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The effect of increasing urbanization and population density on the concentrations of sediment-associated constituents for the conterminous USA

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Abstract In 1991, the US Geological Survey began the first cycle of its multidisciplinary National Water Quality Assessment Program. The Program encompasses 51 river basins that collectively account for >70% of the total water use (excluding power generation), and >50% of the drinking water supply in the USA. One aspect of the first cycle included representative bed-sediment sampling within each of the river basins. Sampling sites were selected to represent the most important land-use categories (e.g. agriculture, undeveloped, urban) in each river basin. Both urban percentage and population density were the only land-use/socio-economic factors that significantly affect sediment-associated chemical concentrations, with the latter appearing to be more significant/consistent than the former. The affected constituents, in decreasing order were: Pb > Hg > Ag > Zn > Cd > Cu > Sb > S > Ni > Sn > Cr > As = TC > Co = Fe = P = TOC.

Key words sediment chemistry; land use; trace elements; major elements; carbon; sulfur

INTRODUCTION

Since the publication of the Hawkes & Webb (1962) treatise on geochemical exploration, as well as the subsequent publication of various geochemical atlases (e.g. Webb *et al.*, 1978), there is a widely accepted perception that land use as well as local mineralogy/petrology (geology) can affect fluvial and/or lacustrine sediment chemistry. There are many studies describing the effects of ore deposits as well as abandoned and/or ongoing mining/smelting operations on aquatic chemistry (e.g. Allan *et al.*, 2002). Evidence for the effects of other types of land use on water quality have come from divergent studies that have attempted to relate land use to surface and groundwater chemistry (e.g. Fitzpatrick *et al.*, 2007), sediment/soil chemistry (e.g. Reimann *et al.*, 2007), and ecological analyses (e.g. Venne *et al.*, 2006). The advent, and subsequently successful application of sediment "fingerprinting" and source ascription to fluvial sediments and flood-plain deposits, has provided additional support for the view that land use can affect sediment chemistry (e.g. Collins & Walling, 2002).

In 1991, the US Geological Survey (USGS) began the first cycle of its multi-decadal, multi-disciplinary, National Water Quality Assessment (NAWQA) Program. The first cycle of the program encompassed 51 river basins (study units) that collectively accounted for >70% of the total water use (excluding power generation), and >50% of the drinking water supply in the USA (Hirsch *et al.*, 1988; Leahy *et al.*, 1990). The selected river basins represent a range of hydrologic settings, rock types (geology), land-use categories, and population densities (Fig. 1). About one-third of the basins are under active investigation for about 3 years at a time; hence, it took 9 years to complete the first cycle. The first cycle included a substantial ecological and bed sediment sampling and analysis component in conjunction with the collection/concatenation of a wide variety of ancillary data including land-use percentages, drainage area, annual discharge, underlying rock type, and population density (Hirsch *et al.*, 1988; Cuffney *et al.*, 1993; Gilliom *et al.*, 1995). Sampling sites were selected to represent important land-use categories (e.g. agriculture, urban) within each basin (Fig. 1). More than 1200 sites were sampled over the 9-year period.

The NAWQA bed sediment data from low population density agricultural and undeveloped sites were used to establish baseline concentrations for selected major and trace elements, as well as for total and organic carbon (TC, TOC), phosphorus (P), and sulfur (S) for the conterminous USA. In addition, based on the ancillary data, all the samples were subdivided according to

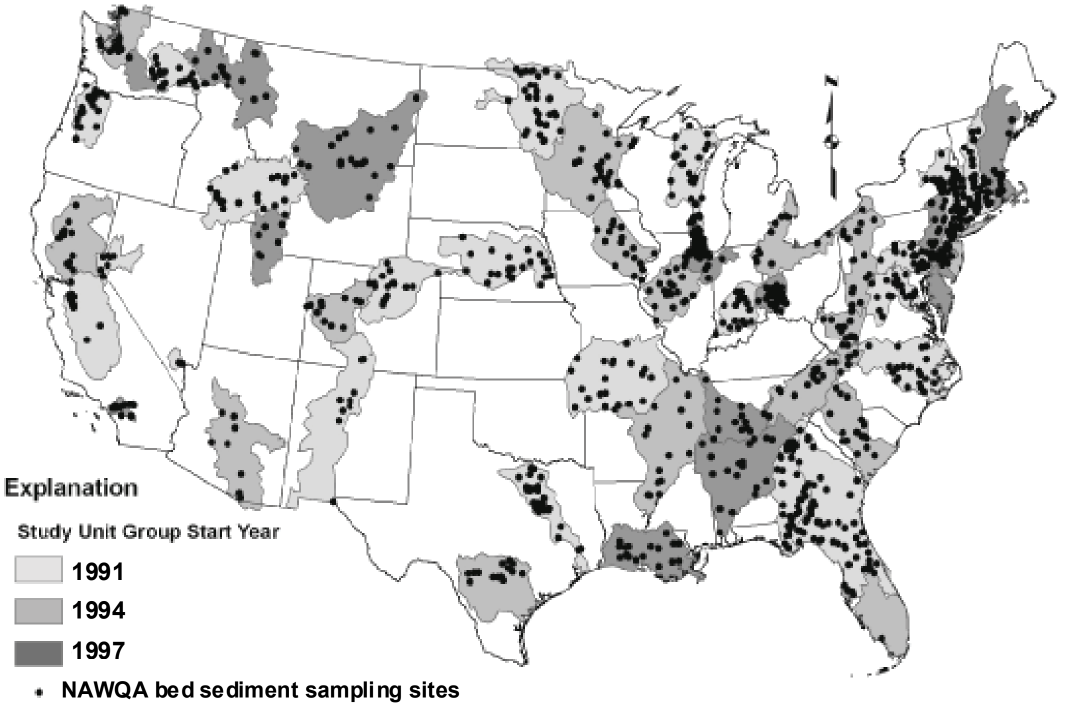


Fig. 1 Map of the NAWQA study units and the location of all the bed sediment sampling sites.

predominant land use (e.g. agriculture, urban), underlying rock type (e.g. metamorphic, intrusive), and population density, and were evaluated against the NAWQA baseline values to determine which factor(s) (geology, land use, and/or population density), if any, affected sediment chemistry. The results from those comparisons/evaluations are described herein.

METHODS

Wherever possible, sampling sites within each study unit were chosen to represent specific land-use categories; in some instances, additional nearby sites were selected to provide upstream/downstream comparisons, or to address land-use gradients. Additional sites were sampled if they represented areas of known and/or likely contamination. Lastly, where feasible within each study unit, at least two sites were selected to try to establish local baseline concentrations.

Sediment sampling was restricted to summer and/or autumn low-flow periods to help minimize seasonal variability (Gilliom *et al.*, 1995). Sediments were collected with a variety of pre-cleaned, non-contaminating devices. On-site sampling was limited to clearly identifiable depositional zones likely to contain substantial amounts of fine-grained sediment. Between 5 and 10 zones per site, near both banks and the centre of the stream, were identified and sampled. The resulting subsamples were composited and thoroughly mixed. Finally, composites for inorganic analyses were wet sieved with native water on site, through 63-µm nylon cloth, to limit the "grain-size effect" and to further facilitate subsequent spatial and temporal comparisons (Horowitz, 1991; Shelton & Capel, 1994).

The USGS analysed the bed sediment samples for a variety of inorganic constituents, as well as total and organic carbon and total sulphur, following procedures detailed in Arbogast (1996). All samples were air-dried prior to analysis. The analyses generated total (≥95% of the constituent present) rather than total-recoverable concentrations. Precision and bias were monitored for all the analytical procedures through the concomitant analyses of a variety of NIST (National Institute of Standards and Technology) and USGS reference materials, as well as replicate samples. Based on the replicate reference material analyses, precision was better than ±10 to 15%, depending on the constituent; no bias was detected (Arbogast, 1996). However, when sediment-associated chemical concentrations approached their respective reporting limits, precision could be as poor as ±100%.

ANCILLARY DATA

The upstream drainage area for each bed-sediment sampling site was calculated using Geographic Information Systems (GIS) and Environmental Systems Research Institute (ESRI) software. The same process was used to calculate the percentage of upstream generalized rock type(s) using the polygon coverage from the digital version of King & Biekman's (1974) Geology of the Conterminous United States. GIS was also used to classify each site according to its dominant upstream land use(s). These land-use classifications were obtained from an enhanced version of the USGS 1992 National Land Cover Data (NCLD) set, which established dominant land use for each 30 m × 30 m grid covering the conterminous USA (Vogelmann *et al.*, 2001; Nakagaki & Wolock, 2005). This led to four initial classifications based on a fixed set of criteria: agricultural, urban, undeveloped, and mixed (Gilliom *et al.*, 2006). The agricultural sites were also subdivided into pasture or cropland, and the undeveloped sites also were subdivided into forested or rangeland (Mueller & Spahr, 2006).

Data from both the 1990 and 2000 censuses were used to assess the population density for each of the NAWQA study units (Hitt, 1994). While the issues of urban gradients and changing amounts of urbanization (increasing amounts of impervious surface) are not directly addressed herein, population density, *per se*, represents a significant socio-economic factor that has, in the past, been positively correlated with changing fluvial sediment chemistry (e.g. Horowitz *et al.*, 1999; Rice, 1999). Hence, upstream population densities were determined for each sampling site. As the first cycle of the NAWQA Program spanned nearly a decade, the mean population density (people (p) km^{-2}) determined from both the 1990 and 2000 censuses was used in this study.

RESULTS AND DISCUSSION

NAWQA data were filtered prior to any statistical calculations and subsequent interpretations. The set was initially culled to eliminate any sites known and/or suspected of being affected by mining or mining-related activities because even though mining or ore-processing tend to be geographically limited, they can exert an areally and compositionally extensive downstream influence over fluvial sediment chemistry (e.g. Moore & Luoma, 1990; Salomons, 1995; Grosbois *et al.*, 2000) and hence, would heavily skew the results for other land-use categories or geologic factors.

A second issue was when/how to assign a specific land-use category to each sampling site because the estimates for the non-mining related locations typically ranged from <1 to >99% for most of the categories used in this study. While there were a few sites that could be termed "true end-members" for any one land use (e.g. ≥90%), the majority represented some type of mixture; albeit, usually one category was dominant. Hence, for the purposes of this study, a ≥50% cutoff for a singular land-use category was used. If no one land-use category represented ≥50%, the site was termed "mixed use". As a result, mixed-use sites were included in the estimation of baseline values and in assessing the effect of population density and rock type (geology), but could not be used to estimate the chemical effects for a specific land-use category. Please note that the effect of upstream drainage area, mean annual discharge and rock type, as well as the agricultural (pasture and cropland), and undeveloped (forested and rangeland) land-use categories displayed very limited or no detectable effects on sediment chemistry. Hence, they are not covered in the following sections.

Background and baseline are concepts that tend to be used interchangeably in the literature. However, background concentrations usually refer to elemental levels that imply the exclusion of anthropogenic effects, whereas baseline concentrations typically are determined at a particular point in time and space (e.g. Gough, 1993). With the advent of the Industrial Revolution, and the concomitant aeolian and fluvial distribution/redistribution of a wide variety of materials and their associated chemical constituents, it is unlikely that true background concentrations can be determined from any surficial material (e.g. Reimann & Garrett, 2005). Hence, a subset of the NAWQA data was used to establish geochemical baselines. Since baseline concentrations can change spatially and temporally, and are more likely to represent a range rather than a single value (e.g. Reimann & Garrett, 2005), those determined for the NAWQA sites could be viewed as decadal (1990–2000) geochemical "snapshots" for the conterminous USA.

For purposes of this study, average baseline values are defined as the median chemical concentrations associated with sites that are: (a) predominantly agricultural or undeveloped; (b) where urban land use was ≤5%; and (c) where population densities were ≤50th percentile (≤27 p km^{-2}). A total of 448 sites met the three criteria. Summary statistics for these sites were calculated (Table 1). Where the concentrations were neither at, or near, the reporting limits of the analytical procedures, the median absolute deviation (MAD) tended to be on the order of 20 to 30% (Table 1). The NAWQA median baseline values are not substantially different from those reported for either global (e.g. Bowen, 1979) or national (e.g. Shacklette & Boerngen, 1984; Horowitz, 1991; Gustavsson *et al*., 2001) data sets that are based on sediment and/or soil samples collected from the conterminous USA. As the Mississippi River drains more than 70% of the conterminous USA (e.g. Meade, 1995), NAWQA baselines also were compared to median values generated for more

Table 1 Baseline chemical concentrations and summary statistics for the NAWQA bed sediment samples.

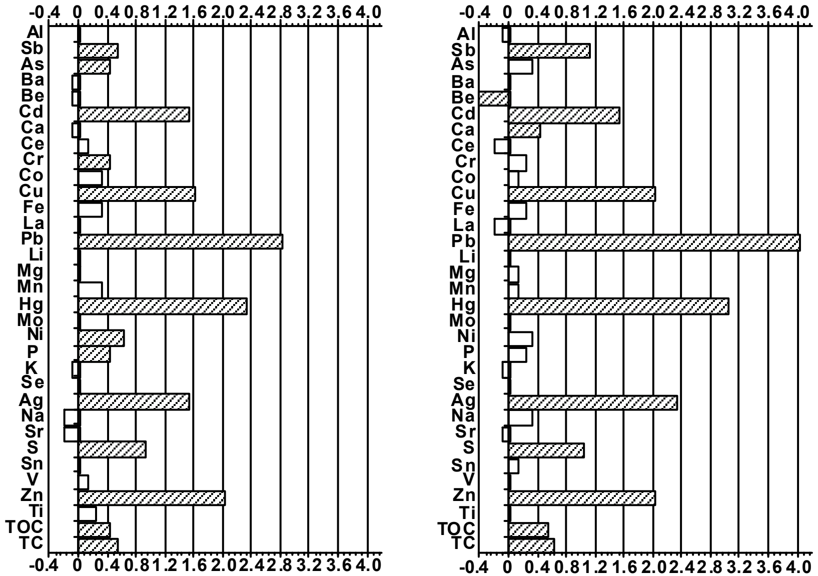
	Al (%)	Sb (mg kg^{-1})	As (mg kg^{-1})	Ba (mg kg^{-1})	Be (mg kg^{-1})	Cd (mg kg^{-1})	Ca (%)	Ce (mg kg^{-1})	Cr (mg kg^{-1})
Count	448	446	447	447	448	445	447	447	447
Min.	0.2	0.1	0.1	7.0	0.1	0.1	0.1	12	6.3
Max.	13.0	3.7	60	1300	7.0	2.8	28	360	270
Mean	6.0	0.8	8.1	470	1.6	0.5	3.0	79	66
Median	5.9	0.7	6.6	490	1.8	0.4	1.8	69	58
MAD	1.0	0.2	2.2	110	0.8	0.2	1.3	15	13

	Co (mg kg^{-1})	Cu (mg kg^{-1})	Fe (%)	La (mg kg^{-1})	Pb (mg kg^{-1})	Li (mg kg^{-1})	Mg (%)	Mn (mg kg^{-1})	Hg (mg kg^{-1})
Count	448	448	448	447	448	448	447	448	448
Min.	0.5	1.0	0.2	6.3	2.0	3.0	0.04	15	0.01
Max.	78	150	10	190	200	97	4.3	9000	3.1
Mean	14	24	3.3	42	24	33	1.0	1100	0.08
Median	12	20	2.9	39	20	30	0.9	840	0.04
MAD	4.0	6.0	0.7	8.0	6.0	10	0.4	360	0.02

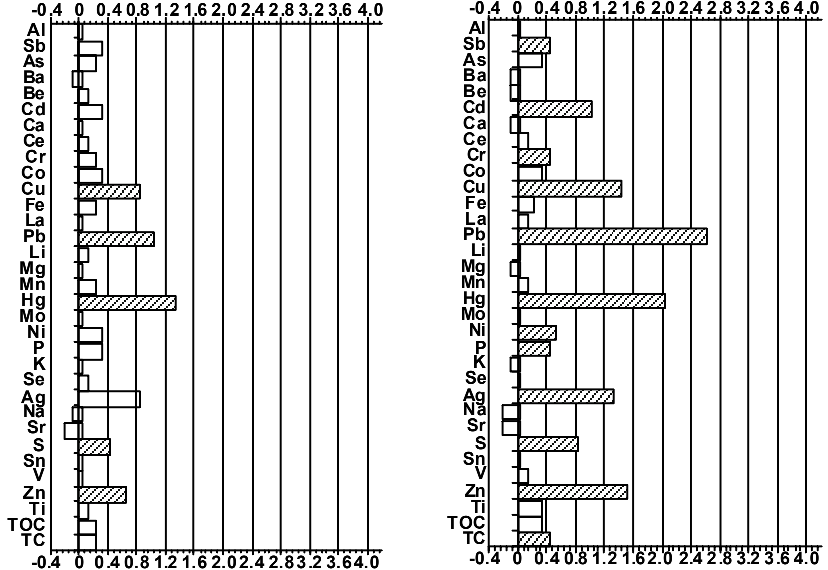
	Mo (mg kg^{-1})	Ni (mg kg^{-1})	P (%)	K (%)	Se (mg kg^{-1})	Ag (mg kg^{-1})	Na (%)	Sr (mg kg^{-1})	S (%)
Count	448	447	447	447	447	445	447	448	439
Min.	0.3	1.0	0.02	0.03	0.1	0.1	0.02	17	0.03
Max.	13	160	0.47	3.1	5.6	4.3	2.2	970	1.5
Mean	1.1	28	0.11	1.4	0.8	0.3	0.7	160	0.12
Median	1.0	23	0.10	1.5	0.7	0.2	0.6	150	0.08
MAD	0.0	7.0	0.02	0.3	0.2	0.1	0.3	60	0.04

	Sn (mg kg^{-1})	V (mg kg^{-1})	Zn (mg kg^{-1})	Ti (%)	OC (%)	TC (%)
Count	433	448	448	444	425	426
Min.	1.2	5.1	5.2	0.04	0.01	0.7
Max.	54	380	430	1.9	25	25
Mean	2.8	92	100	0.38	3.7	4.5
Median	2.5	83	91	0.33	2.4	3.3
MAD	<0.1	21	20	0.08	1.1	1.6

than 10 years of Mississippi River Basin suspended sediment samples collected as part of the revised USGS National Stream Quality Accounting Network Program (Horowitz *et al.*, 2001; Horowitz, unpublished data) and with surficial bed sediments collected from Lake Ponchartrain (Manheim & Hayes, 2002). According to Manheim (pers. comm., 2007), the latter samples are likely to represent Mississippi River Basin sediment-associated concentrations extant around the



≥50% Urban (n = 94) ≥90% Urban (n = 13)



≥50th Popuation Percentile (n = 506; ≥27p km-2) ≥90th Popuation Percentile (n = 102; ≥478p km-2)

Fig. 2 Change ratios (CRs) for the NAWQA ≥50% and ≥90% urban sites, and for those with the ≥50th and ≥90th population percentiles. CRs are calculated by normalizing the median chemical concentrations for a particular land-use or socio-economic factor to median chemical baseline concentrations. Obviously, if the ratioed values were the same, the CR number would be 1. However, by subtracting 1 from the ratio, no difference would be 0, negative numbers indicate depletions and positive indicate enhancements. Calculated CRs were rounded to the nearest tenth. Using this approach, a CR of +1 would indicate that the land-use concentration was double the baseline value, +3 quadruple the baseline value, etc.; negative CRs cannot be lower than –1; hence, a CR of 0.5 indicates that the land concentration is half the baseline value. CRs of <±0.3 should be viewed as falling within the range of analytical/sampling error and/or natural geochemical variance and are not considered significant; the rest are highlighted by cross-hatching in the graphs.

beginning of the 20th century as dredging has brought older material to the surface of the lakebed. Although the data from Lake Ponchartrain and the Mississippi River Basin are not markedly different from the range of NAWQA baseline values, modern Mississippi River suspended sediments appear somewhat elevated in As, Ba, Cr, Cu, Pb, Mn, Hg, Ni, Se and Zn, and somewhat depleted in TOC; contrariwise, the NAWQA baseline values appear marginally elevated in Cd, Co, Fe, Mn, Se and TOC, relative to older (Lake Ponchartrain) sediments.

Urban land use appears to exert a substantial control on downstream sediment chemistry (Fig. 2). The group of affected sediment-associated constituents reads like the "usual list of suspects" typically found within and downstream from urban areas; these constituents, and their potential sources have been identified in numerous prior studies (e.g. Ellis, 1999; Horowitz *et al.*, 1999; Old *et al.*, 2003; Horowitz *et al.*, 2008). The list includes such trace elements as As, Sb, Cd, Cu, Pb, Hg, Ag and Zn; such major elements as Fe, Mn, and S; as well as P, and both TC and TOC (Fig. 2). Trace elements display the largest enhancements (change ratio (CR + 1)), ranging from a low of 1.5 times (e.g. Sb) to as much as nearly 5 times baseline (Pb). Although the patterns can be somewhat noisy, most of the urban-affected constituents tend to display substantially increasing concentrations with increasing urban percentages (Fig. 3(a)).

The correlation between percent urban and population density is 0.92 ($P < 0.001$; $n = 94$); thus, it is not surprising that the latter also exercises a substantial control on the same group of constituents (Fig. 2). The effect of population density also has been noted in previous studies (e.g. Horowitz *et al.*, 1999; Rice, 1999). However, there are some interesting differences between the two factors. Population density enhancements (CR + 1) are not as substantial as those for percent urban (Fig. 2). Further, for many constituents, population density does not begin to exercise a substantial effect until it reaches at least the 50th percentile (i.e. >27 p km^{-2}; Fig. 2). As with the percent urban land-use category, numerous constituents display substantially increasing concentrations with increasing population density; however, the patterns for the latter tend to rise

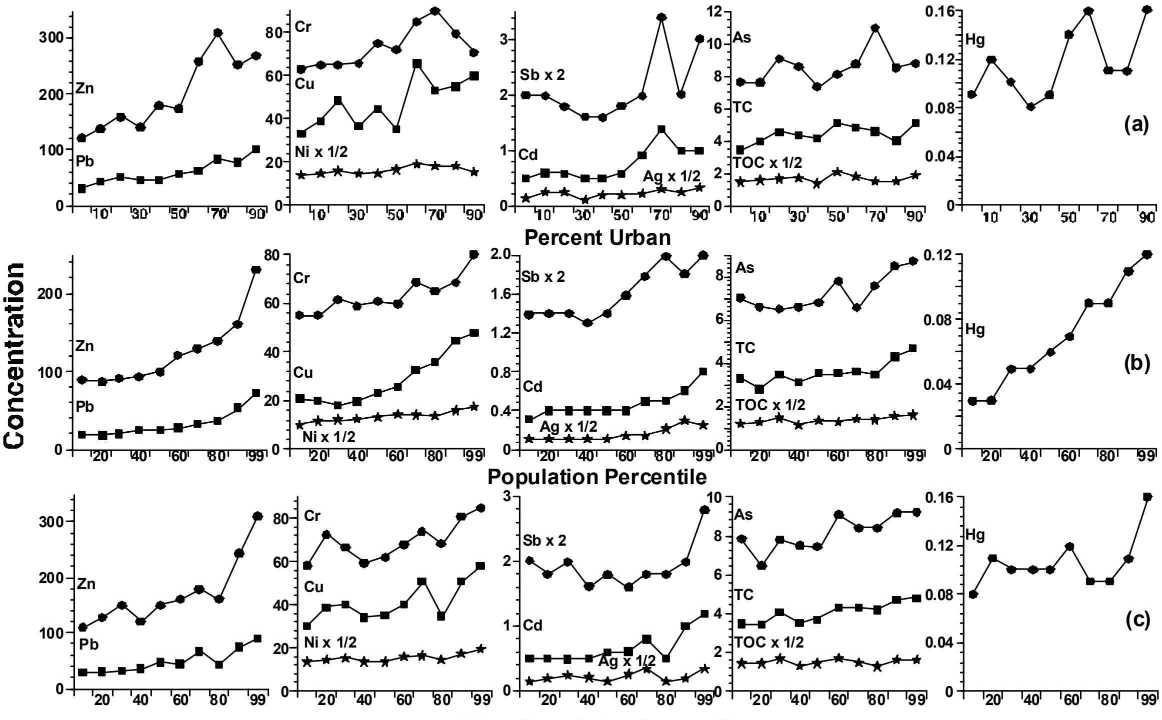


Fig. 3 A comparison of changes in sediment-associated chemical concentrations with: (a) urban percentage, (b) population percentile, and (c) 50% urban sites re-ordered and plotted by population percentile (see text). All concentrations are in mg kg^{-1} except for TC and TOC, which are in weight percent (%).

more steadily, and are markedly less noisy (Fig. 3(b)). Also, the correlations for sediment-associated chemistry and population density tend to be higher than those for percent urban. Lastly, Co, Fe, P, and total S display increasing concentrations with increasing population density, but not with increasing urban percentage (not shown). The seemingly more consistent results obtained using population density, relative to urban percentage, may well result because the former are based on direct counting (census data), whereas the latter are based on potentially less precise photo interpretations. It also may be possible that population density incorporates other factors (e.g. industrial activity) that could affect constituent concentrations, than are represented by urban percentage. The relatively low population density at which constituent effects begin to occur (the 50th population percentile; >27 p km^{-2}) could be viewed as potential support for this contention. Based on the foregoing, it appears that population density represents a better surrogate for predicting the presence of elevated sediment-associated constituent concentrations than urban percentage.

It is possible to combine percent urban and population density into a single composite factor by re-ordering all the designated urban (≥50%) sites by population density, recalculating the CRs, and replotting the data based on population percentile. When this is done, the CRs (not shown) for the enhanced constituents approach those that were determined based on percent urban; however, the linear plots for concentration *vs* increasing population percentile, while smoother than those obtained for urban percentage, are still noisier than those based purely on population percentile (Fig. 3(c)). Further, although the revised plots do pick up the patterns of increasing Co, Fe, and total S, they still do not for P, as occurred with the pure population density plots. Hence, it appears that using a combination of percent urban and population density tends to incorporate some of the advantages/benefits of both factors, albeit not all of them. Relative to the calculated enrichment factors [(CR+1) in parentheses], the sediment-associated constituents most affected, in decreasing order of enrichment are: Pb(4.6) > Hg(4.0) > Ag(3.6) > Zn(3.4) > Cd(3.0) > Cu(2.9) > Sb(2.0) > S(1.9) > Ni(1.7) > Sn (1.6) > Cr(1.5) > As(1.4) = TC(1.4) > Co(1.3) = Fe(1.3) = P(1.3) = TOC(1.3).

SUMMARY

(1) Median baseline concentrations for trace and major elements, P, and carbon (total and total organic) for fine-grained (≤63-µm) bed sediments collected as part of the USGS NAWQA Program are not substantially different from those reported for other sediment and/or soil samples that have been collected from the conterminous USA, or globally.

(2) Most land-use categories (e.g. agriculture, forested, rangeland), upstream/underlying rock type, upstream drainage area, and annual discharge do not appear to exert a substantial influence on the chemical composition of fine-grained bed sediments.

(3) Contrariwise, human activities, as indicated by percent urban and population density, seem to exercise a significant influence on sediment-associated chemical concentrations.

(4) Population density appears to exert a more consistent influence on sediment chemistry than urban percentage, possibly because: (a) it can be measured more accurately; and/or (b) it is a better measure of urban percentage; and/or (c) it is a better measure of other anthropogenic activities likely to increase sediment-associated chemical concentrations.

(5) Relative to baseline concentrations (change ratios (CR)), the constituents most affected by urban percentage/population density are, in decreasing order of enrichment: Pb > Hg > Ag > Zn > Cd > Cu > Sb > S > Ni > Sn > Cr > As = TC > Co = Fe = P = TOC.

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