WASH-OFF OF SOCs FROM ORGANIC FILMS ON AN URBAN IMPERVIOUS SURFACE

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Introduction

Urban areas are characterized by their highly disturbed physical environments and elevated concentrations of numerous chemical compounds. Considerable work has investigated semi-volatile organic compound (SOC) dynamics in naturally occurring media, e.g., air particles, vegetation and soils, however minimal attention has been devoted to the effect of the built environment on SOC dynamics. Using glass windows as a convenient and ubiquitous urban surface, Diamond et al. (1) reported that an organic film develops on impervious surfaces. The film consists of a complex mixture of anthropogenic and biogenic compounds derived from atmospheric deposition. Gas-phase compounds partition into the film, as seen by the correspondence between the film-air partition coefficient, K_{FA}, and the octanol-air partition coefficient, K_{OA}. It is believed that the film increases the dry deposition velocity of air particles (B. Bahavar, unpubl. data) and thus increases the concentration of particle-phase constituents in comparison to those found on "clean" surfaces.

The film is hypothesized to consist of primary and secondary compounds, the latter being polar and lower vapor pressure reaction products of primary emissions, analogous to secondary organic aerosols (e.g., 2). Law and Diamond (3) hypothesized that the polar compounds facilitate the removal of nonpolar SOCs from the film by precipitation. This paper presents evidence that supports the hypotheses that: a) precipitation removes film constituents, and b) the removal is non-selective, i.e., there is little or no relationship between chemical solubility and removal rate.

Methods and Materials

Sample Collection and Preparation. Film wash-off experiments were completed using windows at 3 sites in downtown and 3 sites in suburban Toronto, ON, Canada. The time of last washing was not known. Two sets of samples were collected: total film and residual film remaining after a simulated rain event. The rain event was simulated by spraying ultrapure water at 0.45 L/m^2 or approximately 4 m^2/min, which corresponds to an average rainfall event in Toronto adjusted for that amount falling on a vertical window surface. Windows were sampled by wiping with dry Kimwipes (laboratory tissues), and then dichloromethane (DCM)-wetted Kimwipes (1). Samples were Soxhlet extracted with DCM for at least 12 hours, and then extracts were divided and analysed for PAH/alkanes and organochlorines separately.

Chemical Analyses. 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 100% hexane and contained PCBs. The second fraction was eluted with dichloromethane:hexane (20:80) and contained OC pesticides. After addition of aldrin as a volume corrector, fraction 1 was analysed for 89 individual or coeluting PCBs and fraction 2 for 38 OCs by capillary gas chromatography (GC) with ^{63}Ni electron capture detection (ECD). Recoveries were 90% and 64% for OCN and PCB 30, respectively, and no corrections were made for these recoveries. Blanks were generally less than 5% of sample concentrations. Saturated and unsat-urated hydrocarbons were separated into two fractions on silica/alumina with 100% hexane andhexane:DCM (1:1) as the eluants, respectively and analysed by means of GC-MSD.

Results and Discussion

Film thickness ranged from 125 nm at a site protected by an overhanging roof, to 12 nm at an immediately adjacent site exposed to rainfall (Table 1) which confirms that films are partially, but not completely, removed by natural rainfall. The film contains a range of compounds (Figure 1), some of which originate from the urban area such as PCBs and PAH. Among the most abundant compounds are the penta- and hexa-PCBs which indicate a relatively "fresh" source of chemical, the PAH that are more resistant to photolytic degradation (e.g., phenanthrene, fluoranthene, chrysene), and biogenically derived *n*-alkanes (C-27, C-29 and C-31). The origin of the OC pesticides is likely long-range transport, however higher concentrations are achieved in thicker films that occur downtown and are farthest from source areas. Of the 20 OC pesticides reported, the DDTs and endosulphan were the most abundant. Despite the use of chlordane as a termiticide in certain locations in Toronto, its concentrations in films were very low (< 3 ng/m²).

Film thicknesses and chemical concentrations were higher at urban than suburban sites but chemical composition was strikingly similar. These observations suggest that the urban-suburban air mass is relatively well-mixed and the sources of compounds in the urban-suburban area are relatively uniform, e.g., there are 155 PCB dump sites located throughout Toronto, including near the suburban sites. Concentrations are a function of film thickness, which is controlled by immediate proximity to sources (e.g., distance to roadways), rainfall removal, human washing, and, we suspect, the age of the window which influences surface roughness and microsurface area.

Table 1. Mass of bulk film, film thickness and film SOC concentrations before (total) and after (residual) simulated precipitation, and percentage wash-off. Sample size is 3 urban and 3 suburban locations in Toronto, Canada. Values listed are range, geometric mean.

Sample	Mass, mg/m^2	Thickness, nm	ΣPCB, ng/m^2	ΣPAH, $\mu g/m^2$	ΣOCs, ng/m^2
Total	25–520, 115	6–125, 28	7–300, 53	1.3–18, 4.0	4–57, 14
Urban	50–520, 162	12–125, 40	86–300, 140	2.2–18, 8.4	18–57, 38
Suburban	25–190, 68	6–46, 17	7–165, 20	1.3–2.5, 1.9	4–8, 5.4
Residual			1–96, 15	0.4–3.3, 0.8	1–16, 4.8
Urban			30–100, 43	0.9–3.3, 2.0	4–16, 9.7
Suburban			2–60, 5	0.2–0.7, 0.4	1.5–5, 2.4
% Wash-off			72	79	66
Urban			69	76	74
Suburban			74	82	56

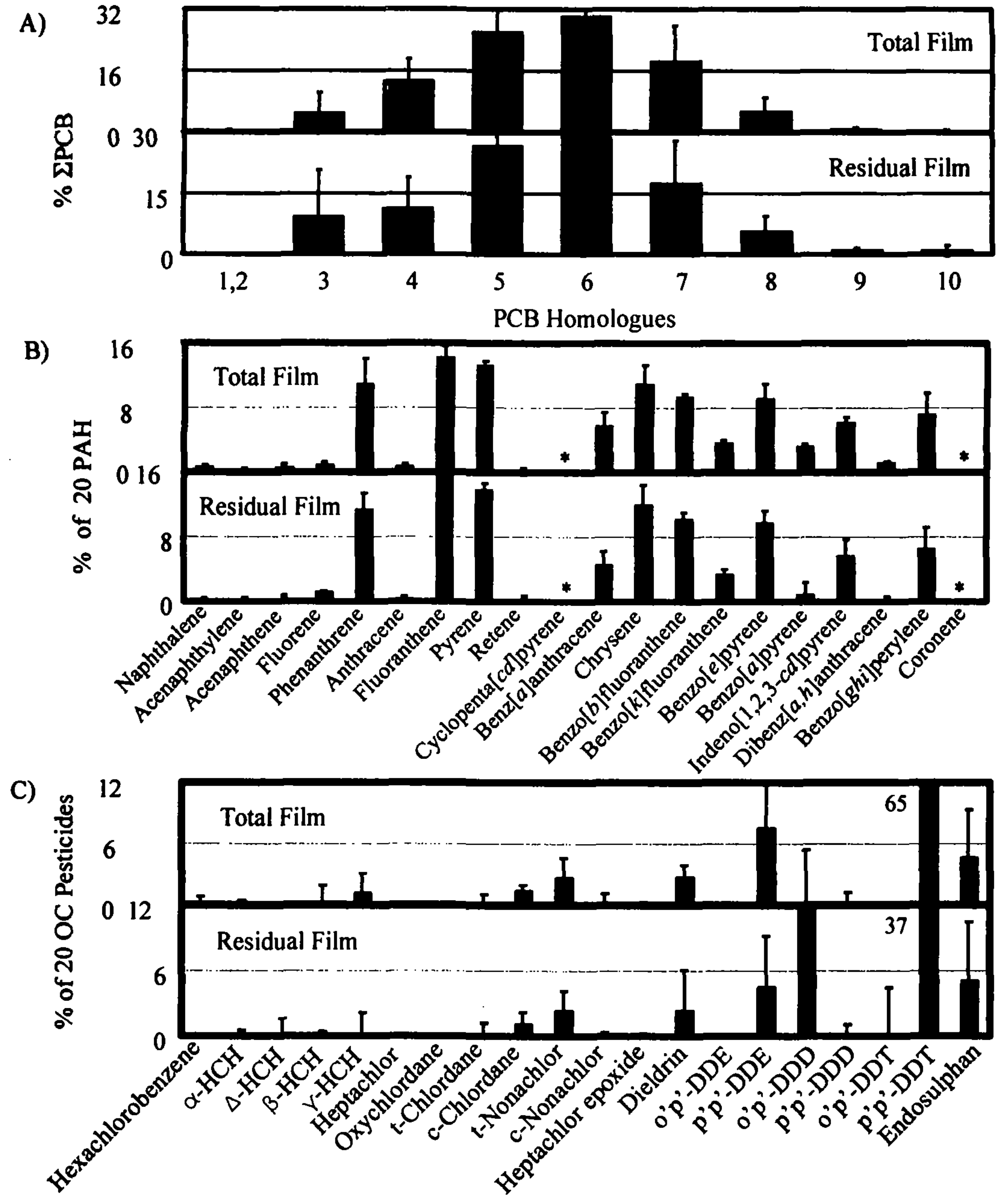

Figure 1. Total and residual film composition, a) PCB homologues, b) PAH and c) OC pesticides.

From 48% (*n*-alkanes) to 79% (PAH) of chemicals were removed from the films by the simulated rain. The removal rate was independent of chemical concentration: regression analyses between total and residual film concentrations yielded R^2 values of 0.98, 0.91, 0.97, 0.995 for individual PCBs, PAH, *n*-alkanes and OC pesticides, respectively. The removal rate was also independent of solubility for all chemicals in all compound classes (Figure 2) and removal rates were similar at urban and suburban sites (ANOVA, $p<0.05$).

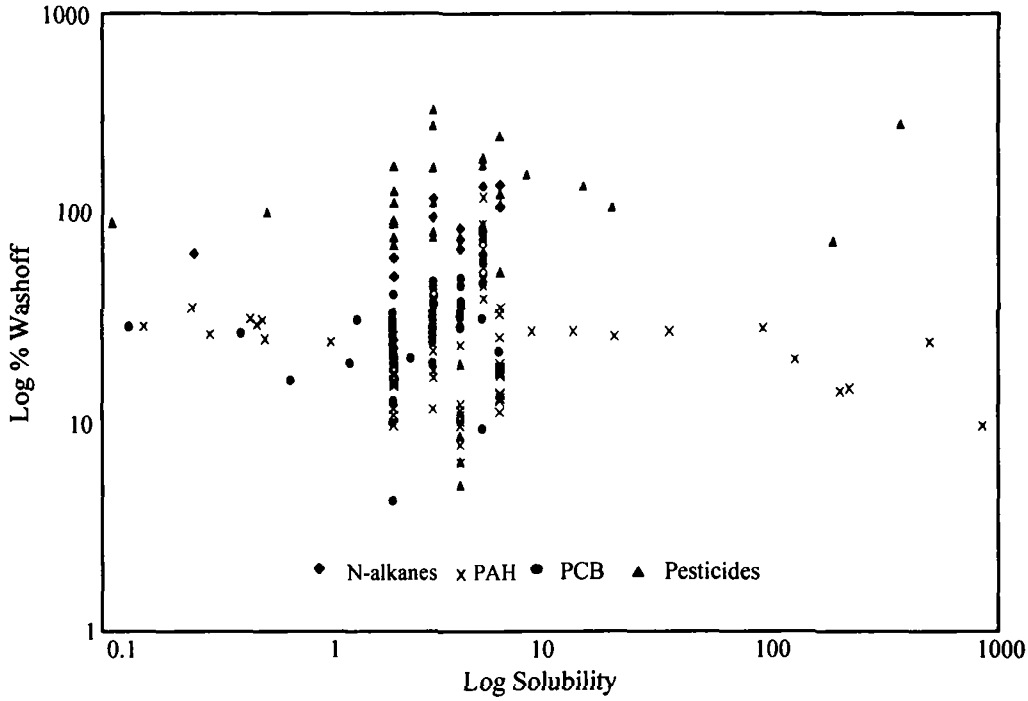

Figure 2. Percentage wash-off versus solubility for *n*-alkanes, PAH, PCBs and OC pesticides.

These results suggest that chemicals in the film, regardless of hydrophobicity, are conveyed to surface waters via precipitation. The role of the film in this transfer lies in the partitioning/ accumulation of gas-phase compounds that would not otherwise be conveyed to surface waters, and increasing concentrations of particle-phase compounds that are captured by the film due to its "greasy" nature. This deduction is confirmed by modeling results which indicate that the film increases SOC air-water transfer and, generally, mobility in urban areas (4).

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