Volatilization of Organochlorine Pesticide Residues
from U.S. Agricultural Soils

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Introduction

Historically, large quantities of organochlorine (OC) pesticides were applied to agricultural soils in the United States. Compounds of concern include toxaphene which was once heavily used in Alabama and other "cotton belt" states, chlordanes which were popular in the "corn belt" states (e.g. Ohio, Illinois, Indiana, Pennsylvania), and DDT and aldrin/dieldrin which received widespread usage. The toxicity, bioaccumulation and environmental persistence of these chemicals resulted in bans and restrictions on use.

All of these OCs have been banned for 10-25 years, yet they still exhibit significant atmospheric burdens and continue to cycle and be dispersed through the global environment (1). One explanation for their prolonged presence is an "old" source - namely re-volatilization of residues from regions where there was significant usage.

This issue is addressed here by first investigating residue concentrations of OC pesticides in "corn belt" (2) and "cotton belt" soils. A dynamic, 3-soil layer, fugacity based model is then used to predict the contribution of these "old" sources to atmosphere. Model results are compared to measured air concentrations.

Experimental Methods

Soil Samples

Surface soil cores (~8 cm) were collected from agricultural fields in Alabama (cotton belt) and several "corn belt" states - Ohio, Illinois, Indiana, Pennsylvania (2). Multiple cores from each field were pooled and sieved to provide uniform samples. Residues were determined by weighing out a ~10g aliquot, mixing with anhydrous sodium sulfate and soxhlet extracting in cellulose thimbles overnight using dichloromethane. Extracts were reduced in volume by rotary evaporation, solvent exchanged into isooctane and reduced to 1 mL using a gentle

stream of nitrogen. Extracts were purified on a 1-g column of neutral alumina (6% added water), eluted with 20 mL of 5% dichloromethane in petroleum ether and the eluate was reduced to 1 mL in isooctane. Analysis was performed by GC-ECD for the "corn-belt" soils and by both GC-ECD (Hewlett Packard 5890) and GC-negative ion mass spectrometry (GCNIMS) (Hewlett Packard 5890GC-5989B MS Engine) in SIM mode for the Alabama samples. Details are presented elsewhere *(2,3)*. Water and organic carbon content were determined for all soil samples.

Air Samples
Air samples were collected using a PS-1 high volume sampler (10 cm dia. glass fibre filter + polyurethane foam (PUF) plug) from January to November 1996 in Muscle Shoals, Alabama. Air volumes were approximately 300 m^3. PUF plugs were soxhlet extracted using petroleum ether. Extracts were reduced by rotary evaporation, transferred to isooctane and reduced to 1 mL by nitrogen blowdown. Extracts were purified on silicic-acid to separate OC pesticides from PCBs. Samples were analyzed by GC-NIMS as discussed above.

Soil-Air Exchange Model
A fugacity-based, 3-soil layer model (Fig. 1) *(4)* was used describe the volatilization of soil residues. The model is a numerical solution (1-day time step) to differential equations describing mass transfer between a well-mixed atmosphere and 3 well-mixed soil compartments of varying depths (0.1cm, 1cm and 10cm). The octanol-air partition coefficient, K_{OA}, was used to describe chemical partitioning between soil and air (soil compartments) and between aerosols and air (atmosphere compartment). Partition coefficients for soil-air (K_{SA}) *(5)* and aerosol-air (K_P) *(6)* were calculated using the following relations:

$$K_{SA} = 0.411 \, f_{OC} \, \rho \, K_{OA} \quad \text{and} \quad \log K_P = \log K_{OA} + \log f_{OC} - 11.91$$

where f_{OC} is the fraction of organic carbon in soil or aerosols and ρ is soil density. Values for K_{OA} were calculated from the literature as $K_{OA}=K_{OW}RT/H$ (where K_{OW} is the octanol-water partition coefficient and H is the Henry's law constant). Values of K_{OA} were corrected for temperature using slopes of sub-cooled liquid vapor pressure, i.e. ΔH_{VAP}. Other model input parameters include soil and air properties, and meteorological parameters.

The model predicts concentrations and fugacities for each soil layer and the atmosphere, and calculates rates associated with each process (arrow) shown in Fig. 1. Predicted air concentrations for Alabama are compared to the 1996 measurements in Muscle Shoals, and the predictions for the "corn belt" are compared with summary data for Sturgeon Point, Lake Erie *(7)*.

Results and Discussion
Soil residues were log-normally distributed *(2)* and geometric mean concentrations for selected chemicals are presented in Table 1. Very high concentrations were observed for toxaphene (221 ng/g soil) reflecting its heavy usage in Alabama during the past. Average soil organic carbon contents were 0.93±0.61% (Alabama) and 2.24±1.3% (corn belt).

Table 1. Geometric mean concentrations (ng/g soil) of selected pesticides in "cotton belt" and "corn belt" (2) soils and measured yearly average air concentrations. (ND=not determined)

	(soil concentrations, ng/g dry wt.)		(model and <u>measured</u> air concentrations pg/m^3)	
	"cotton belt"	"corn belt"	"cotton belt"	"corn belt" *
dieldrin	3.2	1.05	12, <u>49</u>	1.4, <u>27</u>
p,p'-DDE	16	3.75	20, <u>13</u>	0.66, <u>20</u>
t-chlordane	0.18	0.49	1.2, <u>49</u>	0.80, <u>14</u>
c-chlordane	0.25	0.43	1.1, <u>27</u>	0.65, <u>12</u>
toxaphene	221	ND	276, <u>198</u>	ND

* Sturgeon Point, Lake Erie (7)

Using surface soil residues as input, the soil-air model was run for selected chemicals. Results are shown for toxaphene in Fig. 2. Air concentrations predicted by the model are in fairly good agreement with measured values. The sudden increase in air and soil concentrations at Julian day 100 corresponds to a plowing event which acts to homogenize the soil in the top three layers. Over the course of a year only ~40% of toxaphene is depleted in the top 0.1cm of soil, with very little depletion in deeper layers. This depletion is more significant for more volatile chemicals (i.e. chemicals with lower values of K_{OA}) such as dieldrin and the chlordanes.

Modelled and measured air concentrations (Table 1) are in good agreement for dieldrin, p,p'-DDE and toxaphene in Alabama but underestimated for the chlordanes. Chiral analysis of the air in Alabama also suggests little or no contribution of chlordane from soils (8). Non-agricultural usage such as for termiticide control may be an alternate source. In the case of the "corn belt", the model results are lower than measured values for all 4 compounds suggesting a contribution from non-agricultural sources - possibly transport from the southern U.S. or from termiticide use. Lower air concentrations for the corn belt may also be attributed to the higher organic carbon content of these soils (2.2%) which in effect lowers the fugacity gradient for soil to air transfer.

Acknowledgements

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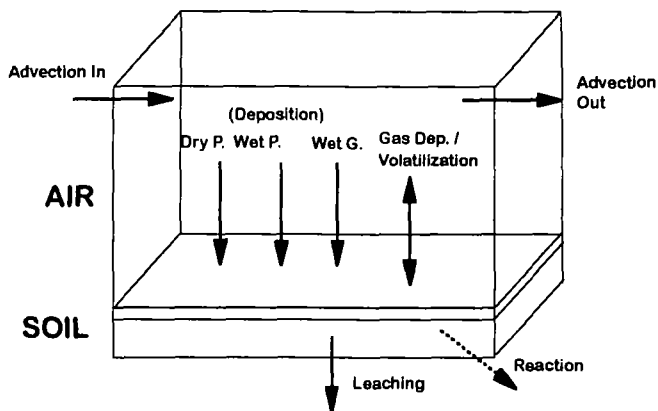(8)   Falconer, R. L. et al *Organohalogen Compd.* (in press)
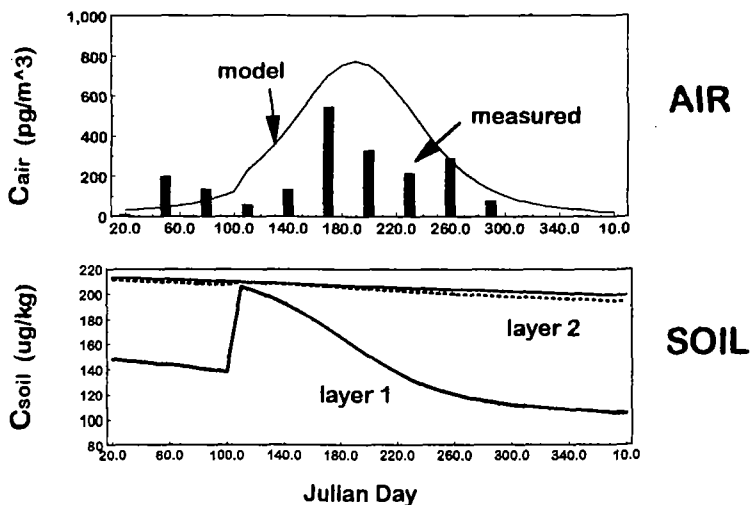
Figure 1. Soil-air exchange model.

Figure 2. Model results for air and soil and measured air concentrations for toxaphene in Alabama.