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Air−Soil Exchange of Organochlorine Pesticides in Agricultural Soils. 1. Field Measurements Using a Novel in Situ Sampling Device

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Initial results are presented for in situ measurements of soil−air partitioning for a range of organochlorine (OC) pesticides in two contaminated agricultural soils. A soil survey was conducted and used to identify high levels of several OC pesticides in two regions of southern Ontario that are known for their intensive agriculture, the Tobacco Belt and the Holland Marsh. Experiments were conducted at one field in each region by sampling air very close to the soil surface using a disc-shaped sampler. The equilibrium status of the sampled air was tested by comparing the chiral signature of the soil with the signature in air sampled by the device and ambient air. Although results showed that 104% of *trans*-chlordane (TC) and 96% of *cis*-chlordane (CC) in the air under the sampler originated from the soil, the propagated errors in these results (34% SD for TC and 26% SD for CC) are too large to provide conclusive evidence for equilibrium. Therefore, a soil−air quotient (Q_{SA}) is reported here instead of the soil−air partition coefficient (K_{SA}). This value is an approximation of the "true" K_{SA}. Results show a linear relationship between log Q_{SA} and log K_{OA} and fit in with the relationship $K_{SA} = 0.411\rho\phi_{OC}K_{OA}$ where ρ is the soil density (kg L^{-1}). Using this relationship, fugacities were calculated in air and soil. Results of this calculation identify a strong disparity that favors soil-to-air transfer. This gradient is confirmed by measurements at different heights over one of the fields. Soil−air exchange is a key process in the overall fate of OC pesticides. The results from this study will improve our ability to model this process and account for differences between soils.

Introduction

Many organochlorine (OC) pesticides that are currently found in the environment were banned decades ago in North America and Europe. However, because of their persistence, they can still be found in the soil and therefore continue to cycle through the environment as soil is a potential source to the atmosphere through volatilization. For example, a soil−air exchange model was used recently to assess the regional fate of pesticides in the U.S. Cotton Belt (*1*). In that study, the soil−air partition coefficient was identified as an important model parameter for regional cycling of pesticides.

The soil−air equilibrium partition coefficient (K_{SA}) describes the partitioning behavior of a gaseous compound between the air and the soil at equilibrium and can be calculated as the concentration in the soil divided by the concentration in air. K_{SA} values have been measured previously using a fugacity meter for a range of persistent organic pollutants (POPs) (*2*−*4*) for one type of soil. Hippelein and McLachlan (*2*) determined a linear relationship between K_{SA} and K_{OA} using an expression derived by Karickhoff (*5*). This model predicts K_{SA} on the basis of the organic carbon fraction of the soil. They found that their results agreed very well with the Karickhoff model for PCBs, chlorobenzenes, and PAHs in a mineral-rich soil (*2*). This is very useful for modeling purposes as the K_{SA} is soil-specific, whereas the K_{OA} is universal and can be measured directly. However, the Karickhoff model was only tested for one type of soil. One purpose of this paper is therefore to check the relationship determined by Hippelein and McLachlan for other soil types with varied organic contents.

A variety of flux chambers have been used in the past for the measurement of contaminant fluxes from the soil into the air. These include passive (or static) samplers, which are mainly applicable for volatile compounds (*6*), and various active (or dynamic) samplers for measuring emissions of volatile organic compounds (*7*), NO_x (*8*), or sulfur (*9*) from soil. However, to our knowledge there has been no study measuring soil−air partition coefficients for POPs directly in the field. Such a sampler is desirable because it would provide useful information regarding the soil−air exchange process that could be used to improve chemical fate models.

This is the first of two papers that address soil−air exchange of OC pesticides. In this paper, we present field experiments conducted at two agricultural regions in southern Ontario. A novel air sampler is described that allows us to measure air concentrations of pesticides at or close to equilibrium with the soil by sampling the air very close to the soil surface. This allows us to derive the in situ soil−air partition coefficient (K_{SA}) in the case of complete equilibrium between the air and the soil or, alternatively, the soil−air quotient (Q_{SA}) in case complete equilibrium is not achieved. It is important to mention that the Q_{SA} or K_{SA} determined here represents the fast or "freely" desorbing fraction. Previous studies have shown that desorption from soil is a two-step process involving an initial fast exchange followed by a more lengthy and slower release of tightly bound chemical (*10*−*12*).

The purpose of this paper is (i) to investigate the potential of agricultural soils to be a source of OC pesticides to the environment, years after the use of these compounds has ceased; (ii) to investigate soil−air partitioning for OC pesticides in the field; and (iii) to check the suitability of a previously derived model to predict K_{SA} in different soils with the aim of using these values in regional air−soil exchange models. In the second paper, a fugacity meter is used to carry out controlled chamber measurements to investigate in more detail how temperature and soil type influence the soil−air exchange (*13*).

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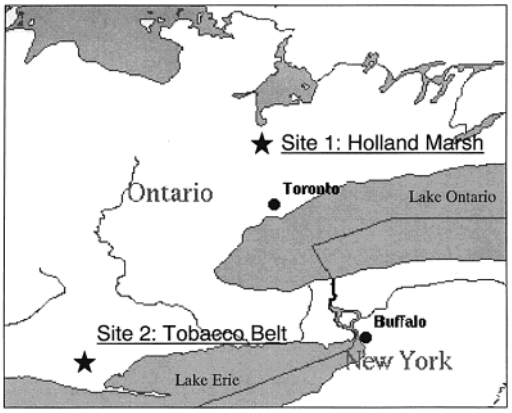

FIGURE 1. Map of southern Ontario showing the two sampling sites in the Holland Marsh (muck crop, site 1) and the Tobacco Belt (soybean, site 2).

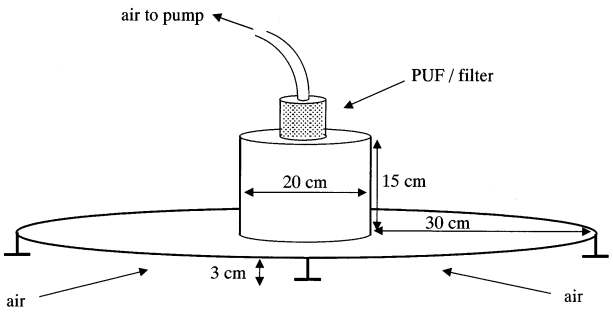

FIGURE 2. Three-dimensional side view of the field sampler.

Study Sites and Soil Description. The field measurements were carried out in the summer of 2000 at two agricultural sites in southern Ontario. Site 1 was situated in the Holland Marsh, north of Toronto, at the Muck Crop Research Station (see Figure 1). The soil was black and peaty with high organic carbon content and high moisture content. This soil had been analyzed for OC pesticides previously and was known to contain high residues of these compounds. To select an appropriate second site, a soil survey was carried out in the Tobacco Belt region (see Figure 1). Four different fields in the region (all within a 5-km radius) were sampled by taking 0−5-cm bulked grab samples. This included a tomato field, a soybean field, a tobacco field, and the Sidney Back conservation area on the site of a former fruit orchard. All fields were sandy agricultural soils with low organic carbon content. On the basis of the OC pesticide residues (see Results section) and sampling convenience (e.g., the presence of a power supply), the soybean field was chosen for site 2.

The characteristics of the soils are as follows: muck crop, water content 72% by mass, mass fraction organic carbon of the dry soil (ϕ_{OC}) 0.44, density of the dry soil solids (ρ_S) 1.53 kg L^{-1}; soybean, water content 20% by mass, mass fraction organic carbon of the dry soil (ϕ_{OC}) 0.018, density of the dry soil solids (ρ_S) 2.54 kg L^{-1}.

Design of the Field Sampler. The field sampler is a "hat-like" stainless steel dome with a 30 cm wide rim around it. The whole device is 80 cm in diameter and is supported by 4 legs to stand about 3 cm above the soil. The top of the dome contains a cylindrical holder for a polyurethane foam (PUF) plug that is connected to a conventional high-volume air sampling pump (see Figure 2) operated at ~200 L min^{-1}. The PUF plug is protected at the bottom of the holder by a glass fiber filter (GFF) that is resting on a steel mesh. Air is drawn under and through the device, and the gas-phase compounds are subsequently trapped on the PUF plug. As we are only interested in compounds present in the gas phase, the GFF serves as a barrier against soil or other particles but is not analyzed.

Because it is close to the soil surface, the sampler collects chemicals in the stagnant layer of air just above the soil surface. The large diameter of the sampler (80 cm) results in a slow face velocity of approximately 2−5 cm s^{-1} at the sampler perimeter. Thus, the stagnant layer is sampled slowly with minimal disturbance.

Calculation of K_{SA} and Q_{SA}. The soil−air partition coefficient (K_{SA}) can be calculated using the following simple equation (*4*):

$$K_{SA} = C_S/C_{A,eq} \quad (1)$$

where C_S is the soil concentration (pg m^{-3}, as determined by solvent extraction) and $C_{A,eq}$ is the equilibrium air concentration (pg m^{-3}, as determined by the K_{SA} apparatus).

If the system is not at complete equilibrium, it is incorrect to use the term K_{SA}. Instead, we then have to use the soil−air quotient (Q_{SA}), which is defined by

$$Q_{SA} = C_S/C_A \quad (2)$$

where C_S is the soil concentration (pg m^{-3}, as determined by solvent extraction) and C_A is the air concentration (pg m^{-3}) determined by the K_{SA} apparatus.

Note that the soil concentration is expressed on a volume basis (obtained by multiplying the soil concentration in pg g^{-1} dry weight by the density of the dry soil solids), so that K_{SA} and Q_{SA} are dimensionless. As mentioned earlier, K_{OA} is often used as a surrogate for environmental organic phases including soil organic matter. It has been used successfully in soil−air exchange models for pesticides (*1*) and PCDD/Fs (*14*). Using an expression derived by Karickhoff (*5*), Hippelein and McLachlan (*2*) predicted the following linear relationship between K_{SA} and K_{OA}:

$$K_{SA} = 0.411\rho\phi_{OC}K_{OA} \quad (3)$$

where ϕ_{OC} is the fraction organic carbon of the soil and ρ is the soil density (kg L^{-1}). They found that their results agreed very well with the Karickhoff model for PCBs, chlorobenzenes, and PAHs in a mineral-rich soil (*2*). In the present study we will investigate whether this predictive model is applicable to OC pesticides in different agricultural soils with varied organic contents.

Methods

Field Measurements. The test area was prepared by clearing a space of several meters in diameter and raking the soil to make it as level and homogeneous as possible, taking away stones, roots, and plants. A composite sample of the top ~2 cm of surface soil was then taken from the raked area for determination of soil residues. The PUF plug and the GFF were loaded in the holder just before the start of the measurement, taking care to avoid contact with any soil. The sampler was then placed carefully over the raked area and adjusted to approximately 3 cm over the soil.

Two measurements were taken using the sampler at the Muck Crop Research Station (site 1, muck crop), and three measurements were taken at the soybean field in the Tobacco Belt (site 2, soybean). Temperature and relative humidity (RH) were measured under the sampler several times during the sampling, using a fast-response digital hygrometer (accuracy: RH ±1.5%, temperature ±0.2 °C; VWR Canlab, Mississauga, ON, Canada) laid on the soil surface without touching the soil directly. We expect this to be a reasonable approximation of the conditions at the soil−air interface. The same setup was used at site 2 (soybean) with the addition of a second sampler (PS-1 semi-high-volume air sampler) at

TABLE 1. Sampling Conditions for Air Measurements at the Muck Crop and Soybean Sites

	date	start	stop	flow (L min^{-1})	air vol (L)	temp (°C)	RH (%)
Site 1 (Muck Crop)							
K_{SA} device	12/7/2000	11:05	14:11	340	63 300	23.8	80
	12/7/2000	14:39	19:15	388	107 000	23.9	94
Site 2 (Soybean)							
K_{SA} device	3/10/2000	09:38	12:23	270	44 600	16.8	88
	3/10/2000	12:29	14:42	257	31 600	18.0	73
	3/10/2000	15:18	18:33	126	24 600	14.7	81
ambient air	3/10/2000	09:50	13:35	340	76 500	21.6	55
	3/10/2000	13:42	18:27	343	97 600	21.4	56

150 cm above the soil for measuring ambient air concentrations (i.e., the conventional high volume method). A summary of sampling conditions is given in Table 1. The maximum variation in temperature during the sampling period was 2 °C at the muck crop site and 7 °C at the soybean site. The RH showed a maximum variation of 25% and 29%, respectively.

Sample Extraction and Analysis. The soils were mixed with Na_2SO_4 and ground using a mortar and pestle until a granular consistency was achieved. They were fortified with a recovery spike containing α-HCH-d_6 and *p,p′*-DDT-d_8 and extracted in a Soxhlet apparatus for 20 h using dichloromethane (DCM). The extracts were reduced in a rotary evaporator under vacuum to ∼5 mL, transferred to a vial and reduced under a gentle nitrogen flow to 0.5−1 mL, and then cleaned on a 1-g alumina column. The column was washed first with 2 vol (∼10 mL) of 5% DCM in petroleum ether and, after application of the sample, was eluted with 10 mL of 5% DCM in petroleum ether under a minimal nitrogen flow. The sample was then reduced again to 1 mL and transferred to a 2-mL GC vial using isooctane. The sample was further reduced to 0.5 mL, and mirex was added as the internal standard for volume correction. The soil extracts were analyzed on a Hewlett-Packard GC-ECD (60 m DB5 column from J&W Scientific, 0.25 mm i.d., 0.25 μm film thickness) operated with hydrogen carrier gas at 50 cm s^{-1}. The temperature program was as follows: 90 °C for 0.5 min, 15 °C min^{-1} to 160 °C, 2 °C min^{-1} to 260 °C, held for 6 min. Injector and detector temperatures were at 250 and 300 °C, respectively.

The PUF plugs were spiked with the deuterated recovery spike and extracted in a Soxhlet apparatus for 20 h using petroleum ether and further cleaned up and analyzed in the same manner as the soils. The GFFs were not extracted. The following OC pesticides were screened for and routinely detected in the samples (in elution order): α-HCH, hexachlorobenzene (HCB), β-HCH, γ-HCH, heptachlor (HEPT), aldrin, heptachlor epoxide (HEPX), *trans*-chlordane (TC), *o,p′*-DDE, *cis*-chlordane (CC), *trans*-nonachlor (TN), dieldrin, *p,p′*-DDE, *o,p′*-DDD, endrin, *p,p′*-DDD, *o,p′*-DDT, and *p,p′*-DDT.

The water content (mass %) of the soils was determined by drying an aliquot of the soil at 105 °C until a constant weight was achieved. The density of the dry soil solids was estimated by drying a portion of the soil and then grinding to a powdery consistency using a mortar and pestle. A known amount of the soil was then added to a known volume of water in a graduated cylinder, and the change in mass and volume was recorded. The organic carbon content (mass %) of the soils was determined as described elsewhere (*15*).

Chiral Analysis and Test of Equilibrium. Several of the OC pesticides measured in this study are chiral, existing as a pair of non-superimposable mirror images, designated as (+) and (−) enantiomers on the basis of their interaction with plane polarized light. These include α-HCH, CC, TC, *o,p′*-DDT, HEPT, and HEPX. The compounds are produced as a racemate with 50% of the (+) form and 50% of the (−) form. Physical processes are not able to distinguish between the two enantiomeric forms; hence, they exhibit identical response factors in chemical analysis and volatilize from soil at the same rate. However, biological processes may preferentially degrade one enantiomer in soil resulting in a nonracemic signature. This signature is described using the enantiomer fraction (EF), which is the fraction of the (+) form that is present (i.e., $EF = A_+/(A_+ + A_-)$ where A is the peak area) (*16*, *17*). By comparing the chiral signature of the air sampled at 3 cm to the signature in the soil and in ambient air, the equilibrium status of the air sampled at 3 cm can be investigated.

Several extracts of soil, ambient air, and air sampled by the field sampler were selected for enantiomeric analysis. Chiral pesticides were determined by gas chromatography−negative ion mass spectrometry (GC−NIMS) on a Hewlett-Packard 5890 GC-5989B MS engine with methane at a nominal pressure of 1.0 Torr and an Agilent 6890 GC-5973 MSD with a methane flow of 2.2 mL min^{-1}. The chiral column used for enantiomeric analysis was the BGB-172 (20% *tert*-butyl dimethylsilylated β-cyclodextrin in OV-1701, 30 m × 0.25 mm i.d., 0.25 μm film thickness, BGB Analytik AG, Switzerland) operating at a He carrier gas flow of 40 cm s^{-1}. The temperature program was 90 °C, hold for 1.0 min, 15 °C min^{-1} to 160 °C, 1.0 °C min^{-1} to 210 °C, hold for 10.0 min, 20 °C min^{-1} to 230 °C, hold for 15.0 min. Other conditions were as follows: splitless injection (split opened after 1.5 min), injector 230 °C, transfer line 230 °C, ion source 150 °C, and quadrupole 100 °C. Resolved enantiomers were (target/qualifier ions): α-HCH (255/257), HEPX (316/318), TC and CC (410/408), and *o,p′*-DDT (246/248). Quality control issues with enantiomeric analysis are precise integration of enantiomer peaks areas and elimination of interferences with the enantiomer peaks. Racemic standards were repeatedly injected to determine the reproducibility of measuring the area of the EF. Average EF values of the standards were 0.500 ± 0.002 for α-HCH, 0.498 ± 0.003 for HEPX, 0.498 ± 0.002 for TC, 0.502 ± 0.003 for CC, and 0.502 ± 0.004 for *o,p′*-DDT. The criterion used for peak purity was agreement of the target/qualifier ion ratio within ±5% of the standard values.

QA/QC. Blanks were included with the soil samples (extraction of a thimble filled with Na_2SO_4; one for every 5 soils extracted) and the air samples (extraction of a PUF field blank; one for every 5 PUFs extracted). Blanks were treated the same as the samples throughout the method. Blanks were pooled to calculate the mean blank, and the limit of detection (LOD) was then calculated as 3 times the standard deviation (SD) of the mean blank. The only compounds routinely detected in the blanks were dieldrin, *p,p′*-DDE, and *p,p′*-DDT. For *p,p′*-DDT, large concentration differences were encountered between blanks, up to 1 order of magnitude. This resulted in a high LOD, which had an impact on the reliability of the results for this compound.

The reproducibility of the soil extraction method was tested by extracting the soils from both sites in triplicate. The relative standard deviation (RSD) ranged from 1.4% to 16.5% for the soybean soil and from 0.9% to 12.4% for the Muck soil for the different compounds.

Recoveries were routinely monitored in every sample using the deuterated recovery spikes (α-HCH-d_6 and *p,p′*-DDT-d_8) that were chromatographically resolved from their unlabeled analogues. The average recovery for α-HCH-d_6 was 87% (range 55−128%), and for *p,p′*-DDT-d_8 it was 97% (range 60−148%). An additional recovery test was performed by spiking a solution containing all OC pesticides into a blank thimble with Na_2SO_4 ($n = 2$). Average recovery after blank subtraction was 102% ranging from 73% to 137%. This excludes the results for *p,p′*-DDT for which the recoveries were very inconsistent because of the large mean blank value

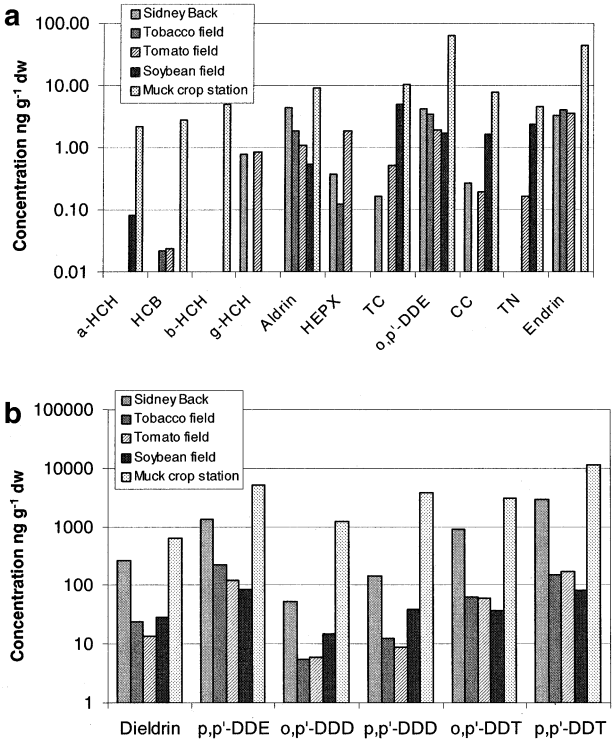

FIGURE 3. Soil concentrations (ng g^{-1} dw) (a) for the fields analyzed in the Tobacco Belt soil survey (Sidney Back conservation area, tobacco field, tomato field, soybean field) and (b) for the soil from the Muck Crop Research Station north of Toronto (note that the *y*-axes are on a log scale).

and the large difference between the various blanks. However, as shown above, the *p*,*p*′-DDT-d_8 recoveries are always within the acceptable range.

Results and Discussion

Soil Concentrations. Southern Ontario has traditionally been a region of intensive agriculture, in particular the two regions selected for this study. Figure 3 shows the soil concentrations from the Tobacco Belt (4 sites: Sidney Back conservation area, tobacco field, tomato field, and soybean field) and Holland Marsh (Muck Crop Research Station). The highest concentrations in all soils were found for dieldrin and the individual DDTs (except *o*,*p*′-DDE). Concentrations for these compounds range between 10 and 10 000 ng g^{-1} dw. The Sidney Back conservation area and the Muck Crop Research Station have consistently higher concentrations of these compounds, generally 1 order of magnitude higher than the other sites (see Figure 3b). The other pesticides are found at concentrations generally ranging from 0.1 to 10 ng g^{-1} dw with no clear differences between the sites. Because there was no power supply available at the Sidney Back conservation area, the soybean field was chosen as the site for the K_{SA} measurements in the Tobacco Belt. The mean pesticide concentrations in soil from the soybean field and from the muck crop field are presented in Table 3. As a comparison, a survey of a range of organic chemicals in Canadian soils conducted in 1989 found the highest concentrations in Ontario to be for *p*,*p*′-DDT (range 7−50 000 ng g^{-1}), *o*,*p*′-DDT (range 1.6−14 000 ng g^{-1}), and *p*,*p*′-DDE (range 1.8−7400 ng g^{-1}) (*19*). In that study, the lowest concentrations of DDT compounds were found in a cornfield, and the highest concentrations were found in an orchard. This agrees with our results for the Tobacco Belt, where the highest concentrations were found in the Sidney Back conservation area, which is on the site of a former fruit orchard. This is consistent with the fact that one of the few applications of DDT allowed

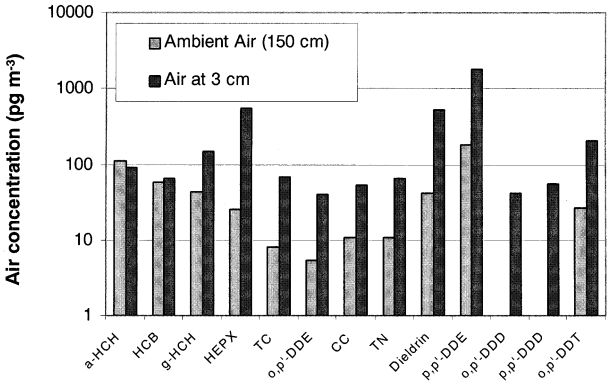

FIGURE 4. Ambient air concentration (at 150 cm) and air concentration measured by the field sampler (at 3 cm) for the soybean soil (pg m^{-3}).

after 1970 was the use for control of pests on apples before it was banned altogether in 1973 (*20*). In another study, which surveyed soil concentrations of DDT in orchards in Ontario, an average of 160 ng g^{-1} DDD, 3600 ng g^{-1} DDE, and 3400 ng g^{-1} DDT were found in orchards near Simcoe in the Tobacco Belt area (*20*). From these results, it follows that southern Ontario soils are a potential source for regional recycling of OC pesticides and are likely to contribute to observed regional air concentrations of these chemicals now and in the future.

Concentration Gradient over the Soybean Field. One way of assessing the source strength of the re-emission process is to look at concentration gradients over the soil, comparing the air concentration at 3 cm (dominated by emissions out of the soil and at/close to equilibrium with it) and the air concentration at 150 cm (combination of re-emissions from the soil and regional/long-range transport). The size and the direction of the gradient provides information about the importance of re-emissions from the soil with respect to the local air concentrations. Figure 4 shows the mean ambient air concentration (at 150 cm) and the mean air concentration at 3 cm for various OC pesticides above the soybean soil (see also Table 3). Note that the *y*-axis is on a log scale. For most compounds, there is a gradient from the soil to the air, indicating that the soil is supplying the air. However, for α-HCH and HCB, the air concentration at 150 cm is very similar to the concentration at 3 cm, suggesting that the ambient air and the soil are at or close to equilibrium for these compounds. This can be expected, as these are the more volatile compounds (have the lowest K_{OA} values of the compounds studied), will have more rapid equilibration times, and are generally well-mixed in the environment (*21*−*23*).

Equilibrium Status of the Air Sampled. Chiral pesticides that exist in soil may experience enantioselective breakdown resulting in a shift in the EF away from the racemic value of 0.5. This signature will be reflected in the stagnant layer of air above the soil if equilibrium exists between the soil and the air. The signature for background or ambient air will most likely be different. In the event that the background air is influenced by LRT of pesticides from areas where these compounds are still used, the background air will reflect a "fresher", less degraded signature with an EF that is closer to racemic (*18*).

Results of chiral analysis of the samples from the soybean soil experiments are presented in Table 2 (mean ± SD from replicate analysis) for TC and CC. Of the two chlordane isomers, TC shows the greatest difference in EF between soil (EF = 0.408 ± 0.008) and ambient air (EF = 0.441 ± 0.010). The air sampled by the K_{SA} apparatus has a mean EF of 0.407 ± 0.008, which is a strong indication that equilibrated air has

TABLE 2. Mean Enantiomer Fractions (EF) in Soybean Soil and Air Samples for *trans*-Chlordane (TC) and *cis*-Chlordane (CC)

	TC		CC	
	EF	SD	EF	SD
soil ($n = 4$)	0.408	0.008	0.557	0.006
air at 3 cm ($n = 9$)	0.407	0.008	0.556	0.007
air at 150 cm ($n = 6$)	0.441	0.010	0.524	0.004

indeed been sampled. The results for CC confirm this suspected equilibrium status, showing a mean EF of 0.556 $\pm$ 0.007 for the air sampled by the K_{SA} apparatus and 0.524 $\pm$ 0.004 for ambient air as compared to an EF of 0.557 $\pm$ 0.006 in soil. Results for other compounds could not be reported because of chromatographic interferences. Using an equation given by Harner et al. (*16*), the fraction of compound in the air residue at 3 cm that originates from the soil can be calculated from the EFs in the soil, in the air at 3 cm, and in the background air at 150 cm. A propagation of errors was also carried out to investigate the uncertainty in this calculation. We calculated that the fraction of compound in the air residue at 3 cm that has originated from the soil is 104.2 $\pm$ 33.5% for TC and 96.3 $\pm$ 26.4% for CC. This calculated fraction is very near the value of 100%, which would be expected in an equilibrium situation. However, even though the precision of the chiral analysis is high (RSD < 2.3%), the propagation of errors shows that there is a substantial uncertainty associated with the calculated fraction. Therefore, we cannot say with absolute certainty that all the air sampled by the apparatus at 3 cm was in equilibrium with the soil. There is a chance that some of the compound sampled at 3 cm originated from ambient air. Because of the much lower ambient air concentrations, it is thus possible that the apparatus actually sampled a significant amount of ambient air, causing our equilibrium air concentration to be underestimated. For example, if the fraction of TC originating from the soil were 85% instead of 100%, this would result in an underestimation of the equilibrium air concentration by a factor 3. If the true mixing ratio of equilibrium and ambient air were known, then a correction could be made to account for this in the calculation of K_{SA}. However, the chiral analysis does not offer enough precision to do this; therefore, we will report Q_{SA} values instead of K_{SA} values throughout the paper. Nevertheless, the chiral analysis shows that the air sampled is close to equilibrium with the soil; therefore, Q_{SA} can be considered an approximation of the "true" K_{SA} value.

Despite these uncertainties, the tracer study using chiral compounds was the most feasible and definitive way of checking the equilibrium condition. An alternative approach would be to alter the sampling rate and observe changes in the air concentration, as was previously done in fugacity meter studies (*2*, *4*). Constant air concentrations over a range of flow rates would be indicative of equilibrium. However, because the required air sampling times are on the order of several hours, it was not possible to vary the flow rate or height of the sampler over a range of values while maintaining constant meteorological conditions (i.e., air and soil temperatures, relative humidity, and wind speed will vary considerably over a period of a few hours, affecting soil–air exchange).

Soil–Air Quotients and Relation with K_{OA}. Mean soil concentrations (C_S, pg g^{-1} dw), mean ambient air concentrations at 150 cm ($C_{A,amb}$, pg m^{-3}), mean air concentrations at 3 cm (C_A, pg m^{-3}), and mean calculated log Q_{SA} values at the muck crop and soybean sites are presented in Table 3. Soil–air quotients were calculated using eq 2. Also included in Table 3 are values for log K_{OA} of selected OC pesticides at 25 °C (*24*). Figure 5a shows the relationship between log Q_{SA} and log K_{OA} for the results obtained at the muck crop and soybean sites, including replicate measurements at each site. K_{OA} values were calculated at the temperature of the experiment using temperature-dependent expressions for K_{OA} (*24*). From Figure 5a, it is clear that the replicate measurements of Q_{SA} agree very well and that a linear relation exists between log Q_{SA} and log K_{OA}. The regression lines for log Q_{SA} with log K_{OA} are similar for the two soils with a slope of 0.748 for the muck crop soil and 0.943 for the soybean soil. Statistical analysis carried out on the regressions (ANOVA) showed that there is no significant difference between the two slopes at the $p < 0.05$ level.

TABLE 3. Mean Soil Concentrations (C_S, ng g^{-1} dw), Mean Ambient Air Concentrations at 150 cm ($C_{A,amb}$, ng m^{-3}), Mean Air Concentrations at 3 cm (C_A, ng m^{-3}), Log Soil–Air Quotients (log Q_{SA}) at Sites 1 and 2, and Measured Log Octanol–Air Partition Coefficients (log K_{OA}) at 25 °C

	site 1 (Muck Crop) (23.9 °C)				site 2 (soybean) (16.5 °C)					
	C_S (ng g^{-1} dw)		C_A (ng m^{-3})	log K_{SA}[a]	C_S (ng g^{-1} dw)		$C_{A,amb}$ (ng m^{-3})	$C_{A,eq}$ (ng m^{-3})	log Q_{SA}[a]	log K_{OA}[b]
	mean	SD	mean	mean	mean	SD	mean	mean	mean	
α-HCH	2.2	0.02	0.40	6.93	0.082	0.014	0.11	0.091	6.38	7.61
HCB	2.7	0.23	0.23	7.27	nd[c]		0.058	0.064		7.38
β-HCH	5.0	0.46	0.35	7.34	nd		nd	nd		8.88
γ-HCH	nd		nd		nd		0.044	0.15		7.85
HEPT	nd		0.038		nd		nd	nd		7.64
aldrin	9.3	1.2	0.20	7.85	0.54	0.046	nd	nd		8.08
HEPX	nd		nd		nd		0.025	0.55		
TC	10	0.47	0.19	7.93	5.1	0.45	0.0082	0.068	8.30	8.87
o,*p*′-DDE	64	2.7	0.66	8.17	1.7	0.21	0.0053	0.039	8.06	
CC	7.8	0.20	0.096	8.09	1.6	0.18	0.011	0.054	7.96	8.92
TN	4.5	0.13	0.047	8.18	2.4	0.28	0.011	0.064	8.05	9.29
dieldrin	640	27	4.4	8.35	29	3.1	0.041	0.53	8.17	8.90
p,*p*′-DDE	5100	310	17	8.65	85	1.1	0.18	1.8	8.08	9.68
o,*p*′-DDD	1200	78	1.7	9.05	15	1.2	nd	0.042	8.97	
endrin	45	0.94	0.20	8.53	nd		nd	nd		8.14
p,*p*′-DDD	3700	220	1.8	9.50	39	2.9	nd	0.056	9.24	10.10
o,*p*′-DDT	3000	160	5.3	8.93	37	4.5	0.027	0.20	8.68	9.45
p,*p*′-DDT	11000	240	8.7	9.31	84	1.2	nd	nd		9.82

[a] Log Q_{SA} was calculated using eq 2. [b] Values at 25 °C (*24*). K_{OA} was corrected for temperature in Figures 6 and 7 using regression constants from ref *24*. [c] nd, not detected.

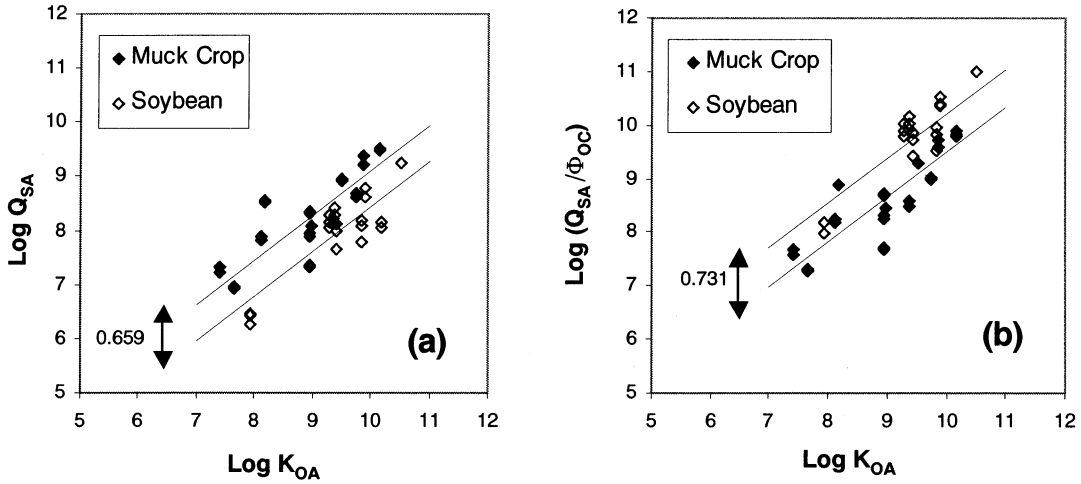

FIGURE 5. Log Q_{SA} vs log K_{OA} for the muck crop soil and the soybean soil showing the replicate measurements. (a) Q_{SA} calculated using eq 2. (b) Q_{SA} corrected for ϕ_{OC}.

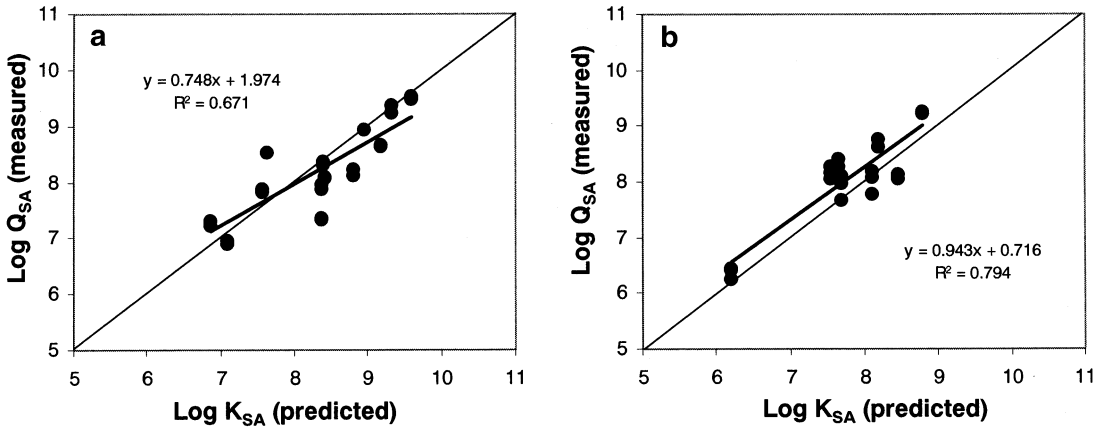

FIGURE 6. Predicted K_{SA} vs measured Q_{SA} for (a) the muck soil and (b) the soybean soil.

It is generally assumed that hydrophobic compounds such as OC pesticides partition mainly into the organic carbon fraction of the soil (*5*, *25*−*27*). The expressions for K_{SA} and Q_{SA} (eqs 1 and 2) do not take into account differences in the organic carbon content of the two soils. In Figure 5b, Q_{SA} values have been corrected for the mass fraction organic carbon (ϕ_{OC}) for each soil. If organic carbon content alone controlled partitioning, correcting for it would bring the two lines closer together. However, Figure 5b shows that (assuming the same slope for both lines using ANOVA) the difference between the intercepts of the lines for muck crop and soybean increases slightly when correcting for organic carbon, suggesting that organic carbon content alone cannot explain the partitioning to these soils. Various authors have shown that the nature of the soil organic matter (e.g., aromaticity) has an influence on the sorbing capacity of the soil for organic chemicals (*25*, *28*, *29*). Another factor that might affect partitioning to soils is the relative humidity of the soil. Various studies have in fact shown that soil sorption is greatly affected by soil water content (*31*, *32*), with increased sorption observed at lower soil water contents (*34*). It is thought in general that sorption to mineral surfaces dominates in soils with low water contents (*30*). Although it is the surface soil that is in exchange with the air, the water content of the surface soil is difficult to measure. Therefore, the water content of the bulk soil was measured. The lower relative humidity of the air above the soil at the soybean site as compared to the muck site suggests that the moisture of the soybean surface soil might have been significantly lower than the moisture of the bulk soil, and this could have led to increased sorption to the soybean soil.

It has been shown previously that eq 3 can accurately predict K_{SA} for a range of POPs in a sandy loam soil (*2*). Here we test eq 3 for OC pesticides in two distinct soil types. Predicted K_{SA} values were calculated by substituting values for the soil density (ρ_S), fraction organic carbon (ϕ_{OC}), and calculated K_{OA} values at the temperature of the experiment into eq 2. The predicted log K_{SA} values are plotted against the measured log Q_{SA} values in Figure 6. The K_{SA} values derived from the Karickhoff relationship (eq 3) are generally within a factor of ∼2−3 of measured Q_{SA} values, and the slopes of the regression lines are 0.748 with a standard error of 0.107 (95% confidence interval 0.527−0.968) and an r^2 of 0.671 for the Muck soil and 0.943 with a standard error of 0.102 (95% confidence interval 0.730−1.155) and an r^2 of 0.794 for the soybean soil. The factor 2−3 difference could be due to an underestimation of the "equilibrium" air concentration under the sampler as explained previously. Alternatively, other uncertainties in the measurements are expected, for example, because of meteorological factors and the large difference in soil type/organic matter content of the soils. Considering these uncertainties, we suggest that the agreement is satisfactory for the use in environmental fate models. However, we also recognize that further studies are required to further investigate the equilibrium question and the influence of soil characteristics and meteorological factors on K_{SA}. For example, the influence of temperature is further investigated in ref *13*.

Fugacity Calculations. Fugacity is a measure of chemical potential or partial pressure of a chemical in a particular medium and controls the movement of chemicals between media. Chemicals strive to establish equilibrium (i.e., equal

TABLE 4. Fugacity Fractions (ff = $f_{soil}/(f_{soil} + f_{air})$) for the Soil−Air System at the Soybean Site[a]

	air at 150 cm	air at 3 cm		air at 150 cm	air at 3 cm
α-HCH	0.65	0.59	dieldrin	**0.99**	**0.80**
TC	**0.99**	**0.81**	*p,p′*-DDE	**0.89**	0.29
CC	**0.94**	0.61	*p,p′*-DDD		**0.74**
TN	**0.91**	0.43	*o,p′*-DDT	**0.98**	**0.76**

[a] Boldface values represent ff values that fall outside the uncertainty range for the equilibrium situation.

fugacity) in the soil−air system (*33*). A detailed explanation of how to calculate fugacities in soil and air is given elsewhere (*1*, *33*). To assess the equilibrium status of the soil−air system, the fugacity fraction (ff) for the chemical in question can be calculated using

$$\text{ff} = f_{soil}/(f_{soil} + f_{air}) \quad (5)$$

A fugacity fraction of 0.5 indicates that the chemical is near soil−air equilibrium. Fugacity fractions greater than 0.5 indicate that more than half of the chemical potential (in the soil−air system) is attributed to the soil, resulting in net transfer of chemical from the soil to the air (i.e., the soil is a source). Values less than 0.5 indicate the opposite—that the soil is a sink and net transfer occurs from the air to the soil. Using the soil and air concentration results from the soybean field, we have calculated fugacity fractions for a selection of OC pesticides. Fugacity fractions for the soil−air system at 3 and 150 cm are shown in Table 4. A propagation of the errors that are inherent in the calculation shows that the equilibrium situation is represented by a ff of 0.5 ± 0.22 (i.e., a range of 0.28−0.72), if we assume a 25% RSD in C_A, C_S, and K_{OA} (used to calculate K_{SA}) and a 5% RSD in temperature (used to calculate Z_{air} and f_{air}). These errors are conservative estimates as the literature shows that RSD of air and soil samples and K_{OA} measurements is usually around 15% (e.g., refs *24*, *34*, and *35*). The fugacity fractions at 3 cm of most compounds fall within or just outside this uncertainty range, and the ff values at 3 cm are lower than at 150 cm for all compounds. The deviation from 0.5 for the measurements at 3 cm is most likely related to the uncertainty in the predicted values of K_{SA} that were used in the calculation of ff. The ff values at 150 cm for all compounds except α-HCH fall outside and above the range of equilibrium values; thus, we can be fairly confident that for these compounds the soil and ambient air at 150 cm are in disequilibrium and that soil will act as a source to the atmosphere. This agrees with the observed concentration gradients in Figure 4. For α-HCH, the large uncertainty associated with the calculation prohibits any definite statements regarding net flux direction, but the ff of near 0.5 agrees with the observed smaller concentration gradient in Figure 4.

Future Work and Recommendations. Although the results from this preliminary study are very useful, there are still some uncertainties associated with the field sampling that will need further investigation. For example, temperature and relative humidity of the air and the soil can vary over the sampling period of several hours and are more difficult to measure than in a controlled environment. The temperature in the very small boundary layer at the air−soil interface is most likely to control the partitioning. However, this is difficult to measure. Therefore, we have to measure the temperature either in the soil or on the soil or in the air just above the soil. This will probably introduce some error in the measurements. Similarly, the moisture content of the surface soil is difficult to measure, and this might influence the results as discussed before. Further validation of the device will be necessary under varying conditions such as soil type, temperature, humidity, and wind speed. Finally, more conclusive evidence is needed on the equilibrium status of the air measured by the sampler.

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