The contribution of particles washed from rooftops to contaminant loading to urban streams

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Abstract

Rooftops are both a source of and a pathway for contaminated runoff in urban environments. To investigate the importance of particle-associated contamination in rooftop runoff, particles washed from asphalt shingle and galvanized metal roofs at sites 12 and 102 m from a major expressway were analyzed for major and trace elements and PAHs. Concentrations and yields from rooftops were compared among locations and roofing material types and to loads monitored during runoff events in the receiving urban stream to evaluate rooftop sources and their potential contribution to stream loading. Concentrations of zinc, lead, pyrene, and chrysene on a mass per mass basis in a majority of rooftop samples exceeded established sediment quality guidelines for probable toxicity of bed sediments to benthic biota. Fallout near the expressway was greater than farther away, as indicated by larger yields of all contaminants investigated, although some concentrations were lower. Metal roofing was a source of cadmium and zinc and asphalt shingles a source of lead. The contribution of rooftop washoff to watershed loading was estimated to range from 6 percent for chromium and arsenic to 55 percent for zinc. Estimated contributions from roofing material to total watershed load were greatest for zinc and lead, contributing about 20 and 18 percent, respectively. The contribution from atmospheric deposition of particles onto rooftops to total watershed loads in stormwater was estimated to be greatest for mercury, contributing about 46 percent.
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1. Introduction

Particle-bound contaminants are widespread in the urban environment, and impair water quality in many urban streams and lakes. The contribution of non-point sources to this impairment is being increasingly recognized, and occurrence of particle-bound contaminants has been documented in a variety of urban media, including air (Franz et al., 1998), stormwater runoff (Garnaud et al., 1999), and stream sediments (Estebe

et al., 1997). Three groups of contaminants are frequently identified in urban aquatic sediments and have sediment quality guidelines (SQG) based on their toxic effects on benthic biota (MacDonald et al., 2000): trace elements, polycyclic aromatic hydrocarbons (PAHs), and organochlorine compounds.

Rooftops are a common feature of the urban environment, as anyone who has flown into a major airport can attest. Rooftops can play an important role in the pathway that contaminants travel between a source (the atmosphere) and a receptor (an urban stream or lake), as they are efficient collectors of particle fallout from the atmosphere and efficient deliverers of those contaminants to urban runoff during storms (Förster, 1999; Davis et al., 2001). Roofs themselves also can be a

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source of contamination through the leaching and disintegration of roofing materials. Metal roofs have been repeatedly shown to be a source of zinc (e.g., Yaziz et al., 1989; Good, 1993; Quek and Förster, 1993; Steuer et al., 1997), and others have reported roofing materials to be a source of copper (Good, 1993; Förster, 1999) and cadmium (Förster, 1999). However, the relative contribution of atmospheric deposition and roofing materials to contamination from rooftops remains to be determined (Mason et al., 1999), as does the overall contribution of rooftop washoff to urban stream and lake contamination.

Several aspects of rooftop runoff remain to be investigated. Most studies of contamination in rooftop runoff have focused on the occurrence of trace elements in aqueous samples of runoff with the objective of determining roof runoff toxicity, but only a few studies have considered the occurrence of PAHs in rooftop runoff (Daub et al., 1994; Steuer et al., 1997; Förster, 1999). PAHs, largely the products of incomplete combustion of petroleum, oil, coal, and wood, represent the largest class of suspected carcinogens (Björseth and Ramdahl, 1985), are prevalent in urban atmospheric deposition (Franz et al., 1998), and are increasing in concentration in urban lake sediments across the United States (Van Metre et al., 2000). Furthermore, most investigators have focused on contaminants in filtered or unfiltered aqueous samples from rooftop runoff, rather than those bound to particles. Contaminated particles, however, are an important component of urban non-point source pollution (Estebe et al., 1997; Mahler and Van Metre, 2003), and can be toxic to benthic biota (MacDonald et al., 2000). Finally, a better understanding of loading at the watershed scale and the relative contributions of atmospheric deposition and roofing materials are needed.

In this study we focus on the trace element and PAH content of fine particles washed off of two types of roofs: galvanized metal and asphalt shingle. The study was designed to address three questions: How do rooftop particle chemistry and contaminant yield vary with distance from a major roadway? What are the relative yields of trace elements and PAHs in particles from atmospheric deposition and from roofing materials? And, how important is the contribution of rooftop washoff to contaminant loading at the watershed scale? To answer these questions, we sampled particles washed from asphalt shingle and galvanized metal roofs with similar geometries, located at two distances from a major expressway in Austin, Texas, on three different occasions. The particles were isolated by filtration and analyzed for concentrations on a per mass basis for a suite of major and trace elements and organic compounds. Yields for particle-bound contaminants were computed and compared to total watershed yields determined by storm-event sampling in the receiving stream. To our knowledge, this is the first study to compare rooftop yields of particle-bound contaminants to measured watershed event yields.

2. Experimental methodology

2.1. Rooftop sampling

This study analyzed the chemistry of particles washed from rooftops on buildings at Camp Mabry, a retired US Army fort in Austin, Texas. Austin has a humid subtropical climate with hot summers and relatively mild winters. Average annual precipitation is approximately 810 mm and precipitation is fairly evenly distributed throughout the year. Camp Mabry is on the edge of the 33.5 km^2 Shoal Creek watershed and is adjacent to the MoPac Expressway about 5 km northwest of the downtown Austin area (Fig. 1). The buildings at Camp Mabry are symmetric, single story, and shed-roofed (approximately 4:12 pitch). They are about 90-m long by 15-m wide and oriented at a right angle to the expressway on relatively flat ground; the lower edge of the roofs is approximately 4 m above the level of the expressway. The predominant wind direction in Austin is from the south–southeast and secondarily from the north–northeast, generally parallel to MoPac in the area of Camp Mabry. Some buildings have asphalt shingle roofs and others have galvanized metal roofs. The east end of these parallel buildings is 12 m from the paved shoulder of MoPac; the west end is 102 m from the roadway. The MoPac Expressway is a limited access, interstate-style roadway with six traffic lanes and a 2-track rail line down the middle (the Missouri–Pacific Railway). Traffic volume for the stretch of highway next to Camp Mabry for 1999 (the most recent year for which data are available) was 134 000 cars per day (CAMPO, 1999).

Rooftop washoff was sampled from four of these buildings and from the adjacent shoulder of MoPac on three occasions (total of 12 rooftop and 3 shoulder samples) following dry weather periods of between two weeks and one month (Fig. 2). To compensate for any effect that roof orientation might have on deposition, each sample was a composite of water recovered from opposite-facing sections of roof of the same type at the same distance from the expressway. The sites sampled were: metal roofs at the east end of buildings 37 and 38 (nearest MoPac) (MNM), metal roofs at the west end of buildings 37 and 38 (farthest from MoPac) (MFM), asphalt shingle roofs at the east end of buildings 31 and 32 (ANM), and asphalt shingle roofs at the west end of buildings 31 and 32 (AFM) (Fig. 1). The roofing materials on all four buildings appeared to be at least several years old and showed moderate wear.

To collect a sample, pre-cleaned 3-m long PVC gutter was installed at the base of an area of roof. Each area
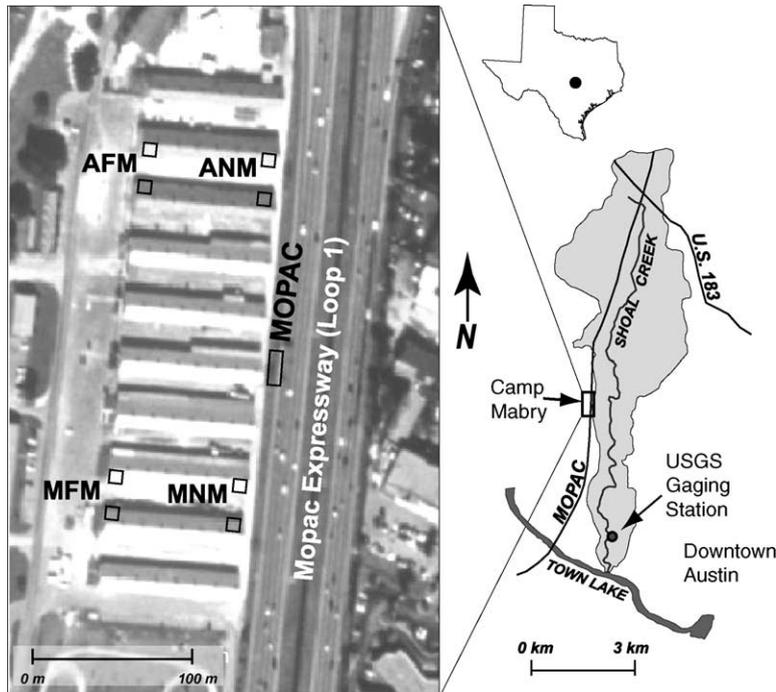
Fig. 1. Location of rooftop sampling sites at Camp Mabry in Austin, Texas, USA. The sites are: metal roofs nearest MoPac (MNM), metal roofs farthest from MoPac (MFM), asphalt shingle roofs nearest MoPac (ANM), asphalt shingle roofs farthest from MoPac (AFM), and the MoPac Expressway shoulder (MoPac).
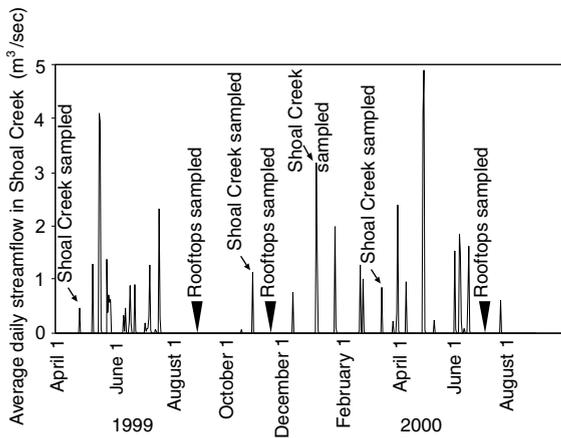

Fig. 2. Timing of rooftop washoff sampling events and Shoal Creek sampling events in relation to rainfall and runoff in Shoal Creek.

was 3-m wide by 8.2-m from the gutter to the peak; two areas (one each from opposite-facing roofs) were washed for each sample for a total area of about 50 m² per sample. A total of 130 l of water was used for each sample, 65 l on each opposite facing section of roof, corresponding to about 2.6 mm (0.1 inches) of depth.

Austin city tap water was pumped into cleaned nalgene carboys and sprayed onto each roof section using a centrifugal pump, tygon tubing, and hand-held sprayer. The effects of sorption and(or) leaching of constituents from the PVC, carboys, and tubing on sediment concentrations were assumed to be minimal because of limited contact time and because suspended sediment, not the dissolved phase, was being analyzed. Austin city water has a total dissolved solids concentration of about 200 mg/l, and a pH of about 10; the eight trace elements analyzed in this study are below detection limits (in µg/l, <2 As, <1.2 Cd, <10 Cr, <6 Cu, <0.36 Hg, <20 Ni, <1 Pb, <20 Zn) (City of Austin, 1999). The water was collected from the down-slope end of the gutter into a funnel, passed through a 63-µm nylon mesh to remove sand-sized and larger particles, which were discarded (including the coarse colored particles used on asphalt shingles), and collected in a 200-l Teflon-bag lined barrel. About 110 l (of 130 l used) was recovered from the metal roofs and about 100 l from the asphalt roofs, as some water was lost to over-spraying, wetting of the roofs, and evaporation.

Particles in water washed off of the shoulder of the MoPac Expressway were also analyzed. Samples were collected similarly to those from the rooftops by spraying 40 l of water onto a 2×14.5 m strip of paved roadway shoulder, for a total area sprayed of 29 m². The

water was contained within the strip by plastic-wrapped sandbags. The runoff was pumped up at the end of the roadway strip, passed through a 63-μm nylon mesh, and collected in Nalgene carboys.

2.2. Sample processing and analytical procedures

Sediment was isolated from water in the barrels on site using inline filtration, following the methods of Mahler and Van Metre (2003). In brief, samples for analysis of major and trace elements were pumped through 142-mm diameter, 0.5-μm poresize Teflon filters in an acrylic filter holder. Sediment was removed from the filter by slipping it into a ziplock bag and gently massaging the filter with a small amount of distilled water. Tests indicate that this process results in nearly 100% recovery of sediment from the filters (Mahler, unpublished data). The sediment–water slurry was freeze dried and ground to a fine powder. Samples were completely digested using a mixture of hydrochloric– nitric–perchloric–hydrofluoric acids and analyzed by inductively-coupled plasma/mass spectrometry (ICP/ MS) or by cold vapor AAS (mercury only) at a USGS laboratory in Denver, Colorado (Arbogast, 1996). Quality assurance was provided by determining the elemental concentrations for duplicate samples and a variety of soil, lake, and marine reference samples.

Samples for analysis of PAHs were pumped through 293-mm diameter, 0.7-μm pore-size baked glass-fiber filters in a stainless-steel filter holder. The filters and the sediments contained were chilled and sent to the USGS National Water Quality Laboratory for analysis. The glass-fiber filters were extracted and analyzed using a variation of the procedures of Furlong et al. (1996). Briefly, sediment was extracted overnight with dichloromethane in a Soxhlet apparatus. The extract was injected into a polystyrene-divinylbenzene gel permeation column and eluted with dichloromethane. The extract was then passed through a silica column cleanup step and analyzed for PAHs and alkyl-PAHs by capillary-column gas chromatography with detection by selected ion monitoring mass spectrometry. Quality assurance was provided by analyzing laboratory duplicate samples, spiked reagent samples, and monitoring recovery of surrogate compounds.

Mass of sediment collected was measured on the freeze-dried samples for elemental analysis, however, mass of sediment could not be directly measured for the organics samples. Samples of unfiltered water were collected during filtration for analysis of suspended-sediment concentration (Guy, 1969). Concentrations of organic compounds were reported by the laboratory as micrograms of constituent per liter of water filtered. The units were converted to mass of constituent per mass of dry sediment based on the volume of water filtered and the suspended sediment concentration of the sample.

3. Results

3.1. Sampling results and statistical testing

Particle-associated contamination from rooftop runoff is evaluated through examination of concentrations as indicators of potential toxicity and yields as indicators of source strength and in the context of total watershed loads. Yield is an expression of the mass of contaminant associated with a unit area and, unlike concentration, is unaffected by the addition of uncontaminated medium (dilution). It is a useful measure of source strength of a contaminant from a given area or source type. Concentrations of selected elements and PAHs in rooftop particles and MoPac Expressway shoulder sediments are presented in Tables 1 and 2. Yields of selected elements and PAHs are presented in Tables 3 and 4. Total PAH as presented here is the sum of 18 parent PAHs and their alkylated homologues.

Statistical differences between groups of samples were tested using the sign test (Helsel and Hirsch, 1992). Trace element and PAH concentrations and yields were compared between the two roof types and between samples collected nearer to and farther from the MoPac Expressway. Samples from asphalt shingle roofs near and far from MoPac were paired with those from metal roofs near and far from MoPac, respectively, to test differences between roofing material types. Samples from both roof types near MoPac were paired with samples from both roof types far from MoPac, to test differences between roof location in proximity to the expressway. In each case, six pairs of samples—three sampling events with two matched pairs of roof type or location for each event—were available for testing. Five of six samples larger than their matched pair resulted in a *p*-value of 0.11 and six of six in a *p*-value of 0.016. We chose to reject the null hypothesis (no difference between the groups) at $p \leqslant 0.11$. For those groups that were determined to be significantly different, a coefficient of difference (C_d) was computed, expressed as the ratio of the median difference between the pairs to the median of all samples; the larger C_d, the larger the difference between the groups. A C_d greater than 0.5 was considered to be large (median difference more than 50 percent greater than median value).

Tables 1 and 2 include event-mean concentrations of contaminants associated with suspended sediments for four runoff events sampled at Shoal Creek during the time period when the rooftop sampling occurred (Mahler and Van Metre, 2003) and, for three of those events, concentrations for a suspended sediment sample collected at the beginning of the rise in stream stage (first flush) (Mahler, unpublished data). The suspended sediment samples from Shoal Creek were collected using automated samplers and isolated from whole water by the same filtration approach and analyzed by the same

Table 1
Concentrations of particulates, organic carbon, and selected trace elements in stream and rooftop particles

Sample	Date	Particulates (mg/l)	Organic carbon (%)	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Hg (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
Shoal Creek first flush	04/26/99	59	NA	11	3.0	82	170	0.37	32	280	830
Shoal Creek first flush	10/30/99	31	NA	12	1.6	74	48	–	34	150	450
Shoal Creek first flush	03/17/00	355	NA	12	0.9	65	45	0.12	30	76	310
Shoal Creek composite	04/26/99	117	3.4	11	0.5	72	29	0.06	26	47	180
Shoal Creek composite	10/30/99	1107	1.4	11	0.5	82	25	–	29	40	160
Shoal Creek composite	01/07/00	901	2.6	9.7	0.5	68	23	0.05	37	36	141
Shoal Creek composite	03/17/00	205	NA	11	0.6	94	30	0.04	34	38	210
Mopac	08/30/99	730	7.8	8.2	3.7	62	95	0.09	44	110	740
Mopac	11/22/99	1460	8.5	9.3	3.8	66	120	0.04	40	100	1200
Mopac	07/07/00	1250	6.6	6.2	1.4	26	35	0.04	23	240	390
ANM	08/30/99	280	13	7.8	4.6	66	98	0.22	32	360	1600
ANM	11/22/99	514	7.7	7.8	3.3	67	88	0.23	29	300	1200
ANM	07/07/00	97	16	7.2	4.3	58	84	0.16	28	390	1900
AFM	08/30/99	72	14	7.9	3.6	60	89	0.22	69	370	900
AFM	11/22/99	249	7.6	9.1	1.9	56	50	0.31	30	300	710
AFM	07/07/00	64	11	7.6	2.5	54	53	0.09	30	220	930
MNM	08/30/99	259	11	6.6	7.6	67	99	0.07	36	120	3800
MNM	11/22/99	220	11	9.3	6.3	80	110	0.06	55	130	4600
MNM	07/07/00	355	13	7.3	7.2	57	96	0.08	31	120	4500
MFM	08/30/99	123	12	9.0	5.6	68	85	0.18	43	170	4300
MFM	11/22/99	178	7.6	11	4.7	57	59	0.06	45	130	3600
MFM	07/07/00	65	12	8.9	7.4	56	77	0.10	36	150	6200
PEC[a]				33	5.0	111	149	1.06	49	128	459
C_d asphalt versus metal (C_d[b] negative if metal > asphalt)				−0.15	−0.63	−0.03	−0.12	0.88	−0.14	0.95	−1.14
C_d near MoPac versus far from MoPac (C_d negative if west > east)		0.86		−0.16	0.32	0.08	0.29		−0.10		

[a] Probable Effect Concentration (PEC) from MacDonald et al. (2000).
[b] Coefficient of difference (C_d) listed only in those cases where the difference between groups was significant.

Table 2
Concentrations of selected PAH compounds and ratios in stream and rooftop runoff particles

Sample	Date	Naph-thalene (µg/kg)	Fluorene (µg/kg)	Phenanth-rene (µg/kg)	Anthra-cene (µg/kg)	Fluo-ranthene (µg/kg)	Pyrene (µg/kg)	Benz(a)-anthra-cene (µg/kg)	Chry-sene (µg/kg)	Benzo(a) pyrene (µg/kg)	Di-benzo(a,h)-anthracene (µg/kg)	Total PAH (µg/kg)	Sum $(2+3)$/ total com-bustion parents
Shoal Crk first flush	04/26/99	142	110	3200	320	8500	7100	2200	5800	3200	640	68 000	0.13
Shoal Crk first flush	10/30/99	94	87	1600	240	6100	4500	1500	3900	2800	580	56 000	0.16
Shoal Crk first flush	03/17/00	12	66	1800	220	4300	3400	1600	3100	2100	340	34 000	0.13
Shoal Crk composite	04/26/99	18	21	640	58	1900	1500	440	1200	650	110	15 000	0.13
Shoal Crk composite	10/30/99	13	14	380	40	1200	900	240	700	430	86	9800	0.15
Shoal Crk composite	01/07/00	14	23	610	51	1900	1400	540	1100	820	100	15 000	0.12
Shoal Crk composite	03/17/00	17	29	960	100	2400	1800	620	1600	980	190	19 000	0.16
Mopac	08/30/99	56	11	270	38	680	490	150	510	220	42	6500	0.36
Mopac	11/22/99	56	10	180	27	430	360	120	320	190	41	5300	0.32
Mopac	07/07/00	20	10	130	17	210	170	50	180	88	24	4200	1.1
ANM	08/30/99	125	31	890	110	2200	1800	640	1400	930	300	22 000	0.21
ANM	11/22/99	78	23	510	64	1200	1000	390	860	600	140	12 000	0.17
ANM	07/07/00	175	30	760	100	2200	1900	640	1800	1100	140	23 000	0.20
AFM	08/30/99	138	41	1200	190	3700	3000	1000	2800	1900	720	34 000	0.14
AFM	11/22/99	72	36	800	100	2100	1700	640	1400	970	220	19 000	0.15
AFM	07/07/00	128	40	1100	150	3100	2600	930	2300	1600	230	30 000	0.17
MNM	08/30/99	135	39	930	120	2400	2000	660	1600	1000	320	22 000	0.18
MNM	11/22/99	169	55	1100	130	2400	2000	680	1600	1100	270	24 000	0.19
MNM	07/07/00	96	28	700	82	1600	1300	390	1200	790	110	17 000	0.19
MFM	08/30/99	81	34	1100	110	3400	2800	730	2100	1400	240	25 000	0.15
MFM	11/22/99	56	35	550	68	1400	1100	450	960	680	150	13 000	0.16
MFM	07/07/00	310	130	3400	380	9200	7700	2500	6800	4800	580	85 000	0.14
PEC[a]		561	536	1170	845	2230	1520	1050	1290	1450			
C_d[b] asphalt versus metal (C_d negative if metal > asphalt)													
C_d east (near MoPac) versus west (far from MoPac) (C_d negative if west > east)		−0.33		−0.42	−0.41	−0.42	−0.33	−0.37				−0.31	0.21

[a] Probable Effect Concentration (PEC) from MacDonald et al. (2000).
[b] Coefficient of difference (C_d) listed only in those cases where the difference between groups was significant.

Table 3
Yields of particulates and particle-bound trace elements from Shoal Creek and expressway and rooftop washoff

Sample	Date	Particu-lates (g/m^2)	As (µg/m^2)	Cd (µg/m^2)	Cr (µg/m^2)	Cu (µg/m^2)	Hg (µg/m^2)	Ni (µg/m^2)	Pb (µg/m^2)	Zn (µg/m^2)
Shoal Creek composite	04/26/99	0.61	6.8	0.32	44	17	0.037	16	29	110
Shoal Creek composite	10/30/99	2.8	29	1.5	229	69	–	81	110	460
Shoal Creek composite	01/07/00	6.8	66	3.0	462	155	0.34	240	240	950
Shoal Creek composite	03/17/00	0.44	4.9	0.28	41	13	0.019	15	17	93
Mopac	08/30/99	1.0	9.6	4.3	72	111	0.100	51	130	860
Mopac	11/22/99	2.0	21.6	8.9	154	276	0.093	93	240	2900
Mopac	07/07/00	1.7	12.5	2.7	53	70	0.080	45	480	790
ANM	08/30/99	0.54	4.4	2.6	37	55	0.12	18	200	900
ANM	11/22/99	0.99	8.0	3.4	69	91	0.24	30	310	1200
ANM	07/07/00	0.19	1.4	0.8	11	16	0.031	5.4	76	370
AFM	08/30/99	0.14	1.1	0.5	8.7	13	0.032	9.9	53	130
AFM	11/22/99	0.48	4.5	0.9	28	25	0.15	15	150	350
AFM	07/07/00	0.12	0.97	0.32	6.9	7	0.012	3.9	28	120
MNM	08/30/99	0.55	3.8	4.3	38	56	0.040	20	71	2200
MNM	11/22/99	0.47	4.5	3.0	39	55	0.029	27	64	2200
MNM	07/07/00	0.75	5.7	5.7	44	75	0.062	25	93	3500
MFM	08/30/99	0.26	2.4	1.5	19	23	0.049	12	47	1200
MFM	11/22/99	0.38	4.2	1.8	22	23	0.023	18	50	1400
MFM	07/07/00	0.14	1.3	1.1	8.1	11	0.014	5.1	21	880
C_d asphalt versus metal (C_d negative if metal > asphalt)				−0.56				−0.12	0.79	−1.0
C_d east (near MoPac) versus west (far from MoPac) (C_d negative if west > east)		0.82	0.58	1.4	0.96	1.6	0.95	0.55	0.89	0.81

methods as used for the rooftop samples. First flush samples were obtained from the first bottle of water collected soon after stream stage began to rise. Event-mean concentrations were determined in flow-weighted composite samples using up to seven discrete samples pumped over the storm hydrograph (Mahler and Van Metre, 2003).

3.2. Bulk sediment characteristics

The sediment analyzed from the rooftops was all in the silt and clay-size range because sand-sized particles (>63 µm) were removed by sieving during collection. Although not sieved, suspended-sediment samples from Shoal Creek were also in the silt and clay-size range, with typically less than 5 percent sand-sized particles in both first flush and composite (event-mean) samples (Mahler, unpublished data).

During the first part of the sampling the water washed off roofs was laden with black particles, but after approximately half of the 2.6 mm per unit area of water was applied, and for the remainder of application, the water recovered was clear. We therefore concluded that the great majority of particles that are easily mobilized

and washed off during rainfall are removed by the first ∼2.6 mm of rain or less. Quek and Förster (1993) reported similar results, finding that the concentration of suspended sediment in runoff reached a minimum after about 1 mm of rainfall. This implies that the rooftop yield of particles occurs early for intense storms, and that the yields calculated are an estimate of the "total rainfall event yield" from the rooftops. Like the rooftop samples, first-flush samples from Shoal Creek were black in color. Samples collected from Shoal Creek later in the storm event and storm-event composite samples were olive gray to dark yellow-brown in color.

The suspended sediment concentration in water recovered during the rooftop sampling varied from 64 to 514 mg/l (Table 1). There was no difference in suspended sediment concentrations between rooftop types, but the concentration and yield washed from sites near MoPac was markedly greater than from sites farther from MoPac (Figs. 3 and 4) (C_d values of 0.86 and 0.82, respectively).

Organic carbon concentrations (Table 1) were similar among rooftop samples, and there was no difference in organic carbon concentrations either between roof types or with distance from the expressway. The median

Table 4
Yields of selected particle-bound PAHs from Shoal Creek and expressway and rooftop washoff

| Sample	Date	Naphtha-lene ($\mu g/m^2$)	Fluorene ($\mu g/m^2$)	Phenanth-rene ($\mu g/m^2$)	Anthra-cene ($\mu g/m^2$)	Fluo-ranthene ($\mu g/m^2$)	Pyrene ($\mu g/m^2$)	Benz(a)a-nthracene ($\mu g/m^2$)	Chrysene ($\mu g/m^2$)	Benzo(a)-pyrene ($\mu g/m^2$)	Dibenzo (a,h)anthra-cene ($\mu g/m^2$)	Total PAH ($\mu g/m^2$)
Shoal Crk composite	04/26/99	0.011	0.012	0.39	0.035	1.1	0.89	0.27	0.76	0.93	0.070	9.2
Shoal Crk composite	10/30/99	0.037	0.039	1.1	0.11	3.5	2.5	0.68	2.0	1.2	0.24	28
Shoal Crk composite	01/07/00	0.098	0.16	4.1	0.35	13	9.8	3.7	7.5	5.6	0.69	100
Shoal Crk composite	03/17/00	0.008	0.013	0.42	0.044	1.1	0.80	0.27	0.71	0.43	0.082	8.4
Mopac	08/30/99	0.066	0.013	0.32	0.045	0.80	0.58	0.18	0.59	0.26	0.050	7.6
Mopac	11/22/99	0.13	0.024	0.43	0.063	1.0	0.85	0.29	0.74	0.45	0.096	12
Mopac	07/07/00	0.040	0.019	0.26	0.034	0.42	0.34	0.10	0.37	0.18	0.048	8.3
ANM	08/30/99	0.070	0.018	0.50	0.062	1.2	1.0	0.36	0.76	0.52	0.17	12
ANM	11/22/99	0.080	0.024	0.52	0.066	1.3	1.1	0.40	0.88	0.62	0.15	13
ANM	07/07/00	0.034	0.006	0.15	0.020	0.42	0.36	0.12	0.34	0.22	0.028	4.5
AFM	08/30/99	0.020	0.006	0.17	0.028	0.54	0.44	0.15	0.40	0.28	0.10	4.9
AFM	11/22/99	0.036	0.018	0.40	0.050	1.0	0.86	0.32	0.68	0.48	0.11	9.6
AFM	07/07/00	0.016	0.005	0.13	0.020	0.40	0.34	0.12	0.30	0.20	0.030	3.9
MNM	08/30/99	0.077	0.022	0.53	0.070	1.4	1.1	0.37	0.92	0.59	0.18	13
MNM	11/22/99	0.082	0.026	0.53	0.062	1.2	0.97	0.33	0.79	0.53	0.130	12
MNM	07/07/00	0.075	0.022	0.55	0.064	1.2	1.0	0.31	0.92	0.62	0.090	13
MFM	08/30/99	0.022	0.009	0.31	0.031	0.92	0.75	0.20	0.57	0.37	0.066	6.9
MFM	11/22/99	0.022	0.014	0.21	0.026	0.53	0.44	0.18	0.38	0.26	0.057	5.2
MFM	07/07/00	0.044	0.018	0.48	0.055	1.3	1.1	0.35	0.97	0.68	0.084	12
C_d asphalt versus metal (C_d negative if metal > asphalt)		−0.18	−0.22	−0.20								
C_d east (near MoPac) versus west (far from MoPac) (C_d negative if west > east)		1.3	0.47	0.42	0.50	0.34	0.33	0.34	0.40	0.37	0.40	0.47
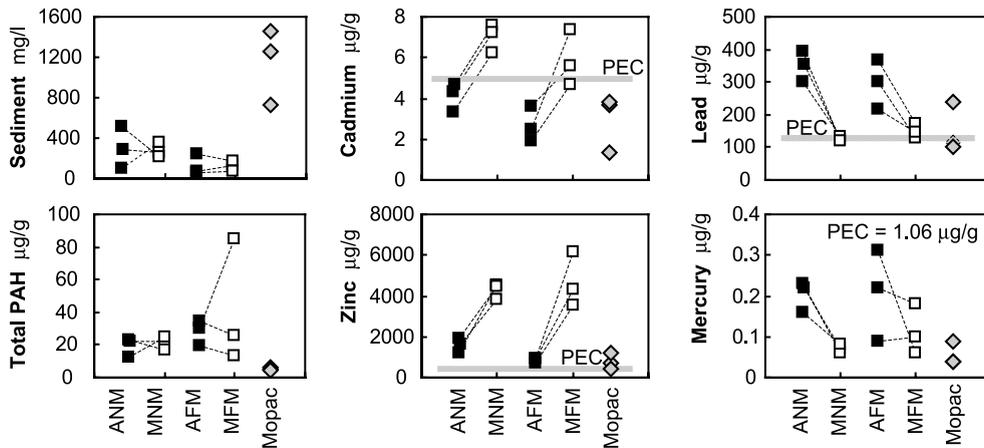
Fig. 3. Effect of roofing material and proximity to the MoPac Expressway on concentrations of selected constituents in rooftop and MoPac shoulder particles. Sites are shown in Fig. 1. Symbols are: asphalt roofs (■); metal roofs (□); MoPac shoulder (◇). Paired samples linked by dashed lines are asphalt versus metal roofs at similar distance from MoPac. PEC is the Probable Effect Concentration SQG (MacDonald et al., 2000). The effect of proximity to the expressway can be seen by comparing the two sets of dark squares to each other and the two sets of open squares to each other.

concentration was 11.6 percent. This is about four times that typical of suspended sediment from Shoal Creek. The organic carbon concentration of the MoPac shoulder samples was a little less than that of the rooftop samples, with a range of 6.6–8.5 percent.

The overall abundance of major elements was similar between all samples, including those from Shoal Creek, and followed the pattern: $Ca > Al > Fe > K \cong Mg > Na \cong Ti > P$. Concentrations of calcium were higher in the samples from the MoPac shoulder than from any of the rooftop samples, probably reflecting local carbonate geology and contribution of roadside soils to particles

on roadways. Concentrations of all major elements except calcium and magnesium were higher from metal rooftops than from asphalt-shingle rooftops suggesting either a difference in particle trapping or dilution of trapped particles by calcium and magnesium from asphalt roofs. Asphalt shingles are reported to contain 8–40 percent limestone, silica, dolomite, or other crushed rock as a filler and stabilizer (California IWMB, 2003). Although calcium concentrations were not statistically greater in asphalt roof samples than metal (4 of 6 sample pairs were greater), the calcium to aluminum ratio was greater in all six sample pairs with a mean of 4.24 versus
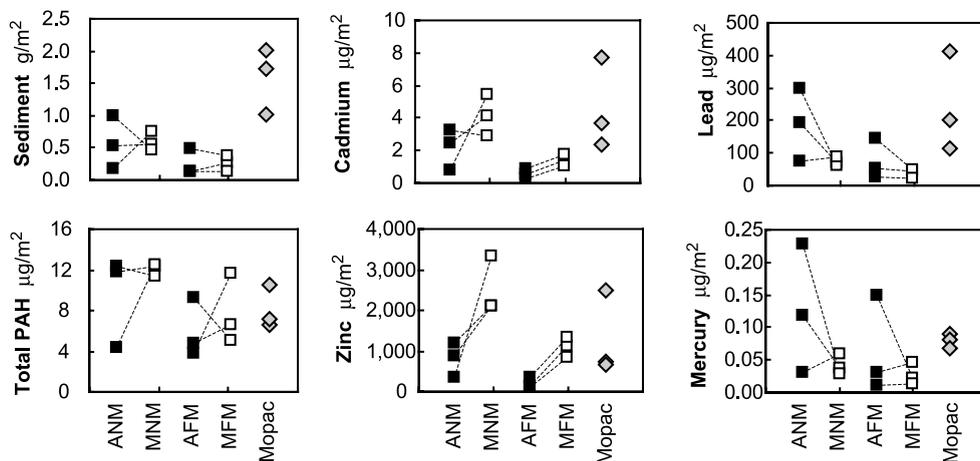

Fig. 4. Effect of roofing material and proximity to the MoPac Expressway on particle-associated yields of selected constituents in rooftop and MoPac shoulder particles. Graphs follow same general layout as Fig. 3.

3.11. A difference in particle trapping on roofs, for example the more efficient trapping of silts by the rougher asphalt shingle roofs, could also cause the differences in major elements.

The major-element assemblages of the rooftop and MoPac shoulder samples were more similar to those of the Shoal Creek first-flush suspended sediment than those of the Shoal Creek event-composite samples. Concentrations of aluminum, potassium, titanium, and magnesium were higher in the Shoal Creek event-composite samples than in those from the rooftop samples from both rooftop types, the MoPac shoulder, and the Shoal Creek first flush samples, suggesting a greater proportion of clay minerals in the Shoal Creek event composite samples.

3.3. Contaminant concentrations associated with rooftop particles

3.3.1. Trace element concentrations

Concentrations of trace elements were compared between the two types of roofs (metal versus asphalt: MNM and MFM versus ANM and AFM) and between the locations of the roofs (near MoPac versus far from MoPac: MNM and ANM versus MFM and AFM) (Table 1; Fig. 3). With the exceptions of lead and mercury, concentrations of trace elements were significantly higher in samples from the metal roofs than those from the asphalt shingle roofs. The differences were most pronounced for cadmium and zinc (C_d values of −0.63 and −1.14, respectively). Lead and mercury concentrations were significantly higher in samples from the asphalt shingle roofs, with relatively high C_d values of 0.95 and 0.88, respectively. Differences for arsenic, chromium, copper, and nickel are relatively small (C_d values range from −0.03 to −0.15) and none were significantly larger from metal roofs if concentrations are normalized to aluminum, suggesting the modest differences could be a consequence of the apparent higher clay content of metal roof sediments. Concentrations of cadmium, chromium, and copper were higher in samples closer to the expressway, and concentrations of arsenic and nickel were higher in samples farther from the expressway, but the differences were not as pronounced as some of those between roof types (Table 1). Mercury, lead, and zinc did not show any spatial differences in concentration.

Concentrations of most trace elements in the Shoal Creek event-composite samples tended to be similar to each other, and, with the exception of arsenic and chromium, were lower in the creek samples than in the rooftop samples, in some cases by as much as an order of magnitude (lead, zinc). In contrast, arsenic and chromium were slightly higher in the creek samples than in the rooftop samples, although a pair-wise statistical test could not be carried out.

3.3.2. PAH concentrations

No differences in concentrations of PAHs were observed between the two types of roofs (Table 2; Fig. 3). This was of interest because the working hypothesis was that deterioration of asphalt shingle roofs contributes PAHs to the environment. Concentrations of 7 of the 10 PAHs statistically tested and total PAH were higher in the samples collected farther from the expressway, with C_d values from 0.31 to 0.42. This too was unexpected, because a second working hypothesis was that PAH concentrations would be higher closer to the expressway. Concentrations of PAHs from rooftops were generally higher than those in Shoal Creek composite samples and lower than those in Shoal Creek first flush samples.

The assemblage of PAH compounds indicates subtle differences in PAH sources for the rooftop and Shoal Creek samples. Uncombusted sources (e.g., decomposing organic matter, oil seeps, petroleum spills) contain predominantly 2- and 3-ringed compounds, whereas combustion (e.g., vehicle exhaust, domestic heating with coal, forest fires) results in predominantly 4- and 5-ringed species (Eganhouse and Gossett, 1991). A decrease in the ratio of 2- and 3-ringed PAH compounds plus homologues to the sum of the major "combustion" PAHs (fluoranthene, pyrene, benz(a) anthracene, chrysene, benzo(b)fluoranthene, benzo(k) fluoranthene, benzo(e)pyrene, benzo(a)pyrene, indeno (1,2,3-cd)pyrene, and benzo(g, h, i)perylene) indicates a shift from uncombusted to combusted fossil fuels as the PAH source (Van Metre et al., 2000). The proportion of non-combustion sources relative to combustion sources is consistently larger in near to MoPac rooftop samples than in the far from MoPac samples. The road shoulder is enriched in non-combustion sources compared to all of the rooftop and creek samples (Table 2). Shoal Creek first flush samples have a PAH source ratio similar to that of the far-MoPac rooftop samples.

3.4. Contaminant yields associated with rooftop particles

3.4.1. Particle yields

Trace element and PAH yields were compared between the two roof types and between samples collected nearer to and farther from the MoPac Expressway (Tables 3 and 4; Fig. 4). Contaminant yield is directly proportional to particle yield, as contaminant yield is computed as the product of contaminant concentration and total particle yield. Near-MoPac total particle yields were significantly larger than far from MoPac particle yields, with a C_d of 0.82.

3.4.2. Trace element yields

Roofing material significantly affected the yields of several trace elements (Fig. 4). Of the eight elements

considered, three (cadmium, nickel, and zinc) had greater yields from metal roofs and the differences for cadmium and zinc were large (C_d values of 0.56 and 1.01, respectively). One element, lead, had a greater yield from asphalt shingle roofs (C_d of 0.79). Although mercury had significantly higher concentrations in particles from asphalt roofs and much greater yields in some samples from asphalt shingle roofs, there was no significant difference in yields. All eight elements considered had significantly higher yields from the near-MoPac rooftops than the far-MoPac rooftops, with C_d values ranging from 0.55 for nickel to 1.55 for copper (Table 1). Yields from the MoPac Expressway exceeded those from all rooftops for arsenic, chromium, copper, and nickel. They exceeded those from asphalt roofs for cadmium and zinc, and exceeded those from metal roofs for mercury and lead. Yields for copper, lead, and zinc were more than an order of magnitude greater than those reported by Barrett et al. (1995) for annual loads from MoPac calculated on a $mg\,m^{-2}\,mm^{-1}$ basis. This is probably because Barrett et al.'s study computed annual loads normalized to total annual precipitation whereas this study analyzed only the first flush.

3.4.3. PAH yields

Little difference in yields of PAH was seen between the roof types (Fig. 4), but PAH yields from the sites nearer to MoPac consistently exceeded those from sites farther from MoPac (Table 4). The three lightest of the individual PAHs had greater yields from metal roofs, but the differences were not large. All 10 individual PAHs and total PAH had greater yields from the near MoPac sites, with C_d values ranging from 0.33 to 0.5 for all PAHs except naphthalene, which had a C_d of 1.3.

3.4.4. Contaminant build-up

Other researchers have noted that contamination on roadways, rooftops, and other surfaces builds up with time (Yaziz et al., 1989; Thomas and Greene, 1993; Mason et al., 1999). Yields of trace elements and PAH in particles from rooftop washoff and associated with suspended sediment in Shoal Creek did not show any correlation with the number of rainless days preceding the washoff or storm. The number of dry days preceding the rooftop washoff experiments ranged from 17 to 38, and the number of dry days preceding the Shoal Creek storm events ranged from 19 to 99. Storm yields on suspended sediment, however, are largely a function of the amount of total runoff in a stream, and considering the small rooftop sample size (3 sampling events) and the possible complications of season and sample variability, little can be concluded regarding contaminant build-up from the rooftop samples.

4. Discussion

In the discussion below, we focus on concentrations to assess the possible toxicity of rooftop particles, and then focus on yields to evaluate the effect of distance from roadway and roofing materials on contamination of rooftop runoff, and to evaluate the contribution of rooftop runoff to contaminant loading in the watershed.

4.1. Relative contamination of particles in rooftop runoff

While many investigators have demonstrated that concentrations of contaminants in rooftop runoff exceed drinking-water guidelines or have documented the toxicity of rooftop runoff to aquatic organisms (e.g., Yaziz et al., 1989; Good, 1993; Thomas and Greene, 1993), the results described here indicate that particle-bound contaminants washed from rooftops may contribute to sediment toxicity in receiving water bodies. The degree of contamination of the particles was evaluated by comparing them to published consensus-based SQGs (MacDonald et al., 2000), in particular the Probable Effect Concentration (PEC), which is the concentration above which bed sediments are shown statistically to frequently have adverse effects on benthic biota. The SQGs were developed to evaluate the toxicity of bed sediments, but are a useful benchmark for assessing the relative contamination of any sediments, particularly if, as is the case for rooftop particles, they are transported to aquatic systems by runoff.

Concentrations of particle-bound zinc, lead, pyrene, and chrysene exceeded the PECs in a majority of samples of rooftop washoff particles (Tables 1 and 2; Fig. 3). Contaminated particles in rooftop runoff are a concern because of the adverse effect they may have on receiving water bodies and because rooftop water is sometimes harvested for domestic drinking water or irrigation. The elevated concentrations of zinc from metal rooftops, lead from asphalt shingle rooftops, and PAHs from both types of rooftops suggest that particles should be removed from rooftop runoff by filtration or sedimentation before the water is diverted to storm sewers or harvested for use.

4.2. Sources of contamination

4.2.1. Major roadways

Comparison of concentrations and loads of contaminants in particles is particularly useful in illustrating the contribution of a major roadway (MoPac Expressway) and associated vehicle (and possibly train) traffic to contaminant deposition on rooftops. Concentrations of some of the trace elements and most of the PAHs were higher in the samples collected far from the expressway than in samples collected near to the expressway, and concentrations from the MoPac shoulder samples were

the lowest of all (Fig. 3). The opposite was seen for yields. Yields of every trace element and PAH tested were significantly greater in the samples collected nearer to the expressway than in those farther from the expressway; yields of the four trace elements not suspected to have a roofing material source, as well as sediment, were greater from the roadway than from the rooftops (Fig. 4).

The apparent contradiction between concentrations and yields is explained by greater contaminant loading combined with sediment dilution near the roadway. We suggest that traffic along the MoPac Expressway is a source of greater contaminant loading near the expressway, while the road shoulder adjacent to the expressway is a source of uncontaminated particles that dilute contaminant concentrations. The effect of proximity to the expressway was greatest for copper and cadmium, two metals with well-defined vehicular sources (copper is used in brake pads; cadmium is found in tires) (Harrison and Johnston, 1985).

The occurrence of higher contaminant concentrations farther from the roadway is seemingly in contradiction with other studies that have reported an inverse relation between contaminant concentration in soils and distance from roadway (Sutherland and Tolosa, 2001). This is because those studies involved collecting samples directly from the ground surface, where contaminants are already mixed with and diluted by soils. Under those sampling conditions concentration is a surrogate for yield.

The spatial evolution of PAH assemblages is consistent with the conclusion that particles from MoPac are accumulating on the rooftops near MoPac. The ratio of the sum of the 2- + 3-ring PAHs to the total combustion parents (Table 2) is highest in the MoPac shoulder samples, decreases with distance from the roadway, and is lowest in the Shoal Creek samples. This indicates a greater uncombusted, or fuel, contribution to the particles washed from the MoPac roadway, which is logical considering the potential for fuel spills on and near the roadway, and that some of these roadway particles are resuspended and deposited on the rooftops near to the expressway.

4.2.2. Roofing material

Roofing material contributed to trace element contamination in roof washoff particles. The metal rooftops were a source of particle-bound cadmium and zinc as reflected by much larger concentrations and yields compared to those from asphalt shingle rooftops (Figs. 3 and 4). Although nickel concentrations and yields were also statistically larger (5 of 6 sample pairs in both cases), the differences are small (C_d values of 0.14 and 0.12) and aluminum-normalized concentrations were not different; therefore, we feel the case for a metal roof source of nickel is inconclusive. Numerous other studies have reported elevated zinc concentrations in runoff from metal roofs (e.g., Yaziz et al., 1989; Davis et al., 2001). Others have reported elevated concentrations of cadmium (Quek and Förster, 1993), copper (Bannerman et al., 1993), and lead (Yaziz et al., 1989) from metal rooftops. Förster (1999) found that partitioning of zinc was dominated by the dissolved phase, but that that effect was diminished when pH was high. The high pH ($\sim$10) of the Austin city water used for this study likely limited the amount of leaching into the dissolved phase, a desirable result as we were specifically trying to characterize particle chemistry. Rainwater, however, which has an average pH of about 5 in central Texas (National Atmospheric Deposition Program, 2000), could potentially release additional trace elements from roofs and rooftop particles by leaching.

The asphalt-shingle roofing material sampled for this study was found to be a source of lead and possibly mercury. Lead concentrations and yields were significantly higher in particles washed from asphalt shingle roofs than in those washed from metal roofs. Asphalt shingle roofs may also be a source of mercury. Concentrations of mercury from asphalt shingle roofs were significantly higher than concentrations from metal roofs, but yields of mercury were not. However, in those cases where mercury yields from asphalt shingle roofs did exceed those from metal roofs, the difference was much greater (3–8 times greater) than when the yields from metal roofs exceeded those from asphalt shingle (1–2 times greater). Regional atmospheric fallout, generally thought to be the major source of mercury in the environment (Swain et al., 1992), does not explain the elevated concentrations of mercury often seen in urban sediments, thus the possibility that asphalt shingle roofs may be a source of mercury to the urban environment is intriguing and warrants further investigation.

Results of analyses of the MoPac shoulder samples support the conclusion that roofing materials are a source of some trace elements. Yields of the three trace elements unassociated with roofing materials (arsenic, chromium, and copper) were greatest in the MoPac shoulder samples. Nickel yields were also greater in the MoPac samples than in rooftop samples (Table 3). In contrast, yields of zinc and cadmium from the MoPac shoulder were greater than those from asphalt shingle roofs but not from metal roofs (a suspected source), while yields of mercury and lead from the MoPac shoulder were greater than those from metal roofs but not from some of the asphalt shingle roofs.

4.3. Contribution of rooftop runoff to urban stream loading

The importance of the role played by rooftop runoff in watershed contaminant loading can be evaluated by comparing estimated hypothetical event loads from

rooftops across the entire watershed to measured event loads in Shoal Creek (Mahler and Van Metre, 2003). The total area of metal and asphalt shingle rooftops in the Shoal Creek watershed was estimated from areal photos of five representative areas of the watershed. The five areas chosen were from 0.2 to 0.4 km^2 and comprised from 19 to 51 rooftops. The type of roof on each building was ground checked. The proportion of the area of each rooftop type to the total area in the photo was then applied to the proportion of that type of landuse in the watershed (Dartiguenave, 1997); roadway, parkland, and undeveloped landuses were assumed to have no rooftops. Asphalt shingle roofs and metal roofs were estimated to make up 25 percent and 4 percent of the total watershed area, respectively.

Hypothetical watershed loads resulting from rooftop runoff were computed three ways. The first estimate is of total rooftop runoff based on the measured yields and the estimated total rooftop area for the watershed. The effect of proximity to a major roadway was removed by using only the far-from-MoPac samples. The mean of the hypothetical rooftop runoff event load was then compared to actual event loads for Shoal Creek. The second estimate is of atmospheric deposition only, computed by including only those roof types with no significant contribution of a contaminant from a roofing material. The third estimate is of roofing material contribution to watershed load of the four contaminants for which roofing material was a significant source: cadmium, nickel, and zinc for metal roofs and lead for asphalt shingle roofs. The roofing material contribution was computed as the product of the difference between the means for the two rooftop types and the total area of that type of rooftop in the watershed. Development of the Shoal Creek watershed was largely completed in about the 1970s and relatively little runoff passes through structural controls. In each case, we assumed that the entire rooftop load would contribute to creek load regardless of the size of the rain event, given the connectedness of impervious cover in urban areas and the ease with which particles were washed from rooftops. The median percent contributions from atmospheric, roofing material, and total rooftop washoff for four runoff events in Shoal Creek are shown in Fig. 5.

Although the yields of contaminants from rooftops were relatively similar for each sampling event, loads and yields in Shoal Creek varied greatly between sampled runoff events, and depended mostly on the magnitude of the event (Tables 3 and 4). Thus, the proportion of the load in the creek that can be explained by rooftop washoff varies inversely with the size of the event and on a large event is relatively small. This suggests that there are relatively large reservoirs of contaminants in storage in the watershed, presumably soils and aquatic sediments, that are accessed and mobilized to varying degrees by runoff.
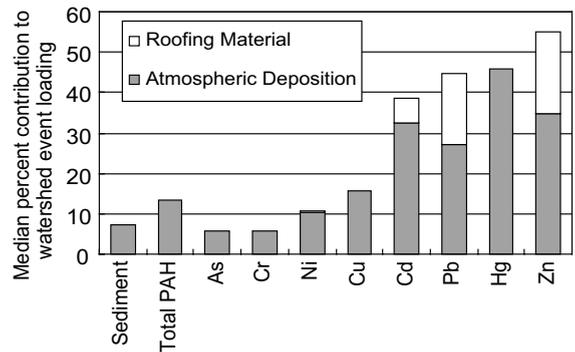

Fig. 5. Median contributions of rooftop runoff, atmospheric deposition onto rooftops, and roofing materials (galvanized metal or asphalt shingle) to event loading in Shoal Creek for sediment, total PAH, and trace elements.

The contribution of rooftop runoff to loading of sediment ranged from 1 to 17 percent (median of 7). Considering that rooftops cover 29 percent of the watershed, this indicates that rooftops are a proportionally small source of sediment. The rooftop contribution to total particle-bound PAH in Shoal Creek runoff was estimated to be from 1 to 18 percent, depending on the size of the event, with a median of 13 percent. This contribution is higher than that found by Steuer et al. (1997) for whole watershed load, probably because the percentage of watershed area comprised of rooftops in the Steuer et al. study was less than half that of this study. Because no difference was found between roof types, the rooftop PAH load is assumed to come from atmospheric fallout. The results of both studies suggest that the bulk of PAH loading originates from sources other than rooftop washoff.

The contribution of rooftop runoff for particle-bound trace elements was in the order $Zn > Hg \cong Pb \cong Cd > Cu \cong Ni > Cr \cong As$ (Fig. 5). The median contribution of zinc is 55 percent (ranging from 8 to 86 percent) compared with 5.7 percent for chromium (ranging from only 1 to 10 percent). When roofing material sources are excluded to estimate atmospheric fallout, the order of contributions shifts slightly with mercury contribution greatest followed by zinc and cadmium (Fig. 5; dark gray bars). These results are somewhat higher than those estimated for copper and zinc in commercial source areas by Bannerman et al. (1993), are proportionally similar to those estimated for zinc and somewhat lower than those estimated for copper by Steuer et al. (1997), and very similar to those estimated in urban commercial stormwater runoff for lead, cadmium, and zinc by Davis et al. (2001).

Of the four elements with a significant roofing material source (Cd, Ni, Pb, and Zn), zinc contributed the most to total watershed loading (median 20 percent),

followed by lead (median 18 percent), cadmium (median 6.2 percent) and then nickel (median 0.3 percent). Metal roofs are widely recognized as being a source of trace elements, but the contribution of asphalt shingle wear to loads of lead in the urban environment has not been previously reported.

5. Summary and conclusions

Concentrations and yields of particle-bound contaminants washed from metal and asphalt-shingle roofs have been evaluated at both the rooftop and watershed scale. Effects of roofing type and proximity to a major expressway were examined. The particles have relatively high concentrations of some contaminants as indicated by comparison to SQGs, in particular zinc, lead, cadmium, chrysene, and pyrene.

Measured yields of contaminants were used to determine the effect of roadway proximity and rooftop type on loading. Yields of all PAHs and trace elements analyzed were elevated in samples collected close to a major expressway (12–15 m) over those collected about 100 m away. The differences were greater for the trace elements than for the PAHs, and were greatest for copper and cadmium. The metal roofing material sampled was a source of particle-bound zinc and cadmium and the asphalt shingles sampled were a source of particle-bound lead and possibly mercury. There was no evidence that asphalt shingle roofs were a source of PAHs.

The contribution of loading from rooftop runoff at the watershed scale was estimated based on the total area of the two different types of rooftops and the yields measured. The contributions from rooftop runoff to particle-bound contaminant loads were greatest for zinc, mercury, and lead, for which the median estimated contributions were 55, 46, and 45 percent of total watershed loading, respectively. Rooftop runoff contributed only about 13 percent of the total particle-bound watershed load of PAHs.

The relative contributions of atmospheric deposition versus roofing material to yields from rooftop runoff were also evaluated. Lack of a roofing material source indicated that PAH, arsenic, chromium, and copper were from atmospheric sources. Nickel was also dominantly from atmospheric sources, however, about 40 percent of the lead, 37 percent of the zinc, and 16 percent of the cadmium in rooftop runoff (median values) were determined to come from roofing materials, with the remainder coming from atmospheric deposition. The possibility that asphalt shingle roofs are a significant source of lead to urban waterbodies has not, to our knowledge, been reported previously. Some mercury may also be contributed by asphalt shingle roofs.

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