# ATMOSPHERIC TRANSPORT AND AIR-WATER EXCHANGE OF HEXACHLOROBENZENE IN LAKE SUPERIOR

Perlinger, Judith A., Rowe, Mark D., and Tobias, David E.
Michigan Technological University, 1400 Townsend Dr., Houghton, MI, 49931 USA

## Introduction

Air-water exchange of semivolatile organohalogen compounds (SOCs) occurs as air flows from coastal land over water. For SOCs that are not equilibrated between phases in coastal regions, air-water exchange may act as a source or a sink of SOCs to/from the water. The direction and magnitude of this exchange is typically estimated using the Whitman two-film diffusive exchange model [1] assuming a homogeneous concentration over the water equal to that measured near- or on-shore. The accuracy of this flux estimation technique is limited, in part, by not accounting for mesoscale atmospheric processes as SOC-polluted air travels offshore in the atmospheric boundary layer. Air-water exchange depends not only on the fugacity of an SOC and the windspeed-dependent roughness of the water surface, but also on the stability of the internal boundary layer (IBL), the layer of air adjacent to the lake surface influenced by surface temperature and roughness [2], and fetch. A stable IBL adds resistance to exchange that is not accounted for in commonly-applied parameterizations of SOC air-water exchange. Fetch-dependent air-water exchange occurs in the dynamic IBL, approaching air-water exchange equilibrium at large fetches. To observe and predict such mesoscale transport and partitioning processes, measurement and modeling tools require adequate precision and spatiotemporal resolution.

Perlinger et al. developed and applied a micrometeorological approach to measure the SOC flux that utilized low-flow multicapillary denuders to rapidly accumulate adequate gaseous SOC mass within a period of atmospheric stationarity [3]. The low-flow devices collect gaseous SOCs at a flow rate of 13 L $min^{-1}$, separating gaseous from particle-associated SOCs as a result of the orders of magnitude higher diffusivities of gaseous SOCs in the capillaries of the device relative to particles, and absorbing gaseous SOCs in the polymeric coating on the inside of the capillary walls. We have also developed apparati and a method to thermally extract analytes directly into a gas chromatograph (GC) [4,5]. High-flow devices that collect SOCs at a flow rate of 300 L $min^{-1}$ have also been recently developed [5,6], allowing proportionately higher SOC masses to be collected, as have apparati and methods to clean up ambient air samples in the gas phase prior to analysis [5,7]. Here, relationships between hexachlorobenzene (HCB) concentration, fetch, and measures of atmospheric stability during one transect experiment in eastern Lake Superior on the morning of July 14 2006 are presented and discussed.

## Materials and Methods

HCB concentrations and micrometeorological parameters were measured along a south to north transect at three stations during offshore flow in eastern Lake Superior on 14 July 2006 using low-flow multicapillary denuders and an energy balance platform onboard the U.S. EPA's *R/V Lake Guardian* (Figure 1). Weather conditions during sampling were initially clear, then progressed to 50 % cloud cover at the last station. Waves were calm to 1 foot. Sampling times, fetches, and averaged wind speed and direction, water surface temperature, and temperatures at the upper and lower sampling platforms at each station are presented in Table 1. Methods described by Perlinger et al. [3] and Tobias et al. [4] were employed with the following modifications to the method for thermal extraction of SOCs from denuders. Oxygen and hydrocarbon traps were added to carrier gas lines for sample extraction, cleanup, and analysis. Diffusion denuders were thermally extracted at 230 °C and a $N_2$ carrier gas flowrate of 750 mL $min^{-1}$ into cooled, Sulfinert-deactivated stainless steel minitubes (4 mm ID, 130 mm bed length) containing PDMS-coated GC packing media (Restek, Bellefonte, PA). The contents of the minitubes were then cleaned by gas-phase thermal elution through minitubes packed with silica gel (Davisil, 35-60 mesh, 150 A pore) into minitubes containing the PDMS-coated packing media at 80 mL $min^{-1}$ flowrate of $N_2$ and 270 °C. The minitubes containing the cleaned extract were thermally extracted into the cooled programmable temperature vaporization inlet of an Agilent 6890 GC equipped with electron capture detection (ECD) for analysis using an aluminum shell inserted into the thermal desorption unit described by Tobias et al. [4] to speed conduction of heat to the minitube in the unit at a helium flowrate of 80 mL $min^{-1}$ and 300 °C. A hot gas spike apparatus was used to introduce surrogate standards, internal standards, and calibration standards into minitubes and diffusion denuders [4]. The GC was calibrated by spiking authentic standards into minitubes, followed by transfer into the GC. Analytes were identified by relative retention time, and quantified by relative response using multi-level calibration curves.

**Results and Discussion**

The denuder samples were extracted 19 months following sample collection. Refrigerated samples have been shown to retain 100±10 % of surrogate polychlorinated biphenyls (PCBs) 14, 65, and 166 over four years of storage, thus no loss of HCB was expected during storage following sampling, and no HCB absorption from indoor air during storage was observed in blanks. Based on modeled and measured SOC gas transmission [8], we predict that HCB was retained in the denuders during the 90-min sampling intervals. Although gaseous HCB is predicted to be retained in the samples, surrogate PCBs 14, 65, and 166 were 27.0±2.6, 75.7±2.6, and 98±4.1% (Avg. Recovery±95%CI) retained, respectively. The surrogates are predicted to be 100 % retained under the sampling conditions. Although PCB 14 has similar retention characteristics to HCB in diffusion denuders, the hot-spike procedure heats the denuder inlet and deposits surrogates some distance into denuder capillaries, reducing their effective breakthrough volumes. This product of the method of loading surrogate standards into denuders explains the discrepancy between modeled and measured retention of surrogate standards in these samples. Concentrations at all fetches were significantly higher than those in the field and trip blank. Field and trip blanks contained HCB concentrations of 3.2 and 1.8 pg $m^{-3}$, respectively. HCB mass in these blanks was less than 6 % of the HCB mass contained in samples at all fetches.

Because the magnitude of the air-water exchange flux is proportional to the concentration difference between the upper and lower platforms using the modified Bowen ratio micrometeorological flux measurement approach [3], it is necessary to determine a measurable concentration difference. This concentration difference is quantified using the student's *t*-test and the relative standard deviation in surrogate PCB recoveries to quantify the uncertainty in the SOC concentration determination. For the dataset reported by Tobias et al. [4], relative standard deviations in recoveries of surrogate PCBs 14, 65, and 166 that were hot-spiked into denuders used to collect ambient air were 19 (14-29), 17 (12-26), and 31 (23-49) %, respectively (mean (95% CI)), with n = 15 for each surrogate. For the dataset presented here, the values were 4 (3-10) and 5 (3-13) % for PCBs 65 and 166, respectively, with n = 6 for each. (The value for PCB 14 is not reported because its precision was affected by variable breakthrough.) The greater uncertainty in surrogate recovery previously is the result of collection, using denuder sampling, and analysis of compounds containing oxygenated moieties in the whole samples, to which the electron capture detector is sensitive [5,7]. These compounds are likely much more abundant in ambient air than are the SOCs in these samples, thus even if they exhibit low responses, baseline noise is increased in the absence of sample cleanup to remove them. The addition of the cleanup step improves the ability to determine SOC concentration differences and thus the ability to apply the modified Bowen ratio to measure air-water exchange fluxes of SOCs.

Potential temperature differences provide measures of mesoscale structure of the lower atmosphere during the transect measurements, during which the averaged direction of airflow at the ship varied by 34 ° or less between stations (Table 1). Temperature differences (upper – lower; not corrected for pressure differences between the two platforms) computed from the temperatures in Table 1 were 0.12, 1.59, and 1.70 at 15.7-, 28.3-, and 58.8-km, respectively (Figure 2). These differences in the lowest 10 m of the atmosphere are indicators of the stability of the IBL with fetch, and are the result, in part, of decreasing surface water temperature with fetch (Table 1). As it traveled north over land to the coast before sunrise at 5:58 am, the air sampled at Station 1 was likely part of a stable nocturnal boundary layer. This air experienced a step change in surface roughness, temperature, and moisture content as it traversed overwater from the coastline. At the first measurement station (15.7-km fetch) shortly after sunrise, a weak temperature gradient was observed. As the transect measurements progressed toward mid-day, the IBL could be expected to grow [2]. The temperature gradient at Station 2 was more than an order of magnitude higher than that at Station 1, and windspeed was lower, supporting this expectation. The temperature gradient at Station 3 (58.8-km fetch) was slightly higher, but windspeed was also higher than that observed at Station 2, suggesting that IBL growth occurred but at a slower rate between Stations 2 and 3 than between the first two stations, and that the IBL approached maximal height and stability at 58.8-km fetch. As IBL height and stability approached maximum values, the volume and stability of air containing HCB undergoing air-water exchange approached constant values.

The upper and lower platform HCB concentrations reported in Table 1 are determined in large part by this mesoscale atmospheric structure. Concentration differences observed at Stations 1, 2, and 3 were 2.1, -2.5, and -10.3 pg $m^{-3}$, respectively (Figure 2). The positive but statistically insignificant concentration gradient at 15.7-km fetch was likely due to efficient vertical mixing from 0 – 15.7 km before sunrise, as indicated by the weak temperature gradient at the first station. The over-water concentrations observed at Station 1 were likely similar to that when the air left the southern shore of the lake at this fetch. Lower platform concentrations increased to a greater extent with fetch than those observed at the upper platform, and the upper-platform HCB concentration decreased from 28.3 – 58.8 km (Table 1; Figure 2). The increasing concentration of HCB at the lower platform and concentration differences that switched from a positive value at 15.7 km to negative values at 28.3 and 58.8 km suggest that, as the air traveled north beyond 15.7-km fetch during the morning, the growing stable IBL accumulated HCB due to HCB efflux out of the lake. The concentration difference at 28.3-km fetch was not sufficiently large so as to be significant. It is interesting that the HCB concentration measured at the upper platform at 28.3-km fetch was higher than that at 58.8-km fetch. A possible explanation for this observation is that the HCB concentration that was present when this air was left the coast during the transect measurements may have decreased during the morning as the nocturnal boundary layer was mixed into the convective boundary layer [9]. At 58.8 km, the concentration gradient was significant and negative, indicating HCB efflux from the lake into the stable IBL. The significant concentration difference between the upper and lower platforms at 58.8 km indicates that air-water exchange equilibrium was not reached at this fetch.

These results demonstrate the applicability of the denuder sampling and cleanup techniques to achieve the spatiotemporal resolution in measurements required to observe mesoscale processes of SOC transport and partitioning behavior. They suggest that during periods of atmospheric stability over surface water, the two-film model will overestimate the magnitude of SOC air-water exchange. For the present case, putting other potential limitations that enter into its application aside, the two-film model would overestimate HCB efflux from the lake and the extent to which the lake purified itself of HCB through air-water exchange. Rowe et al. [10] have developed a two-dimensional (2-D) Lagrangian transport and air-water exchange model that accounts for atmospheric stability in addition to SOC fugacity and surface roughness during offshore flow. We are applying this model to investigate the implications of accounting for fetch and stability in calculation of air-water exchange loadings in the Laurentian Great Lakes.

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**Table 1. Conditions and HCB concentrations at the three sampling stations along a south to north transect in eastern Lake Superior during offshore flow on 14 July 2006.**

| Stn. | Sampling Start Time – End Time (EDT) | Fetch [1] (km) | Avg. Ship WS [2] (m s$^{-1}$) | Avg. Ship WD [2] (°) | Avg. Ship SST [2,3] (° C) | Upper [4] $T_{avg}$ (° C) | Lower [4] $T_{avg}$ (° C) | Upper [HCB] (pg m$^{-3}$) | Lower [4] [HCB] (pg m$^{-3}$) | Deck [HCB] (pg m$^{-3}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0620-0750 | 15.7 | 4.3 | 162.0 | 19.3 | 19.44 | 19.32 | 56.6 | 54.5 | |
| 2 | 0922-1052 | 28.3 | 3.1 | 128.0 | 17.3 | 18.27 | 16.68 | 62.6 | 65.1 | |
| | 104 min. [5] | | | | | | | | | 65.3 |
| 3 | 1318-1448 | 58.8 | 4.9 | 147.3 | 15.5 | 17.84 | 16.14 | 58.0 | 68.3 | |
| | 88 min. [6] | | | | | | | | | 67.6 |

[1] Fetch computed based on 10-m, 6-hr back-trajectories computed using NOAA's HYSPLIT Model and GIS; [2] *R/V Lake Guardian* Log Data; [3] Temperature probe located 2.7 m below the water surface; [4] Average temperatures and HCB concentrations are reported at the upper (8.5 m above the lake surface) and lower (1.0 m above the lake surface) sampling platforms; [5] Collected on deck in the ship's bow during 70 min. in transit from Stn. 1 to Stn. 2 plus 34 min. in transit from Stn. 2 to Stn. 3; [6] Collected during 35 min. in transit from Stn. 2 to Stn. 3 plus 53 min. in transit beyond Stn. 3.

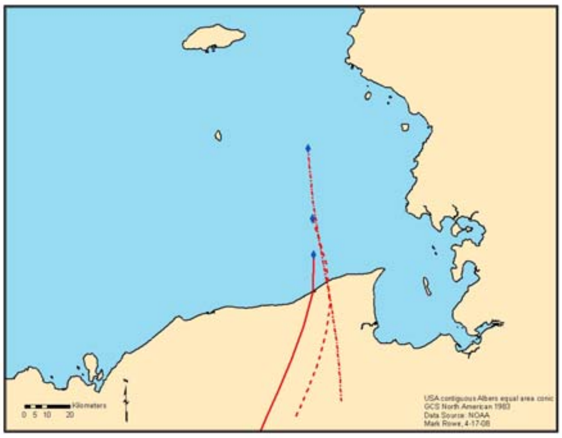

**Figure 1. Location of the three sampling stations during the south to north transect in eastern Lake Superior on 14 July 2006. Fetch was computed as described in the footnote of Table 1.**

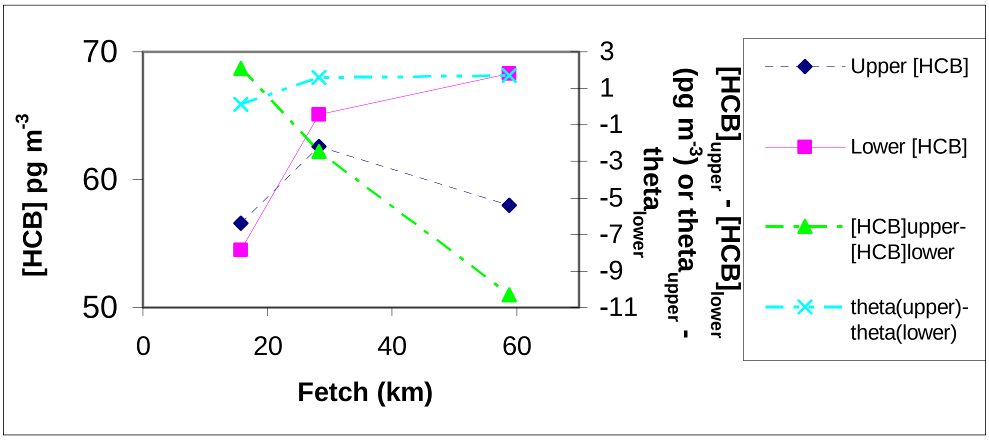

**Figure 2. HCB concentrations measured at the upper and lower platforms, and HCB concentration and potential temperature differences measured at three fetches during the transect (concentration, air temperature, and fetch values reported in Table 1).**