ASSESSMENT OF RISKS TO SOIL QUALITY AND HUMAN HEALTH FROM ORGANIC CONTAMINANTS IN MATERIALS COMMONLY SPREAD ON LAND IN SCOTLAND

FINAL REPORT TO SEPA FROM WCA ENVIRONMENT LIMITED

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EXECUTIVE SUMMARY

Application of organic materials to land can provide many benefits and promote sustainable use of what can be considered to be wastes under some circumstances. The application of these materials is undertaken within robust regulatory frameworks at a local, national and in some cases international level. This regulatory framework ensures that benefits are realised and potential environmental and human health risks are minimised.

However, there may be some circumstances under which exposures of chemicals in organic materials from some sources may present potential risks within the current regulatory framework. This project was aimed at identifying organic chemicals in organic materials that might be spread to land in Scotland and their likely concentrations, and collating environmental and human health related effects data, as well as behaviour and fate information. These outputs were then used to perform a spatial assessment of the potential risks to identify the form, magnitude and characteristics of risks from organic chemicals present in organic wastes spread to land in Scotland.

Animal manures represent the bulk of organic materials going to land in Scotland (over 95%) and, in these materials, the veterinary medicines ivermectin and tetracycline were identified as potentially presenting environmental risks. The spatial assessment, on a Local Authority Area basis, indicated that the southern lowlands, central belt, Angus and Aberdeenshire are areas were a greater level of detailed data would assist in refinement of the assessment.

Some chemicals indentified in organic materials as potentially presenting an environmental risk, such as nonylphenol, phenol and Linear alkylbenzene sulphonate (LAS), have relatively short half-lives in soils and would likely not accumulate.

Tetracycline, ivermectin, triclosan, benzo-a-pyrene, galaxolide, polybrominated diphenylethers, polychlorinated biphenyls (PCBs) and dioxins and dioxin-like PCBs where all modelled spatially to assess potential risks. These assessments demonstrated potential local risks for human and environmental health and indicated that these are most likely to occur in the central belt.

Quantitative risk assessment for human health was undertaken for dietary exposure resulting from the presence of contaminants in waste applied to agricultural land. This considered the potential for dioxins present in exempt waste to transfer and accumulate through the food chain and increase dietary exposure to this class of organic contaminants. The results of the assessment indicated that there was no risk to health even when using worst case assumptions, such as the maximum recorded concentration of dioxins in Mechanical Biological Treatment Compost-Like Output, a high rate of application of waste to land and the assumption that a full range of food groups is produced from waste amended land.

Refinement of the spatial assessments using a probabilistic approach for the three priority chemicals (HHCB, ivermectin, and tetracycline) demonstrated that uncertainties could be

greatly reduced by using measured data, instead of estimates, for the concentrations of chemicals in the materials, and the organic carbon of the receiving soil.

Finally a feasibility study was undertaken to determine the capability of commercial laboratories to undertake determinations of the priority chemicals from this exercise in organic materials. The results from this exercise demonstrated the paucity of commercial laboratories with the skills or experience to determine the concentrations of these types of determinands, with only two of ten laboratories filing a positive return. Of these two laboratories neither could perform determinations for all the priority chemicals and some of the chemicals identified could not be determined by either laboratory.

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GLOSSARY OF TERMS

Term	Explanation
PCB	Polychlorinated biphenyl
HHCB	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-gamma-2-benzopyran or Galaxolide. A polycyclic musk, used as a fragrance.
REACH	Registration, Evaluation, Authorisation and restriction of Chemicals regulation
JRC	Joint Research Centre
PEC	Predicted Environmental Concentration
PNEC	Predicted No Effect Concentration
RCR	Risk Characterisation Ratio
HCV	Health Criteria Value
MBT CLO	Mechanical Biological Treatment Compost Like Output
TEF and TEQ	Toxicity Equivalent Factor and Toxicity Equivalent, expresses the toxicity of dioxins, furans and PCBs in terms of the most toxic form of dioxin, 2,3,7,8-TCDD.
LoD (LOD)	Limit of Detection
PAHs	Polycyclic Aromatic Hydrocarbons
DEHP	Bis(2-ethylhexyl) phthalate (di-2-ethylhexyl phthalate. Plasticiser
LAS	Linear alkylbenzene sulfonate. Surfactant
PDBE	Poly Brominated Diphenyl Ether. Flame retardant
POP	Persistent Organic Pollutants

1 INTRODUCTION

Organic materials (and some inorganic materials) produced as by-products from agricultural, industrial and wastewater treatment activities may offer a range of agronomic and environmental benefits when applied to land. Direct benefits realised through the application of organic material to land include a reduction in the reliance on inorganic chemical fertilizers for macro and micronutrient supplementation. Organic materials can also be used to improve soil structure and drainage or to 'manufacture' soils that can be used for the remediation or improvement of degraded land.

Additional, less direct, environmental benefits have resulted from the development of sustainable end uses for these materials instead of the historic practice of landfilling. Criteria for 'end of waste' decision making for exempted industrial by-products has been explored extensively through the Environment Agency and WRAP's Quality Protocols programme[1].

These benefits are numerous, especially when regulated within well developed management frameworks (e.g. Code for Good Agricultural Practice for Farmers and Landowners; Code of Practice for the use of sludge, compost and other organic materials for land reclamation (SNIFFER 2010)) or legislation (e.g. EU sewage sludge directive 86/278/EEC). Research on the potential environmental and human health risks from the use of manures and sewage sludges on agricultural land have historically been focussed on trace elements and macronutrients, and these findings have been fed into the codes of practice. However, the scientific validity of the limits and restrictions for trace elements in amended soils have largely been shown to be flawed (Environment Agency 2008a). Importantly, relatively little attention has been focussed upon the potential environmental and human health risks of organic chemicals present in these materials. Reasons for this include the practical difficulty of chemical determination of some of these compounds in heterogeneous complex matrices, the relative costs of determination compared to metals and the shear diversity of chemicals likely to be present.

There is therefore a need to undertake an assessment of the potential risks from organic chemicals present in organic materials destined for application to land in Scotland. This project aims to:

- Identify organic chemicals in organic materials likely to be applied to land in Scotland.
- Collate data on likely concentrations of those chemicals in materials (and also effect and no effect concentrations, physico-chemical characteristics, fate and behaviour).
- Develop a prioritisation scheme and ranking of chemicals and materials based on potential risk, and draw conclusions on the relative risks posed in different areas (or environmental/soil conditions) across Scotland.

Specifically, these project aims will be achieved through fulfilling the project objectives, which are:

[1] http://www.environment-agency.gov.uk/business/sectors/142481.aspx

1. Identification of organic chemicals in organic materials spread to land in Scotland and the likely concentrations, with gaps in understanding flagged.
2. For those chemicals identified, collate the environmental and human health related effects data as well as behaviour and fate information, with key reference to the terrestrial compartment.
3. Undertake a spatial assessment of the potential risks to identify the form, magnitude and characteristics of risks from organic chemicals present in organic wastes spread to land.
4. Where potential risks from organic chemicals have been identified assess the feasibility of measuring the concentrations of those chemicals in wastes in order to 'benchmark' the risk assessment process.

In this first section of the report we provide an outline of the plan we are adopting to successfully deliver to the aims of this project, and provide some background as to the relevance of this work. In Section 2 we outline how the literature has been reviewed, and the data collated, synthesised and assessed to specifically undertake a screening risk assessment of organic chemicals potentially present in organic materials going to land. This will provide a priority list of chemicals. The modelling of the potential risks, including a spatial assessment, is given in Section 3. The uncertainties in any risk assessment can often be reduced through the use of more specific measurements of effects or exposures. For organic chemicals in organic materials this can be done through measuring the identified priority chemicals in Scottish organic materials destined for land. However, not all analytical laboratories can undertake this type of analysis at the appropriate levels of performance. In Section 4 we provide a brief review of the methodologies used to determine some the identified priority chemicals in organic materials and also present the results of a brief survey of UK-based laboratories in relation to their analytical capabilities and costs. A summary and some recommendations are provided in Section 5.

1.1 Project plan

The approach that we have taken for this project follows classic paradigms of risk assessment, in that early tasks and assessments will be performed in a generic way using reasonable worst case assumptions of exposure and effects. By taking this risk-based approach, where chemical concentrations in organic wastes and in amended soils are compared to potential effect levels, the outputs from this project can be updated and refined as more data become available (either exposure or effects information). Many of the chemicals that are identified may have incomplete datasets and therefore a full assessment will not be possible. By structuring the project this way and by adopting a relatively precautionary approach in early screening assessments false negatives will also largely be avoided.

Only those organic chemicals and materials identified in the prioritisation will be taken forward in the process for more detailed investigation. This approach ensures effort and resources are focussed upon situations were potential issues have been identified. Figure 1.1 provides a schematic of the process we have followed with the relevant project objectives indicated.

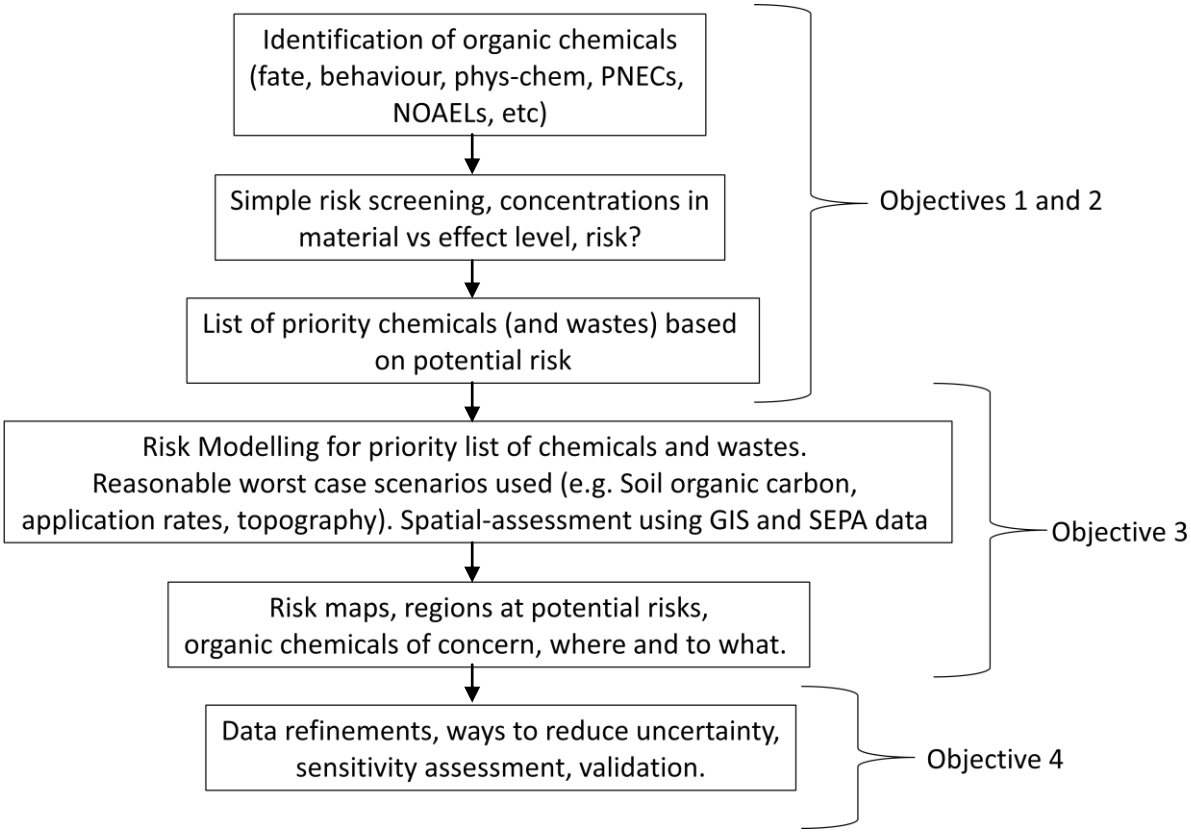


Figure 1.1 Schematic of the risk-based methodology to successfully deliver the aims of the project.

1.2 Background to the project

Increasing regulatory attention is being focussed upon the behaviour and fate of organic chemicals in organic wastes (e.g. Environment Agency 2009a; JRC 2012) and waters (e.g. DWI 2007; Besse and Garric 2008). There are several reviews and research articles in the open literature that provide measured data of organic chemicals in sewage sludges and waste water treatment sludges. Clarke and Smith (2011) have summarised some of these data from around the world for key organic chemicals and this is shown below in Figure 1.1.

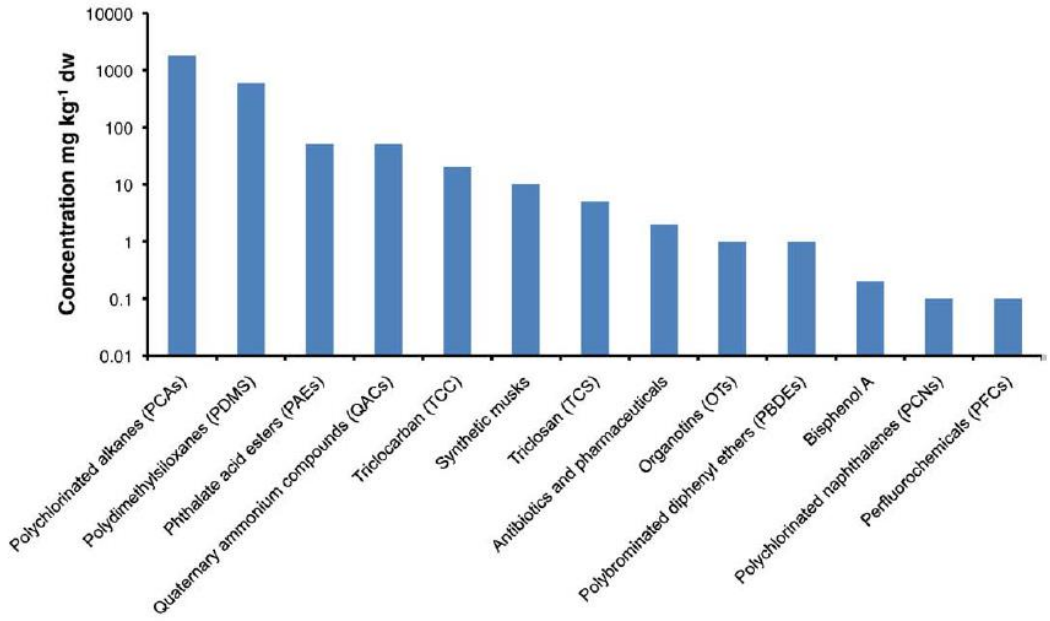


Figure 1.2 Concentrations of selected organic chemicals determined in sewage sludges from around the world (from: Clarke and Smith 2011)

Many of the organic chemicals that are likely to be present in animal wastes, manures (about 96% of the total organic waste material applied to land in Scotland[2]) and sewage sludges, will have specific requirements in order to fulfil registration for safe use under European chemicals, medicines and biocides legislation (e.g. Registration, Evaluation, Authorisation and restriction of CHemicals regulation (REACH)). However, this does not mean that all risks are assessed or that all data are available (Section 2.2.4). Indeed, as recently demonstrated in a survey of sewage sludges by the JRC (2012), organic chemicals that have long been banned are still routinely found in materials destined for application to land (e.g. PCBs).

There are also other circumstances, or specific organic chemicals, that are not covered by the existing chemicals regulatory assessment frameworks in Europe. This may include metabolites or transformation products that may be present in the organic wastes, chemicals derived from treatment processes that are outside of the generic process frameworks described in the guidance, or substances that are used in low tonnages. Such chemical groups include synthetic fragrances, UV filters, antiseptics, antioxidants and insect repellents. Breakdown products are often less toxic than their parent compound but this is not always the case (e.g. Boxall et al. 2003). These chemicals are often difficult to identify in screening type monitoring or review projects because if researchers do not specifically search for a compound, it will not be found.

[2] SEPA's Strategic review of organic waste spread on land.

2 REVIEW OF LITERATURE

In this section of the report we describe the strategy used for identifying organic chemicals likely to be present in organic wastes that may be applied to land in Scotland. In addition to the identification of chemicals and key physico-chemical properties affecting their behaviour and fate we also flag some of the remaining challenges in the identification of chemicals found in organic wastes.

In this section we also present the results from a generic risk screening exercise in order to prioritise the chemicals identified. We have used published (measured or estimated) soil, sewage sludge, manure or other waste concentrations of identified organic chemicals. These values are compared directly to their respective predicted no effect concentrations to allow a preliminary assessment of eco-risks. Health criteria values have also been collated for the chemicals identified and where these are available they are used to advocate prioritisation. Finally a summary section is given including the list of priority chemicals along with a brief summary of the reasoning for their selection.

This section fulfils the objectives 1 and 2 as identified in Section 1.

A Excel™ spreadsheet (EP1302_SEPA Organic Chemicals) has been produced to accompany this project report and represents a repository for the information collated in this section. The references used in this sheet are presented at the end of this report.

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.

Table 2.1 Search strings and results from the literature searching

	Search term	TOXLINE[1]	Thomson Innovation[2]
Group 1	manure AND "organic chemicals"	123	99 (without the quotation marks, since TI won't allow)
	animal manure AND organic contaminants	18	15
	manure AND pops	4	1
	manure AND veterinary medicine	92	31
Group 2	biosolids AND animal manure AND organic contaminants	3	1
	biosolids AND manure AND organic chemicals	7	6
	biosolids AND manure AND pops	0	0
	biosolids AND manure AND veterinary medicine	0	0
	sewage sludge AND animal manure AND organic contaminants	2	1
	sewage sludge AND manure AND organic chemicals	6	16
	sewage sludge AND manure	0	1

	Search term	TOXLINE[1]	Thomson Innovation[2]
	AND pops		
	sewage sludge AND manure AND veterinary medicine	2	2
Group 3	abattoir waste	144	79
	compost AND land	228	591
	dredging	1121	>1000*
	dredging AND land	88	178
	"food waste" AND land	12	TI won't permit quotation marks
	food waste AND land	451	351
	molasses	561	>1000*
	molasses AND land	7	34
	paper waste AND land	1589	846
	"paper waste" AND land	11	TI won't permit quotation marks
	septic tank sludge	54	100
	(waste wood OR waste bark OR waste plant matter) AND (land)	299	292

*Cannot download >1000 results from Thomson Innovation.
[1] Years searched: 1990 – 2013
[2] Years searched: 1993 – 2013

In all 9466 potential articles were initially identified and these were reduced to 6288 following the removal of duplicates and obviously irrelevant papers. These were then reduced to just 88 by reading through the abstracts and applying specific criteria. The criteria by which papers were selected were related to their relevancy to the project aims, including the populating of the Excel™ spreadsheet. In particular papers were selected that contained (or where thought likely to contain based on the abstract):

- Prediction or measurement of an organic chemical 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 Predicted No Effect Concentrations or Health Criteria Values for organic chemicals in the terrestrial environment;
- Environmental fate and behaviour data on organic chemicals, preferably in terrestrial environments.

Of these 88 papers, 35 were identified for closer scrutiny beyond reading the abstract (20 were obtained for free from various sources and 15 were purchased). 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[3], Quality Protocols Programme[4]) research programmes and position statements related to the project aims.

[3] http://esis.jrc.ec.europa.eu/index.php?PGM=ora

2.2 Chemical and data identification

The chemicals selected in this project are not intended to represent an exhaustive list of organic chemicals in organic materials.

Review and regulatory monitoring papers/reports have proved especially useful sources of data for the Excel™ sheet, in particular:

- USEPA (2009) sewage sludge (biosolids) survey of the chemical composition (164 analytes) of sludges randomly sampled from 74 treatment works in 35 states.
- Joint Research Centre's (2012) report on the occurrence and levels of selected compounds in 61 sewage sludge samples from 15 European countries (FATE SEES) (although the UK did not participate in this work).
- Environment Agency's (2006) targeted monitoring study and risk characterisation for 18 veterinary medicines in faeces/litter, soil, water and sediment.
- Clarke and Smith's 2011 international review of emerging organic contaminants in sewage sludges with consideration of potential human and ecological risks.
- Hough et al.'s (2012) generic assessment of risks posed by the use of PAS100 green waste compost to animal welfare and environmental and human health under a range of use scenarios.

The monitoring programmes are heavily biased towards sewage sludges with few comprehensive studies on other organic wastes, aside from those on veterinary medicines and manures (although these often forced to use precautionary assumptions were datasets are limited). This inevitably creates a bias in the data collation but is an inevitable consequence of adopting an evidence-driven approach to the project. The recent studies on the sewage sludges do indicate that the organic chemicals detected include chemicals still widely in use, but also chemicals that have been restricted or banned that are environmentally very persistent (such as congeners of decabrominated diphenylether, e.g. Clarke and Smith 2011). Therefore, all these chemicals are listed in the spreadsheet.

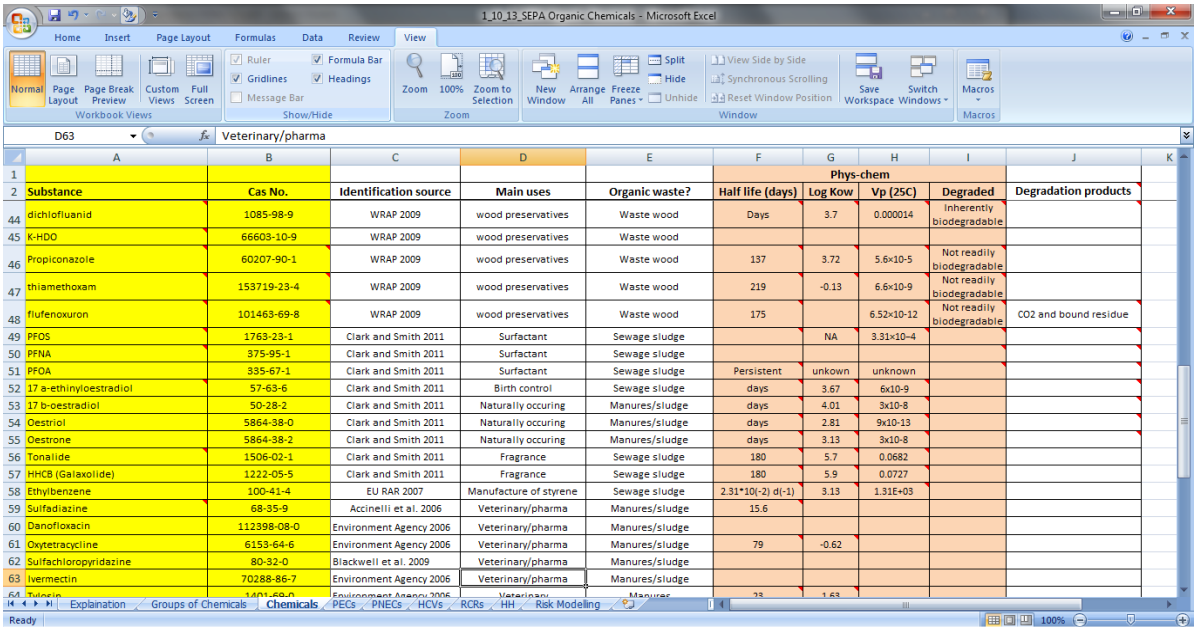
2.2.1 Organic chemicals

Organic chemicals have been identified for inclusion in this assessment if they have been identified from published sources as potentially being present in organic materials that may be applied to land in Scotland. We have not confined our searches to just measured data for Scottish organic materials, as this would greatly limit the project scope. Therefore, we have considered organic chemicals in organic materials as identified from use/exposure modelling (e.g. Clapton et al. 2006), intrinsic hazard (e.g. Selvam et al. 2012), behaviour and fate properties (e.g. Kwon 2011) in addition to global monitoring programmes. Organic chemicals prioritised from material monitoring programmes and/or behaviour and fate studies that were outwith routine or realistic practice in Scotland were not included. For example, studies

[4] http://www.environment-agency.gov.uk/business/sectors/142481.aspx

using materials generated in Mediterranean (e.g. olive production wastes), sub-tropical (e.g. husks from macadamias) or arid (citrus wastes) climates were not included.

The organic chemicals identified are shown on the chemicals tab of the spreadsheet, of which a screen shot is shown in Figure 2.1. The figure shows the substance and CAS Number, the source from which the chemical was identified for inclusion, the chemicals use and the organic material in which it is most likely to be found. In all, 83 chemicals have been identified for inclusion. The physico-chemical data for some of these chemicals are present in columns F, G and H of the spreadsheet. These data will become more relevant in the latter sections of this report and so data have only been collated where needed.



	Substance	Cas No.	Identification source	Main uses	Organic waste?	Phys-chem				
						Half life (days)	Log Kow	Vp (25C)	Degraded	Degradation products
44	dichlofluanid	1085-98-9	WRAP 2009	wood preservatives	Waste wood	Days	3.7	0.000014	Inherently biodegradable	
45	K-HDO	66603-10-9	WRAP 2009	wood preservatives	Waste wood					
46	Propiconazole	60207-90-1	WRAP 2009	wood preservatives	Waste wood	137	3.72	5.6×10-5	Not readily biodegradable	
47	thiamethoxam	153719-23-4	WRAP 2009	wood preservatives	Waste wood	219	-0.13	6.6×10-9	Not readily biodegradable	
48	flufenoxuron	101463-69-8	WRAP 2009	wood preservatives	Waste wood	175		6.52×10-12	Not readily biodegradable	CO2 and bound residue
49	PFOS	1763-23-1	Clark and Smith 2011	Surfactant	Sewage sludge		NA	3.31×10-4		
50	PFNA	375-95-1	Clark and Smith 2011	Surfactant	Sewage sludge					
51	PFOA	335-67-1	Clark and Smith 2011	Surfactant	Sewage sludge	Persistent	unkown	unknown		
52	17 a-ethinyloestradiol	57-63-6	Clark and Smith 2011	Birth control	Sewage sludge	days	3.67	6x10-9		
53	17 b-oestradiol	50-28-2	Clark and Smith 2011	Naturally occuring	Manures/sludge	days	4.01	3x10-8		
54	Oestriol	5864-38-0	Clark and Smith 2011	Naturally occuring	Manures/sludge	days	2.81	9x10-13		
55	Oestrone	5864-38-2	Clark and Smith 2011	Naturally occuring	Manures/sludge	days	3.13	3x10-8		
56	Tonalide	1506-02-1	Clark and Smith 2011	Fragrance	Sewage sludge	180	5.7	0.0682		
57	HHCB (Galaxolide)	1222-05-5	Clark and Smith 2011	Fragrance	Sewage sludge	180	5.9	0.0727		
58	Ethylbenzene	100-41-4	EU RAR 2007	Manufacture of styrene	Sewage sludge	2.31*10(-2) d(-1)	3.13	1.31E+03		
59	Sulfadiazine	68-35-9	Accinelli et al. 2006	Veterinary/pharma	Manures/sludge	15.6				
60	Danofloxacin	112398-08-0	Environment Agency 2006	Veterinary/pharma	Manures/sludge					
61	Oxytetracycline	6153-64-6	Environment Agency 2006	Veterinary/pharma	Manures/sludge	79	-0.62			
62	Sulfachloropyridazine	80-32-0	Blackwell et al. 2009	Veterinary/pharma	Manures/sludge					
63	Ivermectin	70288-86-7	Environment Agency 2006	Veterinary/pharma	Manures/sludge					

Figure 2.1 Spreadsheet of organic chemicals identified as potentially presenting a risk when present in organic materials destined for agricultural land

Additional tabs on the spreadsheet screenshot (Figure 2.1) are for predicted environmental concentrations (PECs) in organic materials and soils (Section 2.2.2), predicted no effect concentrations (PNECs)(Section 2.2.3), Health Criteria Values (HCVs)(Section 2.2.3). Two further tabs are also included for risk characterisation ratios (RCRs) and Exposures, which reflect the outputs from the environmental risk screening presented in Section 2.3.

2.2.2 Predicted environmental concentrations

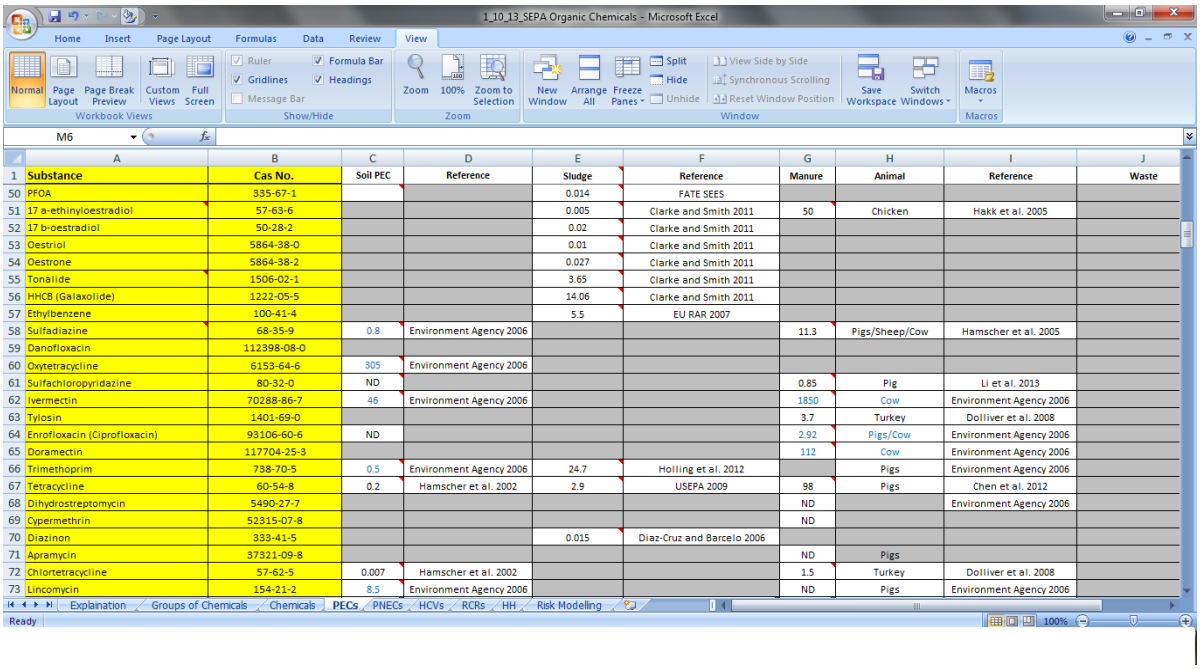
We have adopted a tiered hierarchy of data sources for the collection of predicted (and estimated) environmental concentrations of identified organic chemicals in soils and organic materials. Where measured data are available for the organic chemical in organic wastes in Scotland the maximum or 90th percentile value have been used. For human health assessments, generally the 95th percentile of the frequency distribution of measured chemical data is taken forward as the metric to include in exposure assessments (e.g. CIEH,

2008). However, many of the reference sources used here do not give 95th percentiles, and indeed many do not give percentiles or maximums at all, but just provide averages or means. Where this is the case, comment boxes in the spreadsheet indicate what summary statistic has been used (and also units for the concentration measurement and whether it is dry or wet weight). Where no data for Scotland are available, a data hierarchy has to derive representative data for use in the prioritisation:

1. Measured data in similar waste types from England and Wales.
2. Measured data in similar waste types from similar temperate regions.
3. Any measured data in similar waste types.....from anywhere.
4. Concentrations estimated from "use" data or physico-chemical relationships[5].

The last source is not particularly useful for some of the more persistent organic chemicals where it is believed that the main source in many sludges/composts is actually aerial deposition (e.g. Umlauf et al. 2011).

On the PEC tab in the spreadsheet, as shown in Figure 2.2, some of the values are shown in blue. These values are specifically those values measured in Scotland and the UK. The Soil and Herbage Survey (Environment Agency 2007a) has been used, where appropriate, to provide measured concentrations of some organics in rural Scottish soils.



	A	B	C	D	E	F	G	H	I	J
1	Substance	Cas No.	Soil PEC	Reference	Sludge	Reference	Manure	Animal	Reference	Waste
50	PFOA	335-67-1			0.014	FATE SEES				
51	17 a-ethinyloestradiol	57-63-6			0.005	Clarke and Smith 2011	50	Chicken	Hakk et al. 2005	
52	17 b-oestradiol	50-28-2			0.02	Clarke and Smith 2011				
53	Oestriol	5864-38-0			0.01	Clarke and Smith 2011				
54	Oestrone	5864-38-2			0.027	Clarke and Smith 2011				
55	Tonalide	1506-02-1			3.65	Clarke and Smith 2011				
56	HHCB (Galaxolide)	1222-05-5			14.06	Clarke and Smith 2011				
57	Ethylbenzene	100-41-4			5.5	EU RAR 2007				
58	Sulfadiazine	68-35-9	0.8	Environment Agency 2006			11.3	Pigs/Sheep/Cow	Hamscher et al. 2005	
59	Danofloxacin	112398-08-0								
60	Oxytetracycline	6153-64-6	305	Environment Agency 2006						
61	Sulfachloropyridazine	80-32-0	ND				0.85	Pig	Li et al. 2013	
62	Ivermectin	70288-86-7	46	Environment Agency 2006			1850	Cow	Environment Agency 2006	
63	Tylosin	1401-69-0					3.7	Turkey	Dolliver et al. 2008	
64	Enrofloxacin (Ciprofloxacin)	93106-60-6	ND				2.92	Pigs/Cow	Environment Agency 2006	
65	Doramectin	117704-25-3					112	Cow	Environment Agency 2006	
66	Trimethoprim	738-70-5	0.5	Environment Agency 2006	24.7	Holling et al. 2012		Pigs	Environment Agency 2006	
67	Tetracycline	60-54-8	0.2	Hamscher et al. 2002	2.9	USEPA 2009	98	Pigs	Chen et al. 2012	
68	Dihydrostreptomycin	5490-27-7					ND		Environment Agency 2006	
69	Cypermethrin	52315-07-8					ND			
70	Diazinon	333-41-5			0.015	Diaz-Cruz and Barcelo 2006				
71	Apramycin	37321-09-8					ND	Pigs		
72	Chlortetracycline	57-62-5	0.007	Hamscher et al. 2002			1.5	Turkey	Dolliver et al. 2008	
73	Lincomycin	154-21-2	8.5	Environment Agency 2006			ND	Pigs	Environment Agency 2006	

Figure 2.2 Spreadsheet of predicted environmental concentrations in soils and organic materials destined for agricultural land in Scotland

In the final columns of the PEC tab (G, H, I) are concentrations in manures, the animals from which the manure is derived and a reference. In column J are concentrations of the

[5] ECHA. 2008. Guidance on information requirements and chemical safety assessment Chapter R.7a: Endpoint specific guidance. European Chemicals Agency. May 2008.

organic chemicals in other organic materials, including composts and MBT CLO. These concentrations are all measured.

Where estimates of exposure concentrations have been used for soil concentrations, such as for waste wood and some of the veterinary medicines, the scenario resulting in the highest soil concentration from a single application has been used. In the case of waste wood this is use as a mulch in a horticultural setting and applied to soils with a depth of 20 cm (Peters and Pearce 2011).

The grey shaded boxes are where we currently have no data. This is not say that there *is* no data, but that we have not found it in the searches applied. This provides an opportunity to update the spreadsheet as more data becomes available, especially in relation to the characterisation of data from materials other than sewage sludges and manures, which tend to be relatively well represented in most of the academic and regulatory literature.

We have focussed attention upon data for soils and organic waste concentrations and have limited consideration of transfer of the chemicals to ground and surface waters. This is because for many of the well regulated chemicals, such as pharmaceuticals and common industrial chemicals, these considerations are taken into account in their respective registration systems in Europe. For terrestrial exposures, considerations are often not required to be so rigorous (Section 2.2.4).

2.2.3 Predicted No Effect Concentrations and Health Criteria Values

In an ideal world there would be Predicted No Effect Concentrations (PNECs) and Health Criteria Values (HCVs) for all of the organic chemicals likely to present in organic materials going to land. However, there are a limited number of chemicals for which these values have been derived in the UK (e.g. 12 soil screening values have been derived for ecological risk assessment in the UK, and the status of some of these is currently unclear[6]). This can result in limits from other jurisdictions being selected, or risks for human health and the environment not being assessed (which has happened in some of the previous Quality Protocols). Therefore, we have taken an approach originally put forward in the compilation of the Environment Agency's Hazard Matrix, where, in an effort to ensure consistency in the assessment of risks from the use recycled wastes, a hierarchy of information sources is considered. Limit values were collated for chemicals in freshwaters, the terrestrial environment (primary and secondary sources) and tolerable or mean daily intakes or reference doses for human health assessment (Non-threshold and threshold chemicals) (Environment Agency 2010).

For the terrestrial environment the primary data sources, as assessed by the Environment Agency (2010), for the collation of PNECs for ecological protection are:

- *United States Environmental Protection Agency Ecological Soil Screening Levels (*Eco-SSLs)[7],
- *Canadian Soil Quality Guidelines*[8]

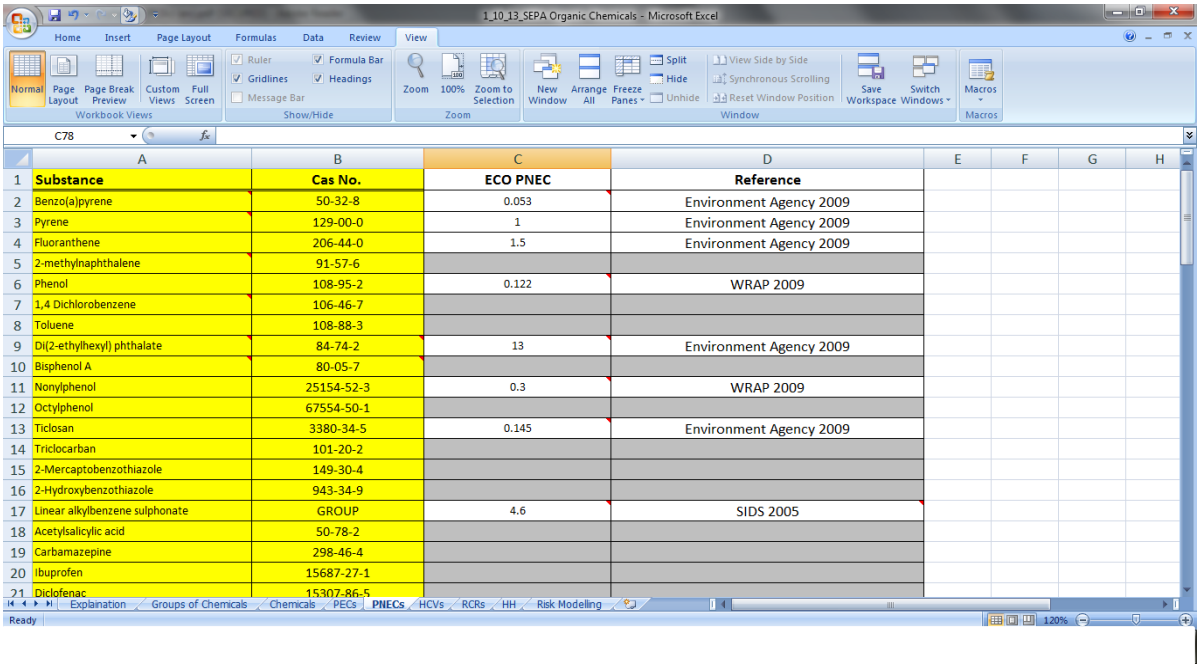
[6] http://www.environment-agency.gov.uk/research/library/consultations/96836.aspx
[7] http://www.epa.gov/ecotox/ecossl/

Secondary sources include:

- *RIVM Maximum Permissible Concentrations (MPCs)*[9].
- *Risk assessments undertaken in support of the Exiting Substances Regulation (793/93/EEC) for high production volume chemicals*[10].

These regulatory sources use similar derivation approaches to those adopted in the UK and the limits are often subject to extensive consultation and peer-review. Importantly, for eco-risks, consideration is also made of direct toxicity and secondary poisoning.

Nevertheless, and not surprisingly, there remain many chemicals (identified as potentially of interest) for which PNECs have not been found in these sources. For these we have used published PNECs from the open literature. While these sources are fully referenced, the PNECs derived have not been subject to regulatory scrutiny (often they have been derived for use in risk screening and prioritisation exercises, e.g. WRAP 2009; Clarke and Smith 2011) so represent a potential source of uncertainty. Figure 2.3 shows the spreadsheet tab for the PNECs.



	Substance	Cas No.	ECO PNEC	Reference
2	Benzo(a)pyrene	50-32-8	0.053	Environment Agency 2009
3	Pyrene	129-00-0	1	Environment Agency 2009
4	Fluoranthene	206-44-0	1.5	Environment Agency 2009
5	2-methylnaphthalene	91-57-6		
6	Phenol	108-95-2	0.122	WRAP 2009
7	1,4 Dichlorobenzene	106-46-7		
8	Toluene	108-88-3		
9	Di(2-ethylhexyl) phthalate	84-74-2	13	Environment Agency 2009
10	Bisphenol A	80-05-7		
11	Nonylphenol	25154-52-3	0.3	WRAP 2009
12	Octylphenol	67554-50-1		
13	Ticlosan	3380-34-5	0.145	Environment Agency 2009
14	Triclocarban	101-20-2		
15	2-Mercaptobenzothiazole	149-30-4		
16	2-Hydroxybenzothiazole	943-34-9		
17	Linear alkylbenzene sulphonate	GROUP	4.6	SIDS 2005
18	Acetylsalicylic acid	50-78-2		
19	Carbamazepine	298-46-4		
20	Ibuprofen	15687-27-1		
21	Diclofenac	15307-86-5		

Figure 2.3 Spreadsheet of predicted no effect concentrations in soils for some of the chemicals identified in Section 2.2.1

In the UK there are very few (< 20) soil guideline values (SGVs) from which acceptable health criteria values (HCVs) can be taken. Most of these will also be for chemicals not identified by the process described earlier in this section. Similar to the approach proposed for terrestrial risk assessment, exposure scenarios can be developed in this project for comparison with the Tolerable Daily Intakes (TDIs), Mean Daily Intakes (MDIs) and

[8] http://ceqg-rcqe.ccme.ca/
[9] http://www.rivm.nl/bibliotheek/rapporten/711701023.html
[10] http://esis.jrc.ec.europa.eu/index.php?PGM=ora

Reference Doses (RfDs) to perform a generic risk assessment for all priority chemicals (Section 2.3.3). Where human health criteria are available these are listed on the HCVs tab of the spreadsheet.

The hierarchy is detailed below in order of preference for source of HCV:

1. Environment Agency Hazard Matrix
2. Recommendations of TDIs and drinking water standards etc by authoritative UK bodies
3. Recommendations made by EU scientific advisory panels and working groups
4. Recommendations by international authoritative organisations (e.g. WHO and associated working groups)
5. Recommendations of other national organisations (e.g. USEPA, RIVM)

For reasons of pragmatism the hazard matrix has been used as the initial source of HCVs as it was populated using this hierarchy of preferred sources relatively recently.

2.2.4 Remaining Challenges

Knowledge of the types and amounts of organic material applied (or intended to be applied in the future) to agricultural land may be readily available from regulatory records. However, it is clear from work undertaken in the Quality Protocols Programme for WRAP and the Environment Agency that limited data are often available on the chemical characteristics of those organic materials beyond very basic macronutrient information. Chemical composition data of a source material that is then processed in some way (e.g. by composting, anaerobic digestion, burning, etc) can be of limited relevance to the final product that is to be applied to land.

Furthermore, the risk assessments that have been undertaken to support the Quality Protocols currently in place on the Environment Agency's website are only available through a freedom of information request. We have obtained those for anaerobic digestate and compost (PAS 100) as these would probably represent greater usage in Scotland than other materials on the protocols list. However, these assessments have not been carried out in a manner consistent with those more recent protocols and organic waste assessments undertaken by the Environment Agency such as for waste wood, Mechanical Biological Treatment Compost-Like Outputs (MBT CLO), road leaf litter sweepings, made topsoil and meat and bone meal ash. These latter risk assessments have been driven by the requirement for full chemical characterisation data of the material, and have actually sometimes failed in this process because such data have not been available. The process undertaken to support the digestate Quality Protocol, likely driven by a lack of compositional data, has focussed upon very generic exposure scenarios delivering semi-quantitative outcomes which are based on a limited number of organic chemicals and groups of organic chemicals (PAHs, DEHP, LAS, NP and NPE, PCBs, PCDD, Antibiotics, Pesticides, Disinfectants, Inks). The selection of these organic chemicals was from just four references, all predating 2007, and therefore adds little to this current project.

Importantly, in the European pharmaceutical registration and approval process[11], very few active ingredients tend to trigger the need for a terrestrial risk assessment. The triggers (for a Tier B Terrestrial assessment) are a K_{oc} of >10,000 L kg^{-1} (OECD 106 or OPPTS 835.1110 study) or a K_d of > 3700 L kg^{-1} or if the active ingredient is not shown to be readily biodegradable (OECD 301). Therefore, for many of the chemicals that are found in sewage sludges there may be limited terrestrial effects data.

Furthermore, in both pharmaceutical and veterinary medicine registration much of the data that would be useful to the performance of a terrestrial risk assessment are not publically available[12]. In order to access these data an agreement is usually required from either the competent authority or the company marketing the active ingredient (cf. Environment Agency 2006).

2.3 Risk Screening

A balance is required to be struck in the risk modelling phase of this project (Section 3) between available resource and the spatial assessment of the most relevant chemicals that present potential risks. There are too many identified chemicals to consider every one for risk modelling. Therefore an evidence-based prioritisation process is required. This has been undertaken through a generic screening exercise whereby data availability is maximised to produce a list of priority chemicals.

Firstly an exposure assessment has been undertaken estimating the likely tonnages of the identified chemicals applied to land in Scotland. This has been used to identify potential priority chemicals based on conservative estimates of the potential quantity applied to land.

Secondly, a preliminary relative environmental risk ranking, using the published PEC in waste materials, historic estimates of the tonnages of different wastes applied to land in Scotland, and PNEC data for terrestrial ecosystems (or PNECs from the literature estimated using equilibrium partition theory) has been used to select potential priority chemicals. These two assessments aim to identify those substances which are of greatest importance within Scotland, but do not consider potential risk at the local scale.

A third approach, which aims to identify substances which may pose potential problems when applied to land in general, and considers annual repeat loadings for 10 years of 8 and 50 t ha^{-1}, has also been applied. Ten years has been considered here as this is in line with early screens undertaken by the Environment Agency in assessing potential risk to terrestrial ecosystems at the sites where the materials are applied to land. This approach only considers single substances and does not account for mixtures.

Finally, a human health related screening exercise has been undertaken based on the preliminary exposure assessment, the magnitude of HCVs and consideration of the findings of similar assessments concerned with the presence of substances of concern in materials applied to land (with a focus on human and veterinary medicines). Ideally, this type of

[11] http://www.ema.europa.eu/ema/index.jsp?curl=pages/regulation/landing/regulation.jsp
[12] www.vmd.defra.gov.uk/.../UKPAR_Documents/UKPAR_314409.doc

screening assessment or prioritisation would incorporate consideration of the potential for chemicals to accumulate in the food chain (i.e. in plants, crops or livestock fed on them) for all compounds having a HCV available and indicated as being applied to land in appreciable quantities (i.e. >1 tpa). However, HCVs or similar metrics have been identified for the majority of chemicals assessed in the initial phase of this project and assessment of the potential to accumulate in the food chain or lead to human exposure by other pathways (e.g. leaching to surface/ground-water and abstraction for potable water) would be a data- and time-intensive exercise that is beyond the scope of this screening assessment. The selection of chemicals for further consideration on the basis of potential harm to human health is therefore based on the following factors:

- Tonnage of compound applied to land (based on estimates from exposure assessment);
- Quotient calculated from Tonnage/HCV;
- Comparison with priority chemicals from previous reviews (e.g. Capleton et al. 2006; Boxall et al., 2003; Hough et al. 2012)
- Confirmation that compounds selected are representative of various chemical groups considered to be priority pollutants.

2.3.1 Grouping of Substances

The various substances identified through the screening literature search have been grouped into a number of broad classes which typically indicate the types of substances and their uses, such as pharmaceuticals, veterinary medicines, and industrial chemicals (see the Spreadsheet). Whilst there are cases where the group to which a substance has been assigned is not the only potentially relevant group for the substance, the grouping of substances is likely to be valuable in instances where some information is unavailable for a particular substance of interest.

Reading across appropriate and relevant information on exposure, fate, or effects may enable provisional indications to be made for substances for which adequate information to perform a reliable assessment is currently not available.

2.3.2 Exposure Sources

The potential sources of each of the substances were identified based primarily on the use patterns of the substances. Virtually all of the types of substances considered here could potentially be found in sewage sludges, due to the diverse range of both domestic and industrial inputs to sewage. Conversely, a much more limited range of substances is expected to be found in animal manures, and these are likely to be limited to veterinary medicines and steroids. Similarly, a restricted range of substances are expected to be present in waste exempt from waste management licensing under paragraphs 7, 9, 12, 19, 45, and 47 (which have been considered in this project), although the specific contaminant substances are likely to vary considerably according to the source industry.

2.3.3 Preliminary Exposure Screening

The estimated concentrations of organic substances in relevant waste materials (sewage sludge, animal manures, etc.) have been combined with historic information on the approximate quantities of these types of materials spread to land in Scotland (SEPA, undated[13]). Agricultural wastes, such as animal manures, were expected to account for the vast majority of organic waste materials which are spread to land in Scotland, with the total quantity estimated to be approximately 15,000,000 tonnes per year. Waste exempt from waste management licensing under paragraphs 7, 9, 12, 19, 45, and 47 and sewage sludge were both spread in much smaller quantities of 367,000 and 2,000,000 tonnes per year respectively.

Combining this information enables estimates of the total quantities of different substances applied to land in Scotland via this route. Where the concentrations of some substances had either not been measured or were not detectable in some waste materials in published surveys the concentrations have been assumed to be zero. The results of this preliminary exposure screening are shown in Table 2.2 for those substances predicted to be applied to land in Scotland in quantities of one tonne per year or more.

Table 2.2 Estimated quantities of organic chemicals applied to soil in Scotland (tonnes per year)

Substance	Group	Tonnes
Tetracycline	Veterinary	1470.6
Linear alkylbenzene sulphonate	Surfactants	357.8
Clopyralid	Pesticide	266.1
Polydimethylsiloxanes	Siloxanes	126.4
Nonylphenol	Alkyphenols	105.3
Di(2-ethylhexyl) phthalate	Phthalates	74.0
Tylosin	Veterinary	55.5
Ivermectin	Veterinary	27.8
Polychlorinated biphenyls	POP	25.8
Chlortetracycline	Veterinary	22.5
Diphenyl ether	Fragrance	19.9
Sulfachloropyridazine	Veterinary	12.8
Phenol	Industrial	10.9
ΣPDBEs(47,99,209)	Halogenated	9.8
HHCB	Fragrance	7.5
PCDD/F (ng kg-1 I-TEQ)	POP	6.7
OTNE	Fragrance	6.1

[13] http://www.sepa.org.uk/science_and_research/data_and_reports/scientific_and_technical.aspx

Substance	Group	Tonnes
Trimethoprim	Veterinary	4.9
Triclocarban	Halogenated	4.8
Triclosan	Halogenated	3.7
AHTN	Fragrance	3.5
HHCB (Galaxolide)	Fragrance	2.8
Doramectin	Veterinary	1.7
Ethylbenzene	Industrial	1.1
1,4 Dichlorobenzene	Industrial	1.1
Fluoranthene	PAH	1.0

The veterinary medicine tetracycline is predicted to be applied to Scottish soils at the highest overall rate of those substances assessed by this screening approach. The concentration of tetracycline in manure used was the maximum concentration reported in pig manure form a study in China (Chen et al. 2012), so is unlikely to be representative of the manures applied to land in Scotland overall. The median concentration of tetracycline reported by this study is approximately 10 times lower (~10 mg kg^{-1}), and this lower concentration would result in predicted loadings more comparable to those of the other high ranking substances. Tetracycline has been identified as being of high potential risk to aquatic ecosystems (Environment Agency 2002), although it was not possible to assess the potential hazard to terrestrial ecosystems. This suggests that it is appropriate for tetracycline to be identified as a potential priority substance in the present study. Animal manures are expected to be the principal source of tetracycline additions to soil, although a small load (<1%) is also expected from sewage sludge spreading, which may result from human medical applications.

The surfactants linear alkylbenzene sulfonate (LAS) and nonylphenol, the silicone monomers polydimethylsiloxanes, and the phthalate plasticiser DEHP are also expected to be deposited to land in significant quantities. Both sewage sludges and waste exempt from waste management licensing under paragraphs 7, 9, 12, 19, 45, and 47are expected to be potentially important sources of these substances, with the exception of the siloxanes which are only expected to be found in sewage sludges due to their widespread use in wash-off personal care products.

The pesticide clopyralid is also expected to be applied to land in considerable quantities. This is due to its potential presence in off-specification composts, which may be applied to land as waste exempt from waste management licensing under paragraphs 7, 9, 12, 19, 45, and 47. It is important to note that the estimation of the total quantities of substances applied to land are based on the levels of substances in specific waste types, and these concentrations have been applied to the entire quantity of exempt industrial waste. Composts were only used to a very limited extent at the time of the review upon which the estimates of the total quantities of waste materials applied to land are based. It is, however,

likely that the application of composts has increased in recent years due to incentives against the use of landfill for waste disposal.

A similar situation also exists for the veterinary medicines which are expected to be applied to land in relatively large quantities. At present the assessment has not considered the different concentrations which might be expected in the manure following treatment of different animals, or the likely average concentrations which might result from occasional or periodic treatments. A further complication regarding veterinary medicines and oestrogens which are added to soil via manures is the quantity of manure deposited directly on pastures. It is not clear whether slurries which are spread on land are more or less likely to contain these substances.

No pharmaceutical substances were predicted to be applied to land in large quantities. Two pharmaceutical substances were estimated to be applied to soil in quantities of between 100 and 1000 kg per year, these are gemfibrozil and metformin and both have been found in sewage sludges at concentrations of approximately 1 mg kg^{-1}.

Sewage sludge is expected to be the major source of pharmaceuticals, substances used in household and personal care products (such as siloxanes, fragrances, and surfactants) and industrial chemicals. Wastes exempt from waste management licensing under paragraphs 7, 9, 12, 19, 45, and 47 are expected to be the major source of some PAH compounds and other industrial chemicals. Manures are only expected to be the main source for steroids and veterinary medicines.

2.3.4 Preliminary Exposure-based Risk Ranking

An assessment of the relative risks posed by some of the substances identified in the initial searches has been performed by comparing the potential annual tonnage of a substance which is applied to land against the PNEC for terrestrial ecosystems (Table 2.3), where this information is available. The relative risk factor was calculated according to the following equation:

Risk Factor = Quantity Applied to Soil (tpa) / PNEC for Terrestrial Ecosystems (mg kg^{-1})

The risk factor expresses the total potential quantity of material applied relative to the sensitivity of terrestrial ecosystems to the substance. A total of only 24 substances could be ranked in this manner. Too many substances have missing information on either the expected concentrations in waste materials, the PNEC for terrestrial ecosystems, or both, to ensure a complete exercise covering all the chemicals that were identified.

Several veterinary medicines are identified as being of relatively high potential risk to soil ecosystems, along with some industrial and household substances. The limited number of pharmaceuticals that were assessed were identified as being of relatively low risk to soil ecosystems, although these substances are expected to be of relatively low toxicity to terrestrial ecosystems. The identification of tetracycline and chlortetracycline as being of high potential risk is consistent with the findings of previous studies (Environment Agency 2002).

Table 2.3 PNEC for terrestrial ecosystems and relative risk factor for risk ranked substances

Substance	Group	$PNEC_{Soil}$ (mg kg^{-1})	Risk Factor
Tetracycline	Veterinary	0.27	5446.6
Tylosin	Veterinary	0.05	1110.0
Chlortetracycline	Veterinary	0.053	424.5
Nonylphenol	Alkyphenols	0.3	350.9
Enrofloxacin (Ciprofloxacin)	Veterinary	0.00013	336.9
Doramectin	Veterinary	0.016	105.0
Ivermectin	Veterinary	0.3	92.5
Phenol	Industrial	0.122	89.7
Linear alkylbenzene sulphonate	Surfactants	4.6	77.8
Polychlorinated biphenyls	POP	0.5	51.6
Polydimethylsiloxanes	Siloxanes	3.77	33.5
Ticlosan	Halogenated	0.145	25.2
HHCB (Galaxolide)	Fragrance	0.32	8.8
Di(2-ethylhexyl) phthalate	Phthalates	13	5.7
PCDD/F (ng kg-1 I-TEQ)	POP	0.000004	2.4
Tonalide	Fragrance	0.32	2.3
Benzo(a)pyrene	PAH	0.053	1.3
Fluoranthene	PAH	1.5	0.6
PFOS	PFOS	0.087	0.6
Pyrene	PAH	1	0.3
Clopyralid	Pesticide	1000	0.3
Sulfachloropyridazine	Veterinary	72	0.2
Metoprolol	Pharmaceuticals	589	4.4E-05
Sotalol	Pharmaceuticals	4095	7.3E-06

Substances for which the main source is sewage sludge, such as surfactants, siloxanes, and fragrances, generally show a lower expected level of risk than the veterinary medicines. Some substances which may potentially be present in both waste exempt from waste management licensing and sewage sludges, such as nonylphenol and phenol, have been identified as being of moderate to high potential risk.

2.3.5 Preliminary Environmental Risk Assessment

To further compliment the exposure screening, a simple generic risk assessment was performed using the data collected in the spreadsheet. Exposure concentrations of organic chemicals in organic materials were calculated from a generic use scenario for a generic soil considering two application rates. Table 2.4 gives the parameters that were used to

calculate the exposure concentrations of organic chemicals over an area of 1 ha (cf. Environment Agency 2009a). The exposure concentrations for each material were calculated for each scenario (1 year of 8 tonnes, 1 year of 50 tonnes, 10 years of 8 tonnes and 10 years of 50 tonnes) and no losses were assumed. These concentrations were then compared to the respective PNEC and risk characterisation ratio calculated.

The drawbacks of this approach include the reliance upon requiring data for both potential exposure (measured concentrations in organic materials) and effects, and the selection of parameters for the calculation of exposures that are realistic for all organic material uses.

Table 2.4 The default parameters and assumptions used in the estimation of exposure concentrations of organic chemicals in soils amended with organic materials

Parameter	Value	Reference
Application rate of compost	50 t ha^{-1} *	Hough et al. 2012
Application rate of sewage sludge/MBT CLO/other organic materials, as dry tonnes ha^{-1}	8 and 50 t ha^{-1}#	Environment Agency 2009
Bulk density of soil receiving organic material	1.3 g cm^{-3}	Environment Agency's WALTER Model
Depth of incorporation for screening level assessment (this assumes all is grassland)	0.1m	Environment Agency 2009a
Area of incorporation	1 ha	Hough et al. 2012

Average application on UK soils, the maximum that can be applied in Scotland per year for newly planted/early establishment crops using sludge cake. For the restoration of derelict land 200 t ha^{-1} may be used outside an NVZ.

The risk characterisation ratios (RCR) of the organic chemicals, for the respective materials for all the scenarios are given in the spreadsheet under the risk characterisation tab. Only the RCRs that are equal to or greater than 1 are shown in Table 2.5. The table shows 12 chemicals indicating a potential risk, but only 7 from single applications. Nonylphenol gives the highest RCR followed by phenol, tetracycline and then LAS in both sewage sludges and other organic materials. Investigation of the degradation properties of those chemicals identified as potential risks after only 10 years of repeat application show limited potential loss for doramectin and a half-life of 180 days for tonalide and up to 100 days for DEHP, suggesting these chemicals could reasonably accumulate in amended soils.

Table 2.5 Risk characterisations ratio equal to, or above, 1 (in red) estimated for generic risk assessment scenarios

Chemical	Sewage Sludge			
	Single application		10 years	
	8t ha^{-1}	50t ha^{-1}	8t ha^{-1}	50t ha^{-1}
Benzo(a)pyrene	0.02	0.13	0.21	1.29
Phenol	2.76	17.2	27.6	172
Nonylphenol	10.1	62.9	101	629

Chemical	Sewage Sludge			
	Single application		10 years	
	8t ha^{-1}	50t ha^{-1}	8t ha^{-1}	50t ha^{-1}
Triclosan	0.19	1.17	1.87	11.7
Linear alkylbenzene sulphonate	0.71	4.43	7.09	44.3
Tonalide	0.07	0.44	0.71	4.39
HHCB	0.27	1.69	2.70	16.9
	Manures			
Tylosin	0.45	2.85	4.55	28.5
Enrofloxacin (Ciprofloxacin)	0.0001	0.0008	1.38	8.64
Doramectin	4.31×10^{-5}	0.0003	0.43	2.69
Tetracycline	2.23	13.9	22.3	139
	Other organic materials			
DEHP	0.08	0.50	0.80	5.03
Nonylphenol	0.40	2.47	3.96	24.7
Triclosan	0.32	2.00	3.20	20.0
Linear alkylbenzene sulphonate	0.92	5.74	9.18	57.4

2.3.6 Preliminary Human Risk Ranking

Prioritisation of chemicals for further consideration on the basis of potential harm to human health via accumulation in the food chain was based on consideration of those substances estimated to be applied to agricultural land in quantities of greater than one tonne per annum (n = 26) and calculation of a relative risk quotient according to the following equation:

Risk Quotient = Quantity Applied to Soil (tpa) / Health Criteria Value (µg/kg bw/d)

The ranking exercise was supplemented by consideration of the potential for various chemical groups to accumulate in the food chain as indicated in a review by Clark and Smith (2011). This study considered various groups of chemicals and assessed their potential risks to the human food chain from sewage sludge land application; ranking the likelihood of risk from this exposure pathway as 'possible' (indicated by ✓ in Table 2.6), 'uncertain' (-) or 'no risk' (x), based on a detailed literature review.

Table 2.6 below details the human health risk ranking for chemicals applied in the highest tonnages and those having a relate risk quotient >1 and/or potential to accumulate in the human food chain.

The highest relative risk quotients are calculated for the human and veterinary medicine tetracyclines (tetracycline and chlortetracycline), ivermectin, tylosin and polybrominated diphenyl ethers. All of these chemicals are also considered to the have potential to accumulate in the food chain following application to land in sewage sludges. Dioxins and PCBs are also well known for their potential to accumulate in food stuffs but calculation of

relative risk quotients was not undertaken at this stage due to the requirement to consider numerous individual congeners.

Table 2.6 Preliminary human health risk ranking

Substance	Group	Tonnes	HCV (µg/kg bw/d)	Relative Risk Quotient	Food Chain Possible (Clark and Smith, 2011)
Tetracycline	Veterinary	1470.6	3	490.2	✓
Linear alkylbenzene sulphonate	Surfactants	357.8	Insufficient data to derive ADI		-
ΣPDBEs(47,99,209)	Halogenated	9.8	0.1	98	✓
Ivermectin	Veterinary	27.8	1	27.8	✓
Tylosin	Veterinary	55.5	6	9.25	✓
Chlortetracycline	Veterinary	22.5	3	7.5	✓
Di(2-ethylhexyl) phthalate	Phthalates	74	10	7.4	x
Nonylphenol	Alkyphenols	105.3	15	7.02	-
Clopyralid	Pesticide	266.1	150	1.774	-
Doramectin	Veterinary	1.7	1	1.7	✓
PCBs	POP	25.8	Data required on individual congeners for TEF approach		✓ (known)
PCDD/PCDFs	POP	6.7			
PCDD/PCDFs	POP	6.7			

2.4 Identification of Priority Chemicals and Waste Materials

From the exposure and risk ranking exercises performed above for the environment and human health, a prioritised list of chemicals has also been collated.

Both the environment and human health exercises are indicative and reliant on numerous assumptions, in particular the availability of environmental and effects/health data. Where a PNEC, HCV or PEC for an organic chemical is not available, and the screening has not been possible, we have "parked" these chemicals. Therefore, the screening represents a process of screening "in" chemicals, rather than screening them "out". If a chemical has not been identified in this process it does not mean that it does not present a potential environmental or human health risk.

From Tables 2.3, 2.5 and 2.6 we have selected candidate chemicals, several of which occur at or near the top of both lists. These candidate chemicals are considered further below with

the aim of having a total of 6-8 to take forward for further consideration in Section 3. The limit of 6-8 substances is one based on practicality and optimal use of resource and is not a reflection of potential risk. The chemicals for initial consideration in the risk modelling exercise (Section 3) are:

- Tetracycline
- Benzo(a)pyrene
- Tylosin
- HHCB
- Nonylphenol
- Doramectin
- Ivermectin
- Phenol
- Linear alkylbenzene sulphonate (LAS)
- PCBs
- PCDD/PCDFDs
- PBDEs

Further examination of these chemicals in relation to inclusion in the risk modelling is outlined in Table 2.7. The criteria for the final selection are:

- The need to ensure that substances are found in representative wastes, i.e. manures, sewage sludges and others (and still used in Scotland, if this is relevant);
- The chemical does not rapidly degrade (i.e. would be present in soils in considerable quantities with the potential to accumulate)

From the list of chemicals in Table 2.7, the immediate selection is:

- Tetracycline – veterinary medicine – manures/animal wastes
- Ivermectin – veterinary medicine – manures/ animal wastes
- Triclosan – biocide- sewage sludges, perhaps manures/animal wastes, other organic wastes (MBT CLO, etc)
- HHCB (Galaxolide) – fragrance – sewage sludges, perhaps household derived organic wastes

This leaves open the possibility of including up to four further organic substances in the assessment. Three of the remaining organic substances (nonylphenol, phenol, and linear alkylbenzene sulphonate) are likely to be found in most organic wastes, but are biodegradable and highly unlikely to persist in soil. These substances were not taken forward for a detailed assessment due to their biodegradation characteristics. Doramectin is a veterinary medicine and two of these have already been selected above and therefore, a third is likely to be a relatively low priority (although manures represent the greatest amount of total applied material). This leaves BaP, Dioxins and dioxin-like PCBs and PDBEs. Due to their ubiquitous occurrence all three have been included in Section 3.

Table 2.7 Final selection and reasoning for screened chemicals.

Substances (or Group)	Reason for selection	To be included in Risk Modelling?
Tetracycline	Identified by all three screening approaches as a priority.	Yes. Half-life in soils likely to be greater than 100 days. Only found in veterinary medicines (perhaps minor quantities in sewage sludges). Identified as a priority by other screening exercises undertaken by the Environment Agency. Used in intensive animal production.
Phenol	Exposure and environmental risk assessment identified phenol.	No. Phenol is readily biodegradable (6.5 days), and although it likely found in most waste materials it is not likely to persist and so would be of relatively low relevance in this exercise.
Nonylphenol	Identified as a priority by all screenings for sewage sludge and other organic wastes.	No. Classified as inherently biodegradable.
LAS	Identified as a priority by all screenings for sewage sludge and other organic wastes.	No. Readily biodegradable, 13-26 days.
Ivermectin	Exposure assessment and human health hazard assessment flagged this as an issue.	Yes. Still used in Scotland as a veterinary medicine, especially in sheep.
Tylosin	Identified by all three screening approaches as a priority.	No. The half-life in soil of tylosin is between 23-97 days.
Triclosan	Potential an environmental risk.	Yes. Will potentially be present in organic materials, including manures and sewage sludges and MBT CLOs. Half-life 266 days under anaerobic conditions, possibly PBT.
BaP	Only identified as a low level risk for environment, not prioritised by the exposure or human health hazard assessment.	Perhaps. Can be used a sentinel organic chemical for all PAHs. Environment and human health toxicity well known. Generally found in all organic materials, assessment perhaps confounded by widespread aerial depositional influence.
Dioxins and dioxin like-PCBs	Only identified as hazard to human health	Perhaps. Likely present in all materials, probably representative of other POPs.
HHCB	Only an environmental risk and only for sewage sludges	Yes. A fragrance and likely present only in sewage sludge (although possibly in household derived waste materials). Represents a group of chemicals often identified in prioritisation.
Doramectin	A potential risk to human health and the environment.	Perhaps. Highest concentrations from intensive livestock.
PDBEs	Only identified as hazard to human health	Perhaps. Likely present in all materials, probably representative of other POPs.

3 RISK MODELLING

In this Section we use the outputs from the previous sections to provide a spatial indication of the potential risks from the chemicals in organic materials that may be applied to land in Scotland. The first part of this section describes how the approach was developed before presenting some of the maps for the prioritised chemicals. The analysis is performed on a Local Authority scale, a map identifying the Local Authorities is included in Appendix D.

3.1 Basis for risk modelling

The potential exposure concentrations of the chemical substances assessed in the present study, which result from the spreading of organic materials to land, were calculated on an average basis for the area of land which was considered to be potentially available for the spreading of such materials. The total area within each Local Authority which was considered to be potentially available for the spreading of organic waste materials was estimated according to the proportion of the population which are considered to live in relatively rural areas, as defined by the Scottish Governments 6-fold Urban Rural classification. The proportion of the population living within the 3 most rural classes (remote small towns, accessible rural, and remote rural) was taken as being indicative of the proportion of land within a Local Authority Area which would potentially be available for the spreading of organic waste materials. Alternative approaches for the assignment of the area of land available for spreading could be based on a classification system such as the Land Use Capability for Agriculture[14], although the information was not available in a compatible format for the present study. This issue is considered in more detail in Section 3.3.1.

The total quantity of material applied to land within each Local Authority Area was normalised to the area of land potentially available for spreading (e.g. tonnes per km^2 of spreading land) (Figure 3.1). The quantities of sewage sludge and wastes exempt from waste management licensing were provided on a Local Authority Area basis by the SEPA Project Team. For veterinary medicines with sources from livestock manures, the following approach was taken: a daily manure production rate for each type of livestock (cows, pigs, sheep, and poultry) was estimated form literature information (e.g. Environment Agency 2006), and this was used to calculate the annual tonnage of manure produced by each type of livestock in each Local Authority Area (Figure 3.2).

The manure production rate for each type of livestock was estimated to be 50 kg d^{-1} for cows, 1 kg d^{-1} for sheep, 15 kg d^{-1} for pigs, and 0.1 kg d^{-1} for poultry (OECD 2006, DEFRA 2009). In the case of cattle particularly, the primary use of the cattle (i.e. dairy or beef) has a large effect on the quantity of manure produced by each animal. A similar issue also applies to pigs and sheep, although the differences between different types of animals are smaller than they are for cattle. As no information on the split between each different type of farming within each Local Authority Area was available, average or intermediate values have been used for the purposes of the present study.

[14] http://www.macaulay.ac.uk/explorescotland/lca_map.pdf

Due to data confidentiality issues in some Local Authority Areas, where a small number of farms contain a large proportion of the local livestock, information could not be provided. In these cases it was assumed that there were none of this type of livestock in the Local Authority Area. This is a pragmatic approach, although it is considered unlikely that any Local Authority Area with very few farms would have very high livestock densities.

Information provided by SEPA indicates that large, PPC part B registered, intensive pig or poultry rearing agricultural activities occur in some Local Authority Areas. Where intensive farming is known to occur it was assumed that 90% of waste from the relevant animals was from intensively farmed sites, and that 50% of the manure from these sites is disposed of via other routes than disposal to land.

The concentration of organic chemicals within each waste type was identified from the literature where possible, and is detailed in the supporting Excel Spreadsheet. In the case of the concentrations of benzo(a)pyrene in bituminous mixtures containing coal tar the concentration was estimated from concentrations of benzo(a)pyrene in coal tar based sealant (estimated as 6 g kg^{-1})[15], and that the sealant constitutes approximately 0.33% of the reused material (from applying a 1mm layer of sealant to a 300 mm layer of roadstone). This results in a concentration of 20 mg kg^{-1} in the reused material.

The types of waste exempt from waste management licensing (as selected from a list provided by SEPA) which were identified as potentially containing the prioritised organic contaminants are listed in Table 3.1, along with their European Waste Catalogue (EWC) codes. The concentrations of the prioritised contaminants in each different waste material type are shown in Table 3.2.

Table 3.1 Concentrations of prioritised organic chemicals in waste exempt from waste management licensing under paragraphs 7, 9, 12, 19, 45, and 47 materials spread to land (mg kg^{-1} dwt)

EWC code	20 02 01	19 05 03	17 03 01	10 01 01	19 06 06	19 12 12
Waste	**Biodegr**	**OSComp**	**Bitumen**	**Ash**	**Digest**	**Other**
Tetracycline	0	0	0	0	98	0
Ivermectin	0	0.17	0	0	1.85	0
Triclosan	0	0	0	0	3.7	7.55
HHCB (Galaxolide)	0	0	0	0	0	0
BaP	0.17	0	20	0.00007	0	0.19
Dioxins and dioxin like PCBs	0	0	0	2.46	0.2	0.63
PDBEs	0	0	0	0	0	25.84

[15] http://austintexas.gov/sites/default/files/files/Watershed/coaltar/PAHs_in_Austin_2005_final.pdf

The concentrations of dioxins and dioxin like PCBs that were in different organic waste materials were generally reported in terms of the total TEQ for the sample. In some cases the levels were reported as a concentration, and in these cases the TEQ for the sample was estimated by assuming the same congener composition as has been identified for UK rural soils (Environment Agency 2009b). Concentrations in soil were calculated assuming standard soil conditions and were calculated as the initial concentration in the topsoil immediately following application and mixing throughout the upper 10 cm of soil (Eq R16-50, ECHA 2012).

Given the spatial resolution of the dataset, which was available for the present study at the Local Authority Area scale, it was not considered to be practical or useful to assess the bioavailability of the organic contaminant sin the soil after application. The reason for this is that whilst bioavailability can be extremely important at a local scale, as the scale of the assessment increases the variability in the bioavailability controlling parameters also increases. This results in considerably greater uncertainty as the assessment scale is increased towards the scale used for the present study. The impact of soil organic carbon concentrations, which are the key bioavailability controlling parameter for the majority of non-polar organic chemicals, on the predicted risk characterisation ratios is considered in the probabilistic analysis (see Section 3.5).

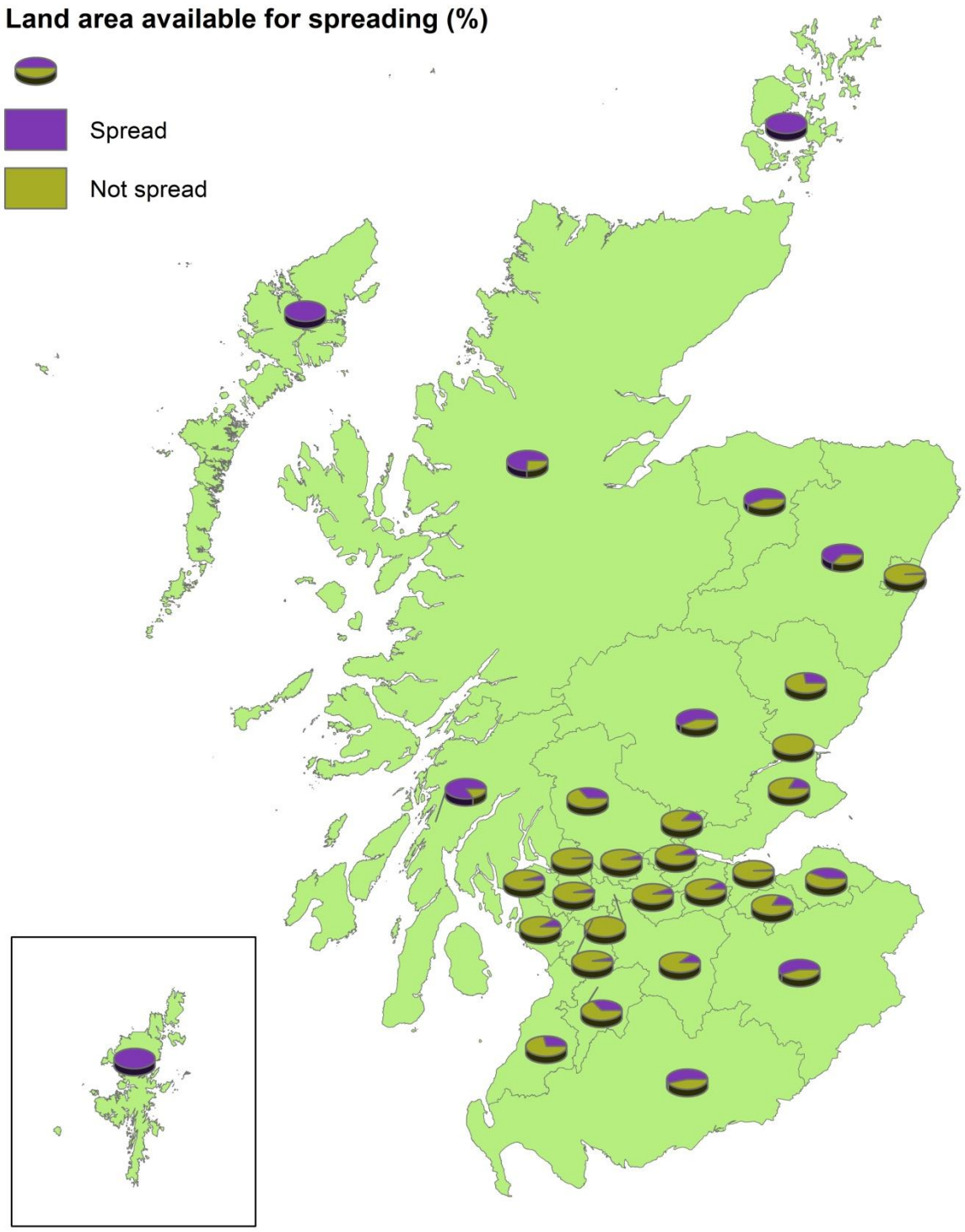


Figure 3.1 Estimated land area for spreading by Local Authority Area in Scotland

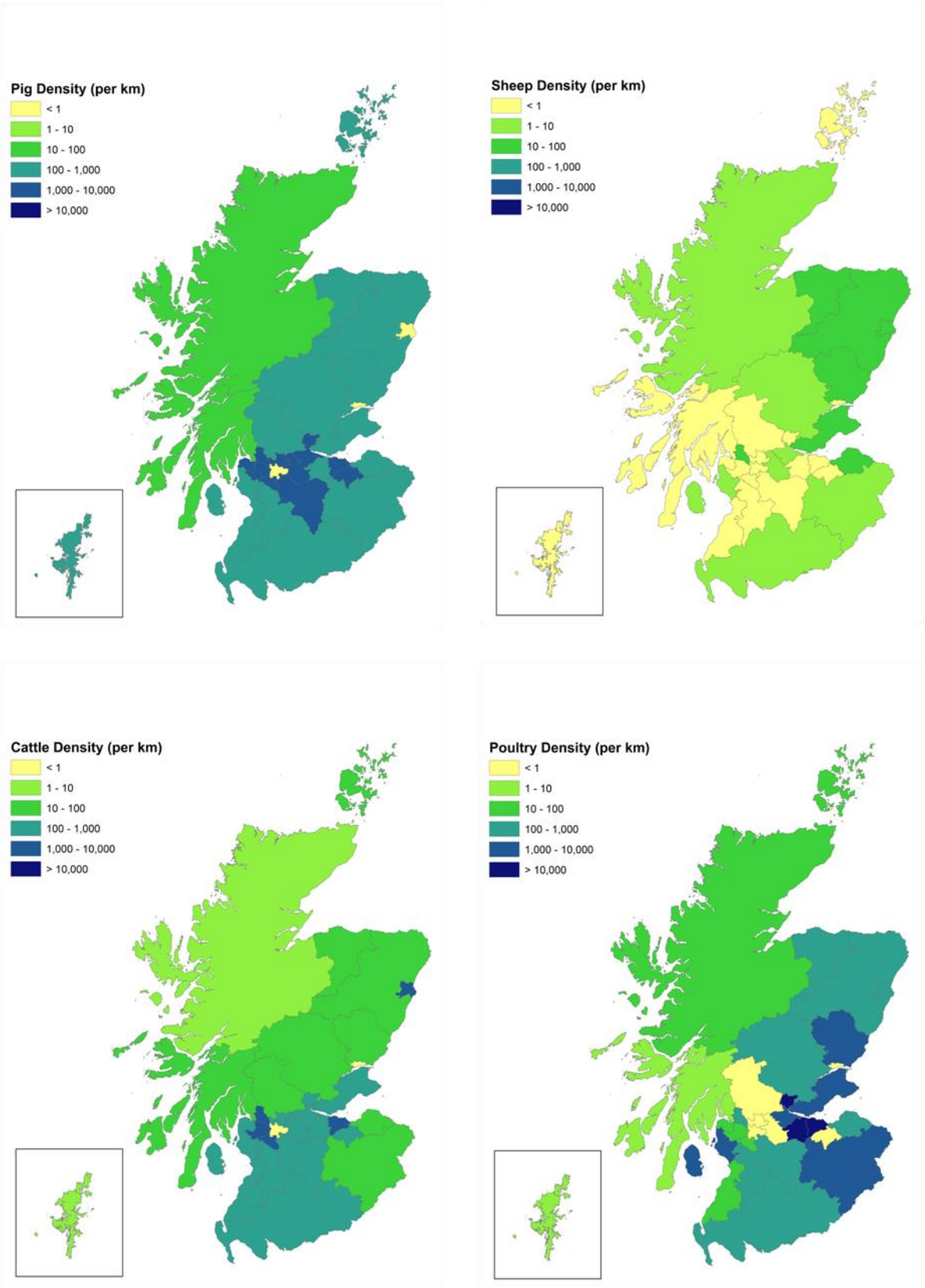


Figure 3.2 Livestock density in Scotland by Local Authority Area

3.2 Spatial assessment

The results of the risk assessment were presented graphically using a GIS (ArcMap 10, ESRI) based on Local Authority Area. The RCR achieved for each substance (ratio of the Predicted Environmental Concentration to the Predicted No Effect Concentration for a substance) in each Local Authority Area were denoted by colour scale, with RCR values <1 (PNEC for a substance not exceeded) displayed in green and values >1 (PNEC value for a substance exceeded) displayed in a colour scale from yellow to red corresponding to an increase in RCR from 1 to 10000.

The relative contribution of each waste type to soil concentrations were then overlaid onto local authority area as pie charts. This "source apportionment" was undertaken across the three main waste types: sewage sludge, animal manures and waste exempt from waste management licensing . Where it was possible to determine the predominant source of a substance in soils the relative contribution of sub-categories of this waste type were displayed on a further map. For example, where animal manures were determined to be the predominant source of a substance in soils, further maps of the relative contribution of cow, sheep, pig and poultry manures to the overall animal manure derived soil contribution of a substance were produced.

3.3 Environmental risk maps

The sources of ivermectin and tetracycline are predominantly from livestock, although both medicines are considered to potentially be found in some waste materials exempt from waste management licensing (see Moray, Figures 3.3 - 3.6). Both medicines may be found in anaerobic digestates, and ivermectrin has also been found in off-specification composts. The entire loading of ivermectin to soils in the Glasgow area is due to the use of off-specification composts, and a significant contribution comes from anaerobic digestates in Moray, and from off-specification compost in South Ayrshire. The only contributions to loadings of tetracycline other than from livestock are from the application of anaerobic digestates, which are particularly concentrated in Moray.

Refinement of the analysis could be undertaken through a more detailed analysis of the different livestock types, and the rates of treatment by various different veterinary medicines. This would provide a more targeted assessment and give a focus for potential prioritisation of manure production types.

For triclosan the key source is clearly sewage sludges and wastes exempt from waste management licensing, mostly off-specification composts, digests and compost-like outputs (CLO). The risks are relatively low, aside from in the Central Belt (Figures 3.7-3.8). Triclosan is readily broken down in treatment processes that are aerobic, but will persist in anaerobic process systems (e.g. Environment Agency 2010). In addition, it has been observed that, due to the variability in source concentrations of the input materials, triclosan concentrations in final organic output materials can also be highly variable, making the derivation of product concentrations challenging.

Triclosan is also likely to be prioritised under the Water Framework Directive as a substance for which an EQS will be set on an EU-wide basis. The UK already has a Specific Pollutant EQS for triclosan. Discussions are on-going in relation to the Persistent, Bioaccumulative and Toxic properties of triclosan; specifically it appears to fulfil both B and T criteria, but there is uncertainty related to P[16].

Despite the widespread, ubiquitous distribution of benzo(a)pyrene in all soils across the industrialised world there are relatively low levels of environmental risks indentified from the use of organic materials on land considered through this project (Figure 3.9). Sewage sludge and wastes make up the key sources and, of these, biodegradable waste (from parks and gardens), bitumen mixtures containing coal tar and other wastes (such as MBT CLO) are the key sources, but it would be expected that the volumes of these materials may be relatively low (Figure 3.10). Benzo(a)pyrene has been selected as a surrogate marker compound for other genotoxic PAHs as it has been demonstrated to be a present at a relatively constant ratio in relation to other genotoxic PAHs in contaminated soils where the PAHs are generally derived from combustion sources. However, this relationship may not be wholly relevant for the BaP sources in the materials considered in this project.

Galaxolide or HHCB is a member of a group of substances used in fragrances and known collectively as the polycyclic musks (Figure 3.11). It can be seen to present relatively low levels of potential environmental risks and its sources are exclusively from sewage sludges (a second figure on the contributions of waste is not shown for HHCB).

Dioxin and dioxin-like PCB data are shown Figure 3.12 and 3.13 with low levels of potential risks identified, outwith the central belt, and the key sources are sewage sludges and wastes exempt from waste management licensing in the form of bottom ashes, anaerobic digestates and MBT CLO (in this case the data are taken from a Spanish sourced biowaste).

For PBDEs only one figure is given that shows the potential risks and also two key sources (Figure 14). From sludge application the environmental risks are predicted to be relatively low, and for one Local Authority Area in the central belt (Glasgow) considerable risks have been identified. The data input to this was from MBT-CLO produced in England, although it is expected that Scottish derived wastes would be similar.

We have provided relatively limited interpretation of the spatial maps, which is an acknowledgement of the semi-quantitative nature of the underlying assumptions and caveats that have been used in their development. The maps provide a tool by which to identify priority chemicals form the short-list and materials and Local Authority Areas where potential environmental risks may be an issue.

[16] http://apps.echa.europa.eu/registered/data/dossiers/DISS-9ea3b5cc-80fb-15ea-e044-00144f67d031/AGGR-a9cc992b-630a-49c8-8d38-190d18284181_DISS-9ea3b5cc-80fb-15ea-e044-00144f67d031.html#AGGR-a9cc992b-630a-49c8-8d38-190d18284181

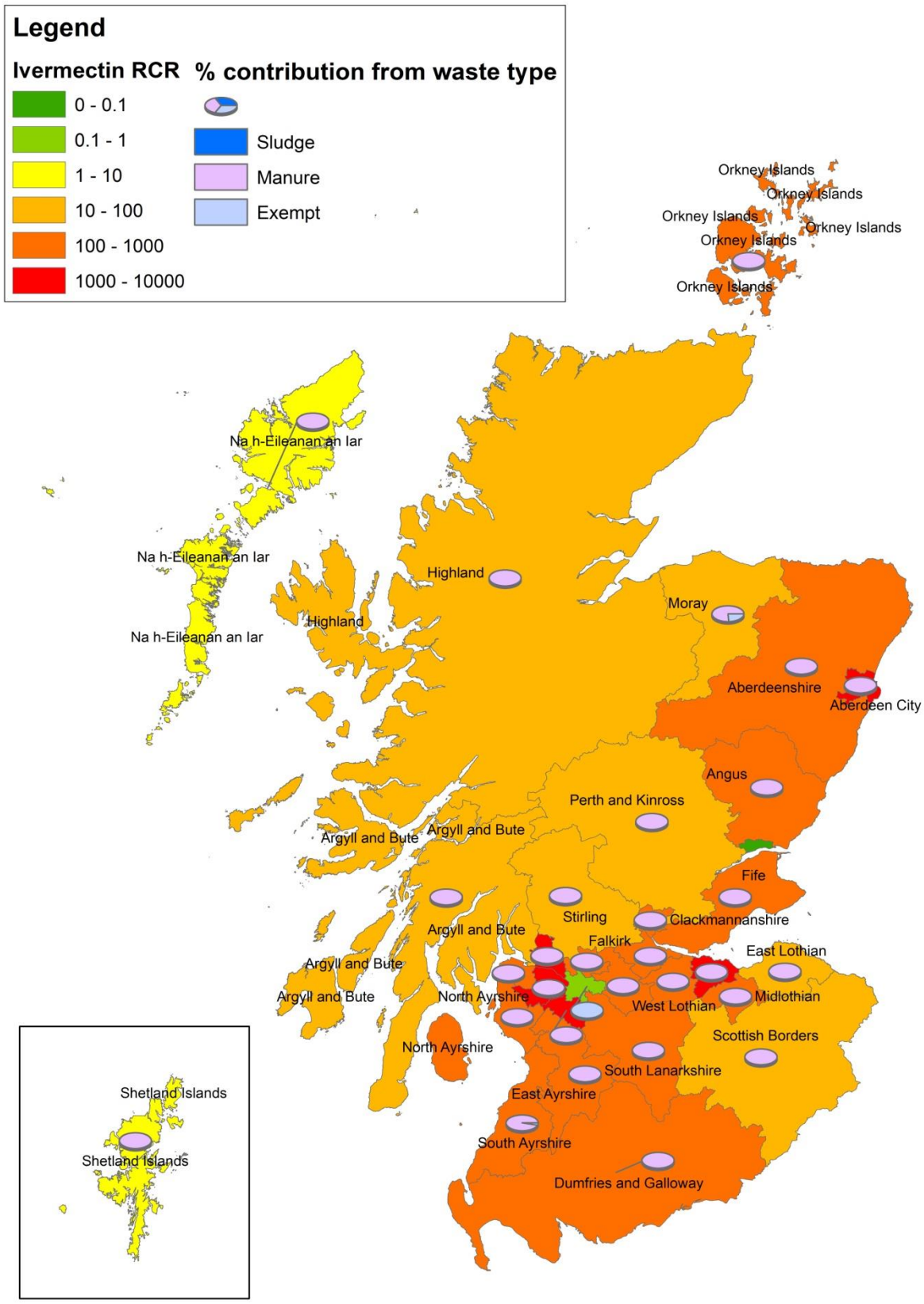


Figure 3.3 Ivermectin risk, with source type contributions

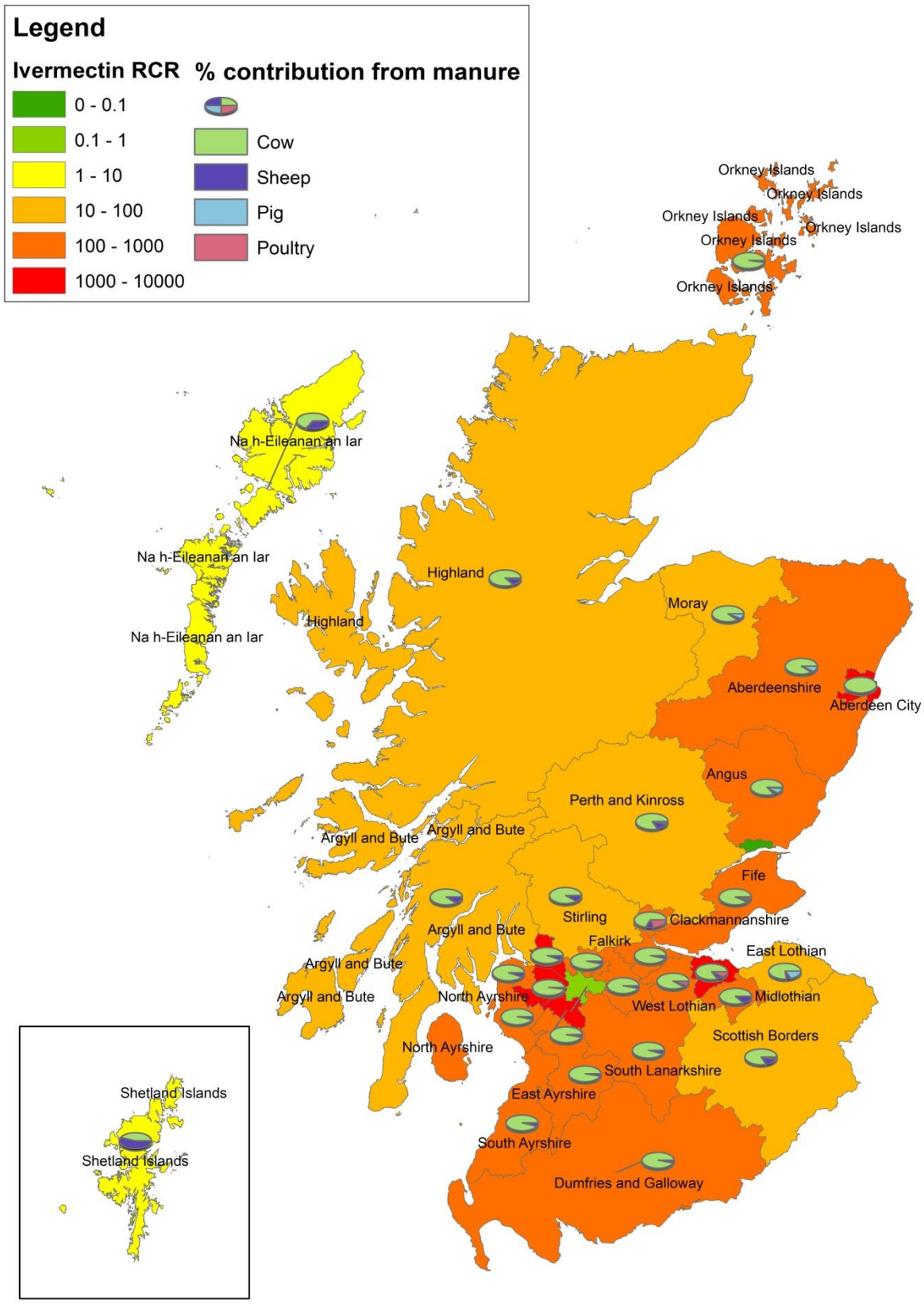


Figure 3.4 Ivermectin risk, with livestock type contributions

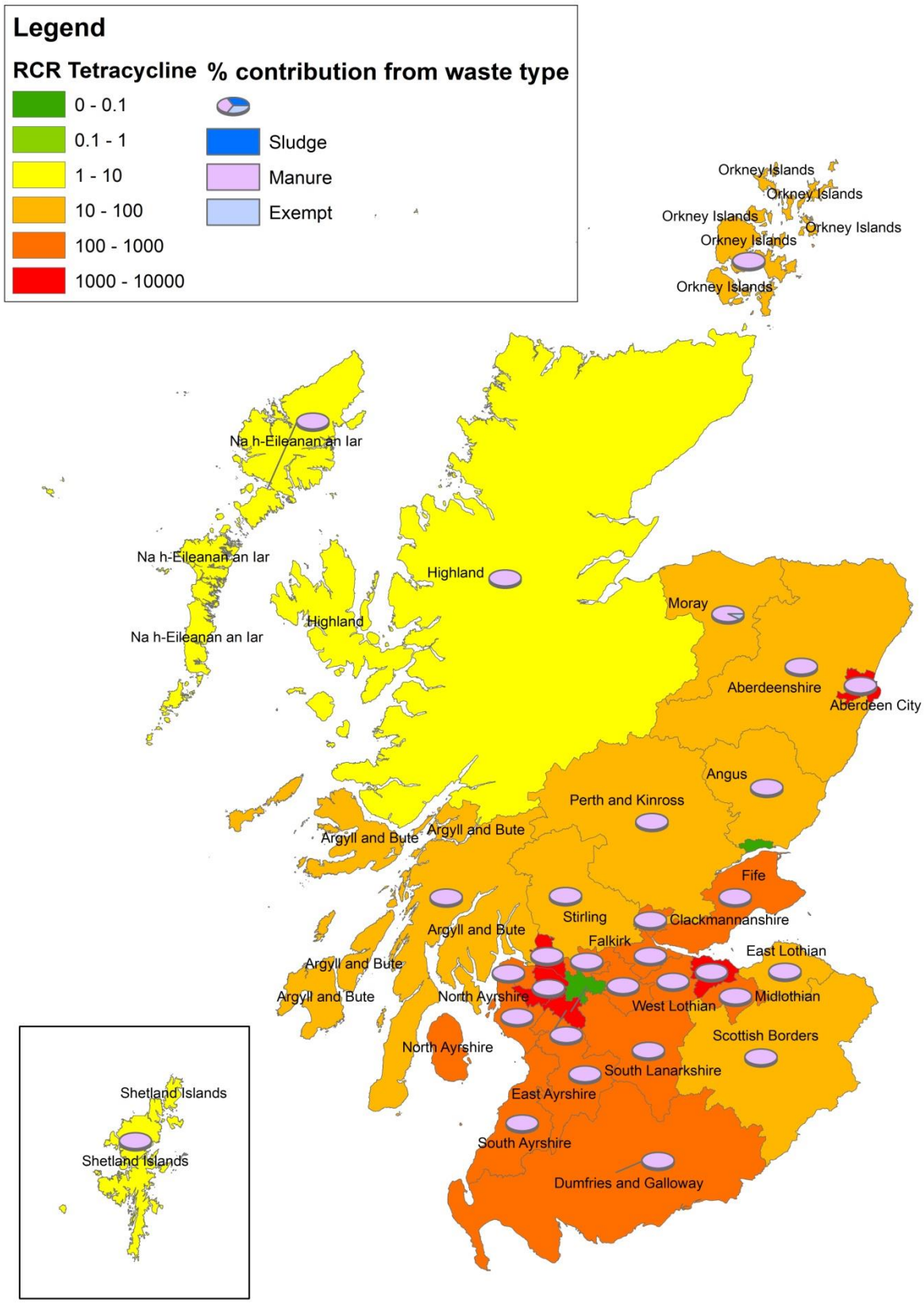


Figure 3.5 Tetracycline risk, with source contributions

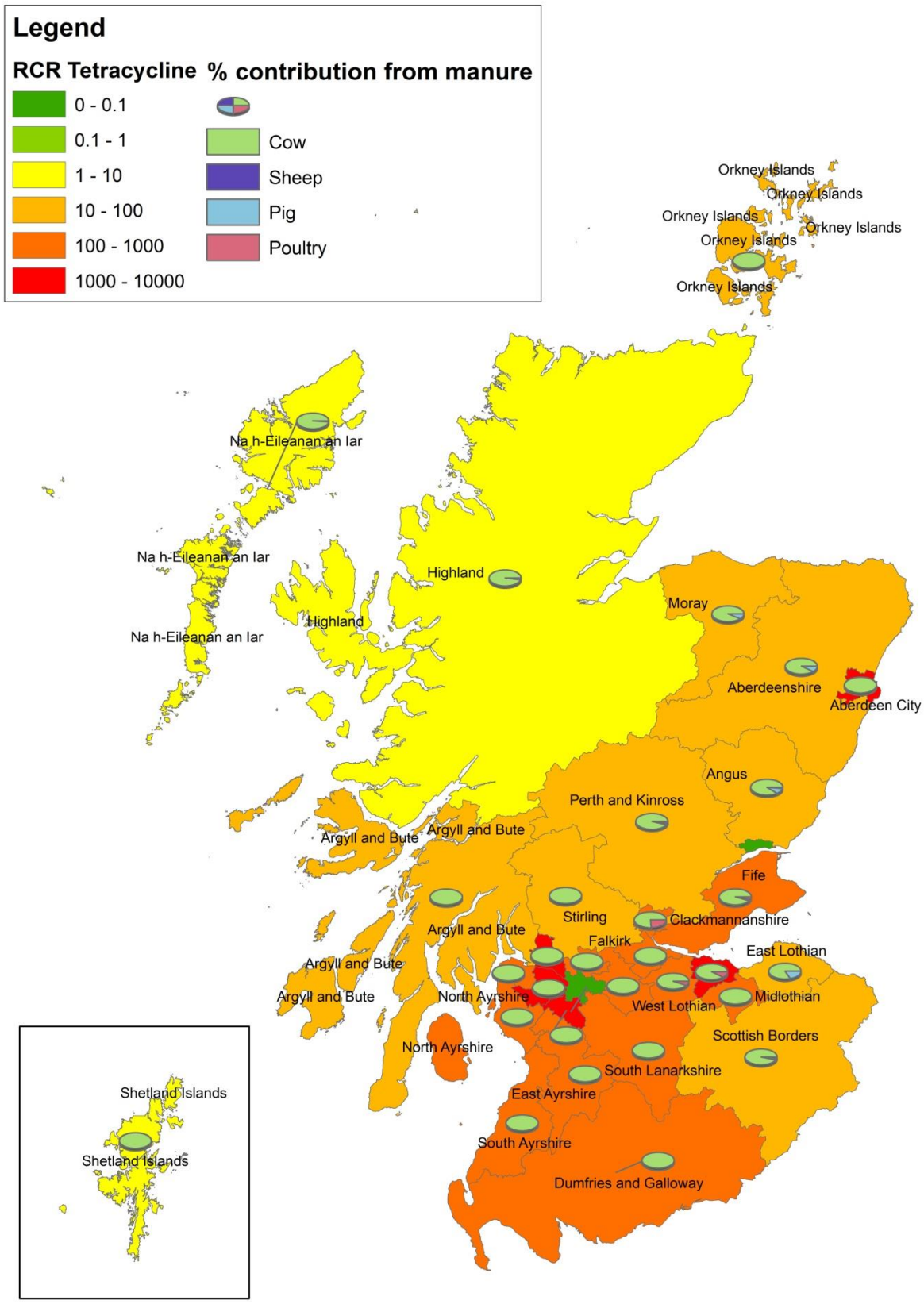


Figure 3.6 Tetracycline risk, with livestock type contributions

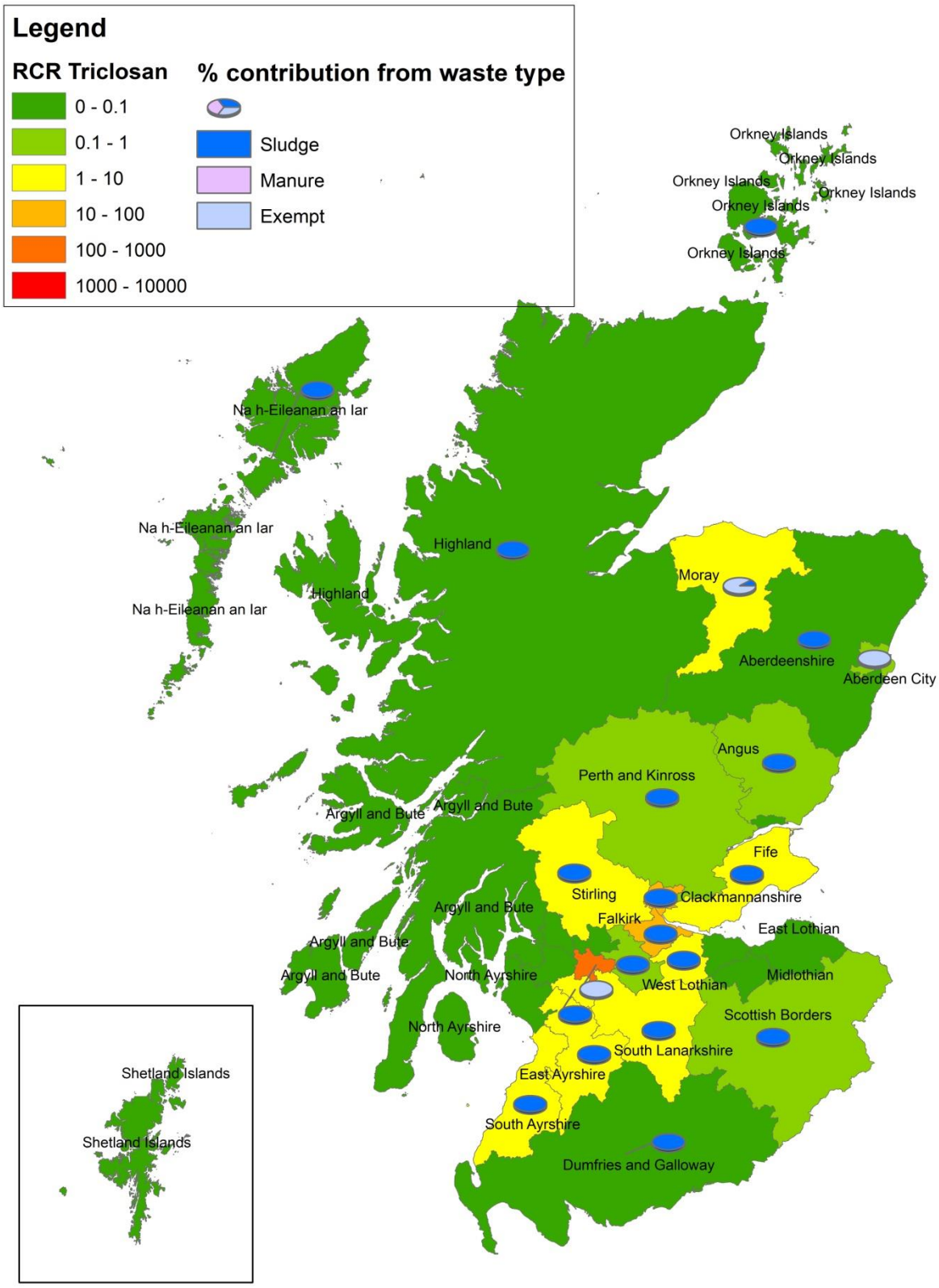


Figure 3.7 Triclosan risk, with source type contributions

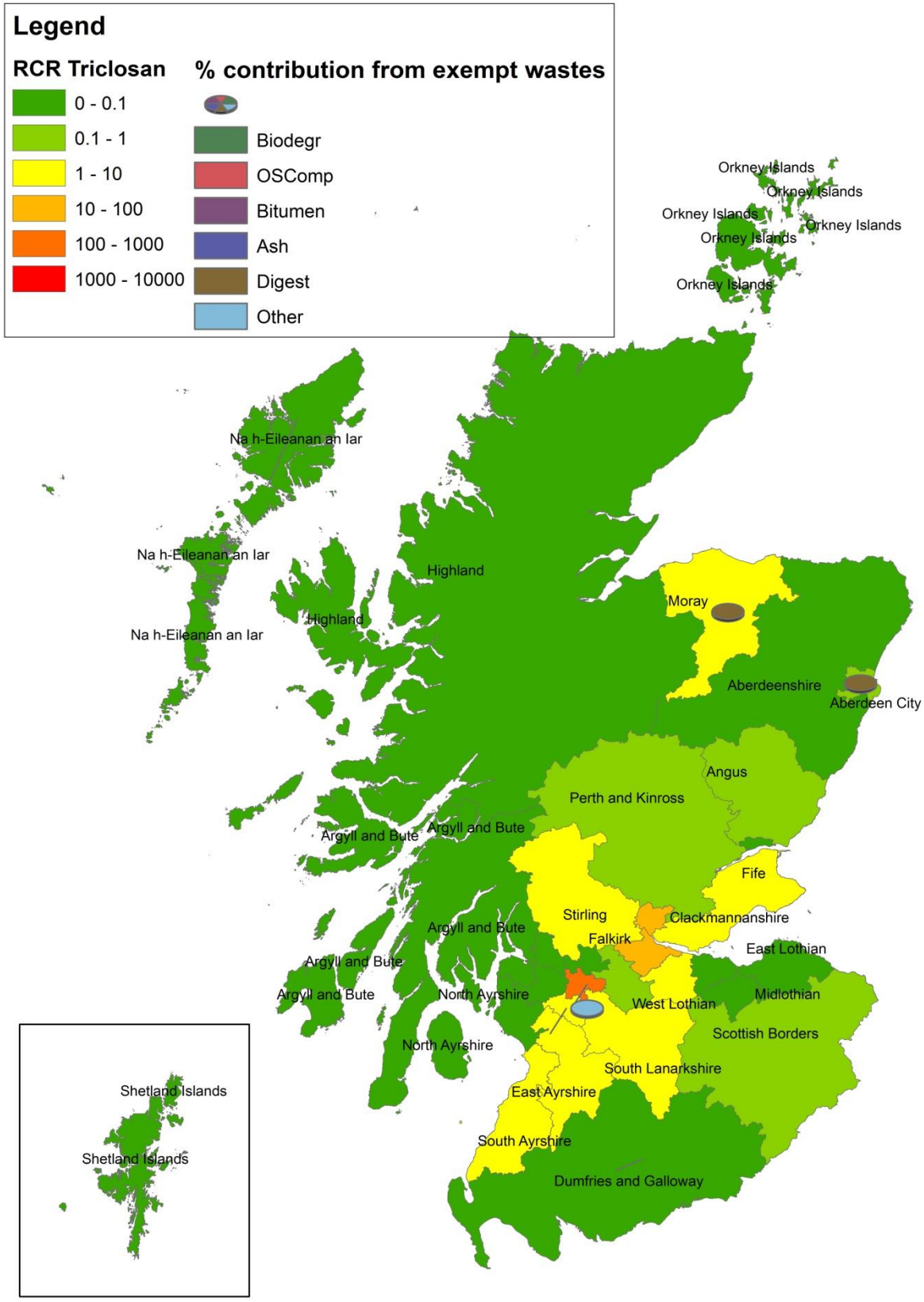


Figure 3.8 Triclosan risk, with waste type contributions

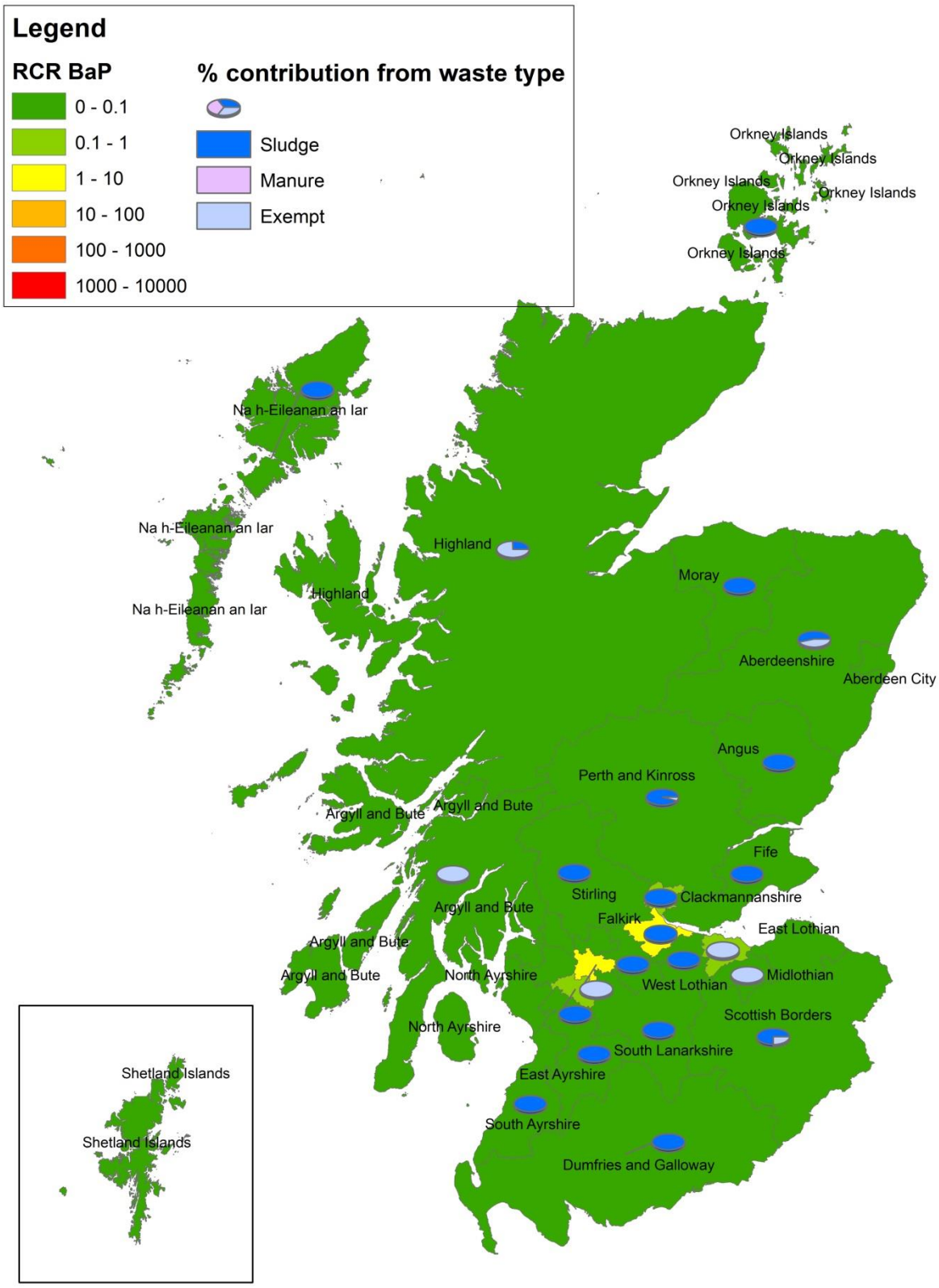


Figure 3.9 Benzo(a)pyrene risk, with source type contributions

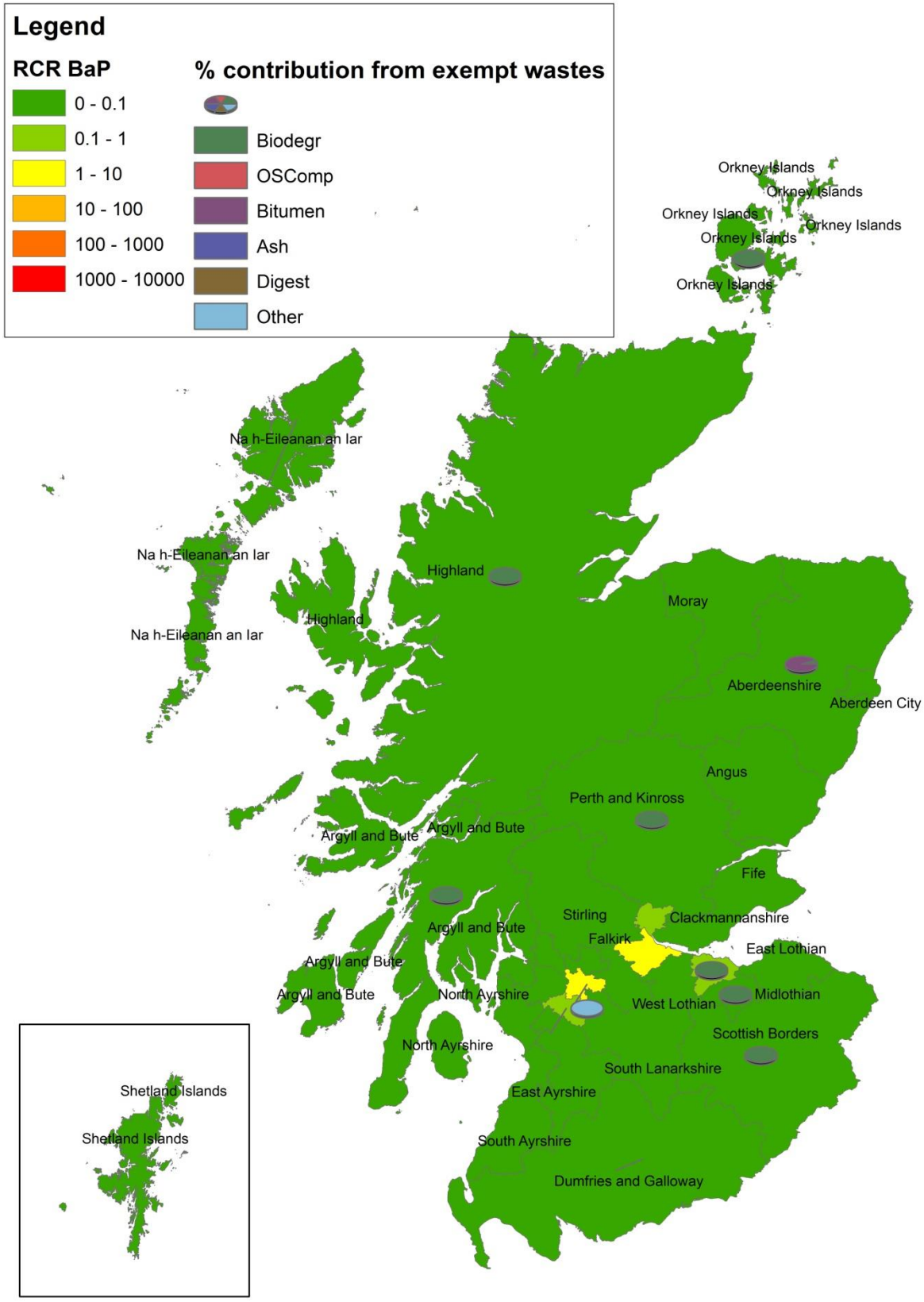


Figure 3.10 Benzo(a)pyrene risk, with waste type contributions

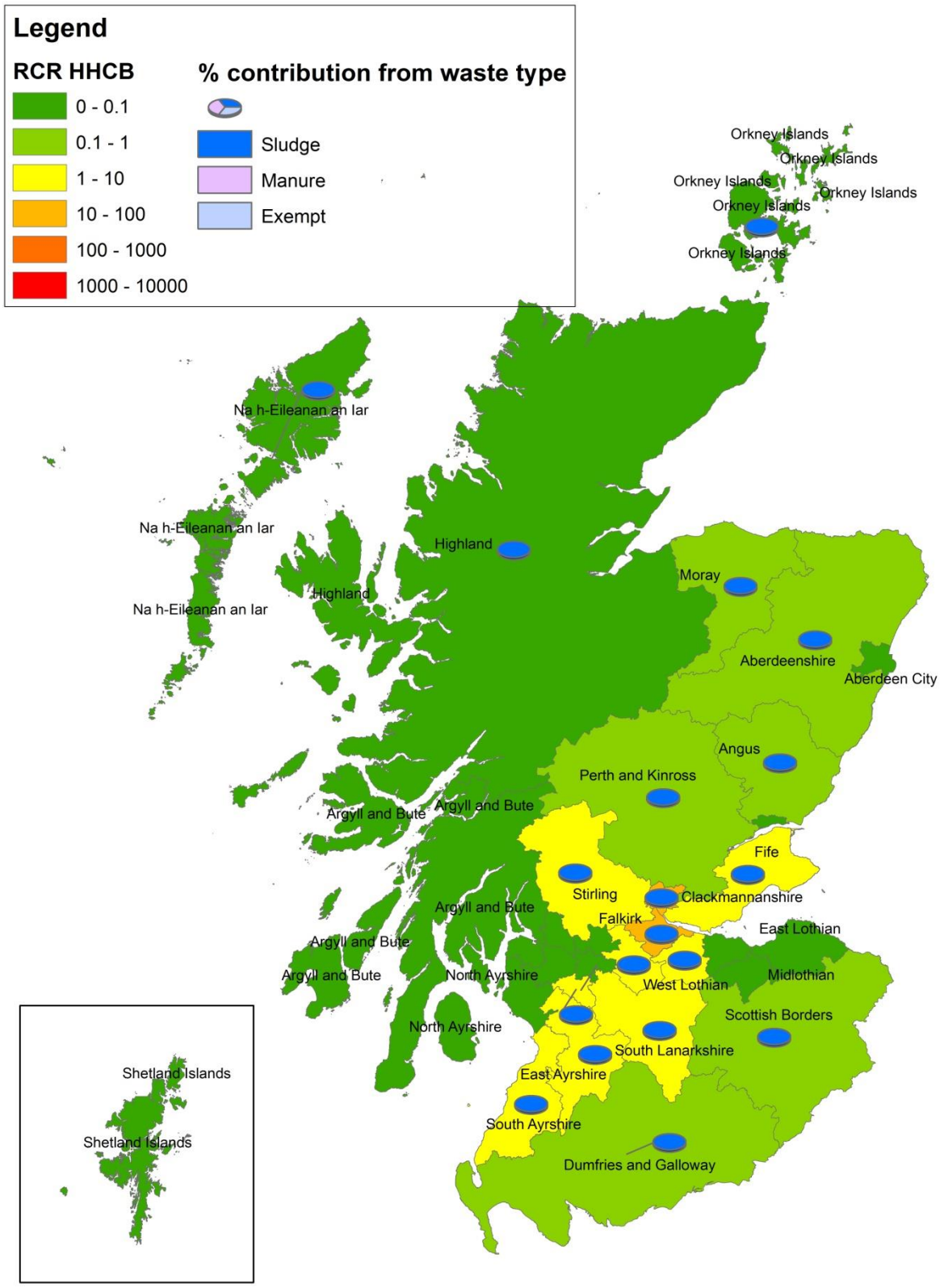


Figure 3.11 HHCB (Galaxolide) risk, with source type contributions

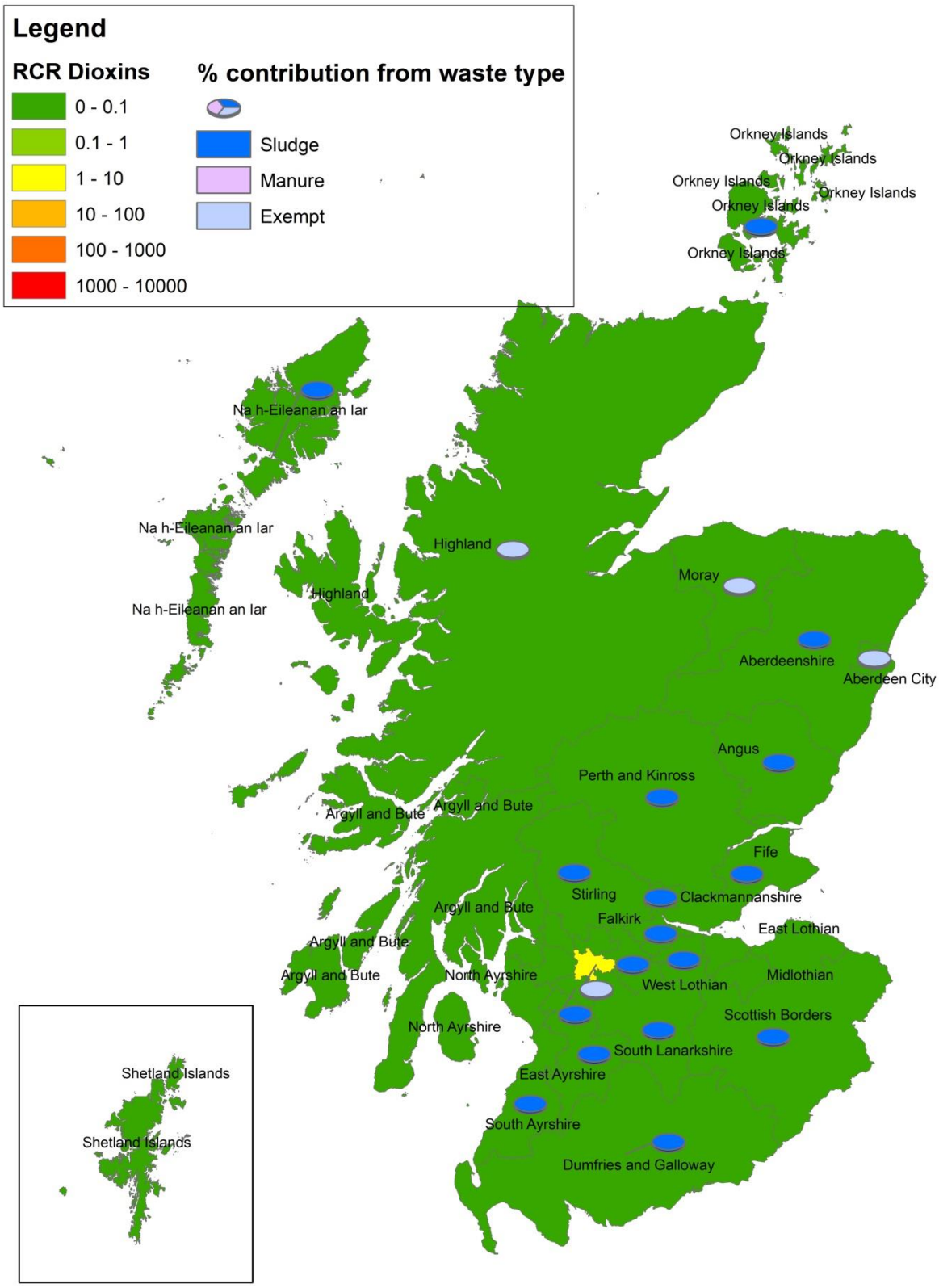


Figure 3.12 Dioxins and dioxin like PCBs risk, with source type contributions

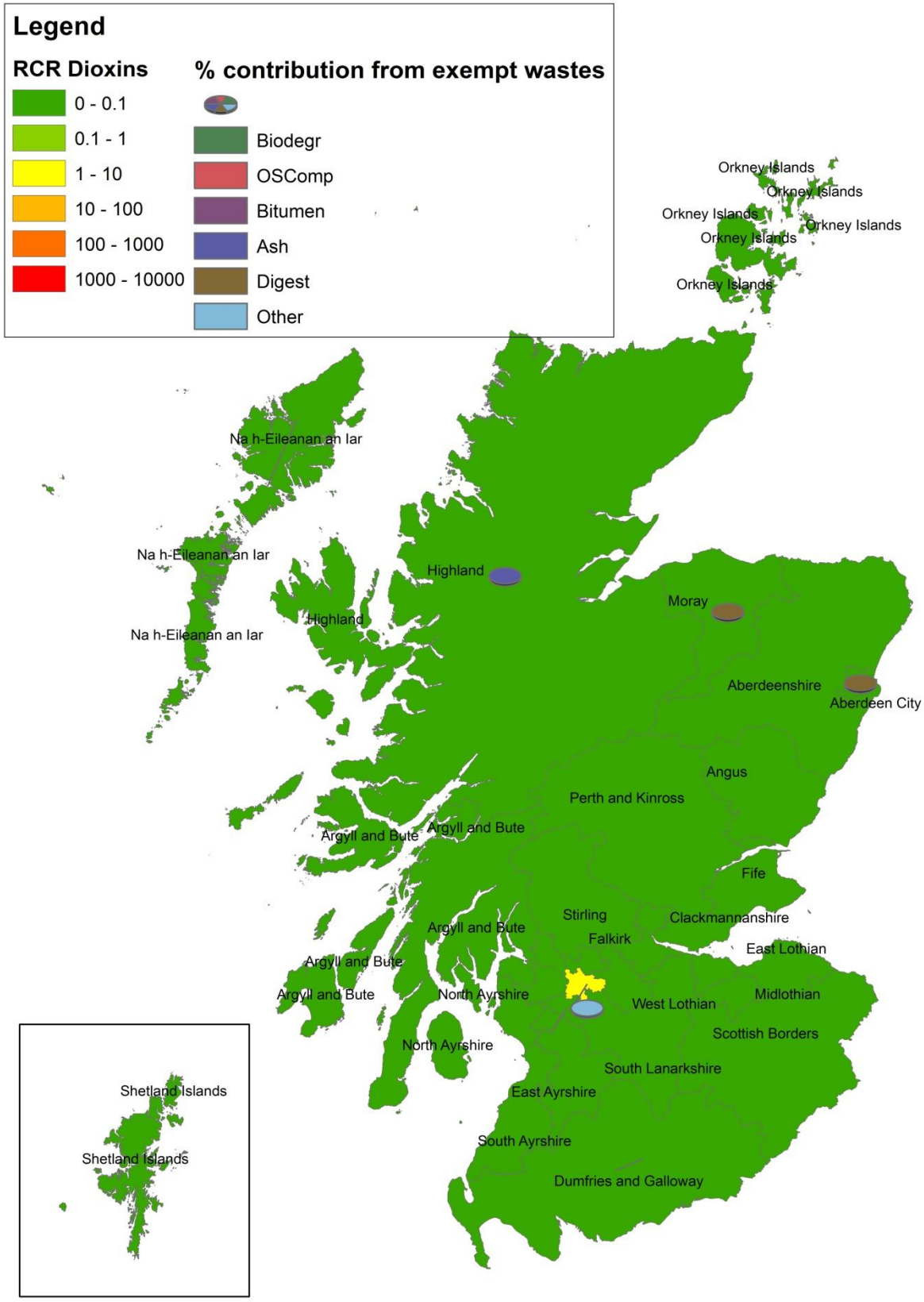


Figure 3.13 Dioxins and dioxin like PCBs risk, with waste type contributions

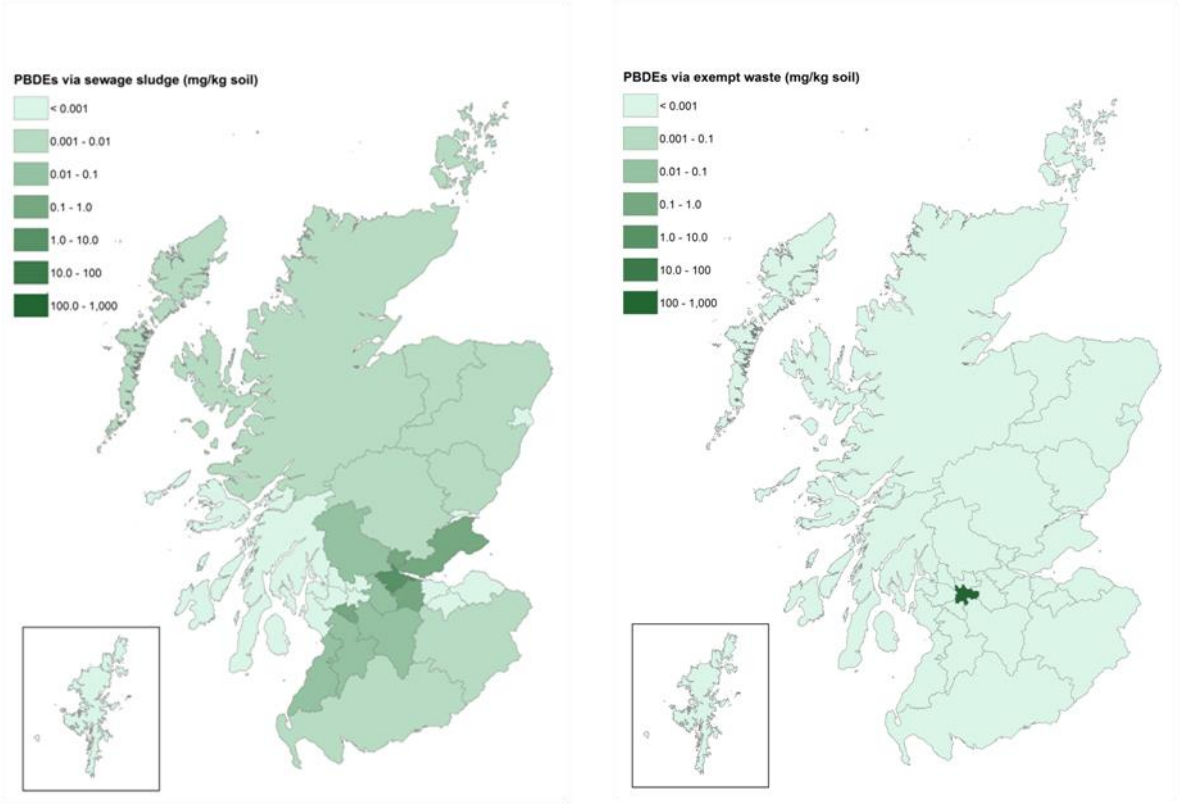


Figure 3.14 Polybrominated diphenylether exposure via sewage sludge and exempt waste

3.3 Exposure calculations

3.3.1 Environmental Exposure Assessment

The area of land potentially available for spreading organic materials has been estimated from the proportion of the population living in rural areas. This is an approximation, but is considered to provide relevant results in that highly urbanised Local Authority Areas (such as Glasgow, Edinburgh, and Aberdeen) have a relatively small area of land expected to be available for spreading, whereas sparsely populated areas (such as the Highland and the islands) have a large area of land which could potentially be used for spreading organic wastes. However, some of this land with be unsuitable for spreading due to physical constraints, such as altitude, gradient, and logistical issues, such as access from a major road network. This tends to result in relatively high risks being predicted for some materials in urban areas due to the limited area of land upon which material may be spread (high transport costs for bulky, low value, materials make this a reasonable assumption).

The use of the Land Capability for Agriculture classifications (if available in a suitable GIS format) would enable a much more refined assessment of the area of land potentially available for the spreading of various different materials. Some materials may be preferentially spread on particular land use types, for example much of the manure produced by livestock will be deposited directly onto grazing land, meaning that the area of

land potentially available for receiving different types of wastes could differ depending upon the source of the waste material. Ideally this information should also be combined with other sources of information, such as topography and land under forestry, as high altitude areas and forested areas are also unlikely to receive applications of waste material.

There is some uncertainty in the manure production rates of the different livestock animals. The quantities of manure produced daily by cattle are much greater than those produced by pigs, sheep and poultry, so a similar number of cattle will produce a much higher loading of manure than other animals. The manure loadings are only important in terms of the quantities of the identified veterinary medicines assessed which are potentially applied to the soil. The medicines are typically dosed according to the body weight of the animals being treated, which means that larger animals like cattle require much larger quantities of the active ingredient for effective treatment than smaller animals.

The predominant sources of the veterinary medicines ivermectin and tetracycline are from animal manures, with cattle providing the greatest contribution in virtually all Local Authority Areas. The only Local Authority Area in which cattle are not expected to be the predominant source of veterinary medicines from animal manures is Shetland, where sheep make a larger contribution than cattle.

Ivermectin is a widely used veterinary medicine and is available in a wide variety of currently authorised formulations for a variety of application methods (e.g. oral solution, pour on, injection, paste, and in-feed treatments) as an antiparasitic treatment for use on pigs, cattle and sheep. Tetracycline is likely to be much more rarely used, as it is available in only a limited number of currently authorised formulations for the treatment of specific conditions in cattle, pigs, and sheep. The exposure assessment assumes a constant concentration in the manure, although this concentration in the manure is only likely to be realised relatively soon after treatment. The proportion of the total herd receiving treatment may be very different for ivermectin, which is likely to be applied to the majority of relevant animals, and tetracycline, which is only likely to be applied to specific animals requiring treatment.

It is possible that some types of products which may have contained tetracycline as an active ingredient in the past have been replaced with formulations containing oxytetracycline or other related substances.

Intensively farmed pigs and poultry do appear to not contribute a particularly large proportion of the overall loading of either of the veterinary medicines assessed. This is likely to be due to two main factors, the relatively small size of these animals compared to cows and consequently lower rates of manure production, and the fact that some of the manure is disposed of by routes other than spreading to land. The same manure concentration of the veterinary medicines has been assumed for all animals, and this may not be unreasonable given that doses are commonly on a body weight basis. The only information available on the concentrations of ivermectin in manure came from a registration study with cattle. Different treatment regimes between conventionally and intensively farmed livestock could lead to different average concentrations in the manure over the course of a year, even if the peak concentrations (i.e. following treatment) are similar. A more detailed assessment of the frequency of use of veterinary medicines, and the total quantities applied for

particular applications would considerably refine this aspect of the assessment. Alternatively, detailed monitoring of a variety of different manure types for a variety of representative veterinary medicines would provide a much clearer picture of the differences in both concentrations and variability between different farming practices.

Concentrations of benzo(a)pyrene in soil resulting from the application of wastes which are exempt from waste management licensing are expected to be relatively low in all cases. There are numerous sources of benzo(a)pyrene into the environment, particularly combustion processes, and it is possible that ambient background concentrations provide a greater contribution to the total soil loading than the applied waste materials, particularly in more urbanised areas. Previous monitoring studies have found higher levels than the additions expected from the present study in Southern and Central Scotland[17].

3.3.2 Human Health Exposure Assessment

3.3.2.1 Methodology

Dioxins and dioxin-like compounds were identified as being present at potentially significant elevated concentrations in one area following application of waste. For materials applied to land as a fertiliser or soil improver the potential impact on human health through 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 and also meats, egg and dairy products (following consumption of silage and forage crops by farm animals).

Dietary exposure assessment has been undertaken using a research modelling tool developed by the Environment Agency (WALTER – **Wa**ste **A**pplications to **L**and: **T**ool for **E**nvironmental **R**isk)[18]. A version of the WALTER modelling tool has been developed specifically to assess the potential risk from dioxins, furans and dioxin-like PCBs in waste materials spread to agricultural land. Concentrations of dioxins in waste material, soil properties and the waste application rate are input to the model to enable calculation of dioxin concentrations in foods and the resultant level of risk to adult and infant consumers, based on their consumption rates for various food types and the relative toxicological potency of the dioxin, furan and PCB congeners. The concentration of dioxins in soil used to calculate plant uptake is based on the existing level in soil (EA, 2009b) plus that added from waste. The food intakes used in WALTER are the mean rates for consumers.

Input parameter values for dietary exposure modelling of dioxins in waste using WALTER are detailed in Table 3.2. The maximum reported dioxin concentration in MBT CLO (36 ng TEQ/kg from EA 2009a) was used for this assessment and the dioxin profile was assumed to be that typical of UK soil (EA 2009b). Dioxins have relatively long biodegradation half-lives and no degradation was assumed for the duration of the assessment.

[17] http://www.macaulay.ac.uk/tipss/

[18] 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.

Table 3.2 Data input to WALTER dietary exposure model for assessment of waste spread to land

Model Parameter	Value
Dioxin concentration in waste applied to land	36 ng TEQ/kg (EA, 2009)
Application rate	8 and 50 t/ha/yr
Application frequency	Once per year
Time period	10 years
Incorporation depth	25 cm (WALTER default for ploughed in application)
Soil density	1500 kg/m^3
Soil organic carbon	5%

3.3.2.2 Results

Modelling of dietary exposure for consumers of food produced by waste amended land does not indicate an unacceptable level of risk based on the maximum recorded concentrations of dioxins in MBT CLO. Summary results of this assessment are presented in Table 3.3

Table 3.3 Results of dietary exposure assessment for dioxins in waste applied to agricultural land

Waste application rate (t/ha/yr)	Adult Intake (ng TEQ/day)	Infant intake (ng TEQ/day)	HCV (ng TEQ/kg bw/day)	Hazard Index (max)
8	0.010	0.0047	0.002	0.31
50	0.018	0.0094	0.002	0.54

The calculated concentrations of dioxins in individual foodstuffs are also below the maximum allowable concentrations for animal feed and for all food for human consumption except for perhaps offal (Environment Agency 2009b).

3.4 Refinements in the assessment

As tools to identify potential risk areas, chemicals and organic materials, the previous estimations and figures provide an evidence-based way forward. Reasonably, it could be asked how the assessments might be refined, in a proportionate way, to deliver greater certainty in the assessment.

The advantage of undertaking the Local Authority Area approach is that it provides an opportunity to focus on specific areas and so use less generic information. In particular, the assessment does not account for any of the soil factors, specifically organic carbon content, that reduce the availability of some organic chemicals, and so their potential risk. To do this on a Scottish-wide scale would be somewhat meaningless in light of the considerable range

of soil carbon contents in Scottish soils. However, summary statistics for soil carbon content become more meaningful when the spatial scale that they represent is reduced. Where applicable, the soil PNECs, which are usually derived for a soil of 3.4% organic matter (2% organic carbon), can be normalised to the soil (PEC) under consideration. Examples of this process have been developed for Soil Screening Values, by the Environment Agency (2008b), and follows European chemicals risk assessment guidance (REACH R16). It is perhaps pertinent to recall that many of the materials considered in this report are added to soil to improve the organic matter content.

Where SEPA undertake compliance monitoring of the application of wastes which are exempt from waste management licensing to land soil organic carbon is routinely measured for the land upon which the application takes place, taking account of spatial variability. In the case of specific applications, at specific locations, and with known soil properties, it is possible to take account of the bioavailability of the chemicals which are present. When considered at larger spatial scales the influence of bioavailability is considerably more uncertain, and a more generic assessment approach which assumed a uniform, typical (but relatively low) organic carbon content for soil is generally considered to be more appropriate.

In addition to the normalisation, account could also be taken of loss mechanisms of the organic chemical on application. In a screening assessment, as performed here, this is probably not appropriate, but as the number of areas that require consideration is reduced this becomes a reasonable refinement. Degradation rates for some chemicals are given in the Excel sheet accompanying this report and an approach might be to incorporate a loss parameter in the annual loading calculation, e.g. an average concentration lost from a soil over a year. This, together the normalisation step, would reduce uncertainties in the assessment of potential risks.

The measured data for organic chemical concentrations have in some cases been taken from relatively few non-UK studies. Relatively high percentiles of these concentrations (e.g. 90^{th} percentile) or maxima have been used, which is appropriate for a screening assessment. More comprehensive data are available for sewage sludges with an excellent coverage of many priority organic chemicals. Whilst municipal sewage sludges are relatively consistent in their nature, specific information about the sludge in question could be especially important if there are industrial sources of prioritised substances discharging to sewage treatment plants in which the sludge is generated.

A key uncertainty arising from the analysis of livestock manures if the different treatment regimes which may be applied to different farming practices and animal husbandry approaches, and the effect that this may have upon the resulting concentrations of veterinary medicines in the manure. The findings of the present study suggest that intensive farming of pigs and poultry is unlikely to be a major contributor to the overall risk. This assumes that 50% of the manure from these facilities is disposed of by other means than spreading to land, and that the concentrations of the veterinary medicines in manure is equivalent to that from other types of livestock and farming practices. Cattle appear to present the greatest potential risk, due to their high stocking densities and large size, which

requires larger doses of medicines and results in greater manure production. There can be a relatively large difference in the manure production rates of different types of cattle (e.g. dairy or beef), and they may also require different treatment regimes for some veterinary medicines. This issues could be important in terms of different kinds of livestock giving rise to different concentration of chemicals in their manure. A further issue which is often unclear form the literature information is whether or not concentrations relate to peak concentrations soon after treatment, or to averaged concentrations over a longer period of time. Whilst the peak concentrations may be of interest the average concentrations are more relevant to an analysis of the potential for accumulation of chemicals in soil.

The challenge remains obtaining these types of data for other organic materials that are applied to land, in order to improve the certainty of the assessment. A fallacious argument heard in the production of risk assessments for the Quality Protocols was in relation to certain organic compounds having not been found in materials and so there was likely low risk. However, if the organic compound wasn't looked for then it is unlikely to be found.

3.5 Using probabilistic approaches to refine the assessment

In order to refine the assessment further, for those chemicals and areas for which environmental risks had potentially been identified, a probabilistic assessment of the loadings of ivermectin to soils from cattle in North Ayrshire, and galaxolide to soils from sewage sludge in Falkirk, has been performed. Both of these scenarios represent relatively high predicted risk situations.

The following input parameters were considered as variables for the calculation of ivermectin exposures and risks:

- the fraction of land available for spreading (normal, mean ~0.01, std dev ~0.01)
- the number of head of cattle (normal, mean 36467, std dev 3647)
- the manure production rate of cattle (bimodal, beef ~30 & dairy ~60)
- the ivermectin concentration in manure (log-normal, mean 0.3, std dev 0.25)
- the quantity of sewage sludge spread (normal, mean 4848, std dev 485)
- the galaxolide concentration in sewage sludge (log-normal, mean 10.8, std dev 8.4)
- the soil mixing depth (normal, mean 0.1, std dev 0.2)
- the bulk density of the soil (normal, mean 1500, std dev 150)
- the soil organic carbon content (log-normal, mean 0.05, std dev 0.03)
- the degradation half-life of ivermectin in soil (normal, mean 128, std dev 33)
- the degradation half-life of galaxolide in soil (normal, mean 128, std dev 15)

The risk characterisation ratios for ivermectin in soil immediately after spreading, and one year following spreading, are shown in Figures 3.15 and 3.16 respectively. The contributions of the various different uncertainties to the overall uncertainty in the predicted risk characterisation ratios both immediately after application, and one year after application, are shown in Figures 3.17 and 3.18 respectively.

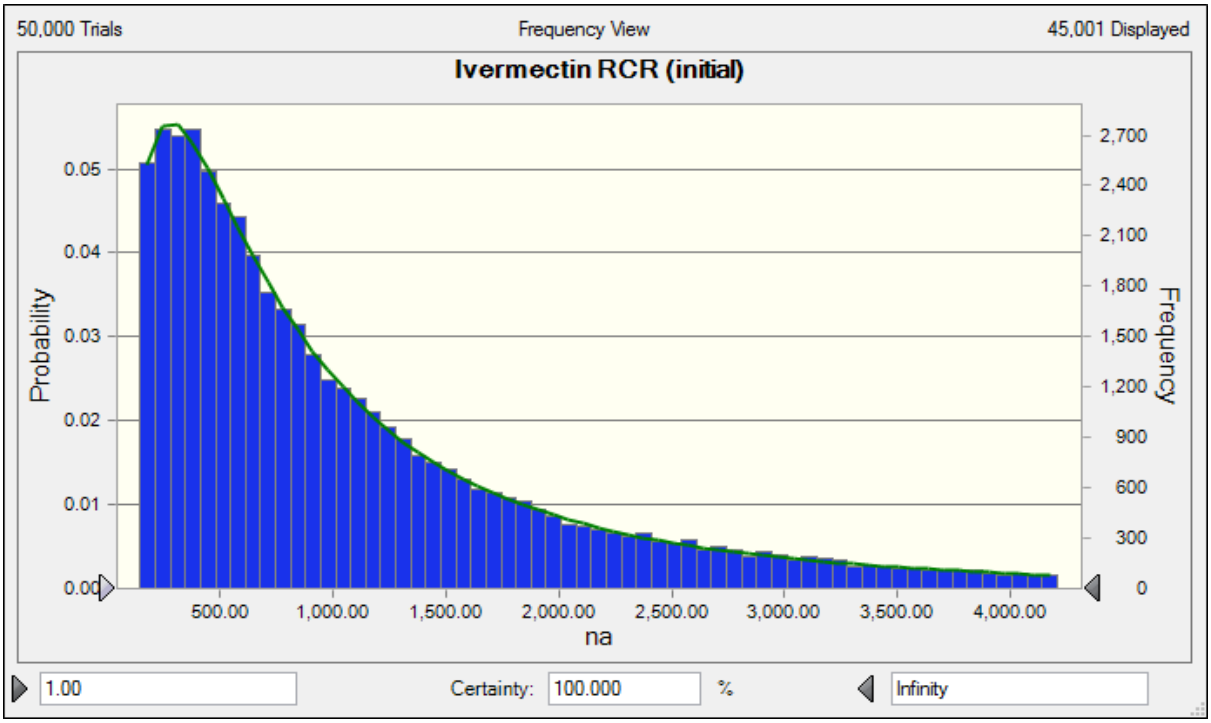


Figure 3.15 **Risk characterisation ratios for ivermectin immediately after application to soils in North Ayrshire**

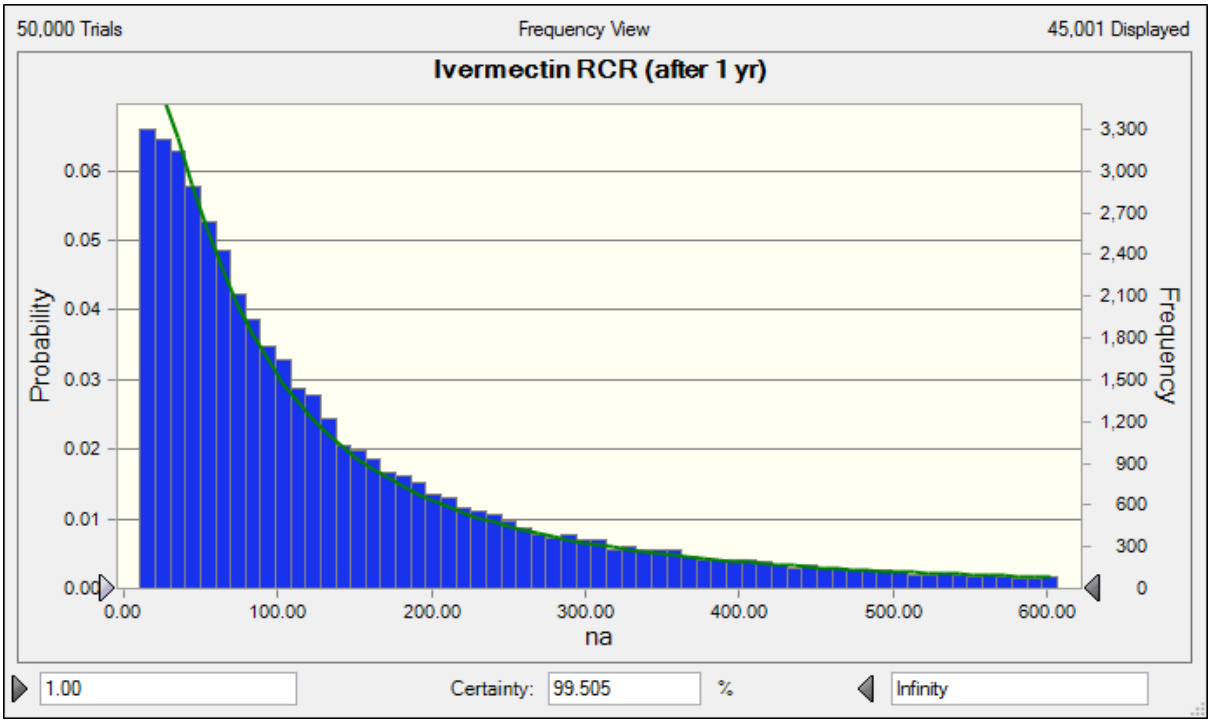


Figure 3.16 **Risk characterisation ratios for ivermectin one year after application to soils in North Ayrshire**

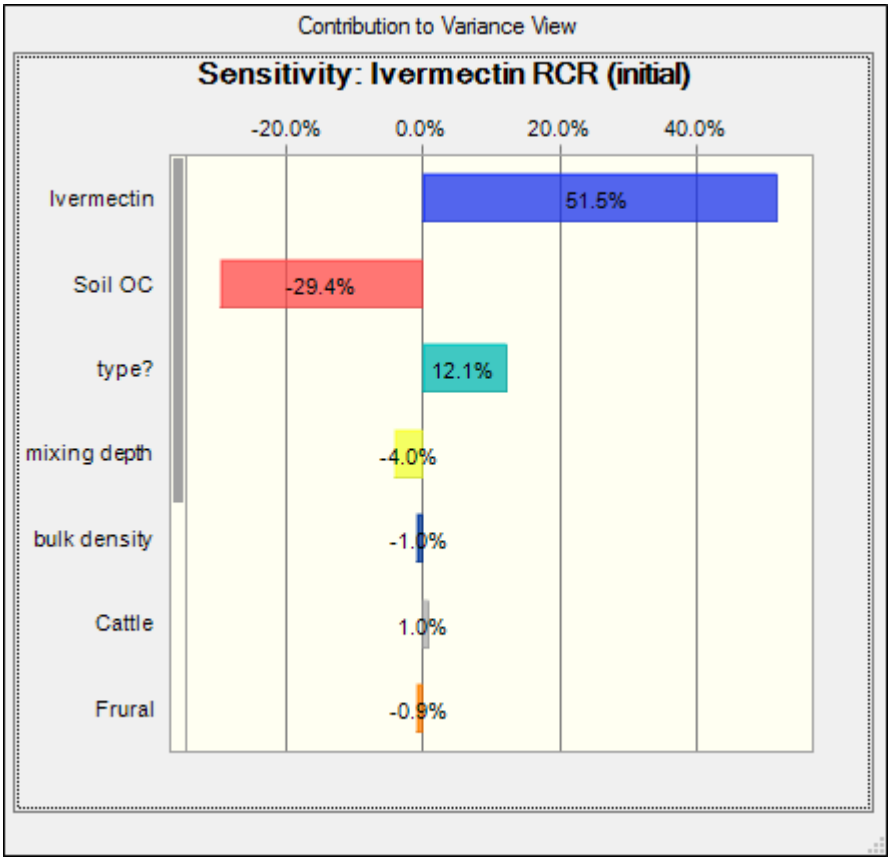


Figure 3.17 Contribution to uncertainty in risk characterisation ratios for ivermectin immediately after application to soils in North Ayrshire

The predicted risk characterisation ratios, both initially (Figure 3.15) and one year after application (Figure 3.16) follow a log-normal distribution pattern. The calculated risk characterisation ratios are high in both cases (median 786 immediately after application and 90 one year after application). The principal source of uncertainty (see Figures 3.17 and 3.18) in both calculations is the concentration of ivermectin in the manure, which should ideally reflect the average concentration over a period of a year. Higher concentrations of ivermectin in the manure result in higher predicted risk characterisation ratios, and are therefore displayed as a positive contribution to the uncertainty in the figures. The next most important factor in the uncertainty for the initial risk is the organic carbon content of the soil, because higher soil organic carbon results in lower availability of the contaminants and a higher organic carbon corrected PNEC is calculated (higher organic carbon concentrations result in lower risks, and the uncertainty is consequently displayed as a negative value). For the situation after 1 year, the half-life of ivermectin in soil is a key uncertainty. Ivermectin degradation in soils is noted as being highly variable[19], and it has been suggested that this may be due to the availability of ivermectin for degradation within the soil, with readily available fractions undergoing relatively rapid degradation, but degradation being limited by desorption from the soil.

[19] http://www.fda.gov/ucm/groups/fdagov-public/@fdagov-av-gen/documents/document/ucm072090.pdf

The concentration of ivermectin in the manure and the organic carbon content of the soil collectively account for over 80% of the uncertainty in the estimation of the initial risks (Figure 3.17). The same factors, along with the soil half life, account for over 85% of the uncertainty in the risk characterisation ratio one year after application (Figure 3.18). The only other factor to make a significant contribution to the uncertainty is the type of farming practice, i.e. whether the cattle are beef or dairy cattle, because this has potentially important implications for the rate of manure production. Dairy cattle are expected to result in higher risks than beef cattle, although animal husbandry practices and treatment regimes of veterinary medicines may mean that the assumption that the concentration of ivermectin in the manure is the same for both types of farms is inappropriate. Undertaking monitoring of different manure types for veterinary medicines would enable a considerable improvement in the reliability of this assessment.

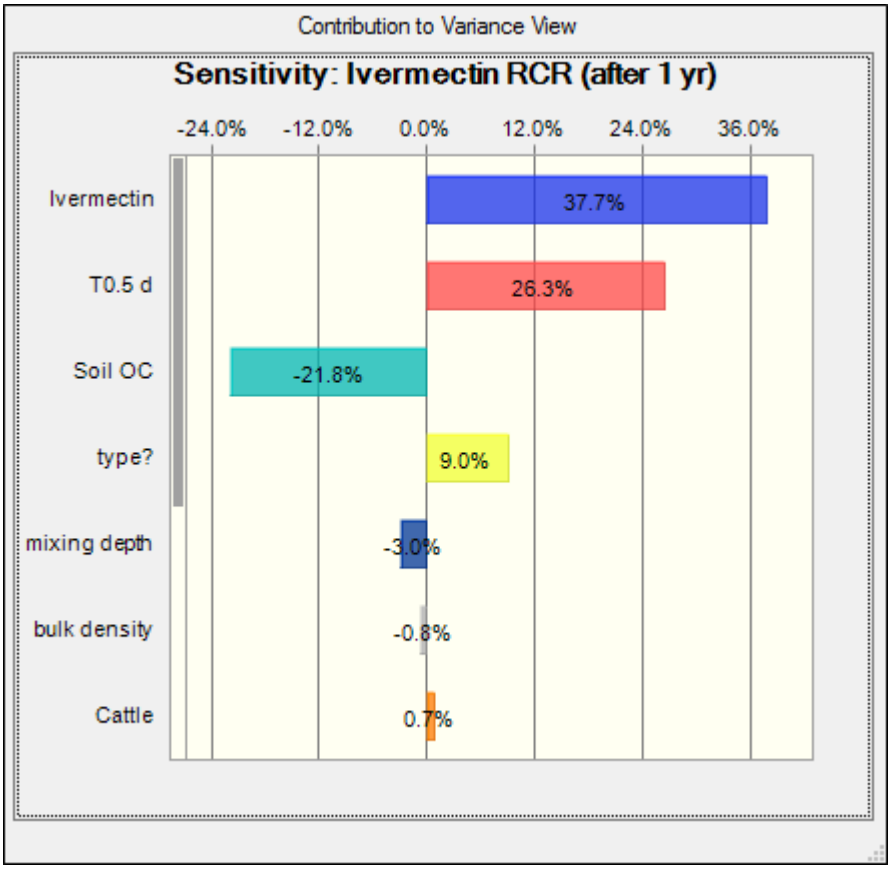


Figure 3.18 Contribution to uncertainty in risk characterisation ratios for ivermectin one year after application to soils in North Ayrshire

The risk characterisation ratios for galaxolide in soil immediately after sewage sludge spreading, and one year following spreading, are shown in Figures 3.19 and 3.20 respectively. The contributions of the various different uncertainties to the overall uncertainty in the predicted risk characterisation ratios both immediately after application, and one year after application are shown in Figures 3.21 and 3.22, respectively.

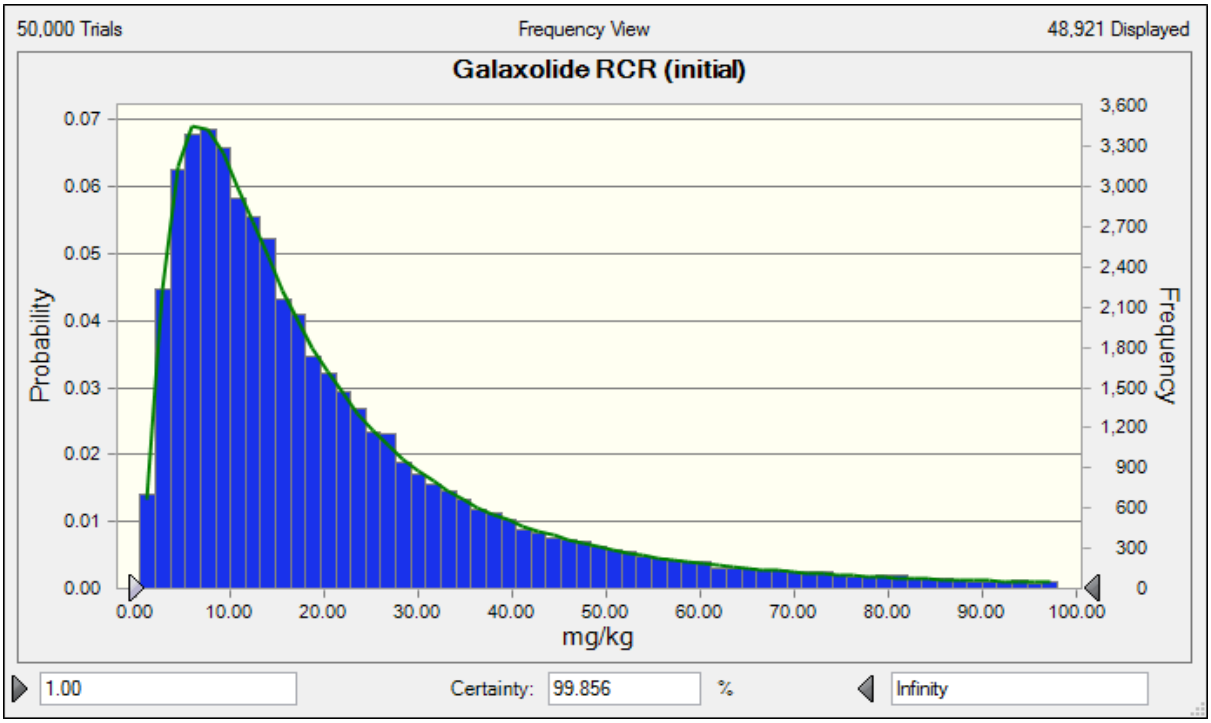


Figure 3.19 Risk characterisation ratios for galaxolide immediately after application to soils in Falkirk

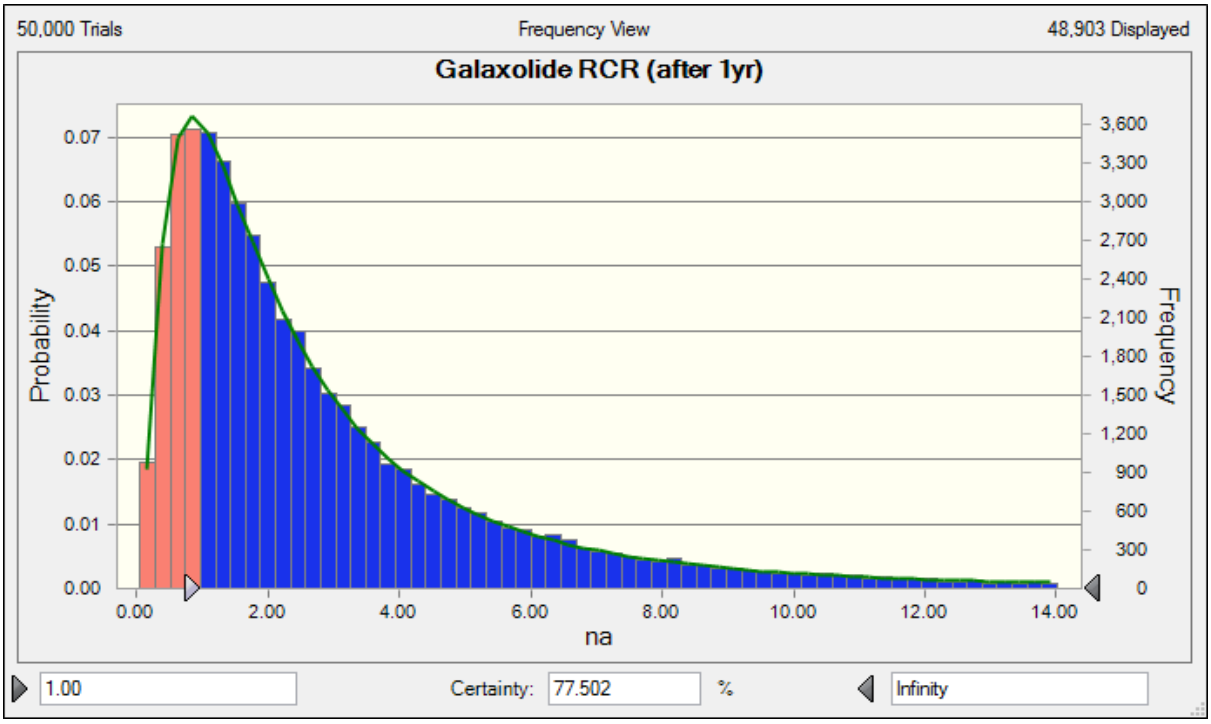


Figure 3.20 Risk characterisation ratios for galaxolide one year after application to soils in Falkirk

The predicted risk characterisation ratios calculated for galaxolide both immediately after application and one year after application follow a log-normal distribution. The risk characterisation ratios are almost entirely above one (>99% probability, median 15)

immediately after application, but are reduced appreciably after one year in the soil. The likelihood of failure (RCR > 1) is still relatively high after one year (77.5% probability, median 2). As was observed for ivermectin, the concentration of galaxolide in sewage sludge is the principal uncertainty in this analysis, and the concentration of organic carbon in the soil is also an important factor in the predicted risk. The degradation half-life of galaxolide in soil is rather less variable than that of ivermectin, which results in this parameter being a less important source of uncertainty for galaxolide.

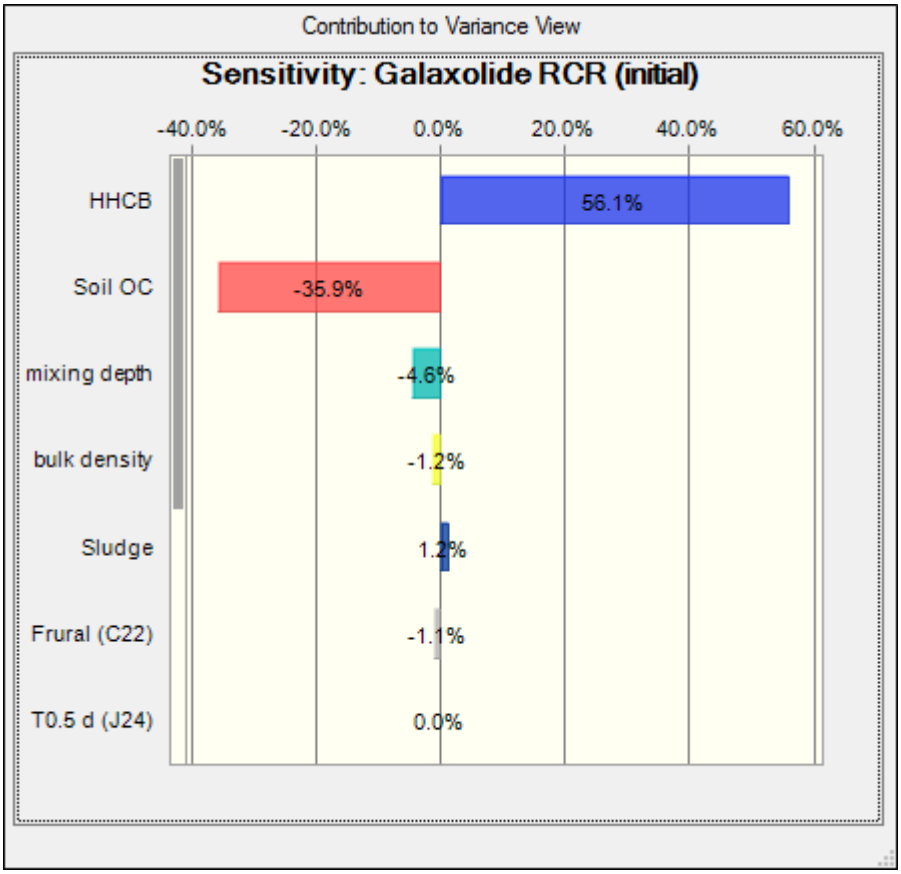


Figure 3.21 Contribution to uncertainty in risk characterisation ratios for galaxolide immediately after application to soils in Falkirk

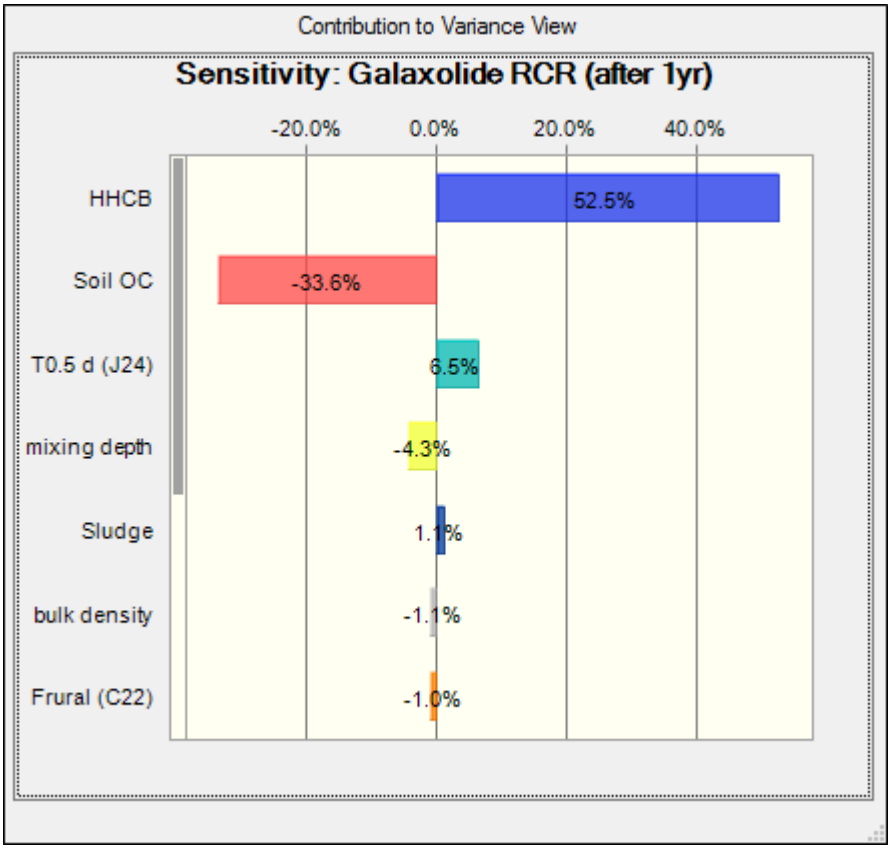


Figure 3.21 Contribution to uncertainty in risk characterisation ratios for galaxolide one year after application to soils in Falkirk

The probabilistic analysis of the key sources of uncertainty in the risk assessments performed suggest that the most important parameters for refinement are the concentrations of the substances of interest in the waste materials applied to land, and the organic carbon content of the soil to which it is applied. Degradation rates may also be important in some cases, especially where repeated applications of material are made to the same area of land over an extended period of time.

4 DATA INTERPRETATION

In this section of the report we also provide a brief review on the analytical challenges faced when attempting to determine organic chemicals in complex, often heterogeneous, solid matrices. This section addresses objective 4 of the project and therefore will also a give summary of responses from analytical chemistry service providers in the UK to a questionnaire in relation to their capabilities in determining the priority chemicals identified in Section 2 and 3 for a range of organic materials. A confidential subsection of this survey including costs has been provided to the SEPA project team.

The first part of this section highlights some of the challenges faced by commercial laboratories in determining the identified chemicals in organic material through a brief review of the open literature and regulatory surveys.

4.1 Analytical Challenges

A lack of standardised extraction procedures have been highlighted by Kester et al. (2005) and EC (2004) as they key analytical challenge associated with the analysis of organic waste material. Current analytical procedures for the extraction of organic samples in the laboratory do not specify which clean-up techniques and extraction methods need to be performed. This is important, as standard methods require modification to distinguish organic compounds of concern from benign compounds. A similar finding is highlighted in EC (2004) which identifies the lack of a harmonised extraction method as a major issue in the analysis of organic wastes. The lack of a clearly defined procedure and the potential for inexperienced laboratory staff dealing with complex matrices can have the effect of critical analytical decisions being poorly made, which would affect quantification levels, therefore it is recommended that without significantly experienced laboratory staff, organic waste results should be treated with suspicion (Kester et al. 2005).

4.2 Laboratory Survey

Based on the information available on the UKAS website[20], and with correspondence with the SEPA project team, ten laboratories were contacted and requested to complete a questionnaire regarding their capabilities to perform analysis in organic wastes of the chemicals identified in Section 2. The full laboratory questionnaire has been provided in Appendix 1, and the laboratories contacted and their responses are detailed here in Table 4.1.

Table 4.1 Laboratories contacted regarding their capabilities to perform analysis of selected chemicals in organic wastes

Laboratory	Returned Questionnaire	Comments
Lab 1	No	A questionnaire was supposed to be returned however, despite following up enquiry no questionnaire was received
Lab 2	No	No returned response received

[20] http://www.ukas.com/

Laboratory	Returned Questionnaire	Comments
Lab 3	No	Currently have no accredited methods for the media of interest
Lab 4	No	No returned response received
Lab 5	Yes	Results of returned questionnaire in Table 4.2
Lab 6	Yes	Results of returned questionnaire in Table 4.2
Lab 7	No	Only perform analysis on water samples
Lab 8	No	Cannot perform analysis requested
Lab 9	No	No returned response received
Lab 10	No	Cannot perform analysis requested

As can be seen in Table 4.1, only 2 completed questionnaires were received by wca. The results of these are summarised in Table 4.2. The other laboratories contacted where unable to perform the analysis and therefore contacted wca directly without completing the questionnaire or did not complete questionnaire despite several emails and phone call (Table 4.1)

From Table 4.2, it can be seen that neither the Lab 6 or Lab 5 perform analysis for all the prioritised compounds in organic wastes. Typical method LoDs are in the µg kg^{-1} range, with some analysis, for example Benzo-a-pyrene at Lab 5, having LoDs in the ng kg^{-1} range. Turn around for samples are typically 7 to 10 days, though for dioxin analysis this can increase to 14 days.

Table 4.2 Results of the returned questionnaires from Lab 5 and Lab 6

Determinand	Laboratory	Brief method overview	Analytical performance, all of dry weight basis.				Details of accreditation or validation (information on requirements to achieve validation if suitable)	Sample volume required (units)	Turn-around time
			Method LOD (units)	Method precision (%)	Method bias (%)	Concentration range of method (with and without dilution of extract)			
Tetracycline	Lab 6	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
	Lab 5	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
Phenol	Lab 6	Solvent Extraction HPLC	1000µg kg^{-1}	Better than 15% RSD	Better than 30% Bias	0-10mg kg^{-1} range may be extended with dilution	UKAS – validated to WRC NS30	Minimum 50 grams per sample	10 Working Days
	Lab 5	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
Nonylphenol	Lab 6	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
	Lab 5	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
Linear alkylbenzene sulphonates	Lab 6	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
	Lab 5	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
Ivermectin	Lab 6	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
	Lab 5	LC-MS/MS	10µg kg^{-1}	Matrix dependent	Matrix dependent	N.R.	N.R.	100gms	7 – 10 days
Tylosin	Lab 6	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
	Lab 5	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
Triclosan	Lab 6	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
	Lab 5	LC-MS/MS	10µg kg^{-1}	Matrix dependent	Matrix dependent	N.R.	N.R.	100gms	7 – 10 days

Determinand	Laboratory	Brief method overview	Analytical performance, all of dry weight basis.				Details of accreditation or validation (information on requirements to achieve validation if suitable)	Sample volume required (units)	Turn-around time
			Method LOD (units)	Method precision (%)	Method bias (%)	Concentration range of method (with and without dilution of extract)			
Benzo-a-pyrene	Lab 6	Solvent Extraction/ GCMS	20µg kg^{-1}	Better than 15% RSD	Better than 30% Bias	0-500µg/kg for PAHs, Can be extended with dilution	UKAS – validated to WRC NS30	Minimum 50 grams per sample	10 working days
	Lab 5	HR-GCMS	10ng kg^{-1}	Matrix dependent	Matrix dependent	N.R.	N.R.	100gms	7 – 10 days
Dioxins and dioxin like-PCBs	Lab 6	Accelerated Solvent Extraction/ HR GCMS	0.3 to 4ng kg^{-1}	Better than 15% RSD	Better than 30% Bias	0 – 2µg kg^{-1} which may be extended by dilution	Unaccredited – validated to WRC NS30	Minimum 50 grams per sample	14 working days
	Lab 5	HR-GCMS	10ng l^{-1}	Matrix dependent	Matrix dependent	N.R.	UKAS	100gms	7 – 10 days
HHCB (Galaxolide)	Lab 6	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
	Lab 5	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
Doramectin	Lab 6	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
	Lab 5	LCMS/MS	10µg kg^{-1}	Matrix dependent	Matrix dependent	N.R.	N.R.	100gms	7 – 10 days
Polybrominated diphenyl ethers (ΣPDBEs(47,99,209))	Lab 6	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
	Lab 5	HR-GCMS	10µg kg^{-1}	Matrix dependent	Matrix dependent	N.R.	N.R.	100gms	7 – 10 days

5 SUMMARY AND RECOMMENDATIONS

In this report we have followed classic risk assessment paradigms in order to assess the potential human and environmental risks from organic chemicals in organic materials going to land in Scotland. Animal manures represent the greatest volume of organic material being applied to land, but other sources of organic chemicals from organic materials to land include sewage sludges, composts and numerous exempt materials that include off-specification composts, digestates, food and garden waste.

A literature search of open and grey sources was used to identify commonly found or priority chemicals in organic materials from around the world. These sources were reviewed and an Excel-based spreadsheet constructed listing the chemicals, the materials they are found in, their physico-chemical properties (likely to govern fate and behaviour) and their concentrations in those materials. Several key review and regulatory monitoring papers were very useful and a relevancy hierarchy was established to ensure that only data from organic sources likely to be encountered in Scotland were included.

In addition to measured data in the organic materials, PNECs and HCVs were also collated for the key chemicals. For many organic materials that are waste exempt from waste management licensing under paragraphs 7, 9, 12, 19, 45, and 47, little organic chemical data are available. We have shown in this report that this remains probably the largest uncertainty in assessing potential risks. Another key uncertainty is the organic carbon content of the soil, because of its effect on the bioavailability of organic chemicals, and is best considered as part of a site specific assessment.

Risk screening has been performed for potential environmental risks using an exposure and an effects based approach. This screening is limited to those substances for which there are data. The exercise screens chemicals in, but does not screen chemicals out (i.e. just because a chemical is not selected does not mean it might not present a potential risk, if no data are available). A crude human health related screening was also undertaken. These screening approaches were used to provide an evidence based method to reduce the chemicals to a manageable number for which to perform more in-depth assessment. The chemicals initially selected were; tetracycline, ivermectin, triclosan, HHCB, BaP, dioxins and dioxin-like PCBs and PDBEs.

Spatial risk modelling was performed with these chemicals from a range of organic material applied to land. The area available to receive land-spread materials was calculated for each Local Area Authority in Scotland. A range of assumptions were used to calculate animal manure loadings. Maps have been presented showing the risk characterisations ratios for chemicals in materials applied to soils and the contributions from waste type. From these maps the greatest potential risks appear to be from the veterinary medicines, with localised risks identified for the other chemicals, especially galaxolide.

A probabilistic approach was then taken to assess the sensitivity of the risk calculations for the veterinary medicines and the fragrance to the range assumptions. Included in these calculations was an account for degradation and also the soil organic carbon content. From

the outputs of the probabilistic approach it was clear that in order to refine the risk assessments the factors of greatest importance are concentration data for the chemical in the organic material, soil organic carbon content, and for ivermectin, the degradation rate following application.

An assessment of the capabilities of commercial laboratories to perform analysis of organic materials for the prioritised chemicals was undertaken. The results from this exercise demonstrated the paucity of commercial laboratories with the skills or experience to measure the concentrations of these types of determinands, with only two of the laboratories filing a positive return and of these no one lab could perform all the required determinands (and for many no UKAS accreditation was available).

The key recommendations from this report are that:

- Widely used veterinary medicines, such as antiparasitic treatments, are likely to be of greatest concern in cattle due to the greater quantities of active ingredient required for treatment.

- Where particular exempt industrial waste materials are known to be spread in large quantities, particularly within a limited area, consideration should be given as to whether or not those waste materials are likely to contain any organic substances of potential concern. Data are very limited for many of these materials.

- The concentrations of veterinary medicines in the manure of different animals should be combined with data on the relative importance of the different animals in terms of the manures which are spread to land. It may be appropriate to consider targeted assessments for specific animals in some areas if there are high concentrations of particular farming activities. Monitoring the concentrations of these chemicals in these organic materials, and the carbon contents of the soils to which they are being applied, would greatly reduce uncertainty in the assessment of environmental risks.

- However, this monitoring could be focus upon delivering the greatest reduction in uncertainties for the least costs. Focusing upon more readily analysed substances, where the perceived level of risk is comparable, would provide a greater clarity of potential risks for lower cost.

- Monitoring of veterinary medicines in a range of different livestock manure types would enable a valuable refinement in the assessment, especially if the levels of the various veterinary medicines differ for different types of farming practices, e.g. dairy and beef cattle, or intensively and conventionally farmed pigs.

- A more detailed analysis of the different types of waste exempt from waste management licensing under paragraphs 7, 9, 12, 19, 45, and 47 which are applied to land should be undertaken, with a particular focus on those which are expected to contain significant levels of organic contaminants.

- Quantitative risk assessment for human health based on dietary exposure to dioxins in food produced on waste amended land indicated that there was no risk to health

even when using worst case assumptions, such as the maximum recorded concentration of dioxins in MBT CLO, a high rate of application of waste to land and the assumption that a full range of food groups is produced from the waste amended land.

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ANNEX 1: LABORATORY QUESTIONNAIRE

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today's consultants for tomorrow's challenges

LABORATORY SPECIFICATION

QUESTIONNAIRE ON THE DETERMINATION OF ORGANIC CHEMICALS IN ORGANIC WASTES FOR REGULATORY USERS

November 2013

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1 INTRODUCTION

The analytical challenges associated with the determination of organic chemical concentrations in organic waste materials are considerably greater than those for waters, soils and sediments[21]. Reviews detail some of the methods that can be used, but it is clear that laboratory experience of organic materials (such as sewage sludge, composts, CLO, animal manures) and in-depth knowledge of the behaviour of the determinand in analytical systems are very important to accurately and precisely quantify many organic chemicals.

Regulatory organisations are becoming increasing concerned about organic chemicals in organic materials going to land. However, data on the concentrations of chemicals in these materials are often lacking. This questionnaire has been developed to establish which commercial laboratories have the capability and expertise to undertake analysis of a priority list of chemicals identified through a generic screening assessment. SEPA have commissioned this work by wca and are keen to assess capabilities in this area in order to support evidence-based management of organic materials applied to land. This management is likely to involve undertaking a sampling and assessment programme, for the purpose of this questionnaire we may consider 50 samples would be taken.

The aim of this questionnaire is to set out the requirements of a potential testing programme for organic materials in order to assess the capabilities of commercial laboratories in performing these analyses to a required specification, as detailed in Section 2. Selected laboratories will be asked to return their completed questionnaires by **the 29th November**.

It is important that this questionnaire is completed with reference to your current, routine laboratory performance. The information collated needs to represent the current capability of the laboratory community since if samples of organic materials were distributed for analysis of these selected determinands in the near future no new method development would be possible. Previous, similar exercises undertaken by wca on such capabilities have shown that there can be a significant mismatch between what is promised and what can be reasonably delivered.

The results of the questionnaires will be made anonymous and a summary sent back to you for your information, with an indication of where your performance sits compared to others. All commercial information related to prices will be treated in confidence and will not be shared in the summary document.

1.1 What do you need to do?

Please read the next section and then complete Tables in Appendices A, C and D. Also, provide additional comments where necessary. Any queries please contact Iain Wilson at wca environment (iain.wilson@wca-environment.com).

[21] Kester GB, Brobst RB, Carpenter A, Chaney RL, Rubin AB, Schoof RA, Taylor DS. 2005. J. Environ. Qual. 34:80–90.

2 LABORATORY REQUIREMENTS

The determinands of interest, the required analytical performance and the associated performance requirements for the laboratories that will perform the testing are outlined in this section;

2.1 Analytical Method Performance

Method performance should meet specific requirements including the precision, accuracy (or bias), linearity, concentration range and Limit of Detection (LoD).

The MCERTs guidance[22] suggests precision targets of 15% for PAHs and PCBs. Analytical methods employed should be able to achieve precision targets equal to or better than those specified in these guidance. Suggested limits of detection for selected determinands are provided in Appendix A along with the full list of required determinands. Analytical methods employed should, as a reasonable minimum, be able to achieve these LoDs in all organic materials, unless otherwise detailed. The LoDs have been calculated based on the derived environmental or human health limit value.

Use of any certified reference materials (CRMs) for the determinand should be noted. For replicate organic material analyses, the results must not differ by more than the precision specified for each determinand. Please see Appendix B.

2.2 Accreditation and Validation

Accreditation status must be stated for all determinands and if the accreditation requires sample submission in specific bottle types or if these are supplied, this must be stated. Evidence of laboratory accreditation to ISO 17025, and participation in relevant external Proficiency Testing schemes (where applicable) and statistically derived method performance validation data should be provided, together with a summary of the validation methodology. If validation is not yet complete, information on the remaining analyses to complete the validation and produce the statistically-derived method performance data and the date for provision of the validation data should be given. If non-accredited analyses are included, quality control mechanisms should be stated.

2.3 Sample Volume

As the sample weights required for analysis will depend on the methods employed, information on sample weight required for the full suite of analyses should be specified by the participating laboratories.

2.4 Timescales

[22] Environment Agency. 2012. Performance Standard for Laboratories Undertaking Chemical Testing of Soil. Version 4.

Typical laboratory analysis times for the parameters should be detailed, including any use of subcontractors. This should include the time taken from sample receipt, preparation analysis and reporting. The maximum and minimum number of samples in an accepted batch should be provided.

2.5 Costs

Costs should be provided using the table in Appendix C and should be based on a per sample basis and linked to sample turn-around time (assume a total of 50 samples per batch). Please note that it is expected that the 'per sample' charge will cover the cost of analysing the required AQC samples (e.g. any CRMs and blanks) in each batch as these will not count as 'samples' or be paid for separately.

These data will be treated in confidence and only used in the final, restricted, report to SEPA and *will not* be given in the Summary Report circulated to all participants.

APPENDIX A

FULL LIST OF DETERMINANDS AND LIMITS OF DETECTION (LOD) FOR SOME SELECTED ANALYTES

The analytical methods employed in the study should be able to achieve, at a minimum, the LODs presented in Table below.

Table A.1; Minimum required LoDs for some of the determinads of interest

Determinand	CAS No.	LOD (mg kg^{-1}) (dry weight basis)
Tetracycline	60-54-8	0.081
Phenol	108-95-2	0.001
Nonylphenol	25154-52-3	0.09
Linear alkylbenzene sulphonates	Group	1.38
Ivermectin	70288-86-7	0.0002
Tylosin	1401-69-0	0.0005
Triclosan	3380-34-5	
Benzo-a-pyrene	50-32-8	0.0001
Dioxins and dioxin like-PCBs	Group	0.010
HHCB (Galaxolide)	1222-05-5	0.096
Doramectin	117704-25-3	0.0048
Polybrominated diphenyl ethers (ΣPDBEs(47,99,209))	Group	>0.0002

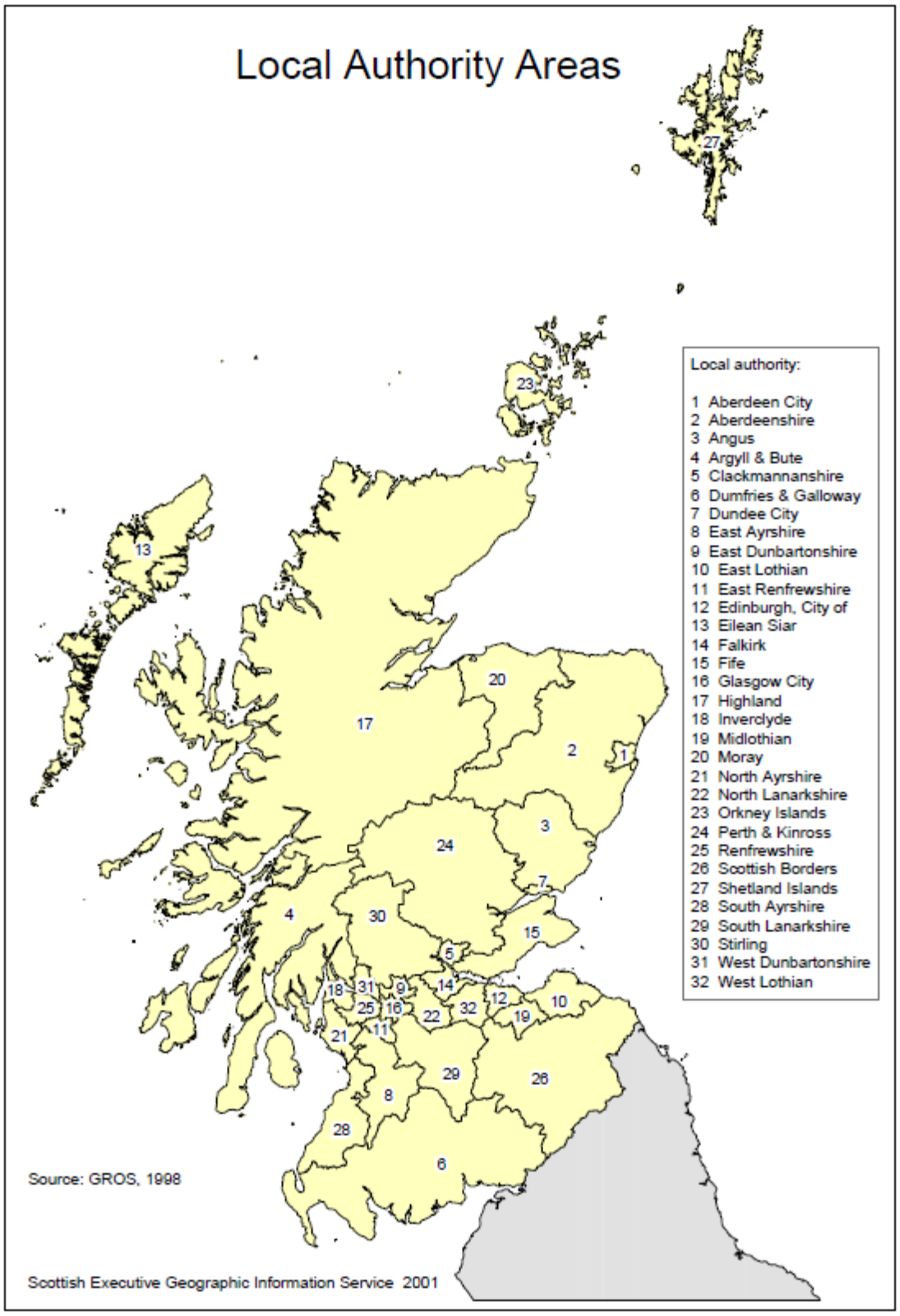
APPENDIX B – LABORATORY REQUIREMENTS INFORMATION TABLE – CAPABILITIES

Please provide information on your capabilities with respect to each requirement using the table below as a template.

Table B.1; Laboratory requirements information table

Determinand	Brief method overview	Analytical performance, all of dry weight basis.				Details of accreditation or validation (information on requirements to achieve validation if suitable)	Sample volume required (units)	Turn-around time
		Method LOD (units)	Method precision (%)	Method bias (%)	Concentration range of method (with and without dilution of extract)			
Tetracycline								
Phenol								
Nonylphenol								
Linear alkylbenzene sulphonates								
Ivermectin								
Tylosin								
Triclosan								
Benzo-a-pyrene								
Dioxins and dioxin like-PCBs								
HHCB (Galaxolide)								
Doramectin								
Polybrominated diphenyl ethers (ΣPDBEs(47,99,209))								

APPENDIX C – MAP OF SCOTTISH LOCAL AUTHORITY AREAS



http://www.scotland.gov.uk/Resource/Doc/933/0009386.pd