Endosulfan, pentachlorobenzene and short-chain chlorinated paraffins in background soils from Western Europe

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Abstract

Soils are major reservoirs for many persistent organic pollutants (POPs). In this study, "newly" regulated POPs i.e. Σendosulfans (α-endosulfan, β-endosulfan, endosulfan sulfate), pentachlorobenzene (PeCB), and short-chain chlorinated paraffins (SCCPs) were determined in background samples from woodland (WL) and grassland (GL) surface soil, collected along an existing latitudinal UK-Norway transect. Statistical analysis, complemented with plots showing the predicted equilibrium distribution and mobility potential, was then explored to discuss factors controlling their spatial distribution. SCCPs were detected with the highest average concentrations (24~~35~~±72~~100~~ ng/g soil organic matter (SOM)), followed by Σendosulfans (3~~2~~±4~~3~~ ng/g SOM) and PeCB (~~1~~0.6±0.5~~4~~ ng/g SOM). PeCB and Σendosulfans share many similarities in their distribution in these background soils as well as with several legacy POPs. A steep decline in concentrations of SCCPs with increasing latitude indicates that their occurrence is dictated by proximity to source regions, while concentrations of Σendosulfans peaked in regions experiencing elevated precipitation rates.

Capsule

Processes affecting the occurrence and latitudinal distribution of some "newly" regulated POPs in background soils.

Keywords

Short-chain chlorinated paraffins, Endosulfan, Pentachlorobenzene,

Background soils, Soil organic matter

1   Introduction

Soils have a large affinity and capacity for sorbing and storing persistent organic pollutants (POPs) (Meijer et al., 2003). Yet, the storage capacities of soils are expected and observed to vary significantly across the globe, reflecting differences in e.g. proximity to global source regions of POPs, soil organic matter content, and climatic conditions (Meijer et al., 2003). Soils from boreal regions are of particular interest, due to the low temperatures, high organic matter content, and slow decomposition associated with this type of environment (Moeckel et al., 2008). Hence, soils from boreal regions are expected to have elevated storage capacities for POPs (Dalla Valle et al., 2005).

Soils located remote from potential sources such as e.g. industrial or populated regions and agricultural areas are defined as background soils (Meijer et al., 2003). The POP contamination of background soils is mainly due to atmospheric deposition. Background soils may therefore be utilized to study potential pollution gradients as mediated by atmospheric transport, e.g. from potential source regions towards remote areas. A latitudinal transect of background soil sites, extending from southern parts of the UK towards northern Norway (UK-Norway transect), was established in 1998 (Meijer et al., 2002). Past studies from the UK-Norway transect have reported data on the occurrence and distribution of legacy POPs such as polychlorinated biphenyls (PCBs) (Meijer et al., 2002; Schuster et al., 2011), polybrominated diphenyl ethers (PBDEs) (Hassanin et al., 2004), polycyclic aromatic hydrocarbons (PAHs) (Nam et al., 2008b), polychlorinated dibenzodioxins and dibenzofurans (PCDDs/Fs) (Hassanin et al., 2005) and selected organochlorine pesticides (Schuster et al., 2011). While the UK-Norway transect has been considered a suitable "model environment" for empirical evaluation of long-range atmospheric transport (LRAT) behaviour of legacy POPs, studies of "new" (i.e. recently regulated) POPs have still been lacking. The overall goal of the study is to obtain a quantitative

58　and mechanistic understanding of the occurrence, fate, and distribution in background soils

59　from North-western Europe of the following three substances/substance groups, collectively

60　referred to as "new" POPs in this study.

61

62　*(i)*　Endosulfan is an organochlorine pesticide, which is banned in many parts of the world.

63　　　Technical mixtures of endosulfan contain two isomers, α- and β-endosulfan (α/β) in a

64　　　7/3 or 2/1 ratio, depending on the origin of the technical mixture (Weber et al., 2010).

65　　　Technical endosulfan was listed under the Stockholm Convention on POPs (Annex A) in

66　　　2011 (UNEP, 2011).

67　*(ii)*　Pentachlorobenzene (PeCB) has been used in production of the pesticide quintozene

68　　　(pentachloronitrobenzene) and in a variety of chlorobenzene mixtures in order to

69　　　reduce the viscosity of dielectric fluids. Current sources of PeCB to the environment

70　　　include various combustion and industrial processes, as well as degradation of other

71　　　chemicals (Bailey et al., 2009). PeCB was listed in Annex A and C under the Stockholm

72　　　Convention in 2009 (UNEP, 2009), in addition to being adopted under the 1998 Aarhus

73　　　protocol in 2009 (UNECE, 2010).

74　*(iii)*　Short-chain chlorinated paraffins (SCCPs) are a complex mixture of polychlorinated *n*-

75　　　alkanes. The alkane chain length can reach up to 13 carbons with chlorine content

76　　　ranging between 30-70% (Houde et al., 2008). SCCPs have the general chemical formula

77　　　$C_xCl_yH_{2x+2-y}$ where x is the number of carbon atoms (x=10-13) and y is the number of

78　　　chlorine atoms (y=1-13) (Muir et al., 2000). SCCPs have been utilized in e.g. metal-cutting

79　　　fluids, sealants, paints, lubricants, flame-retardants, and as softeners in different

80　　　materials (UNECE ad hoc expert group on POPs, 2003; van der Gon et al., 2007). They

81　　　have a potential to be released into the environment through production, storage,

82　　　leaching, and/or volatilization (Muir et al., 2000). SCCPs have been adopted under the

83　　　1998 Aarhus protocol (UNECE, 2010) and are being evaluated by the Persistent Organic

84　　　Pollutants Review Committee (POPRC) under the Stockholm Convention on POPs (UNEP,

85　　　2012).

86　There are few studies which have reported levels and distribution of these new POPs in

87　background soils. However, endosulfans have previously been studied in forest soils in Canada

88　and UK (Wong et al., 2009) and Tajikistan (Zhao et al., 2013), PeCB has been measured in

89   Estonian (Roots et al., 2010) and Antarctic soils (Borghini et al., 2005) while SCCPs have been

90   reported in background soils from China (Wang et al., 2013).

91   **2   Materials and methods**

92   **2.1   Sampling**

93   Background surface soil samples were collected in 2008 (Schuster et al., 2011), along an

94   existing transect of 39 sites (Meijer et al., 2002). This transect includes a number of United

95   Kingdom (UK) sites (n=16) and Norwegian sites (n=23), covering remote/rural areas from

96   50.58-70.47° N and -6.20-27.95° E. Site descriptions are provided in Table A1 while a map is

97   provided in Figure A1 in the Supplementary Data (SD). The soil sampling strategy together with

98   information on soil characteristics has been presented earlier (Schuster et al., 2011), and only

99   a brief summary is given here. The soil samples were collected to represent two types of

100   remote soils, i.e. grassland soils (GL, n=25) and woodland (coniferous/deciduous) soils (WL,

101   n=34). 59 surface soil samples in total were sampled and analysed. The samples were collected

102   with a stainless steel hand-held corer and the targeted sampling depth was the upper layer

103   (0-5 cm). Ten cores were taken to cover an area over several square meters and pooled to

104   obtain a composite sample from each site (Meijer et al., 2002). The lumped samples were

105   placed in zip-locked bags and stored in a freezer at ~-18 °C until further sample preparation.

106

107   **2.2   Sample preparation, clean-up, and analysis**

108   In the following section, a short overview of the sample treatment is given. More detailed

109   information of the sample preparation, including drying, sieving, extraction, clean-up and

110   analysis of the soil samples, is available in the SD (Sect A2.1-A2.3).

111   Wet soil samples were placed on aluminium foil and dried in an oven at low temperature (~27

112   °C), to minimize the potential for volatilization of target compounds. The time required to

113   obtain complete dryness was approximately two weeks. Diatomaceous earth (DE) was

114   prepared along with the soil samples, in order to address possible laboratory contamination

115   from drying and clean-up procedures. Dried soil samples were afterwards sieved with a pre-

116   cleaned sieve and stored cold in clean, brown glass bottles, covered with aluminium foil and

117   a polypropylene (PP)-lid until extraction.

118 Extraction of the soil samples was performed by use of a Dionex Accelerated Solvent Extractor

119 (ASE-200, 1995) unit (California, USA). An ASE cell was packed with soil samples that had been

120 pre-mixed with DE for better extraction efficiency (see Figure A2). In addition, a mixture of

121 internal standard was added. The extraction was carried out with acetone/*n*-hexane 1/1

122 (w/w). The content of soil organic matter (SOM) was determined by loss on ignition (LOI) at

123 550 °C (A2.6).

124 The soil extracts were divided into two aliquots prior to the clean-up procedures (A2.2.2), i.e.

125 an endosulfan fraction (α-endosulfan, β-endosulfan and endosulfan sulfate), referred

126 collectively to as Σendosulfans, and an acid stable fraction (PeCB, SCCPs). The aliquot for the

127 determination of Σendosulfans was cleaned using a silica column only, while the aliquot for

128 the determination of the acid stable compounds was treated with sulphuric acid followed by

129 a fractionation with a silica column (A2.2.2). Subsequently, both aliquots were reduced to ~50

130 µl by nitrogen and recovery standards were added (see A2.3). There were some problems with

131 sedimentation in the endosulfan extracts, and it was necessary to centrifuge the samples (see

132 A2.2.2) prior to instrumental analysis. ΣEndosulfans and SCCPs were determined with high

133 resolution gas chromatography coupled to mass spectrometry in an electron capture negative

134 ion mode (GC/HRMS(ECNI)), while PeCB was determined using gas chromatography coupled

135 to high resolution mass spectrometry in an electron impact (EI) mode (GC/HRMS(EI)) (see

136 Table A2). More information concerning the general method validation (QA/QC) is given in SD

137 (A2.4 and A2.5).

138

2.3 Statistical analysis

139

140 Statistical analysis was performed with Microsoft Office Excel 2007 (Albuquerque, New

141 Mexico, USA). Pearson correlation coefficients (r) were calculated to evaluate any linear

142 relationships between the included variables, while the significance (p) was estimated by use

143 of a Student`s t-distribution (see A2.8). A correlation with a $p < 0.05$ was defined as statistically

144 significant. For statistical summaries of overall results, samples with concentrations below

145 method detection limit (MDL) (see A2.5) were assigned a value of ½ MDL. Prior to the

146 correlation analyses, data below MDL and outliers were removed. The dataset was reviewed

147 for possible outliers using a z-score test, and a z-score value ≥3 was determined as an outlier

148 (A2.8.1). Additional parameters explored in the statistical analysis were bulk density (BD),

black carbon (BC), SOM content, and concentrations of HCB, PBDEs and PCBs which were all adapted from Schuster et al. (2011), with the exception of SOM. All data, with the exception of values for latitude and land use, were log transformed prior to the correlation analysis.

2.4 Mapping phase distribution and fate in soils

The distribution of organic compounds within environmental compartments is largely determined by their environmental partitioning behaviour which, in turn, is dictated by their physical-chemical properties (Gouin et al., 2000). Following Wong and Wania (2011), the phase distribution and mobility potential of individual substances in soils can therefore be plotted in chemical partitioning space maps (Figure 1). This simple graphical technique facilitates mechanistic insights into the likely partitioning and fate in soils and is used to complement interpretation of measurement data and results obtained based on the statistical analysis. Physical-chemical properties used to represent the various substances were adopted from the literature. Data for PCBs and PBDEs (Li et al., 2003; Wania and Dugani, 2003), HCB, PeCB, α-, β-endosulfan (Shen et al., 2005), endosulfan sulfate (U.S. EPA, 2011) and SCCPs (European Chemicals Bureau, 2008; Gawor and Wania, 2013)). The SCCPs are represented by a 38 formula groups, each representing the average properties of all isomers within each group (Krogseth et al., 2013), as well as the average property derived for SCCPs in the European Union (EU) Risk Assessment Report (RAR) (European Chemicals Bureau, 2008). For details, see SD (sect. A2.7). However, we caution that uncertainties remain with regards to the physical-chemical properties for SCCPs and refer to Gluege et al., (2013) for a detailed analysis and discussion.

3 Results and discussion

3.1 Overall results

Table 1 presents a summary of overall results for Σendosulfans and its individual constituents as well as for PeCB and SCCPs, expressed as ng/g SOM. Table A4 shows the same results, but expressed on a ng/g dw basis, while Table A5 presents concentrations for individual compounds and sampling sites, expressed as ng/g dw and ng/g SOM. A few results were considered invalid and excluded from further analysis, either because of matrix related disturbances (Σendosulfans; n=2, SCCPs and PeCB; n=1) or a low recovery of less than 10% (PeCB; n=5) (see also A2.4). Due to the complexity of SCCP mixture, a complete separation of

the individual congeners was not achieved (Sverko et al., 2012; Tomy et al., 1997), consequently introducing higher uncertainty into the quantified results of this compound group. The results for SCCPs should therefore be interpreted with caution. Concentrations were often below MDL for several of the studied compounds (see A2.5). Following removal of invalid data and data below MDL, one or more endosulfan constituents were detected in 56 out of the 57 samples considered valid (Table A5).

Within the group of Σendosulfans, endosulfan sulfate was most frequently detected (n=56), followed by β-endosulfan (n=17) and α-endosulfan (n=13) (Table 1). PeCB was detected in 52 samples, while SCCPs were detected in 23 samples. The average concentration of SCCPs analysed (n=58) was by far the highest among the "new" POPs with 24~~35~~ ng/g SOM (SD±~~100~~72 ng/g SOM), ranging from < MDL (0.8~~6~~ ng/g SOM) to 417~~570~~ ng/g SOM. The average concentration of Σendosulfans in all background soil samples (n=57) was 2~~3~~ ng/g SOM (SD±4~~3~~ ng/g SOM), and ranged from < MDL (0.02 ng/g SOM) to 26~~20~~ ng/g SOM. The average concentration of PeCB for all sites studied (n=53) was 0.6~~1~~ ng/g SOM (SD±0.5~~1~~ ng/g SOM), ranging from < MDL (0.03~~8~~ ng/g SOM) to 3~~6~~ ng/g SOM.

For comparison, Table 1 additionally includes previously published data for some legacy POPs (PCBs, PBDEs and HCB) collected during the same sampling campaign (Schuster et al., 2011). Table A4 additionally includes concentration ranges for endosulfans, PeCB and SCCPs from other localities around the world. While a direct comparison is somewhat difficult because of differences in methodologies, it is encouraging to note that the concentration ranges reported in the literature are generally similar to the levels measured in this study (Table A4). The average concentrations of SCCPs in all soil samples were highest among all compounds listed in Table 1, followed by Σ_{31}PCBs (6±5 ng/g SOM). This pattern was consistent also for each sub-set of samples listed in Table 1 (UK, Norway, GL, and WL). ΣEndosulfans came out third for all soils combined (32~~43~~ ng/g SOM) including the Norwegian, UK and WL sub-sets. ~~For all soils combined~~Concentration of~~,~~ HCB (1±1 ng/g SOM) ~~was~~ were approximately twice that of~~more or less at the same level as~~ PeCB (0.6~~1~~±0.5~~1~~ ng/g SOM) ~~which in turn exceeded that of~~and Σ_5PBDEs (0.6±0.8 ng/g SOM) for all soils combined. The same pattern was evident for Norwegian together with ~~and~~ WL and GL soils, but not for UK ~~and GL~~ soils. Here PeCB was found at the same level as~~exceeded both~~ HCB and Σ_5PBDEs ~~in UK and GL soils~~ (Table 1).

209   Table 1:

3.2 Correlation analysis

3.2.1 Removal of outliers

Outliers were removed prior to the correlation analysis. Results for PeCB (Birkenes, WL, Norway), Σendosulfans (endosulfan sulfate, β-endosulfan) and Σ_{31}PCBs (Onsøy, WL, Norway), SCCPs (Tamokdalen, GL, Norway) and Σ_5PBDEs (Okehampton, WL, UK) were consequently excluded (A2.8.1). Correlation analysis was then performed on the full remaining dataset (Table 2), as well as individually for UK, Norway, GL, and WL soils (Tables A6-A9).

3.2.2 Correlations between compound groups

For all soils combined, a highly significant correlation was found between the Σendosulfans and HCB ($r=0.82$, $p<0.001$), Σendosulfans and Σ_{31}PCBs ($r=0.73$, $p<0.001$) as well as between Σendosulfans and PeCB ($r=0.58$, $p<0.001$) (Table 2). These results show that Σendosulfans share some similarities in their distribution and fate in these background soils with other POPs known to be relatively volatile (i.e. log $K_{OA} < \sim10$, see Fig. 1a). The correlation between Σ_5PBDEs (log $K_{OA} > \sim10$) and Σendosulfans was significant, but weaker ($r=0.38$, $p<0.01$).

Significant correlations were also found between PeCB and HCB ($r=0.63$, $p<0.001$) and between PeCB and Σ_{31}PCBs ($r=0.62$, $p<0.001$) for all soils combined (Table 2), which is attributed to similarities in their predicted phase partitioning and distribution in soil (Fig. 1a). PeCB and Σ_5PBDEs displayed a weaker correlation for all soils ($r=0.49$, $p<0.001$) (Table 2), which might be partly explained by a more divergent distribution partitioning behaviour as the Σ_5PBDEs are less volatile (Fig. 1a, b).

SCCPs were not significantly correlated with any other POPs listed in Table 2 nor in any sub-sets (Tables A6-A9) with the notable exceptions of a weak and significant correlation with Σ_5PBDEs for all soils combined ($r=0.27$, $p<0.05$) (Table 2) as well as for GL soils only ($r=0.50$, $p<0.05$) (Table A8). These results indicate that SCCPs are comparatively less prone to LRAT (see also Fig. 2c, f).

235   Figure 1.

236

3.2.3   *Correlation with site variables*

238   It is well established that POPs and SOM are typically correlated in soils (e.g. Seth et al., 1999)

239   which is also observed in this dataset (Table 2). For all GL soils (n=24), the SOM content varied

240   from 11 to 93 % (w/w), while the SOM content ranged from 13 to 98 % within the WL soils

241   (n=34). A confounding factor in the correlation analysis is the strong and significant correlation

242   between SOM and BC for all soils combined (r=0.63, p<0.001) (Table 2). BC is a by-product of

243   incomplete combustion of fossil fuels and biomass (Schmidt and Noack, 2000), and POPs may

244   have the potential to be emitted with BC from an emission source (Nam et al., 2008a). SOM is

245   composed of amorphous organic matter (AOM) and carbonaceous matter such as BC (Nam et

246   al., 2008a). The sorption capacity of carbonaceous materials (BC) is considered to be

247   remarkably higher compared to AOM, and BC is thought to be responsible for a large part of

248   the sorption of organic contaminants in soils (Cornelissen et al., 2005; Lohmann et al., 2005).

249   Consequently, correlations between POPs and SOM should be evaluated with caution as high

250   correlations between POPs and SOM may in part be due to the sorption properties of BC.

251   Another confounding variable is bulk density (BD) which is inversely proportional to SOM;

252   hence SOM rich soil has low BD.

253   Highest correlations between BC and the "new" POPs for all soils combined (Table 2) were

254   seen with PeCB (r=0.57, p<0.001) followed by Σendosulfans (r=0.46, p<0.001). Strong and

255   significant correlation was also seen between SOM and Σendosulfans (r=0.80, p<0.001) albeit

256   weaker for SOM and PeCB (r=0.70, p<0.001). In contrast to Σendosulfans, PeCB is known to

257   be emitted from a variety of industrial sources and combustion processes (Bailey et al., 2009;

258   Doring et al., 1992). As PeCB experienced the strongest correlation with BC among all POPs

259   listed in Table 2, this indicates that PeCB and BC may to some extent be co-emitted from

260   various combustion processes.

261   SCCPs showed no significant correlations (p>0.05) to any of the soil parameters, i.e. BD, BC

262   and SOM, either for all soils combined nor for any sub-sets (Table 2, A6-A9). This indicates that

263   the distribution of SCCPs in soil is probably more influenced by proximity to sources, rather

264   than soil characteristics.

265   Table 2:

266   **3.3   ΣEndosulfans, endosulfan constituents and distribution within the soil subsets**

267   Within the Σendosulfans, endosulfan sulfate was the dominant component and was detected

268   in all samples except one, while the α- and the β- endosulfan isomers were detected in 13 and

269   17 samples, respectively (Table 1, Table A5). Endosulfan sulfate contributed with 97 % to the

270   average concentration of Σendosulfans, while α-and β- endosulfan isomers contributed with

271   ~1.4 % and ~ 1.6 %, respectively.

272   The elevated concentration of endosulfan sulfate, compared to α and β-endosulfan, is because

273   the former is the effective transformation product of the parent endosulfan compounds in

274   soils (Antonious et al., 1998; Walse et al., 2003). The α/β ratio of technical mixtures are

275   reported to be 7/2 or 2/1, depending on the mixture (Weber et al., 2010). For sites where both

276   α- and β-endosulfan were above MDL (n=7), the observed ratio in soils ranged from 0.1 to 0.9.

277   These findings clearly imply a depletion of α-endosulfan in soils, relative to in the technical

278   mixtures. We believe this depletion in part can be explained by Figure 1, which shows that α-

279   endosulfan is more volatile and less prone to atmospheric deposition (Fig. 1a) as well as more

280   prone to evaporate from soils (Fig. 1b) in comparison to β-endosulfan and endosulfan sulfate,

281   which are relatively more prone to erosion and leaching, respectively. These findings are

282   consistent with a study by Rice and co-workers (2002) where α-endosulfan was found to be

283   more volatile than β-endosulfan in soils. Furthermore, while strong and significant

284   correlations are seen between Σendosulfans and endosulfan sulfate (r=0.99, p<0.001) as well

285   as between Σendosulfans and β-endosulfan (r=0.91, p<0.001) in background soils, there is no

286   statistical significance between Σendosulfans and α-endosulfan (r=0.49, p>0.05) which

287   indicates divergent behaviour and fate of the latter isomer (Table 2). However, as α and β-

288   endosulfan were often below or close to MDL, the focus in the following is on Σendosulfans.

289   Results for the Σendosulfan concerning the UK and Norwegian soil revealed essentially the

290   same distribution pattern with respect to the soil parameters, i.e. BC, BD and SOM (Table A6

291   and A7). Several studies have revealed that the forest may act as filter for airborne

292   contaminants by enhancing the rate of deposition (Horstmann and McLachlan, 1998; Wania

293   and McLachlan, 2001). The average endosulfan concentration in WL soil was higher than in GL

294   soil with 34 ng/SOM and 0.74 ng/g SOM, respectively (Table 1). Our data therefore suggest

295   that Σendosulfans are influenced by the forest filter effect, although the partitioning

296   properties (Fig. 1a) for β-endosulfan in particular are slightly outside the forest filter "window"

297   (i.e. log K_{OA} and log K_{AW} around 9-10 and -2 to -3, respectively) as proposed by Wania and

298   McLachlan (2001). A confounding factor, which might help to explain the enrichment of

299   Σendosulfans in WL soils compared to GL soils, is that the forest soils are higher in SOM (Table

300   A1). The capacity of WL soils rich in SOM (average SOM 0.66 g/g dw) to retain Σendosulfans

301   may thus exceed that of GL soils (average SOM 0.44 g/g dw). The strong and significant

302   correlation between Σendosulfans and SOM is displayed in Figure 2g). Here the concentration

303   of Σendosulfans increased with amount of SOM both for GL and WL soil.

304   Figure 2a) and 2d) display the latitudinal distribution of Σendosulfans expressed on SOM and

305   on a dry weight basis, respectively. The concentration of Σendosulfans for both WL and GL soil

306   tends to increase towards 60 °N, followed by a slight decrease at higher latitudes, irrespective

307   of the normalization. The elevated concentrations of Σendosulfans seen at mid-latitudes

308   (~60°N) may in part be caused by an orographic effect, which enhances wet deposition in

309   southern parts of Norway compared to central and northern Norway (Aamot et al., 1996;

310   Becker et al., 2011). The average concentration of Σendosulfans for the Norwegian sites

311   (n=32) was also higher than for the UK sites (n=24), with 3 and ~~2~~ 1 ng/g SOM, respectively

312   (Table 1). An orographic effect on the spatial distribution of Σendosulfan concentrations also

313   seems plausible as Σendosulfans are among the more water-soluble substances in our data

314   set (Fig. 1a). ΣEndosulfans are furthermore positively correlated with latitude in GL soils, albeit

315   with limited significance (r=0.47, p<0.05) (Table A8), yet negatively correlated (and not

316   significant) for the Norwegian sub-set (Table A7). It is interesting to note that α-endosulfan is

317   slightly positively correlated with latitude (r=0.24), whereas β-endosulfan as the more water-

318   soluble substance is slightly negatively correlated (r=-0.11) for all soils combined (Table 2).

319   However, none of these two correlations nor any correlations between average precipitation

320   rates and Σendosulfans, including its constituents, were significant (Tables 2 and A6-A9).

321   Figure 2 (a-i)

322   **3.4   Pentachlorobenzene (PeCB) and distribution within soil subsets**

323   The average concentration of PeCB in UK soils (n=21) was ~~about twice~~somewhat higher than

324   the average concentration for the Norwegian soils (n=31) with 0.8~~2~~ ng/g SOM and 0.5~~1~~ ng/g

325   SOM, respectively (Table 1). The higher concentration of PeCB in UK soils may be due to

326   proximity to past or ongoing source regions (Bailey et al., 2009; Nam et al., 2008a). It is

327   interesting to note that this pattern is different from the one previously reported for HCB,

328   where concentrations in Norwegian soils were found to exceed UK soils by a factor of about

329   two (Table 1) in spite of close similarities in their partitioning behaviour (Fig. 1). Taken together

330   with the strong association noted between PeCB and BC in soils, this provides further support

331   for our hypothesis that PeCB may be co-emitted with BC from combustion processes.

332   Combustion processes are also implicated as major emission sources of PeCB in the literature

333   (Bailey et al., 2009; Tiernan et al., 1983). Studies have furthermore revealed that fly-ash from

334   combustion processes contain PeCB (Liu et al., 2013; Nie et al., 2011). Furthermore, it is

335   interesting to note that the correlation between PeCB and SOM was slightly stronger in

336   Norwegian soils (r=0.80, p<0.001) (Table A7) compared to UK soils (r=0.71, p<0.001) (Table A6)

337   which suggests that SOM may be somehow more important in controlling the occurrence in

338   background soils in more remote regions of this transect.

339   The average concentration of PeCB in GL soils (n=19) was more or less at the same level as WL

340   soils (n=33), i.e. 0.6~~1~~ ng/g SOM (Table 1). This suggests that PeCB is not affected by the forest

341   filter effect. PeCB showed significant correlation with BC for GL soil (r=0.66, p<0.01) (Table

342   A8), but to a lesser extent with BC in WL soil (r=0.41, p<0.05) (Table A9). This may be explained

343   by the lower and weaker correlation between BC and SOM in WL soil (r=0.42, p<0.05) (Table

344   A9) compared to in GL soil (r=0.79, p<0.001) (Table A8). The latter could be due to a higher

345   influence of fresh input of organic matter containing organic carbon in forest soils, versus

346   carbonaceous carbon (BC) (Agarwal and Bucheli, 2011), causing a possible dilution of BC in WL

347   soils.

348   Figure 2b) and 2e) present the latitudinal distribution of PeCB on a SOM and dry weight basis,

349   respectively. Concentrations of PeCB based on ng/g SOM for both WL and GL soil were

350   generally somewhat higher between ~ 50-55°N (>~~1.5~~0.8 ng/g SOM in most samples),

351   compared to higher latitudes (typically less than ~~1.0~~0.5 ng/g SOM) (Fig. 2b). Nonetheless, the

13

352 concentration of PeCB is more or less uniformly distributed with exception ~~from~~ of ~~two~~ one

353 site~~s~~ (Fig. 2b). Figure 2h) shows the concentration of PeCB expressed on dry weight basis

354 versus the content of SOM in all soil samples. The figure clearly illustrates how the

355 concentrations of PeCB for both WL and GL soil increase with increasing amounts of SOM. This

356 increase furthermore appears particularly steep at low SOM content (~30%). These findings

357 are supported by the strong and significant correlation between PeCB and SOM seen for all

358 soils and each sub-set (Tables 2, A6-A9).

359

3.5 Short-chain chlorinated paraffins (SCCPs) and distribution within soil subsets

361 The average concentration of SCCPs for the UK sites was ~~approximately~~ almost twice the

362 average concentration for the Norwegian sites, with ~~50~~ 31 ng/g SOM and ~~22~~ 18 ng/g SOM,

363 respectively (Table 1). The higher concentrations found in UK soil may reflect closer proximity

364 to source regions (van der Gon et al., 2007). This is consistent with findings by Barber et al.,

365 (2005), who noted a significant temporal and spatial variability of SCCPs in UK air.

366 No sign of a forest filter effect could be observed as the average SCCP concentration in GL soils

367 was ~~59~~ 38 ng/g SOM, which is ~~more than~~ close to 3 times higher than the average

368 concentration in WL soils (14~~17~~ ng/g SOM) (Table 1).

369 Figures 2c) and 2f) illustrate the concentration of SCCPs as a function of latitude on an ng/g

370 SOM and on a dry weight basis, respectively. The results show that the higher concentrations

371 are typically seen at lower latitudes and that no sites at higher latitudes (> 62°N) experienced

372 concentrations of SCCPs above MDL. This further suggests that SCCPs have a limited potential

373 for LRAT as levels in soils decline relatively fast with increasing distance from suspected source

374 regions. However, previous studies by Reth et al., (2006) and Tomy et al., (1999) show that

375 SCCPs have been found in biota and sediments in the Arctic. Figure 2i) displays the

376 concentrations of SCCPs on a dry weight basis versus SOM content (%) which further confirms

377 the lack of correlation between SCCPs and SOM (Table 2, A6-A9).

4 Conclusion

379 The occurrence of Σendosulfans, PeCB, and SCCPs in background surface soils from Western

380 Europe has been evaluated by the use of statistical analyses, distribution maps and mobility

381 plots in soil, as well as data on concentrations of legacy POPs (PCBs, HCB and PBDEs). Overall,

382 the statistical analysis and mobility plots showed that Σendosulfans and PeCB share many

383 similarities with selected old POPs in their distribution in background soils. Moreover, PeCB

384 and Σendosulfans were highly correlated with each other, and soil characteristics as SOM and

385 BC were both important in explaining their occurrence and distribution. Concentrations of

386 Σendosulfans peaked in areas experiencing elevated precipitation rates and were strongly

387 dominated by endosulfan sulfate (~97%). PeCB was found with higher concentrations in UK

388 soil compared to Norwegian soil. A particularly strong association between BC and PeCB

389 suggests that emissions of PeCB in part may be attributed to various combustion processes,

390 and therefore retained closer to source regions. SCCPs do not share many similarities with

391 Σendosulfans and PeCB nor most legacy POPs in these background soils, with the exception

392 of PBDEs. A steep decline in SCCP concentrations with increasing latitude indicates a limited

393 potential for long-range atmospheric transport. Further, the lack of correlation between soil

394 concentrations and key soil characteristics, such as SOM, indicate that the occurrence of SCCPs

395 is largely dictated by proximity to source regions. This study also demonstrates that simple

396 chemical distribution and mobility plots (chemical space maps) are useful as complementary

397 tools to assess whether any inferences made from statistical analysis of observations are

398 reasonable from a mechanistic standpoint.

407

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565

566   Figure captions in the order of appearance

567   Figure 1: Chemical partitioning space maps for selected POPs, a) equilibrium phase distribution, b)

568   mobility potential in soils (modified after Wong and Wania (2011). Data for the compound groups is

569   referred to in section 2.4.

570

571   Figure 2 (a-i): Latitudinal distribution for Σendosulfans, PeCB and SCCPs on ng/g SOM (a, b, c) and dry

572   weight basis (d, e, f). Also included is the log concentration (ng g^{-1} dw) versus SOM (g, h, i). Woodland

573   (WL, ▲) and grassland (GL, O) soil samples are plotted separately. One outlier for each compound was

574   omitted (2.8.1).

Figure 1 a), b)

1.5 fitting image

a)

"VOLATILE"   "LIPOPHILIC"

$C_{10}Cl_2$

log K_{AW}

log K_{OA}

- PCBs
- PBDEs
- HCB
- PeCB
- Endosulfans
- SCCPs

alfa
RAR
sulfate
beta
log K_{OW} = 9
$C_{13}Cl_{12}$
log K_{OW} = 3
"WATER-SOLUBLE"

b)

EVAPORATION

$C_{10}Cl_2$

log K_{AW}

log K_{OC}

- PCBs
- PBDEs
- HCB
- PeCB
- Endosulfans
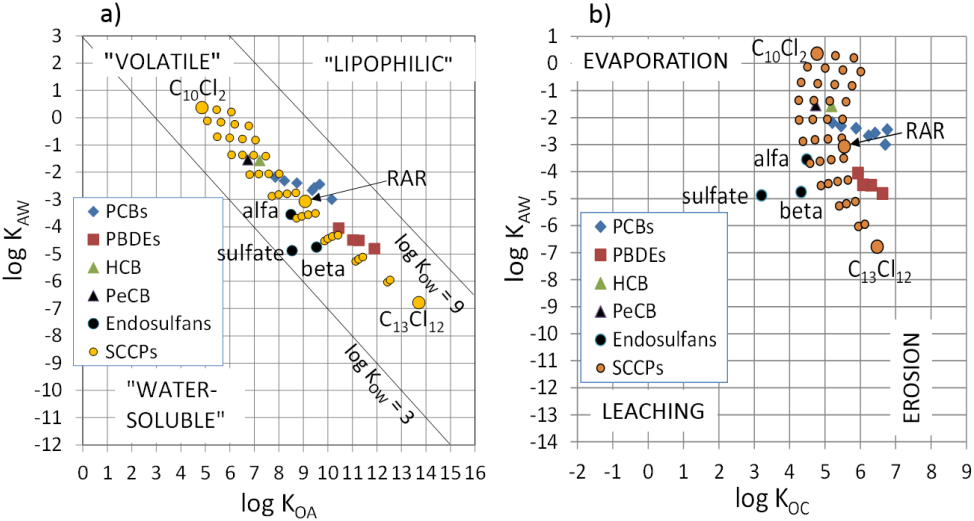- SCCPs

RAR
alfa
sulfate
beta
$C_{13}Cl_{12}$
LEACHING
EROSION

Table 1: Average soil concentrations ± standard deviation and ranges, for Σendosulfans and its constituents, PeCB and SCCPs for all soils combined (ng/g SOM). Samples which failed to meet the specified QA/QC criteria were excluded (see 3.1). The table also includes Σ_{31}PCBs, Σ_5PBDEs and HCB (Schuster et al., 2011).

	>MDL	Σendosulfans	endosulfan sulfate	α-endosulfan	β-endosulfan	PeCB	SCCPs		Σ_{31}PCBs	Σ_5PBDEs	HCB
				Aritmetric average ± standard deviation							
				Range (min-max)							
All 2008	**All 2008**	2±4	2±4	0.02±0.02	0.04±0.1	0.6±0.5	24±72	**All 2008**	6±5	0.6±0.8	1±1
n = 57/53/58	n = 56/52/23	<0.02[2]-26	<0.003[2]-25	<0.005[2]-0.08	<0.003[2]-0.7	<0.03[2]-3	<0.8[2]-417	n = 70	0.2-27	0.01-4	0.04-7
Norway	**Norway**	3±5	3±5	0.02±0.02	0.06±0.1	0.5±0.4	18±73	**Norway**	8±6	0.3±0.4	1±1
n= 32/32/32	n= 32/31/9	0.08-26	0.04-25	<0.005[2]-0.07	<0.003[2]-0.7	<0.03[2]-2	<0.8[2]-417	n= 40	0.2-27	0.01-2	0.2-5
UK	**UK**	1±2	1±2	0.02±0.02	0.02±0.03	0.8±0.6	31±71	**UK**	5±3	1±1	0.8±1
n= 25/21/26	n= 24/21/14	<0.02[2]-10	<0.003[2]-10	<0.005[2]-0.08	<0.003[2]-0.1	0.2-3	<0.9[2]-317	n= 30	0.5-10	0.1-4	0.04-7
GL	**GL**	0.7±0.9	0.6±0.9	0.02±0.02	0.01±0.01	0.6±0.7	38±103	**GL**	5±5	0.5±0.8	1±1
n= 23/20/24	n= 22/19/9	<0.02[2]-4	<0.003[2]-4	<0.005[2]-0.08	<0.003[2]-0.06	<0.03[2]-3	<0.9[2]-417	n= 30	0.2-23	0.02-4	0.06-7
WL	**WL**	3±5	3±5	0.02±0.02	0.06±0.1	0.6±0.4	14±37	**WL**	8±6	0.7±0.7	1±1
n= 34/33/34	n= 34/33/14	0.1-26	0.1-25	<0.005[2]-0.07	<0.003[2]-0.7	0.2-2	<0.8[2]-205	n= 40	0.6-27	0.01-3	0.04-5

[1] Number (n) of sites for which Σendosulfans, PeCB and SCCPs were determined, respectively.

[2] One or more samples were below MDL (½ MDL used for statistical summaries).

[3] Data from (Schuster et al., 2011)

Figure 2 (a-i): Latitudinal distribution for Σendosulfans, PeCB and SCCPs on ng/g SOM (a, b, c) and dry weight basis (d, e, f). Also included is the log concentration (ng g^{-1} dw) versus SOM (g, h, i). Woodland (WL, ▲) and grassland (GL, O) soil samples are plotted separately. One outlier for each compound was omitted (2.8.1).