EVIDENCE FOR AN ORGANIC FILM ON IMPERVIOUS URBAN AND RURAL SURFACES

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Introduction

Law and Diamond (1) have hypothesized that an organic film develops on impervious surfaces in urban areas as a result of high emissions of VOCs and SOCs as well as oxidants and other reactive atmospheric species. According to the hypothesis, a film develops from deposition of primary emissions largely from vehicles, and compounds formed secondarily as a result of oxidation or nitrogenation. Law and Diamond suggested that the film could 1) act as a sink for gas phase compounds which could partition into the film and 2) increase the accumulation of particle phase compounds by increasing the dry deposition rate of particles. These effects could influence POPs fate in urban areas and contribute to potential toxicological impacts.

Diamond et al. (2) have presented evidence to support the hypothesis, showing that a range of POPs accumulate on urban windows which were used as a test impervious surface. Their results indicate that concentrations in the film of *n*-alkanes, PAH, PCBs and polychlorinated alkanes (PCAs) differ from building-to-building, however profiles of compound abundance are highly repeatable. Further, they showed that the film acts as a compartment into which gas phase compounds partition, the evidence for which is the comparability of the film-to-air ratio with measured values of the octanol-air partition coefficient, K_{OA}, for a range of PAH and PCBs. This paper presents the first evidence for the presence of an organic film on rural as well as urban impervious surfaces. We also discuss the significance of the film in terms of POPs fate.

Materials and Methods

Sample Collection and Preparation. Samples of urban surface films were collected from the windows of 7 buildings located in downtown Toronto, Ontario and 3 rural buildings in southern Ontario, Canada. The buildings were chosen and are identified according to date of construction. Methods of sample collection and analysis are fully explained by Diamond et al. (2). Windows were sampled by wiping with dry Kimwipes, and then dichloromethane (DCM) wetted Kimwipes. Gravimetric analysis was performed to measure the total mass of material on windows. Samples were Soxhlet extracted with DCM for at least 12 hours, and then extracts were divided between PAH/alkane and organochlorine analysis.

Chemical Analysis. For PCB analysis, sample extracts were separated into three fractions of increasing polarity on Florisil (8 g; 1.2 % v/w water deactivated). The first fraction was eluted with hexane and contained PCBs. After addition of aldrin as a volume corrector, this fraction was analysed for 89 individual or coeluting PCBs by capillary gas chromatography (GC) with ^{63}Ni

electron capture detection (ECD). Florisil fractions two and three were combined for analysis of short chain PCAs (3). High resolution gas chromatography electron capture negative ion high resolution mass spectrometry (HRGC-ECNI-HRMS) was done in the selected ion mode (SIM).

Results and Discussion

Organic Film on Windows. The total mass of extracted material from urban and rural samples varied according to how "dirty" the windows were. Film thicknesses, that were calculated assuming an organic matter density of 826 kg/m^3 for octanol, were within the range of 2.5 nm to 1 μm reported in the literature for monolayer or multilayer films on fog droplets and air-water interfaces.

Table 1. Summary of mass, thickness and total chemical concentrations in film samples.

Sample		Mass, mg/m^2	Film thickness, nm	EPCB, ng/m^2	EPCA, ng/m^2
Urban	Range	50 – 430	25 – 240	8 – 5800	40 – 1900
	mean[1]	130	70	110	200
Rural	Range	16 – 28	8 – 15	0.6 – 7	5 – 18
	mean[1]	23	12	1.8	11

[1]geometric mean.

PCBs. Absolute amounts (Table 1), homologue profiles (Figure 1), and congener abundances varied predictably between urban and rural sites. All urban samples, except one, were dominated by P_6CBs and P_7CBs. Two samples, (typified by 1963/6) were comprised of almost 50% P_7CBs, followed by 20-30% P_6CBs with congeners typical of Aroclor 1260. These profiles suggest local sources such as building materials (e.g., window caulking, exterior paints) and interior or nearby transformers or capacitors. These buildings were constructed prior to the bans on PCB importation and usage. If so, the film on the exterior of the windows reflects PCBs degassing from the interior to the exterior of the buildings where they are available to exchange with the ambient air mass.

The other urban samples were comprised of 30 and 25% P_6CB and P_7CB, respectively, with congeners typical of Aroclor 1254. Interior sources of PCBs are unlikely for these buildings which were constructed after the ban, however their congener pattern suggests proximity to relatively "fresh" sources of PCBs in contrast to atmospheric profiles that are dominated by lighter congeners. Rural samples had lower EPCB concentrations than urban samples and homologue patterns that were dominated by the P_3CBs, which is consistent with atmospheric patterns found at distance from sources. Congeners 153, 138 and 180, that are highly resistant to oxidative and metabolic degradation, are among the most abundant in the urban samples as well as in fish, meat and milk products and human breast milk (4), but not in rural film samples.

PCAs. EPCA concentrations in urban samples were not related to film thickness, but covaried with PCB concentrations. Similarly to PCBs, there was high variation in the quantity of PCAs but compound profiles were consistent among samples. C_{12} compounds with 6-8 chlorines comprised 35-45% in all urban samples (Figure 2).

Rural concentrations were about 20 times lower than urban concentrations. The abundance profiles

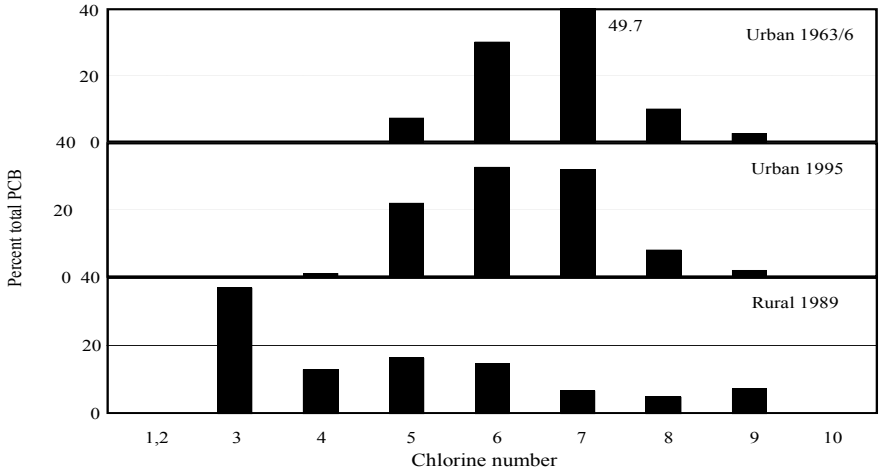

Figure 1. Distribution of PCB homologue groups in urban and rural

were shifted to lighter compounds, consisting of 40-50% C_{11} compounds, and particularly C_{11}-Cl_7.

One rural sample from Egbert (an Environment Canada laboratory) was dominated by C_{12}-Cl_6 PCA, resembling the urban profiles. The rural film profiles are dominated by two to four compounds in contrast to an air profile from Ebgert that has contributions from most formula groups (5).

PCAs are used for industrial and commercial purposes such as high temperature lubricants, plasticizers, flame-retardants, and additives in adhesives, paints, rubber and sealants (5). Commercial PCAs are complex mixtures comprised of numerous formula groups. As expected from their usage, urban film samples have higher concentrations and profiles indicative of "fresher" sources of PCAs with higher chlorination than rural samples

Discussion

The results indicate that POPs do accumulate on impervious surfaces in both urban and rural areas. Mean concentrations are 20 to 60 times higher in urban than rural samples. Urban profiles indicate proximity to "fresher" sources whereas the rural sites reflect chemical aging. The rural sites are less than 1 hour travel time (average air velocities) from locations contributing emissions leading to film development and about 2 to 4 hours from major source locations of PCBs and PCAs. Alteration of the source PCB and PCA profile is expected due to reaction during atmospheric transport and while on window surfaces, and due to washoff from precipitation.

Regarding the effect of the film on POPs fate, Diamond et al. (2) have shown that gas phase compounds partition into the film and as such, the film acts as a reservoir for these compounds. However, because of the film's high surface-area to volume ratio, the residence time of compounds in the film is extremely short. This suggests that gas phase compounds in the film likely respond rapidly to changes in ambient air concentrations and as well, could affect air concentrations.

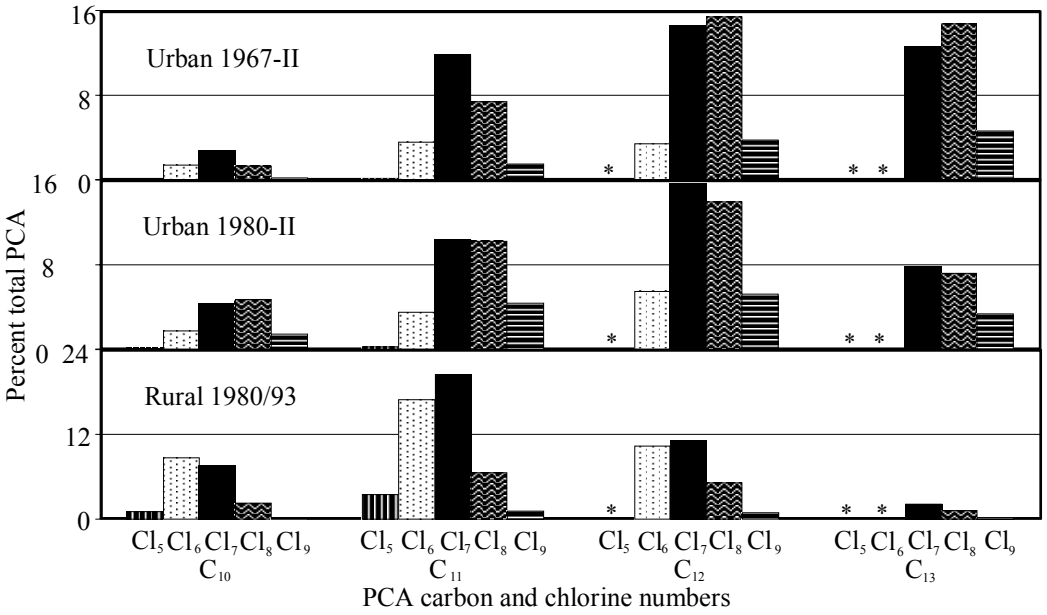

Figure 2. PCA formula group abundance profiles in urban and rural film samples.
* denotes compound not analyzed.

In this sense, the film may be behaving similarly to vegetation from which POPs undergo diurnal volatilization/condensation cycles (6).

In conclusion, these results confirm that an organic film exists on impervious surfaces in both urban and rural areas and the concentrations and patterns are consistent with proximity to source locations. The film is a newly recognized compartment that 1) accumulates particle and gas phase POPs, the latter of which are in dynamic equilibrium with air; 2) influences the fate of POPs through surface-air exchange; and 3) because of the high reproducibility of compound abundance, may be used to obtain a time-integrated sample of air constituents.

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