizer. No single method is currently available to assess the possible magnitude of these abiotic processes under such environmental conditions. The large uncertainty in estimating degradation in soil contrasts with the acknowledged importance of these processes in soil CTO fate. Even more than for the other soil fate pathways, comparison with literature findings (where available) is therefore an essential and integrative part of its assessment.

2.7. Plant uptake

The transfer of contaminants from the rhizosphere to the roots is primarily mediated by the regular water uptake in plants. Predicting plant uptake based on measured soil concentrations is therefore not straightforward. An additional challenge is that soil conditions in the rhizosphere might be quite different from those in bulk soil due to root-induced alteration of the physical, biological and physical–chemical properties in the rhizosphere (Hinsinger et al., 2009). Subsequent transport of contaminants from the root system to the stem (i.e. translocation, one of the target endpoints of our assessment), leaves and storage organisms occurs via the vascular transport system. The contaminants have to penetrate several plant tissues during translocation. The translocation and accumulation of contaminants in above-ground plant parts therefore depends on a combination of their aqueous solubility, which promotes their transport via water in the vascular system, and their lipophilic properties, which promote their transport across the lipidic plasma membrane of cells (McFarlane, 1995).

As an effect of this complex situation, plant uptake models are mainly semi-mechanistic models based on empirical studies, and are mostly limited to neutral organic compounds. Nearly all such models depend on the octanol–water partitioning coefficient K_{ow} to predict plant uptake. The general trend noted in all models regarding predicted shoot concentrations is that uptake declines with increasing K_{ow}, which is consistent with the observation that root-to-shoot transport processes are mainly controlled by passive transpiration within the xylem (Collins et al., 2006). In addition, lipophilic chemicals are more likely to be sorbed to soil organic matter and less available for uptake via the soil solution. From among these models, we selected the Stem Concentration Factor (SCF) model of Ryan et al. (1988), see Supplementary information C, for non-ionic organic chemicals from soils. In the assessment of Collins et al. (2006), SCF was found to be the best performing model for predicting shoot concentrations (our target end point), showing a reasonably good performance over a broad (0–6.5) log K_{ow} range.

Similar calculations could not be performed for ionic substances. Trapp's (2004) model for uptake into roots and translocation of ionic compounds is highly complex and includes processes such as lipophilic sorption, electrochemical interactions, ion trap, and advection in xylem. A recently proposed simple, equilibrium

Table 2
PPCP mass fraction w_c analytically determined in STP sludge and pig slurry samples (S: sludge or slurry sample; nd: not detected) and estimated in soil after raw residue, compost or fertilizer application. *A* and *B* refer to the scenarios (Fig. 2).

PPCP chemical	$w_{c,\ \mathrm{sludge/slurry}}$ (ng/g dry weight)			PAR (%)	$w_{c,\ \mathrm{Soil},\ t0}$ (ng/g dry weight)			
	S1	S2	S3		*A* low	*A* high	*B* low	*B* high
Diclofenac	37	24	17	50–80	1.5	6.2	0.2	2.1
Piroxicam	3	12	11	40–60	0.2	2.0	0.1	0.8
Ketoprofen	228	304	209	40–60	17.4	50.7	4.6	20.1
Pravastatin	4	281	25	40–60	0.3	46.8	0.1	18.5
Loratadine	4	4	4	40–60	0.3	0.7	0.1	0.3
Furosemide	30	198	33	40–60	2.5	33.0	0.7	13.1
Erythromycin	216	192	211	70–90	16.0	36.0	1.1	7.1
Ofloxacin	329	349	399	70–90	27.4	66.5	1.8	13.2
Ciprofloxacin	358	545	583	70–90	29.8	97.2	2.0	19.2
Sulfamethoxazole	4	16	11	70–90	0.4	2.7	0.0	0.5
Trimethoprim	725	700	783	70–90	58.3	131	3.9	25.8
Doxycycline	nd	nd	nd	–	–	–	–	–
Spiramycin[a,b]	nd	nd	nd	–	–	–	–	–
Lincomycin[a]	35	67	16	60–80	1.7	14.1	0.1	1.5
Tetracycline[a]	133	32	40	60–80	3.4	27.9	0.2	2.9
Oxytetracycline[a]	1819	590	6140	60–80	62.0	1289	3.3	135.6
Sulfadiazine[a]	nd	3687	nd	60–80	0.0	774.3	0.0	81.4
Marbofloxacin[a]	120	931	70	60–80	7.4	196	0.4	20.6
β-Estradiol	nd	nd	nd	–	–	–	–	–
EE2	626	45	141	30–50	3.7	104	1.2	48.2
Methylparaben	140	138	89	50-80	7.4	23.3	1.0	7.7
Triclosan	nd	nd	nd	–	–	–	–	–
Tolyltriazole	16	20	39	30–50	1.3	6.6	0.4	3.0
Octylphenol	nd	nd	nd	–	–	–	–	–
Nonylphenol	18	8	28	90	0.7	4.7	0.0	0.3
TCPP	928	4640	23,200	50–80	77.3	3866	10.2	1276
PFOS[c]	46			0–20	3.8	7.7	2.0	5.1
PFOA[c]	4			0–20	0.3	0.7	0.2	0.4
Galaxolide[c]	8600			50–80	716.7	1433	94.6	473.0
Tonalide[c]	890			50–80	74.2	148	9.8	49.0
Benzo[a]pyrene	210	180	230	40–60	15.0	38.3	4.0	15.2
Benzo[b]fluoranthene	150	210	190	40–60	12.5	35.0	3.3	13.9

PAR: processing abatement range (see Supplementary information B). 'high' $w_{c,\ \mathrm{Soil},\ t0}$ estimates are based on the combination of highest $w_{c,\ \mathrm{sludge/slurry}}$, the lower limit of the processing abatement range (scenarios *B*), and lower limit of the soil density range. 'low' $w_{c,\ \mathrm{Soil},\ t0}$ estimates are based on the combination of the opposite limits.

[a] Denotes chemicals analyzed in pig slurry, thus referring to the *Slurry* scenarios.

[b] Analyzed in both sludge and slurry samples.

[c] Indicates chemical concentrations not analytically determined but based on a recent EU-wide survey (Tavazzi et al., 2012).

partitioning based approach to assess plant uptake in the BASL4 organic chemical fugacity model does not generate satisfactory results (Hughes and Mackay, 2011). An AGAP uptake indication is proposed for some ionic substances on the basis of published findings, while taking into consideration the "environmentally realistic" concentrations used in experimental studies (since uptake depends on applied concentrations: Stahl et al., 2009) and how they compare to our scenarios. Where available and obtained through "compatible" experiments, uptake ratios are applied and combined with crop yield in order to obtain a realistic indication of the ionic substance harvested tissue concentration.

When interpreting AGAP quantification results, attention should be focused not only on a compound's hydrophobicity, but also on its molecular size. As listed in Hughes and Mackay (2011), several studies have shown that compounds of high hydrophobicity and molecular size tend to be found in high concentration only on or near the root surface. Other studies have also indicated that translocation of chemicals from roots to above-ground plant parts is not normally a major process for hydrophobic chemicals. Hughes et al. (2005) summarize findings on the relation between K_{ow} and plant uptake (incl. internal transport). Selected published ionic substance plant uptake findings combined with their interpreted size and lipophilicity characteristics have been used for qualitative appraisal of the risk of the presence of other ionic substances in sugarcane stalk tissue, one of the endpoints of interest in our assessment.

2.8. Leaching

As indicated in Fig. 2, one of the assessment targets is the amount of contaminants possibly leached into deeper soil horizons, below the root zone. This was accepted beforehand as a relevant proxy for drinking water concentration, i.e. the ideal indicator: sugarcane is cropped on steep slopes with highly permeable soils and bedrock in which locally dense strata create deep and fragmented water tables. It is widely known that under these conditions hydro-geologists are unable to assess the relationship between infiltration and drinking water wells. Information on soil water partitioning and water infiltration is required to estimate contaminant leaching. Both are combined in the calculation of a theoretic first-order daily 'removal through leaching' rate, while real infiltration occurs in seasonal peak events: fields are irrigated, with irrigation 'mixing' solutes in the root zone but not inducing deep soil seepage—what matters is infiltration beyond the root zone, not surface infiltration. This can be estimated but occurs mainly during a limited number of rain storms during the rainy season. The soil water partitioning coefficient is a dynamic parameter as it depends on the fractions of the three soil phases (ECB, 2003). Contrary to the average situation (as considered under volatilisation and plant uptake, see Supplementary information C), soil porosity in this calculation is considered to be dominated by water in order to obtain a meaningful 'daily' rate estimate.

3. PPCP fate assessment results and discussion

3.1. PPCPs in organic wastes

For the vast majority of sludge PPCPs, the concentrations were found to be quite similar among the three samples (Table 1). Variations exceeding one order of magnitude are limited to 3 out of 23 chemicals, indicating that these results may be representative of western Reunion PPCP sludge contamination. No drug consumption related seasonal contamination variation is expected in the tropical setting considered. As expected, slurry drug concentrations from individual pig farm storage pits are more spiked, exceeding one order of magnitude variation among the three samples for 3 out of 6 chemicals.

3.2. Soil applied PPCPs

The estimated initial soil concentrations (i.e. $w_{c,\ \mathrm{Soil},\ t0}$) are at least 5-fold lower than the sludge/slurry concentrations (Table 1). However, the application scenario has a considerable impact on initial soil concentrations, with maximum differences exceeding one order of magnitude for all chemicals analyzed. *A* and *B* scenario soil concentrations are clearly distinct, with the respective low-high concentration ranges showing no overlap for 10 out of the 27 substances present at detectable levels. For the sludge scenarios, this difference is exacerbated when accounting for the different soil depths considered (~30 cm for *Sludge A* and ~10 cm for *Sludge B*), but this is also related to the marked differences in application frequency (Fig. 2).

3.3. PPCP plant uptake

With the exception of perfluorinated compounds (PFCs), all of the non-pharmaceutical selected chemicals (Table 1) present in the samples (Table 2) are likely non-ionized in soils. In the absence of a model based estimate, two peer-reviewed experimental studies focused on crop uptake of sludge-contained PFCs provide useful estimates. Stahl et al. (2009) showed that PFOA/PFOS concentrations in plants vary greatly depending on the concentrations applied to the soil. However, the lowest PFC concentration studied (250 μg/kg soil) is about two to three orders of magnitude higher than our estimated $w_{c,\ Soil,\ t0}$: if we extrapolate their regressions for maize stalks (accepting maize stalks as a proxy for cane stalks) for our t_0 PFC mass fractions, we come up with predicted cane concentrations that are well below the background concentrations found in their control experiments. The uptake–soil concentration ratio obtained by Yoo et al. (2011) is comparable to that of Stahl et al. Provided that no accumulation will occur in soil at the current loading rate, as the results presented in the subsequent sections indeed suggest, the above findings suggest that sugarcane stalk PFC concentrations will not be detectable.

Contrary to the situation for non-pharmaceuticals, a majority of the pharmaceuticals present in our samples (11 out of 16) were likely dominantly ionized in at least part of the soils studied. This concerns all analgesics, lipid regulators and diuretics, 3 out of 5 human antibiotics and 3 out of 5 veterinary antibiotics. Peer-reviewed experimental studies, the sole remaining source regarding the crop uptake risk for these pharmaceuticals, so far have largely been focused on antibiotics (reviewed by Kim et al., 2011). From among the six mostly ionic antibiotics useful uptake rates have been reported only for trimethoprim. Boxall et al. (2006) calculated low (res. 0.06 and 0.08) trimethoprim soil-based uptake factors (UF). However, trimethoprim $w_{c,\ Soil,\ t0}$ was among the highest of our substances (Table 2). If one would accept the UF of lettuce as a proxy for the SCF of sugarcane, the high end estimates of the *A* and *B* scenarios would be res. 5 and <1 ng/g fresh weight. Our sulphonamide-class antibiotics sulfamethoxazole (human) and sulfadiazine (veterinary) have the lowest molecular weights of all of our pharmaceuticals (res. 253 and 250 g/mol). While this makes extrapolation of the sulfamethazine findings (Dolliver et al., 2007) tempting, their log K_{ow}s are well below 1 which, according to Hughes et al. (2005), would make them too lipophobic to enter the root system. Boxall and Ericson (2012) indeed concluded that developing a clear relationship between uptake and pharmaceutical properties, such as hydrophobicity, is difficult as some pharmaceuticals are taken up by some organisms and not by others, and uptake into similar organisms in different environments can vary. Holling et al. (2012) suggested that the rhizosphere conditions, particularly the presence of dissolved organic matter, might be one of the critical factors in determining the mobilization and bioavailability of xenobiotic compounds such as PPCPs.

Studies are currently emerging on crop uptake of pharmaceuticals other than antibiotics. Dodgen et al. (2013), for example, studied diclofenac uptake, which they found to be inferior to nonylphenol uptake. Regarding the low SCF estimated for the latter (Table 3), this provides an indication of a low uptake risk. Indeed, Cortés et al. (2013) did not observe any diclofenac uptake when applied at 22 ng/g dry weight in sludge, which is very similar to our values. No experimental reports are available for the other non-antibiotic ionic pharmaceuticals.

Table 3 reports SCF and $w_{c,\ Shoot}$ estimates for the non-ionic chemicals. Clearly, the SCF value ranges are very broad for many of the 14 compounds. The influence of K_{ow} on SCF is overshadowed by the value range of the component that Ryan et al. (1988) added to the original solution concentration based K_{ow}–SCF relation to account for the effect of soil sorption on the soil solution concentration, thus allowing estimation of SCF on a total soil concentration basis. While this value range is partly the effect of real parameter variability (soil bulk density, soil water content and soil organic carbon fraction respectively vary in studied soils by 2-, 3- and 2-fold), most of its variation stems from the uncertain organic carbon partitioning coefficient: K_{oc} estimates vary between minimum and maximum by at least 20–30-fold (in the case of musks, corrosion inhibitors, preservatives and surfactants) up around 1500-fold (synthetic oestrogen EE2 and the anti-histamine loratadine). SCF estimates nevertheless provide useful insight: the entire value range is very low to negligible for HAP, musks, nonylphenol, tetracycline and oxytetracycline, i.e. 7 out of the 14 chemicals. Out of the remaining 7 chemicals, two pharmaceuticals have low to negligible minima with maxima that remain within the lowest 10% of the empirical values used to establish the original K_{ow}–SCF relation. Ciprofloxacin has a quite constant, moderate SCF value (0.15–0.65). The four remaining compounds exhibit highly uncertain uptake behaviour with value ranges of negligible minima and moderate to high maxima. The highest maximum, that of EE2 (2.7), indeed corresponds to the upper range of the empirical values reported in Ryan et al.

The $w_{c,\ Shoot}$ estimates, one of our targets, reported in Table 3 correspond to application of the minimum and maximum SCF values to the low and high $w_{c,\ Soil,\ t0}$ values of the *A* and *B* scenarios, respectively (Table 2), thus exacerbating the $w_{c,\ Shoot}$ estimate range. For a number of chemicals (particularly loratadine), the low $w_{c,\ Soil,\ t0}$ values rendered the large SCF value ranges irrelevant. For both *A* and *B* scenarios, the lower bound $w_{c,\ Shoot}$ estimates are all negligible (less than 3 ng/g). The higher bound $w_{c,\ Shoot}$ estimate for Scenario *B* is significant for EE2 and TCPP. The latter is even very high under scenario *A* (2.7 μg/g), but it should be kept in mind that this extreme concerns only the first harvest after a decadal application.

No experimental plant uptake studies have been published for most of the non-pharmaceutical compounds in Table 3. The sole indication that the model estimates are not unrealistic is that two out of the four high SCF chemicals, i.e. methylparaben and tolyltriazole, have log K_{ow} values of 1.7–2.0, making them the only chemicals of Table 3 in the 1.0–2.5 range (the most likely to be taken up into the xylem and phloem and transported to different parts of the plant, according to Hughes et al., 2005). The other two,

Table 3
Predicted stem concentration factors (SCFs) and resulting predicted $w_{c,\ Shoot}$ mass fractions for non-ionic PPCPs.

	Minimum soil parameter value SCF		Maximum soil parameter SCF		$w_{c,\ Shoot}$ (ng/g fresh weight)			
	min K_{ow}	max K_{ow}	min K_{ow}	max K_{ow}	*A* low	*A* high	*B* low	*B* high
Loratadine	0.19	0.13	0	0	0	0.1	0	0
Ofloxacin	0.23	0.32	0.05	0.07	0.9	13.5	0	0.9
Ciprofloxacin	0.44	0.65	0.15	0.22	2.9	39.6	0.1	2.6
Tetracycline[a]	0.03	0.03	0	0	0	0.2	0	0
Oxytetracycline[a]	0	0.08	0	0	0	22.8	0	2.4
EE2	2.25	2.72	0	0	0	178.8	0	27.5
Methylparaben	1.45	1.49	0.05	0.05	0.2	22.0	0	2.4
Tolyltriazole	1.31	1.50	0.06	0.07	0.1	6.2	0	1.0
Nonylphenol	0.05	0.03	0	0	0	0.1	0	0
TCPP	1.13	1.13	0	0	0.2	2766.0	0	304.3
Galaxolide	0.06	0.04	0	0	0.3	53.0	0	5.8
Tonalide	0.08	0.03	0	0	0	7.1	0	0.8
Benzo[a]pyrene	0	0	0	0	0	0.1	0	0
Benzo[b]fluoranthene	0.01	0	0	0	0	0.2	0	0

'Soil parameter' refers to all parameters of the model of Ryan et al. other than K_{ow}: soil bulk density, soil water content, soil organic carbon fraction, but also K_{oc}. *A* and *B* refer to the scenarios (Fig. 2).

Chemicals in italics are based on concentrations given in a recent EU-wide survey (Tavazzi et al., 2012).

[a] Denotes chemicals analyzed in pig slurry, thus referring to the *Slurry* scenarios.

i.e. TCPP and EE2, have a log K_{ow} of about 3.7, but the experimental relationship of Ryan et al. indicates that uptake only clearly diminishes for chemicals of log $K_{ow} > 4.5$.

3.4. PPCP soil fraction dynamics

Table 4 presents the first-order rate constants k for removal from topsoil as well as the first-order rate constants for biodegradation and leaching (indicated as a percentage of k). k_{Plant} represents 0.2% of k at most for the neutral compounds (TCPP in ‘high’ variants of the scenarios), with k_{Plant} thus being of little significance in the soil balance, hence its value range is not presented here. The same accounts for $k_{\mathrm{Volatilisation}}$, contributing <0.1% except for the *A* scenarios high end estimate of musks (0.2%) and the exceptionally high perfluorinated chemical *A* scenarios k shares (PFOS: 52–96%; PFOA: 96–99%). Except for the latter case of PFOS and PFOA, the k values are identical among *A* and *B* scenarios. But the low–high k value ranges are broad throughout, varying by 20- to 35-fold (for PFOS/PFOA they are res. 300 and 183). The values are lowest for chemicals known to be ‘recalcitrant’ (according to the Biowin 4.10 model, US-EPA, 2012; see Supplementary information C): TCPP, loratadine, erythromycin and ofloxacin, followed by those that, according to Biowin's ultimate biodegradation model, would have a half-life of some months (EE2, ciprofloxacin, tetracycline, oxytetracycline, musks and HAP). Indeed, Table 4 indicates that biodegradation would account for most of the removal for nearly all substances and the entire k value range. $k_{\mathrm{Biodegradation}}$ even accounts for 94% or more of k except for antibiotics, piroxicam, furosemide and PFOS/PFOA. Lower shares generally indicate a significant contribution to removal by leaching (which could even come to dominate removal in the case of ofloxacin).

Sugarcane has a long annual crop cycle. As fertilisation and regrowth occur once a year, estimating $w_{\mathrm{c,\ Soil,}\ t1}$ at that time horizon (Table 4) is the most relevant ‘residual soil presence’ information for sugarcane farmers and the industry. While low-end residual mass fraction estimates, obtained by applying the high-end k values to the low end $w_{\mathrm{c,\ Soil,}\ t0}$ (Table 2) values, all equal zero after 1 year, high-end estimates exceed a couple of ng/g for about a third of the chemicals. High-end estimates are structurally (except for PFOS/PFOA) substantially higher (by 2–10-fold) under *A* as compared to *B* scenarios. Note that the *Sludge A* scenario application frequency differs (decadal instead of yearly), although the same accounts for the considered soil depth (0.3 m under this scenario, instead of 0.1 m for the others). While three out of the 27 chemicals (oxytetracycline, TCPP and galaxolide) could possibly exceed the 100 ng/g dry weight mass fraction range under scenario *A*, only TCPP could possibly exceed that level under scenario *B*.

While even for high-end estimates the removal after 1 year is nearly complete for a large majority of the PPCPs considered, Fig. 3 also indicates that the removal dynamics in the first months vary over a very wide range. There is even some overlap between the high-end removal dynamics estimation domain and the low-end domain, indicating that at its lowest removal rate estimate, the most quickly removed PPCPs still dissipate faster than the most recalcitrant PPCPs at their highest removal rate estimate.

Chemicals that would be most persistent in soil also were expected to be relatively persistent upon processing (see Supplementary information B: e.g. oxytetracycline (Combalbert et al., 2010), EE2 (Bruchet et al., 2005; Cajthaml et al., 2009)). The same holds for those supposed to be efficiently removed (e.g. nonylphenol (Soares et al., 2008)). The predicted ‘ultimate’ biodegradation (complete mineralization) cannot be readily

Table 4
Calculated first-order soil removal rate constants k (d^{-1}) value ranges per scenario.

	k				$k_{\mathrm{Biodegradation}}/k$		k_{Leaching}/k		$w_{\mathrm{c,\ Soil,}\ t1}$	
	A low	*A* high	*B* low	*B* high	*A*/*B* low	*A*/*B* high	*A*/*B* low	*A*/*B* high	*A* high	*B* high
Diclofenac	0.016	0.331	0.016	0.331	98.6	94.4	1.2	5.4	0.02	0.01
Piroxicam	0.016	0.359	0.016	0.359	99.8	87.0	0.2	12.9	0.01	0.00
Ketoprofen	0.039	0.814	0.039	0.814	99.3	95.8	0.6	4.1	0.00	0.00
Pravastatin	0.039	0.831	0.039	0.831	99.0	93.8	0.9	6.1	0.00	0.00
Loratadine	0.002	0.033	0.002	0.033	100	99.0	0.0	0.9	0.37	0.15
Furosemide	0.011	0.243	0.011	0.243	92.0	80.4	7.8	19.5	0.69	0.27
Erythromycin	0.003	0.113	0.003	0.113	94.9	57.6	4.9	41.9	10.3	2.05
Ofloxacin	0.002	0.083	0.002	0.083	68.2	39.1	31.7	60.9	27.9	5.53
Ciprofloxacin	0.006	0.148	0.006	0.148	81.1	65.8	18.8	34.2	10.9	2.15
Sulfamethoxazol	0.016	0.358	0.016	0.358	99.8	87.2	0.2	12.7	0.01	0.00
Trimethoprim	0.010	0.234	0.010	0.234	98.6	83.5	1.3	16.5	3.56	0.70
Lincomycin[a]	0.017	0.365	0.017	0.365	92.3	85.5	7.7	14.5	0.03	0.00
Tetracycline[a]	0.005	0.149	0.005	0.149	95.8	65.5	4.2	34.5	4.37	0.46
Oxytetracycline[a]	0.005	0.148	0.005	0.148	97.4	66.0	2.6	34.0	208.0	21.9
Sulfadiazine[a]	0.016	0.360	0.016	0.360	99.2	86.8	0.8	13.2	2.50	0.26
Marbofloxacin[a]	0.010	0.248	0.010	0.248	95.4	78.6	4.6	21.4	4.72	0.50
EE2	0.005	0.101	0.005	0.101	100	96.4	0.0	3.5	17.6	8.15
Methylparaben	0.020	0.400	0.020	0.400	99.7	97.4	0.3	2.5	0.02	0.01
Tolyltriazole	0.020	0.402	0.020	0.401	99.5	97.2	0.5	2.8	0.01	0.00
Nonylphenol	0.019	0.390	0.019	0.390	100	100	0.0	0.0	0.00	0.00
TCPP	0.002	0.034	0.002	0.034	99.9	94.6	0.1	5.2	2138	705.4
PFOS[b]	0.007	2.055	0.003	0.088	47.3/99.5	3.2/73.9	0.2/0.4	1.1/25.3	0.63	1.54
PFOA[b]	0.084	15.40	0.003	0.087	3.9/98.7	0.4/74.9	0.0/1.1	0.1/24.2	0.00	0.13
Galaxolide[b]	0.005	0.098	0.005	0.098	100	99.6	0.0	0.2	242.2	80.0
Tonalide[b]	0.005	0.098	0.005	0.098	100	99.6	0.0	0.2	25.1	8.28
Benzo[a]pyrene	0.005	0.098	0.005	0.098	100	100	0.0	0.0	6.48	2.57
Benzo[b]fluor.	0.005	0.098	0.005	0.098	100	100	0.0	0.0	5.92	2.34

$k_{\mathrm{Biodegradation}}/k$ and k_{Leaching}/k share are indicated as percentages. Two values are given for PFOS and PFOA, representing res. the *A* and *B* scenario shares. The high-end $w_{\mathrm{c,\ Soil,}\ t1}$ (ng/g dry weight) is obtained by applying the low-end k values to the high end $w_{\mathrm{c,\ Soil,}\ t0}$ (Table 2) values. The values presented correspond to $t_1 = 1$ year. The low-end $w_{\mathrm{c,\ Soil,}\ t1}$ at that time horizon all equal 0.

[a] Denotes chemicals analyzed in pig slurry, thus referring to the Slurry scenarios.

[b] Indicates chemical concentrations not analytically determined but based on a recent EU-wide survey (Tavazzi et al., 2012).

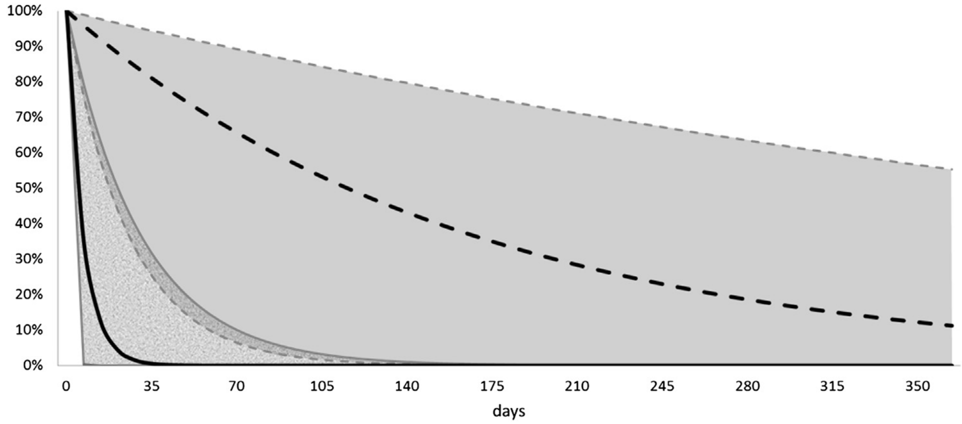


Fig. 3. High-end (textured area bounded by solid grey lines) and low-end (grey area bounded by dashed grey lines) 1 year topsoil removal dynamics domains of all PPCPs considered. Thick black (solid and dashed) lines are the median values of each domain.

compared to experimental results because the mere disappearance of the parent compound indicates biotransformation of an unknown degree, and not necessarily mineralization. However, the predicted predominant role of biodegradation in PPCP depletion in soil has been widely confirmed in the literature (Boxall et al., 2004a,b; Boxall and Ericson, 2012), although the process is not well understood (Boxall and Ericson, 2012). Looking at specific molecules, published findings on antibiotics highlight a broad range of dynamics that both in relative and absolute (semi-quantitative) terms mostly prove to be compatible with the predicted dynamics, e.g. “moderate degradation of various tetracyclines within 180 days” (Du and Liu, 2012), “only a small proportion of … ciprofioxacin, ofloxacin, … degrade even after 30 to 80 days” (Kumar et al., 2005). These studies confirm the influence of temperature on biodegradation rates. Our predicted dynamics may be conservative in some cases, e.g. erythromycin was found to completely biodegrade within 30 days at 20–30 °C temperatures by Kumar et al. (2005), and Cajthaml et al. (2009) cite several references giving evidence of rapid degradation of EE2 on temperate agricultural land. Stumpe and Marschner (2009) offer a more in-depth understanding of EE2 biodegradation and highlight the fact that EE2 degradation follows a specific mineralization pathway, largely involving phenol degraders. Degradation results may thus depend on agricultural practices. If organic residues are left on the (tropical) soil surface, fungi dominate the microbial activity, while bacteria play a greater role when substrates are mixed into the soil (Juo and Franzluebbers, 2003). Fungi prevail over bacteria when the soil pH is low, but Lienhard et al. (2013) demonstrated that in tropical soils agricultural practices that generate environmental stress (tillage) decrease fungal richness and diversity while increasing bacterial richness and diversity. Regarding the very low tillage frequency in sugarcane fields, our predicted EE2 dynamics may well be conservative for low pH soils.

In the light of recent research results on pharmaceuticals, the fact that in most cases the predicted removal dynamics are dominated by the biodegradation factor indicates that the term ‘removal’ should be qualified—abiotic process may contribute to the soil's so-called ‘biodegradation’ (Kim et al., 2011; Xia et al., 2005), but particular sorption mechanisms could preclude a chemical's biodegradation (Boxall and Ericson, 2012; Kim et al., 2011; Kumar et al., 2005; Soares et al., 2008). It may well be that in the volcanic soil studied, the predicted ‘removal’ will include a portion that has become what Boxall and Ericson call “irreversibly bound” to soil, echoing the interesting discussion on bioavailability (as well as outright analytical extractability) in Hughes and Mackay (2011). Although perhaps not as significant for other chemicals, this is of interest for pharmaceuticals since, according to Boxall and Ericson, it is one of the predominant end pathways since residues become either potentially depleted and/or inactivated as they are incorporated into humic acids during the mineralization and stabilization of soil organic matter. Though still debated, evidence suggests that such bound residues are essentially removed (Boxall and Ericson, 2012). This yet unquantifiable aspect should nevertheless not be overlooked when reporting on the sheer presence of PPCPs in soil.

3.5. PPCP leaching

While a substantial portion of some compounds have been predicted to leach to the deeper soil (>4% of total removal after 1 year at minimum to 20% or more at maximum for 6 out of 27 chemicals), Table 4 indicates that, for 12 chemicals, 5% or less may leach to below the root zone. Given these uncertain estimates, the absence of an operational model to quantitatively simulate chemical leaching and the unconsidered importance of (erratic) rainfall timing (with respect to fertilizer application), we did not attempt to transform k_{Leach} into $m_{\text{c, Seepage}}$. However, compounds that are predicted to be present in the highest relative initial soil concentrations (Table 2) belong to the latter low leaching potential group, with the exception of pig slurry bound oxytetracycline, frequently present in substantial concentrations and for which leaching may represent up to a third of removal. Regarding their relatively modest concentration, substances predicted to be of the highest mobility (erythromycin, ofloxacin, ciprofloxacin) might produce appreciable $m_{\text{c, Seepage}}$ only in the event of substantial rainfall shortly after a high rate decadal *Sludge A* application (corresponding to 5 t/ha DW of sludge, see Supplementary information C), when other, more gradual, removal processes would yet have had little effect.

Hardly any of our chemicals have so far been studied in leaching experiments. Oxytetracycline, the one compound studied in several reported experiments, is either not detected in leachates (Blackwell et al., 2009; Kumar et al., 2005) or only in scant concentrations (Kwon, 2011). This sheds some doubt on our projections for oxytetracycline and tetracycline leaching, as further put in question by Boxall et al. (2004b) who conclude, on the basis of experimental findings, that tetracyclines, macrolides and sulphonamides have a low potential to leach to groundwater, while other authors (Kwon, 2011; Zhang et al., 2011) report higher leaching of the smaller

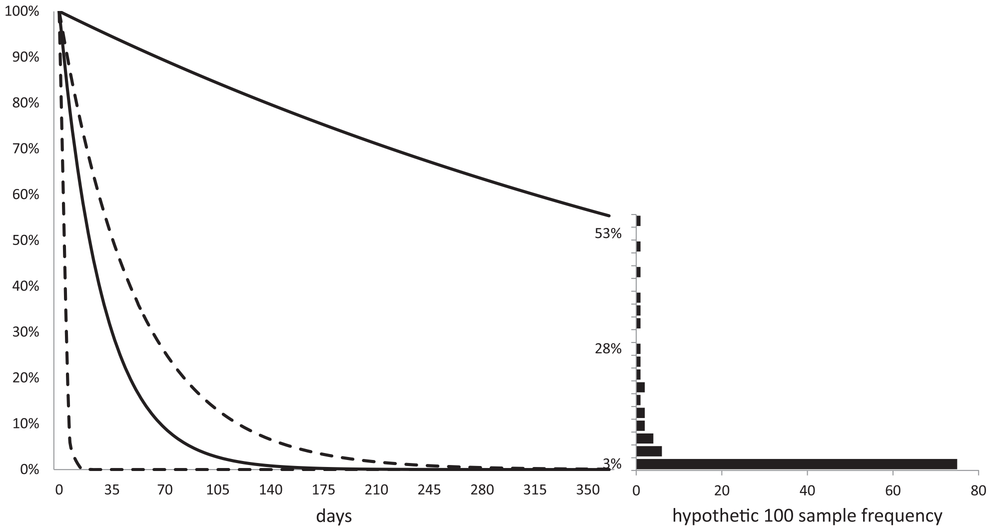


Fig. 4. Interpretation of upper and lower bounds based removal dynamics. Solid lines indicate high and low *k* TCPP dynamics, recalcitrant when compared, for instance, to nonylphenol (dashed lines). The histogram on the right indicates the frequency distribution that would be obtained between these high and low removal limits from a hundred samples after 1 year if the *k* distribution would be uniform.

sulphonamides. These latter observations contrast with the relatively low predicted k_{Leach} fractions of the two sulphonamides we considered (Table 4). A local experimental study on herbicide leaching (Bernard et al., 2005) documented leaching below predicted values, and the strong sorption characteristics of the tropical volcanic soils was identified as one explanatory factor. The present projections are therefore unlikely to underestimate the extent of leaching.

3.6. Quantitative PPCP fate assessment

This study is a first attempt to obtain quantitative estimates on PPCP fate indicators deemed relevant by decision makers and which consider the specific system characteristics as far as possible. Given the currently very limited extent of knowledge, just providing best- and worst-case possibility ranges at all levels seemed to be a sound approach, despite the obvious drawback related to the difficult interpretation of the resulting often broad value ranges. Much of the informative value of results resides in the relative differences predicted among chemicals: despite broad possibility ranges, such differences remain very appreciable for all three assessment targets.

While beyond the scope of this paper, interpretation of the target value estimates in absolute terms requires reference values whose choice depends on the stakeholder to be informed. Are indicator values that prove high in relative terms (i.e. with respect to that of other substances) to be valued as high in absolute terms? Scenario A's TCPP $w_{\text{c, Shoot}}$ was labelled ‘very high’ because of its detectability, which is the interpretation criterion for this target's most concerned stakeholder. As the detection limit of current analytical equipment is roughly a couple of ng/g, at most only two out of the 27 chemicals considered would *possibly* exceed their risk criterion under the *B* scenario. Although far from being precise, this constitutes clear and useful information and helps to design follow-up and monitoring decisions. However, such a stakeholder criterion should not preclude (1) an objective fate assessment down the industrial processing chain, or (2) the appreciation of a human health risk this could represent. For TCPP and others (see Table 1) this would require putting such risks into perspective with respect to possible background concentrations. Such *STEP 5* aspects are beyond the scope of the present paper.

Our work was focused on establishing the extremes in order to grasp the possibility range induced by uncertainty and variability. The distribution of values between these extremes remains unknown, and much care should be taken in interpreting these values. This especially concerns the soil removal dynamics. While interpretation of the first-order *k* value ranges is, for example, quite straightforward, Fig. 4 shows that the log transform of the calculation of $w_{\text{c, Soil, }t1}$ on the basis of $w_{\text{c, Soil, }t0}$ and k leads to a distribution between the extremes that is far from uniform or normal. The histogram on the right of Fig. 4 illustrates the 1 year $w_{\text{c, Soil, }t1}$ ‘residual fraction’ distribution for TCPP that would result from a hypothetical *uniform* distribution of *k* between its extremes: ¾ of the frequency distribution is located in the 1st 5% bin (up to 2.8 in the TCPP 0–55% residual fraction range), with more than 90% of the distribution having a residual fraction of less than 20%.

4. Conclusion

While the above results indicate that there would be little reason for concern about accumulation in soil under the given scenarios, they also indicate that the conclusions could change substantially when considering other sludge/slurry based fertilizer use scenarios, particularly short crop cycle market gardening. The same accounts for crop uptake regarding the predicted and reported proportionality with soil concentrations. Interpretation of PPCP leaching ‘risk’ is far less clearcut, because: (1) the uncertainty is such that no meaningful quantification can be produced as yet; (2) leaching cannot be meaningfully related to groundwater contamination in our hydrogeologic conditions; and (3) concerned stakeholders do as yet not dispose of reference values for interpretation.

The estimated indicator value ranges resulting from the proposed possibility range method may be expected to correctly reflect the cumulative effect of uncertainty and variability of each of the individual parameters considered. This of course is not the case for properties that are not explicitly considered, but whose variation may limit the conditions under which the individual models employed are valid. While the results constitute useful ‘best possible’ indications that may be appreciated by stakeholders, there are at least two sets of properties that are known to be of great influence, while they were only considered to a limited extent in the development of the models used: plant and soil properties. 25 years ago, Ryan et al. (1988) already noted that "there has been no systematic examination of plant responses to organic chemicals in soil", while citing studies that since the 1960s demonstrate that variations in uptake between species, as well as between varieties of a single species, are high. While various species were considered in the development of their model, in its assessment by Collins et al. (2006) and in the recent experimental results cited in this paper, its validity for sugarcane has yet to be confirmed. Only one other tropical C4 plant (maize) has so far been considered by some authors. The same accounts for soil properties. Soil sorption properties are known and acknowledged to result from a complex set of processes and properties. They hence vary to a very large extent among soil types, whereas the still limited number of studies have so far of course not been able to assess them broadly, experimentally, or to untangle them analytically. Given the very strong mineral sorption properties of some Réunion soils, it cannot be excluded that some of the 'best possible' indicator value ranges are not broad enough to be accurate. These observations constitute a call for future experimental studies to focus on relevant yet contrasting situations.

Clearly, research still has a long way to go before providing reliable ex-ante indicator estimates for specific situations. In the meantime, and despite its obvious shortcomings, appraisals like the one presented provide useful approximations: by informing and objectively discussing the TOC presence and fate, it could potentially unlock development which is held back by mistrust and ignorance.

Acknowledgements

This study was financially supported by the French Ministry of Food, Agriculture and Fisheries (without any involvement), special account for agricultural and rural development grant number 10004, and the local water company La Créole (that financed the sludge sample analysis). Pig slurry sampling was facilitated and carried out in collaboration with the Regional Federation of Agricultural Cooperatives FRCA.

Appendices A, B and C. Supplementary material

Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.jenvman.2014.09.015.

References

Alrøe, H.F., Kristensen, E.S., 2002. Towards a systemic research methodology in agriculture: rethinking the role of values in science. Agric. Hum. Values 19, 3–23.

Beck, A.J., Johnson, D.L., Jones, K.C., 1996. The form and bioavailability of non-ionic organic chemicals in sewage sludge-amended agricultural soils. Sci. Total Environ. 185, 125–149.

Bernard, H., Chabalier, P.F., Chopart, J.L., Legube, B., Vauclin, M., 2005. Assessment of herbicide leaching risk in two tropical soils of Reunion Island (France). J. Environ. Qual. 34, 534. http://dx.doi.org/10.2134/jeq2005.0534.

Blackwell, P.A., Kay, P., Ashauer, R., Boxall, A.B., 2009. Effects of agricultural conditions on the leaching behaviour of veterinary antibiotics in soils. Chemosphere 75, 13–19. http://dx.doi.org/10.1016/j.chemosphere.2008.11.070.

Boxall, A.B.A., Fogg, L.A., Blackwell, P.A., Blackwell, P., Kay, P., Pemberton, E.J., Croxford, A., 2004a. Veterinary medicines in the environment. Rev. Environ. Contam. Toxicol. 180, 1–91. http://dx.doi.org/10.1007/0-387-21729-0_1.

Boxall, A.B.A., Johnson, P., Smith, E.D., Sinclair, C.J., Stutt, E., Levy, L.S., 2006. Uptake of veterinary medicines from soils into plants. J. Agric. Food Chem. 54, 2288–2297.

Boxall, A.B.A., Kay, P., Blackwell, P.A., Fogg, L.A., 2004b. Fate of veterinary medicines applied to soils. In: Kummerer, K. (Ed.), Pharmaceuticals in the Environment. Springer, Berlin, Heidelberg, Germany, pp. 103–119.

Boxall, A.B.A., Rudd, M.A., Brooks, B.W., Caldwell, D.J., Choi, K., Hickmann, S., Innes, E., Ostapyk, K., Staveley, J.P., Verslycke, T., Ankley, G.T., Beazley, K.F., Belanger, S.E., Berninger, J.P., Carriquiriborde, P., Coors, A., DeLeo, P.C., Dyer, S.D., Ericson, J.F., Gagné, F., Giesy, J.P., Gouin, T., Hallstrom, L., Karlsson, M.V., Larsson, D.G.J., Lazorchak, J.M., Mastrocco, F., McLaughlin, A., McMaster, M.E., Meyerhoff, R.D., Moore, R., Parrott, J.L., Snape, J.R., Murray-Smith, R., Servos, M.R., Sibley, P.K., Straub, J.O., Szabo, N.D., Topp, E., Tetreault, G.R., Trudeau, V.L., Van Der Kraak, G., 2012. Review pharmaceuticals and personal care products in the environment: what are the big questions? Environ. Health Perspect. 120, 1221–1229.

Boxall, A.R., Ericson, J.F., 2012. Environmental fate of human pharmaceuticals. In: Brooks, B.W., Huggett, D.B. (Eds.), Human Pharmaceuticals in the Environment: Current and Future Perspectives, Emerging Topics in Ecotoxicology, vol. 4. Springer, New York, pp. 63–83. http://dx.doi.org/10.1007/978-1-4614-3473-3_4.

Bruchet, A., Castillo, L., Esperanza, M., Janex-Habibi, M.-L., Herry, G., Huyard, A., Pasanau, J., 2005. Présence et devenir des perturbateurs endocriniens dans les stations de traitement des eaux résiduaires urbaines (Angers, France).

Cajthaml, T., Kresinová, Z., Svobodová, K., Sigler, K., Rezanka, T., 2009. Microbial transformation of synthetic estrogen 17alpha-ethinylestradiol. Environ. Pollut. 157, 3325–3335. http://dx.doi.org/10.1016/j.envpol.2009.06.027.

Collins, C., Martin, I., Fryer, M., 2006. Evaluation of Models for Predicting Plant Uptake of Chemicals from Soil (Bristol, UK).

Combalbert, S., Capdeville, M.-J., Pourcher, A.-M., Budzinski, H., Dabert, P., Bernet, N., Hernandez-Raquet, G., 2010. Impact des systèmes de traitement du lisier dans le transfert des perturbateurs endocriniens et des antibiotiques vers l'environnement naturel. In: Journées Recherche Porcine. INRA-IFIP, Paris, France, pp. 291–296.

Cortés, J.M., Larsson, E., Jönsson, J.T., 2013. Study of the uptake of non-steroid anti-inflammatory drugs in wheat and soybean after application of sewage sludge as a fertilizer. Sci. Total Environ. 449, 385–389.

Daughton, C.G., Ternes, T.A., 1999. Pharmaceuticals and personal care products in the environment: agents of subtle change? Environ. Health Perspect. 107 (Suppl. I), 907–938.

Dodgen, L.K., Li, J., Parker, D., Gan, J.J., 2013. Uptake and accumulation of four PPCP/EDCs in two leafy vegetables. Environ. Pollut. 182, 150–156.

Dolliver, H., Kumar, K., Gupta, S., 2007. Sulfamethazine uptake by plants from manure-amended soil. J. Environ. Qual. 36, 1224–1230. http://dx.doi.org/10.2134/jeq2006.0266.

Du, L., Liu, W., 2012. Occurrence, fate, and ecotoxicity of antibiotics in agro-ecosystems. A review. Agron. Sustain. Dev. 32, 309–327. http://dx.doi.org/10.1007/s13593-011-0062-9.

ECB, 2003. Technical Guidance Document on Risk Assessment (Ispra, Italy).

Eriksen, G.S., Amundsen, C.E., Bernhoft, A., Eggen, T., Grave, K., Halling-Sørensen, B., Källqvist, T., Sogn, T., Sverdrup, L., 2009. Risk Assessment of Contaminants in Sewage Sludge Applied on Norwegian Soils. VKM, Oslo.

Funtowicz, S.O., Martinez-Alier, J., Munda, G., Ravetz, J.R., 1999. Information Tools for Environmental Policy under Conditions of Complexity (Copenhagen).

Funtowicz, S.O., Ravetz, J.R., 1991. A new scientific methodology for global environmental issues. In: Costanza, R. (Ed.), Ecological Economics: the Science and Management of Sustainability. Columbia University Press, New York, pp. 137–152.

Halling-Sorensen, B., Nielsen, S.N., Lanzky, P.F., Ingerslev, F., Lützhoft, H.C.H., Jorgensen, S.E., 1998. Occurrence, fate and effects of pharmaceutical substances in the environment – a review. Chemosphere 36, 357–393.

Hinsinger, P., Bengough, A.G., Vetterlein, D., Young, I.M., 2009. Rhizosphere: biophysics, biogeochemistry and ecological relevance. Plant Soil 321, 117–152.

Holling, C.S., Bailey, J.L., Vanden Heuvel, B., Kinney, C.A., 2012. Uptake of human pharmaceuticals and personal care products by cabbage (*Brassica campestris*) from fortified and biosolids-amended soils. J. Environ. Monit. 14, 3029–3036.

Hughes, L., Mackay, D., 2011. Model of the fate of chemicals in sludge-amended soils with uptake in vegetation and soil-dwelling organisms. Soil Sedim. Contam. 20, 938–960. http://dx.doi.org/10.1080/15320383.2011.620046.

Hughes, L., Webster, E., Mackay, D., Armitage, J., Gobas, F., 2005. Development and Application of Models of Chemical Fate in Canada – Modelling the Fate of Substances in Sludge-amended Soils (Peterborough, Ontario, Canada).

INERIS-ONEMA, 2011. Banque Nationale des Ventes distributeurs [WWW Document]. URL: https://bnvd.ineris.fr/.

Jelić, A., Petrović, M., Barceló, D., 2009. Multi-residue method for trace level determination of pharmaceuticals in solid samples using pressurized liquid extraction followed by liquid chromatography/quadrupole-linear ion trap mass spectrometry. Talanta 80, 363–371. http://dx.doi.org/10.1016/j.talanta.2009.06.077.

Juo, A.S.R., Franzluebbers, K., 2003. Tropical Soils: Properties and Management for Sustainable Agriculture. Oxford University Press, New York.

Kim, K., Owens, G., Kwon, S., So, K., Lee, D., Ok, Y.S., 2011. Occurrence and environmental fate of veterinary antibiotics in the terrestrial environment. Water Air Soil Pollut. 214, 163–174. http://dx.doi.org/10.1007/s11270-010-0412-2.

Kumar, K., Gupta, S.C., Chander, Y., Singh, A.K., 2005. Antibiotic use in agriculture and its impact on the terrestrial environment. Adv. Agron. 87, 1–54.

Kwon, J., 2011. Mobility of veterinary drugs in soil with application of manure compost. Bull. Environ. Contam. Toxicol. 87, 40–44. http://dx.doi.org/10.1007/s00128-011-0297-9.

Leeuwis, C., 2000. Reconceptualizing participation for sustainable rural development: towards a negotiation approach. Dev. Change 31, 931–959. http://dx.doi.org/10.1111/1467-7660.00184.

Lienhard, P., Terrat, S., Prévost-Bouré, N.C., Nowak, V., Régnier, T., Sayphoummie, S., Panyasiri, K., Tivet, F., Mathieu, O., Levêque, J., Maron, P.-A., Ranjard, L., 2013.

Pyrosequencing evidences the impact of cropping on soil bacterial and fungal diversity in Laos tropical grassland. Agron. Sustain. Dev. 1–9.

Mackay, D., Shiu, W.Y., Ma, K., Lee, S.C., 2006. Handbook of Physical–Chemical Properties and Environmental Fate for Organic Chemicals, second ed. CRC Press, Boca Raton, FL.

Mackay, D., Webster, E., 2006. Environmental persistence of chemicals. Environ. Sci. Pollut. Res. 13, 43–49.

McFarlane, J.C., 1995. Anatomy and physiology of plant conductive systems. In: McFarlane, J.C. (Ed.), Plant Contamination – Modeling and Stimulation of Organic Chemical Processes. Lewis Publishers, Boca Raton, Florida, pp. 38–68.

Ryan, J.A., Bell, R.M., Davidson, J.M., O'Connor, G.A., 1988. Plant uptake of non-ionic organic chemicals from soils. Chemosphere 17, 2299–2323.

Smital, T., 2008. Acute and chronic effects of emerging contaminants. In: Hutzinger, O., Barceló, D., Kostianoy, A. (Eds.), Handbook of Environmental Chemistry, vol. 5, Part S, vol. 1. Springer-Verlag, Berlin, Heidelberg, Germany, pp. 105–142. http://dx.doi.org/10.1007/698.

Soares, A., Guieysse, B., Jefferson, B., Cartmell, E., Lester, J.N., 2008. Nonylphenol in the environment: a critical review on occurrence, fate, toxicity and treatment in wastewaters. Environ. Int. 34, 1033–1049. http://dx.doi.org/10.1016/j.envint.2008.01.004.

Stahl, T., Heyn, J., Thiele, H., Hüther, J., Failing, K., Georgii, S., Brunn, H., 2009. Carryover of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) from soil to plants. Arch. Environ. Contam. Toxicol. 57, 289–298. http://dx.doi.org/10.1007/s00244-008-9272-9.

Stumpe, B., Marschner, B., 2009. Factors controlling the biodegradation of 17beta-estradiol, estrone and 17alpha-ethinylestradiol in different natural soils. Chemosphere 74, 556–562. http://dx.doi.org/10.1016/j.chemosphere.2008.09.072.

Tavazzi, S., Locoro, G., Comero, S., Sobiecka, E., Loos, R., Gans, O., Ghiani, M., Umlauf, G., Suurkuusk, G., Paracchini, B., Cristache, C., Fissiaux, I., Riuz, A.A., Gawlik, B.M., 2012. Occurrence and Levels of Selected Compounds in European Sewage Sludge Samples – Results of a Pan-European Screening Exercise (FATE SEES) (No. JRC76111), JRC Scientific and Policy Reports. Ispra, Italy. http://dx.doi.org/10.2788/67153.

Trapp, S., 2004. Plant uptake and transport models for neutral and ionic chemicals. Environ. Sci. Pollut. Res. 11, 33–39.

US-EPA, 2012. Estimation Program Interface Suite.

Wassenaar, T., Doelsch, E., Feder, F., Guerrin, F., Paillat, J., Thuriès, L., Saint Macary, H., 2014. Returning organic residues to agricultural land (RORAL) – fuelling the follow-the-technology approach. Agric. Syst. 124, 60–69.

Xia, K., Bhandari, A., Das, K., Pillar, G., 2005. Occurrence and fate of pharmaceuticals and personal care products (PPCPs) in biosolids. J. Environ. Qual. 34, 91–104.

Yoo, H., Washington, J.W., Jenkins, T.M., Ellington, J.J., 2011. Quantitative determination of perfluorochemicals and fluorotelomer alcohols in plants from biosolid-amended fields using LC/MS/MS and GC/MS. Environ. Sci. Technol. 45, 7985–7990. http://dx.doi.org/10.1021/es102972m.

Zhang, Q., Yang, C., Dang, Z., Huang, W., 2011. Sorption of tylosin on agricultural soils. Soil Sci. 176, 407–412.