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Simulated rain events on an urban roadway to understand the dynamics of mercury mobilization in stormwater runoff

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ABSTRACT

This research focuses on mercury (Hg) mobilization in stormwater runoff from an urban roadway. The objectives were to determine: how the transport of surface-derived Hg changes during an event hydrograph; the influence of antecedent dry days on the runoff Hg load; the relationship between total suspended sediments (TSS) and Hg transport, and; the fate of new Hg input in rain and its relative importance to the runoff Hg load. Simulated rain events were used to control variables to elucidate transport processes and a Hg stable isotope was used to trace the fate of Hg inputs in rain. The results showed that Hg concentrations were highest at the beginning of the hydrograph and were predominately particulate bound (HgP). On average, almost 50% of the total Hg load was transported during the first minutes of runoff, underscoring the importance of the initial runoff on load calculations. Hg accumulated on the road surface during dry periods resulting in the Hg runoff load increasing with antecedent dry days. The Hg concentrations in runoff were significantly correlated with TSS concentrations (mean $r^2 = 0.94 \pm 0.09$). The results from the isotope experiments showed that the new Hg inputs quickly become associated with the surface particles and that the majority of Hg in runoff is derived from non-event surface-derived sources.

1. Introduction

Urban stormwater runoff is a leading cause of water quality impairment and is a regulatory priority due to high concentrations of numerous pollutants (US EPA, 2002; Novotmy and Olem, 1994). Furthermore, the volume of urban stormwater runoff can be up to 16 times higher than from natural catchments of equivalent area due to the high percentage of impervious surfaces, often resulting in a large mass of pollutants transported to surface waters (Schueler, 1994). Most studies on urban runoff have focused on total suspended solids (TSS) (Chebbo and Gromaire, 2004; Gupta and Saul, 1996), nutrients (Vaze and Chiew, 2002; Hook and Yeakley, 2005), and heavy metals associated with vehicle use such as lead and copper (Ozdilek et al., 2007; McPherson et al., 2005). Elevated mercury (Hg) concentrations have been found in urban waterways (Hurley et al., 1995; Lawson et al., 2001); however, very little research has been conducted on the mobilization of Hg in urban stormwater runoff (Eckley and Branfireun, 2008b). Most research on Hg in runoff has been conducted in natural areas (Allan and Heyes, 1998; Allan et al., 2001); however, it is also important to study this phenomenon in cities because many urban waterways are used for subsistence fishing (Murkin et al., 2003; Kraft, 2000) and often empty into larger water bodies, such as the Great Lakes, resulting in potential impairment of ecosystem function and fisheries.

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The elevated Hg concentrations in urban waterways have been found to be most pronounced during stormflow periods and are predominantly transported in association with particles (HgP) (Hurley et al., 1995; Lawson et al., 2001). The source of the HgP has not been identified and could originate from internal sources such as bank erosion or particle resuspension and/or from external sources such as road surfaces via urban stormwater runoff. Potential sources of Hg on urban surfaces include street dust from pavement and vehicle abrasion, soil, leaf litter, and atmospheric deposition (wet and dry) (Eckley and Branfireun, 2008a; Hopke et al., 1980). Consequently, source attribution of the Hg in runoff presents a challenge, yet is imperative since internal versus external sources require different reduction strategies.

The results from Eckley and Branfireun (2008b) showed that the Hg load in runoff from urban catchments varied within and between events. For example, *within* a given event the Hg concentrations were highest during the leading edge of the hydrograph, which could result from the higher Hg concentrations in rain at the start of an event. Alternatively, the elevated Hg concentrations in the initial runoff could have resulted from a loosely bound fraction of the surface Hg load that is easily transported in the initial runoff but is quickly exhausted, resulting in a decrease in the runoff concentration. Variability in the Hg loads transported *between* runoff events could also result from differences in the Hg concentrations in rain, which can have a large range in concentrations between events (Eckley and Branfireun, 2008b; Poissant and Pilote, 1998; Riedel et al., 2000), but alternatively could result from differences in the amount and/or intensity of rain. The impact energy of rain has been shown to be important in liberating particles bound to the surface, and the runoff discharge influences the entrainment of surface particles (Vaze and Chiew, 2002, 2003; Saget et al., 1996). Furthermore, since Hg can accumulate on a surface from dry deposition, the number of dry days before a given rain event (i.e. the antecedent conditions) could also contribute to the between event variability in Hg loads.

Monitoring Hg in urban stormwater runoff is important to understand the total load that a waterway receives; however, it cannot easily identify the individual influence of any of the abovementioned variables because of concomitant changes within and between events. Furthermore, sampling stormwater runoff cannot elucidate the fate of the Hg in rain or determine whether the Hg in runoff was derived from the rain or from the surface. While the Hg inputs in rain may be of similar magnitude to the outputs in runoff (as observed for several events in Eckley and Branfireun, 2008b), this does not necessarily indicate that the Hg in runoff originated from the rain and that there was no surface contribution. Hg inputs in rain may become retained by surface interactions while the runoff generated may entrain Hg that had accumulated on the surface from preceding wet or dry deposition. Identifying the influences and dynamics of Hg in runoff is imperative to develop process-based models that can predict Hg in urban runoff.

Rainfall simulation experiments have been successfully used to control variables, which can help to elucidate processes involved in pollutant mobilization in runoff (Vaze and Chiew, 2003; Van Metre and Mahler, 2003). Stable isotopes have also been used to trace environmental transport and fate of some pollutants (Harris et al., 2007). This study uses both of these tools to better understand the transport dynamics of Hg in urban runoff from a typical asphalt roadway. Specifically, the objectives of this research are to determine: 1) how the transport of surface-derived Hg changes during an event hydrograph; 2) the influence of antecedent dry days on the Hg load in runoff; 3) the influence of rain event duration on Hg mobilization; 4) the relationship between suspended sediments and Hg transport; and 5) the fate of new inputs of Hg in rain and its relative importance to the runoff Hg load.

2. Methods

2.1. *Site description*

The study was performed during the summer of 2006 at the University of Toronto Mississauga (UTM) campus (43° 33′ N, 79° 40′ W) in the Toronto metropolitan area. The impervious surface studied was the main road (asphalt with concrete curb) that circles the campus. The surface temperature of the road was measured during each simulated rain event using a digital thermometer and ranged between 24 and 35 °C. The road receives moderate weekday use associated with the University (11,500 students) that is mainly accessed via personal automobile transportation. The specific section of road studied has a slight slope (1°) and drains to a low point in the road where a break in the curb diverts runoff water to an infiltration swale.

2.2. *Rainfall simulation*

Nine rainfall events of varying size (3.4–21.9 mm) and antecedent dry days (1.5 h–14 days) were simulated using a simple irrigation system. The characteristics of the simulated rain were within the range of values for real rain events recorded during the 3-month study period. There were 12 natural rain events during this time, totaling 152 mm, and ranging in size and intensity from 0.2 to 35 mm and 3 to 42 mm/h respectively. The average number of dry days between the natural rain events was 7 and the longest dry period was 21 days. During the experiments, the road was temporarily closed to traffic. Water was brought to the road via a hose connected to an external municipal water source. Immediately before the irrigation line, the water was filtered to remove particulate matter and to reduce the concentration of chlorine that is added to the municipal water supply (Rainfresh® ceramic filter with an activated carbon core) and passed through a pressure regulator (30 psi). The pressure was recorded at the end of the hose and did not vary more than 6% within or between events. The hose was connected to 25 m of irrigation line with 14 sprinklers inserted every 1.8 m. Each individual sprinkler wetted a wedge shaped area of ~7 m^2 and together they created a continuously wetted area of 3.0 m by 27.8 m (83.4 m^2). The flow from each sprinkler was measured during each event and varied between 0.033 and 0.045 L/s. There was little variation in the rainfall intensity between events (20–24 mm/h). The Hg concentration in the simulated rain was low; however, other ions were higher than natural rain (with the exception of nitrate) (Table 1). While the chemistry of