



# **THE ASSESSMENT OF ORGANIC CONTAMINANTS IN MATERIALS SPREAD ON LAND**

## **FINAL REPORT TO SEPA FROM WCA**

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## EXECUTIVE SUMMARY

For decades organic materials that would otherwise need to be disposed of have been spread to land, conferring many benefits to soils. However, chemicals including pharmaceuticals, veterinary medicines, personal care products and industrial chemicals, hereafter referred to collectively as contaminants, in organic materials that may be recycled to land are becoming an increasing concern. These organic materials can provide agronomic benefits due to nutrient and organic matter content and may include sewage sludges, animal manures and composts. However, there is a balance to be struck in using these materials between the benefits and potential human and environmental health risks from the contaminants present in them.

This project has refined the findings of a previous desk-based SEPA risk assessment through the identification, prioritisation and measurement of contaminants in organic materials applied to land in order to inform the risk-benefit balance described above. The measurement of prioritised contaminants in UK organic materials destined for land application means that risk assessors no longer need to rely upon data from other parts of the globe and so provides a higher degree of relevance in assessments compared to previous work.

Contaminants were selected for monitoring from a list of >200 contaminants previously identified in sewage sludge, animal manure and compost based on initial screening of their persistence and bioaccumulation potential, followed by an environmental risk ranking exercise. For each type of organic material, contaminants with the highest risk ranking that met the initial screen for persistence and/or bioaccumulation potential in soil were taken forward. The number of contaminants that were monitored was based on level of risk and resources available for the project.

Samples of sewage-derived biosolids were provided by Scottish Water and compost samples were provided by commercial producers of plant/ and plant/food-derived compost. A number of farms in England and Scotland provided samples of manure from pigs, cattle and poultry in addition to information about their usage of the veterinary medicines being assessed as the prioritised contaminants for these types of organic material. Materials were sampled in the specific condition in which they are applied to land in Scotland and England.

Most priority contaminants measured in biosolids from two Scottish sewage treatment plants (STPs) occurred at lower concentrations than previously reported in the literature for unprocessed sewage sludge. A similar trend was also observed for the manure and compost samples. The synthetic musk fragrance chemical HHCB (galaxolide) was the contaminant measured at the highest concentrations in biosolids (up to 42 mg kg<sup>-1</sup> dry weight). Soil amendment scenarios were run in the refined risk assessment that considered application rates dependent on the organic material and either a one year timespan with a single application or a ten year timespan with annual applications. In the case of HHCB, the assessment for application of biosolids following long term application to land indicates a potential risk to soil organisms, with risk characterisation ratios (RCRs) up to 6.2 for the longer term application scenario for biosolids generated from anaerobic digestion (an RCR >1 indicates there is a risk). Ciprofloxacin has also been identified as posing a potential risk to soil from biosolids applications for modelled scenarios with multiple applications. However,

the derivation of the threshold for adverse or toxic effects (the predicted no effect concentration, PNEC) for this substance is uncertain and likely overly precautionary; this means there is considerable uncertainty regarding the actual risk posed. It should also be noted that there is no consideration of removal by biodegradation following application to soil in this assessment, which adds significant conservatism to the estimated risks for HHCB and ciprofloxacin.

Lower concentrations measured in biosolids in this project compared with the literature may be due to analysis of treated material compared to untreated sludge in previous studies, or alternatively reduction in the use of the prioritised contaminants since those studies were published. Differences in results between the sludges from the two STPs may be due to variation in input or the type of technique used for sludge treatment. Further work is required to elucidate these observations.

In most scenarios assessed by this project, no risks were identified for veterinary medicines to soil and human health from the use of animal manures on land. It was found during the sample collection phase of the project that veterinary medicine use by food producers was low and undertaken only as a last resort to safeguard animal welfare. Because samples were collected only from food producers that had confirmed use of the veterinary medicines in the past six months, there was an inherent bias in the data collected and most typical manures would not be expected to contain any of the medicines investigated. Only in the case of the most conservative scenario considered (multiple applications as a surface dressing at the highest applicable rates) was a small potential risk to soil health identified for enrofloxacin and sulfamethoxazole measured in poultry manures. However, there are significant conservative assumptions in this assessment including no consideration of chemical losses from soil over time and some considerable uncertainties in the PNECs used.

Overall, this project indicates there is only a limited potential for risks from organic contaminants in organic materials applied to agricultural soil. However, this limited dataset only presents a snapshot for a small number of contaminants. The results indicate the potential need for monitoring of certain medicines and personal care products, such as synthetic musks, with respect to exposure in agricultural soils.

Many of the PNECs used to characterise the environmental risks of contaminants applied to land in organic materials have low levels of certainty. These are likely to be precautionary but are an area for which obvious refinement could be made, especially for the human and veterinary medicines.

Human health risk assessment, based on dietary exposure and using data generated from analysis of materials applied to land in this project, suggests that there is a low level of risk to health arising from this exposure pathway for the selected contaminants at the concentrations measured in biosolids, manure and compost.

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# 1 INTRODUCTION

The Scottish Environment Protection Agency (SEPA) has taken a stepwise approach to identify the organic contaminants, hereafter referred to simply as contaminants, in material applied to land in Scotland that pose the greatest risks to human health and/or the environment. Previous work has undertaken a literature search and risk-based prioritisation to identify those contaminants present in various types of material applied to land<sup>1</sup>; contaminants modelled spatially to assess risks levels were tetracycline, ivermectin, triclosan, benzo-a-pyrene, galaxolide (HHCB), polybrominated diphenylethers, polychlorinated biphenyls (PCBs) and dioxins and dioxin-like PCBs, of which HHCB, ivermectin and tetracycline were deemed of greatest concern (see section 1.2, Table 1.1). This project represents the next stage of this process, which is focussed on updating the knowledge base from published literature and most importantly, seeking to confirm previous findings by measuring concentrations of the prioritised contaminants in materials applied to land identified as posing the highest potential human and environmental risks.

This project is focussed on the organic materials identified as the most important for application to land in Scotland and includes agricultural manures and slurries, sewage sludge, compost, digestates and some ashes (although these are not organic). Additional financial and technical support provided by the Environment Agency allowed a greater number of manure and slurry samples to be collected than had initially been envisaged when scoping the project. This allowed sampling of manures and slurries from a much wider range of pig, poultry and cattle producers. These additional samples were collected from farms in England, but it is expected that veterinary treatments applied by English commercial producers will be similar to those applied in Scotland as government guidance, veterinary advice and food standards between England and Scotland are closely aligned.

Different contaminants can occur in each of the materials, e.g. veterinary medicines in animal manure, and human medicines and personal care products (PCPs) in sewage sludges, so the focus here was only to analyse for the contaminants most likely to be found in each organic material<sup>2</sup>.

## 1.1 Project aims and objectives

The project objectives are:

- Objective 1: Carry out representative sampling and analysis for high risk contaminants in a range of different organic materials that are frequently spread on land in Scotland.
- Objective 2: Use typical concentrations of contaminants in each material analysed to estimate a maximum safe spread rate. For each material, comment on the likelihood of this rate being exceeded.

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<sup>1</sup> <https://www.sepa.org.uk/media/138585/ep1302-sepa-organic-chemicals-nc.pdf>

<sup>2</sup> It is also important to note that different waste treatment technologies also influence the form and concentrations of contaminants in organic waste materials (Legros et al. 2017). However, financial and time constraints in this project mean that it is unlikely that enough samples will be collected from enough materials to identify such differences.

- Objective 3: Determine whether spreading and/or land management practise is likely to affect level of risk posed by contaminants in materials spread to land.

Specifically, these objectives will be achieved through delivering to the following aims, which are:

1. To determine typical concentrations of the highest risk contaminants in representative samples of organic materials that are spread on land in Scotland.
2. To estimate maximum safe spread rates for these organic materials on the basis of typical concentrations of contaminants found in them.
3. To determine if spreading and/or land management methods need to be altered due to contaminant concentrations in spread materials.

How the project aims and objectives are to be met are covered in the following sections, with an overarching strategy detailed below.

## **1.2 Background**

Increasing numbers of synthetic chemicals are being monitored for and detected in organic materials that may be recycled to agricultural land (e.g. USEPA 2009a). This is due to greater awareness of potential risks and at the same time, analytical methods are continually improving and detection limits are getting lower (e.g. Schwesig et al. 2011). It is therefore important to provide context to the detection of these contaminants in organic materials going to land by making the distinction between hazard and risk. Detection alone does not always indicate potential risk to environment or human health. Furthermore, some of the research performed on presence and fate and behaviour of contaminants in organic materials may not necessarily reflect genuine operating conditions. It is essential that any review and challenge to current practices needs to be robust and evidence-led. Furthermore, it is critical that regulatory management actions to ensure the sustainability of organic material recycling to land delivers specific and measurable needs and benefits while ensuring environmental protection.

'Benchmarking', activities to investigate the presence and concentration of previously unidentified contaminants in materials applied to land, is currently ongoing in many global regulatory jurisdictions, including Australia (New South Wales Environment Protection Agency are currently reviewing all the chemicals they routinely monitor in biosolids; Mike McLaughlin pers. comm.), Canada (CCME 2010) and the UK<sup>3</sup>. The reasons for this are largely similar for all jurisdictions; there is uncertainty with regard to the environmental and human health risk associated with contaminants in materials destined for application to land with the possibility of effects that manifest through terrestrial exposure and via animal and human food chains. It is also unclear to what extent risks to the environment and human health are enhanced due to persistence and accumulation of contaminants through repeated applications and these investigations are seeking to improve knowledge of this.

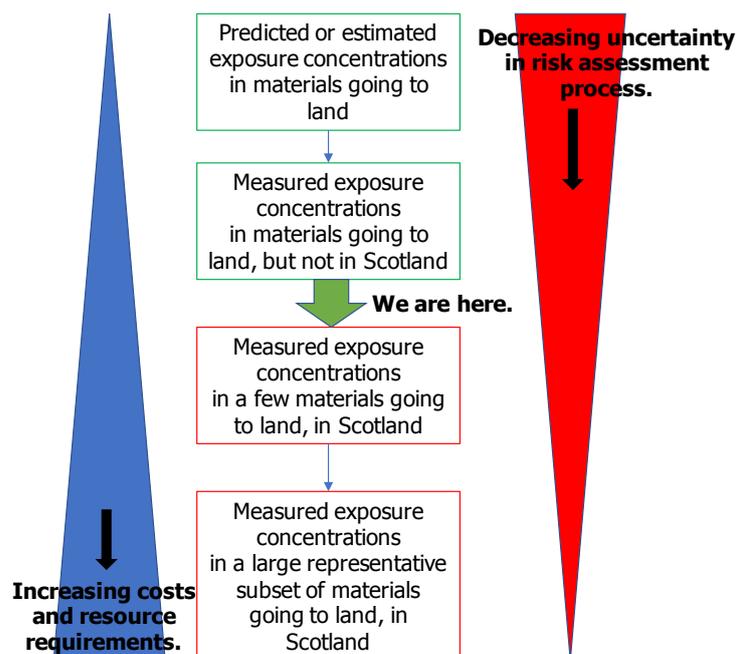
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<sup>3</sup> UKWIR have recently let a project on "Biosolids to Market. A strategic proposal to explore the threats to biosolids to land – now and in the future".

There is a clear need to deliver an assessment in this report based on current and future potential exposure that accounts for the main contaminants of relevance. Some recent studies eg Rigby et al. (2015) focussed on contaminants that are of concern to human health via the food chain and not to the wider environment. In addition, this current study has included animal manures and human and veterinary medicines. Consideration of animal-derived manures and slurries is important because these materials account for 95% of the organic material applied to land in Scotland (SEPA 2014).

In Australia, the New South Wales Environmental Protection Authority (NSWEPA) and New South Wales Office of Environment and Heritage, Environment Protection Science Branch have recently (2015 and 2016) completed reviews of potential human and environmental health risks from contaminants in biosolids and mixed waste composts (i.e. Mechanical Biological Treatment Compost-Like Outputs, MBT CLO). wca undertook the risk-based review of the chemicals in biosolids on behalf of NSWEPA (Stutt and Merrington 2017) and a key finding from this research was that the risk posed by chemicals currently monitored in New South Wales (e.g. trace metals and banned organo-chlorine pesticides) is low when considering exposure arising from land application of biosolids. Following their risk-based review, wca recommended that other contaminants, for example triclosan and HHCB (galaxolide), should be monitored as a priority based on predicted risk to the terrestrial environment. For contaminants for which there was only limited measured data available, such as benzo(a)pyrene (BaP) (taken as being representative of PAHs as a group), cashmeran, decamethylcyclopentasiloxane, di(2-ethylhexyl)phthalate (DEHP), hexabromocyclododecane (HBCDD), perfluorooctanoic acid (PFOA) and tonalide, as well as microplastics, there were large uncertainties in the predictions of potential risk, meaning that further validation was required for these contaminants.

Such further validation marks a refinement in risk assessment processes that follow an initial screening or precautionary assessment using predicted data or measured data with a relatively high level of uncertainty (i.e. not specifically from the geographical region of interest). In order to take forward the assessment of materials applied to land in Scotland (building on the SEPA 2014 project) this validation is also necessary, as shown in Figure 1.1.



**Figure 1.1 Schematic of balance between regulatory certainty and costs and resource requirements with regard to measuring chemical contaminants in organic materials going to land in Scotland.**

The 2014 SEPA report identified priority contaminants in organic materials that are spread on land that presented potential environmental and human risks. Table 1.1 shows the waste materials and the priority contaminants in them identified from the 2014 screening exercise.

It is important to note that the 2014 SEPA study was limited because virtually no information about the levels of contaminants in wastes which are applied to land in Scotland was available. Much of the information used to prioritise the chemicals came from Europe, the USA and Australia. However, using information from other areas likely to have broadly similar chemical usage allowed SEPA to identify contaminants which might be likely to cause problems if they are allowed to accumulate in soils through the repeated application to land of organic materials containing traces of them.

**Table 1.1 Waste materials assessed and potential contaminants of concern identified, from the 2014 SEPA Report.**

Material	Determinand							
	Tetracycline	Ivermectin	Triclosan	HHCB	BaP	Dioxin <sup>1</sup>	Doramectin	PBDEs
Sewage Sludge								
Organic manures								
Compost wastes								
Digestates								
Papermill sludge								
Ashes <sup>2</sup>								

<sup>1</sup>Also includes Dioxin-like PCBs

<sup>2</sup>Includes meat and bone meal ash (MBMA) and furnace bottom ash (FBA)

Since the 2014 SEPA report, the assessment criteria for many of the chemicals previously assessed for both the terrestrial environment (Predicted No Effect Concentrations) and human

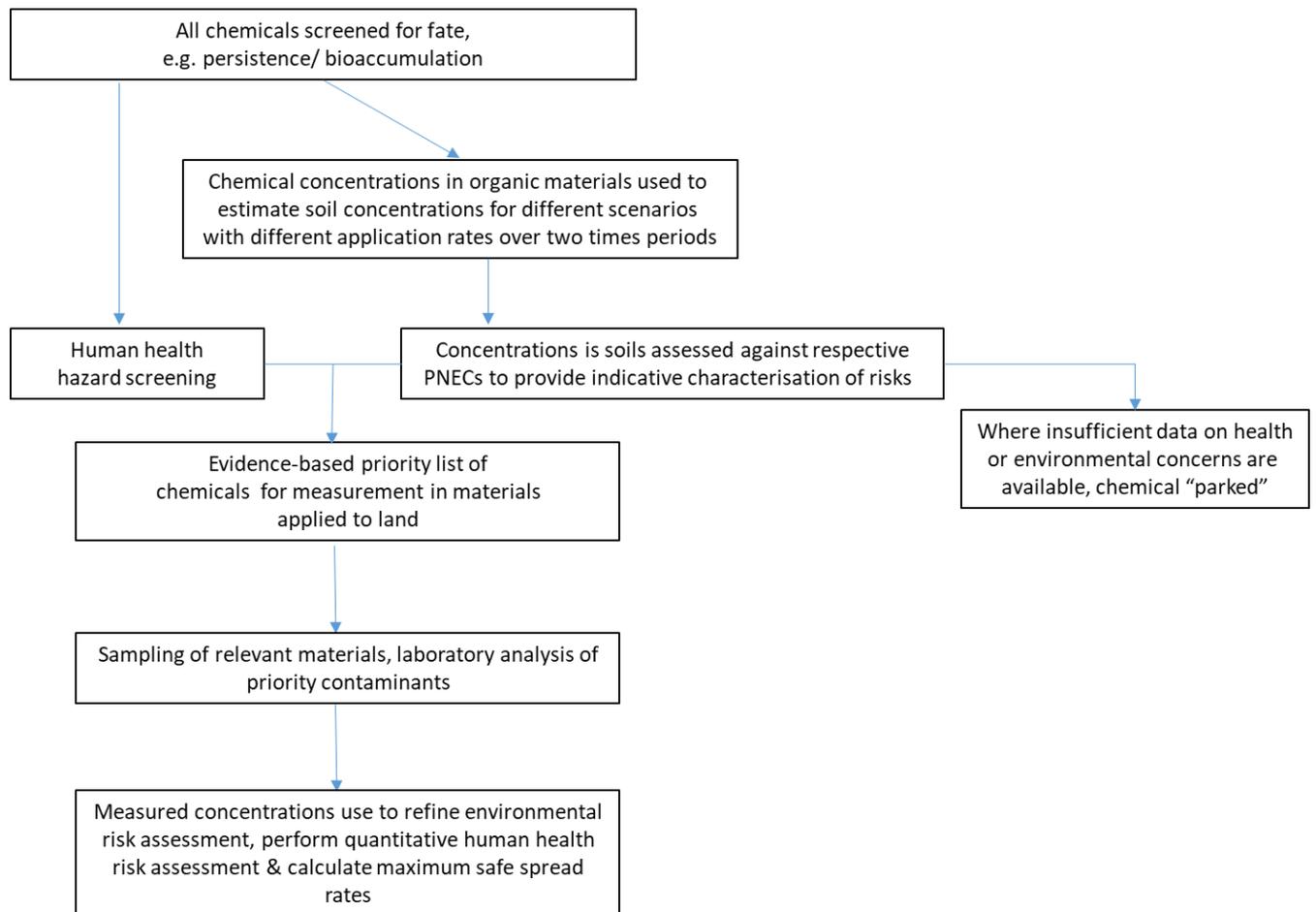
health (Health Criteria Values) have been developed further. For example, the Environment Agency (2017) has recently published revised soil screening values for assessing ecological risk to soil organisms. These guidelines are of direct relevance as they have been specifically developed for screening the risks to soil from chemicals released through the land spreading of waste-derived materials.

Furthermore, additional studies to determine the environmental concentrations of chemicals in organic materials that may be applied to land will provide additional relevance to exposure scenarios where data are still limited (e.g. Kullik and Belknapy 2015).

The risk assessment paradigm for regulation and followed in this report considers chemicals and their risk individually, whereas in reality soils, soil organisms, and crops that are grown in agricultural soils are exposed to a mixture of contaminants. Although approaches to mixture assessment are yet to be accepted in regulation, this fact adds another source of uncertainty to any risk assessment.

### **1.3 Report structure**

Section 2 of this report outlines the project strategy followed and the methodology used to search the literature, review and collate relevant information; the chemical prioritisation and generic risk screening exercise; and how the risk assessment is to be refined. Section 3 details the results from this screening and prioritisation methodology and Section 4 presents the sampling and analytical results from the sampling exercise. The potential risks from organic materials spread to land now and in the future assuming little change to current practices, are discussed in Section 5, before conclusions are given in Section 6 and recommendations in Section 7. Figure 1.2 provides a schematic detailing the overall approach to the project.



**Figure 1.2 Schematic of the key process steps followed in this project.**

## 2 METHODOLOGY

This section describes the strategy used for identifying contaminants likely to be present in organic wastes that may be applied to land in Scotland. In addition to the identification of contaminants and key physico-chemical properties affecting their behaviour and fate some of the remaining challenges in the identification of contaminants found in organic wastes are also flagged. This section fulfils objective 1 and part of objective 2, as identified in Section 1.

An Excel™ spreadsheet (24\_11\_17\_Priority Chemicals for SEPA\_updated) has been produced to accompany this project report and represents a repository for the information collated in this section. The references used in this spreadsheet are presented at the end of this report.

The potential for contaminants detected in waste-derived materials to pose a risk following application to agricultural land is assessed in two stages with an initial screen based on fate and behaviour properties followed by preliminary environmental risk assessment and screening of potential human health hazard.

The spreadsheet accompanying this report details groups of contaminants and individual contaminants identified from the literature search quantified in high relevance studies along with physico-chemical and environmental fate data. For those contaminants likely to persist in organic material/soil and/or accumulate in the food chain the spreadsheet details predicted no effect concentrations (PNECs) and health criteria values (HCVs), which are used in semi-quantitative assessment of risks to the environment and human health screening, respectively. The sources of these PNECs and HCVs are given in the spreadsheet, which is constructed to allow the user to change these values if so required to perform a different type of assessment. It is important to stress that this assessment is indicative and not definitive as numerous assumptions and caveats apply (all of which are detailed in the relevant sections of the report); it should also be noted that most assumptions are conservative in nature. For example, in the selection of concentrations in biosolids to be used in the assessment a hierarchy of preferences has been followed:

- Scottish or wider UK data;
- 90<sup>th</sup> percentiles (typically used as a reasonable worst case in exposure assessments; see ECHA 2016);
- Maximum concentrations;
- Means, where only these were available.

This conservatism is reasonable and conforms to the classic risk assessment paradigm in that early screening is generally 'reasonable worst case' with regard to assessment inputs ensuring limited false negatives (Type II errors) but enabling refinement when better data becomes available.

### 2.1 Literature screening strategy

The search strings used for the literature search and the databases searched, along with the number of 'hits' are shown in Table 2.1. The strings used were identical to the searches conducted in 2014, except for the exclusion of the molasses search strings, due to this material

not being identified as a risk in the 2014 report. Also, seven additional search strings (italicised in Table 2.1) were run that were not performed in 2014 to extend the scope of the literature survey and to include composts.

**Table 2.1 Search strings and results from the literature searching**

<b>Search term</b>	<b>TOXLINE<sup>1</sup></b>	<b>Thomson Innovation<sup>2</sup></b>
manure AND "organic chemicals"	36	5
animal manure AND organic contaminants	7	20
manure AND pops <sup>3</sup>	0	1
manure AND veterinary medicine	36	35
biosolids AND animal manure AND organic contaminants	1	3
biosolids AND manure AND organic chemicals	0	22
biosolids AND manure AND pops	0	0
biosolids AND manure AND veterinary medicine	0	2
sewage sludge AND animal manure AND organic contaminants	0	2
sewage sludge AND manure AND organic chemicals	1	155
sewage sludge AND manure AND pops	0	0
sewage sludge AND manure AND veterinary medicine	0	3
abattoir waste	11	29
compost AND land	28	406
dredging	121	1466
dredging AND land	6	122
"food waste" AND land	79	79
food waste AND land	79	329
paper waste AND land	61	417
"paper waste" AND land	61	1
septic tank sludge	9	45
(waste wood OR waste bark OR waste plant matter) AND (land)	24	197
((sewage sludge OR biosolid OR manure OR waste wood OR waste bark OR waste plant matter) AND (Scotland))	43	97
<i>((biosolid OR sludge) AND (chemical))</i>	661	2475*
<i>((biosolid) AND (chemical))</i>	34	30
<i>((sewage sludge) AND (contaminant))</i>	29	251
<i>((biosolid OR sludge) AND (persist* OR bioaccum* OR ecotox*))</i>	144	388
<i>((biosolid OR sludge) AND (PEC OR PNEC OR HCV OR partition coefficient))</i>	6	40
<i>Compost* AND contaminant</i>	325	478
<i>digestate* AND contaminant</i>	6	19

\*Cannot download >1500 results from Thomson Innovation.

<sup>1</sup> Years searched: 2014 – 2017

<sup>2</sup> Years searched: 2014 – 2017

<sup>3</sup> Persistent Organic Pollutants

The organic materials forming part of the search strings listed above were selected on the basis of the volumes applied to agricultural soil in Scotland, as determined by advice from SEPA.

### **2.1.2 Information review and collation**

A total of 5622 potentially relevant articles were initially identified (excluding 2475 results that could not be downloaded from Thomson) and these were reduced to 4340 following the removal of duplicates and obviously irrelevant papers. The number of studies requiring further consideration was then further reduced by reading through the abstracts and applying specific criteria related to the project aims. Specifically, on the basis of their abstract, papers were selected that contained (or where thought likely to contain) one or more of the following:

- Prediction or measurement of an organic chemical or contaminant in an organic waste that might be used in Scotland (sewage sludge, composts, digestates, manures & non-agriculturally derived organic materials, e.g. papermill sludges, MBT CLO, distillery wastes, food wastes, waste wood);
- Derived effect concentrations, preferably terrestrial PNECs or HCVs;
- Environmental fate and behaviour data on contaminants identified in relevant materials, preferably in terrestrial environments.

Of these papers, 59 were identified for closer scrutiny beyond reading the abstract. In addition to these papers, regulatory websites in Europe, North America (Environment Canada, USEPA) and Australia (CSIRO, Queensland and NSW Government Agencies) were also searched for 'grey literature sources' including monitoring surveys, registration dossiers (for veterinary medicines, pharmaceuticals, etc.), risk assessments (such as those used for the Existing Substances Regulation<sup>4</sup>, Quality Protocols Programme<sup>5</sup>), research programmes and position statements related to the project objectives.

### **2.1.3 Literature draft weighting criteria**

Weighting criteria have been developed to assess all the literature identified by the above search strings and used to assign a score of 1-4 to each reference. These criteria and scoring are detailed below:

1. A report with this score will be a regulatory report or survey with extensive monitoring data from multiple sites/countries. Any sources that contain Scottish data will be given this score;
2. A study with a score of two will have been peer reviewed and published in a high quality journal. This can be applied to both reports and survey data;
3. A reference that is considered less reliable will be assigned a score of 3. An example of when this score will be applied is a survey where a limited number of sites have been investigated and perhaps only a paper focussed upon a method or an academic study undertaking chemical "stamp collecting";

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<sup>4</sup> <http://esis.jrc.ec.europa.eu/index.php?PGM=ora>

<sup>5</sup> <http://www.environment-agency.gov.uk/business/sectors/142481.aspx>

4. This score will be assigned to literature that is not considered relevant to this project.

## 2.2 Fate Screening

An initial screening for the contaminants identified from the literature was performed by a review of physico-chemical properties and environmental fate and behaviour characteristics. The following criteria<sup>6</sup> were used to screen out chemicals from further consideration that were considered unlikely to persist and accumulate in organic materials and soils:

- Log K<sub>ow</sub> <4.5 (to indicate a lack of bioaccumulation potential and lower sorption potential to organic matter);
- Classification as readily or inherently biodegradable;
- Half-life <120d in soil, sludge or compost<sup>7</sup> (ECHA 2016).

Contaminants meeting any of these criteria are considered unlikely to accumulate in soil following application of organic material and are screened out from further consideration, bar some exceptions described in the next paragraph. Those not meeting these criteria were taken forward to the next stage of the assessment and are considered further in Sections 2.3 and 2.4.

For pharmaceuticals and veterinary medicines a slightly different screening approach was used to align with the triggers for undertaking a terrestrial risk assessment during registration of a pharmaceutical active ingredient in the EU. Briefly, the triggers, following recognised laboratory test guidelines, (for a "Tier B" Terrestrial assessment) are:

- an organic carbon-water partition coefficient ( $K_{oc}$ ) >10,000 L kg<sup>-1</sup> **or**
- an adsorption coefficient ( $K_d$ ) > 3700 L kg<sup>-1</sup> **or**
- if the active ingredient is not shown to be readily biodegradable

The partition coefficient between octanol and water, namely a Log K<sub>ow</sub> of >4.5, is used as a relatively conservative proxy for  $K_{oc}$  of >10,000 L kg<sup>-1</sup>.

## 2.3 Environmental risk screening

A simple generic environmental risk assessment has been performed for those contaminants selected by the initial physico-chemical screen and for which PNECs are available (as per Figure 1.2). The references for the PNECs are all provided in the reference section at the end of this report.

The PNECs are taken from a range of regulatory jurisdictions, with a variety of protection goals and regulatory purposes, but are suitable for use in this precautionary generic level risk assessment (Environment Agency 2017). For some of the contaminants, it has not been possible to obtain a suitable PNEC (see spreadsheet, PNECs tab, marked n/a in column C),

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<sup>6</sup> Contaminants' vapour pressures were also retrieved but treated only with secondary importance and were not used to screen out chemicals on the basis of a potential to volatilise from soil; this conservative approach was taken as partitioning occurs between different compartments in soil (e.g. partitioning to organic carbon may retard tendency to volatilise).

<sup>7</sup> This includes biological and chemical removal processes (e.g. biodegradation and hydrolysis)

and these contaminants are 'parked' for further investigation as new information becomes available (these 'parked' chemicals are shown on a separate tab in the Excel™ spreadsheet).

Exposure concentrations of the contaminants in soils following application of the specific organic source material were calculated from a generic use scenario for a generic soil considering two application rates over two separate time periods. Table 2.2 details the parameters and their origin that have been used to calculate the exposure concentrations of contaminants over an area of 1 ha. The exposure concentrations in the soils were calculated for each of four scenarios for each material:

- 1 year application of 8 tonnes per hectare;
- 1 year of 50 tonnes per hectare;
- 10 years of 8 tonnes per hectare per year; and,
- 10 years of 50 tonnes per hectare per year.

These estimated concentrations of the chemicals from each scenario were then compared to the respective PNECs and risk characterisation ratios (RCRs) were calculated<sup>8</sup>. The results of this assessment are given in Section 3.1.

No contaminant losses were assumed over the two spreading periods. This is a very conservative assumption, especially in the cases of the 10-year scenarios, as it disregards degradation, leaching, volatilisation and other factors like soil ageing of organic chemicals. In addition, it should be noted that a further conservative assumption is made in that the organic material is only applied as a surface dressing and not ploughed in. Higher contaminant concentrations in soil are expected in surface dressing scenarios as the material spread is not 'diluted' by being mixed through the soil. However, both of these assumptions are in line with a reasonable worst-case risk assessment paradigm.

When undertaking such an assessment it is assumed that at all times 'good practice' has been followed in organic material use. In a generic screening level assessment, it is not practically feasible to consider other types of behaviour.

**Table 2.2 The parameters and assumptions used in the estimation of exposure concentrations of organic chemicals in soils amended with organic materials for this project (generic scenario)**

Parameter	Value	Reference
Application rate of biosolids, as dry tonnes ha <sup>-1</sup>	8 and 50 t ha <sup>-1</sup>	Environment Agency 2009
Bulk density of soil receiving organic material	1.7 g cm <sup>-3</sup>	Environment Agency 2010
Depth of incorporation	0.05 m	EUSES <sup>9</sup>
Area of incorporation	1 ha	

<sup>8</sup> RCR = PEC/PNEC, value = or > 1 indicates potential risk

<sup>9</sup> <https://ec.europa.eu/jrc/en/scientific-tool/european-union-system-evaluation-substances>

There are several assumptions made in performing this environmental screening assessment, as presented here and in the accompanying spreadsheet, that may be considered to influence the assessment. Specifically, these include:

- No account has been taken for the ambient background concentrations of contaminants already present within the soil or deposited from airborne particulate matter to the soil. This would include some of the organics such as PAHs and likely results in a lack of conservatism;
- No account has been taken for degradation or loss of any of the contaminants from the waste derived materials or in the amended soils. This is likely to have a precautionary influence on the outcome;
- Generally, maximum or 90<sup>th</sup> percentile concentrations of contaminants in the organic materials have been used for the derivation of the predicted environmental concentrations (PECs), this is reasonable worst case;
- No account for bioavailability has been taken for the contaminants in this report;
- The organic material is not ploughed in.

## 2.4 Indicative human health chemical ranking

Risk assessment for human health has the objective of assessing dietary exposure resulting from the presence of contaminants in organic materials applied to agricultural land. This considers the potential for persistent organic pollutants with high bioaccumulative potential present in materials to transfer and accumulate through the food chain and increase dietary exposure to these contaminants. Full quantitative risk assessment would require a detailed modelling exercise which is beyond the scope of this project. Instead an indicative human health screening has been undertaken for the selected contaminants, based on a ranking system comprising an assessment of toxicity and exposure potential.

Contaminants are ranked by their toxicological potency according to a scoring scheme devised for Health Criteria Values (HCVs) and other similar measures of toxicological potency (ADIs<sup>10</sup>, RfDs<sup>11</sup>). For substances with a readily available HCV or similar accredited level of acceptable human exposure, scores are allocated to each contaminant according to the following scheme for oral HCVs (Table 2.3).

**Table 2.3 Potency scoring scheme for contaminants with HCVs**

Health Criteria Value ( $\mu\text{g kg}^{-1} \text{ bw day}^{-1}$ )	Ranking Score
< 0.01	10 (high hazard)
1 to 0.01	8
1 to 10	6
10 to 100	4
>100	2 (low hazard)

<sup>10</sup> Acceptable Daily Intake (ADI is a measure of the amount of a specific substance (originally applied for a food additive, later also for a residue of a veterinary drug or pesticide) in food or drinking water that can be ingested (orally) on a daily basis over a lifetime without an appreciable health risk.

<sup>11</sup> Reference Dose (this terminology is commonly used by the US Environment Protection Agency for oral exposure; Reference Concentration, RfC, is used for inhalation exposure)

### 3 RESULTS OF PRIORITISATION EXERCISE

In this section, the results from the initial fate and behaviour screening and also the outcomes from the environmental risk screening and the indicative human health hazard ranking are presented. A summary is provided at the end of this section including the list of prioritised chemicals, the materials in which they may present a potential risk when applied to land and a summary of the reasoning for their selection.

#### 3.1 Chemical prioritisation

Using the criteria described in Section 2.2, contaminants identified as being present in materials destined to be applied to agricultural land were screened for their potential to persist and/or bioaccumulate. Here we indicate the contaminants that are then taken forward to the next level of assessment.

##### 3.1.1 Chemicals 'screened in'

Following the screening exercise, from the initial list of 229 chemicals found in organic materials for which screening was possible, 65 contaminants were deemed likely to persist in amended soils. The contaminants in Table 3.1 are those screened in for further assessment (37 contaminants). Where groups of compounds had initially been identified in the occurrence data, generally only one contaminant was taken forward as being representative of that group (for example BaP rather than all PAHs) to ensure the list was a manageable size (those represented in a group shown in italics in table 3.1). Decamethylcyclopentasiloxane (D5) and Dodecamethylcyclohexasiloxane (D6) were also screened in due to the on-going proposed restriction of their use in wash-off applications.

**Table 3.1 Contaminants screened into risk assessment**

Substance	Category and representative (if relevant)	Substance	Category and representative (if relevant)
Alpha- chlordane		Sulfamethoxazole	
<i>Benzo(a)pyrene (BaP)</i>	PAH; used as representative	Thiabendazole	
Cashmeran		<i>Pyrene</i>	PAH
Decabromodiphenyl ethane (DBDPE)		Ivermectin	
<i>Decamethylcyclopentasiloxane (D5)</i>	Siloxanes	Cypermethrin	
<i>Di(2-ethylhexyl) phthalate (DEHP)</i>	Phthalates	Enrofloxacin	
Dichlorodiphenyl dichloroethane (DDD)		1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE)	
Dichlorodiphenyldichloroethylene (DDE)		di(2-ethylhexyl)-2,3,4,5-tetrabromophthalate (TBPH)	
Diclofenac		Hexabromobenzene (HBB)	
Dieldrin		perfluorodecanoate	
Dodecamethylcyclohexasiloxane (D6)	Siloxanes	PFNA	

Substance	Category and representative (if relevant)	Substance	Category and representative (if relevant)
Hexabromocyclododecane (HBCD)		Sulfanilamide	
HHCB (galaxolide)		Sulfathiazole	
PCDD/DFs		<i>Perylene</i>	PAH
<i>BDE-47 (2,2',4,4'-tetrabromodiphenyl)</i>	PBDEs; Representative = sum of BDE-47, BDE-99 and BDE-209	Naproxen	
<i>BDE-99 (2,2',4,4',5-pentabromodiphenyl)</i>		Ofloxacin	
<i>BDE-153 (2,2',4,4',5,5'-hexabromodiphenyl)</i>		Trimethoprim	
<i>BDE-209 (decabromodiphenyl)</i>		Chlorotetracycline	
<i>Penta BDE</i>		Clarithromycin	
PFOA		Sarafloxacin	
PFOS		Virginiamycin	
Tonalide		Tamoxifen	
Triclocarban		<i>Benzo(a)anthracene</i>	PAH
Triclosan		<i>Benzo(b)fluoranthene</i>	PAH
Ciprofloxacin		<i>Benzo(e)pyrene</i>	PAH
Oxytetracycline		<i>Benzo(g,h,i)perylene</i>	PAH
Doramectin		<i>Benzo(k)fluoranthene</i>	PAH
Apramycin		<i>Chrysene</i>	PAH
<i>Fluoranthene</i>	PAH	<i>Dibenz(a,h)anthracene</i>	PAH
Short-chain chlorinated Paraffins: C10-C13		<i>Dibenzo(a,e)pyrene</i>	PAH
Medium-chain chlorinated Paraffins: C14-C17		<i>Dibenzo(a,h)pyrene</i>	PAH
Gemfibrozil		<i>Dibenzo(a,l)pyrene</i>	PAH
Norfloxacin		<i>Indeno(1,2,3-cd)pyrene</i>	PAH

## 3.2 Results of environmental risk screening

The risk screening for the terrestrial environment was undertaken based on reasonable worst case assumptions and using the available data on exposure levels gathered during the literature search (i.e. measured concentrations of the contaminants in the materials that may be applied to land). The generic scenarios are possibly worst case, and may not be completely appropriate for all the materials, but they do facilitate a cross-material comparison to some extent (although in general sewage sludge is the most studied material in terms of measured contaminant concentrations). As indicated in the previous section, those contaminants for which a risk characterisation ratio (RCR) is equal to or greater than 1 may present a potential risk when applied in specific organic materials to land. Table 3.2 lists the contaminants for each material for the four specific scenarios that give RCR values equal to or greater than 1. The following short sub-sections discuss each organic material considered.

### 3.2.1 Sewage sludge

The first generic exposure scenario is for one 8 tonne ha<sup>-1</sup> application to soil in a year. This single application of sewage sludge shows potential risks for the four medicines ciprofloxacin (RCR of > 29), sulfamethoxazole and gemfibrozil (RCRs < 10). Table 3.2 shows a further 7

chemicals with RCR > 1 when 10 repeated applications are made to the same soil at 8 tonnes ha<sup>-1</sup> over 10 years, but notably the RCRs are less than those observed for the four medicines.

With a single application at the 50 tonnes ha<sup>-1</sup> rate, dieldrin, HHCb (galaxolide), triclosan, oxytetracycline and norfloxacin give RCRs greater than 1, in addition to the four medicines at the lower tonnage. At the higher rate for the longer period of application, 19 contaminants give RCRs values greater than or equal to 1.

### **3.2.2 Composts**

For composts, as with sewage sludge, a single application gives RCRs of greater than 1 for ciprofloxacin (>35) and enrofloxacin (<10). With 10 repeat applications of compost only norfloxacin (another antibiotic) is added to the list. These same three contaminants also give RCRs above 1 when a single 50 tonne ha<sup>-1</sup> application is made, and only PFOS and sulfamethoxazole show risks at the highest tonnages and applications. These results are based on the limited data, from other countries, available for measured concentrations of organic contaminants in compost. However, the source of these medicines in compost is unclear and these results may be of little relevance to the situation in Scotland, because animal manure is not used as a source material for compost generation.

### **3.2.3 Manures**

The manures assessment has been split to include all types of manure, under a general category and then specifically, where exposure data are detailed enough to allow individual assessments for cows, pigs, poultry and manure-based digestates.

#### **3.2.3.1 General**

Three medicines were identified as having RCRs greater than 1 following one application of manure at 8 tonne ha<sup>-1</sup>. The results for ciprofloxacin (RCR > 60) and enrofloxacin (RCR > 50) indicated high risks, as well as oxytetracycline. With repeat applications or increased tonnages in a single application, norfloxacin and sulfamethoxazole were also identified as a potential environmental risk, with the larger tonnage and rate (50 tonnes over 10 years) also flagging doramectin.

#### **3.2.3.2 Cow manure**

For cow manure, ciprofloxacin (RCR >180) and enrofloxacin again gave potential risks at the lowest rate and from a single application. With increased spread rates and number of applications oxytetracycline, ivermectin, norfloxacin and oxytetracycline also give RCRs > 1.

#### **3.2.3.3 Pig manure**

For pig manure, sulfamethoxazole, oxytetracycline, ciprofloxacin and enrofloxacin gave potential risks at the 8 tonne ha<sup>-1</sup> with a single application. The RCR for both enrofloxacin and ciprofloxacin was >200. As spread rates and number of applications increased, norfloxacin also gave potential risks.

#### **3.2.3.4 Poultry manure**

Poultry manures showed RCRs greater than 1 for oxytetracycline, norfloxacin and sulfamethoxazole, at the lowest spread rate and a single application. As spread rates and number of applications increased enrofloxacin and ciprofloxacin were also identified as giving potential risks.

#### **3.2.4 Digestate**

Finally, digestates showed no potential risks from the chemicals examined here under any of the exposure scenarios, where measured concentration was available. The highest RCRs were seen for PFOA and PFOS, but these were less than 0.6 at the higher spread rate for repeated applications over 10 years.

**Table 3.2 Organic substances giving an RCR of greater than or equal to one for one of the four generic exposure scenarios and the specific material in which this occurs.**

Generic exposure scenario	Sewage sludge	Compost	Manure (general)	Manure (cow)	Manure (pig)	Manure (poultry)	Digestate
8 tonnes ha <sup>-1</sup> , 1 year	<b>Ciprofloxacin</b> Gemfibrozil Sulfamethoxazole	<b>Ciprofloxacin</b> Enrofloxacin	<b>Ciprofloxacin</b> Oxytetracycline <b>Enrofloxacin</b>	<b>Ciprofloxacin</b> <b>Enrofloxacin</b>	<b>Ciprofloxacin</b> Oxytetracycline Sulfamethoxazole <b>Enrofloxacin</b>	Oxytetracycline <b>Norfloxacin</b> <b>Sulfamethoxazole</b>	
8 tonnes ha <sup>-1</sup> , 10 years	Dieldrin HHCB (galaxolide) PFOA PFOS Triclosan <b>Ciprofloxacin</b> Oxytetracycline <b>Gemfibrozil</b> Norfloxacin <b>Sulfamethoxazole</b> Enrofloxacin	<b>Ciprofloxacin</b> Norfloxacin <b>Enrofloxacin</b>	<b>Ciprofloxacin</b> <b>Oxytetracycline</b> Norfloxacin Sulfamethoxazole <b>Enrofloxacin</b>	<b>Ciprofloxacin</b> Oxytetracycline Norfloxacin Ivermectin <b>Enrofloxacin</b>	<b>Ciprofloxacin</b> <b>Oxytetracycline</b> Norfloxacin <b>Sulfamethoxazole</b> <b>Enrofloxacin</b>	<b>Oxytetracycline</b> <b>Norfloxacin</b> <b>Sulfamethoxazole</b>	
50 tonnes ha <sup>-1</sup> , 1 year	Dieldrin HHCB (galaxolide) Triclosan <b>Ciprofloxacin</b> Oxytetracycline Gemfibrozil Norfloxacin <b>Sulfamethoxazole</b> Enrofloxacin	<b>Ciprofloxacin</b> <b>Enrofloxacin</b> Norfloxacin Sulfamethoxazole	<b>Ciprofloxacin</b> <b>Oxytetracycline</b> Norfloxacin Sulfamethoxazole <b>Enrofloxacin</b>	<b>Ciprofloxacin</b> Oxytetracycline Norfloxacin Ivermectin <b>Enrofloxacin</b>	<b>Ciprofloxacin</b> <b>Oxytetracycline</b> Norfloxacin <b>Sulfamethoxazole</b> <b>Enrofloxacin</b>	<b>Oxytetracycline</b> <b>Norfloxacin</b> <b>Sulfamethoxazole</b>	
50 tonnes ha <sup>-1</sup> , 10 years	BaP* Cashmeran Decamethylcyclopentasiloxane (D5) DEHP <b>Dieldrin</b> Hexabromocyclododecane (HBCD) <b>HHCB (galaxolide)</b> PFOA PFOS <b>Triclosan</b>	PFOS <b>Ciprofloxacin</b> <b>Norfloxacin</b> Sulfamethoxazole <b>Enrofloxacin</b>	<b>Ciprofloxacin</b> Oxytetracycline Doramectin <b>Norfloxacin</b> <b>Sulfamethoxazole</b> <b>Enrofloxacin</b>	<b>Ciprofloxacin</b> <b>Oxytetracycline</b> <b>Norfloxacin</b> Sulfamethoxazole <b>Ivermectin</b> <b>Enrofloxacin</b>	<b>Ciprofloxacin</b> <b>Oxytetracycline</b> <b>Norfloxacin</b> <b>Sulfamethoxazole</b> <b>Enrofloxacin</b>	<b>Oxytetracycline</b> <b>Norfloxacin</b> <b>Sulfamethoxazole</b> Enrofloxacin	

Generic exposure scenario	Sewage sludge	Compost	Manure (general)	Manure (cow)	Manure (pig)	Manure (poultry)	Digestate
	<b>Ciprofloxacin</b> <b>Oxytetracycline</b> Penta-BDE <b>Gemfibrozil</b> <b>Norfloxacine</b> <b>Sulfamethoxazole</b> Thiabendazole <b>Enrofloxacin</b>						

Contaminants in bold have RCR >10.

\*BaP is included in this list as a representative of PAHs; the full list of PAHs with RCR > 1 are included in the assessment spreadsheet

Due to the lack of available PNECs the following compounds (18 substances) listed in Table 3.3 were 'parked', as an adequate assessment could not be performed.

**Table 3.3 Organic substances 'parked' for environmental screening assessment**

Substance	
1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE)	Perylene
di(2-ethylhexyl)-2,3,4,5-tetrabromophthalate (TBPH)	Naproxen
Hexabromobenzene (HBB)	Ofloxacin
perfluorodecanoate	Trimethoprim
PFNA	Chlorotetracycline
BDE-153 (2,2',4,4',5,5'-hexabromodiphenyl)	Clarithromycin
BDE-99 (2,2',4,4',5-pentabromodiphenyl)	Sarafloxacin
Sulfanilamide	Virginiamycin
Sulfathiazole	Tamoxifen

### 3.3 Results of indicative human health ranking

As detailed in Section 2.4, contaminants are ranked by their toxicological potency according to a scoring scheme devised for Health Criteria Values (HCVs) and other similar intake values (e.g. ADI and RfDs). The output of this ranking exercise is detailed below in Table 3.4 and in the 'HCVs' tab of the spreadsheet. It should be noted that the organic compounds considered here have  $\log Kow > 4.5$  and therefore have some potential to bioaccumulate in the food chain or are medicines (human and veterinary) with potential to persist in the terrestrial environment. Quantitative assessment of this exposure pathway and possible risks to human health from dietary intake would require a detailed modelling exercise that is beyond the scope of this phase of the project that is dedicated to chemical prioritisation.

It is recommended that any detailed assessment of dietary intake starts with the most toxicologically potent compounds highlighted by this ranking exercise.

**Table 3.4 Ranking of prioritised chemicals for toxicological significance**

<b>Score = 10 Very high potency</b>	BaP (PAHs), PCDD/DFs (dioxins and furans)
<b>Score = 8 High potency</b>	Alpha-chlordane, Diclofenac, Dieldrin, Doramectin, PBDEs (47, 99 & 153), PFOS*, Sarafloxacin
<b>Score = 6 Moderate potency</b>	DEHP, DDD, DDE, HBB, PFOA*, Ciprofloxacin, medium-chain chlorinated paraffins, Trimethoprim, Enrofloxacin, Ivermectin, BDE-209
<b>Score = 4 Low potency</b>	HHCB, Tonalide, Oxytetracycline, Apramycin, short-chain chlorinated paraffins, Chlorotetracycline, Thiabendazole, Virginiamycin, Cypermethrin
<b>Score = 2 Very low potency</b>	Decamethylcyclopentasiloxane, Dodecamethylcyclohexasiloxane, Triclosan, Gemfibrozil
<b>'Parked' No HCV</b>	BTBPE, Cashmeran, DBDPE, TBPH, HBCD, Perfluorodecanoate, PFNA, Triclocarban, Naproxen, Norfloxacin, Ofloxacin, Sulfamethoxazole, Clarithromycin, Sulfanilamide, Sulfathiazole, Tamoxifen

\*On December 13<sup>th</sup> 2018, the European Food Safety Authority (EFSA) published a proposal for revised Tolerable Weekly Intake (TWI) values for PFOS and PFOA that are around 80 and 1,800 lower than previously published values (EFSA, 2018a). If the revised TWI values for PFOS and PFOA were used, it is likely that both of these substances would have a score of 10, corresponding to 'very high potency'. However, as of January 18<sup>th</sup> 2019, the new TWI values were disputed due to the use of epidemiological data, rather than mammalian toxicology data, in their derivation (EFSA, 2018b). Therefore, for the purpose of this report, it was decided to continue using Tolerable Daily Intake (TDI) values for PFOS and PFOA published in 2008 (EFSA, 2008) as a basis for calculations of risk to human health from these substances associated with organic material spreading to land.

Of the contaminants highlighted as high or very high potency the majority have also been highlighted by the preliminary environmental risk assessment (i.e. BaP, PCDD/DFs, dieldrin, doramectin and PBDEs) and would be strong candidates for prioritisation. Alpha-chlordane is no longer approved for use and sarafloxacin has been withdrawn from clinical use, which precludes them from further assessment. This leaves just diclofenac as a contaminant that could warrant consideration purely on the basis of hazard to health.

### 3.4 Final chemical prioritisation

Tables 3.2 and 3.4 detail the results of the screening prioritisation of chemicals in organic materials destined for application to land for environmental risks and human health hazards, respectively. From these results we have identified priority contaminants, on the basis of risk and hazard, relevance to the various materials and resources available. The result of this final prioritisation is summarised in Table 3.5.

For sewage sludges representatives of different classes of pharmaceutical (enrofloxacin and its active metabolite, ciprofloxacin; oxytetracycline, ivermectin and sulfamethoxazole) were selected along with two personal care products (triclosan and HHCB), to represent specific groups of contaminants that present potential risks to the terrestrial environment. Three

hazardous and persistent contaminants (BaP (as part of the SVOC suite), PFOS and PBDEs) were selected for sampling in biosolids on the basis of high toxicological potency and predicted risk to the environment at repeated higher tonnage applications. Dieldrin (as part of the OC suite) was also selected based on the environment and toxicological potency; however, if all results are <LOD an exposure assessment will not be performed, due to dieldrin being banned by the Stockholm convention.

For cattle, poultry and pig manures, ciprofloxacin, enrofloxacin and oxytetracycline are forecast to present the largest risk to the environment. These veterinary medicines were selected for analysis in these types of manure along with ivermectin for pigs and cattle and sulfamethoxazole for poultry.

For ashes, only dioxins were selected as potentially important. No contaminants were identified as presenting an environmental risk or health hazard from the data reviewed for digestates. Composts, based on the health hazard screening samples, were analysed for dieldrin and BaP<sup>12</sup>, along with DEHP<sup>11</sup> due to its general potential environmental risk, presence in the SVOC suite and its potential for use as a marker for some types of plastic contamination. As discussed in section 3.2.2, the pharmaceuticals identified as posing a risk based on literature data were not taken forward as they are likely to be of little relevance to the situation in Scotland, because animal manure is not used as one of the source materials for compost generation.

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<sup>12</sup> BaP and DEHP were part of the SVOC suite

**Table 3.5 Prioritised contaminants selected for analysis**

Sample Type		Biosolids	Compost	Pig Manure	Cattle Manure	Poultry	Ash
Determinands	Ciprofloxacin	✓	x	✓	✓	✓	x
	Enrofloxacin	✓	x	✓	✓	✓	x
	Oxytetracycline	✓	x	✓	✓	✓	x
	Ivermectin	✓	x	✓	✓	x	x
	Triclosan	✓	x	x	x	x	x
	Sulfamethoxazole	✓	x	x	x	✓	x
	HHCB (galaxolide)	✓	x	x	x	x	x
	Dioxins	x	x	x	x	x	✓
	PFOS	✓	x	x	x	x	x
	PBDEs <sup>1</sup>	✓	x	x	x	x	x
	SVOC Suite <sup>2</sup>	✓	✓	x	x	x	x
	OC Pesticide <sup>3</sup>	✓	✓	x	x	x	x
OP Pesticide <sup>4</sup>	✓	✓	x	x	x	x	
<b>Number of samples<sup>5</sup></b>		16	4	10	6	5	3

<sup>1</sup> polybrominated diphenylethers; <sup>2</sup> Semi-volatile organic compounds (SVOC) suite analysis includes PAH, BaP and DEHP analysis; <sup>3</sup> organochlorine pesticides, including dieldrin; <sup>4</sup> organophosphate pesticides; <sup>5</sup> see section 4.1 below

## **4 Sampling of materials and analysis of prioritised contaminants**

The contaminants of interest in specific materials applied to land were identified by the prioritisation exercise detailed in Section 3 and are listed in Table 3.5. The organic materials collected for analysis included treated sewage sludge (also known as 'biosolids'), manure from cattle, pigs and poultry and compost. Samples of virgin wood ash were also provided for analysis of dioxins.

Sample numbers and analysis undertaken for each material are summarised in Sections 4.1 and 4.2. Summary statistical analysis were performed on the analytical data and this is reported in Section 4.3.

### **4.1 Sampling, Sample Numbers and Locations**

The sample sites were identified through discussions with numerous stakeholders, and direct contact by partner organisations of the research project. The final sample locations are detailed in Table 4.1. In the case of animal manures, possible sample locations were pre-screened for veterinary use of the prescribed medicines of interest to avoid costly analysis of samples from herds and flocks that had not been recently exposed to these medicines. In Scotland and elsewhere in the UK, veterinary medicines are only used by food producers as a last resort to treat outbreaks of disease and to protect and enhance animal welfare. Therefore the samples collected for this project include an inherent bias and do not reflect the average concentration of veterinary medicines in most farmyard manures.

All samples, except the samples from the STPs, were provided by the stakeholders, using materials provided by wca, following sampling guidance provided for the project. Following sampling the materials were transported to the laboratory for analysis in the shortest timeframe possible; this was usually the day after sampling. Samples were not transported chilled, as although this is typically performed for sample analysis, in this project samples were taken in the form that they are applied to land, and in the field these materials are not stored chilled. The processed biosolids samples were taken by a commercial consultancy with expertise in field sampling, due to difficulties regarding logistics of the stakeholder following the same procedure performed by the stakeholders during sampling.

The number of samples and analytical determinands for each material and location providing samples are detailed in Table 4.1 below. The determinands selected for each material were based on the prioritisation exercise, and for manure samples, recent usage of target veterinary medicines at the site was also taken into consideration.

**Table 4.1 Sample types, locations and number of samples**

Locations	Sample Type	Number of Samples	Determinand(s) Analysed
Compost 1	Green Waste Compost <sup>1</sup>	4	SVOC Suite; OC Pesticide; OP Pesticide
Compost 2	Food & Green Waste Compost <sup>1</sup>	2	
Farm 1	Pig manure <sup>2</sup>	3	Ciprofloxacin; Enrofloxacin
Farms 2 & 3 <sup>3</sup>	Pig manure <sup>4</sup>	4	Oxytetracycline
	Cattle Manure <sup>4</sup>	3	Oxytetracycline; Ivermectin
Farm 4	Pig manure <sup>4</sup>	3	Oxytetracycline; Ivermectin
	Cattle Manure <sup>4</sup>	3	Oxytetracycline; Ivermectin
Farm 5	Poultry manure <sup>2</sup>	2	Ciprofloxacin; Enrofloxacin
Farm 6	Poultry manure <sup>2</sup>	3	Sulfamethoxazole
STP 1	Processed biosolid from STP using liming treatment	8	Ciprofloxacin; Enrofloxacin; Oxytetracycline; Ivermectin; Triclosan; Sulfamethoxazole; HHCB (Galaxolide); PFOS; DEHP; PBDEs; SVOC Suite; OC Pesticide; OP Pesticide
STP 2	Processed biosolid from STP using anaerobic digestion	8	
Ash	Virgin wood ash <sup>1</sup>	3	Dioxins

<sup>1</sup> From a commercial compost producer in Scotland

<sup>2</sup> From a commercial farm in England

<sup>3</sup> Farm 2 and 3 were from the same location; however different contact persons were provided for the different medias, and therefore, different unique identifiers were provided

<sup>4</sup> From a research farm in Scotland

## 4.2 Analysis

The analysis of the samples was conducted by Socotec (Bretby)<sup>13</sup>. Samples were air-dried and then extracted using a variety of techniques, typically either solvent extraction or a Quick Easy Cheap Effective Rugged Safe (QuEChERS) (as detailed in Table 4.2). Analytical methods for ciprofloxacin, enrofloxacin, oxytetracycline, ivermectin, triclosan, sulfamethoxazole and HHCB (galaxolide) are not routinely developed by commercial laboratories and so their analysis was performed using bespoke Good Laboratory Practise methods developed for the objectives of this project; all other analyses were performed using routine in-house laboratory methods.

<sup>13</sup> Specialist Chemistry, SOCOTEC, Etwall Building, Bretby Business Park, Ashby Road, Burton Upon Trent, DE15 0YZ. <https://www.socotec.co.uk/our-services/infrastructure-energy/chemical-analysis/>

The analytical techniques and typical limits of detection (LoDs) for each determinand or suite, as appropriate, are detailed in Table 4.2.

**Table 4.2 Extraction method, analysis technique and Limit of Detection**

Determinand or Suite	Extraction method	Analytical Method	LOD ( $\mu\text{g kg}^{-1}$ dwt)
Ciprofloxacin	Solvent extraction	GC/MS	10
Enrofloxacin	Solvent extraction	GC/MS	10
Oxytetracycline	Solvent extraction	GC/MS	10
Ivermectin	Quick Easy Cheap Effective Rugged Safe (QuEChERS)	LC-MS/MS	10
Triclosan	QuEChERS	GC/MS	10
Sulfamethoxazole	QuEChERS	GC/MS	1
HHCb (Galaxolide)	Solvent extraction	GC/MS	10
Dioxins	Solvent extraction	HR- GC/MS	0.001 – 0.07
PFOS	Solvent extraction	LC-MS/MS	0.03
PBDEs	Solvent extraction	GC/MS	0.001
SVOC Suite	Solvent extraction	GC/MS	100 to 14,500
OC Pesticide	Solvent extraction	GC/MS	1 – 30
OP Pesticide Suite	Solvent extraction	GC/MS	1 - 10

Additionally, selected samples from each material were also analysed for moisture content for comparison to typical literature values of different organic materials. This information was required as application rates are typically estimated as wet weights.

## 4.3 Results of Sample Analysis

Summary statistics of the analytical results for the processed biosolids, cattle, pig and poultry manures, compost and ash samples are summarised in the sections below. Summary statistics are only presented for the substances that were selected from the prioritisation exercise. However, where analysis suites have been utilised the results for all suite constituents are included in the available spreadsheets that support this report. The summary statistics calculated for each material are minimum, maximum, 90<sup>th</sup> percentile, mean, median and standard deviation. For datasets where there is 100 % censored data the upper bound median and upper bound 90<sup>th</sup> percentile are equal to the LOD and therefore not calculated in the summary tables. For datasets where censored data<sup>14</sup> are reported both the lower and upper bound mean and median have been calculated. Outlier analysis has also been performed for determinands with greater than three samples per media<sup>15</sup>.

### 4.3.1 Manures

Manures from pig, poultry and cattle farms were analysed for prioritised veterinary medicines. The summary statistics for the pig, cattle and poultry manures are detailed in Tables 4.3 to 4.5.

<sup>14</sup> Samples <LoD

<sup>15</sup> Outlier analysis undertaken using the ESI CIEH statistical tool

Samples were collected from farms and facilities in both England (with the help of the Environment Agency) and Scotland. It proved difficult to identify food producers where the veterinary medicines of interest had been used on livestock within the past six months and where samples of fresh or recently stored manures could be obtained. Therefore the overall sample numbers are lower than originally anticipated. However, the anecdotal observation that veterinary medicine use is not widespread at the food producers approached is itself an important finding.

**Table 4.3 Summary statistics for the Pig Manure samples**

	<b>Ciprofloxacin</b>	<b>Enrofloxacin</b>	<b>Oxytetracycline</b>	<b>Ivermectin</b>
Number of Samples	3	3	7	3
Number of Samples <LoD	3	3	0	3
Minimum ( $\mu\text{g kg}^{-1}$ dwt)	<LOD	<LOD	20	<LOD
Max ( $\mu\text{g kg}^{-1}$ dwt)	<LOD	<LOD	740	<LOD
90P ( $\mu\text{g kg}^{-1}$ dwt)	N.A.	N.A.	500	N.A.
Lower Bound Mean ( $\mu\text{g kg}^{-1}$ dwt)	N.A.	N.A.	209	N.A.
Upper Bound Mean ( $\mu\text{g kg}^{-1}$ dwt)	N.A.	N.A.	209	N.A.
Lower Bound Median ( $\mu\text{g kg}^{-1}$ dwt)	N.A.	N.A.	140	N.A.
Upper Bound Median ( $\mu\text{g kg}^{-1}$ dwt)	N.A.	N.A.	140	N.A.
Standard Deviation ( $\mu\text{g kg}^{-1}$ dwt)	N.A.	N.A.	259	N.A.

**Table 4.4 Summary statistics for the Cattle Manure samples**

	<b>Oxytetracycline</b>	<b>Ivermectin</b>
Number of Samples	6	6
Number of Samples <LoD	1	5
Minimum ( $\mu\text{g kg}^{-1}$ dwt)	<LOD	<LOD
Max ( $\mu\text{g kg}^{-1}$ dwt)	120	10
90P ( $\mu\text{g kg}^{-1}$ dwt)	115	N.A.
Lower Bound Mean ( $\mu\text{g kg}^{-1}$ dwt)	592	N.A.
Upper Bound Mean ( $\mu\text{g kg}^{-1}$ dwt)	60	N.A.
Lower Bound Median ( $\mu\text{g kg}^{-1}$ dwt)	50	N.A.
Upper Bound Median ( $\mu\text{g kg}^{-1}$ dwt)	50	N.A.
Standard Deviation ( $\mu\text{g kg}^{-1}$ dwt)	50.4	N.A.

**Table 4.5 Summary statistics for the Poultry Manure samples**

	<b>Ciprofloxacin</b>	<b>Enrofloxacin</b>	<b>Sulfamethoxazole</b>
Number of Samples	2	2	3
Number of Samples <LoD	2	1	0
Minimum ( $\mu\text{g kg}^{-1}$ dwt)	<LOD	<LOD	10
Max ( $\mu\text{g kg}^{-1}$ dwt)	<LOD	30	27
90P ( $\mu\text{g kg}^{-1}$ dwt)	N.A.	N.A.	24.6
Lower Bound Mean ( $\mu\text{g kg}^{-1}$ dwt)	N.A.	N.A.	17.3
Upper Bound Mean ( $\mu\text{g kg}^{-1}$ dwt)	N.A.	N.A.	17.3
Lower Bound Median ( $\mu\text{g kg}^{-1}$ dwt)	N.A.	N.A.	15.0
Upper Bound Median ( $\mu\text{g kg}^{-1}$ dwt)	N.A.	N.A.	15.0
Standard Deviation ( $\mu\text{g kg}^{-1}$ dwt)	N.A.	N.A.	8.74

Outlier analysis performed on the manure samples identified two potential outlier results; one oxytetracycline result for pig manure and one ivermectin result for cattle manure (these datapoints are highlighted in the associated spreadsheet). After reviewing the results of these samples, although they are statistically flagged as outliers, they are not considered as erroneous results. For the oxytetracycline result, the sample analysed was 100 % pig dung and therefore, a higher concentration would be expected in this sample than in samples from other locations that were analysed, as the latter samples consisted of pig dung mixed with straw.

#### **4.3.2 Processed biosolid**

Samples of processed biosolid were taken from two STPs in Scotland and analysed for a variety of personal care products, medicines, and other priority contaminants. The two sites sampled utilised different treatment regimes. STP 1 utilises liming of the sludge to produce the sludge cake, and STP 2 utilises anaerobic digestion. Due to the different treatment techniques used at the sites, and the different locations, the summary statistics have been calculated for each site separately, rather than for a combined biosolids dataset. The summary statistics are detailed in Tables 4.6 and 4.7 below.

**Table 4.6 Summary statistics for STP 1 (liming treatment) biosolid samples**

	Ciprofloxacin	Enrofloxacin	Oxytetracycline	Sulfamethoxazole	Triclosan	Ivermectin	HHCb	PFOS	BaP	DEHP	BDE-209	Dieldrin
Number of Samples	8	8	8	8	8	8	8	8	8	8	8	8
Number of Samples <LoD	0	8	0	8	0	8	0	5	8	0	0	8
Minimum ( $\mu\text{g kg}^{-1}$ dwt)	60	<LOD	600	<LOD	210	<LOD	4200	<LOD	<LOD	1100	0.005	<LOD
Max ( $\mu\text{g kg}^{-1}$ dwt)	160	<LOD	1300	<LOD	340	<LOD	12000	0.05	<LOD	2100	0.078	<LOD
90P ( $\mu\text{g kg}^{-1}$ dwt)	160	N.A.	1230	N.A.	333	N.A.	11300	0.043	N.A.	2058	0.07	N.A.
Lower Bound Mean ( $\mu\text{g kg}^{-1}$ dwt)	128	N.A.	917.50	N.A.	288	N.A.	7212.50	0.02	N.A.	1613	0.04	N.A.
Upper Bound Mean ( $\mu\text{g kg}^{-1}$ dwt)	128	N.A.	917.50	N.A.	288	N.A.	7212.50	0.03	N.A.	1613	0.04	N.A.
Lower Bound Median ( $\mu\text{g kg}^{-1}$ dwt)	145	N.A.	910	N.A.	300	N.A.	6350	0.015	N.A.	1630	0.04	N.A.
Upper Bound Median ( $\mu\text{g kg}^{-1}$ dwt)	145	N.A.	910	N.A.	300	N.A.	6350	0.03	N.A.	1630	0.04	N.A.
Standard Deviation ( $\mu\text{g kg}^{-1}$ dwt)	39.9	N.A.	243.82	N.A.	50.6	N.A.	2876.72	0.01	N.A.	392	0.02	N.A.

**Table 4.7 Summary statistics for the Sewage Treatment Plant 2 (Anaerobic digestion) biosolid samples**

	<b>Ciprofloxacin</b>	<b>Enrofloxacin</b>	<b>Oxytetracycline</b>	<b>Sulfamethoxazole</b>	<b>Triclosan</b>	<b>Ivermectin</b>	<b>HHCb</b>	<b>PFOS</b>	<b>BaP</b>	<b>DEHP</b>	<b>BDE-209</b>	<b>Dieldrin</b>
Number of Samples	8	8	8	8	8	8	8	8	8	8	8	8
Number of Samples <LoD	0	8	0	8	0	8	0	6	8	3	0	8
Minimum ( $\mu\text{g kg}^{-1}$ dwt)	90	<LOD	250	<LOD	720	5.00	36000	0.02	<LOD	<LOD	0.021	<LOD
Max ( $\mu\text{g kg}^{-1}$ dwt)	190	<LOD	500	<LOD	1200	5.00	42000	0.08	<LOD	389	0.12	<LOD
90P ( $\mu\text{g kg}^{-1}$ dwt)	183	N.A.	486	N.A.	1200	5.00	41300	0.06	N.A.	315	0.12	N.A.
Lower Bound Mean ( $\mu\text{g kg}^{-1}$ dwt)	154	N.A.	376	N.A.	945	5.00	38000	0.03	N.A.	206	0.06	N.A.
Upper Bound Mean ( $\mu\text{g kg}^{-1}$ dwt)	154	N.A.	376	N.A.	945	10	38000	0.04	N.A.	244	0.06	N.A.
Lower Bound Median ( $\mu\text{g kg}^{-1}$ dwt)	165	N.A.	360	N.A.	845	5.00	37000	0.02	N.A.	218	0.05	N.A.
Upper Bound Median ( $\mu\text{g kg}^{-1}$ dwt)	165	N.A.	360	N.A.	845	10	37000	0.03	N.A.	218	0.05	N.A.
Standard Deviation ( $\mu\text{g kg}^{-1}$ dwt)	35.8	N.A.	94.7	N.A.	190	0.00	2268	0.02	N.A.	65.9	0.04	N.A.

When outlier analysis was performed on the prioritised determinands in the sewage treatment plant cake, one outlier was identified. The outlier was for the maximum measured PFOS concentration at STP 2 of 0.08  $\mu\text{g kg}^{-1}$ . This concentration is approximately 2.5 standard deviations above the mean results; although it is not sufficiently outlying to be excluded from the analysis due to the limited size of the dataset.

### 4.3.3 Compost

Compost samples were provided from two commercial composters in Scotland; one producing compost from green waste only (Compost 1) and one from combined food and green waste (Compost 2). For compost samples organochlorine (OC) and organophosphate (OP) pesticide suites and SVOC analytical suite were performed. Summary statistics are presented in Table 4.8 for the phthalate DEHP, BaP and dieldrin, substances identified during the prioritisation exercise.

**Table 4.8 Summary statistics for analysis on the compost samples**

	DEHP	BaP	Dieldrin
Number of Samples	6	6	6
Number of Samples <LoD	4	6	6
Minimum (mg kg <sup>-1</sup> dwt)	<LOD	<LOD	<LOD
Max (mg kg <sup>-1</sup> dwt)	0.473	<LOD	<LOD
90P (mg kg <sup>-1</sup> dwt)	0.341	N.A.	N.A.
Lower Bound Mean (mg kg <sup>-1</sup> dwt)	0.180	N.A.	N.A.
Upper Bound Mean (mg kg <sup>-1</sup> dwt)	0.247	N.A.	N.A.
Lower Bound Median (mg kg <sup>-1</sup> dwt)	<LOD	N.A.	N.A.
Upper Bound Median (mg kg <sup>-1</sup> dwt)	<LOD	N.A.	N.A.
Lower Bound Standard Deviation (mg kg <sup>-1</sup> dwt)	0.150	N.A.	N.A.
Upper Bound Standard Deviation (mg kg <sup>-1</sup> dwt)	0.111	N.A.	N.A.

### 4.3.4 Virgin Wood Ash samples

Three virgin wood ash samples were provided by a commercial supplier in Scotland. The ash was analysed for dioxins, furans and dioxin-like PCBs; the lower and upper bound total WHO TEQ were determined for each sample, as well as the median and mean for the dataset (Table 4.9).

Outlier analysis was not performed on the virgin wood ash samples due to only three samples being analysed.

**Table 4.9** Lower and Upper Bound Total WHO TEQ equivalents for the virgin wood ash samples

<b>Total WHO TEQ ng kg<sup>-1</sup> dwt</b>		
	<b><i>Lower bound</i></b>	<b><i>Upper bound</i></b>
Sample A TEQ	40.1	43.0
Sample B TEQ	40.8	41.0
Sample C TEQ	32.0	32.0
Median	40.1	41.0
Mean	37.6	38.7

## 5 REFINED RISK ASSESSMENT

### 5.1 Material specific scenario development

Organic wastes used as fertilisers for agricultural land are applied at different rates depending on the source, form and nutrient content of the material. Therefore, for each material specific spreading rates were determined based on typical nitrogen content and moisture content of each material<sup>16</sup> (ADHB, 2018) to calculate a maximum application of 170 kg N/ha (Defra and EA, 2017) as well as values based on low and high spread rates; this information is summarised in Table 5.1. For manures two spread rates have been calculated based on the variation in the moisture content. The mixing depths used for each material were defined based on typical application methods, i.e. either surface dressing or soil incorporation. As an initial worst case scenario application of manures and compost was considered as a surface dressing using a mixing depth of 5 cm. Biosolids are typically ploughed into soils so the deeper mixing depth of 20 cm was used for exposure assessment of these materials (ECHA, 2016). If no risks were identified for the relatively conservative surface dressing scenario then no further refinement was required. For any contaminants for which risks were identified for the surface dressing exposure scenario for single and ten consecutive annual applications<sup>17</sup>, they were also assessed using the deeper soil incorporation mixing depth.

**Table 5.1 Spreading characteristics for refined exposure assessment**

Material	Fraction dry matter	Total N (kg N/t)	Based on 170 kg N/t	For risk assessment		Years spreading		
			Calc max spread rate (t/ha) <sup>1</sup>	Low spread (t/ha) <sup>1</sup>	High spread (t/ha) <sup>2</sup>	HHRA	Env RA	
Limed sludge cake (STP 1)	0.95	40	4.3	n/a	5	10	1	10
Anaerobic digestion sludge cake (STP2)	0.4	8.5	20.0	n/a	30			
Cattle manure <sup>3</sup>	0.25	6	28.3	8	30	10	1	10
Pig manure	0.25	7	24.3	8	30	10	1	10
Layer poultry manure	0.35	19	8.9	4	10	10	1	10
Broiler poultry manure	0.6	30	5.7					

<sup>1</sup> Based on materials with lower moisture content

<sup>2</sup> Based on materials having higher moisture content

<sup>3</sup> Compost spreading also used this scenario (i.e. based on the highest spread rate calculated for other materials)

<sup>16</sup> The typical dry matter fraction was compared to the moisture content determined for the analysed samples and application rates adjusted as required

<sup>17</sup> If a potential risk was identified in 10 application scenario, but the datasets was 100 % LoD, this was not further assessed in the soil incorporation scenario because of the likelihood of propagation of a false positive result since worst case assumptions were used in the soil dressing scenario for LoD results.

## 5.2 Refined Risk Assessment for Terrestrial Environment

### 5.2.1 Methodology

The refined risk assessments for the environment were performed using both the upper-bound 90<sup>th</sup> percentile concentration and the upper-bound median contaminant concentrations determined from the sample analysis (see Section 4). The 90<sup>th</sup> percentile and median concentrations were selected as they are calculated from the distribution of the datasets; the 90<sup>th</sup> percentile and median concentrations are the concentrations at which 90 % and 50 % of observations are at or below this concentration. To calculate upper-bound concentrations, samples less than the LoD have been used in calculation of the median and 90<sup>th</sup> percentile concentrations as equivalent to the method LoD, as this is a worst-case assumption. For specific materials where contaminants were reported as less than the LoD for all samples then the LoD was used in the assessment. The 90<sup>th</sup> percentile concentration is used as a reasonable-worst case in risk assessment, and the median concentration is representative of typical values (the central tendency within the distribution of the results).

The parameters used for the soil properties in the refined risk assessments are detailed in Table 5.2:

**Table 5.2 The parameters and assumptions used for the two scenarios utilised in the refined risk assessment**

Parameter	Soil dressing scenario	Soil incorporation scenario	Reference
Bulk density of soil receiving organic material	1.7 g cm <sup>-3</sup>		ECHA 2016
Depth of incorporation	0.05 m	0.20 m	
Area of incorporation	1 ha		Standard Unit

The refinement of the environmental risk assessment involved the following steps:

- The PNECs of the prioritised contaminants were reviewed and where updated for BaP, HHCB (galaxolide) and PFOS as new PNECs had been derived since the initial risk screening;
- Updating the spread-rates for each material based on the data detailed in Tables 5.1 and 5.2;
- Conversion of the laboratory reported dry weight concentrations to wet weight concentrations;
- Calculation of the upper-bound 90<sup>th</sup> percentile and median concentrations for the wet weight concentrations.

By performing these refinements, a more realistic material specific scenario is provided than the initial risk assessment, as it accounts for variations in the spread-rates and typical application methods.

In the refined risk assessments, potential risks are identified in red text. Some RCRs greater than 1 are identified in orange text. In these cases, all samples had levels less than the limit of detection but PNECs were lower than the achieved LoD. Based on the accepted conservative assumption of concentration (concentration = LoD), the RCR was still greater than 1 so there is considerable uncertainty associated with these potential risks.

Key for results tables in section 5:

\* Chemicals marked with asterisk indicate that all samples were <LoD

2.3 RCR>1 based on quantified measurement (i.e. >LoD)

Where a potential risk has been identified for a contaminant in a material in a surface dressing scenario and the determinand is not less than the LoD in all samples, a soil incorporation scenario has also been performed.

### **5.2.2 Refined Risk Assessment for Manures**

As detailed in Section 5.1, the terrestrial environment risk assessment for manures was initially performed assuming a soil dressing application scenario (a soil incorporation depth of 0.05m). The results of the refined risk assessments for soil dressing application using pig manures are detailed in tables 5.3 and 5.4, cattle manures in tables 5.5 and 5.6, and poultry manures in tables 5.7 and 5.8.

None of the single application scenarios, where the manures are applied as a surface dressing, identified any potential risks to soil from the contaminants measured in cattle, pig and poultry manures. In the scenarios where manures were applied for ten consecutive annual applications, small exceedances for enrofloxacin (RCR 1 and 2.2) and sulfamethoxazole (RCR 1.1 and 2.2) were found only for poultry manure applications at the highest rate of 10 tonnes per hectare. No risks were subsequently identified for poultry manures ploughed-in to soils to a mixing depth of 0.2m (see tables 5.9 and 5.10).

It is important to also note that the risks identified for enrofloxacin should be treated with caution, as there is considerable uncertainty in the derived PNEC (see section 2.3 and associated spreadsheet tab "PNECs") Therefore, this assessment should be treated as indicative.

**Table 5.3 Refined risk assessment for pig manures for surface dressing application scenario using the upper bound 90<sup>th</sup> percentile concentration**

Substances	Cas No.	PNEC (mg kg <sup>-1</sup> ww)	Manure (90 P) (mg kg <sup>-1</sup> ww)	PEC 8t/1app (mg kg <sup>-1</sup> ww)	RCR	PEC 8t/10app (mg kg <sup>-1</sup> ww)	RCR	PEC 30t/1app (mg kg <sup>-1</sup> ww)	RCR	PEC 30t/10app (mg kg <sup>-1</sup> ww)	RCR
Ciprofloxacin*	85721-33-1	1.47E-03	0.0025	2.35E-05	0.016	2.35E-04	0.16	8.82E-05	0.060	8.82E-04	0.60
Enrofloxacin*	93106-60-6	1.47E-03	0.0025	2.35E-05	0.016	2.35E-04	0.16	8.82E-05	0.060	8.82E-04	0.60
Oxytetracycline	6153-64-6	1.81	0.247	2.32E-03	1.28E-03	2.32E-02	0.01	8.72E-03	0.00	8.72E-02	0.05
Ivermectin*	70288-86-7	6.35E-02	0.01	9.41E-05	1.48E-03	9.41E-04	0.01	3.53E-04	0.01	3.53E-03	0.06

**Table 5.4 Refined risk assessment for pig manures for surface dressing application scenario using the upper bound median concentration**

Substances	Cas No.	PNEC (mg kg <sup>-1</sup> ww)	Manure (median) (mg kg <sup>-1</sup> ww)	PEC 8t/1app (mg kg <sup>-1</sup> ww)	RCR	PEC 8t/10app (mg kg <sup>-1</sup> ww)	RCR	PEC 30t/1app (mg kg <sup>-1</sup> ww)	RCR	PEC 30t/10app (mg kg <sup>-1</sup> ww)	RCR
Ciprofloxacin*	85721-33-1	1.47E-03	0.0025	2.35E-05	0.016	2.35E-04	0.16	8.82E-05	0.060	8.82E-04	0.60
Enrofloxacin*	93106-60-6	1.47E-03	0.0025	2.35E-05	0.016	2.35E-04	0.16	8.82E-05	0.060	8.82E-04	0.60
Oxytetracycline	6153-64-6	1.81	0.126	1.19E-03	6.54E-04	1.19E-02	0.01	4.45E-03	0.00	4.45E-02	0.02
Ivermectin*	70288-86-7	6.35E-02	0.01	9.41E-05	1.48E-03	9.41E-04	0.01	3.53E-04	0.01	3.53E-03	0.06

**Table 5.5 Refined risk assessment for cattle manures for surface dressing application scenario using the upper bound 90<sup>th</sup> percentile concentration**

Substances	Cas No.	PNEC (mg kg <sup>-1</sup> ww)	Manure (90 P) (mg kg <sup>-1</sup> ww)	PEC 8t/1app (mg kg <sup>-1</sup> ww)	RCR	PEC 8t/10app (mg kg <sup>-1</sup> ww)	RCR	PEC 30t/1app (mg kg <sup>-1</sup> ww)	RCR	PEC 30t/10app (mg kg <sup>-1</sup> ww)	RCR
Oxytetracycline	6153-64-6	1.81	0.001725	1.62E-05	8.95E-06	1.62E-04	8.95E-05	6.09E-05	3.36E-05	6.09E-04	3.36E-04
Ivermectin	70288-86-7	6.35E-02	0.0002	1.88E-06	2.97E-05	1.88E-05	2.97E-04	7.06E-06	1.11E-04	7.06E-05	1.11E-03

**Table 5.6 Refined risk assessment for cattle manures for surface dressing application scenario using the upper bound median concentration**

Substances	Cas No.	PNEC (mg kg <sup>-1</sup> ww)	Manure (median) (mg kg <sup>-1</sup> ww)	PEC 8t/1app (mg kg <sup>-1</sup> ww)	RCR	PEC 8t/10app (mg kg <sup>-1</sup> ww)	RCR	PEC 30t/1app (mg kg <sup>-1</sup> ww)	RCR	PEC 30t/10app (mg kg <sup>-1</sup> ww)	RCR
Oxytetracycline	6153-64-6	1.81	0.008	7.53E-05	4.15E-05	7.53E-04	4.15E-04	2.82E-04	1.56E-04	2.82E-03	1.56E-03
Ivermectin	70288-86-7	6.35E-02	0.00175	1.65E-05	2.60E-04	1.65E-04	2.60E-03	6.18E-05	9.73E-04	6.18E-04	9.73E-03

**Table 5.7 Refined risk assessment for poultry manures for surface dressing application scenario using the upper bound 90<sup>th</sup> percentile concentration**

Substances	Cas No.	PNEC (mg kg <sup>-1</sup> ww)	Manure (90P) (mg kg <sup>-1</sup> ww)	PEC 4t/1app (mg kg <sup>-1</sup> ww)	RCR	PEC 4t/10app (mg kg <sup>-1</sup> ww)	RCR	PEC 10t/1app (mg kg <sup>-1</sup> ww)	RCR	PEC 10t/10app (mg kg <sup>-1</sup> ww)	RCR
Ciprofloxacin*	85721-33-1	1.47E-03	0.010	4.71E-05	0.032	4.71E-04	0.32	1.18E-04	0.080	1.18E-03	0.80
Enrofloxacin	93106-60-6	1.47E-03	0.0275	1.29E-04	0.088	1.29E-03	0.88	3.24E-04	0.22	3.24E-03	2.2
Sulfamethoxazole	723-46-6	1.35E-03	0.0246	1.16E-04	0.09	1.16E-03	0.86	2.89E-04	0.21	2.89E-03	2.2

**Table 5.8 Refined risk assessment for poultry manures for surface dressing application scenario using the upper bound median concentration**

Substances	Cas No.	PNEC (mg kg <sup>-1</sup> )	Manure (median) (mg kg <sup>-1</sup> ww)	PEC 4t/1app (mg kg <sup>-1</sup> ww)	RCR	PEC 4t/10app (mg kg <sup>-1</sup> ww)	RCR	PEC 10t/1app (mg kg <sup>-1</sup> )	RCR	PEC 10t/10app (mg kg <sup>-1</sup> )	RCR
Ciprofloxacin*	85721-33-1	1.47E-03	0.0055	2.59E-05	0.018	2.59E-04	0.18	6.47E-05	0.044	6.47E-04	0.44
Enrofloxacin	93106-60-6	1.47E-03	0.0125	5.88E-05	0.040	5.88E-04	0.40	1.47E-04	0.0998	1.47E-03	1.0
Sulfamethoxazole	723-46-6	1.35E-03	0.012	5.65E-05	0.04	5.65E-04	0.42	1.41E-04	0.10	1.41E-03	1.1

**Table 5.9 Refined risk assessment for poultry manures in the soil incorporation scenario using the upper bound 90<sup>th</sup> percentile concentration**

Substances	Cas No.	PNEC (mg kg <sup>-1</sup> ww)	Manure (90 P) (mg kg <sup>-1</sup> ww)	PEC 4t/1app (mg kg <sup>-1</sup> ww)	RCR	PEC 4t/10app (mg kg <sup>-1</sup> ww)	RCR	PEC 10t/1app (mg kg <sup>-1</sup> ww)	RCR	PEC 10t/10app (mg kg <sup>-1</sup> ww)	RCR
Enrofloxacin	93106-60-6	1.47E-03	2.75E-02	3.24E-05	0.022	3.24E-04	0.22	8.09E-05	0.055	8.09E-04	0.55
Sulfamethoxazole	723-46-6	1.35E-03	2.46E-02	2.89E-05	0.02	2.89E-04	0.21	7.24E-05	0.05	7.24E-04	0.54

**Table 5.10 Refined risk assessment for poultry manures in the soil incorporation scenario using the upper bound median concentration**

Substances	Cas No.	PNEC (mg kg <sup>-1</sup> ww)	Manure (median) (mg kg <sup>-1</sup> ww)	PEC 4t/1app (mg kg <sup>-1</sup> ww)	RCR	PEC 4t/10app (mg kg <sup>-1</sup> ww)	RCR	PEC 10t/1app (mg kg <sup>-1</sup> ww)	RCR	PEC 10t/10app (mg kg <sup>-1</sup> ww)	RCR
Enrofloxacin	93106-60-6	1.47E-03	1.25E-02	1.47E-05	0.010	1.47E-04	0.1	3.68E-05	0.025	3.68E-04	0.25
Sulfamethoxazole	723-46-6	1.35E-03	1.20E-02	1.41E-05	0.01	1.41E-04	0.10	3.53E-05	0.03	3.53E-04	0.26

### 5.2.3 Refined Risk Assessment for processed biosolids samples

The refined risk assessments for each sewage treatment plant have been conducted separately due to the different treatment used at each site. The refined risk assessments for processed biosolids have been performed using the soil incorporation scenario only for the one spread rate calculated for each sludge (STP 1, 5 t ha<sup>-1</sup>; STP 2, 30 t ha<sup>-1</sup>). The refined risk assessment for STP 1 (liming) for the 90<sup>th</sup> percentile and upper-bound median concentration are detailed in Tables 5.11 and 5.12, and for STP 2 (anaerobic digestion treatment) in Tables 5.13 and 5.14.

From these refined assessments it can be seen that potential risks have been identified for the following contaminants:

- STP 1 (liming treatment); Ciprofloxacin at ten applications for both the median and 90<sup>th</sup> percentile concentration. A risk was also identified for ten applications for HHCB (galaxolide) for the 90<sup>th</sup> percentile concentration (RCR = 1.13) but not for the median concentration (RCR = 0.72). Although the median concentration does not identify a potential risk, the 90<sup>th</sup> percentile concentration does; the 90<sup>th</sup> percentile is equivalent to a reasonable worst case concentration and is more appropriate for this assessment due to the limited dataset available and the lack of temporal variation in the samples taken. HHCB (galaxolide) at STP 1 was detected in all samples (range = 4.2 to 12 mg kg<sup>-1</sup>, standard deviation = 3.33 mg kg<sup>-1</sup>)
- STP 2 (anaerobic digestion); Ciprofloxacin at ten applications for both the median and 90<sup>th</sup> percentile concentration. A risk was also identified for ten applications for HHCB (galaxolide) for the 90<sup>th</sup> percentile and median concentration.

No risks were identified for the other prioritised contaminants for analysis in the processed biosolid samples for either STP1 or STP 2 at either the 90<sup>th</sup> percentile or median concentration.

Several risks have been identified for ciprofloxacin. However risks for ciprofloxacin and enrofloxacin should be treated with caution, as there is considerable uncertainty with the derived PNEC for these substances (see section 2.3 and associated spreadsheet tab "PNECs") Therefore, this assessment should be treated as indicative.

**Table 5.11 Refined risk assessment for lime stabilised sludge cake from STP 1 using the upper bound 90<sup>th</sup> percentile concentration**

Substances	Cas No.	PNEC (mg kg <sup>-1</sup> ww)	Sludge (90 P) (mg kg <sup>-1</sup> ww)	PEC 5t/1app (mg kg <sup>-1</sup> ww)	RCR	PEC 5t/10app (mg kg <sup>-1</sup> ww)	RCR
Ciprofloxacin	85721-33-1	1.47E-03	0.16	2.35E-04	0.16	2.35E-03	1.597
Enrofloxacin*	93106-60-6	1.47E-03	0.01	1.47E-05	0.010	1.47E-04	0.0998
Oxytetracycline	6153-64-6	1.81	1.23	1.81E-03	9.98E-04	1.81E-02	9.98E-03
Sulfamethoxazole*	723-46-6	1.35E-03	1.00E-03	1.47E-06	1.09E-03	1.47E-05	1.09E-02
Triclosan	3380-34-5	0.147	0.333	4.90E-04	3.32E-03	4.90E-03	0.03
Ivermectin*	70288-86-7	6.35E-02	1.00E-02	1.47E-05	2.32E-04	1.47E-04	2.32E-03
HHCb (galaxolide)	1222-05-5	0.147	11.3	1.66E-02	0.11	1.66E-01	1.13
PFOS	1763-23-1	1.59E-02	4.30E-05	6.32E-08	3.99E-06	6.32E-07	3.99E-05
BaP*	50-32-8	0.17	0.2	2.94E-04	1.73E-03	2.94E-03	1.73E-02
DEHP	117-81-7	14.7	2.06	3.03E-03	2.05E-04	3.03E-02	2.05E-03
Dieldrin*	60-57-1	2.27E-02	5.00E-03	7.35E-06	3.24E-04	7.35E-05	3.24E-03
BDE-209 (decabromodiphenyl)	1163-19-5	98.6	6.75E-05	9.93E-08	1.01E-09	9.93E-07	1.01E-08

**Table 5.12 Refined risk assessment for lime stabilised sludge cake from STP 1 using the upper bound median concentration**

Substances	Cas No.	PNEC (mg kg <sup>-1</sup> ww)	Sludge (median) (mg kg <sup>-1</sup> ww)	PEC 5t/1app (mg kg <sup>-1</sup> ww)	RCR	PEC 5t/10app (mg kg <sup>-1</sup> ww)	RCR
Ciprofloxacin	85721-33-1	1.47E-03	0.128	1.88E-04	0.127	1.88E-03	1.273
Enrofloxacin*	93106-60-6	1.47E-03	1.00E-02	1.47E-05	0.010	1.47E-04	0.10
Oxytetracycline	6153-64-6	1.81	0.918	1.35E-03	7.44E-04	1.35E-02	7.44E-03
Sulfamethoxazole*	723-46-6	1.35E-03	1.00E-03	1.47E-06	1.09E-03	1.47E-05	1.09E-02
Triclosan	3380-34-5	0.147	0.288	4.23E-04	2.87E-03	4.23E-03	0.03
Ivermectin*	70288-86-7	6.35E-02	1.00E-02	1.47E-05	2.32E-04	1.47E-04	2.32E-03
HHCb (galaxolide)	1222-05-5	0.147	7.21	1.06E-02	0.07	1.06E-01	0.72
PFOS	1763-23-1	1.59E-02	2.44E-05	3.58E-08	2.26E-06	3.58E-07	2.26E-05
BaP*	50-32-8	0.17	0.200	2.94E-04	1.73E-03	2.94E-03	1.73E-02
DEHP	117-81-7	14.7	1.61	2.37E-03	1.61E-04	2.37E-02	1.61E-03
Dieldrin*	60-57-1	2.27E-02	5.00E-03	7.35E-06	3.24E-04	7.35E-05	3.24E-03
BDE-209 (decabromodiphenyl)	1163-19-5	98.6	3.60E-05	5.29E-08	5.37E-10	5.29E-07	5.37E-09

**Table 5.13 Refined risk assessment for anaerobically digested sludge cake from STP 2 using the upper bound 90<sup>th</sup> percentile concentration**

Substances	Cas No.	PNEC (mg kg <sup>-1</sup> ww)	Sludge (90P) (mg kg <sup>-1</sup> ww)	PEC 30t/1app (mg kg <sup>-1</sup> ww)	RCR	PEC 30t/10app (mg kg <sup>-1</sup> ww)	RCR
Ciprofloxacin	85721-33-1	1.47E-03	4.58E-02	4.04E-04	0.274	4.04E-03	2.740
Enrofloxacin*	93106-60-6	1.47E-03	2.50E-03	2.21E-05	0.015	2.21E-04	0.1497
Oxytetracycline	6153-64-6	1.81	0.122	1.07E-03	5.91E-04	1.07E-02	5.91E-03
Sulfamethoxazole*	723-46-6	1.35E-03	2.50E-04	2.21E-06	1.64E-03	2.21E-05	1.64E-02
Triclosan	3380-34-5	0.147	0.300	2.65E-03	1.80E-02	2.65E-02	1.80E-01
Ivermectin*	70288-86-7	6.35E-02	2.50E-03	2.21E-05	3.48E-04	2.21E-04	3.48E-03
HHCB (galaxolide)	1222-05-5	0.147	10.3	9.11E-02	0.62	9.11E-01	6.18
PFOS	1763-23-1	1.59E-02	1.48E-05	1.30E-07	8.20E-06	1.30E-06	8.20E-05
BaP*	50-32-8	0.17	2.50E-02	2.21E-04	1.30E-03	2.21E-03	1.30E-02
DEHP	117-81-7	14.7	7.87E-02	6.94E-04	4.71E-05	6.94E-03	4.71E-04
Dieldrin*	60-57-1	2.27E-02	1.25E-03	1.10E-05	4.87E-04	1.10E-04	4.87E-03
BDE-209 (decabromodiphenyl)	1163-19-5	98.6	2.95E-05	2.60E-07	2.64E-09	2.60E-06	2.64E-08

**Table 5.14 Refined risk assessment for anaerobically digested sludge cake from STP 2 using the upper bound median concentration**

Substances	Cas No.	PNEC (mg kg <sup>-1</sup> ww)	Sludge (Median) (mg kg <sup>-1</sup> ww)	PEC 30t/1app (mg kg <sup>-1</sup> ww)	RCR	PEC 30t/10app (mg kg <sup>-1</sup> ww)	RCR
Ciprofloxacin	85721-33-1	1.47E-03	4.13E-02	3.64E-04	0.247	3.64E-03	2.470
Enrofloxacin*	93106-60-6	1.47E-03	2.50E-03	2.21E-05	0.0150	2.21E-04	0.1497
Oxytetracycline	6153-64-6	1.81	9.00E-02	7.94E-04	4.38E-04	7.94E-03	4.38E-03
Sulfamethoxazole*	723-46-6	1.35E-03	2.50E-04	2.21E-06	1.64E-03	2.21E-05	1.64E-02
Triclosan	3380-34-5	0.147	0.211	1.86E-03	1.27E-02	1.86E-02	1.27E-01
Ivermectin*	70288-86-7	6.35E-02	2.50E-03	2.21E-05	3.48E-04	2.21E-04	3.48E-03
HHCB (galaxolide)	1222-05-5	0.147	9.25	8.16E-02	0.55	8.16E-01	5.54
PFOS	1763-23-1	1.59E-02	7.50E-06	6.62E-08	4.17E-06	6.62E-07	4.17E-05
BaP*	50-32-8	0.17	2.50E-02	2.21E-04	1.30E-03	2.21E-03	1.30E-02
DEHP	117-81-7	14.7	5.44E-02	4.80E-04	3.26E-05	4.80E-03	3.26E-04
Dieldrin*	60-57-1	2.27E-02	1.25E-03	1.10E-05	4.87E-04	1.10E-04	4.87E-03
BDE-209 (decabromodiphenyl)	1163-19-5	98.6	1.29E-05	1.14E-07	1.15E-09	1.14E-06	1.15E-08

#### **5.2.4 Refined Risk Assessment for compost samples**

A refined risk assessment was also performed for the compost samples; this assessment was performed at both eight and 30 tonnes per hectare application rates using the soil dressing mixing depth (5 cm) (Tables 5.15 and 5.16).

This assessment did not identify a risk for the prioritised contaminants DEHP, BaP and Dieldrin for compost. As no risk was identified for the soil dressing scenario, it was not deemed necessary to perform an assessment for the soil incorporation scenario.

**Table 5.15 Refined risk assessment for compost using the surface dressing scenario for the upper bound 90<sup>th</sup> percentile concentration**

Substances	Cas No.	PNEC (mg kg <sup>-1</sup> )	Compost (90P) (mg kg <sup>-1</sup> ww)	PEC 8t/1app (mg kg <sup>-1</sup> ww)	RCR	PEC 8t/10app (mg kg <sup>-1</sup> ww)	RCR	PEC 30t/1app (mg kg <sup>-1</sup> ww)	RCR	PEC 30t/10app (mg kg <sup>-1</sup> ww)	RCR
DEHP	117-81-7	14.7	0.171	1.60E-03	1.09E-04	1.60E-02	1.09E-03	6.02E-03	4.08E-04	6.02E-02	4.08E-03
BaP*	50-32-8	0.17	0.100	9.41E-04	5.54E-03	9.41E-03	5.54E-02	3.53E-03	2.08E-02	3.53E-02	2.08E-01
Dieldrin*	60-57-1	2.27E-02	2.50E-02	2.35E-04	1.04E-02	2.35E-03	1.04E-01	8.82E-04	3.89E-02	8.82E-03	3.89E-01

**Table 5.16 Refined risk assessment for compost using the surface dressing scenario for the upper bound median concentration**

Substances	Cas No.	PNEC (mg kg <sup>-1</sup> ww)	Compost (Median) (mg kg <sup>-1</sup> ww)	PEC 8t/1app (mg kg <sup>-1</sup> ww)	RCR	PEC 8t/10app (mg kg <sup>-1</sup> ww)	RCR	PEC 30t/1app (mg kg <sup>-1</sup> ww)	RCR	PEC 30t/10app (mg kg <sup>-1</sup> ww)	RCR
DEHP	117-81-7	14.7	0.100	9.41E-04	6.39E-05	9.41E-03	6.39E-04	3.53E-03	2.40E-04	3.53E-02	2.40E-03
BaP*	50-32-8	0.170	0.100	9.41E-04	5.54E-03	9.41E-03	5.54E-02	3.53E-03	2.08E-02	3.53E-02	2.08E-01
Dieldrin*	60-57-1	2.27E-02	2.50E-02	2.35E-04	1.04E-02	2.35E-03	1.04E-01	8.82E-04	3.89E-02	8.82E-03	3.89E-01

## 5.3 Human Health Risk Assessment

### 5.3.1 Methodology

For materials applied to land as a fertiliser or soil improver the potential impact on human health from the contaminant via the food chain is the most significant exposure pathway. Dietary exposure assessment for materials spread to land involves calculating the uptake of contaminants from soil into plants such as fruits, vegetables and cereals and subsequent transfer to humans through the consumption of these foods as well as meats, egg and dairy products (following consumption of silage and forage crops by farm animals).

Dietary exposure assessment has been undertaken for contaminants measured in organic materials applied to land and having a significant hazard to human health<sup>18</sup>. Exposure assessment and estimation of risk used a modelling tool developed by the Environment Agency, WALTER (**W**aste **A**pplications to **L**and: **T**ool for **E**nvironmental **R**isk)<sup>19</sup>. Concentrations of contaminants in waste material, physico-chemical properties of the contaminants, soil properties and the material application rates were inputted to the model to calculate concentrations in foods and the resultant level of risk to adult and infant consumers based on their consumption rates for various food types. Soil:plant uptake factors are calculated within the model and the food intakes used in WALTER are the mean rates for consumers.

Input parameter values for the exposure scenario used to characterise modelling of dietary exposure to priority contaminants in organic waste applied to land using WALTER are detailed in Table 5.17. As for the environmental risk assessment, surface dressing with 5 cm mixing depth was considered as an initial worst case scenario for manures and compost. Soil incorporation via ploughing (25 cm mixing depth in WALTER) was used for application of biosolids. Physico-chemical properties of the contaminants are detailed in Appendix 2 and representative contaminant concentrations used as input to the assessment are detailed in Tables 4.3 – 4.7. Maximum or 90<sup>th</sup> percentile (90P) concentrations of contaminants measured in materials were used for initial modelling as a reasonable worst case. The priority contaminants selected for assessment have relatively long biodegradation half-lives and no degradation is assumed for the duration of the assessment; it has already been acknowledged that this a relatively conservative approach that could be refined in the future if required.

**Table 5.17 Data input to WALTER dietary exposure model for assessment of contaminants in waste spread to land**

Model Parameter	Value
Application rate	STP 1: 5 t/ha (dw <sup>20</sup> ) STP 2: 30 t/ha (ww) Compost, Cattle & pig manure: 30 t/ha (ww) Poultry manure: 10 t/ha (ww)

<sup>18</sup> Defined as those contaminants scored >6 for hazard to human health (see Table 3.4 in Section 3.3)

<sup>19</sup> While every effort has been made to ensure that the calculations are implemented correctly, the Environment Agency accepts no liability for their use and provides no warranty whatsoever.

<sup>20</sup> Biosolids from STP 1 are subjected to liming and have negligible moisture content

<b>Model Parameter</b>	<b>Value</b>
Application frequency	Once per year
Time period	10 years
Incorporation depth(s)	5cm (WALTER default for surface dressing) 25 cm (WALTER default for ploughed in application)
Soil density	1300 kg/m <sup>3</sup> (WQP Sandy Loam, WALTER)
Soil organic carbon	3.4% (EA 2017)

Ww =wet weight; dw = dry weight

### **5.3.2 Human Health Risk Assessment Results for Organic Material applied to Land**

Summary results of the human health risk assessment are presented in Tables 5.18 to 5.23. For all contaminants and scenarios the hazard quotients (HQs) are considerably less than 1. For biosolids and compost predicted HQs range from  $5.0 \times 10^{-6}$  to 0.03 and for manures from  $8.9 \times 10^{-6}$  to  $8.7 \times 10^{-5}$ . These results indicate that dietary exposure to the prioritised contaminants in food produced from waste-amended land is unlikely to pose an unacceptable level of risk to health at the contaminant concentrations measured in organic wastes for this project.

### **5.3.3 Wood Ash data**

The data for the 'dioxin' content of the three virgin wood ash samples indicated a mean concentration of 39 ng/kg WHO-TEQ (upper bound) and a maximum concentration of 43 ng/kg WHO-TEQ. The mean value is nearly four times higher than the average dioxin content recommended in the Quality Protocol for poultry litter ash used as a fertiliser (EA 2012) and commonly used in the health risk assessment of materials applied to land. Significantly, the dioxin content of all samples is higher than the maximum allowed concentration of 20 ng/kg WHO-TEQ. As these results were considerably higher than would be expected, the operator was consulted and stated that though these three samples breach the standard in the Quality Protocol for poultry litter ash used as a fertiliser (EA 2012), there is not enough data at this stage to make any judgement on whether action is required in response to this. Further analysis will be carried out using a UKAS accredited method and should this identify dioxin-like compounds in the ash close to or above the standard, additional testing of individual biomass streams will then be undertaken to identify the origin.

**Table 5.18 Results of dietary exposure assessment for sewage sludge biosolids from STP 1 applied to agricultural land (5 t/ha)**

Substance	90P Contaminant concentration (mg/kg)	Soil concentration (mg/kg)	Adult Intake (mg/day)	Infant intake (mg/day)	HCV (mg/kg bw/day)	Hazard Quotient (max)
DEHP	2.06	1.71E-01 <sup>21</sup>	6.24E-03	4.86E-03	1.00E-02	0.0295
PFOS*	4.3E-05	5.08E-07	4.59E-06	5.67E-06	3.00E-04	2.17E-03
BDE 209	6.75E-05	9.87E-07	2.83E-09	3.06E-09	7.00E-03	5.02E-08
Ciprofloxacin	0.16	1.67E-03	5.84E-06	2.31E-06	6.20E-03	4.28E-05

\*Note that if the revised (ESFA, 2018a) TWI were used for PFOS, a higher Hazard Quotient would be achieved, although it would still be below 1 as the revised PFOS TWI is only 80 times higher than the previous ESFA (2008) value, whilst the hazard quotient is 3 orders of magnitude below 1. Please also see footnote to Table 3.1.

**Table 5.19 Results of dietary exposure assessment for sewage sludge biosolids from STP 2 applied to agricultural land (30 t/ha ww)**

Substance	90P Contaminant concentration (mg/kg)	Soil concentration (mg/kg)	Adult Intake (mg/day)	Infant intake (mg/day)	HCV (mg/kg bw/day)	Hazard Quotient (max)
DEHP	0.315	1.53E-01 <sup>22</sup>	2.93E-03	2.30E-03	1.00E-02	0.0263
PFOS*	5.9E-05	1.04E-06	9.45E-06	1.17E-05	3.00E-04	4.47E-03
BDE 209	1.20E-04	2.63E-06	7.55E-09	8.16E-09	7.00E-03	1.34E-07
Ciprofloxacin	0.183	2.87E-03	1.00E-05	3.96E-06	6.20E-03	7.33E-05

\*Note that if the revised (ESFA, 2018a) TWI were used for PFOS, a higher Hazard Quotient would be achieved, although it would still be below 1 as the revised PFOS TWI is only 80 times higher than the ESFA (2008) value, whilst the hazard quotient is 3 orders of magnitude below 1. Please also see footnote to Table 3.1.

<sup>21</sup> Including background concentration of 0.153 mg/kg DEHP measured in Scottish arable soil (Rhind *et al.* 2013)

<sup>22</sup> Calculated soil concentration following application of waste in addition to background concentration of 0.153 mg/kg DEHP measured in Scottish arable soil - model calculates no enrichment of background concentration

**Table 5.20 Results of dietary exposure assessment for pig manure applied as surface dressing (30 t/ha ww)**

Substance	Max Contaminant concentration (mg/kg)	Soil concentration (mg/kg)	Adult Intake (mg/day)	Infant intake (mg/day)	HCV (mg/kg bw/day)	Hazard Quotient (max)
Ivermectin	0.01	1.06E-03	1.03E-05	7.60E-06	1.00E-02	8.74E-05
Ciprofloxacin	0.01	7.83E-04	1.12E-06	4.81E-07	6.20E-03	8.91E-06

**Table 5.21 Results of dietary exposure assessment for cattle manure applied as surface dressing (30 t/ha ww)**

Substance	90P Contaminant concentration (mg/kg)	Soil concentration (mg/kg)	Adult Intake (mg/day)	Infant intake (mg/day)	HCV (mg/kg bw/day)	Hazard Quotient (max)
Ivermectin	0.03	1.10E-03	1.03E-05	7.60E-06	1.00E-02	8.74E-05

**Table 5.22 Results of dietary exposure assessment for poultry manure applied as surface dressing (10 t/ha ww)**

Substance	Max Contaminant concentration (mg/kg)	Soil concentration (mg/kg)	Adult Intake (mg/day)	Infant intake (mg/day)	HCV (mg/kg bw/day)	Hazard Quotient (max)
Ciprofloxacin	0.03	1.10E-03	1.56E-06	6.73E-07	6.20E-03	1.25E-05

**Table 5.23 Results of dietary exposure assessment for compost applied as surface dressing (30 t/ha ww)**

Substance	90P Contaminant concentration (mg/kg DW)	Soil concentration (mg/kg)	Adult Intake (mg/day)	Infant intake (mg/day)	HCV (mg/kg bw/day)	Hazard Quotient (max)
DEHP	0.341	0.214 <sup>3</sup>	3.72E-03	2.30E-03	1.00E-02	0.033

## 6 CONCLUSIONS

In the initial phase of the project more than 200 contaminants were identified that had been measured in sewage sludges, manures and composts. A prioritisation exercise was undertaken based on the screening of persistence and bioaccumulation potential followed by risk assessment using calculated concentrations in soil following application to land and available predicted no effect concentrations (PNECs). Priority contaminants identified by this exercise for further assessment included human and veterinary medicines, biocides, plasticisers, industrial chemicals and personal care products.

Previously undertaken risk assessments of contaminants in organic materials applied to land have several limitations in that the analysis has not been carried out on the material directly prior to application to land. Furthermore, the assessments have often used data from geographical locations and climatic regions that are not entirely relevant to the UK. These issues have been addressed here by analysing samples of composts and processed sewage sludge from Scotland and animal manures from Scotland and England in the specific condition in which they are applied to land.

Samples of processed biosolids were provided by Scottish Water and compost samples were provided by commercial producers of plant/ and plant/food-derived compost. A number of food producers in England and Scotland have provided samples of manure from pigs, cattle and poultry in addition to information about their usage of the veterinary medicines prioritised for assessment in this project.

Prioritised contaminant concentrations were determined in processed biosolids from two STPs. Results (Tables 4.6 and 4.7) show that concentrations of the medicine sulfamethoxazole and the organochlorine pesticide dieldrin are below the analytical limits of detection. Concentrations of the plasticiser DEHP and the fluorosurfactant PFOS are significantly lower in the sampled biosolids than values previously reported in the literature for unprocessed sewage sludge (Clarke and Smith, 2011; JRC, 2012). It is uncertain whether this is due to reduced concentrations in the sewerage system or whether treatment of the sludge has led to reduced levels. Triclosan was also detected at much lower concentrations than previously reported in the literature at both STPs (Clarke and Smith, 2011). This may be due to sludge treatment, or more likely its phasing out for a number of consumer uses (in 2015 ECHA's Biocidal Products Committee decided that Triclosan should not be approved for use as a disinfectant in human hygiene products). Risk assessment for the application of processed biosolids containing the levels of triclosan, PFOS and DEHP measured in this study indicates a low level of risk to the terrestrial environment. However, the synthetic musk HHCB (galaxolide) was measured at concentrations comparable to, and exceeding, those previously reported in the literature (JRC, 2012). Concentrations of HHCB were significantly higher at STP2 than STP1, indicating a difference in either the sewage influent characteristics or in the removal efficiency of different types of sewage treatment. Risk assessment for biosolid application to land indicated a potential risk from HHCB to the terrestrial environment following repeated application. The antibiotics ciprofloxacin and oxytetracycline were detected in all STP samples; concentrations were also lower than those previously reported in the literature (Clarke & Smith 2011; Chen *et al.* 2013). Potential risks to soil organisms were identified for Ciprofloxacin, but

these must be treated with caution because there is considerable uncertainty with the derived PNEC, hence they can only be considered as indicative. Levels of oxytetracycline were well below risk levels.

In pig manure, ciprofloxacin, enrofloxacin and ivermectin were below the analytical limit of detection ( $10 \mu\text{g kg}^{-1}$ ) in all samples. Ciprofloxacin was also below the LoD in all poultry manure samples. It is important to also note that these were samples taken from herds and flocks treated with the veterinary medicine within the last six months. The prioritised determinands were measured in at least one sample for other manures but these concentrations were all below the maximum reported literature concentrations (Bloem *et al.* 2017; Environment Agency 2006; Zhang *et al.* 2015). Risk assessment for manure applications to land found no risk to soil health for most of the manures and application scenarios. A small potential risk from the application of poultry manures (RCR 1 – 2.2) was identified only at the highest application rates for consecutive applications as a surface dressing (a soil incorporation depth of 0.05m). It should also be recognised that the risk assessment did not take into account any reduction in soil concentrations due to abiotic and biotic degradation, leaching or offtake, which might have made a considerable effect over a ten-year period. In addition, there is considerable uncertainty in the PNECs for ciprofloxacin and enrofloxacin.

In the compost, BaP and dieldrin were less than the LoD in all samples. DEHP was less than LoD in four of the six samples, with the maximum concentration measured being  $0.473 \text{ mg kg}^{-1}$ ; approximately four times lower than the maximum measured concentration in the literature of  $1.98 \text{ mg kg}^{-1}$  (Brändli *et al.* 2006).

The potential risks identified for terrestrial organisms from the refined environmental risk assessment are summarised in Table 6.1.

**Table 6.1 Identified potential risks for organic waste materials and specific chemicals at different application rates (applied as a surface dressing with a soil incorporation depth of 0.05m)**

Material	Concentration	Single Application		x 10 applications	
		Low spread-rate	High spread-rate	Low spread-rate	High spread-rate
Limed sludge cake (STP 1)	90th Percentile	N.A.	-	N.A.	Ciprofloxacin; HHCB (galaxolide)
	Median	N.A.	-	N.A.	Ciprofloxacin
Anaerobically digested sludge cake (STP2)	90th Percentile	N.A.	-	N.A.	Ciprofloxacin; HHCB (galaxolide)
	Median	N.A.	-	N.A.	Ciprofloxacin; HHCB (galaxolide)
Pig manure	90th Percentile	-	-	-	-
	Median	-	-	-	-
Cattle manure	90th Percentile	-	-	-	-
	Median	-	-	-	-
Poultry manure	90th Percentile	-	-	-	Enrofloxacin; Sulfamethoxazole
	Median	-	-	-	Enrofloxacin; Sulfamethoxazole
Compost	90th Percentile	-	-	-	-
	Median	-	-	-	-

- = No risk identified  
N.A. = Not assessed

An initial screening risk assessment based on concentrations reported in literature (usually taken from other parts of the world) suggested that many contaminants in materials spread to land posed risks and that these risks occurred even where spread rates were low and single applications used (Table 3.2; section 3.2). Undertaking a refined risk assessment based on measured concentrations in materials spread to land in Scotland and England established that relatively few contaminants were identified at the levels found in the previous literature and that the potential risks were limited only to the high spread rate scenarios with multiple applications of materials (Table 6.1). This demonstrates that environmental risks from contaminants in materials spread to land in Scotland and England are likely to be much lower than predicted by the screening assessment and illustrates the importance of characterising materials in the condition in which they are applied to land in the UK.

Modelling of human dietary exposure to selected contaminants in organic materials applied to agricultural land indicates a negligible level of risk arising from this exposure pathway for these contaminants at the concentrations measured in biosolids, manure and compost. It is therefore unlikely that these contaminants pose a risk to human health as constituents of

organic waste spread to land. However, there were a number of prioritised contaminants for which health criteria values could not be identified meaning that they could not be considered as part of the hazard screening or risk assessment for human health (see 'parked' chemicals in Table 3.4).

## **6.1 Potential long-term risks from organic chemicals in materials spread to land with current practices**

The measured concentrations of contaminants in material spread to land and risk assessment undertaken in this project indicate that it is likely to be a low risk to human health and the environment under current application practices (and following good practice) from the prioritised chemicals for which hazard data are available. It is not currently possible to establish maximum safe spread rates for any of the materials examined due to residual uncertainties in factors such as field degradation rates and PNECs.

In the spreadsheets developed for this project it is possible to assess the influence of changing rates of application for alternative uses of these materials such as reclamation.

## **6.2 Future potential risks**

The contaminants prioritised for analysis in organic materials applied to land have been selected on the basis of behaviour, fate and potential hazard to both human health and the soil environment. The measured data collected in these materials is very limited in terms of scope, but it does represent a useful starting point and is perhaps the first time samples have been collected and contaminants measured in Scotland if not the UK with the explicit aim of assessing potential human and environmental health risks.

A refinement of the risk assessment would be required in order to identify future potential risks. Three specific areas would need to be addressed in order to do this:

- Evaluation of the regulatory certainty of the existing PNECs. The methodology used to derive these PNECs usually relies upon the use of large assessment factors (10-100) when ecotoxicity data are limited. This delivers a considerable amount of conservatism into the characterisation of potential risk.
- It is well recognised that social behaviours and animal rearing practices can dramatically influence the concentrations of some chemicals in organic materials. In order to gain an understanding of this more samples across a greater number of STPs and farms in England and Scotland would be required.
- Finally, there are many chemicals in wide-spread use, a fraction of which have been prioritised here, and there are many for which no assessment of the potential risks has been possible. These may reasonably present risks now, but there is currently not enough available information from which to make even a rudimentary assessment of current or potential future risks. National and international collaborative working would seem like the most expedient way to fill this clear information gap.

The prioritisation undertaken in this project is reliant upon finding in the literature measured concentrations of chemicals in the materials of interest (i.e. the 'known, knowns'). However,

many chemicals that may be present in these materials are used in relatively small amounts and European authorisation and registration data requirements are limited. For these chemicals it is especially difficult to judge the potential risks they may present. Importantly, articles imported to the European Union that may have specific chemicals present (such as PFOS) are not strongly controlled under existing legislation.

## 7 DISCUSSION AND RECOMMENDATIONS

This project has reported a step-wise risk-based approach to determining potential risks from chemicals in organic materials applied to land in Scotland and England. The measurement of chemical concentrations in samples of material directly prior to their spreading on land has enabled the undertaking of a more relevant risk assessment and helped to identify the next areas for refinement. We have drawn the following conclusions from this project:

- Many of the chemicals prioritised for measurement in the materials going to land were not routine determinands for commercial laboratories, which suggests that few of these substances are being measured regularly.
- Difficulties in method development undertaken by the laboratory emphasised the complexity of the matrices being assessed.
- Sampling of biosolids was undertaken at the end of the winter period when the use of many medicines, especially antibiotics, is likely to be at its highest level.
- Most priority contaminants measured in biosolids from two Scottish STPs occurred at lower concentration than previously reported in the literature from outside the UK, for unprocessed sewage sludge. A similar trend was also observed for the manure and compost samples.
- Triclosan concentrations appear to be declining concurrent with the removal of this biocide from consumer products. PFOS and PBDE concentrations in biosolids were significantly lower than previously reported for sewage sludge in the literature.
- The synthetic musk HHCB (galaxolide) was the contaminant measured at the highest concentrations (up to 42 mg kg<sup>-1</sup>) and risk assessment for application of biosolids to land indicates a potential risk to soil organisms following long term application. Multiple application of biosolids containing HHCB (galaxolide) produce RCRs up to 6.18 for 10 applications at 30 tonnes per hectares for anaerobically digested sludge cake. Currently there is no consideration of biodegradation of HHCB over this period; a half-life in soil of 180 days is reported by Clarke et al. (2011), which would indicate the potential for removal of this compound by microbial degradation. Further modelling work and possibly field monitoring could be undertaken to assess the extent to which biodegradation of HHCB and similar compounds prevents their accumulation in soil.
- Ciprofloxacin has been identified as a potential risk in multiple sludge application scenarios that were modelled; however, the derivation of the PNEC is uncertain and is associated with a high degree of uncertainty and likely conservatism; this means there is considerable uncertainty regarding the actual risk posed.
- Enrofloxacin and sulfamethoxazole in multiple applications of poultry manure at the highest spreading rates with limited soil incorporation have been identified as a potential risks; however, there is a large degree of uncertainty in the PNEC for enrofloxacin.
- Lower concentrations measured in biosolids for this project may be due to analysis of treated material compared to untreated sludge or the reduced use of the prioritised chemicals. Differences in results between the two STPs may be due to variation in input or the type of technique used for sludge treatment. Further work is required to elucidate these observations.

- Farms indicated much reduced use of antibiotics; there is no longer prophylactic use of this type of veterinary medicine and farm owners reported that they are only using these substances when absolutely necessary. Indeed, it was difficult to obtain samples of manure from farms that had recently treated their animals with the veterinary medicines identified from our prioritisation exercise. Therefore the manure samples used in this study are inherently biased towards higher concentrations and it is likely that typical manures spread to land contain none of the medicines considered here.
- This project indicates only limited potential for risks from organic compounds in organic material applied to agricultural soil. However, this limited dataset only presents a snapshot for a small number of contaminants and the results indicate the need for monitoring of certain medicines and personal care products, such as synthetic musks. Many of the hazard-based metrics (e.g. PNECs) used to characterise the environmental risks of chemicals applied to land in organic materials have low levels of regulatory certainty. These are likely to be precautionary but this is an area for which obvious refinement could be made, especially for the human and veterinary medicines.
- Human health risk assessment based on dietary exposure and using data generated from analysis of materials applied to land suggests that there is a low level of risk to human health arising from this exposure pathway for these compounds at the concentrations measured in biosolids, manure and compost.
- It was not possible to establish maximum safe spread rates for any of the organic materials included in the study because of residual uncertainties in PNECs and contaminant degradation rates. This also means that it is not currently possible to determine if spreading and/or land management methods need to be altered due to contaminant concentrations in spread materials.

Recommendations arising from this project are in line with those that would be expected in any refinement of a risk assessment, including the collection of more, targeted, locally relevant data from organic materials and the development of robust metrics by which to characterise potential risks. The antibiotics assessed in this study have especially poorly developed environmental hazard profiles and we would strongly recommend working with the producers and manufacturers of these drugs to develop better PNECs for the terrestrial environment. Additionally, those substances that have no PNEC also require greater characterisation and investigation otherwise there is the risk that they remain “parked” indefinitely despite being a potential cause for concern. The risk assessments for long term spreading in this report assumed contaminants accumulate in soils with no removal mechanisms. This conservative assumption could be refined in the future. More generally, the risk assessment paradigm for regulation used here has considered chemicals and their risk individually whereas in reality soils, soil organisms, and crops that are grown in agricultural soils are exposed to a mixture of contaminants. When approaches to mixture assessment become accepted in regulation that are relevant for the topic assessed in this project, they should be applied.

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## Appendix 1 Physico-chemical data input to WALTER model for HHRA

Property	Ciprofloxacin		Ivermectin	
	Value	Source	Value	Source
<b>K<sub>aw</sub> (at 10°C)</b>	5.23E-15	Boethling & Mackay 2000 <sup>i</sup>	5.23E-15	Boethling & Mackay 2000 <sup>i</sup>
<b>D<sub>a</sub> (m<sup>2</sup> s<sup>-1</sup>)</b>	2.92E-06	SPARC <sup>ii</sup>	1.27E-06	SPARC
<b>D<sub>w</sub> (m<sup>2</sup> s<sup>-1</sup>)</b>	3.96E-10	SPARC	1.99E-10	SPARC
<b>log K<sub>ow</sub></b>	0.28	HSDB <sup>iii</sup>	4.86	Drugbank <sup>iv</sup>
<b>log K<sub>oc</sub> (L kg<sup>-1</sup>)</b>	4.54	EA 2006	5.662	EPIWIN <sup>v</sup>
<b>MW (g mol<sup>-1</sup>)</b>	331.34	Merck Index <sup>vi</sup>	875.106	PubChem <sup>vii</sup>
<b>Vap (Pa) (at 10°C)</b>	5.79E-13	SPARC	9.79E-36	SPARC
<b>Sol (mg L<sup>-1</sup>)</b>	30000	HSDB	8.88E-04	EPIWIN
<b>K<sub>d</sub> (L kg<sup>-1</sup>)</b>	NR		NR	
<b>Degradation type</b>	Inherently biodegradable	Liao <i>et al.</i> (2016) <sup>viii</sup>	Inherently biodegradable	UK Marine SACS <sup>ix</sup>
<b>CF<sub>cereals</sub> (kg kg<sup>-1</sup> DW)</b>	Calculated by WALTER		Calculated by WALTER	
<b>CF<sub>greenveg</sub> (kg kg<sup>-1</sup> DW)</b>	Calculated by WALTER		Calculated by WALTER	
<b>CF<sub>rootveg</sub> (kg kg<sup>-1</sup> DW)</b>	Calculated by WALTER		Calculated by WALTER	
<b>CF<sub>fruit</sub> (kg kg<sup>-1</sup> DW)</b>	Calculated by WALTER		Calculated by WALTER	
<b>CF<sub>grasses</sub> (kg kg<sup>-1</sup> DW)</b>	Calculated by WALTER		Calculated by WALTER	
<b>CF<sub>meat</sub> (kg DW kg<sup>-1</sup> FW)</b>	0.04	EA 2018 <sup>x</sup>	0.03	EA 2018
<b>CF<sub>offal</sub> (kg DW kg<sup>-1</sup> FW)</b>	0.3	EA 2018	1.5	EA 2018
<b>CF<sub>milk</sub> (kg DW kg<sup>-1</sup> FW)</b>	0.03	EA 2018	0.43	EA 2018
<b>CF<sub>egg</sub> (kg DW kg<sup>-1</sup> FW)</b>	0.05	EA 2018	2.43	EA 2018

<sup>i</sup> Derived by approach outlined by Boethling & Mackay (2000) using HLC at 10 deg C calculated by SPARC

<sup>ii</sup> SPARC predictive software <http://www.archemcalc.com/sparc.html>

<sup>iii</sup> Hazardous Substances Databank (HSDB) <https://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB>

<sup>iv</sup> Drugbank entry for Ivermectin <https://www.drugbank.ca/drugs/DB00602>

<sup>v</sup> US EPA EPIWIN predictive software package

<sup>vi</sup> Cited in HSDB

<sup>vii</sup> PubChem <https://pubchem.ncbi.nlm.nih.gov/compound/ivermectin#section=Top>

<sup>viii</sup> <https://www.ncbi.nlm.nih.gov/pubmed/26762935>

<sup>ix</sup> UK Marine SACS Project [http://www.ukmarinesac.org.uk/activities/water-quality/wq8\\_23.htm](http://www.ukmarinesac.org.uk/activities/water-quality/wq8_23.htm)

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