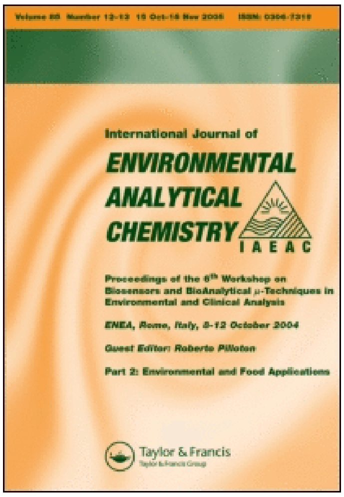

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DEVELOPMENT AND EVALUATION OF SAMPLING AND ANALYTICAL TECHNIQUES FOR INVESTIGATING AIR-WATER EXCHANGE OF CHEMICALS

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Gas exchange across the air-water interface is one of the three major transport pathways for atmospheric inputs of organic pollutants in the Great Lakes. It is essential to advance our knowledge of the air-water exchange processes to improve our understanding of the environmental pathways and fate of a variety of persistent and toxic chemicals. Two complementary prototype devices were developed and tested for direct characterization of air-water exchange processes. One was a sparger device which was used to determine the (truly) dissolved concentration of a given chemical in water, and hence its potential for diffusive transfer at the air-water interface. The other was a flux chamber with which the chemical mass transfer rate from the water surface to the atmosphere (or vice versa) was determined. Ambient air and air from the sparger and flux chamber were collected/concentrated on multi-bed adsorbent tubes, followed by thermal desorption GC-MS analysis. Collected water samples were filtered and then concentrated on adsorbent tubes which were subject to similar thermal desorption GC-MS analytical procedures. The combination of these techniques provides a useful means for the estimation of the mass transfer rates of chemicals across the air-water interface.

KEY WORDS: Atmospheric deposition, volatilization, air-water gas exchange, persistent and toxic organic pollutants, sparger, flux chamber.

INTRODUCTION

Atmospheric deposition of chemicals to water and volatilization from water to the atmosphere can be significant processes influencing both media and generally contribute to determining the fate of environmental contaminants. For example, gas exchange across the air-water interface is one of the three major transport pathways for atmospheric inputs of organic pollutants in the Great Lakes[1]. Different from wet and dry (atmospheric) deposition processes which are uni-directional, air-water exchange is a "two-way street", with the magnitude as well as the direction of the mass transfer determined by a number of parameters[2,3]. For many organic pollutants such as PCBs and DDTs, volatilization is a major output pathway in some lakes[4,5]. Recently it has been shown that air-water exchange is the most important process controlling PCB levels in both the air and water in Lake Superior[6]. It is essential to advance our knowledge of the

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air-water exchange process in order to improve our understanding of the environmental pathways and fate of a variety of priority chemicals.

While the direction and magnitude of the mass transfer of particular chemicals across the air-water interface can be estimated based on the measured air and water concentrations of the chemicals and their Henry's Law constants, uncertainties in gas exchange estimates are very large and the process is thus poorly quantified[3]. Direct measurement of the fluxes of persistent organic pollutants between the atmosphere and surface water represents an important topic in contemporary scientific research. Two complementary prototype devices were therefore developed and tested for direct characterization of air-water exchange processes. One was a sparger device which was used to determine the (truly) dissolved concentration of a given chemical in water, and hence its potential for diffusive transfer at the air-water interface. The other was a flux chamber with which the chemical mass transfer rate from the water surface to the atmosphere (or vice versa) was determined.

Acquisition of reliable analytical data was of crucial importance to the success of this study. This included two equally important procedures: 1) collection of surface water and ambient air samples, along with effluent air samples from the sparger and the flux chamber, and 2) chemical analysis of these samples for compounds of interest. Since the target compounds were present at very low concentrations in both air and water, high analytical sensitivities were required. Several sampling and analytical methods were evaluated or developed for determination of the target compounds in air and water samples, in order to permit the direct characterization of air-water exchange processes of chemicals in conjunction with the sparger and flux chamber sampling devices.

EXPERIMENTAL SECTION

Chemicals and supplies

The chemicals selected as target compounds for the sampling and analytical development represent typical organic compounds present in both the atmosphere and the waters of the Great Lakes, and are also a subset of the priority chemicals being considered in Annex 15 of the U.S.—Canada Great Lakes Water Quality Agreement. These compounds (and the purities and suppliers of the respective chemicals used in testing) are chloroform (99.8% min., Caledon Laboratories Ltd., Georgetown, ON), toluene (99.7% min., Caledon), chlorobenzene (99.5% min., Caledon), 1,4-dichlorobenzene (99+%, Aldrich Chemical Company, Inc., Milwaukee, WI), 1,3-dichlorobenzene (98%, Aldrich), naphthalene (certified, Fisher Scientific Company, Fair Lawn, NJ), α-hexachlorocyclohexane (99%, Aldrich), γ-hexachlorocyclohexane (97%, Aldrich), hexachlorobenzene (99%, Aldrich), and 2,4,6-trichlorobiphenyl (99+%, Ultra Scientific, Kingstown, RI). Two deuterated compounds, toluene-d_8 (99+ atom %, Aldrich) and 1 ,2-dichloroethane-d_4 (2000 μg/mL in methanol, Supelco Canada, Oakville, ON) were used in recovery tests and as internal/external standards during field sample analyses. Ultra high purity (UHP) helium for GC-FID and GC-MS operation and for adsorbent tube cleaning, zero gas grade hydrogen and air for the FID, UHP nitrogen for GC-ECD operation and sample preparation were all supplied by Medigas, Toronto, ON. HPLC grade water (Caledon) was used in recovery tests.

Carbotrap® B and Carbotrap® C (20/40 mesh, supplied by Supelco Canada) were tested as adsorbent materials to trap the target compounds. Sampling tubes were prepared in the laboratory by packing these two adsorbents (300 mg each, separated and held by quartz wool) in 11.5 cm × 6 mm o.d. (i.e., 4.5" × 1/4" o.d.) glass tubes (Supelco Canada). The analytes were extracted from these tubes with 2 mL of pentane (glass distilled, BDH Inc., Toronto, ON). The Carbotrap® 300 multi-bed adsorbent tubes (stainless steel, 7" × 1/4" o.d.) used for air sampling followed by thermal desorption were also supplied by Supelco Canada. Thermal desorption adsorbent tubes (glass, 4.5" × 1/4" o.d.) used for concentration of water samples were packed in the laboratory with Tenax TA (60/80 mesh, Chromatographic Specialties, Inc., Brockville, ON). The Carbotrap and Tenax TA tubes, respectively, were thermally cleaned at 350°C and 250°C for at least one hour with UHP helium purging (30 mL/min) prior to use.

Air samples were drawn through the adsorbent tubes by means of personal air sampling pumps (Model LFS 113D, Gilian Instrument Corp., Wayne, NJ). Water samples were collected from the sampling site with 500 mL precleaned amber jars (Chromatographic Specialties, Inc.) and filtered with Whatman #1 filters (Fisher Scientific) in the laboratory to remove suspended particles prior to concentration with the adsorbent tube.

A large steel water tank was used for laboratory testing of the sparger and flux chamber devices. This rectangular tank with acrylic walls measured 1.11 m by 1.22 m with a depth of 1.04 m, and was capable of holding 1,400 L of water. It was filled with 1,000 L of tap water and a colour tracer (red ink) or chemicals were spiked into the water when needed.

Sparger

The two new spargers were constructed of stainless steel and each mounted in a robust floatation system which included a gas bottle and an electronic gas (mass) flow measurement unit. The major changes to previous versions[7,8] were: 1) the use of stainless steel for construction of the sparger chamber; 2) addition of an "umbrella", which prevented sparging air bubbles from escaping, at a mid point of the sparger; 3) the use of a longer pressurization section to allow higher gas flow rates; and 4) the re-design of the floatation system which employed a life buoy float topped with a circular PVC mount to hold the air supply/control module and the adsorbent tubes.

The life buoy had an outside diameter of 0.76 m and a water replacement capacity of 27.2 kg when completely immersed. A Dolphin "pony" scuba air cylinder with a capacity of 377 L at the maximum pressure of 3000 psi was contained in a PVC holder which was immersed in water and suspended on the PVC mount supported by the life buoy. The air first entered a variable area flowmeter (model G–03229–11, Cole-Parmer Inc. Montreal, PQ) with a needle valve for flow control, and passed an adsorbent tube which was either a Carbotrap 300 or Tenax TA tube. The air cleaned by this adsorbent trap was then conveyed to the sparger chamber via Teflon tubing, the stainless steel tube inside the sparger and the fritted glass head. The sparging air also acted as a bubble pump to draw fresh water into the sparger chamber via the three holes on the bottom of the cylindrical chamber. The outflow water exited the chamber via the six holes in the cylinder wall. The "umbrella" or "skirt", as shown in Figure 1, prevented the air bubbles from escaping with the outflow water stream. This ensured that all sparging air bubbles exit via the outlet on the top of the cylindrical chamber to the sampling adsorbent tube, where the chemicals sparged out from the water and carried by the air stream were collected. The air was exhausted via a model 8112 mass flowmeter (Matheson Gas Products Canada, Whitby, ON). The pressure in the sparger chamber was indicated by means of a Cole-Palmer G-68930-01 gauge. The air supply was sufficient for 40 to 50 hours of continuous operation at flow rates of 100 to 150 mL/min.

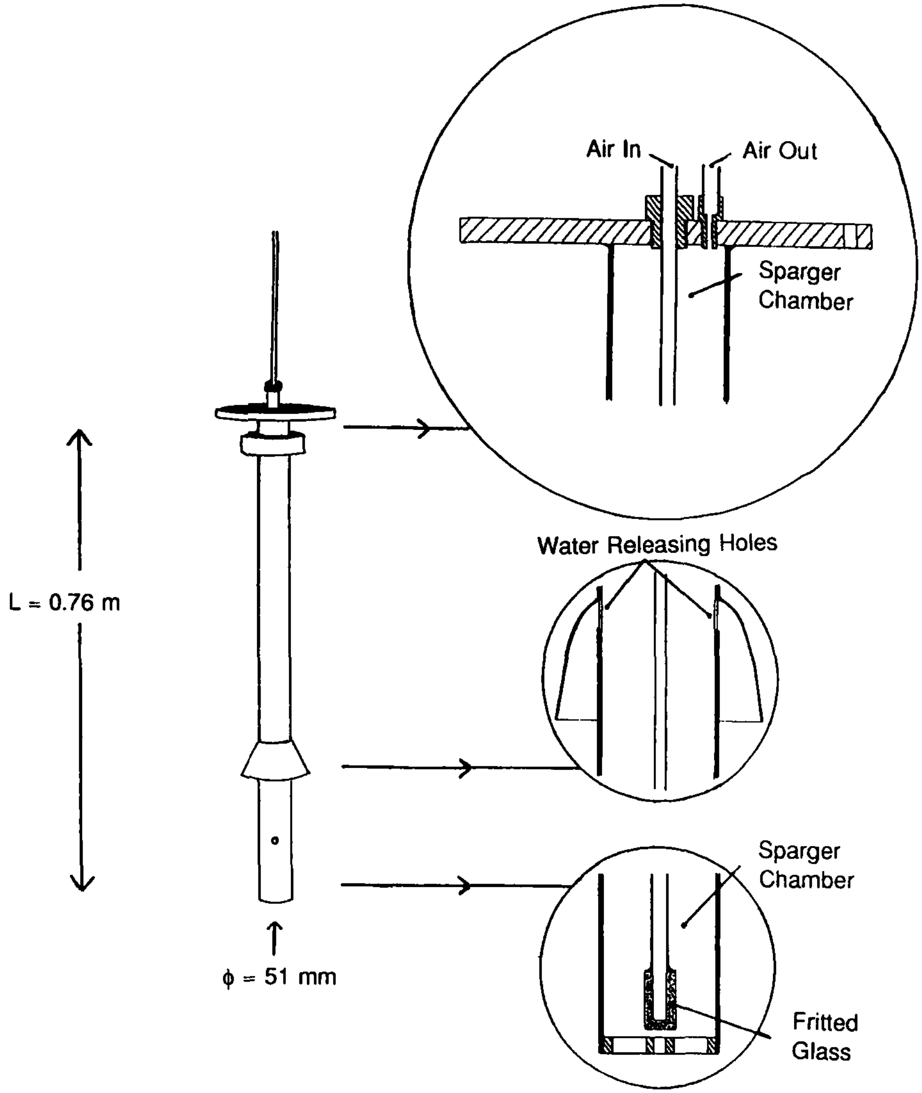

Figure 1 Sparger schematic (sparging chamber only, float and flow control unit not shown).

Flux chamber

The flux chamber used in this work (Figure 2) was constructed with plexiglass (1/4" thickness) and consisted of a main body 80 cm long, 50 cm wide and 50 cm high, with both ends tapered as showed in Figure 2a. One end was separated from the chamber, with its lower part used as a buoyancy compartment and its upper part as a storage compartment (with a lid) for batteries, sampling pumps, etc. The main body was separated by a panel into upper and lower parts with openings on both ends to allow internal air circulation driven by four fans mounted near the middle of the upper part

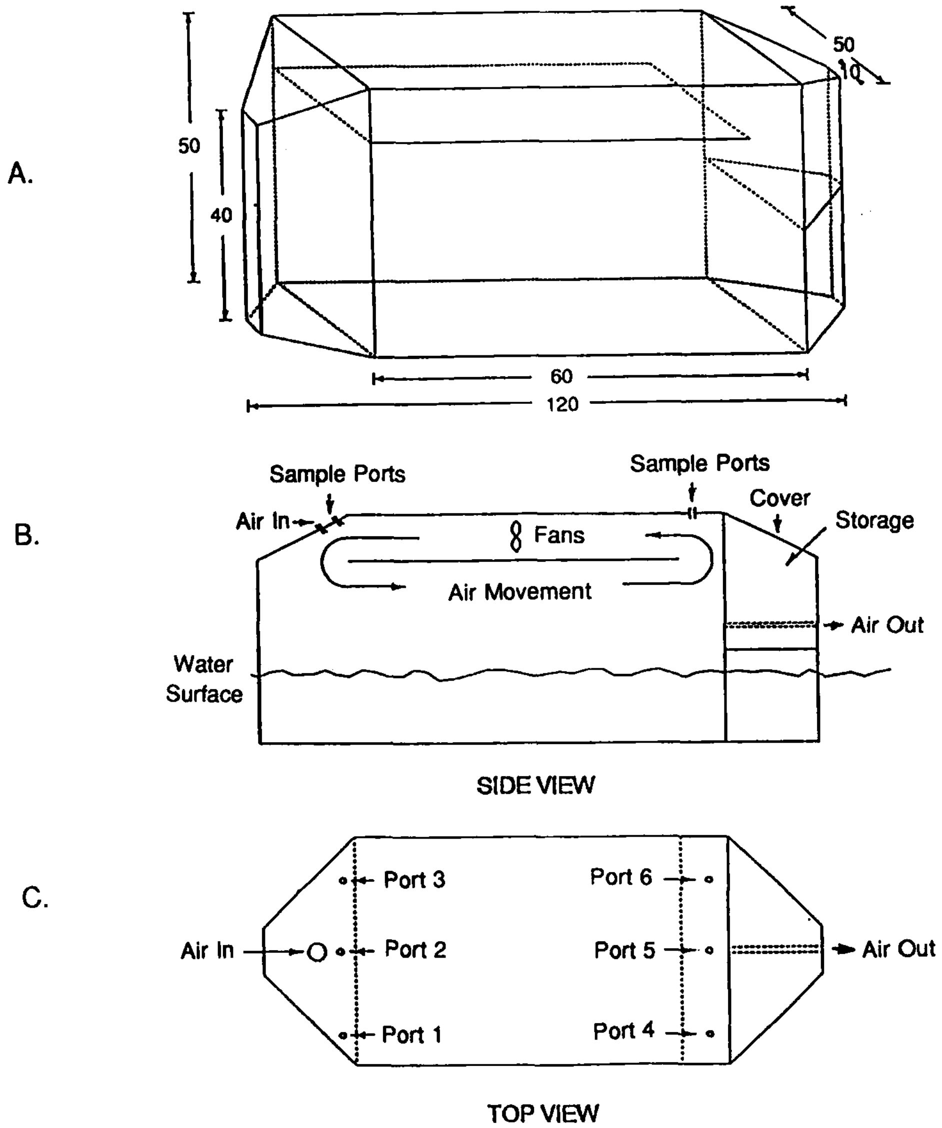

Figure 2 Flux chamber schematic (all dimensios in centimeters; floats, air sampling pumps and tubes not shown).

(Figure 2b). The top surface of the chamber was covered by a layer of clear Mylar sheet. The chamber covered a surface of 0.46 m^2 and had an operational air volume of 160 L. It was held by two large and two small boat floats to achieve sufficient buoyancy and demonstrated better stability than a previous prototype[8]. Approximately 15 cm of the chamber skirt was below the water surface.

Ambient air entering the chamber from the inlet port was circulated by the fans before the main air flow being drawn out of the chamber by a pump (Cat. No. 7411–70, Canadawide Scientific Ltd., Toronto, ON) via the outlet port (Figure 2c). A critical orifice maintained the air flow rate at 10 L/min. A small fraction of the air was drawn out of the chamber with personal air sampling pumps via one or more of the six air sampling ports (Figure 2c) during air sample collection.

Field sample collection and preparation

Air samples (ambient, sparger and flux chamber) were collected with Carbotrap 300 tubes at air flow rates in the range of 100 to 600 mL/min for periods of 1 to 2.5 hours. Grab samples of water were taken at the beginning, middle and near the end of air sampling period. Upon returning to the laboratory, air samples were stored at 4°C until analysis by means of thermal desorption GC-MS. The water samples were first filtered and then pushed, at a flow rate of ca. 10 mL/min under a slight pressure of ultra high purity nitrogen, through the Tenax TA tubes, where the analytes were adsorbed and concentrated. The Tenax TA tubes were centrifuged with a model CL centrifuge (International Equipment Co., Needham Hts, MA) for 20 minutes to remove water and further dried for 20 minutes in a desiccator evacuated to minus 30 inches of mercury. The Tenax tubes (glass) suitable for concentration of water samples were not designed for use with the thermal desorber coupled to the GC-MS, the analytes were therefore thermally desorbed and transferred to Carbotrap 300 tubes, from which the analytes were thermally desorbed into the GC-MS for analysis.

Analytical instrumentation and procedures

A Hewlett Packard (Avondale, PA) HP5890 GC-FID equipped with a 30 m × 0.25 mm J&W Scientific (Folsom, CA) DB-5 capillary column and a Hewlett Packard HP5890 GC-ECD equipped with a 30 m × 0.25 mm HP-5MS capillary column (Hewlett Packard), were used for analyses of some laboratory testing samples which were prepared with solvent extraction and solid phase microextraction (SPME). A Supelco SPME Fiber Assembly (100 μm polydimethylsiloxane coating) was tested for solid phase microextraction of air and water samples. The analytes extracted onto the fiber were thermally desorbed by inserting the needle holding the fiber into the GC injection port at 250°C.

Sample transfer from the 4.5" Tenax TA tubes to the 7" Carbotrap 300 tubes was performed by means of a Dynatherm Analytical Instruments Model 850 Thermal Desorber (supplied by Supelco Canada) at a temperature of 250°C for 6 minutes with a purge gas (He) flow of 30 mL/min. Analytes on the Carbotrap tubes were desorbed with an *AERO*Trap 6000 Thermal Desorber (Tekmar Company, Cincinnati, OH) with desorption temperature at 350°C, cryo-focusing temperature at –180°C, and desorption purge gas (He) flow rate at 30 mL/min. A Hewlett Packard 5890 Series II Plus GC equipped with a 5872A MSD and a J&W Scientific DB 624 column (75 m × 0.53 mm × 3 μm) was used for thermal desorption GC-MS analysis. The GC column temperature was held at 40°C for 1 minute and then increased to 170°C at a rate of 10°C/min. The GC carrier gas (He) flow rate was 5 mL/min.

Recovery tests

Extraction efficiencies for the target compounds from the Carbotrap® B and Carbotrap®C adsorbents were determined by spiking known amounts of the compounds onto the adsorbent materials and measuring the amounts recovered in the extracts of an appropriate solvent. Thermal desorption efficiencies were obtained by comparing results of direct injection of known amounts of analytes onto the GC with those of the same amounts of analytes spiked on the adsorbent tubes and transferred to the GC via thermal desorption. The collection efficiencies of Tenax TA for the analytes from water samples were determined by means of 1) spiking known amounts of analytes onto the adsorbent tubes, passing different volumes of water through the tubes and determining the amounts of analytes retained by the adsorbent tubes, and 2) spiking known amounts of analytes in water to prepare solutions with defined concentrations, passing different volumes of this fortified water through the adsorbent tubes and determining the amounts of analytes retained by the adsorbent tubes.

RESULTS AND DISCUSSION

Sparger theory and initial testing

The sparger is actually an "*in-situ*, dynamic purge and trap" apparatus. Although significant improvements have been made and new features added to the current prototype as compared to previous versions[7,8], it still operates on the same principle[7] for determination of the (truly) dissolved concentration of a given chemical in water, and hence the chemical's potential for diffusive transfer at the air-water interface[9]. When an equilibrium is established between the air bubbles sparging through the water column in the sparger chamber, the dissolved concentration (C_w) of a given chemical in water, in ng/m^3, is given by:

$$C_W = \frac{C_{SA}}{K_{AW}} \qquad (1)$$

where C_{SA} (ng/m^3) is the concentration of the chemical in the sparger air and K_{AW} the dimensionless air-water partition coefficient. The flux, or the emission rate (E) of the chemical across the air-water interface, in ng/m^2.min, can be determined based on:

$$E = K\,(C_W - \frac{C_{AA}}{K_{AW}}) \qquad (2)$$

where K (m/min) is the overall mass transfer coefficient across the air-water interface and C_{AA} (ng/m^3) the concentration of the chemical in the ambient air near the water surface.

Before the new spargers were used in field measurements of chemical fluxes across the air-water interface in conjunction with the flux chamber and the sampling and analytical methods developed, they were first tested in the laboratory for air flow control, effectiveness of replenishing the chamber with fresh water and blank levels of target compounds in the sparging air. With a pressure drop of ca.16" of water, the sparger was capable of operating with a maximum air flow rate of 200 mL/min, which was the full scale range of the mass flowmeter used. Experiments in the test tank with water spiked with red ink demonstrated that the rising air bubbles in the sparger also worked as a "pump" to generate a constant water flow through the chamber, entering via the holes at the bottom of the chamber and exiting via the releasing holes near the middle of the chamber. The "umbrella" acted as expected to prevent the air bubbles from escaping from the water releasing holes. Analysis of the trapping and sampling adsorbent tubes also indicated that the trapping tube worked effectively in removing any target compounds which might be present in the air from the scuba gas bottle.

The spargers were also tested for floating steadiness in the test tank and a large body of open water. The life buoy float was about 75% submerged. In the tank, one side of the buoy was pressed down until this end was completely submerged and then released suddenly. The sparger righted itself with some swinging motions. It again behaved well when artificial waves with an amplitude of about 0.3 m were generated using a paddle. The sparger was steady on the surface of a large body of open water with surface wind velocities up to 5 m/s. Higher wind velocities were not encountered during the test.

Flux chamber theory and initial testing

Flux chambers have been used for measurement of chemical fluxes across the air-water interface[8,10–13]. When an isolation chamber is deployed on a surface, the chemical mass balance requires that the change in mass of a specific compound in the chamber is equivalent to the sum of the chemical fluxes due to net surface emission and any input from the purge gas minus the removal of this compound through various loss mechanisms. Therefore, if wall losses are negligible, mass transfer to the chamber can be represented by the following equation:

$$\frac{d(VC)}{dt} = EA + C_iF - C_oF \tag{3}$$

where V is the volume of the chamber (L), C the concentration of the compound in the chamber (ng/L), E the flux, or emission rate, ng/m^2/min, of the compound, A the area covered by the chamber (m^2), C_i the concentration (ng/L) of the compound in the input purge gas, C_0 the concentration (ng/L) of the compound in the output gas and F the purge gas flow rate (L/min).

If C_i is zero and complete mixing is achieved, then C_0 equals C and at steady state the net flux across the air-water interface, i.e. the emission rate, ng/ m^2/min, of a compound can be determined by:

$$E = \frac{CF}{A} \tag{4}$$

where C, F and A are all measurable quantities with units as specified above. Since the chamber concentration reaches 95% of the steady state concentration at $t = 3\tau$ where τ represents the time for one complete flushing of the air in the monitor chamber, a period of time ($\geq 3\tau$) should elapse after deploying and before sampling. It was also recognized that the air and water boundary layers are disturbed by the presence of the chamber and, therefore, the data obtained should be treated with caution.

The flux chamber was deployed on the water surface of the test tank and a Drager Air Flow Tester was placed near the inlet port for introduction of a tracer smoke into the chamber in order to test the mixing of air in the flux chamber. It took less than 5 minutes and more than 25 minutes, respectively, for the chamber to be filled completely by the smoke with and without the fans on. The water was then spiked with chloroform and well mixed. The flux chamber was re-deployed and air samples were taken from the sampling ports at intervals of 10 minutes. The concentration of chloroform reached a plateau (i.e., the steady state) ca. 50 minutes after chamber deployment. This agreed well with the theoretical value of 48 minutes. At steady state, the concentrations from different sampling ports were within a relative standard deviation, i.e. RSD, of 4%. The RSD was greater than 15% without the fans operating. This confirmed that the internal circulation fans (an addition to this new prototype) helped to achieve better mixing in the chamber. The fans also generated air flows with linear velocities up to 3.2 m/sec across the water surface to simulate effects of air movement inside the chamber.

The floating steadiness of the flux chamber was also confirmed by testing it side by side with the spargers on the surface of a large body of open water. However, the flux chamber was less mobile than the spargers which were completely self-sustained, i.e. without the need for external power supply. In contrast, the current prototype of flux chamber required an air supply with a pump which relied on an external power supply. This imposed additional logistic requirements.

Air analysis

Due to the anticipated low concentrations of the target compounds (parts-per-trillion) in the atmosphere and natural waters, identification and quantitation of these compounds are not easy tasks. Sample collection and preparation procedures have to be considered in association with the analytical finish to achieve sufficient overall method sensitivity and reliability. Determination of HCHs in air may require collection of a sample greater than 100 m^3 on PUF plugs[14], followed by lengthy solvent extraction and pre-concentration steps before the final extract is analyzed by GC-ECD. This sampling method is not suitable for the volatile compounds, because they break through the collection media and further losses occur during the extraction and pre-concentration processes due to their high volatility. Also the flux chamber and sparger do not permit collection of air samples of such a large volume within the desired time limit of a few hours. A much smaller sample volume is required to prevent volatile compounds such as chloroform from breaking through the collection media and to be accommodated by the flux chamber and the sparger techniques. However, the sensitivity of the analytical instrument is very likely insufficient to detect the amount of collected HCHs, which are normally present in air at concentrations lower than 100 pg/m^3. Sampling with multi-sorbent tubes is considered the method of choice for collection of air samples since no single sorbent can quantitatively and effectively collect compounds with such a wide range of volatility.

The solvent (pentane) extraction efficiencies for the target compounds from the adsorbent tubes packed with Carbotrap® B and Carbotrap® C were found in the range of 70% (2,4,6-trichlorobiphenyl) to 95% (chloroform). The GC-ECD detection limits determined in our laboratory for the target compounds ranged from ca. 0.2 pg per injection for HCHs and HCB,1 pg per injection for chloroform, to ca.100 pg per injection for chlorobenzene. (The ECD is not responsive to toluene and naphthalene.) When sampling with these adsorbent tubes followed by solvent extraction and GC-ECD analytical finish, a sample volume of at least 40 L is required in order to detect chloroform in air at the level of 50 ng/m^3. Such a sample volume is manageable in terms of compatibility with the sparger and flux chamber devices and does not result in sample breakthrough. However, it is impractical to use this technique for the determination of HCHs in air since a minimum air volume as big as 14 m^3 is required (assuming 2 mL solvent for extraction and 1 µL injection onto the GC) to detect these compounds, due to the fact that their concentrations are possibly as low as 30 pg/m^3.

The SPME technique[15,16] was tested for sampling air. The SPME probe was exposed to whole air samples and then inserted to the GC injection port for desorption. This technique is based on partitioning of the analyte in the gas (or water) phase and the stationary phase coated on a fused silica fibre. No sample volume was involved in calculation of method sensitivity, provided that the amount of the analyte adsorbed onto the stationary phase is relatively small compared to the total amount of the analyte in the whole air sample, i.e., the depletion of the analyte in air does not cause starvation of the stationary phase. The detection limits of the technique combined with GC-ECD were below 10 ng/ m^3 for HCB and HCHs, at least 20 times better than direct injection of 1 mL air sample onto the GC-ECD, and comparable to the technique of adsorbent tube sampling (with a 40-L air sample) followed by solvent extraction and GC-ECD (2 mL solvent and 1 μL injection). However, the method sensitivity was still insufficient for determination of HCHs at concentration levels which are normally below 0.1 ng/m^3 in air.

Water analysis

A number of established concentration methods exist for water samples. These methods include the purge and trap technique for volatile organics, solvent extraction and solid phase extraction followed by solvent elution or extraction[17]. The typical purge and trap technique (followed by thermal desorption) provides method sensitivities at the ppb (μg/L) level, which is insufficient for volatile analytes at low ppt (ng/L) and sub-ppt levels in natural water, although this technique can be modified by increasing the sample volume from the normally used 5 to 25 mL to 1 L or greater to allow collection of sufficient amounts of analytes for analysis. Similar sensitivities can be achieved with the other two methods in association with further concentration procedures. Higher sensitivities are possible but the procedures can be extremely tedious. Solid phase extraction of water samples followed by lengthy clean-up and concentration steps prior to GC-ECD analysis has been used for determination of HCHs in water.[2]

The SPME technique was examined for sampling the target compounds in water and the detection limits (with GC-ECD) determined in our laboratory for HCB and HCHs were found to be ca.10 ng/L. The detection limits for other chlorinated target compounds were 5 times (2,4,6-trichlorobiphenyl) to 100 times (chlorobenzene) worse than those for HCB and HCHs. While this technique proved to be much simpler and provide lower detection limits for semi-volatile compounds than the purge and trap technique and demonstrated its potential for some difficult analytical tasks, the commercial product currently available still lacks the sensitivity for determination of the target compounds at the concentration levels in natural water. It is therefore necessary to develop much more sensitive methods for the determination of the target compounds in water as well as air.

Air and water analysis by Adsorption/Thermal Desorption GC-MS

It was realized that it would be difficult to determine the complete list of 10 target compounds using the same sampling/analytical procedures. The target compounds were therefore divided into two sub-groups. With the intention of demonstrating the usefulness of the sparger and flux chamber for the estimation of the mass transfer rates of chemicals across the air-water interface, our efforts were directed to the development of a simple, less time-consuming sample collection and concentration technique to achieve the necessary method sensitivity for determination of the more volatile target compounds (chloroform, toluene, chlorobenzene,1,4-dichlorobenzene,1,3-dichlorobenzene) in water and (ambient, sparger and flux chamber) air samples. The method for the less volatile target compounds (naphthalene, α- & γ-HCHs, HCB, and 2,4,6-PCB) is expected to be similar conceptually to that for the more volatile compounds, although the sampling and analytical conditions will be quite different.

Adsorbent tubes have been used widely for collection and concentration of air samples[18-20]. This sample collection method can normally provide ppbv level sensitivity with solvent extraction[18-19] followed by GC analysis. For the anticipated concentrations at the pptv (ng/m^3) level, it is particularly advantageous to apply the thermal desorption technique[20] since the total amount or a large fraction of compounds collected may be transferred, without dilution, to the GC for quantitation. Thus, much higher sensitivity can be achieved with thermal desorption compared to solvent extraction. The thermal desorption efficiencies of the five more volatile target compounds from the Carbotrap 300 and Tenax TA tubes were tested and found to be 95 ± 15%. The breakthrough air volumes of the target compounds from these adsorbent tubes were known to be greater than 40 L. The combination of the Tekmar thermal desorber and the Hewlett-Packard GC-MSD proved to be adequate for determination of chloroform in air (50 ng/m^3) with a sample volume of ca. 10 L. Tests also confirmed that although the MSD provided an additional benefit of positive identification of analytes, its much lower sensitivities to chlorinated compounds compared to the ECD still made it inappropriate for determination of HCHs in air, even in conjunction with the thermal desorption technique. At least 1 m^3 of air was required to facilitate determination of these compounds at levels below 100 pg/m^3, but a sample volume this big was incompatible with the sparger and flux devices and with which breakthrough of volatile compounds such as chloroform occurred.

Only a few applications of adsorbent tubes for concentration of water samples followed by thermal desorption have been reported[21,22], and hence the recoveries of the target compounds from water were required to be determined. The recovery test was conducted in several different ways. In the first test, two deuterated compounds (1,2dichloroethane-d_4 and toluene-d_8) each at 33 ng were spiked onto the Tenax TA adsorbent tubes and different volumes of water (0.2 to 1.0 L) were passed through the adsorbent tubes. Also, known amounts (13 to 23 ng) of the five volatile target compounds were spiked onto the adsorbent tubes and 0.2 L water was passed through the tubes. This experiment was repeated with much higher amounts (120 to 1200 ng) of chloroform to examine the effect of loading on recovery. The test results are tabulated in Table 1. The most volatile compounds (chloroform and 1,2dichloroethane-d_4) and the other test compounds were recovered > 80% with a sample volume of 0.2 L. In fact, the recovery of toluene d-8 was satisfactory even with 0.5 L of water, and 1,2-dichloroethane-d_4 recovery apparently decreased with an increase in sample volumes.

In the second recovery test, different volumes (0.2,0.4 and 0.6 L) of fortified water containing the five target compounds and toluene-d_8 were passed through the adsorbent tubes and the recoveries are listed in Table 2. The recoveries of toluene-d_8 were lower compared to those in Table 1, probably due to adsorption losses to the glass container for preparing the fortified water samples. The recoveries of chloroform were also lower than those obtained in Test 1, possibly for the same reason and/or volatilization after preparation, and the trend that the recovery decreased with increasing sample volume was demonstrated. The facts that the recoveries of toluene were greater than 100% and there were relatively large uncertainties associated with the determination of the recoveries of both toluene and chloroform may be attributed to the high blank levels of these two compounds in water (Table 2) and contamination through handling (i.e. exposure of sample tubes to air containing these two compounds as the result of frequent usage of these two solvents in a chemical laboratory). Build-up of artifacts on adsorbents have been observed in our laboratory and by other workers, especially for toluene[23].

Table 1 Recovery test with spiked adsorbent tubes.

Sample Volume (L)	*0.2*	*0.25*	*0.5*	*1.0*
1,2-Dichloroethane-d_4	90%	86%	60%	28%
Toluene-d_8	95%	96%	99%	77%
Note:	1,2-dichloroethane-d_4 & toluene-d_8: 33 ng each			
Compounds	Amount Spiked (ng)			Recovery
Chloroform	23			92 ± 25%
Toluene	13			82 ± 15%
Chlorobenzene	17			90 ± 7%
1,3-dichlorobenzene	20			97 ± 11%
1,4-dichlorobenzene	20			101 ± 6%
Note:	Water sample volume: 0.2 L			
Amount Spiked (ng)	120	360	600	1200
Chloroform	95%	96%	111%	96%
Note:	Water sample volume: 0.2 L			

Table 2 Recovery test with fortified water.

Target Compound	*Concentration in Water (ng/L)*	*Water Sample Volume (L)*			*Adsorbent Blank*	*Water Blank*
		0.2	*0.4*	*0.6*	*ng/tube*	*ng/0.2-L*
Chloroform	145	81 ± 23%	103 ± 24%	44 ± 22%	< 0.2	30.0 ± 5.0
Toluene-d8	180	95 ± 7%	79 ± 11%	82 ± 3%	< 0.2	< 0.2
Toluene	85	141 ± 41%	107 ± 31%	111 ± 32%	1.2 ± 1.2	13.3 ± 3.9
Chlorobenzene	108	97 ± 8%	81 ± 11%	86 ± 5%	< 0.2	0.3 ± 0.6
1,3-Dichlorobenzene	125	99 ± 9%	87 ± 11%	88 ± 2%	< 0.2	0.3 ± 0.3
1,4-Dichlorobenzene	123	107 ± 16%	90 ± 15%	92 ± 1%	< 0.2	0.3 ± 0.3

The blank levels of chlorobenzene and two dichlorobenzenes were low and the recoveries for these three compounds were quite good and comparable in the two tests (Table 1 and Table 2). Their recoveries did not vary with sample volume in the tested range (0.2 to 0.6 L).

Field measurements

In the Summer and Fall of 1994, the flux chamber and two spargers were deployed from a shoreline location in a harbour of Lake Ontario. Ambient, flux chamber and sparger air samples were taken with sample volumes ranging from 12 to 72 L. Water samples near these sampling devices were also collected. Air and water samples collected were analyzed using the adsorption/thermal desorption GC-MS method described previously. Results based on the analyses of samples collected showed good agreements between the flux chamber, sparger and water measurements. More field measurements will be conducted and the results will be reported later.

CONCLUSION

Preliminary results have demonstrated the potential of the adsorption/ thermal desorption GC-MS method for the study on the air-water exchange processes of organic chemicals. The method sensitivities for the target compounds tested were at the levels of 1 to 5 ng/L for 0.2-L water samples, and 30 to 50 ng/m^3 for 10-L to 30-L air samples. Unequivocal identification by MS and its applicability to non-chlorinated compounds were advantages over ECD detection in GC-ECD. Coupling thermal desorption with GC-ECD is expected to provide much higher sensitivity for the chlorinated target compounds and should be explored, but certain difficulties (e.g., the compatibility of the two techniques) are also anticipated. In conjunction with the analytical method developed, the sparger and flux chamber devices provide a useful means for the estimation of the mass transfer rates of chemicals across the air-water interface and thus enable us to study one of the most important aspects of the environmental fate of many persistent and toxic chemicals. Further efforts are required to improve the existing sampling and analytical methods to allow the determination of the types of air and water samples required for the direct *in situ* measurement of fluxes of the target compounds across the air-water interface in the natural environment.

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