Comparison of Concentrations and Loadings of PCBs and PAHs in Urban and Rural Streams during Base Flow and Storm Events

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Introduction

It is now widely acknowledged that large urban centres are sources of a range of pollutants to the wider environment[1-4]. One pathway through which this occurs is via the movement of pollutants into and through urban waterways. In Toronto, Canada, six streams flow from upstream rural/agricultural land north of the city, through the urbanized area, to an ultimate output to Lake Ontario. Minimal work has been done to characterize loadings of trace contaminants in these rivers, particularly with respect to storm flow events. Urban rivers, and in particular urban storm events, are well known to transport significant loads of nutrients and metals[5,6]. The greatest loadings often occur during the "first flush" or beginning of the storm event when accumulated materials during the antecedent dry period are mobilized[5]. This is accentuated by the speed with which the first flush occurs in areas largely covered by impervious surfaces.

To investigate the riverine aspect of contaminant transport and loadings to Lake Ontario, bulk water samples were collected from urban and suburban stream sites across the Greater Toronto Area (GTA) during low flow and high flow events over 3 months. The comparison of data across the different watersheds and differing land uses can provide insight into the factors and sources influencing the transport of persistent organic pollutants (POPs) through urban areas. In addition, more frequent sampling was conducted during a high flow event at one urban site (Mimico), in order to clarify the transport and loading dynamics of polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) throughout these type of events. To further elucidate the contaminant pathways and transport, a seasonal campaign of air, atmospheric deposition, soil, sediment sampling was also undertaken.

Site Selection and Sampling Methods

Ten stream sites were selected across 6 Toronto watersheds. The sites represent different drainage basin sizes and hydrologic parameters, as well as varying degrees of urban development (Table 1). Samples were collected at base flow and high flow conditions for all 10 sites from September to November 2006.

All samples (18L) were collected from fixed lines with an ISCO 6712 sampler. Following collection samples were fractionated into both the dissolved phase and particulate phase, using a glass fibre filter and XAD fractionation train. All of the samples were then extracted using a Dionex ASE 300. Samples were cleaned up using 1 g Silica SPE tubes. PAH were analyzed using a HP 5890 GC and 5972A MSD fitted with a 30m DB-5 column. PCBs were analyzed using a Agilent 6890 GC and Micromass Autospec-Ultima high resolution MSD fitted with a 30m DB-5 column. Alongside of this all samples were also analysed for a range of general water quality parameters. One field blank and one lab blank were included with each set of samples. All samples were blank corrected.

Results and Discussion

PCBs

The concentration of 32 PCBs in stream water increased from rural sites to urban sites for base flow and high flow (Table 2). The arithmetic mean base flow concentrations of ΣPCBs at rural and urban sites were 16.2 and 928 pg/L, respectively. The mean high flow concentrations of ΣPCBs at rural and urban sites were 922 and 2053 pg/L, respectively. Instantaneous loadings of PCBs were calculated using the measured discharge at the time of sample collection. The loadings followed a similar trend to the concentrations. The instantaneous base flow loadings averaged 0.005 and 1.84 μg/s for rural and urban sites, and 6.53 and 81.3μg/s for instantaneous high flow loadings at rural and urban sites, respectively.

PAHs

The concentration of PAHs in river water also showed an increasing trend from rural to urban sites, with an even greater increase between urban and rural sites, as well as between base and high flow events (Table 2). The mean base flow concentrations of 18 PAHs at rural and rural sites were 7.85 and 75.8 ng/L, respectively. At high flow, the mean concentrations of PAHs at rural and urban sites were 15.7 and 600 ng/L, respectively. Instantaneous loadings of PAHs averaged 6.5 and 84.6 μg/s for rural and urban base flow. PAHs loadings showed a dramatic increase to 47.6 and 23076 μg/s, between rural and urban sites for high flows. Urban-to-rural gradients were only 10-fold for base concentrations but 485 times for instantaneous loadings at high flows.

Flow Event Samples

Samples collected at 1 urban site (Mimico) over the course of a storm event illustrate the dynamics of contaminant transport during the event, as well as the distribution of contaminants between dissolved and particulate phases. Concentrations of PCBs in river water increased from base flow, through first flush, reached the peak concentration at peak flow, then decreased along with flow on the falling limb of the hydrograph (Figure 1). However, an examination of the dissolved phase/particulate phase distribution of PCBs demonstrates that the large increase in PCB concentration at peak flow was entirely due to increased concentrations of particulate-phase PCBs, as the concentration in the dissolved phase remained relatively constant over the entire storm event. An identical trend was seen for PAHs over the same event.

The loadings of particulate-associated contaminants to the river during base and high flow events were expected to be from one of two major sources: (1) wash-off of particles from urban surfaces into streams, and (2) remobilization of bed sediment. The particulate-associated contaminants are most likely from a combination of both these inputs. Stein et al.[5] identified that for PAHs a first flush effect is generally seen when the particle-bound PAHs are washed-off from impervious surfaces, where they accumulated during antecedent dry periods, during the early portions of storms. The efficiency with which particles are mobilized from impervious surfaces depends on precipitation intensity. A first flush effect was not observed for PCBs or PAHs at Mimico. Rather, concentrations peaked with flows which suggested their source is remobilized bed sediment due to bed scour. This conclusion is further supported by a comparison of the relative distribution of PAH compounds in base flow water, high flow water, sediment (Figure 2). The relative distributions of PAH compounds match closely between base flow, high flow and bed sediment which is consistent with bed sediment as a source. However, due to the widely variable hydrologic conditions between sites, this is not a uniform state for all Toronto streams. Comparison of low flow, base flow and sediment PAH distributions for other sites show that Mimico is the only site where PAH profiles in water at high flow and bed sediment are similar. At 6 sites (Markham, Mill, Etobicoke, Broda, Highland and Pottery) the PAH concentrations appeared to be derived from bed sediment under high flow events only, and for the 3 most rural sites (Albion, Dicksons, King), the PAH concentrations did not appear to be sediment-derived during either low or high flow conditions.

It is challenging to understand trace contaminant fate in streams, given the variability in contaminant sources, differences in antecedent dry conditions, dynamics between sites, and variability among storm events. As an example, the instantaneous peak loadings at Mimico varied from 51.1 μg/s to 202 μg/s between the flow events within a two month period.

Conclusions

Urban stream sites yielded higher concentrations and loadings of PCBs and PAHs than rural streams, supporting the contention that urban areas are important sources of POPs to the wider environment. Furthermore, the relative importance of urban areas as a source increases dramatically during wet weather, high flow events.

Acknowledgements:
NSERC, Ontario Ministry of the Environment, Toronto and Region Conservation Authority, Environment Canada, and Great Lakes Atmospheric Deposition Program.

References:
1. Wong, F., Harner, T., Liu, Q., Diamond, M.L. 2004. *Environmental Pollution* 129:387.
2. Offenberg, J.H., Baker, J.E. 1997. *Environ. Sci. Technol.* 31(5): 1534.
3. Motelay-Massei, A., Ollivon, D., Garban, B., Teil, M.J., Blanchard, M., Chevreuil, M. 2004. *Chemosphere*. 55: 555.
4. Harrad, S., Hunter, S. 2006. *Environ. Sci. Technol.* 40(15): 4548.
5. Stein, E.D., Tiefenthaler, L.L., Schiff, K. 2006. *Environ. Toxicol. Chem*. 25(2): 373.
6. Tiefenthaler, L.L., Stein, E.D., Schiff, K.C. 2008. *Environ. Toxicol. Chem*. 27(2): 277.

Table 1: Site Characteristics. Site names and data in regular type are rural and in italics are urban.

Site	Watershed	Population Density (people/km^2)	Drainage Area (km^2)	Upstream Land Use	Mean Discharge (m^3/s)	Distance from Urban Centre (km)
Albion	Humber River	74	N/A	Forested	0.37	47.8
King	Humber River	56	94.8	Agricultural	0.63	33.9
Dicksons	Rouge River	106	N/A	Agricultural	0.59	31.9
Broda	Humber River	662	303	Agricultural	1.93	28.5
Markham	*Rouge River*	*982*	*186*	*Urban*	*1.76*	*26.0*
Highland	*Highland Creek*	*2794*	*88*	*Urban*	*1.56*	*20.7*
Etobicoke	*Etobicoke Creek*	*2390*	*204*	*Urban*	*2.99*	*15.3*
Mimico	*Mimico Creek*	*3104*	*70.6*	*Urban*	*0.992*	*11.2*
Mill	*Humber River*	*4384*	*800*	*Urban*	*8.01*	*9.2*
Pottery	*Don River*	*7021*	*316*	*Urban*	*4.25*	*4.3*

Table 2: Total PCB (32 congeners) and total PAH (18 compounds) concentrations and loadings for base flow and storm events. Site names and data in regular type are rural and in italics are urban.

Site	PCB Concentrations (pg/L)		PAH Concentrations (ng/L)		PCB Instantaneous Loadings (µg/s)		PAH Instantaneous Loadings (µg/s)	
	Base Flow	High Flow	Base Flow	High Flow	Base Flow	High Flow	Base Flow	High Flow
Albion	39.8	6.5	1.1	29.5	0.0094	0.0106	0.3	48.2
King	18.8	3643.9	14.9	5.4	0.0041	26.1194	3.3	38.6
Dicksons	2.0	0.2	2.1	4.9	0.0004	0.0001	0.5	2.4
Broda	4.1	0.8	13.3	23.1	0.0067	0.0037	22.1	101.1
Markham	*3359.0*	*376.0*	*54.3*	*20.6*	*9.0894*	*5.8265*	*147.0*	*318.9*
Highland	*193.1*	*1135.9*	*12.1*	*447.8*	*0.0135*	*6.8153*	*0.8*	*2686.8*
Etobicoke	*714.5*	*2367.3*	*22.8*	*389.2*	*0.4215*	*127.4839*	*13.5*	*20959.2*
Mimico	*766.1*	*6948.0*	*247.4*	*2218.2*	*0.1310*	*201.6300*	*42.3*	*64372.2*
Mill	*133.1*	*454.9*	*28.9*	*95.5*	*0.3784*	*51.8313*	*82.3*	*10882.2*
Pottery	*404.2*	*1034.5*	*89.5*	*431.7*	*1.0024*	*94.0326*	*222.0*	*39237.1*

Figure 1: Turbidity and concentrations of PCBs in stream water over the course of a storm event at Mimico

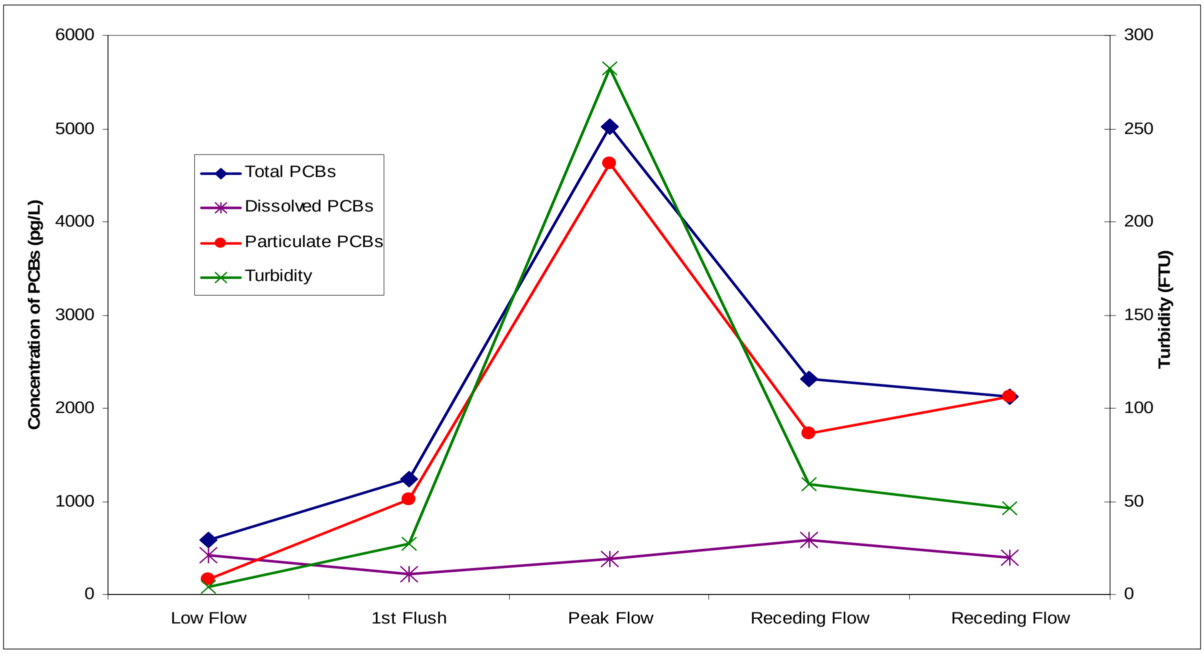

Figure 2: Comparison of relative PAH distributions for Mimico high flow, base flow and sediment