Atmos. Chem. Phys., 11, 12799–12811, 2011
www.atmos-chem-phys.net/11/12799/2011/
doi:10.5194/acp-11-12799-2011

Atmospheric Chemistry and Physics

Soil-Air exchange controls on background atmospheric concentrations of organochlorine pesticides

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Received: 7 July 2011 – Published in Atmos. Chem. Phys. Discuss.: 19 September 2011
Revised: 6 December 2011 – Accepted: 9 December 2011 – Published: 19 December 2011

Abstract. Soils are the major terrestrial reservoir of persistent organic pollutants, and thus net volatilization from soil, when it happens, may exert a control on the atmospheric occurrence and variability of organic pollutants. Here, we report and discuss the concentrations of legacy organochlorine pesticides (OCPs) such as hexachlorobenzene (HCB), hexaclorocyclohexanes (HCH) and dichlorodiphenyltrichloroethane (DDT) in the atmosphere and in soils, their measured fugacities in soil, the soil-air partition coefficients (K_{SA}) and soil-air fugacity ratios (f_s/f_a) in rural background areas of N-NE Spain and N-NW England. Four sampling campaigns were carried out in Spain and UK to assess seasonal variability and differences between sampling sites. K_{SA} values were significantly dependent on soil temperature and soil organic matter quantity, and to a minor extent on organic matter type. HCH isomers and DDT metabolites in soil are close to equilibrium with the overlying atmosphere at rural background areas of Spain with a tendency to volatilize and deposit during warm and cold periods, respectively. The mixture of HCH and DDT found in the atmosphere is clearly strongly influenced by the mixture of HCH and DDT which escapes from soil, with significant correlations between them (r^2 ranging between 0.63–0.76 and p-level$<$0.001 for the Ebro sampling sites), thus suggesting a close coupling of air and soil concentrations, demonstrating that net volatilization from soil control the atmospheric levels of OCPs in the Northern Spain background atmosphere. Conversely, soils at rural UK sites were usually a sink for atmospheric DDT and HCH, but not for HCB. The negative statistically significant relationship found between log K_{SA} and the log (f_s/f_a) ratio, suggests that high latitude regions, due to the high soil organic matter content and lower temperatures, will act as larger traps and accumulate more atmospheric OCPs. Thus, the extent to which soils are secondary sources to the atmosphere is currently dependent on the reservoir potential of soils for OCPs and shows a marked seasonality in their strength.

1 Introduction

Legacy organochlorine pesticides (OCPs) were used heavily in the past, such as hexachlorocyclohexanes (HCH) for pest control, dichlorodiphenyltrichloroethane (DDT) for malaria control, or for industrial and agricultural purposes such as hexachlorobenzene (HCB). Most have been banned or restricted in industrialized countries and are now being eliminated under the United Nations Economic Commission for Europe (UN-ECE) and the Stockholm Convention on persistent organic pollutant (POPs). However, due to their long environmental lifetimes, semi-volatility, and hydrophobicity, residues still persist in the local and global environment (Gregor and Gummer, 1989; Blais et al., 1998; Grimalt et al., 2001; Ribes et al., 2002). In background regions with no historical direct inputs, the occurrence of OCPs in the atmosphere and soils is influenced by their volatilization from soils and atmospheric deposition events, with atmospheric transport as the main vector for their spatial re-distribution from secondary and potential primary regional sources. Several studies over the past years (Zhang et al., 2007, 2011) have recognized the importance of the amount and composition of soil organic matter (SOM) to explain the sorption and the availability for biological degradation, vertical transport or volatilization of OCPs from the soil surface to the atmosphere. Soils are the major environmental reservoir of POPs (Dalla Valle et al., 2005), and volatilization of OCPs from soil can be a continuous and diffuse source of atmospheric contamination, which must be assessed to determine the relative contribution of "legacy" residues (secondary sources) and ongoing usage (primary sources). Sampling air and soil

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Published by Copernicus Publications on behalf of the European Geosciences Union.

at the same sites may allow statements on the atmosphere-surface exchange of OCPs and the determination of in-situ soil and ambient air fugacities will provide quantitative evidence of the direction of soil-air exchange of OCPs. In this study, we investigate in detail the factors controlling OCPs gradients between soils and the atmosphere and the soils controls on atmospheric concentrations in selected temperate background areas. This is achieved by means of determining the OCPs concentrations in the atmosphere, in soils, their fugacities in surface soils, and fugacity ratios between soil and the atmosphere by using the soil fugacity sampler (Meijer et al., 2003a; Cabrerizo et al., 2009). Therefore, the main objective is to study the influence of soils as a control of the atmospheric levels of OCPs by means of (i) studying the effect that temperature and soil organic matter quantity and quality have on soil OCPs fugacity, concentrations in soil, and the soil-air partition coefficients (K_{SA}), (ii) quantifying soil/air fugacity ratios to determine the direction of soil-air exchange and (iii) exploring the factors affecting the atmospheric concentrations of OCPs. This study has been performed in background rural and semi-rural areas of the Ebro river basin (Spain) and northwest England and is a companion assessment of the recently reported studies on polycyclic aromatic hydrocarbons (PAHs) (Cabrerizo et al., 2011a) and polychlorinated biphenyls (PCBs) (Cabrerizo et al., 2011b).

2 Materials and methods

2.1 Soil and air sampling

Nine background sites in Spain and UK were selected. All of them were non-agricultural rural or semirural sites (See Fig. S1 and Table S1 in the Supporting Information (SI) for sampling sites locations and information). There were six rural sites: Borau, Alfaro, Nájera, Lasieso, Uruñuela located along the Ebro river basin (N-NE Spain) and Langden (near Lancaster, UK); and three semi-rural: Tudela, Sabiñanigo (Ebro river basin-Spain) and Hazelrigg (near Lancaster, UK). Sampling sites in Alfaro and Tudela were close to land used for fruit crops but these and all other sites are non agricultural sites. Three sampling campaigns were carried out in June 2006, November 2006 and September 2007 in the Ebro river basin. Sampling in the UK sites was performed during August–September 2008.

Ambient air samples and air equilibrated in-situ with the soil surface samples were collected using a low volume sampler proposed by Cabrerizo et al., 2009. As in commercial high volume samplers, the air passes through a glass fiber filter to remove dust particles and a polyurethane foam (PUF) plug in which the compounds from the gas phase are retained. Filters and PUF used in this sampler are quartz fiber filters (GF/F) of 47 mm of diameter and 10 × 2 cm PUF. The main advantage of this sampler is that allows for accurately determining the OCPs soil fugacity by sampling the air which has been equilibrated for enough time with the soil, thus OCPs soil fugacities were determined. Unlike a commercial high volume sampler, the flow rate is much lower (8–10 $\mathrm{l\,min^{-1}}$), thus allowing for air that passes below the sampler to equilibrate in terms of OCPs concentrations with the soil surface (Cabrerizo et al., 2009). In parallel, another sampler located at 1.5 m is operating at the same condition in order to determine ambient air fugacities. Each sample is an integration of 24 h of sampling with a total air volume of 10–14 $\mathrm{m^3}$.

Soil samples were taken after soil fugacity sampling, by gently collecting the soil surface layer (approximately top 0.5–1 cm). Concerning this study, a total of 43 soil fugacity measurements, 41 ambient air concentrations, and 20 top surface soils were sampled and analyzed. After sampling, air and soil samples were stored in freezers at −20 °C until analysis.

2.2 Analytical methods

Soil and air samples were Soxhlet extracted for 24 h in dichloromethane:methanol (2:1) and acetone:hexane (3:1), respectively. Extracts were cleaned and fractionated using alumina chromatography. Soil samples were also treated with activated copper to avoid chromatogram interferences by sulfur. Samples taken in the Ebro river basin (Spain) were analyzed by gas chromatography coupled with electron capture detection (GC/ECD) and those taken in the UK by gas chromatography coupled to mass spectrometry (GC/MS) with an EI+ source operating in selected ion mode (SIM). Details of the temperature programs and monitored ions are given elsewhere (Ockenden et al., 1998; Thomas et al., 1998; Gouin et al., 2002; Cabrerizo et al., 2011b). The following OCPs were analyzed: HCB, HCH isomers (α-HCH, β-HCH, γ-HCH, δ-HCH) and DDT and its metabolites (p,p′-DDT, o,p′-DDT, p,p′-DDD, o,p′-DDD, p,p′-DDE, o,p′-DDE). Unfortunately, o,p′-DDD was omitted in this study due to a co-elution with PCB82 when analyzed by GC/ECD. In the same way, HCB did show a co-elution in some air samples taken only in the first sampling campaign (June 2006), so these samples were not considered. No breakthrough of OCPs is observed with the sampling conditions, due to the small sampling volumes (10–14 $\mathrm{m^3}$) and the PUFs size which are 10 cm long × 2 cm of diameter. The breakthrough for OCPs has been estimated to be around 80 $\mathrm{m^3}$ for the more volatile OCPs(HCB) during the summer. Reference to the sum of isomers groups of HCHs (ΣHCH) and DDTs (ΣDDT) considers the aforementioned isomers.

Quality Assurance/Quality Control. All analytical procedures were monitored using strict quality assurance and control measures. Laboratory blanks and field blanks constituted 21 % of the total number of samples processed. δ-HCH, p,p′-DDE and p,p′-DDT were detected in both laboratory blanks and field blanks at low concentrations, ranging between 2 and 10 % of levels found in samples, indicating minimal contamination during storage, sampling, transport and processing. Therefore, samples were not blank corrected. Method quantification limits were derived from the lowest standard in the calibration curve, ranged from 0.35 pg m^{-3} and 0.5 pg g^{-1} for air and soil samples processed with GC/ECD and between 3.5 pg m^{-3} and 10 pg g^{-1} for air and soil samples processed with GC/MS. Recoveries were routinely monitored using PCB65 and PCB200 and $^{13}C_{12}$-PCBs (28, 52, 101, 138, 153, 180) and they ranged from 53 ± 17 to 76 ± 14 and from 58 ± 3 to 101 ± 26 for soil and gas phase respectively, so samples were not corrected by recoveries.

Meteorological data. Concurrent meteorological data were monitored where possible using a wireless weather station or were provided by the nearest weather station to the sampling site by the Spanish Meteorological Agency (AEMET). The following physico-chemical characteristics of samples were measured by standard methods described elsewhere (Cabrerizo et al 2011a, b): soil temperature (soil T), ambient air temperature (air T), soil water content (SWC) and precipitation, soil organic carbon (TOC) or organic carbon fraction (f_{OC}), surface soil pH and redox potential, fraction of nitrogen (f_N) and altitude. The four last parameters were used as indirect "proxy parameters" for the organic matter type/quality.

3 Results and discussion

3.1 Occurrence of organochlorine pesticides in ambient air

All the measured ambient air concentrations, air T and precipitation in the Ebro river basin and UK sites are listed in the SI (Table S2a–d). Average concentrations of individual organochlorine pesticides ΣHCH, ΣDDT and HCB are also reported. The range in the ΣHCH, ΣDDT and HCB concentration in ambient air for Ebro sites (Spain) were 0.019–0.352 ng m^{-3}, 0.006–0.111 ng m^{-3} and 0.018–0.066 ng m^{-3}, respectively. Overall, the highest concentrations of HCH isomers and DDT metabolites were observed in warm periods campaigns (June 2006 and September 2007), suggesting a seasonal variability. ΣHCH, ΣDDT and HCB concentrations in ambient air for UK sites (Hazelrigg and Langden) were in the ranges 0.023–0.078 ng m^{-3}, 0.012–0.016 ng m^{-3}, and 0.034–0.037 ng m^{-3} respectively. These atmospheric levels are in the same order of magnitude to those reported in other studies at background areas (Barber et al., 2005; Gioia et al., 2007; Růžičková et al., 2007; Halse et al., 2011). Overall, the concentration of OCPs in ambient air increased when air T also increased ($p\text{-level} < 0.05$) (Fig. 1), suggesting that atmospheric concentrations of OCPs vary seasonally, with concentrations reaching a maximum of ambient air concentrations during warmer periods. The 24 h back trajectories were calculated using the US National Atmospheric and Oceanic Administration (NOAA) H-Split model for individual OCPs in those samples for which there was a significant difference between maximum and minimum at the same temperature. Examples of back trajectories for selected OCPs were calculated at 10 m and 100 m above ground level in order to identify where the air masses were originated. Figure S2a–c shows, that the back trajectories for maximum and minimum concentrations at the same ambient air temperature do not correspond to a predominant direction of air masses, which suggest that re-emissions of OCPs from local sources in these background environments, consistent with volatilization from soil, may be playing an important role in controlling their ambient air concentration. Ambient air concentrations for selected sites in the Ebro river basin are shown in Fig. S3 and presented as fugacities (or partial pressures in Pa) by

$$f_a = 10^{-9} C_A \mathrm{RT/MW} \tag{1}$$

where C_A is the measured air concentration in ng m^{-3}, R is the gas constant (8.314 Pa m^3 mol^{-1} K^{-1}), MW is the chemical molecular weight (g mol^{-1}), and T is the temperature (K).

3.2 Occurrence of pesticides in surface soils

Soil concentrations for individual OCPs, ΣHCH and ΣDDT in ng g dw^{-1} (ng g soil dry weight (dw)) at each site are shown in the SI (Table S3a, b). Concentrations of HCB, ΣHCH and ΣDDT in soils are in the range between detection limit and 0.49 ng g dw^{-1} with a mean value of 0.11 ng g dw^{-1}; between detection limit and 0.52 ng g dw^{-1} with a mean value of 0.06 ng g dw^{-1}; and between 0.02 and 4.73 ng g dw^{-1} with a mean value of 0.79 ng g dw^{-1}, respectively. The concentrations in soil reported here are similar to those reported in previous studies for non-agricultural and background soils (Meijer et al., 2003b; Grimalt et al., 2004; Borghini et al., 2005). Overall, p,p′-DDE was the main contributor (up to 60 %) to the ΣDDT for most soils. This is consistent with the fact that DDT in soil is subject to microbial degradation to more stable and toxic metabolites such as p,p′-DDE. The ratios p,p′-DDE/p,p′-DDT have been successfully used to distinguish the source of DDT (Harner et al., 2004; Liu et al., 2009; Wang et al., 2009). Therefore, if the ratio of p,p′-DDE/p,p′-DDT is >1, it indicates aged DDT, while ratios <1 indicate fresh inputs. From the data set reported here ($N = 20$), almost all soil samples had ratios of p,p′-DDE/p,p′-DDT >1, indicating aged DDT. Only 3 samples collected in the Ebro basin in different sampling campaigns had values <1 in both soil samples and air equilibrated with soil (soil fugacity measurements) (Sabiñánigo (0.53), Lasieso (0.74) and Nájera (0.03)) which could suggest a recent use of this OCPs in the area. Regarding HCH isomers, γ-HCH and δ-HCH were found to be the dominant isomers in these soils, although α-HCH was also detected in some soils. It is usually considered in the literature that

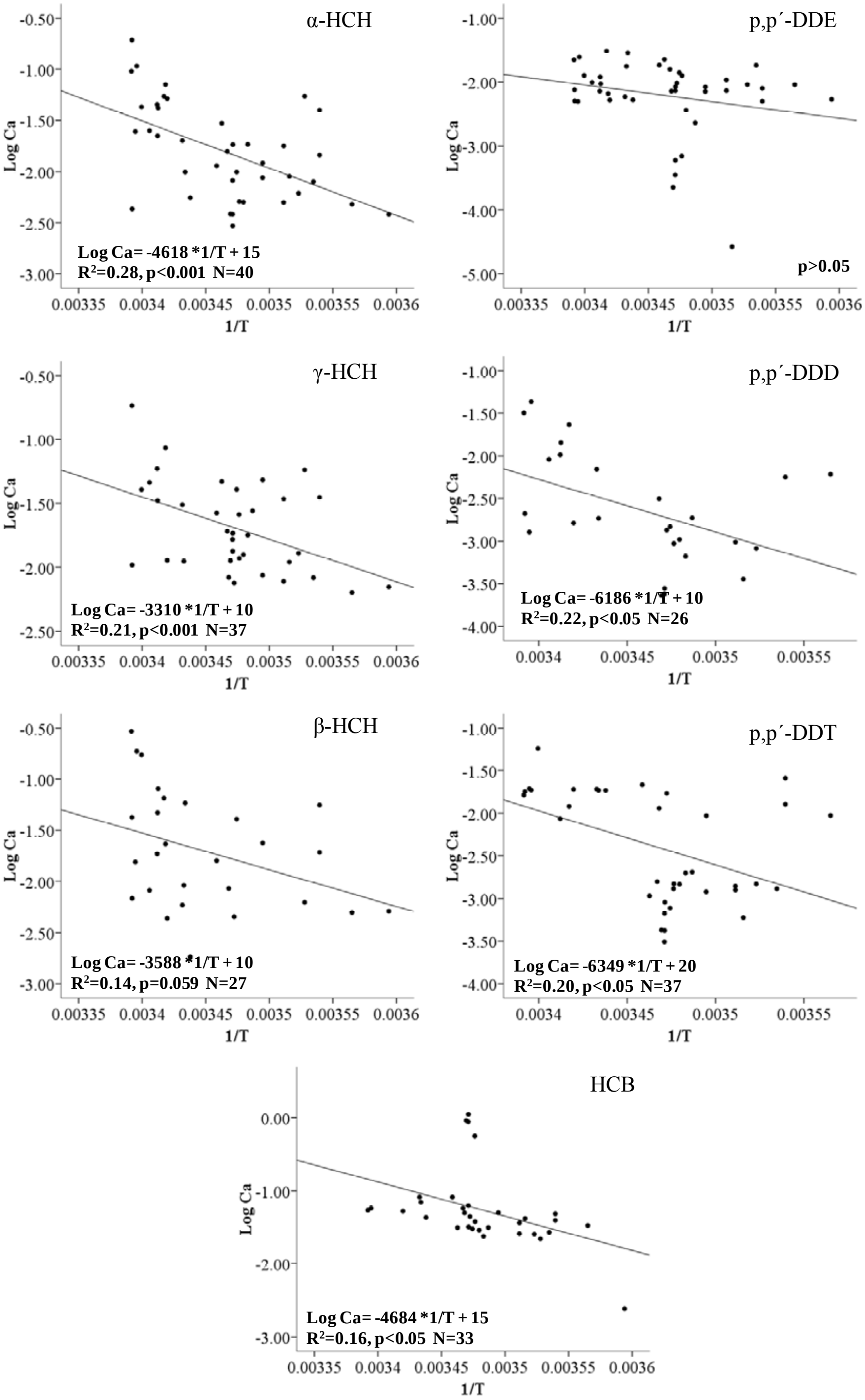

Fig. 1. Ambient air concentration (Log Ca in ng m^{-3}) regressed against $1/T$ for selected HCH isomers, DDT metabolites and HCB.

if the ratio α/γ-HCH are in the range of 4-12 (Breivik et al., 1999; Lee et al., 1999; Vijgen, 2011) it is representative of technical HCH mixture, while lower values or nearly 1 represent lindane input. For the data set reported here, generally, the ratio α/γ-HCH in soils had values lower than 4 and most of them lower or close to 1, which exception of 2 soil samples, which suggest the predominant use of lindane instead of the technical HCH mixture in the study area. In order to study the influence of physico-chemical properties on the occurrence of OCPs in soils, a regression analysis was performed. Regressions were calculated between the soil OCPs concentrations and the following variables: soil T, air T, SOM quantity and proxies for soil type. HCB, ΣDDT and ΣHCH concentrations in soils (ng g dw^{-1}) were significantly correlated (p-level$<$0.05) with soil organic carbon (Fig. 2) suggesting that SOM is clearly an important parameter influencing the concentration of OCPs in background soils, consistent with previous studies (Meijer et al., 2003b). The major contributors among HCH isomers and DDT metabolites to ΣHCH and ΣDDT which correlated against soil organic carbon are presented in Fig. S4. A strong relationship (steep slope, less scatter) was observed for HCB (r^2 = 0.73 and p-level$<$0.001). This implies that the reservoir of OCPs is larger for soils with larger SOM, and that processes like atmospheric transport and re-distribution through air-soil exchange are important in influencing the soil OCPs concentration, since no direct sources are known for the sampling sites. A statistically significant correlation (p-level$<$0.05) was observed between soil concentration normalized to soil organic carbon and SOM quality ($f_{\mathrm{OC}}/f_{\mathrm{N}}$) for selected DDT metabolites (p,p′-DDE and o,p′-DDT), with r^2 ranging between 0.23–0.24, while no significant correlation were found for HCH isomers, thus suggesting a variable but modest influence of the soil OCPs reservoir with respect of the SOM type. Concerning temporal trends, there were no statistically significant differences in soil concentrations of OCPs with respect to soil or ambient air temperature for the three sampling periods in the Ebro, consistent with the fact that the inventory of POPs in soil is generally believed to be considerably larger than the annual fluxes in and out of the soil (Kurt-Karakus et al., 2006). No significant correlation was observed with soil pH or soil redox. There were significant (p-level$<$0.001 and p-level$<$0.05) correlations between the different POPs families' concentrations (Table S4) for HCB, ΣHCH, ΣDDT, ΣPCBs and ΣPAHs across the whole set of soils, which is clear evidence of the common role of organic matter quantity as a descriptor of the burden of hydrophobic pollutants. This was also observed by Nam et al. (2008) in other European background soils.

3.3 OCPs fugacity in soils

Only those OCPs present in the exchangeable fraction of soil will be able to escape from the soil surface to the atmosphere. The recent development of a new soil fugacity sampler (Cabrerizo et al., 2009) allows for direct determination of the pollutants fugacity in soils. In this study, OCPs fugacity in soil was determined directly under field controlled conditions by:

$$f_{\mathrm{s}} = 10^{-9} C_{\mathrm{SA}} \mathrm{RT/MW} \tag{2}$$

where C_{SA} (ng m^{-3}) is the gas phase concentration that has been equilibrated with the soil surface as measured using the soil fugacity sampler. To establish the role of temperature and SOM in the magnitude of the emission of OCPs in soils, a least squares regressions of log f_{S} = a + b (1/T) and log f_{S} = a + b (log f_{OC}) were applied for individual HCH isomers, DDT metabolites and HCB which were detected in at least 15 of the samples (N≥15). Results show that lower soil fugacities correspond to low temperatures (Figure S5)

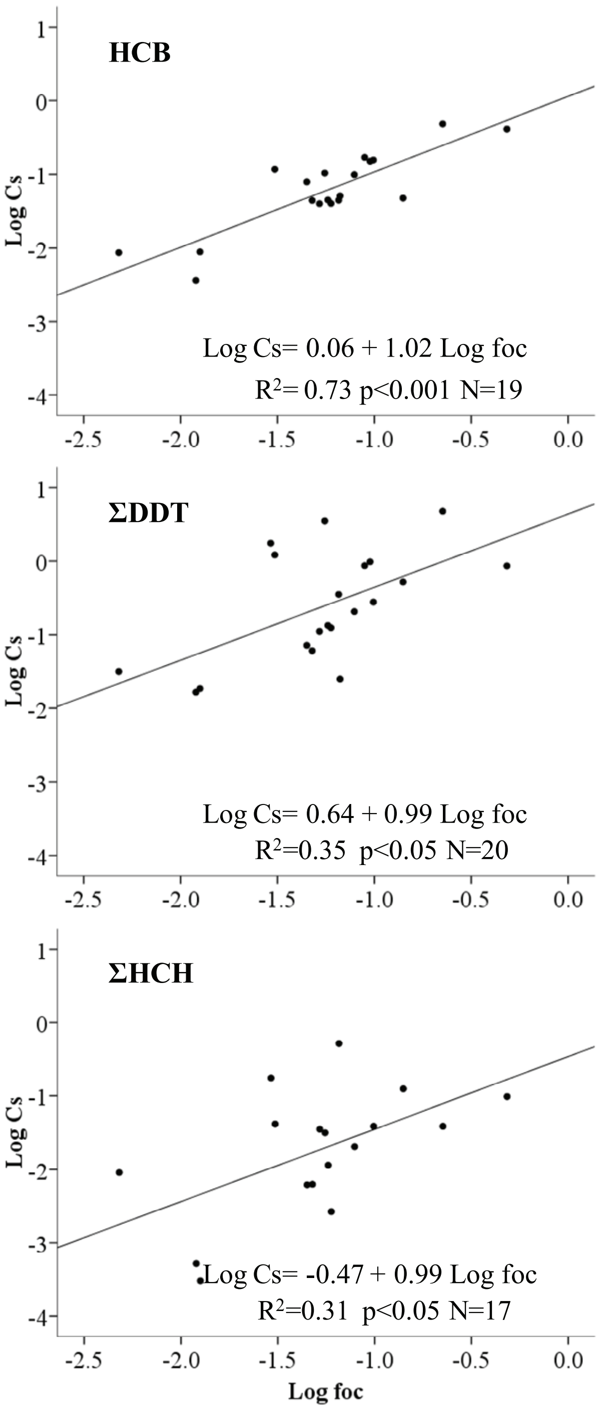

Fig. 2. Concentrations in soil (Log Cs in ng gdw^{-1}) versus soil organic carbon (Log f_{OC}).

with r^2 ranging between 0.25–0.38 (p-level<0.05) and to higher amounts of SOM, with r^2 ranging between 0.15 and 0.35 (p-level<0.05) for α-HCH, o,p′-DDT and p,p′-DDT (Table S5a).

Soil fugacities of those DDT metabolites which were not affected by the SOM quantity (ex. o,p′-DDE, p,p′-DDE, p,p′-DDD) were regressed against SOM quality ($f_{\mathrm{OC}}/f_{\mathrm{N}}$) and soil pH (see Tables S5b-c). Results show that lower soil fugacities correspond to high $f_{\mathrm{OC}}/f_{\mathrm{N}}$ ratios with r^2 ranging between 0.26–0.42 (p-level<0.05) for o,p′-DDE, p,p′-DDE, p,p′-DDD, and that the soil fugacity decreases with decreasing pH with r^2 ranging between 0.47–0.67, thus suggesting that both SOM quantity and quality (especially for DDT metabolites) may be important parameters retarding the emission of OCPs to the atmosphere and therefore soils with high concentration of SOM and lower pH are favored in the accumulation of POPs as described in previous studies (Ockenden., et al 2003; Cabrerizo et al., 2011b). Ratios of α/γ-HCH during net volatilization, in both air equilibrated with soil (fugacity in soil) and ambient air also shows lower values of α/γ-HCH ratio consistent with the predominant use of lindane instead of technical HCH mixture, which is in agreement with results of α/γ-HCH ratio in soils.

There was a high variability for HCB soil fugacities and no statistically significant trend could be observed.

3.4 Factors affecting the soil-air partitioning of organochlorine pesticides

As there are currently no fresh applications of the studied OCPs in Spain and UK, their air concentration variability, with higher concentrations during warm periods, is presumably related to their volatilization from soils. As shown above, the soil fugacity depends on temperature, SOM quantity and type, thus the soil-air exchange and partitioning will be dominated by several physical and chemical properties of the soil and atmosphere, among which the vapor pressure, the enthalpy of vaporization of the chemicals (ΔH) (Mackay et al., 1986; Bidleman, 1999) and the SOM quantity and type are the most important. ΔH has been calculated from the slope of the regression resulting when the soil-air partitioning coefficient (K_{SA}) is plotted against $1/T$ (Fig. 3). K_{SA} (L kg^{-1}) was calculated as:

$$K_{\mathrm{SA}} = C_{\mathrm{S}}/C_{\mathrm{SA}} \tag{3}$$

Characteristic examples of the influence of temperature on K_{SA} for selected HCH isomers and DDT metabolites are shown in Fig. 3. Log K_{SA} was significantly positively correlated with $1/T$, in agreement with previous studies (Cortes et al., 1998; Haugen et al., 1998; Su et al., 2006), even though these previous studies usually estimated the enthalpies from the ambient gas phase concentrations variability. For those HCH isomers and DDT metabolites which show a significant dependence of temperature (p-level<0.05), it is possible to calculate the enthalpy of volatilization (ΔH, KJ mol^{-1}) from the slope of the regression by:

$$\Delta H = \frac{\text{slope}}{2.3} R \tag{4}$$

where R is the gas constant and 2.3 the conversion factor from decimal to natural log. The values of ΔH for α-HCH, γ-HCHs and δ-HCH are 40 ± 12, 80 ± 13 and 64 ± 12 KJ mol^{-1} respectively. The difference in temperature dependence between α-HCH and γ-HCH isomers has also been observed in other studies (Haugen et al., 1998; Cortes et al., 1998; Poissant and Koprivnjav, 1996). Calculated values of ΔH for p,p′-DDE, o,p′-DDT and p,p′-DDT are 49 ± 14, 39 ± 16 and 38 ± 12 KJ mol^{-1}. These air-soil enthalpies are consistent with previously reported values from other studies. Grimalt et al., 2004 reported ΔH values of 88 kJ mol^{-1} for α-HCH and 43 for γ-HCH; Buehler et al., 2003 reported ΔH between 50–65 kJ mol^{-1} for γ-HCH, between 21–27 kJ mol^{-1} for α-HCH and between 47–61 kJ mol^{-1} for ΣDDT. Aulagnier and Poissant (2005) also reported values in the range 24–36 kJ mol^{-1} for DDE and between 14–92 kJ mol^{-1} for DDT. Air-soil phase exchange enthalpies reported in this study for OCPs and in other studies for other POPs are consistent, but in general slightly lower than the enthalpies for volatilization of the pure compound and the associated with the phase change of a chemical from octanol to air (ΔH$_{\mathrm{OA}}$) which are 61.9 and 65.4 for α-HCH, γ-HCHs (Hinckley et al., 1999) respectively and 97.8 and 88 for p,p′-DDE and p,p′-DDT respectively (Shoeib and Harner, 2002), suggesting that OCPs sorption to SOM is weaker than sorption to the octanol phase.

However, no significant correlation with temperature was observed for HCB. A breakthrough of HCB has been considered in the literature (Lee et al., 1999) as a potential artifact to explain the lack of temperature dependence in air concentrations, due to the high vapor pressure of HCB in comparison to the rest of OCPs. However its vapor pressure is in the same range of those for phenanthrene for which temperature dependence was observed in a previous reported study at the same sites (Cabrerizo et al., 2011a). This together with the low sampling air volumes (10–14 m^3) and the estimated breakthrough to be on 80 m^3 for this study, suggest that this artifact may not be important in our results. The dependence of HCB partitioning with temperature is not clear in the literature. While some studies (Kaupp et al., 1996; Cortes et al., 1998; Lee et al., 1999) show temperature dependence of atmospheric concentrations with relatively low ΔH values, such as 5 kJ mol^{-1} at Eagle Harbour, 1.9 and 17 kJ mol^{-1} in the UK, other studies show a lack of dependence. Su et al., 2006 reported that the monthly variations of HCB in the Arctic atmosphere were less than a factor of 2, while the temperature varied up to 20 °C. Liu et al., 2009, reported a spatial trend for HCB in winter and spring but not in summer and autumn, while Aulagnier and Poissant, 2005 reported a negative correlation of HCB with temperature and so

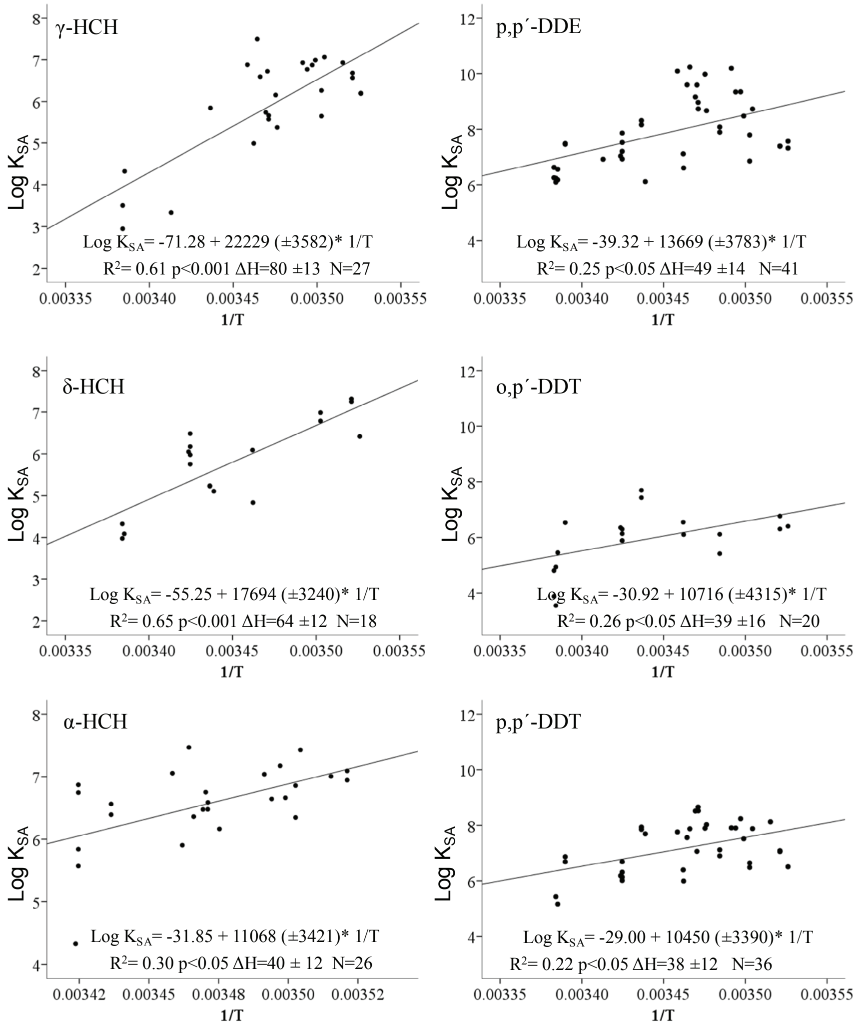

Fig. 3. Regression of soil-air partition coefficient (Log K_{SA}) versus temperature ($1/T$) for selected HCH isomers and DDT metabolites.

apparent negative enthalpies of volatilization. Then, it is possible that the enthalpy of volatilization from the pure compound is similar to the enthalpy of solubilization to SOM in the case of HCB. These suggest that HCB is weakly temperature dependent and other processes are strongly affecting the partitioning behavior, consistent with the lack of temperature dependence of its K_{SA} in this study and other observations. The lack of HCB measurements in the campaign performed in June resulted also in a dataset with available data for a narrower range of temperatures that makes it more difficult to detect significant trends.

Several studies over the last years (Bidleman et al., 1998; Finizio et al., 1998; Bidleman and Leone, 2004, Kurt-Karakus et al., 2006; Kurt-Karakus et al., 2007) have provided evidence that biodegradation of OCPs is occurring in field soils by looking at chiral signatures of selected OCPs such as α-HCH, o,p′-DDT and o,p′-DDD and studying the preferential breakdown in field samples in order to assess fresh inputs or aged OCPs re-emissions. Certainly, the use of chiral ratios is useful for elucidating the influence of volatilization from soil in atmospheric concentrations, but the chiral ratios were not determined here. In this study, soil fugacity measurements were done under equilibrium conditions, thus degradation may not be affecting the K_{SA}. If degradation is occurring in these soils, the degradation products of OCPs will potentially be more bioavailable than the parent compound and so will be more prone to undergo in soil-air exchange.

To elucidate differences in soil retention capacity for the selected OCPs in the different sampling sites, the soil organic carbon-air partition coefficient (K_{OCA}) was calculated from the soil-air partition coefficient (K_{SA}), where K_{OCA} is given by:

$$K_{OCA} = K_{SA}/f_{OC} \tag{5}$$

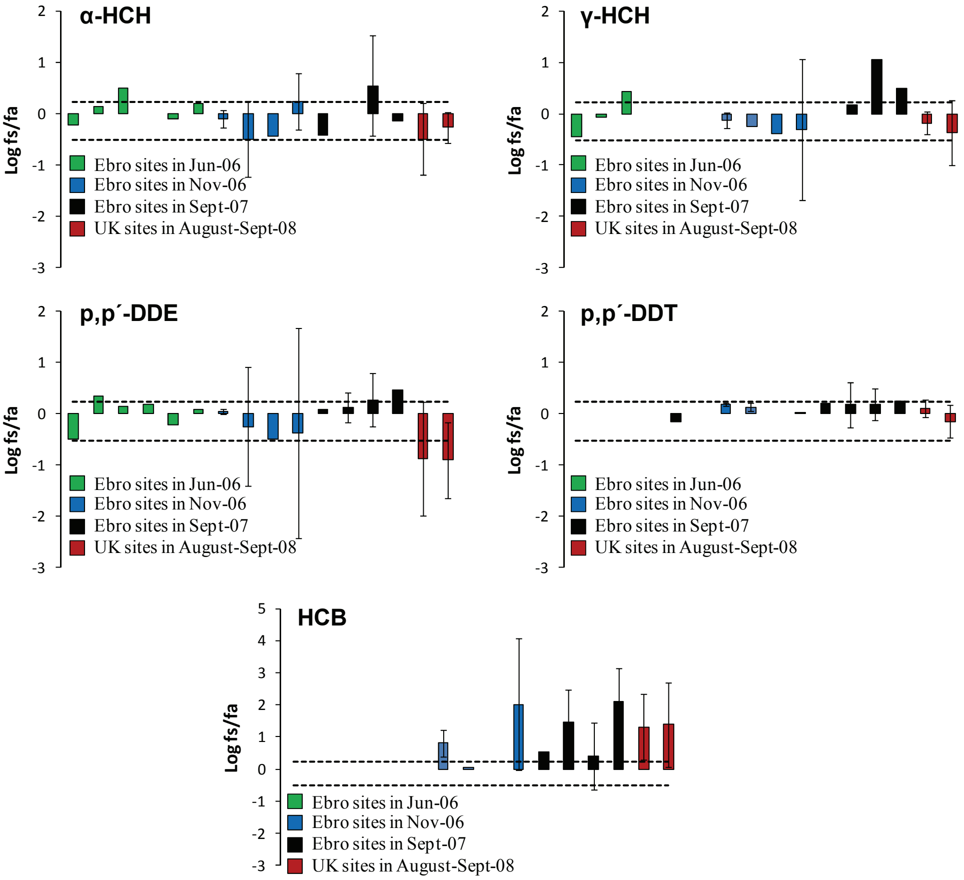

Fig. 4. Soil to air fugacity ratio (f_S/f_a) in logarithmic scale for the different sampling campaigns in Ebro (Spain) and UK. Dash lines indicates equilibrium (range +0.23, −0.52).

K_{OCA} were regressed against the octanol-air partition coefficient (K_{OA}). Figure S6 shows the log K_{OCA} versus log K_{OA} for the sampling campaigns, in different seasons, in the rural and semi-rural Ebro sites (Spain) and for the 2 sampling sites (Hazelrigg and Langden) selected in the UK. K_{OA} values for individual HCH isomers, DDT metabolites and HCB were estimated using the values proposed by Shoeib and Harner, 2002 and corrected by the in-situ measured temperature at each sampling site. The plots of log K_{OCA} versus log K_{OA} suggest that K_{OA} is an excellent descriptor of soil-air partitioning, with r^2 ranging from 0.27–0.74 and p-level<0.001 when all pesticides and all sampling sites are considered. As shown in Fig. S6, log K_{OCA} values obtained at different sampling sites lie in a range of 2 log units for HCH isomers and HCB (left part of the Figure) and 5 log units for DDT metabolites (right part of the Figure), which indicates differences in the soil retention capacity depending on the site. Sampling sites in the UK show, in general, similar or slightly higher values of log K_{OCA} for low molecular weight organochlorine pesticides (HCH isomers and HCB) at the same log K_{OA} value than sampling sites in the Ebro River's watershed. However, higher values of log K_{OCA} were observed for DDT isomers in UK sites than in the Ebro River's watershed, highlighting the Langden site. In order to obtain compound specific values for the fitting parameters, explaining the potential role of temperature and organic matter type, compound specific K_{OCA} values were correlated with the various variables (temperature, altitude, f_{OC}/f_N, pH....). Single regressions were performed using the equation Log K_{OCA} = a + b (X_n), with a and b being the fitting parameters and X_n the parameters considered. Statistical analyses were only done for those OCPs having at least $n = 15$ pairs of soil-air measurements (Fig. S7 and Tables S6a–c). Altitude, Soil T and pH were statistically correlated ($p < 0.05$) when regressed against HCH isomers and DDT metabolites K_{OCA} in single regressions, while f_{OC}/f_N, an indirect parameter of the organic matter quality, was only statistically positively correlated when regressed against K_{OCA} for DDT metabolites but not statistically correlations were observed for HCH, thus suggesting that the differences in the soil retention capacity may be attributed to differences in the SOM type as well.

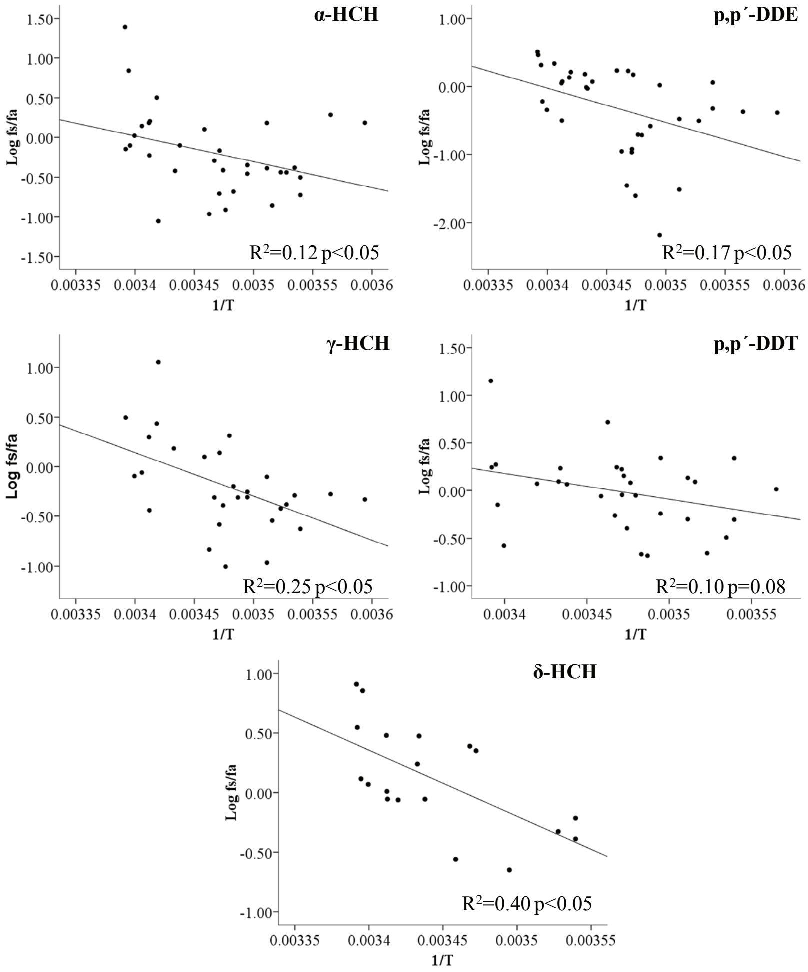

Fig. 5. Examples of soil to air fugacity ratio (Log f_s/f_a) regressed against $1/T$.

3.5 Secondary sources and soil-air exchange controls on atmospheric concentrations of OCPs

Measurements of the air concentration equilibrated with the soil and the atmospheric concentration, both transformed into fugacities of OCPs in soil and ambient air, were compared to infer the direction of air-soil exchange. When fugacity in soil is higher than in ambient air there is a net volatilization of chemical. In contrast, if the fugacity in ambient air is higher than in soil, there is a net deposition of the chemical. Figure 4 shows soil/air fugacity ratios (f_s/f_a), in logarithmic scale, for the three sampling campaigns, at different seasons, in the rural and semi-rural Ebro sites and for UK sampling. Bars represent the different sampling sites. Since there is an analytical error of 20 % when analyzing gas phase concentrations with the low volume of sampled air and the soil fugacity sampler is averaging the signal for 24 h, there is an uncertainty associated to the soil-air fugacity ratios, estimated to be lower than 70 % (Cabrerizo et al., 2011a, 2011b). With this in mind, equilibrium would be represented by log f_s/f_a in the range of +0.23 and −0.52, being the real uncertainty, lower than this range for many sampling sites. f_s/f_a, in the Ebro river campaigns, indicates near equilibrium conditions for selected HCH isomers (α-HCH, γ-HCH) and DDT metabolites (p,p′-DDE, p,p′-DDT), although a trend for soils to move from equilibrium towards becoming a net source to the atmosphere was observed during warmer periods (sampling campaigns carried out in early and late summer, June 2006 and September 2007). Conversely, during colder sampling periods (November 2006) the soils tended to move from equilibrium towards a net sink of atmospheric OCPs. Kurt-Karakus et al., 2006, in a study of OCPs at different heights, also reported net volatilization gradients of DDTs in agricultural soils in Canada, with highest concentration reported at 5 cm than at 200 cm from the soil surface. Soils appear to move from equilibrium (p,p′-DDT) to net atmospheric sinks (γ-HCH and p,p′-DDE) even in the late summer in the NW England environment. The fact

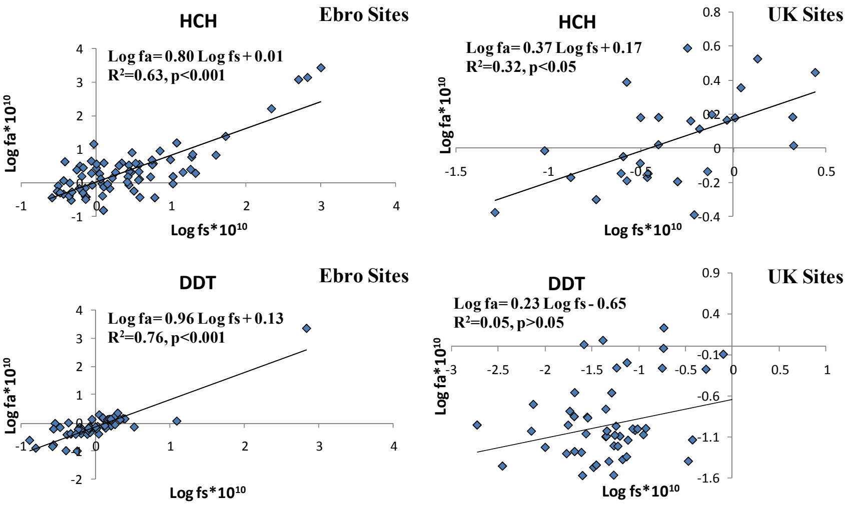

Fig. 6. Fugacity in soil (f_s) versus fugacity in air (f_a) for all HCH (α-HCH, γ-HCH, β-HCH, δ-HCH) isomers and all DDT metabolites (p,p′-DDE, p,p′-DDD, o,p′-DDT and p,p′-DDT) for sampling sites in Spain (Figures on the left) and sampling sites in UK (Figures on the right.

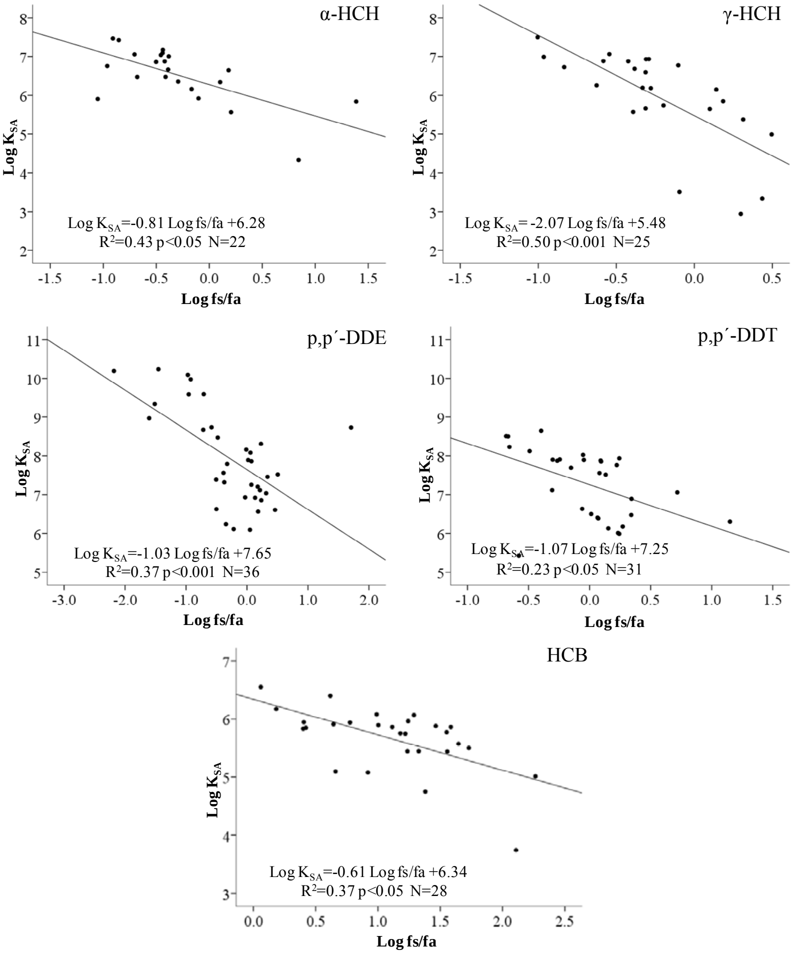

Fig. 7. Soil-air partition coefficient (Log K_SA) regressed versus the soil-air fugacity ratio (Log $f_\mathrm{s}/f_\mathrm{a}$) for selected OCPs

that UK soils behave as sinks of atmospheric OCPs may be due to higher SOM content or lower temperatures. In fact, Fig. 5 shows f_s/f_a ratios regressed against $1/T$ for individual HCH isomers and DDT metabolites. Higher f_s/f_a ratios were observed when increasing the temperature, suggesting that the tendency of the soil to act as a secondary source of OCPs to the atmosphere is temperature dependent. The behavior of HCB is interesting since all soils seem to be moving from equilibrium to act as a clear net source of HCB to the atmosphere, even in Ebro's sites in winter and in the UK. Unfortunately the behavior of Ebro soils in summer could not be assessed due to the chromatographic co-elutions as previously was pointed out.

In those sampling periods when there is net volatilization, and to a lesser extent when air and soil are close to equilibrium, it is possible that soils act as significant sources controlling the atmospheric occurrence of OCPs. Indeed, the left part of Figure 6 shows significant correlations between fugacities in soil and in ambient air when all HCH isomers (α-HCH, β-HCH, γ-HCH, and δ-HCH), and all DDT metabolites (p,p′-DDE, o,p′-DDD, o,p′-DDT and p,p′-DDT) for the Ebro sampling sites are considered. Therefore, in the Ebro River's water shed atmosphere, in which there is a seasonal net source of OCPs to the atmosphere with a net volatilization of HCH and DDT during warm periods, the soils exert a clear control on the atmospheric occurrence of OCPs. Indeed, the levels of HCH and DDT found in the atmosphere are significantly correlated with HCH and DDT which escape from soil (fugacity in soil) with r^2 ranging between 0.63 and 0.76 ($p < 0.001$) independent on the season. Similarly, the soil fugacity of individual HCH isomers was statistically correlated ($p < 0.001$) with their ambient air fugacity, with r^2 ranging between 0.69–0.84 (Fig. S8a). This trend is in agreement with results for PCBs reported elsewhere (Cabrerizo et al., 2011b), and indicates that atmospheric levels of banned HCH, DDT, and PCB in the Ebro River basin atmosphere are mostly controlled by re-emissions from soils. This trend is not as clear at UK sampling sites (right part of Fig. 6), as we have observed the soil is still a net sink for most OCPs. Therefore, the comparisons between regions show a spatial pattern. These findings suggest that secondary sources at mid latitudes, as is the case of background soils from NE Spain are playing an important role as sources, and OCPs are currently being exchanged between the soil and the atmosphere. In contrast, regions where log K_{SA} values are elevated, due to higher SOM content or lower temperatures, as is the case at the UK sampling sites, soils will act as larger traps and accumulate more OCPs, since soils are still under-saturated with respect to the atmospheric OCPs levels. Therefore, these soils will need longer times, during which primary sources of OCPs decrease, to become a secondary source to the atmosphere. The extent of secondary sources may be related to K_{SA}, which depends on T, SOM and to a lesser extent soil type. Soils with higher retention potential (higher K_{SA}) may still be net sinks of legacy POPs. If this is the correct scenario, then the log K_{SA} should be inversely correlated with the log f_s/f_a ratio. Figure 7 shows the negative correlation between log K_{SA} and log f_s/f_a for the data set reported here, for selected HCH isomers, DDT metabolites and HCB. This is consistent with the results reported in a previous paper (Cabrerizo et al., 2011b) for other POPs, PCBs, for which we observed the same trend only for some of the more volatile PCB congeners, those having similar physico-chemical properties than OCPs, while no statistically significant correlation was observed for most chlorinated congeners. Figure 7 clearly shows that at high K_{SA} values, soils act as a sink of atmospheric OCPs (f_s/f_a <1), while in regions and periods with low K_{SA} (low SOM content and high T), soils are a source of OCPs to the atmosphere (f_s/f_a >1). This finding is important since after decades of restriction in the use of OCPs, soils at higher latitudes and in cold environments are still important sinks of atmospheric POPs. This is in agreement with the studies of Schuster and co-workers, 2010 and 2011, in European background regions of UK and Norway. In these regions with soils with high SOM content and low temperatures, they found evidence that diffuse primary sources of POPs are still dominating the atmospheric burden of POPs at high latitudes and secondary sources, such as re-volatilization from soil surfaces are playing a minor role.

4 Conclusions

The present study shows that in the current balance of primary and secondary sources of OCPs in European temperate regions, soils with low SOM and relatively warm climate are a seasonal secondary source of HCH and DDT to the atmosphere, while soils in colder climates and regions with high SOM will act as a net sinks, because soil concentrations are still under-saturated with respect the atmospheric concentrations and diffuse primary sources may still be playing an important role. Whereas biodegradation completely removes OCPs from the environment, volatilization from secondary sources leads to the re-cycling of OCPs between environmental compartments mediated by atmospheric re-mobilization. This volatilization from low latitudes may have an important effect on levels and inputs in other regions such as the high latitude compartments.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys.net/11/12799/2011/ acp-11-12799-2011-supplement.pdf.

Acknowledgements. This research project was funded by the European Commission under the Global Change and Ecosystems (FP6) Water Cycle and Soil Related Aspects (AQUATERRA, Project number 505428 GOCE and from the Spanish Ministry of Education and Science through the SCARCE Consolider project. A. C acknowledges a Ph.D. pre-doctoral fellowship from the Spanish Ministry of Science and Innovation.

Edited by: R. Ebinghaus

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