Environmental characterization of surface runoff from three highway sites in Southern Ontario, Canada: 1. Chemistry

T. Mayer, Q. Rochfort, J. Marsalek, J. Parrott, M. Servos, M. Baker, R. McInnis, A. Jurkovic and I. Scott

ABSTRACT

Highway runoff is a significant source of contaminants entering many freshwater systems. To provide information on effects of highway runoff on aquatic biota, runoff samples were collected from three sites representing different classes of highways with low, intermediate and high traffic intensities. Samples were analysed for chloride, trace metals and polycyclic aromatic hydrocarbons (PAHs). Runoff from a major multilane divided highway, with the highest traffic intensity, contained the highest levels of chloride (45–19,135 mg/L) and metals. Runoff solids from this highway contained the highest levels of PAHs (19.7–2142 mg/kg). PAHs were also high (9.83–237 mg/kg and 26.4–778 mg/kg) at the intermediate and low traffic intensity sites, respectively. High concentrations of potent mutagens and carcinogens such as benzo(a)pyrene (0.414–124.62 µg/g) and indeno-pyrene (0.549–50.597 µg/g) were measured in the particulate phase of all runoff samples. Chloride concentrations of winter and early spring runoff were significantly higher ($P < 0.001$, $t = 2.66$) than during the rest of the year. Levels of contaminants depended on traffic intensity, road condition (age, composition, maintenance), the condition of metal structures (drains, guardrails, etc.) and seasonal conditions. A companion paper discusses spatial and temporal aspects of contaminant-associated toxicity of highway runoff.

Key words | contaminants, highway runoff, PAHs, road salts, trace metals

T. Mayer
Q. Rochfort (corresponding author)
J. Marsalek
J. Parrott
R. McInnis
A. Jurkovic
National Water Research Institute,
Environment Canada,
867 Lakeshore Rd,
Burlington, ON,
Canada L7R 4A6
E-mail: *Quintin.Rochfort@ec.gc.ca*

M. Servos
Department of Biology,
University of Waterloo,
Waterloo, ON,
Canada N2L 3G1

M. Baker
Health Canada,
2720 Riverside Drive,
Ottawa, ON,
Canada K1A 0K9

I. Scott
Agriculture and Agri-Food Canada,
1391 Sandford St,
London, ON,
Canada N5V 4T3

INTRODUCTION

Highway runoff has been identified as a significant contributor of non-point source pollution, containing a broad variety of contaminants, which enter receiving waters and add to loads from other sources. Many of these substances, which originate from the operation of automobiles and maintenance of highways, are known to occur at levels that can be toxic to freshwater organisms. Increased emphasis on controlling the non-point sources of pollution has intensified the need to discern the toxicological effects of complex mixtures, such as highway runoff.

A network of highways covering over 100,000 km crosses the landscape in highly urbanized Southern Ontario,

Canada. However, the effect of stormwater runoff from these highways on the receiving water bodies is not well understood. Environmental studies of highway runoff can be divided into two groups: those describing the chemical composition of highway runoff (Hoffman *et al.* 1985; Ellis *et al.* 1997; Marsalek *et al.* 1997; Sansalone & Buchberger 1997; Ball *et al.* 1998; Legret & Pagotto 1999; Turer *et al.* 2001; Westerlund *et al.* 2003; Westerlund & Viklander 2006) and others addressing highway runoff toxicity, but typically on the basis of limited biotesting results, which are hard to extrapolate to other biological levels (Gjessing *et al.* 1984; Rokosh *et al.* 1997; Novotny *et al.* 1998; Buckler & Granato 1999;

Van Dolah *et al.* 2005; Sanzo & Hecnar 2006; Kayhanian *et al.* 2008). Furthermore, information on the mutagenic and genotoxic effects of highway runoff on biota is lacking.

A number of authors have attempted to identify the sources of highway runoff toxicity. Maltby *et al.* (1995) and Boxall & Maltby (1995, 1997) reported that highway runoff was toxic to aquatic organisms in streams receiving such runoff and identified hydrocarbons, copper and zinc as potential toxicants. More recent studies of Van Dolah *et al.* (2005) and Meland *et al.* (2010) attributed the adverse effects of highway runoff to multiple stressors, rather than to a particular contaminant. Concerns about road salt releases into the environment led to studies confirming that road salt constituents (e.g. Cl [Mount *et al.* 1997]) played a major role in the toxicity of the highway runoff during winter months (Mayer *et al.* 1998). Yet there have been relatively few studies investigating the chemistry and toxicity of highway runoff in cold climates (Meland *et al.* 2010) employing multiple target organisms in toxicity biotesting. To advance the understanding of environmental impacts of highway runoff on the receiving water bodies, a comprehensive approach examining chemical and toxicological status of highway runoff needs to be taken, and toxicity should be addressed by biotesting at various biological levels.

A seasonal study of highway runoff was carried out in Southern Ontario, with the objectives to: (i) characterize the chemical composition of highway runoff and determine the effect of traffic intensity as well as of other factors on the chemistry of runoff, (ii) establish the linkages between the chemistry and toxicity of runoff by relating the toxicity of runoff to its chemical characteristics and (iii) address the temporal variation in highway runoff toxicity.

The first of the two companion papers follows and addresses the chemical characterization of highway runoff, which is the first objective of the study. Towards that end, the runoff chemistry was assessed at three highway sites with different intensities and composition of traffic, for a number of runoff events occurring during various seasons. The list of constituents studied followed the findings of earlier research (Marsalek *et al.* 1997; Viklander 1997, 1998) and included trace metals, polycyclic aromatic hydrocarbons (PAHs) and road salts, which have been shown to be the most abundant contaminants in highway runoff in cold climates. Recognizing that ferrocyanide compounds are commonly added to road salt as anti-caking agents, several winter runoff samples and solutions of two different concentrations of commercial road salts were also analysed for total and free cyanide.

MATERIALS AND METHODS

Study sites and sample collection

Three sites, each located on a highway with different traffic characteristics, were selected for this study. The sites differed by traffic intensity (Table 1) and the composition of vehicular traffic. Two of the study sites were located on major provincial highways, the Queen Elizabeth Way (QEW) and Highway #2 (Hwy 2), which at the time of the sample collection (1996–1998) served as major transportation routes in Southern Ontario. The QEW is a multilane divided highway and Hwy 2 was (at the time of our sampling) a major arterial road between Hamilton and Brantford, Ontario. Since completion of our sampling program, Hwy 2 became a local road of much lesser importance, because Highway 403 (a multilane divided highway) has been extended through this region and now carries the bulk of traffic that used to travel along the investigated section of Hwy 2. The third site was located on an urban/residential road in Burlington, Ontario, a city with a population of 150,000 (at the time of the study). While the exact breakdown between the trucks and personal vehicles was not available for the studied highways, the major

Table 1 | Physical characteristics of sampling sites at the time of sample collection (1996–1998)

Sampling site	Traffic intensity (vehicles/day)	Length of road between drains (m)	Width of the road between drains (m)
Skyway Bridge (SW), Queen Elizabeth Hwy	92,000	29.25	17.4
Fairchild Creek (FCC), Hwy 2	31,100	6.30	10.8
Plains Road (RBG)	15,460	54.70	10.8[a]

[a]Estimated value.

highway sites were characterized by a substantially heavier volume of truck traffic than the site on the urban/residential road. The QEW, which was comprised of four lanes in each direction at the study site, had the highest intensity of traffic (Table 1) and the greatest number of heavy trucks. This site was followed by Hwy 2, which at the study site was comprised of two lanes in each direction. The Plains Road site in Burlington with two lanes in each direction had the lowest intensity of traffic (Table 1). The sampling site on the QEW was located on the north foot of the James N. Allen Burlington Bay Skyway Bridge (referred to herein as Skyway Bridge) and is denoted here as the SW site. The sampling site on Hwy 2 was located on the bridge over Fairchild Creek and is referred to as the FCC site. Lastly, the sampling site in Burlington was situated on the bridge near the Royal Botanical Gardens parking lot and is referred to as the RBG site. All roads at the sampling sites were paved with asphalt. The lengths of the road drained, represented by the distances between the road drains, are given in Table 1.

The study was conducted over a period of 24 months (1996–1998) encompassing all seasons. In total, 47 samples were collected and analysed. Not all samples collected were analysed for all the runoff constituents discussed in the paper due to limitations in sample volumes and analytical laboratory capacities. At each site, samples were collected by diverting flow from the bridge deck drains into large (200-L) plastic barrels. The runoff samples were taken from the barrels immediately after the individual events and the conductivity and pH of samples were measured. Sub-samples were split for chemical and toxicological analysis. Sub-samples used for chemical analyses were preserved according to the National Laboratory for Environmental Testing, NLET (1998) protocols and stored at 4 °C until analysis.

To determine intra-event variations in runoff quality, manual grab samples of runoff from the SW site were collected at short time intervals during two rain events and used for the time series experiments. The time interval is reported here as the average collection time and represents the mean interval time from the onset of the event.

Sample analysis

Runoff samples were analysed for a broad range of constituents, including trace metals, de-icing salt constituents (Cl, Na, Ca, Mg and K) and PAHs. Inductively coupled plasma (ICP) was used to determine the concentrations of total and dissolved metals. Dissolved metals were determined on samples filtered through 0.45-µm membrane filters. Chloride concentrations were determined using the thiocyanate colorimetric method, which is based on the displacement of the thiocyanate ion (SCN) from mercuric thiocyanate by the chloride ion and subsequent reaction of the liberated thiocyanate with ferric ion to form the coloured ferric thiocyanate complex.

Winter runoff samples and solutions of two different concentrations of commercial road salt (10 and 20 g/L) were analysed for total and free cyanide by the Ontario Ministry of Environment (MOE) analytical laboratory at Rexdale, Ontario. The total cyanides, which include free cyanide, simple cyanides and metal-cyanide complexes, including iron cyanide complexes, were determined colorimetrically using ultraviolet (UV) light digestion and distillation. Cyanides were converted to cyanogen chloride by reaction with chloramine-T, which forms a red complex with iso-nicotinic and barbituric acids. The absorbance of this complex was measured at 600 nm. The free cyanide method measures concentrations of HCN liberated after acidification to pH 4. This method is similar to the method used for the determination of the total cyanides, except that no UV irradiation is used (which avoids the conversion of complexed cyanides).

PAHs were determined in both the aqueous and particulate phases of samples. PAH analysis of the particulate phase was carried out on the material collected on the solvent-cleaned Millipore AP Filter (142 mm diameter). The dry weight of solids was recorded and used for the calculation of concentrations per unit of mass. The PAHs in aqueous phase were determined on the filtrate. The analyses were performed according to NLET protocols no. 03-3261, 03-3751 (NLET 1998). Summaries of the methods used in these analyses are provided below.

Aqueous phase analysis employed an Empore disk extraction followed by GC/MS determination. In this analysis, a 1-L water sample, to which deuterated PAH surrogates had been added, was passed through a 45-mm octadecylsilica (C_{18}) Empore disk using a vacuum at 137–172 kPa. The disks were allowed to dry, then primed with 2 mL of acetone and extracted with 15 mL of cyclohexane. The

cyclohexane was solvent-exchanged with iso-octane and concentrated to 1 mL. This extract, to which external standards were added, was analysed by GC/MSD using selected ion monitoring. The GC/MSD system equipped with a 60 m × 0.25 mm ID fused silica DB-5 column and a mass selective detector was used for determination. The PAHs in particulate phase were extracted with a 1:1 mixture of acetone and hexane. The concentrated extract was partitioned with water and back-extracted with dichloromethane (CH_2Cl_2). The combined extract was concentrated, cleaned up and fractionated using a 3% (w/w) deactivated silica gel column. An extract re-concentrated to a final volume of 10 mL was used for GC/MS determination. The GC/MS conditions were the same as those for the aqueous phase.

RESULTS

Metals, chloride and cyanides

A comprehensive chemical analysis, which would examine organic and inorganic contaminants identified in the literature as potential sources of toxicity in highway runoff, can serve to facilitate source identification without a full-scale Toxicity Identification Evaluation. The most prominent inorganic contaminants in highway runoff in cold climates are heavy metals, including Cu, Zn, Pb, Mn, Fe, Cd and chloride (Westerlund *et al.* 2003). To assess the potential contribution of metals to the observed toxicity, concentrations of metals in runoff samples were determined and, as discussed in the companion paper, related to the toxicity data. The analytical procedures used were designed to differentiate between the total and dissolved metals. Without this distinction, the levels of bioavailable metals may be grossly overestimated, particularly in samples with high sediment concentrations. The concentrations of total and dissolved metals are presented in Table 2. Because of high variations in metal concentrations at all sites, the means presented in Table 2 are geometric means. The close association of metals with sediments is readily apparent from Table 2 and confirmed by high values of the Pearson-moment correlation coefficients (r) between the total suspended solids (TSS) and total elemental concentrations ($r > 0.83$, significant at 99.9% confidence levels). Metal concentrations in

the majority of samples exceeded Canadian Council of Ministers of the Environment (CCME) Guidelines (Table 2), largely because of the high sediment concentrations. While statistically significant differences ($P < 0.01$) were observed between the three sites for many of the total metal concentrations (Table 2), it is clear that they are largely due to sediment concentrations in runoff samples. With the exception of Zn, the inter-site differences in dissolved metal concentrations, however, are much less apparent. The mean dissolved Zn concentration, Zn(D), was significantly ($P < 0.02$) higher at the RBG site than at the remaining two sampling sites (Table 2). The high Zn(D) concentrations at the RBG site were attributed to the input of Zn from new galvanized drainage structures and fittings, recently installed at the bridge during renovations.

The dissolved metal concentrations ($Me_{Dissolved}$) increased with increasing salinity of runoff, suggesting a decrease of partitioning coefficients ($\Pi = ((Me_{Total} - Me_{Dissolved})/(TSS \times Me_{Dissolved}))$). The relation was particularly significant ($P < 0.01$, $n = 33$) for Cd and Cu (Figure 1). The concentrations of dissolved metals in runoff are a function of total metal and ligand concentrations in runoff. The presence of organic and inorganic ligands increases the concentrations of dissolved metals in runoff. Chloride originating from winter road maintenance is a significant contributor to inorganic ligands, enhancing the complexation of metals, thus potentially increasing their concentrations in the aqueous phase.

The field data show a broad range of chloride concentrations, ranging from 4 mg/L to as much as 19,135 mg/L Cl, with geometric mean concentrations 3,219, 397 and 1,213 mg/L for SW, FCC and RBG sites, respectively (Table 2). The elevated concentrations were, as expected, associated with winter and early spring conditions, and the peak concentrations coincided with snowmelt and snowstorm events (i.e. when road salts are applied on highways). The seasonal differences were statistically significant ($P < 0.001$, $t = 2.66$). In general, the highest concentrations of chloride were observed in runoff from the SW site (Table 2).

Low concentrations of total and free cyanides (Table 3), the known additives to road salts, were detected in winter and spring runoff. With the exception of one sample (SW 46, Table 3), the free cyanide (an uncomplexed form of

Table 2 | Ranges and geometric means[a] of concentrations of chloride, total suspended solids (TSS) and total (T) and dissolved (D) metals at the three highway runoff sampling sites[b] over the 2-year sampling period. For comparison, included are the CCME (2011) Guidelines for Protection of Aquatic Life

Constituent	CCME (2011) Guidelines (mg/L)	Concentration (mg/L)					
		SW		FCC		RBG	
		Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range
Chloride		3,219 ± 5,167	45–19,135	397 ± 515	28–1,480	1,213 ± 2,943	4–9,350
TSS		629 ± 597	81–2,288	348 ± 274	34–885	145 ± 105	36–300
Fe(T)	0.300	23.950 ± 16.795	4.2–54.2	10.620 ± 7.489	2.2–24.2	3.650 ± 2.851	1.66–10.5
Fe(D)		0.097 ± 0.118	0.0174–0.496	0.159 ± 0.168	0.0152–0.512	0.041 ± 0.037	0.0073–0.138
Mn(T)		3.770 ± 5.331	0.293–17.9	0.970 ± 0.893	0.198–2.65	0.260 ± 0.199	0.124–0.77
Mn(D)		0.228 ± 0.143	0.0295–0.497	0.190 ± 0.279	0.0175–0.888	0.094 ± 0.065	0.036–0.253
Pb(T)	0.001–0.007[c]	0.264 ± 0.289	0.314–0.974	0.100 ± 0.088	0.0063–0.234	0.037 ± 0.026	0.0145–0.0999
Pb(D)		0.001 ± 0.001	0.0001–0.0028	0.001 ± 0.001	0.0001–0.0027	0.000 ± 0.000	0.0001–0.0013
Zn(T)	0.03	1.259 ± 0.838	0.269–2.72	0.501 ± 0.374	0.0525–1.22	0.609 ± 0.470	0.263–1.82
Zn(D)		0.045 ± 0.038	0.0066–0.146	0.039 ± 0.026	0.0106–0.0991	0.213 ± 0.173	0.0589–0.554
Cd(T)	0.00017[c]	0.007 ± 0.005	0.0011–0.0169	0.002 ± 0.002	0.0005–0.0046	0.001 ± 0.001	0.0005–0.0032
Cd(D)		0.001 ± 0.001	0.00001–0.0053	0.000 ± 0.000	0.00001–0.0003	0.000 ± 0.000	0.0001–0.0014
Cu(T)	0.002–0.004[c]	0.296 ± 0.165	0.0752–0.653	0.105 ± 0.081	0.012–0.234	0.060 ± 0.046	0.0207–0.16
Cu(D)		0.056 ± 0.058	0.0007–0.184	0.018 ± 0.011	0.0052–0.0366	0.025 ± 0.021	0.0043–0.057
Cr(T)		0.086 ± 0.089	0.0117–0.303	0.051 ± 0.05	0.0056–0.138	0.019 ± 0.01	0.0089–0.341
Cr(D)		0.004 ± 0.004	0.0004–0.0153	0.002 ± 0.001	0.0007–0.0039	0.007 ± 0.003	0.0024–0.0128
n		16		10		10	

n = Sample size.

[a]Geometric mean ± SD (standard deviation).

[b]Highway sampling sites: SW = Skyway Bridge, Queen Elizabeth Highway; FCC = Fairchild Creek, Hwy 2; RBG = Royal Botanical Gardens, Plains Road.

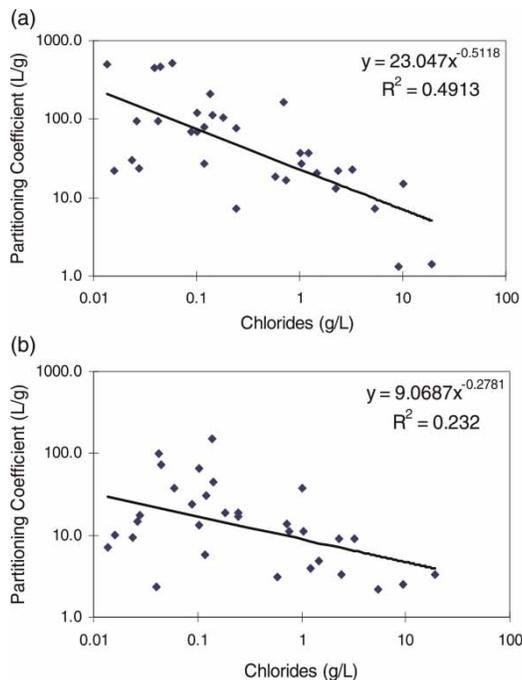[c]Concentrations of Cd, Cu and Pb are water hardness dependent.

(a)

(b)

Figure 1 | Solubility of (a) cadmium and (b) copper as a function of chloride concentrations in runoff ($n = 36$) (Partitioning coefficient $\Pi = ((Me_{Total} - Me_{Dissolved})/(TSS \times Me_{Dissolved}))$).

Table 3 | Cyanide and free cyanide (CN) concentrations in highway runoff and the CCME (2011) Water Quality Guidelines for the Protection of Aquatic Life

Sample ID	Sampling time	Conductivity (µS/cm)	Total cyanide (µg/L as CN)	Free cyanide (µg/L as CN)
SW 40A	November 14 1997	13,000	61.1	5.6
RBG 44	February 12 1998	15,000	18.7	2.3
SW 45	March 18 1998	21,500	67.1	5.0
SW 46	March 26 1998	2,000	55.2	1.8
CCME (2011)				5

CN) accounted for about 10% of the total cyanides. The concentrations of free cyanides (CN) in two out of four samples reached or exceeded Canadian Environmental Quality Guidelines for the Protection of Aquatic Life (5 µg/L) recommended by the CCME (2011). This form of cyanide is toxic to living organisms. The free cyanides are formed by photodecomposition of ferrocyanides. Their concentrations

in solution at any given time are a function of the reaction kinetics of photodecomposition and volatilization. The concentration of total CN measured in commercial road salt was 113 mg/kg (or 113 ppm) and was similar to that (100 mg/kg of road salt, or 100 ppm) commonly specified by the Salt Institute during the time of the study (Bruce Bertram, Salt Institute, unpublished data). In recent years, the use of cyanides in commercial road salts has been targeted for further reductions.

PAHs

PAHs are generally thought to be the most prevalent of the organic contaminants in highway runoff (Marsalek *et al.* 1997). Both solid phase and aqueous phase components of PAH contamination were considered to be important. PAHs in the aqueous phase may have greater immediate effects; however, particulate PAHs are also of concern, as they may be transported and deposited in receiving water bodies, where they may enter and subsequently bioconcentrate through the aquatic food chain.

The chemical analyses revealed that in most samples, PAHs in the aqueous phase were below the detection limits of the instruments used, although their presence can be inferred. The bulk of the PAHs in highway runoff (91%) were in the particulate phase. This was expected, as higher molecular weight PAHs tend to be associated with the particulate matter. High concentrations of those particulate PAHs commonly associated with vehicular emission (phenanthrene [PHEN], fluoranthene [FLUOR] and pyrene [PYR]) were measured at all three sites (Figure 2), although
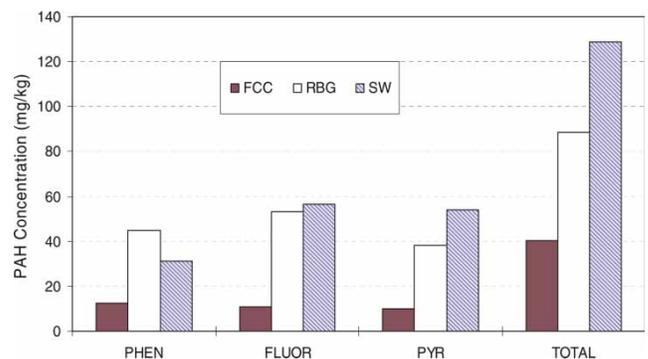

Figure 2 | Mean concentrations of phenanthrene (PHEN), fluoranthene (FLUOR), pyrene (PYR) and total PAHs in runoff sediments from the three sampling sites.

the highest concentrations were usually measured at the SW site. The concentrations of these PAHs (Table 4) exceeded the CCME Guidelines in nearly all samples. High concentrations of potent mutagens and carcinogens such as benzo(*a*)pyrene (0.414–124.62 μg/g) and indeno-pyrene (0.549–50.597 μg/g) were also observed in the particulate phase of runoff (Table 4). Because of the high variations in PAH concentrations at all three sites, the means presented in Table 4 are geometric means. The mean concentration of the benzo(*a*)pyrene at the SW site was about 5.5 times higher than the mean concentration at the FCC site but, surprisingly, only 1.6 times higher than that at the RBG site. Likewise, concentrations of indeno-pyrene were comparable for both sites. The mean concentration of total PAHs (the sum of the 16 priority USEPA pollutant PAHs) was more than three times higher at the SW site than at the FCC site, and nearly one and a half times higher than that at the RBG site (Table 4). Surprisingly, PAH concentrations were higher at the RBG site than at the FCC site, even though the opposite would be expected from the traffic type and intensity. It was noted that the RBG section sampled had recently been repaved due to bridge deck renovations. This likely contributed to elevated PAH concentrations in runoff solids. On the whole, the PAH data confirm notably higher contamination of runoff from the SW site than that observed at the FCC and RBG sites (Figure 2 and Table 4). Runoff particulates (Table 4) collected during the event of July 21 and used for the mixed function oxidase (MFO) induction experiment exhibited the highest concentrations of PAHs at the SW site, followed by the RBG and FCC sites.

DISCUSSION

Seasonal and inter-event variation

A broad variety of factors affect the chemical composition of highway runoff (Marsalek *et al.* 1997; 1999a), including climatic variables, such as temperature; frequency, intensity and duration of precipitation; solar radiation; and anthropogenic factors such as intensity and composition of vehicular traffic, road design and conditions, road structures and appurtenances (e.g. guardrails, signs) and road maintenance.

Table 4 | Concentrations (geometric means and ranges; $n = 11$) of PAHs in solid phase of runoff and PAH concentrations from the selected storm event on July 21. For comparison, presented in the table are also Sediment Quality Guidelines for the Protection of Aquatic Life (CCME 2011)

Site/sample ID	Data type	Phenanthrene (mg/kg)	Fluoranthene (mg/kg)	Pyrene (mg/kg)	Chrysene (mg/kg)	Benzo(a)pyrene (mg/kg)	Indeno-pyrene (mg/kg)	Total PAHs[a] (mg/kg)
SW	Geometric mean	31.16	56.63	54.06	29.85	14.91	8.48	128.7
	Range	1.43–231.07	3.83–415.4	3.32–389.44	1.857–215.49	1.012–24.62	0.611–29.078	19.7–2142
FCC	Geometric mean	12.25	10.64	9.83	3.88	2.69	4.21	40.5
	Range	0.719–98.76	0.394–46.78	0.431–46.78	0.373–13.488	0.526–7.491	0.804–11.645	9.83–237
RBG	Geometric mean	44.92	53.15	38.10	19.26	8.90	11.18	88.6
	Range	2.02–33.51	1.07–213.09	1.170–153.73	0.122–121.64	0.414–43.134	0.549–50.597	26.4–778
SW	July 21	20.76	30.51	20.76	12.12	9.97	8.82	155.8
FCC	July 21	0.81	1.83	1.69	1.11	0.62	1.03	12.2
RBG	July 21	8.12	14.22	11.66	0.12	0.41	0.55	38.43
PEL[b]		0.515	2.355	0.875	0.862	0.782		7.11

[a]Sum of the 16 priority USEPA pollutant PAHs.
[b]PEL = Probable Effects Levels, CCME Canadian Environmental Quality Guidelines, 2011.

The above factors account for most of the seasonal, inter-event and intra-event variations in runoff quality.

Seasonal variation in runoff chemistry generally occurs as a result of changing road maintenance requirements. In climates such as that found in Southern Ontario, freeze/thaw cycles occur in winter, making driving conditions difficult. To keep highways open and maintain safe driving conditions during the winter months, chemical de-icers, typically road salts, such as sodium chloride and/or calcium chloride, are applied to the roads. As a result, substantial loads of salts may be added to other contaminants in runoff during the winter months, enhancing the contaminant burden of winter road runoff (Mayer *et al.* 1999; Ramakrishna & Viraraghavan 2005). As discussed in the companion paper (Mayer *et al.* 2011 – this issue) and Mayer *et al.* (1998) road salt was a significant contributor to runoff toxicity. Because inorganic salts are highly soluble and their constituents behave conservatively (i.e. their concentrations in water are not affected by typical physical, chemical or biological processes), they are not removed by conventional runoff treatment methods like other contaminants. Source control and dilution are the only methods that can be used to reduce the salt concentrations in receiving environments. A substantial dilution of runoff is needed to mitigate the adverse effects of road salt on the aquatic ecosystems. This makes small receiving water bodies, with limited dilution capacities, particularly vulnerable to large seasonal pulses of chloride and associated cations. Furthermore, high concentrations of dissolved salts and metals in runoff may adversely impact groundwater, including water quality in the vadose and saturated zones. Mitigation measures for this class of highway contaminants will have to be different from those for PAHs or metals, which tend to bind to particulates. In Canada, due to concerns about the large quantities of chloride released to the environment and potential adverse effects, the Code of Practice (Environment Canada 2004) was developed and implemented to improve road salt practices with respect to storage, application and snow disposal.

In winter, snow and ice berms are often formed along the side of the road, where they trap pollutants and concentrate them (Viklander 1999; Reinosdotter & Viklander 2005). Solids, metals, PAHs and road salts may build up for long time periods over the winter, and may be collectively washed off during major snowmelt events, such as those observed during our study (Mayer *et al.* 1998 and Table 1 in Mayer *et al.* 2011). This can result in a large toxic load (usually of de-icing salts, metals and oil) in the runoff. High levels of chloride from the application of de-icing salts also alter partitioning of metals between the particulate and aqueous phase, particularly Cd and Cu, increasing their concentrations in the dissolved phase (Figure 1). Similar trends concerning increasing concentrations of dissolved metals (Cd, Cu, Pb, Zn) with increasing chloride concentrations were observed by Novotny *et al.* (1998), Bäckström *et al.* (2003) and Reinosdotter & Viklander (2007) confirming adverse impacts of runoff salinity on the partitioning of heavy metals in road runoff. Major sources of metals in road/highway runoff include highway metal structures and appurtenances, worn tires, corroding car bodies and engine parts, brake shoes and linings and car/truck exhausts. Additional enhancement of the toxicity of runoff containing road salts comes from the presence of cyanides, whose concentrations (Table 3) at the point of discharge occasionally reached or exceeded the values (0.005 mg/L free CN) stipulated by the Canadian Water Quality Guidelines for protection of aquatic life (CCREM 1987; CCME 2011). However, the cyanide concentrations in receiving waters are expected to be sufficiently low due to the upstream dilution, so no adverse effect would be anticipated from these compounds. In the late spring, summer and fall, concentrations of road salt constituents remain low, as expected (4–185 mg/L Cl).

The event characteristics have important implications for the contaminant loads in runoff. Generally, higher intensity rainfall events and longer antecedent dry periods are responsible for greater contaminant loads in runoff (Marsalek *et al.* 1999a, b). In this study, the runoff event with the largest rainfall depth, 24.2 mm, but a zero antecedent dry period, had the highest concentration (74.2 mg/kg) of 16 priority PAHs in the runoff solids. Runoff with the second highest concentration of PAHs (36.6 mg/kg) was collected from the rainfall event characterized by 9.8 mm rainfall and a 3-day antecedent dry period. Lastly, runoff with the lowest concentration of PAHs (26.6 mg/kg) was collected from the lowest rainfall, 5.4 mm, and a zero antecedent period.

Intra-event variation

Pollutants build up over time if they are not removed from the roadways (by either sweeping/cleaning or rainfall). The time between rainfall events is known as the antecedent dry period; the longer this period is, the greater the pollutant build-up will be. Rainfall events mobilize pollutants, which tend to accumulate on the road surface during the antecedent period. When a significant rainfall occurs, the pollutant flux tends to be concentrated in the first portion of the runoff event (Marsalek *et al.* 1999b). This phenomenon is known as the 'first flush' and has been observed to be the most toxic part of the runoff (Marsalek *et al.* 1999b; Shinya *et al.* 2000; Kayhanian *et al.* 2008). The most mobile substances (e.g. soluble salts) wash off the roadway first, while some other materials (such as old oil deposits and larger particles) require larger volumes of water or greater runoff flow velocity to mobilize. This trend is also evident from our study, which shows declining Zn concentrations in runoff collected over the course of an event at the SW site. The data show that the concentrations of dissolved Zn dropped from 1.01 mg/L at the beginning of the event to 0.65, 0.43 and 0.17 mg/L at 13.5, 17.5 and 47.5 min into the rain event, respectively. Our findings are consistent with those of Shinya *et al.* (2000), who showed that more than half of the total pollutant load was washed off during the initial phase of runoff.

Site variation

It has been documented (Marsalek *et al.* 1999a) that the traffic intensity has a major effect on the chemical composition of highway runoff. This trend is apparent (Table 2) from the TSS and most of the metal concentrations, except for Zn. The examination of data showing chemical composition of runoff indicates that the RBG site had the highest levels of dissolved Zn (Table 2), although the traffic volume was the lowest. Input of Zn from the galvanized bridge drain (replaced as part of bridge renovations) was believed to be responsible for the elevated concentration of this metal in runoff and (as shown in Mayer *et al.* 2011) in higher runoff toxicity.

As shown by the spatial differences in the levels of PAHs in runoff solids (Figure 2, Table 4), volume and composition of traffic had a major effect on the levels of these contaminants. Runoff solids from the SW site had the highest PAH concentrations (19.7–2,142 mg/kg, Table 4). This site was located on a major multilane highway, which not only had the highest traffic intensity, but also had the largest number of diesel-driven vehicles. The concentrations of PAHs (Figure 2 and Table 4) in road solids at the RBG site were higher than anticipated from the traffic intensity at that site. This site had also the lowest number of diesel-driven vehicles of the three sites. The reason for higher than expected PAH concentrations may be, as mentioned earlier, a contribution of particles from recently repaved asphalt at this site or a substantially longer segment (Table 1) of the road contributing the sampled runoff. Thus, the data show that in addition to traffic volume and composition, highway structures and the road conditions (age and composition of the road) as well as the road design have significant effects on the chemical composition of runoff. Since our study, methanol-containing additives are increasingly used to reduce PAHs emission (Wu *et al.* 1999) and there is a tendency to use improved materials for road and bridge construction. Coal-tar based pavement sealants, which are a major source of PAHs (Van Metre *et al.* 2009), have already been banned by the State of Washington (Stormwater 2011). All of these measures should serve to improve the overall quality of highway runoff.

CONCLUSION

Chemical analyses of runoff samples show that PAHs, metals and road salts constitute major classes of contaminants in highway runoff. Different sources contribute different classes of contaminants to runoff. As shown by this study, in addition to vehicular traffic, highway structures (e.g. galvanized bridge drains) can be important contributors of metals to runoff. Furthermore, road conditions (age and composition of pavement) can be important contributors of PAHs. Finally, road salt constituents are contributed by applications of chemical de-icers during winter road maintenance. These constituents (chloride) not only have an adverse effect on the salinity of runoff, they are also a contributing factor to the increased concentrations of dissolved heavy metals, their

mobilization and bioavailability. While continuous changes in technology (gasoline additives) are improving the performance of automobiles since the study was carried out and Best Management Practices in Road Salts Use have been implemented, vehicular transport and road mainten-ance remain major sources of metals, PAHs and road salts to aquatic environments.

ACKNOWLEDGEMENTS

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