PAPER

A novel fractionation approach for water constituents – distribution of storm event metals†

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A novel fractionation method, based on both particle size and settling characteristics, was employed to examine metal distributions among five fractions. In-stream and stormwater runoff samples were collected from four land use types: highway, urban, agricultural (storm event and irrigation), and natural. Highway samples contained the highest dissolved concentrations for most metals, and freshwater ambient water quality criteria were exceeded for Cd, Cu, Pb, and Zn in the first storm of the water year. Anthropogenic sources were indicated for Cu, Zn, Cd, and Pb in highway and urban samples, and total metal loadings (mg km^{-2}) were observed to be as follows: highway > urban > agricultural storm event $\sim$ natural > agricultural irrigation. Notably, $\sim$10-fold higher suspended solids concentration was observed in the agricultural storm event sample, and suspended solids-associated metals were correspondingly elevated. Distribution coefficients revealed the following affinities: Zn, Ni, Cd, and Pb to large dense particles; and Cu, Zn, Cr, Ni, and Pb to colloidal organic matter.

Environmental impact

Fractionation is a means of assessing the distribution of pollutants in an environmental matrix, where the distribution has implications on the pollutants fate, transport, and effects. In this study, a novel fractionation approach is demonstrated for the fractionation of metals from storm event samples. The developed fractionation approach utilized both size and settling fractionation methods, which is unique from previous fractionation methods. Metal distributions from four land uses are assessed, and six metals of interest are highlighted (Cd, Cr, Cu, Ni, Pb, and Zn). Sample evaluation includes: metal loads (by land use), metal enrichment as an indicator of anthropogenic sources (by land use), metal distribution among five fractions that encompasses both size and inferred composition (by sample), and distribution coefficient evaluation (K_d by land use).

1 Introduction

According to the U.S. Environmental Protection Agency, greater than half of assessed surface waters were deemed "impaired" and causes frequently included nonpoint sources of suspended solids (SS), metals, and organic matter (OM).[1] Within the environmental matrix, the components interact, and the associations (*e.g.*, particle-bound or OM-complexed) influence the fate, transport, and effects of the constituent of concern. Suspended particles interact with dissolved metals, which are affected by thermodynamically dependent equilibrium conditions as well as kinetic limitations. The interactions are influenced by the metal, particle concentration and characteristics (*e.g.*, adsorption site density and heterogeneity), and solution chemistry including pH, ionic strength, and concentration of competitive sorbates.[2,3]

Larger particles ($d_p > 10 \ \mu m$) and their associated constituents (*i.e.*, OM or metals) are more likely to be removed *via* sedimentation in engineered structural Best Management Practices (BMPs) or quiescent natural conditions.[4,5] Within the sediment, the particles may proceed toward a new equilibrium with the surrounding pore water. Desorption, due to elevated salinity, OM concentration, and changes in redox conditions, can affect dissolved concentrations and often allow for the export (mobilization) of dissolved metals to the overlying or underlying waters.[5] A study of detention basin sediments by Camponelli *et al.* found that Cu and Zn were elevated at sediment depths $\sim$0.5 m indicating that Cu and Zn are somewhat mobile.[6] The benthic community will be exposed to the constituents associated with sediments and pore water. Colloids are not likely to settle even provided quiescent conditions, and will be advectively transported. Both organic and inorganic colloids are typically present in surface water. Colloids' high specific surface area provides many reaction sites, and increased Brownian motion potentially contributes to aggregation of colloids and subsequent sedimentation, particularly with changes in local aqueous chemistry such as increased ionic strength. Freely dissolved constituents (*e.g.*, Cu^{2+} or Zn^{2+}) are typically considered the bioavailable and toxic forms.[7]

Environmental water quality criteria (WQC) were established in the 1970s in both Europe and the United States with the

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primary goal of protecting water as a resource to support human activities. Over time, this view has expanded to include the protection and preservation of aquatic environments because the ecosystems have intrinsic value.[8] WQC are beginning to evolve beyond total or dissolved constituent concentrations, and some WQC now partially acknowledge the complex inter-connectedness of constituents and the matrix in which they are found.[9] Examples of this include the adjustments to several metals' WQC to account for the effects of water hardness on toxicity (*e.g.*, Cd and Pb), or in the case of copper, the WQC is based on the Biotic Ligand Model (BLM) which further accounts for the effects of pH, alkalinity, and dissolved organic carbon (DOC; another measure of OM) concentration.[7]

Researchers have attempted to divide the matrix components (*i.e.*, fractionate) to better understand fate and implications of the pollutants. Fractionation efforts have been applied to engineered[6] and natural[6,10,11] systems, as well as both inorganic[6,10,12] and organic[11] pollutants. Previous water column fractionation approaches have largely relied on separation based independently on size (*e.g.*, sieving, sequential filtering or ultrafiltering)[6,12,13] or on settling (*e.g.*, settling columns and centrifugation).[13,14] Smullen *et al.* proposed that land use may be partially responsible for concentration differences that had been observed in runoff, and land use-dependent statistically significant runoff concentrations were observed by Pitt *et al.*[15,16] In addition to land use-dependent concentration differences, it is possible that land use may also effect the contaminant distribution (*i.e.*, associations or complexations) within the runoff matrix, where such differences could be elucidated with an appropriate fractionation method. The objective of this work was to employ a new water column fractionation approach to discern metal distributions and associations in samples collected from four associated land uses, and to examine the implications of the phase distribution information. The new approach combines fractionation by size and settling characteristics, from which the fraction's density and composition (*i.e.*, organic or inorganic) can be inferred, thereby improving understanding of mechanisms driving constituent distributions.

2 Methods

2.1 Sampling sites

Four sampling sites were selected to represent four types of land uses: highway, urban, agricultural, and natural. Each of the selected sampling sites is predominately the land use of interest, where urban was characterized by intensive use with extensive structural coverage, agriculture was primarily devoted to food and fiber production, and natural landscape was covered by mixed coniferous vegetation. Sampling occurred during the 2009–10 winter, and higher intensity storms were targeted (>0.65 cm in a six hour period, which exceeds the US EPA NPDES storm definition of 0.25 cm total depth). California's central valley, which contains all of the sampling sites, receives a vast majority of its precipitation during the winter (*e.g.*, typically 85% of the precipitation in Davis, CA occurs between November and March). Eight sampling events were

conducted. Highway samples were collected from the west-bound lanes of Interstate 80 (I-80) near Vacaville, CA (38.328°N, 122.022°W; three samples) and the site has an annual average daily traffic (AADT) load of 161 000 vehicles per day; this section was re-surfaced during summer 2009. A temporary drop-drain was constructed on-site so that the entire flow could be collected to ensure representative sampling. The urban, agricultural, and natural sites (*i.e.*, rivers or streams) were collected instream from the top 30 cm of the water column within the current; instream sampling was employed to reflect the many upstream contributors, however the sample collection location included only dissolved and suspended solids (*i.e.*, not bed-load). Arcade Creek (38.624°N, 121.457°W), the urban site (one sample), is a small (88 km^2) and densely urban (79% urban) catchment within the Sacramento, CA metropolitan area.[17] Colusa Basin Drain (38.812°N, 121.774°W), the agricultural site (three samples), drains 4274 km^2, of which 65% is agriculture (1% urban); the primary crop in the region is rice, and herbicide/insecticide application typically occurs in May–June,[17] while flood irrigation is typically employed April–August. One agricultural storm-event samples was collected (labeled A1), and an additional two samples (labeled A2 and A3) were collected from the agricultural site during the flood irrigation season and were included as additional overland flow samples. The natural site (one sample) was located on the S. American River just above the entrance to Folsom Reservoir (38.772°N, 121.034°W). The watershed above the sampling point is ~99% natural (2175 km^2 total), but river flows are dam modulated. The watershed has some anthropogenic influences: U.S. highway 50 (13 000 AADT) runs adjacent to the river for approximately 55 km; includes several small towns, the largest town having ~10 000 residents; and a mining legacy.[18] Stream flows and precipitation data (based on a tipping bucket gauge) for the natural, urban, and agricultural sites were from California Department of Water Resources (CA DPR) gauges. There wasn't an appropriate CA DPR precipitation gauge near the highway site; instead, data from a CIMIS precipitation gauge of an unknown type was used. A map of sampling locations, weather stations, and stream gauges is shown in ESI (Fig. S-1†).

2.2 Sample collection and processing

The highway and urban sites are small catchments and largely impervious, thus the peak of the storm was targeted for sampling. The agricultural and natural sites included large catchments with very little impervious surface, so sampling was targeted 6–12 for hours after the storm peak. Samples were processed *via* filtration, centrifugation, and ultrafiltration (UF) as shown in Fig. 1. Samples were passed through a 1.7 mm stainless steel sieve to remove large particles, and then to a flow through centrifuge (FTC; 9000 Gs, retention time ~ 40 s) to separate and retain particles. Based on FTC residence time and rotation speed, a spherical particle with a density (ρ) of 2000 kg m^{-3} and a diameter (d_p) > 0.3 μm would be retained; experimentally, particles 0.5 < d_p < 0.79 μm (the smallest measured size bin) were >99.5% retained.[19] To preserve the particle size distribution, all
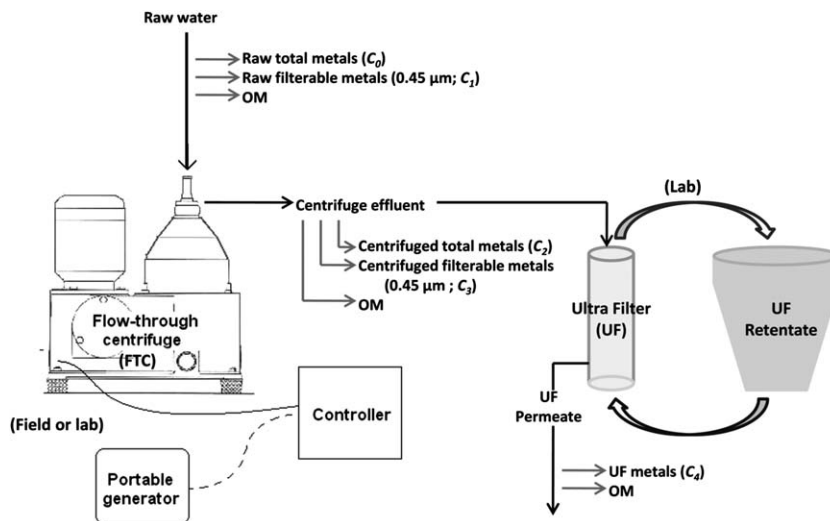
Fig. 1 Sample processing with a flow-through centrifuge (FTC) and ultrafilter (UF).

centrifugation and 0.45 μm filtering was done within six hours of collection,[20] either in the field or at the UC Davis campus. When weather permitted, the FTC was operated in the field with the support of a generator and sample was continuously processed for 4.5 hours. This time frame generally did not include the entire storm; storm and sampling timing (*i.e.*, start and stop times) and volume of sample centrifuged can be found elsewhere.[21] High winds prevented field use of the FTC for three sampling events. In the field, 20 L of centrifuge effluent were collected every 30 minutes (time weighted composite; HDPE carboys) for a total of 200 L collected. When laboratory operation of the FTC was required, 20 L of sample were collected every 30 minutes over 4.5 hours, transported back to the UC Davis campus, and promptly centrifuged (all FTC effluent was collected). Grab samples were collected every 30 minutes to assess SS, metals concentrations, and OM concentrations; all grab samples were stored on ice during transport to UC Davis. Total and filterable metals samples (Millipore 0.45 μm PVDF) were collected both pre- and post-centrifugation. At UC Davis, metals and OM samples were acidified (HNO$_3$ and H$_2$SO$_4$, respectively) and stored at 4 °C prior to analysis. Samples were analyzed within the recognized holding times as follows: SS (seven days), metals (six months), and OM (28 days).

The collected FTC effluent was ultrafiltered (10 kDa cutoff with Δp = 15 psi; Pall, Microza polysulfone) in a semi-batch manner – 20 L of FTC effluent were ultrafiltered until ∼1 to 2 L remained, and then the next batch was added. UF retentate was only removed when the system became too clogged (insufficient permeate flow) or after the entire sample had been ultrafiltered. UF processing was initiated upon returning to the lab but required up to four days to complete the process which may have affected metal partitioning among colloidal and dissolved phases; samples were stored at 4 °C in the dark both pre- and post-UF processing. Constituents in the UF permeate were operationally defined as dissolved. Permeate samples were collected following each semi-batch.

The FTC and UF apparatuses were both disassembled and washed between sampling events, and were pre-conditioned with 20 L of double distilled water. In total, 12–42 and 52–124 samples were collected per event (sampling duration and FTC location dependent) for OM and metals analysis, respectively.

Gravimetric analysis of SS was conducted according to Standard Method 2540,[18] but control total dissolved solids (TDS) samples showed contamination of the filtrate, therefore TDS data are not presented. Particulate, colloidal, and dissolved OM were determined by "loss on ignition" (Volatile Solids, Standard Methods 2540), where the method detection limit was 1.7 mg L^{-1} and the duplicate's relative standard deviation (RSD) was typically less than 5%. Metals analysis was completed using an inductively coupled plasma mass spectrometer (ICP-MS; Agilent 7500i, Ar plasma at 1350 W) on dilute acid extracted samples (1% HNO$_3$) according to EPA method 6020;[19] ICP-MS tuning and analysis settings can be found elsewhere.[20] In all cases, metals were measured on dilute acid extracted samples, which accesses more than the exchangeable metals, but does not include the refractory minerals.[21]

Standard reference material 1643e (SRM) was used to check recoveries, which were as follows (average ± standard deviation): Cd (74 ± 23%), Cr (82 ± 23%), Cu (79 ± 18%), Ni (78 ± 17%), Pb (43 ± 11%), and Zn (77 ± 42%). Recoveries varied among analysis batches, therefore the results have been normalized to the batch SRM recovery. Limit of detection (LOD; seven blanks, $\mu + 3\sigma$) was in the single or low tens of ppb for the more abundant crustal elements (Ca, Fe, K, and Na) as well as Zn. Cr, Ni, and Cu had 0.1 < LOD < 1 ppb, and Cd and Pb had LOD < 0.1 ppb. All presented results are sampling event time-weighted average concentrations, which provide an approximation of the event mean concentration (EMC). EMC approximation could be improved through the use of flow-weighted average concentrations collected over the duration of the storm, but were not possible because flow data was not available and the entire storm was not monitored for all events.

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2.3 Quasi solid–liquid distribution coefficients (K_d^*), enrichment factors (EF), and loadings

The distribution coefficient (K_d) is the ratio of the equilibrium solid phase-bound metal concentration (mass/mass) to the dissolved metal concentration (mass/volume) and has been used to provide insights into the fate and transport of constituents of interest. K_d is typically calculated for equilibrium partitioning between phases. Samples were processed as quickly as possible to preserve the samples in their native (potentially non-equilibrium) state, however changes in solid–liquid distribution may have occurred during necessary processing time. In this study, the solid phase concentrations were not known for each fraction. The solid phase concentration was approximated by summing the fractionated concentrations, as determined by the ICP-MS, of the following elements: Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Se, V, and Zn. This includes the six most abundant crustal metals, plus many of the next ten most abundant elements. The conventional equation for K_d and the approximation used in this study are shown below:

$$K_d = \frac{A_i\ [\mu g\ g^{-1}]}{C_{i,4}\ [\mu g\ mL^{-1}]} \approx \frac{C_{i,j}\Big/{\sum C_{z,j}}\ [\mu g\ g^{-1}]}{C_{i,4}\ [\mu g\ mL^{-1}]}$$

$$= K_d^*\ [mL\ g^{-1}\ \text{or}\ L\ kg^{-1}]$$

where A_i was the particle-sorbed concentration and was approximated by the concentration of element i found in fraction j ($C_{i,j}$) divided by the sum of the concentrations of all measured elements (z) found in fraction j ($\sum C_{z,j}$). The denominator ($C_{i,4}$; UF permeate) was the dissolved concentration of element i. This approximation allows for phase association comparisons within this study, however the partitioning coefficient values cannot be directly compared to other published values because the ICP-MS summed elements ($\sum C_{z,j}$) underestimates the true solid phase mass in each fraction. In particular, fractions that were predominantly organic – composed primarily of carbon, oxygen, and hydrogen which are not measured by the ICP-MS – would be represented here as having lower solids concentrations, thus the A_i estimate would be higher as would the approximated partitioning coefficient value. To avoid confusion, the estimated distribution coefficient values discussed in this study will be referred to as K_d^*.

Enrichment factors (EF) are an established approach for assessing the relative elemental contributions and have been applied to a variety of environmental matrices.[10,22] EFs were calculated as the ratio $[(X/Y)_{sample}]/[(X/Y)_{reference}]$ where X is the element of interest, Y is the normalizer which is typically representative of crustal contributions, and the reference is selected to represent the unimpacted elemental ratio. Aluminum was the normalizer used in this study (Y) and sample N1 was used as the reference. EF > 1 signified enrichment and suggested an anthropogenic source, EF < 1 signified depletion, and values close to unity were considered unimpacted.

Area normalized elemental loads were calculated based on $L = C_{i,0}V/A$ where L is the load (mass/contributing area), $C_{i,0}$ is the average raw water total concentration for element i, V is the total stream flow or runoff volume associated with the storm event, and A is the watershed area. V was determined from published monitoring stations (agricultural and natural sites) or as the product of the storm depth, watershed area, and assumed runoff coefficient (1 and 0.5 for highway and urban sites, respectively). Sensitivity analysis of the runoff coefficient assumptions indicated that there was no change in their relative order if the runoff highway or urban runoff coefficients were changed by ±0.25.

2.4 Sample fractionation calculations

Metal concentrations were determined for five fractions labeled as follows: (F1) large dense particles, (F2) light particles, (F3) dense colloids, (F4) light colloids, and (F5) dissolved. Large dense particles (F1) are expected to be removed from the water column *via* sedimentation and contribute to sediment constituent load. Dense colloids (F3), presumed inorganic, have slow settling velocities (*e.g.*, $v_{st} \sim 0.3$ mm h^{-1} as calculated by Stoke's law for colloid of diameter $d_p = 0.35$ μm and density $\rho = 2600$ kg m^{-3}). Fractions F2 and F4 are described as "light" to indicate "less dense," which would affect the particle's centrifugal removal. F2 and F4 are assumed to have greater OM content (less dense), however settling velocity may also be decreased *via* increased surface roughness or nonspherical particle shape. Light particles (F2) were differentiated by their low density and assumed to principally include particulate OM (POM) likely of terrestrial origins (not produced in-stream),[23] while fraction F4 contains less dense OM colloids. Constituents that passed through the ultrafilter (10 kDa) were operationally defined as dissolved (C_4 = F5). The F5 fraction contained considerable OM that could complex metals, therefore F5 is not necessarily freely dissolved or even limited to inorganically complexed metals. Fulvic acids are <10 kDa (F5), and smaller sized OM is associated with increased bioreactivity.[23] Humic acids are larger and may be found in both F4 and F5 fractions. Humin and other non-humic OM (*e.g.*, carbohydrates and polysaccharides) are typically higher molecular weight and are therefore expected to be contained in the F4 fraction. Metal distribution results often vary considerably among studies, likely due, in part, to differences in matrices, methods, and operational definitions. In their review of urban stormwater, Makepeace *et al.* concisely summarized individual metals' distributions; their summary is used for comparison throughout this study.[24]

Elemental concentrations in each size fraction were determined by difference as shown in Fig. 2, where calculated negative concentrations were set to zero. Filtration and UF were assumed to differentiate solely on particle size, while centrifugation was assumed to remove particles based on both size and density (refer to Stoke's law, shown in ESI†). Owing to the different removal mechanisms and the size–density interaction on centrifugal removal, there was no clear expected relationship between the elemental concentrations in the centrifuge effluent (C_1) and the 0.45 μm filtrate (C_2). Therefore, two sets of equations were developed for fractionation (Fig. 2). To illustrate the sensitivity of inferred particle size to its assumed density, 100%
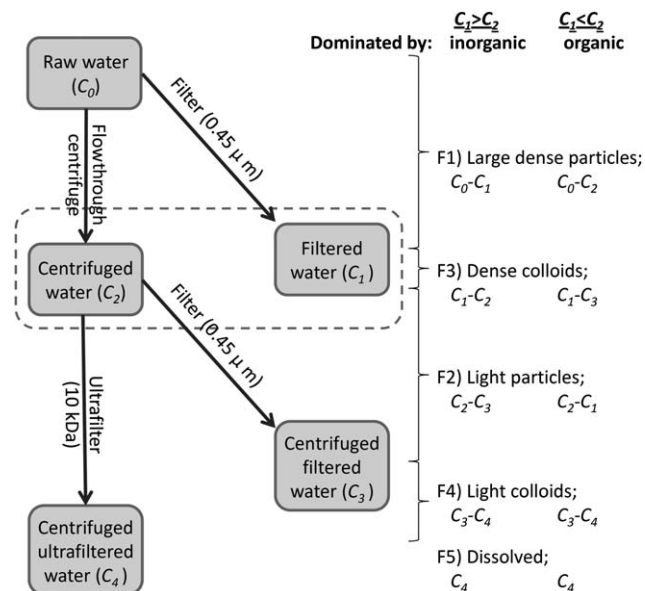
Fig. 2 Schematic of the physical fractionation processing (left side; C_i are measured concentrations) and mathematic expressions applied to ICP-MS results to determine fraction concentrations (right side; F_i are calculated fraction concentrations). No relationship was assumed between C_1 and C_2.

FTC capture of particles $d_p > x$ μm for various densities were calculated: 100% of particles $d_p > 0.31$ μm would be collected for particles with $\rho = 2000$ kg m^{-3} (*e.g.*, clay mineral particles), while for $\rho = 1900$ kg m^{-3} (*e.g.*, OM coated clay mineral particles) or $\rho = 1050$ kg m^{-3} (*e.g.*, particulate OM), 100% removal would occur for $d_p > 0.33$ and 1.37 μm, respectively.

OM fractionation was calculated based on the assessed volatile solids concentrations, and three fractions were calculated as follows: particulate ($C_0–C_2$), colloidal ($C_2–C_4$), and dissolved (C_4). The complete fractionation method could not be employed for OM since only total, centrifuged, and UF permeate OM samples were collected.

3 Results and discussion

3.1 Collected samples

Storm, sample collection, and sampling event designator information are shown in Table 1. The limited number of collected samples, combined with the substantial variability in the storm characteristics, likely influenced this study's outcomes, but the results can still highlight major trends and areas worthy of further research. The following sections will discuss observed TSS and OM concentrations, total and dissolved metal concentrations, metal distributions *via* the new fractionation approach, anthropogenic indicators, and metal loadings.

3.2 Suspended solids (SS) and organic matter (OM) concentrations

Bar charts in Fig. 3 show each samples' fixed and volatile SS (FSS and VSS, respectively) and OM distributions. TSS was observed to be far greater in the storm event agricultural sample (A1) than in any other sample, which is possibly due to erosion of the tilled fields by overland flow. The fraction of SS that was volatile ranged from 5% (A3) to ~35% (H2 and H3), indicating that the SS ($d_p > 0.7$ μm by filtration) are predominantly inorganic. VSS (Fig. 3A; filtration) was expected be similar to but not equal to particulate OM (Fig. 3B; centrifugation), however the results were not strongly related, which is likely due to the differences in removal mechanisms.

Sample event average total OM concentrations were 14–38 mg L^{-1}. The observed concentrations were greater than typical natural values, but were not considered extreme, and are in line with typical highway runoff OM values; elevated OM concentrations can lead to oxygen depletion in receiving waters.[23,25] In this study, a majority of the OM was considered dissolved (<10 kDa by UF) for all samples except sample A1 where dissolved and particulate concentrations were equal (~40% each; Fig. 3). Among the highway samples, the lowest

Table 1 Hydrologic and sample collection data for the six storm events and the two irrigation samples

Site	Designator	Date	Max intensity[a] (mm h^{-1})	Storm total[a] (mm)	pH	Conductivity (μS cm^{-1})	Field centrifuge?
Natural – American River near Folsom, CA							
	N1	2/27/2010	61.0	64.0	7.2	90.7	Yes
Highway – westbound Interstate 80 near Vacaville, CA							
	H1	10/13/2009	21.1	88.4	6.9	54.0	No
	H2	12/12/2009	2.8	11.4	6.6	39.4	Yes
	H3	2/23/2010	4.3	16.8	6.7	49.8	Yes
Urban – Arcade Creek in Carmicheal, CA							
	U1	4/11/2010	6.4	11.7	7.2	54.0	No
Agricultural drainage – Colusa Basin Drain near Knight's Landing, CA							
	A1	1/20/2010	15.2	87.9	7.3	438.9	No
	A2[b]	7/8/2010	—	—	8.2	757.4	Yes
	A3[b]	8/3/2010	—	—	8.1	522.9	Yes

[a] Prior or during sampling period. [b] Non-storm event; flood irrigation season.
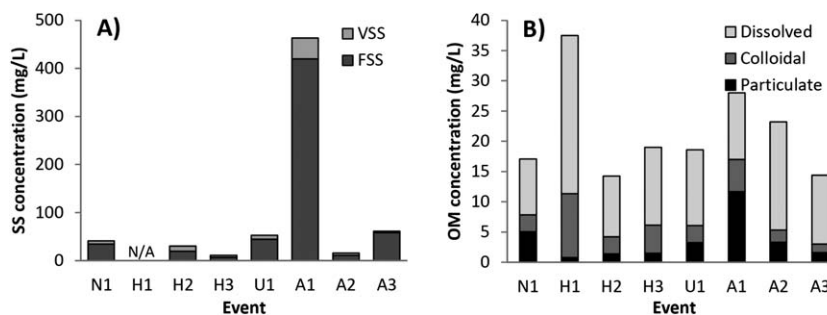
Fig. 3 Average concentration of suspended solid (A) and organic matter (B) concentrations for collected environmental field samples.

concentrations of OM were found in the particulate phase, while for all other samples, the colloidal OM fraction was the smallest. Lower molecular weight natural OM (NOM) is generally expected to be more bioavailable,[23] and OM can bind metals, thereby increasing their mobility relative to settleable particle bound constituents, however such complexation can also potentially decrease the metals' bioavailability.[7,23]

3.3 Metals concentrations and enrichment factors

Total and dissolved metal concentrations can be seen for the six elements (Cd, Cr, Cu, Ni, Pb, and Zn) in the bar chart in Fig. 4; tabular data can be found in ESI (S-1†). Among the six emphasized elements, raw water samples exceeded LOD values, except irrigation samples (A2 and A3) which contained raw Cd concentrations that were below the LOD. Raw water elemental concentration relative standard deviations were typically <30%
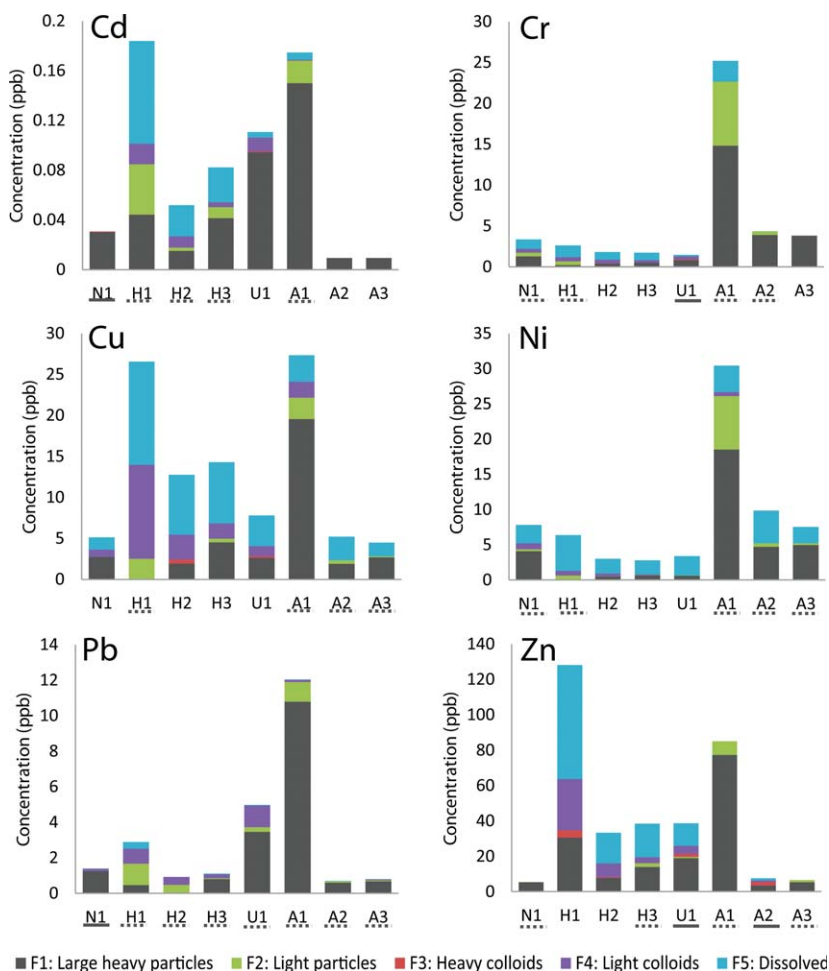

Fig. 4 Fractionation results for select metals. Samples with $C_1 > C_2$ (inorganic dominance) are underlined with a solid bar (—), and samples with $C_1 < C_2$ (organic dominance) are underlined with a dashed bar (---); samples with $C_1 \sim C_2$ (within 5%) are not underlined.

within a sampling event, indicating that concentration variability was moderate. The USEPA's National WQC for Cd, Cr^{3+}, Pb, Ni, and Zn are hardness dependent and therefore nominally different for each sample, while Cu WQC are more complex and based on the BLM which incorporates many parameters including pH, OM, SO_4^{2-}, temperature, and alkalinity.[7,9] Only the highway runoff samples exceeded any relevant criteria, most notably the Zn criterion in all three highway samples. Not all of the necessary water quality parameters were assessed to determine compliance with the BLM-based Cu criterion, however all highway runoff dissolved Cu concentrations exceeded the former hardness-based Cu criterion by factors of 5–10.

Event average concentrations were also compared to the USEPA's Criterion Continuous Concentration (CCC) which is intended to protect again chronic exposure.[9] Cd and Pb in sample H1 were found to be greater than their respective CCCs, as were Cu concentrations for all three highway samples. The highway runoff samples were characterized by low hardness (<15 mg L^{-1} as $CaCO_3$) and had higher dissolved metals' concentrations for Cd, Cu, and Zn. Upon entering adjacent surface waters, dilution and changes in aqueous chemistry (e.g., hardness) would likely occur, which would affect the metals' toxicity and nominal criteria. These three metals and Pb have previously been identified as problematic metals in highway runoff.[26]

Zn and Cu were the most abundant elements of concern in the highway and urban samples (total concentration). Ni was the most abundant among the natural (N1) and the two agricultural irrigation samples (A2 and A3). Sample A1 had the highest total Pb concentration and also the highest TSS concentration. Among the highway samples, the highest total metals concentrations for all six metals were all observed in the first sample (H1). H1 was the first storm of the wet season, had the highest intensity rain, and was the first washing of new pavement. Antecedent dry period has been associated with increased particulate buildup and elevated metals concentrations in stormwater runoff,[25] increased rain intensity and volume are associated with mobilizing larger particles,[13] and the new pavement may all have contributed to the elevated concentrations observed during this first storm. Pavement exposed to pH-adjusted, double-deionized, low OM water did not significantly leach metals,[27] however the presence of other ions or OM, as are present in stormwater, may competitively displace or promote metal leaching, as was demonstrated by the increased leaching of metals from road dust when exposed to river water (containing OM and other ions) compared to distilled water.[28] The agricultural storm event sample (A1) also exhibited higher total metal concentrations than the irrigation samples (A2 and A3) for all metals; this is at least in part due to the substantially elevated SS concentration in A1 (>4-fold difference).

Among the elements considered, Zn and Cu were the most abundant dissolved constituents in the highway and urban samples. Among all samples, Ni dissolved concentrations were 2–5 ppb, which includes highway and urban samples where >70% of the Ni was found in the dissolved fraction. Pb was always found to be <20% dissolved. Agricultural samples contained the highest dissolved Cr concentrations, but the dissolve

Cr concentration varied between storm (2.5 ppb) and irrigation samples (<0.02 ppb). Sample H1 exhibited the highest dissolved concentrations for the other metals. Gobel et al. asserted that most of the dissolved metals in highway runoff originate as part of wet deposition,[29] however there are known transportation sector sources[26] which are likely responsible for the comparatively high highway runoff dissolved concentrations observed in this study (shown in Fig. 4; compared to the other samples).

Fig. 5 shows calculated bulk (total metals) EFs. The highway samples and especially sample H1 were enriched in many of the metals, particularly Cu, Zn, Cd, and Pb. The urban sample was also enriched in Zn, Cd, and Pb. By contrast, the agricultural samples were typically depleted in almost all the elements, possibly due to slightly elevated Al background (e.g., aluminosilicate clay minerals) in the agricultural samples compared to the reference.[30] Irrigation samples (A2 and A3) had noteworthy Cd and Pb depletions. Drainage canal current was minimal at these sampling times, and therefore large inorganic particles were less likely to be suspended in the water column and included in the sample. These two elements were also observed to be principally associated with the larger denser particles, contributing to the observed depletion.

Fractionation results for Cd, Cr, Cu, Ni, Pb, and Zn are shown in Fig. 4, with in-depth discussions in the following sections. The metal-specific C_1–C_2 relationship for each sampling event is shown in Fig. 4, where inorganic dominated samples ($C_1 > C_2$) are underlined with a solid line, while organic dominated samples ($C_2 > C_1$) are underlined with a dashed line. Calculated K_d^* values are summarized in Table 2 and reported in full in the ESI (Table S-2†). Allison and Allison conducted a
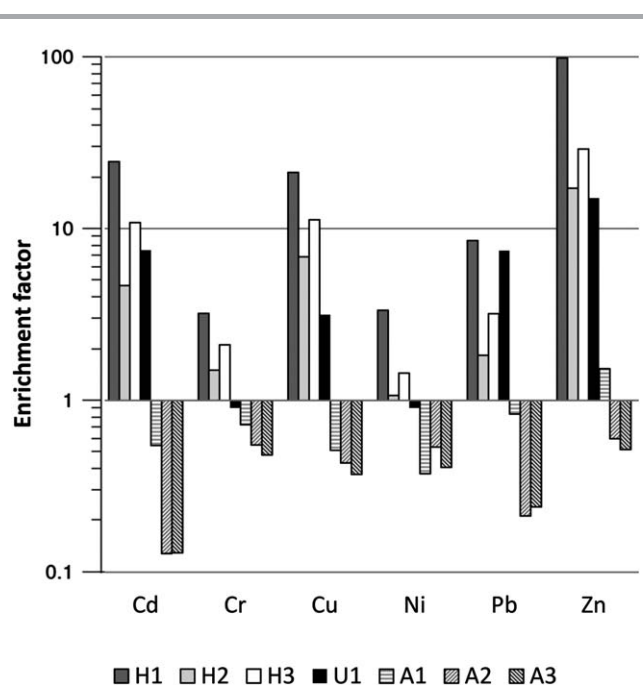

Fig. 5 Calculated enrichment factors for the total water samples; Al was used as a normalizer and natural sample (N1) as the reference. Sample enrichment (EF > 1) indicates an anthropogenic source, as is observed for highway (H) and urban (U) samples for most metals.

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Table 2 Summary of log quasi distribution coefficients (log K_d^*). Only the principal fraction is shown, or in cases where two fractions were nearly equally strong (within 0.1 log units), they both are shown and ordered based on the value[a]

Element	Sample type (samples)				
	Natural (N1)	Highway (H1, H2, H3)	Urban (U1)	Agricultural storm (A1)	Agricultural irrigation (A2, A3)
Cd	NA	F1	F1	F1	NA
Cr	F4	F4	F2	F2	F2
Cu	F1, F4	F4	F4	F1, F4	F2
Ni	F1, F4	F4, F1	F1	F1, F2	F2
Pb	F1	F4, F1	F4, F1	F1	F4
Zn	NA	F1, F4	F1, F4	NA	F4

[a] NA = not applicable; constituent dissolved concentration ≤0 ppb.

literature review of metals' K_d values for suspended solids and DOC; mean K_d values were determined and used for comparison in this study.[2] Among SS-bound metals, the metals' partition coefficients typically were: Pb > Zn > Cu = Cd > Ni.[2] The fraction specific K_d^* values (*e.g.*, $K_{d,F1}^*$) in this study generally followed the established trend, though the relative order between Zn and Cu were sometimes mixed. This study did not assess bulk or fraction-specific mobility or toxicity, but mobility and toxicity are both important for environmental implications, and therefore are included in the following discussion.

3.4 Cadmium

Samples H1 and A1 exhibited similar total Cd concentrations, however far more of the Cd in sample H1 was dissolved while in sample A1 Cd was largely particle bound. The freshwater criterion for Cd is based on dissolved concentration and is adjusted for hardness; H1, which was a soft water and therefore had a comparatively low criterion concentration, exceeded the freshwater continuous criterion (measured dissolved = 0.082 ppb; CCC = 0.06 ppb). Cd fraction distributions varied widely and fraction percentage ranges were: F1 24–100%; F2 0–22%; F4 0–17%; and F5 0–48%. Cd and the other metals in this study were not significantly associated with fraction F3 – assumed to be inorganic colloids. This was likely due to the filter pore size employed in the sample fractionation, which was selected prior to sample analysis by ICP-MS. In samples A2 and A3, all of the detected Cd was in the F1 fractions; these two samples, along with N1, contained no detectable Cd in the dissolved (F5) fraction. Calculated K_d^* values were consistently highest for the F1 fraction. The review of urban stormwater revealed that Cd was typically dissolved or colloidally associated.[24]

Davis *et al.* assessed wet and dry deposition and found them to be the first and third most important vectors of Cd at 41% and 19% respectively,[31] possibly from industrial emission sources.[24] By contrast, Gobel *et al.* identified roadways as the most significant source of Cd, with four times higher Cd concentrations in roadway runoff than from typical "gardens, grassed areas, cultivated land" runoff (referred to as cultivated lands here forth).[29] Brakes have been identified as a source of

Cd (typically representing 10% of the Cd loads),[31] however this may not account for after-market Cd-plated brakes which produce Cd wash-off concentrations more than 1200 times higher than typical brakes.[32] In this study, highway runoff Cd concentrations were more than five-fold higher than those of irrigation samples. Biosolids (*i.e.*, treated sewage sludge in California) may be an important source of labile Cd in the agricultural samples as it is enriched ∼10-fold over world soil averages.[33]

3.5 Chromium

Sample A1 had a notably higher total Cr concentration than any other sample. While fraction F1 of sample A1 contained a majority of the Cr, the Cr distribution was less skewed toward the large, dense particles than those for other metals from the same sample (*i.e.*, Zn, Cd, and Pb). Among the highway samples, the dissolved fraction was >50% of the total Cr. Light colloids (F4) contributed 10–25% for all non-agricultural samples; A2 and A3 had non-detectable Cr in the F4 fractions (F1 > 90%). Makepeace *et al.* reported that Cr is primarily associated with SS,[24] as it was for the irrigation samples in this study. K_d^* values were highest for the F4 fraction for the non-agricultural samples, and were highest in fraction F2 for samples A1 and A2, all indicating that Cr favors OM complexation.

Roadways were found to be the principal source of Cr in the urban setting,[29] and tires and yellow paint have been identified as sources of Cr[26,34] both of which could release Cr in the form of mechanically produced particles or as dissolved leachate. These sources may contribute to the observed enriched highway Cr concentrations. Previous research found typical highway runoff to contain three-fold more Cr than typical cultivated lands;[29] by contrast, all agricultural samples in this study contained higher Cr concentrations than the highway runoff samples. Biosolids have been found to contain two times the amount of Cr compared with background soil,[33] but Cr enrichment was not observed in the agricultural samples, which indicates that the observed elevated Cr concentrations were likely due to mobilized soil.

3.6 Copper

Highway and urban samples contained both the highest nominal dissolved Cu concentrations and the highest percent dissolved Cu. Sample H1 was distinct from the other samples as virtually all (>90%) of the Cu was found in either colloidal or dissolved fractions (F3–F5). These finding were congruent with previous reports that Cu was primarily dissolved and associated with colloidal material,[24] but previous reports of distribution in highway runoff varied widely.[12] Wet deposition, storm characteristics, and roadway usage were likely responsible for the reported incongruities.[13,29] Large dense particles were the other dominant fraction (F1); in sample A1, >80% of the Cu was particle bound (F1 and F2). Cu distributions in samples N1, A2, and A3 were similar (mostly F1 and F5) and contained the lowest total and dissolved Cu concentrations (∼≤5 ppb). Cu K_d^* values were greatest for the F4 fraction in all non-agricultural samples. In sample A1, $K_{d,F1}^* \sim K_{d,F4}^*$ while for samples A2 and

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A3 the highest K_d^* values were observed for F2, indicating an affinity for OM. Previously, OM has been observed to substantially complex Cu in many matrixes[6,35] and mean DOC K_d values were roughly half an order of magnitude higher than those of suspended sediment.[2]

Cu is present in the natural soil in trace amounts – average unimpacted CA soil contains 28.7 mg Cu per kg [30] – however anthropogenic Cu sources exist for each of the impacted land uses in this study. Brakes, building siding/roofing, and dry deposition each can contribute substantial Cu loadings (47%, 22%, and 14% respectively),[31] with the roofing loadings dependent on the prevalence of Cu roofs.[29] All three highway samples contained higher Cu concentrations than did the urban sample. Braking produces particles that are copper laden (10.8% Cu);[36] several studies have demonstrated Cu to be enriched in finer road-associated particles.[6,10] Cu from roofing material has been found in the dissolved fraction (*i.e.* filtrate),[37] while copper from brakes likely originates as particles.[34]

The agricultural samples were not found to be Cu enriched, but anthropogenic agricultural Cu sources include pesticides (select pesticides contain up to 80% Cu by dry mass[38] and biosolids. Previous research found biosolids to contain ~20-fold higher Cu concentrations than average soil and Cu in these samples was typically OM- or carbonate-complexed, resulting in limited bioavailability.[33] Cultivated lands – which are influenced by dry deposition, soil composition, and any applied anthropogenic compounds – were found to contain Cu at concentrations that were ~10% of those of main roads.[29] In the present study, total agricultural storm event Cu was equal to total highway Cu (A1 ~ H1), while irrigation concentrations in samples A2 and A3 were approximately only 15% of the average highway Cu concentrations.

3.7 Nickel

None of the samples exceeded EPA freshwater Ni criteria. Similar to results for Cr, the highest concentrations of Ni were observed for sample A1, with a majority of Ni in fraction F1, moderate Ni portions in fractions F2 and F5, and traces in F4. Ni was >80% dissolved (F5) for the highway and urban samples. By contrast, Makepeace *et al.* reported that Ni was typically associated with suspended particulate matter and OM.[24] In this study, N1 and the agricultural samples were predominantly F1 associated. The K_d^* values highlighted the associations with the F1 fractions, and F4 also had high K_d^* values. U1 $K_{d,F1}^*$ was over an order of magnitude higher than the distribution coefficients for the other U1 fractions. Among the agricultural samples, K_d^* values were highest for the F2 fraction. F2 and F4 were both assumed to contain organic particles/colloids; published K_d values for DOC are roughly half an order of magnitude higher than those for suspended sediment.[2] In road-associated particles, Ni has shown increased enrichment in finer particles (0.1 < d_p < 63 μm)[10] and particle–OM content increased with decreasing particle size (<20 to 2000 μm).[11] Among traffic sources, Ni is primarily associated with tires, and to a lesser extent brakes,[26,32] both of which would be expected to originate as particles. Ni concentrations in roadway runoff were 5–10

times greater than cultivated land runoff concentrations.[29] In this study, the agricultural samples contained more Ni than did the highway runoff, however the agricultural samples were not Ni enriched. Biosolids have previously been observed to contribute labile Ni, which may preferentially wash off, but at concentrations that are similar to those from soil.[33]

3.8 Lead

The highest total Pb concentrations were found in sample A1, followed by U1 and H1. Lead was predominantly associated with fraction F1, especially in N1 and the agricultural samples. Pb was also found associated with the light particles and colloids (F2 and F4), especially in the highway samples. Very little Pb was found in the F5 fraction; sample H1 contained the highest dissolved Pb concentration (0.38 ppb; 13%). The K_d^* values indicate that Pb was preferentially associated with the F1 and F4 fractions. Previous work has also shown Pb to be associated with SS.[24] Historic use of leaded gasoline is typically considered the primary source, and the greatest concentrations have been observed in road runoff,[29] however among current sources, building sidings represent 79% of the total Pb load.[31] Biosolids have also been observed to contain elevated Pb concentrations (~5× world soil averages),[33] which may have contributed to the elevated Pb concentration observed in sample A1 this study.

3.9 Zinc

All three of the highway samples exceeded the maximum and continuous EPA freshwater hardness-dependent criteria for dissolved Zn. In the case of H1, the dissolved Zn concentration (96 ppb maximum) was more than four times the criterion maximum concentration (CMC). Samples N1, A2, and A3 had comparatively low dissolved Zn concentrations (<10 ppb) which were well below the relevant criterion. In the natural and agricultural samples, F1 contained the highest Zn concentration followed by F2. The highway and urban samples contained a considerable fraction of dissolved Zn (F5 > 33%) with a moderate fraction associated with light colloids which was consistent with previous findings that Zn was primarily dissolved, but also easily sorbed to colloidal and suspended particulate matter.[24] Among the other samples, dissolved Zn was minimal (F5 ~ 15%) or not detected. Among samples with F5 > 0, F1 and F4 had the highest K_d^* values which is similar to reported mean K_d values ($K_{d,SS} \sim K_{d,DOC}$).[2] In sample A2, the $K_{d,F4}^*$ was several orders of magnitude higher than that for any other fraction.

Zn has significant natural sources (CA average soil: 149 mg kg^{-1}),[30] in addition to important anthropogenic sources. Tires, which abrade and release particles during use, were frequently listed as a key anthropogenic source as they contain ~1% Zn by mass[39] and were responsible for 25% of the urban anthropogenic Zn loads.[31] However, building siding/roofing is the dominant urban Zn source (65%).[29,31] Though Zn was not considerably enriched in agricultural samples, possible sources include commonly used pesticides (~1 to 17% Zn)[38] or biosolids (~9 times soil background and quite labile).[33] Cultivated land

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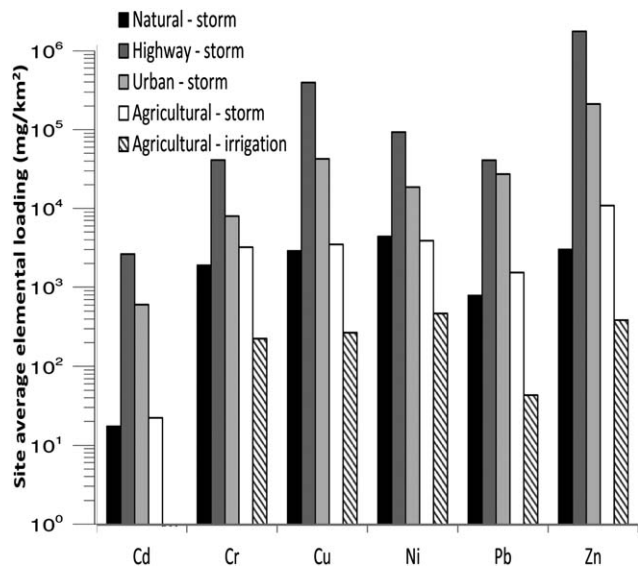This journal is © The Royal Society of Chemistry 2013

Fig. 6 Average elemental loadings by land use (site), presented on a log scale. Agricultural samples are differentiated by storm event (A1) and irrigation (A2 and A3) samples.

Zn concentrations were found to be ~25% of roofing material and main road concentration,[29] which was similarly observed among irrigation and highway samples in this study.

3.10 Metal loadings

Elemental loads were calculated on a mass per contributing area (mg km^{-2}) basis and are shown in Fig. 6. Among the three agricultural samples, the irrigation samples (A2 and A3) were observed to have similar characteristics, while the storm-event sample (A1) was different (demonstrated in Fig. 4). Therefore two classes of agricultural samples are shown. Storm characteristics are expected to play a significant role in mass loadings, therefore the loadings presented here should be interpreted as potential general trends rather than definitive values. Highway runoff contained the highest loads for all metals, followed by urban. Highway and urban loads exceeded natural loads, while the agricultural storm loadings were typically similar to natural loads, and agricultural irrigation loadings were less than natural storm loadings for all metals. The EF and loading results highlight that highways and urban areas are important sources of metals to surface waters. Irrigation samples likely exhibit lower loads than the agricultural storm sample due to the comparatively lower SS concentration.

4 Conclusions

Understanding constituent (i.e., metal) associations, which can be assessed with an appropriate fractionation approach, is important for understanding and predicting the constituent's fate (e.g., associations/complexation), transport (e.g., mobility), and effects (e.g., bioavailability). The fractionation approach developed in this study allows for the inference of fraction composition due to difference of separation mechanisms

between size- and settling-based methods. Cu was generally found in the dissolved phase and complexed by OM and is therefore likely mobile. Ni and Zn were primarily dissolved and should also be considered mobile. Pb mobility is likely comparatively low, as it was associated with SS, as was Cd in non-highway samples. Metals in highway runoff potentially pose the greatest ecological threat due to elevated dissolved concentrations (Cd, Cu, Ni, Pb, and Zn) and minimal hardness; highway runoff Cd, Cu, Pb, and Zn each exceeded USEPA freshwater criteria. Highway samples contributed the highest loads (mg km^{-2}) for all metals, which were likely from anthropogenic sources. Notably higher TSS and particle-associated metals (Cr, Cu, Pb, and Ni) were observed in the storm event agricultural sample (A1), which represents a future potential source of bioavailable metals following the change in the aqueous chemistry that is likely to occur following sedimentation.

The combined approach presented in this study has many potential applications for both engineered and natural systems, can be applied to a suite of constituents, or could be adapted to be used in other matrices. The approach can be adapted to small sample volumes through the use of a conventional centrifuge and centrifugal ultrafilters; additionally, the method can be adapted to suit the size and density range of interest by adjusting centrifugation parameters and nominal pore size. Finally, the results could be improved via direct detection of dissolved constituents, which could be accomplished for metals or organic constituents (e.g., Donnan membrane technique and solid phase micro extraction, respectively).

Acknowledgements

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