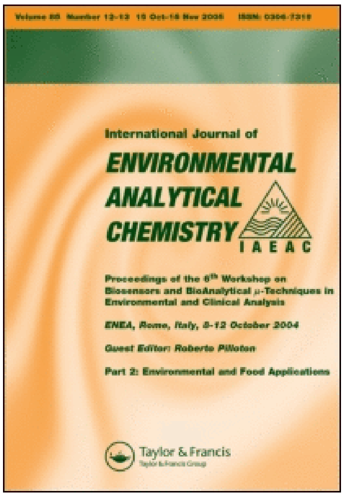

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Heavy Metals and Their Relationship to Solids in Urban Runoff

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Although a considerable amount of work has been done in order to develop models for estimating metal loadings in urban runoff, some basic information on the relationships between various storm water parameters is still lacking. In a previous study at a viaduct road runoff site in Pullman, WA, metal input from sources other than motor vehicles was excluded and a definite relationship was observed between total solids and metal concentrations. This study was undertaken to determine if the same models can be used for storm events occurring at a different location where the input of solids and metals from sources other than motor vehicles was not controlled. Storm runoff was collected at 20 different roadside sites during each of two separate storm events at the non-industrialized area of Logan, UT. The samples were analyzed for total solids and metals (lead, copper, zinc, iron, chromium and cadmium). Since several methods of digestion of runoff samples are given in the literature, the two most common procedures were compared. After predigestion with HNO_3, the 40 samples were each separated into two aliquots. One aliquot was digested with HCl–HNO_3 while the other was digested with HF–HNO_3. The two digestion procedures did not provide significant differences in metal levels suggesting that the time consuming HF–HNO_3 digestion procedure is not required. Significant correlations were observed between metals vs. total solids and regression equations were developed for the two parameters. The models were compared to those obtained from the earlier study. It was observed that the regression models are only similar in the case of chromium and lead vs. total solids at the two locations indicating that simple models for the two metals might be used to estimate metal loadings at different geographical areas.

KEY WORDS: Urban runoff, heavy metals, storm runoff models, digestion techniques.

INTRODUCTION

Background

Many advances have been made in the last few years by water quality researchers in defining the impact of various pollutants in urban runoff.

Motor vehicles have been shown to be a major source of heavy metals in urban road runoff[1] and therefore produce a constant input of metals to the aquatic environment. The characterization of metals in urban runoff is important due to their potential toxic effects to aquatic life[2] as well as the possibility that they may find their way to drinking water supplies and thus create a public health hazard. A similar situation has occurred in the past with the contamination of drinking water supplies by road de-icing salts.[3] Urban runoff is oftentimes not contained nor treated previous to discharge, and the amount of material discharged is not controlled. Consequently, this so called "non-point" source pollution has become a significant by-product of increasing urbanization in the U.S.[4]

Several workers have attempted to model metal loadings in road runoff using variables such as rainfall intensity,[1] days elapsed since a previous storm event,[5] and vehicle density[6] but there is some question as to the application of such complicated models at different geographical areas.[7] In addition, there exists an inconsistency among various studies in the actual procedures used for analysis of metals in runoff. Difficulties have evolved in comparing data of several investigators when each used a different method of sample preparation or digestion technique.

Modeling metal loadings in runoff

In determining those factors involved in modeling metal loadings in runoff, several authors have used study areas where the source of metal input was not entirely vehicle related.[5,8,9] These sources consisted of soil runoff, industry related fallout, rooftop drainage etc. Investigators chose either to ignore these sources or to attempt to include them in their runoff models. A novel approach used by Bourcier and Hindin[10,11] involved a viaduct study area (Pullman, WA) where runoff from non-vehicle sources was virtually eliminated. This allowed producing a simple regression model that could be used to predict vehicle related metal loadings in runoff. The preliminary model was of the form:

$$Y = mx + b \tag{1}$$

where: Y = metal concentration (mg/l)
m = slope
x = total solids concentration (mg/l)
b = Y-intercept.

Since the volume unit (l) existed on both sides of the equation, it was disregarded and a model describing metal loading vs. total solids loading was evolved. It was also found from actual stormwater measurements that the ratio of grams of accumulated solids to volume of accumulated runoff for a storm event was consistently 100 g/cu ft. This relationship when substituted into the above model (1) resulted in the following:

$$\text{metal (g)} = m\ (100\ \text{g/cu ft} \times \text{runoff vol. in cu ft}) + b \qquad (2)$$

Thus, a simple model was generated which made it possible to predict metal loadings at a drainage area for a particular storm event with only the runoff volume in cu ft to be determined.

In order to determine if the above model developed at Pullman, WA could be used at another geographical area required a comparison of the original regression model (1) of the relationship between total solids (TS) and metal concentrations in runoff. This study was initiated, then, to perform the above-mentioned comparison using the data from the Pullman, WA† study and that obtained from Logan, UT‡ where the input of metals is largely due to motor vehicles although other sources of metals may be involved.

Comparison of runoff digestion techniques

The methods of preparation of runoff samples are somewhat inconsistent in the literature. In some cases the method of digestion is not specified. Two widely used procedures, however, consist of digestion with either nitric-hydrofluoric acid as proposed in two publications[6,12] or a less time consuming method using nitric-hydrochloric acid as is described in an EPA report[13] and in *Standard Methods*.[14] In order to alleviate some of the confusion surrounding the subject, the two methods were conducted simultaneously but separately on runoff samples and the results compared by statistical means.

EXPERIMENTAL

Metal loading models for urban runoff

Runoff samples were obtained from 20 randomly selected sampling points during two storm events in November, 1978. The study area consisted of a three mile stretch of U.S. Route 91 in the non-industrialized City Center of Logan, Utah. Runoff was collected at street drains along both sides of the roadway. The urban runoff drainage system in Logan is such that a majority of the street runoff is diverted to larger drains and ultimately

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†Pullman, Washington, population 20,509 (1970), longitude 117° W, latitude 47° N, altitude 2341 ft.

‡Logan, Utah, population 22,333 (1970), longitude 112° W, latitude 42° N, altitude 4535 ft.

discharged to the Logan River. No attempt was made to measure flow at the study area since the runoff originated from several small urban watersheds and these would have been very difficult to monitor. Total solids were determined in samples as prescribed in *Standard Methods*[14] and total metals (Pb, Cu, Zn, Fe, Cd and Cr) were measured in sample digests after appropriate digestion (the description follows). Various statistical calculations were performed[15] on the data to describe the relationship between the above mentioned water quality parameters.

Comparison of digestion techniques

A total of 40 runoff samples were collected in 250 ml polyethylene bottles, acidified with 1.0 ml concentrated nitric acid and refrigerated at 4°C prior to digestion. A 150 ml aliquot of each runoff sample was transferred to a glass beaker on a hot plate after the addition of 10 ml of HNO_3. Glass covers were placed on the beakers and the samples heated slowly until a volume of approximately 40 ml was obtained. The digests were then transferred to 50 ml volumetric flasks and diluted to volume. Each sample digest was then separated into two, 25 ml aliquots using 25 ml volumetric flasks. One aliquot was digested with $HF–HNO_3$ and the other with $HCl–HNO_3$ as is described below in (a) and (b), respectively.

(*a*) $HF–HNO_3$ digestion:

The 25 ml aliquot was transferred to a 50 ml Teflon beaker and 5 ml HNO_3 added. The samples were then heated to almost dryness and 5 ml HF and 5 ml HNO_3 added. The samples were heated again to almost dryness. The above procedure was then repeated and when digestion was complete, the sample digests transferred to 25 ml volumetric flasks and brought to volume. Samples were then stored in polyethylene bottles and refrigerated at 4°C prior to analysis.

(*b*) $HCl–HNO_3$ digestion:

A separate 25 ml aliquot was digested using the same procedure as is given in (a) except that HCl was used in place of HF and glass beakers were utilized rather than Teflon ones.

The above mentioned digestion scheme resulted in concentrating the digests by a factor of 3. This was a useful analytical technique as it oftentimes increased metal levels in digests to within a measurable range. Both a deionized, glass-distilled water blank and three, 1.0 mg/l Pb standards were carried through each digestion procedure duplicating the above mentioned methods. Metal levels in deionized, distilled water were non-detectable before and after the digestion. Analysis of the six Pb digests (three from each digestion procedure) of 1.0 mg/l Pb resulted in a recovery of 97.0 ± 3.2† percent of the added lead.

Total metal measurements were performed by atomic absorption spectrophotometry (Jerrell–Ash, model 810). Lead, zinc, iron and chromium were measured solely by flame techniques (air–acetylene flame). A Teflon, corrosion resistant nebulizer was installed in the instrument to allow flame measurement of acidic digests. Cadmium and copper were analysed by both flame and flameless (Jerrell–Ash, FLA-10 graphite furnace system) techniques, depending on the relative concentrations of metals in the digests. Background correction was carried out by utilizing the A–B mode of the instrument whereby channel A referred to the absorbing line of the metal to be determined and channel B, a non-absorbing line of the same element. All standards were obtained from Fisher Chemical Co. All acids were analytical grade and all glassware was acid washed (HNO_3) and thoroughly rinsed with deionized, glass distilled water before use.

RESULTS AND DISCUSSION

Comparing runoff digestion methods

Results of metal analysis and the comparison of digestion techniques are presented in Table I. The mean values observed for each metal are similar

TABLE I

Results of metal analysis of urban runoff after $HCl–HNO_3$ and $HF–HNO_3$ digestion

Metal	Digestion method	Mean ± SD[a] (mg/l)	Range (mg/l)
Lead	HCl	3.71 ± 3.75	0.07–14.73
	HF	3.32 ± 3.42	0.07–13.87
Copper	HCl	0.08 ± 0.09	0.003–0.38
	HF	0.08 ± 0.08	0.010–0.31
Zinc	HCl	0.93 ± 0.87	0.01–4.25
	HF	0.91 ± 0.82	0.01–4.11
Iron	HCl	27.75 ± 38.70	0.67–146
	HF	25.20 ± 31.65	0.67–120
Cadmium	HCl	4.12 ± 2.94	0.61–13.73
	HF	4.00 ± 2.94	0.61–13.73
Chromium	HCl	0.11 ± 0.13	0.01–0.46
	HF	0.11 ± 0.11	0.01–0.42

[a] $n = 40$.

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†Mean ± standard deviation.

to the corresponding mean values obtained from a survey of reported values conducted by Bradford.[16] The large standard deviation relative to the mean is also typical of urban runoff. The individual metal concentrations obtained from HF–HNO_3 digestion were subtracted from the corresponding values of HCl–HNO_3 digestion and the resulting mean ±SD are provided in Table II. The HCl–HNO_3 method produced higher mean concentrations except in the case of Cr. The p-values given (Table II) refer to the results of a paired t-test performed on the differences, whereby levels >0.05 indicate that the metal concentrations are statistically equivalent using either digestion method. This was the case with all metals with the exception of Pb. Although a low significance level exists for Pb, when the individual metal ratios for Pb were calculated, i.e., HCl digestion method/HF digestion method, a mean of 1.12±0.17 was obtained which indicated that HCl values were consistently slightly higher than HF values. No conclusive explanation for this occurrence can be provided although it was observed that levels higher than 10 mg/l Pb (corresponding to 30 mg/l in the sample digests) showed the greatest variation amongst the two digestion methods. At such elevated metal levels, variation may occur due to the over-abundance of atoms in the flame upon analysis. It may be that the difference of sample matrix between the two digestion procedures is accentuated at such high concentrations of Pb. Dilution of samples prior to analysis may have provided statistically comparable results. When the four pairs of lead values above 10 mg/l are disregarded, the two methods showed no significant difference ($p<0.05$).

TABLE II

Results of the comparison of HCl–HNO_3 vs. HF–HNO_3 digestion of urban runoff samples

Metal	$\bar{x}$ of differences (HCl–HF)	p-value[a]
Lead	0.391	0.006
Copper	0.005	0.089
Zinc	0.018	0.307
Iron	2.540	0.125
Cadmium	0.124	0.534
Chromium	−0.005	0.481

[a] Level of significance testing the hypothesis that $u_{HF}=u_{HCl}$ using paired t-test, $n=40$.

Since the HF procedure is known to result in digestion of metal silicates while the HCl method will not, it would be expected that higher metal levels would occur after HF rather than HCl digestion due to the availability of the silicate bound metals. The relative amount of metals released may be so small, however, that they do not seem to be of consequence.

Overall, it appears that the HCl–HNO_3 method of digestion produces results equivalent to the HF–HNO_3 method and due to the special equipment and additional time necessary for HF digestion, the HCl technique should be adequate for the purpose.

Correlation coefficients for metals as well as for metals vs. TS are presented in Table III. High correlation was found between the various metals and between metals and total solids. This phenomenon suggests that either a single source of metals and solids exists or that two or more sources are contributing at the same rate. It has been shown previously that motor vehicles are responsible for metal input at a roadway in a non-industrialized area[10] and are likewise, the probable single significant source of metal input observed at the Logan, Utah location.

TABLE III

Correlation coefficients (*r*) among metals and total solids (TS) for road runoff samples at Logan, UT

Parameter	TS	Pb	Cu	Zn	Fe	Cd
Pb	0.646	—	—	—	—	—
Cu	0.638	0.924	—	—	—	—
Zn	0.731	0.940	0.922	—	—	—
Fe	0.601	0.786	0.885	0.821	—	—
Cd	0.587	0.727	0.775	0.775	0.735	—
Cr	0.646	0.891	0.938	0.892	0.940	0.755

Note: HCl–HNO_3 digestion method was used, all values significant at $p<0.001$, $n=40$.

Modeling heavy metals in runoff

Although it has been a practice in the past to relate heavy metals in urban runoff to a number of hydrologic parameters, describing metals concentrations in relation to total solids may be a more useful indicator as was mentioned earlier. Since the HF–HNO_3 procedure was common to the Pullman, WA study as well as the investigation reported here, HF digestion values were used in the statistical tests comparing regression lines. The pairs of regression equations are presented along with correlation coefficients and corresponding levels of significance in Table IV. All correlation coefficients showed *p*-values less than 0.05 which indicated

TABLE IV

Comparison of regression equations developed for total solids (TS) vs. metals in road runoff at two different geographical locations

Site	Regression equation[a]	Correlation coefficient, r	Correlation, p-value[b]	Comparison of slopes, p-value[c]
P[d]	$\text{Pb} = 5.28 \times 10^{-4}(\text{TS}) + 0.32$	0.91	<0.001	0.18
L[e]	$\text{Pb} = 8.96 \times 10^{-4}(\text{TS}) + 1.39$	0.65	<0.001	
P	$\text{Zn} = 5.02 \times 10^{-3}(\text{TS}) + 8.47$	0.53	0.004	<0.005
L	$\text{Zn} = 2.38 \times 10^{-4}(\text{TS}) + 0.39$	0.72	<0.001	
P	$\text{Fe} = 2.0 \times 10^{-2}(\text{TS}) + 70.27$	0.76	<0.001	0.007
L	$\text{Fe} = 8.12 \times 10^{-3}(\text{TS}) + 7.65$	0.63	<0.001	
P	$\text{Cr} = 5.02 \times 10^{-5}(\text{TS}) + 0.03$	0.81	<0.001	>0.50
L	$\text{Cr} = 2.88 \times 10^{-5}(\text{TS}) + 0.05$	0.63	<0.001	

[a] All values in mg/l.

[b] Value <0.05 indicates sig. correlation.

[c] Value >0.05 indicates sig. equivalence of slopes of regression lines.

[d] Pullman, WA, $N = 28$.

[e] Logan, UT, $N = 40$.

significant correlation. The basis for the test was the t-statistic as described by Snedecor and Cochran.[15] In addition, a comparison of slopes of regression lines of each pair was conducted using the F-statistic.[15] Both lead and chromium vs. TS showed statistically identical slopes ($p > 0.05$) among geographical locations with p-values of 0.18 and >0.50, respectively (Table IV).

A similar test was then performed on the relative heights of the regression lines of the two metals. A significant difference ($p < 0.05$) was found to exist for Pb vs. TS in the heights of the regression lines from the two locations while those for chromium vs. TS were statistically equivalent ($p > 0.05$). The plots of metals vs. TS are given in Figs. 1 and 2 for Pb and Cr, respectively. Only Pb and Cr show similarity of regression lines between the two locations. Since runoff from the Pullman study was collected from a single drainage area during three storm events while the Logan samples were collected from a number of smaller drainage systems selected at random during two storm events, a larger deviation of values around the regression line occurred as was expected from the Logan samples. This is most likely due to the natural hydrologic variability within the several drainage areas at the Logan study site. Lead and chromium are primarily related to vehicle operation while Zn and Fe may be related to other sources as well, such as soil runoff. This may be responsible for the similarity of the Pb and Cr models from the Logan area with those from Pullman, WA site where non-vehicle related runoff

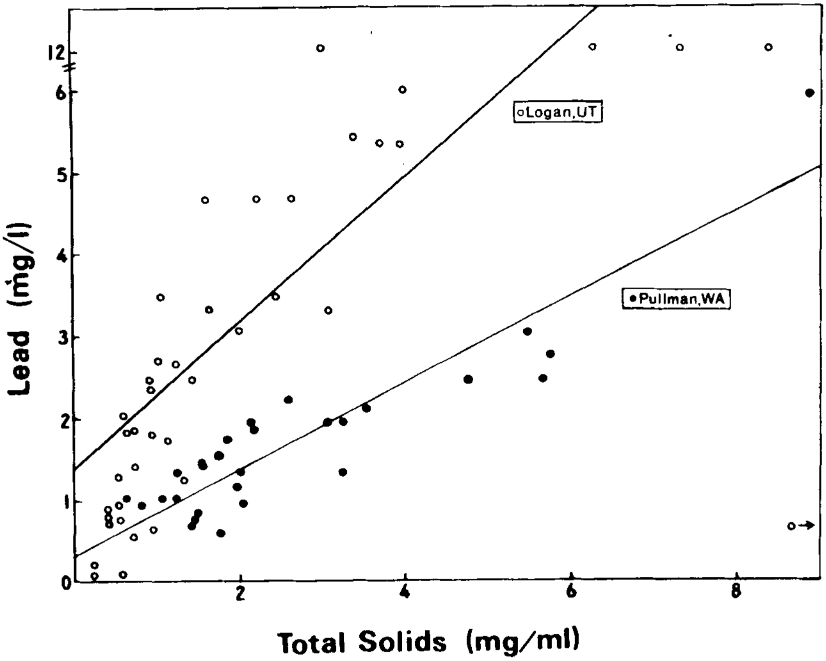

FIGURE 1 Plot of regression equations for total solids vs. lead concentrations in road runoff at two locations (→ refers to a total solids value of 11.6 mg/ml).

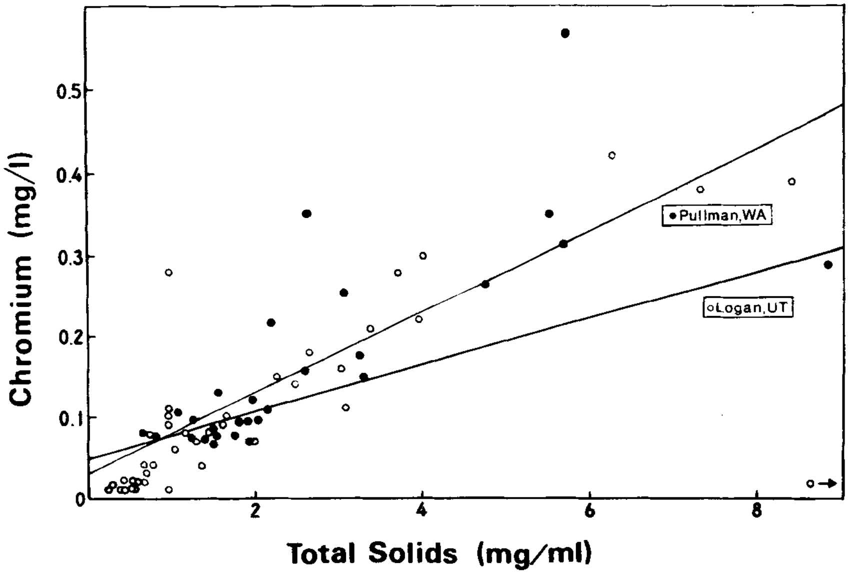

FIGURE 2 Plot of regression equations for total solids vs. chromium concentrations in road runoff at two locations (→ refers to a total solids value of 11.6 mg/ml).

was excluded. The fact that average Zn concentrations in runoff at the Pullman, WA were a factor of 10 greater than those at the Logan, UT area as well as those found in a nationwide survey,[16] leaves discrepancies in the Zn vs. TS correlation which remain unexplained. At the Logan area, one would expect a greater contribution of organic matter in addition to soil derived runoff which should both be relatively low in Pb and Cr in relation to TS concentrations compared to the Pullman, WA area. This was not the case, however, and, in fact, the opposite was found in terms of Pb vs. TS while that for Cr vs. TS was statistically equivalent.

More conclusive data is needed before it can be determined if a somewhat universal model can be used to predict metal loadings in urban runoff. It appears that at least in the case of Pb and Cr, statistically sound evidence exists suggesting the possible use of the models at different locations.

CONCLUSIONS

No significant difference was observed between the HF–HNO_3 and HCl–HNO_3 digestion procedures for all metals tested except in the case of Pb where similar results were obtained when levels <30 mg/l were present in the sample digests.

In terms of comparing metals vs. TS regression models developed at different locations, both Pb and Cr show significantly similar models with Cr attaining highly significant equivalence with the model developed at another geographical area. This information should be valuable as a basis for further investigations into the possibility of using simpler, less complicated regression models as methods of estimating metal loadings in urban runoff.

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