Development of a Solid Phase Fugacity Meter:

Initial Experiments with Spruce Needles

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Introduction

The atmosphere is the dominant pathway for the transport and dispersion of many organic pollutants in the environment. The high concentrations in arctic ecosystems of anthropogenic contaminants originating in the temperate regions is one manifestation of this process (Norstrom et al, 1988). Air bound compounds can re-enter the terrestrial environment by means of precipitation, particulate deposition, or direct transfer between the gas phase and solid surfaces. The latter phenomena is suspected to be the most significant process for plant accumulation of a large class of semi-volatile organic pollutants (Bacci et al, 1990). A thorough understanding of gas phase-solid surface transfer is thus essential for modelling environmental chemical fate.

Transport between the gaseous and solid phases is thought to be a reversible partitioning process controlled by concentration gradients. The mathematical description of such processes is simplified by introducing the fugacity concept. The fugacity of a substance can be understood as its tendency to escape from a phase (Mackay et al, 1981). If this tendency is equal in two adjoining phases, then a state of equilibrium exists. Differences in the fugacity of adjoining phases result in diffusive transport to the phase with the lower fugacity at a rate proportional to the fugacity difference. In order to determine the extent and direction of gas phase-solid transport, it is necessary to know the air and solid surface fugacities of the substance. While the gaseous fugacity can be easily determined from the air concentration, we are aware of no method for determining fugacities on solid surfaces.

In this paper we report on the development of a procedure to measure the fugacity of organochlorine compounds on spruce needle surfaces. This method also serves to check the hypothesis that gas phase-solid surface transfer is a reversible equilibrium process.

The Measurement Concept

We measured the needle surface fugacity indirectly. The needle surface was first allowed to come into equilibrium with a contacting air mass. At equilibrium the fugacities of the needle surface and the air must be identical by definition, assuming a reversible partitioning process. The concentrations of the compounds in this air mass were then measured, and the air fugacities (and hence needle surface fugacity) were calculated using the simple relationship below:

$$f = c*R^{-1}*T^{-1}*M^{-1} \quad \text{(MacKay et al, 1981)} \quad (1)$$

f: fugacity (Pa)
c: concentration $(g*m^{-3})$
R: gas constant $(mole*Pa^{-1}*m^{-3}*K^{-1})$
T: temperature (K)
M: molecular weight $(g*mole^{-1})$

Artificially contaminated needles were used for the initial experiments to reduce the size of the apparatus and to simplify the analysis. Spruce needles were exposed to a contaminated particulate free atmosphere for three weeks. It was assumed that an air-needle surface equilibrium was reached during this period. The substance concentrations in the contaminated atmosphere were measured. They allowed a

theoretical initial needle surface fugacity to be calculated, which served as the basis of comparison for the subsequent fugacity measurements.

The needles were then placed in a glass column, clean air was passed over them, and the substance concentrations in the outflowing air were measured. During the first set of experiments the flow rate of the air in the column was varied to determine the residence time at which equilibrium between the air and the needle surface was reached. This residence time was used for the subsequent measurements. A time series was then conducted, in which successive air samples were drawn over the same needles to obtain information about changes in the needle surface fugacity over time.

Experimental

Ten-year-old spruce trees (Picea omorica) were exposed to a contaminated atmosphere in a gas chamber containing the following substances: TCB (tetrachlorobenzene), QCB (pentachlorobenzene), HCB (hexachlorobenzene), -HCH und -HCH (hexachlorocyclohexane isomers), p,p'-DDE, p,p'-DDT, PCBs (polychlorinated biphenyls, a mixture of arochlor standards). The air concentrations in the chamber were maintained approximately constant at levels 1000 to 50,000 times above normal ambient air.

The concentrations in the gas chamber were determined by drawing 300 L of air through a trap containing 18 g of activated florisil. Every florisil trap was dosed with a mixture containing ^{13}C labelled standards of the following compounds: TCB, QCB, HCB, -HCH, p,p'-DDE, p,p'-DDT, PCB 101, PCB 153 (PCB numbering according to Ballschmitter and Zell, 1980). The florisil trap was subsequently eluted with 250ml n-hexane and the extract was evaporated to 25μl. GC/MS analysis was performed in the SIM mode on an HP-MSD 5890 equipped with an HP Ultra 2 fused silica capillary column.

After three weeks in the chamber the twigs containing the last year's growth were removed from the tree, packed in aluminum foil, and stored at -16°C. The substance concentrations in the needle were determined to aid in the interpretation of the results. The extraction and clean-up was conducted according to the method of Reischl (Reischl et al, 1987).

The fugacity meter is illustrated in Figure 1. It consists of a glass column enclosed in a water jacket and with a glass frit at the lower end. For the fugacity measurements 40g of the frozen needles complete with twigs were loosely packed into the 230 ml sample volume of the column. The air from a compressed air cylinder was introduced into a florisil trap to remove possible contaminants. It then flowed through a reflux cooler which helped bring the air to the desired column temperature (22°C for these experiments). After passing through the sample the air flowed through a glass fibre filter which removed any particulate bound matter in the gas stream. The contaminants which had diffused from the needle surface into the air were then collected on a 10 g florisil trap, which was extracted and analysed using the method described above. A flow meter measured the volume of the outflowing air, which ranged from 30 to 600 L per analysis. Preliminary experiments had shown no breakthrough of the substances on a 10g florisil trap using a 1000 L sampling volume.
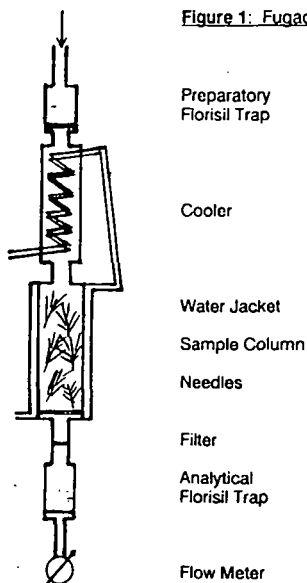

Figure 1: Fugacity Meter

Preparatory Florisil Trap

Cooler

Water Jacket

Sample Column

Needles

Filter

Analytical Florisil Trap

Flow Meter

Results

Figures 2 and 3 show the results of the residence time experiments for two typical compounds, QCB and -HCH. Concentration units were chosen for the graphs for the sake of clarity, but the fugacities can easily be calculated using equation 1. The residence time of the air in the column was varied from 4 to 170 s. Initially the air concentrations rose with increasing residence time, but extending the residence time beyond 30 s led to no further increase. Hence it was concluded that a residence time of 30 s was sufficient for the establishment of an equilibrium between the needles and the flowing air. This rapid achievement of equilibrium supports the assumption that an air-needle surface equilibrium was achieved during the 3 week exposure in the gas chamber.

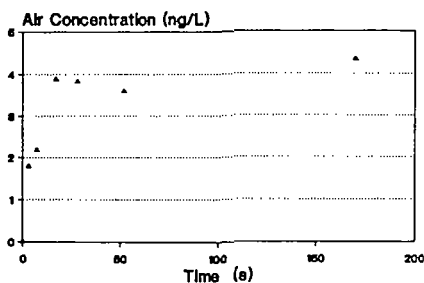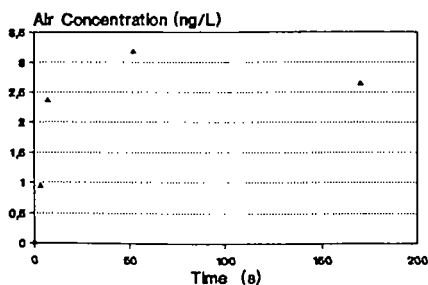Figure 2: Air Concentration of QCB for Different Residence Times

Figure 3: Air Concentration of -HCH for Different Residence Times

The upper lines in Figures 4 and 5 show the results for PCB 52 and HCB of the time series conducted with one needle sample. A total of 1260 L of air were blown through the column. The air concentrations are seen to decrease exponentially with time. One possible explanation is that the needle's contaminant burden was largely depleted by the experiment, leading to an ever lower fugacity. However, the measured needle concentrations showed that only 11% of the total burden of PCB 52 and 9% of HCB was lost to the air stream. This would explain a fugacity decrease of at most 11%, but over 75% was observed.

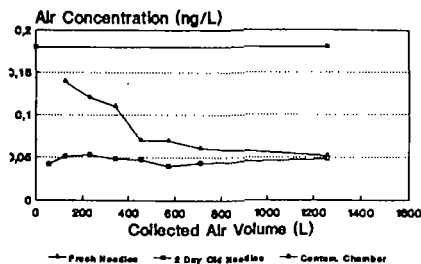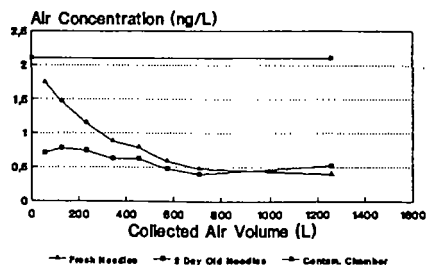Figure 4: Air Concentration of PCB 52 from Spruce Needle Time Series

Figure 5: Air Concentraion of HCB from Spruce Needle Time Series

The explanation for this lies with the short exposure of the tree in the gas chamber. Although the three weeks were likely sufficient for the establishment of an air-surface equilibrium, this was not the case for the needle interior. Investigations of the kinetics of air-whole needle accumulation have determined half lives of up to 20 weeks for these substances (McLachlan et al, 1989). The observed decrease in the needle surface fugacity is due to the diffusion of the contaminants from the needle surface into the needle interior.

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This hypothesis was tested by storing a sealed needle sample at room temperature for two days before packing it in the column. The results are illustrated on the lower lines of Figures 4 and 5. As expected, the initial surface fugacities are much lower than those from the freshly thawed samples. In this case the contaminants had no opportunity to leave the needles. During the two days at room temperature they diffused further into the needle, resulting in a decrease in the surface concentration (and hence fugacity).

Due to the various phenomena described above the initial needle surface fugacities had to be estimated by extrapolating the measured air concentrations to the 0 L value. From Figures 4 and 5 it is seen that an extrapolation of the air concentrations to the y-axis gives a value very close to the air concentration in the contamination chamber (represented by the horizontal line in the figures). Thus the theoretical and the measured surface fugacities are in near perfect agreement, well within the range of analytical error. This confirms that the air-needle surface transfer is a reversible process governed by equilibrium considerations. Furthermore, it demonstrates that surface fugacities can be measured using the method presented here.

Conclusions

1. Equilibrium between the desorbing needle surface and the gaseous phase is rapidly achieved for the compounds investigated (max. 30sec).
2. Contaminant transport from the gaseous phase to the needle surface is faster than transport within the needle.
3. The transfer process air-needle surface is a reversible phenomena governed by equilibrium considerations.
4. Contaminant fugacities on needle surfaces can be measured using the method presented here.

Further experiments are planned to clarify the influence of temperature and atmospheric humidity on the measurement of surface fugacity. This should yield valuable information on the influence of these parameters on air-plant partitioning of organic pollutants.

There is a considerable scientific effort currently investigating the use of plants as biomonitors of organic air pollutants (McLachlan et al, 1989; Bacci et al, 1987). They are based on correlations between plant concentrations and air concentrations of contaminants. This approach has several drawbacks, including variablity in the accumulation properties of plants with age and location, and interpretaiton difficulties caused by the plant's rapid accumulation but slow depuration of compounds in a variable environment. The fugacity meter could eliminate many of these problems. It investigates only the outer surface of the plant, which responds much more quickly to environmental changes than the complete organism. Moreover, the method is independent of plant properties. Further investigations of this application of the fugacity meter are intended.

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