

Surface Organic Films: Growth Dynamics and Partitioning Characteristics

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Introduction:

Urban areas have been identified as a source of contaminants to which resident human and animal populations may be exposed. These contaminants, many of which are carcinogens and/or endocrine disruptors, present a health risk to these populations and to receptor ecosystems in the larger regional environment. It is therefore important to understand the sources and fate of these contaminants including their partitioning and exchange dynamics in urban centres. In 2000, Diamond et al.¹ showed the formation of a surface organic film on impervious urban surfaces. It is believed that the film is formed through the condensation of primary and secondary organic aerosols, followed by the deposition of particulates. Compounds found in the gas phase are capable of partitioning into the organic film, increasing the dry deposition rate of semi-volatile organic compounds, a category of compounds in which many urban contaminants are found. The compounds can then be released back into the atmosphere through volatilization or to water bodies through surface washoff².

Materials and Methods:

Two separate studies were carried out in downtown Toronto on the rooftop of a University of Toronto building (Physical Geography Building – PGB). The purposes of these studies were threefold: to study the rate of organic film growth; to measure the film concentrations of polychlorinated biphenyls (PCBs); and to examine film-air partitioning characteristics of PCBs.

In both studies, 30 trays of 3 mm glass beads were set out approximately 1.5 m above the rooftop. The beads were deployed on aluminum screens that allowed the glass surface to be exposed to ambient air from all directions. The trays were sheltered from direct precipitation and sunlight. In the first study (September – December 2003), beads were collected every 2 or 3 days. In the second study (July 2004 – April 2005), beads were collected every 1-2 weeks.

To determine film mass, 50 g of beads from each tray was taken and extracted twice with dichloromethane (DCM). The DCM was poured into a pre-weighed glass vessel and evaporated to dryness with a gentle stream of nitrogen. The film mass was determined by difference.

To determine PCB mass, the film was then re-constituted with DCM and blown down with nitrogen to a few milliliters. The residue was cleaned with alumina and extracted with a 5% solution of DCM:hexane. The solution was then blown down and solvent exchanged into iso-octane. PCBs were analyzed by gas chromatography, electron capture detection (GC-ECD), using Mirex as the internal standard on a 30 m DB-5 column. The temperature program consisted of an initial oven temperature of 90°C, ramping up to a temperature of 160°C at 15.0°C/minute. The temperature was then increased to 270°C at 3.0°C/minute and finally increased once more to 290°C at 20.0°C/minute. A total of 13 PCB congeners dominant in the extract were quantified, including PCB-8, PCB-18, PCB-28, PCB-52, PCB-49, PCB-101, PCB-118, PCB-153, PCB-105, PCB-137/138, PCB-156, PCB-180 and PCB-209.

To determine the K_{fa} value for the film, 20 g of beads were measured into a glass chamber and a gentle stream of nitrogen blown through at approximately 100 mL/minute (see Figure 1). The nitrogen was trapped with C18 bonded silica, then extracted with a solution of 50:50 DCM:hexane. The solvent was blown down then solvent exchanged into iso-octane (ISO) and analyzed by GC-ECD with Mirex as the internal standard. The K_{fa} was calculated as:

$$K_{fa} = \frac{C_{film}}{C_{air}}, (1)$$

where K_{fa} is the film-air partition coefficient, C_{film} is the film concentration in pg/L and C_{air} is the air concentration in pg/L. C_{film} was determined from the film mass, assuming a film density of 1 g/mL.

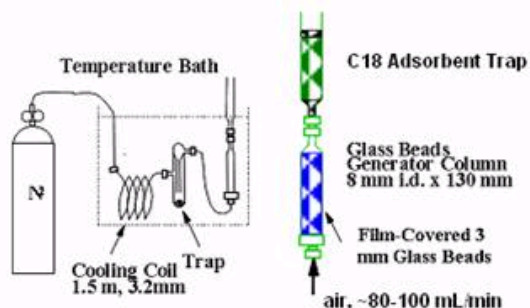


Figure 1 Apparatus for measuring film-air partition coefficient (K_{fa})

The method was initially tested using ethylene vinyl acetate (EVA) as a synthetic film. EVA was dissolved in DCM (8 g/400 mL of DCM) and spiked with a known amount of a PCB and organochlorine pesticides mixture. 3-mm glass beads were coated with the EVA-DCM mixture and the DCM allowed to evaporate. The glass beads were placed in the glass chamber as described in figure 1 and a known amount of air passed through the chamber. The EVA-air partition coefficient was taken as:

$$K_{EVA-air} = \frac{C_{EVA}}{C_{air}}, (2)$$

where $K_{EVA-air}$ is the EVA-air partition coefficient, C_{EVA} is the PCB concentration in pg/L and C_{air} is the concentration in pg/L. The EVA-air partition coefficient was verified using the octanol-air partition coefficients (K_{oa}) of the various compounds of interest.

Results and Discussion:

Film Mass and PCB Content

Figures 2 and 3 summarize the rate of film growth for the two Toronto studies. Figure 2 is the initial study of 90 days. The film evolved at a rate of approximately 1.90 nm/day and experienced linear growth up to day 89. Figure 3 describes the second PGB rooftop study, where film growth is also linear but increasing at a slightly higher rate of 2.5 nm/day, up to day 273. However, a t-test analysis indicated that the slopes of the two sampling campaigns were not significantly different, with a confidence level of 95%.

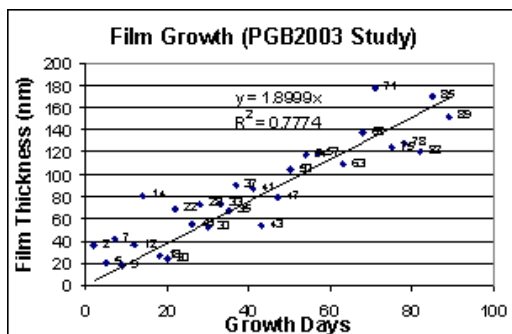


Figure 2 Results from the fall-winter 2003 film growth study showing linear growth

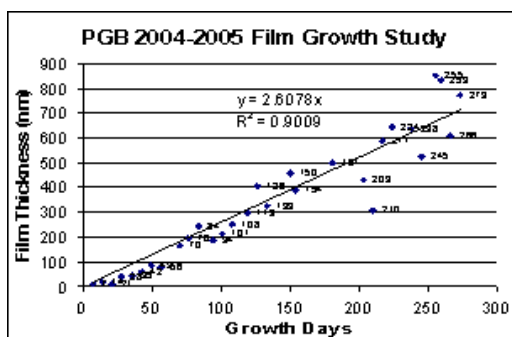


Figure 3 Results from the 2004 film growth study, with linear film growth up to 273 days

Figure 4 shows the PCB content of the film from the first rooftop study in 2003. The PCB mass increased at a similar rate as the film mass, suggesting that film-air equilibrium exists for PCBs. These results are consistent with previous kinetic work showing rapid equilibrium of PCBs in thin films³.

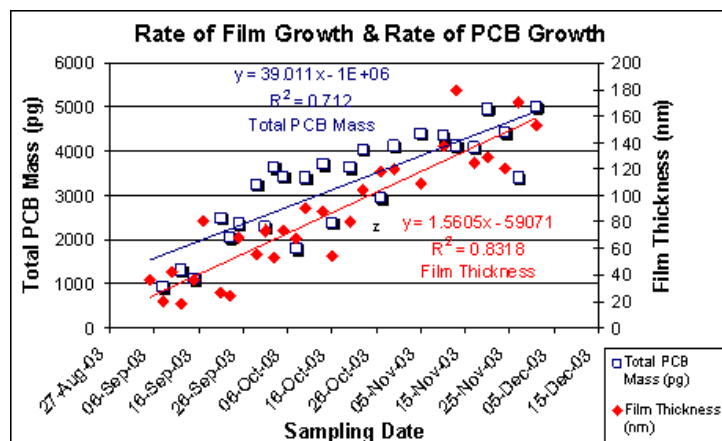


Figure 4 Linear PCB mass accumulation compared to film growth (PGB 2003 study)

EVA-Air Partition Coefficient

Figure 5 is a summary of the relationship between the laboratory-measured EVA-air partition coefficient (K_{EVA-a}) and the literature octanol-air partition coefficient (K_{oa}) of certain PCBs and organochlorine pesticides. There is a good log-log relationship that compares well to previous measurements by Harner et al.³, Wilcockson and Gobas⁴ and Wilford et al. (unpublished results). The near-linear slopes from all four studies are an indication that EVA-air partitioning can be predicted based on the octanol-air partition coefficients for PCBs.

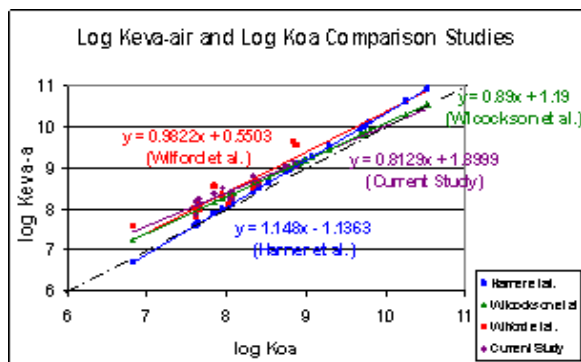


Figure 5 Comparison of the log Keva-air and log Koa values from 4 separate studies

Results from the EVA work also served to prove the validity of the method as described in Figure 1 to measure partition coefficients. This method was subsequently used to measure partitioning of PCBs in real surface organic films collected in Toronto. In the absence of these laboratory data, it is also possible to calculate field-derived values for the film-air partition coefficient. These K_{fa} values were calculated using the film concentrations of PCB from the bead deployment study and average PCB air concentrations for downtown Toronto (Gouin et al., unpublished). Figure 6 is a plot of log K_{fa} versus log K_{oa} for 13 PCBs.

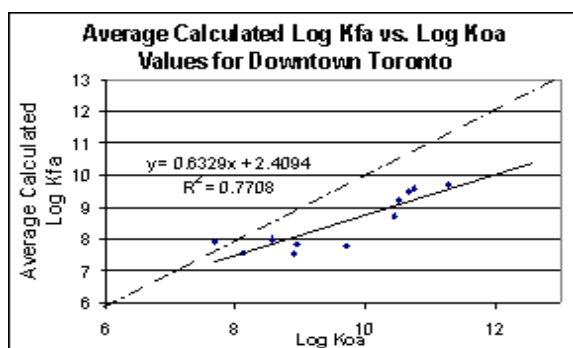


Figure 6 Comparison of the calculated log Kfa value with the log Koa value

If the film had the same partitioning properties as octanol and film-air equilibrium was established for PCBs, the data would have a slope near unity and fall near the 1:1 line. The regression line in Fig. 6 has a slope of 0.63 with the low molecular weight PCBs near the 1:1 line and the higher molecular weight PCBs deviating below the line. The deviation for the higher molecular weight PCBs may indicate insufficient time for them to establish equilibrium with the film. In other words, for the higher molecular weight PCBs, the film is growing faster than the PCBs could maintain equilibrium. Similar results were obtained in a study conducted by Wong et al.⁵, who examined experimental and forest soils to investigate polycyclic aromatic hydrocarbons (PAHs) uptake over a deployment period of ~165 days. Their results showed that the soil-air partition coefficient of lower molecular weight PAHs agreed well with an equilibrium model based on K_{oa} but not for higher molecular weight PAHs. This was an indication that the soils had not reached equilibrium for high molecular weight PAHs.

Harner et al.³ conducted kinetic uptake studies for thin polymer films (POGs). Based on these results, a ~0.2 μm film (this was the thickness of the film on the beads used to calculate K_{fa} in Figure 6) would require several days to weeks to achieve equilibrium for low molecular weight PCBs and up to several months for high molecular weight PCBs. The period of film growth in this case (Figure 6) was 2 months, which explains the deviation from equilibrium for the higher molecular weight PCBs.

In summary, the results presented here indicate that films may develop quickly on impervious surfaces that are typical in cities. These films accumulate PCBs and other chemicals which are then subject to dynamic film-air exchange.

This has been shown to be well described by K_{oa} . Process studies on film-air partitioning are required to develop multimedia models for evaluating the fate of PCBs and other semi-volatile pollutants in urban environments.

Acknowledgements:

The authors would like to acknowledge Jennifer Truong of the University of Toronto for providing field assistance and NSERC for funding this study (Project #STP-258056).

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