Monitoring suspended sediment and associated trace element and nutrient fluxes in large river basins in the USA

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Abstract In 1996, the US Geological Survey converted its occurrence and distribution-based National Stream Quality Accounting Network (NASQAN) to a national, flux-based water-quality monitoring programme. The main objective of the revised programme is to characterize large USA river basins by measuring the fluxes of selected constituents at critical nodes in various basins. Each NASQAN site was instrumented to determine daily discharge, but water and suspended sediment samples are collected no more than 12–15 times per year. Due to the limited sampling programme, annual suspended sediment fluxes were determined from site-specific sediment rating (transport) curves. As no significant relationship could be found between either discharge or suspended sediment concentration (SSC) and suspended sediment chemistry, trace element and nutrient fluxes are estimated using site-specific mean or median chemical levels determined from a number of samples collected over a period of years, and under a variety of flow conditions.

Key words large river basins; monitoring; nutrient fluxes; suspended sediment fluxes; trace element fluxes

INTRODUCTION

The United States Geological Survey's (USGS) National Stream Quality Accounting Network programme (NASQAN) began in 1973 and was designed to determine the occurrence and distribution of a wide variety of water quality parameters (Ficke & Hawkinson, 1975; OWQ, 1996). The programme operated more-or-less continuously using this approach, until 1995, and at its height, incorporated more than 500 sites. In 1994, in response to substantially diminishing resources, changes in data requirements, and to better integrate the programme with other USGS ambient water-quality monitoring programmes, NASQAN was redesigned (OWQ, 1996). Initially, the new programme, which began in late 1995 (the 1996 water year), had two data objectives: (a) to characterize large US river basins by measuring the mass flux of selected constituents at critical nodes in various systems; and (b) to determine the fluxes of a variety of chemical constituents to the coastal zone. An important secondary goal was to provide error estimates for all the calculated fluxes. After the first year, the second objective was dropped due to a lack of sufficient spatial coverage. Based on historical data, the revised NASQAN network should account for >80% of the annual movement of water within the conterminous USA, as well as the discharge of more than 260 Mt of suspended sediment, to the coastal zone (Meade & Parker, 1985).

SAMPLING DESIGN AND METHODS

The revised NASQAN programme sampling design was predicated on evaluating the movement of water and a variety of water-quality-associated parameters in large rivers, where individual point sources tend to have only relatively local impacts. As such, water and dissolved constituents tend to behave conservatively; hence, large river segments tend to be compositionally homogeneous. Thus, contributions from sizeable portions of a basin, and/or potential sources or sinks for a variety of chemical parameters, can be estimated by adding/subtracting the contributions/losses of large river segments. Hydrophilic substances tend to move through large basins along with the water itself. Hence, sampling the same segment of water (i.e. Lagrangian sampling) as it moves through the system should permit the delineation of concentration changes and, if the discharge or water velocity is known, travel time(s) for the segment may be predicted.

Contrariwise, suspended sediment does not behave conservatively; it moves in and out of suspension, and there are constant exchanges between the water column, the riverbed, and banks. Thus, the particles making up a "packet" of sediment, and their associated chemical constituents, continuously change as material moves in (deposition) and out (resuspension) of "storage" as the packet moves downstream. As such, the packet rarely retains its original composition, even over relatively short distances, and travel times for individual particles are unpredictable. Thus, suspended sediment and sediment-associated chemical constituents display much more marked spatial and temporal variability than dissolved constituents (e.g. Horowitz, 1995). As a result of this non-conservative behaviour, contributions from sizeable portions of a basin, and/or potential sources or sinks for a variety of sediment-associated chemical parameters, cannot be reasonably estimated by adding/subtracting the contributions/ losses of large river segments. As a result of the behavioural differences between water and suspended sediment, a sampling programme designed to monitor dissolved fluxes may not be applicable to monitoring sediment and sediment-associated chemical fluxes. This dichotomy can create network design problems that may necessitate separate sampling schemes (both spatial and temporal) for water and suspended sediment.

Each revised NASQAN site was instrumented to determine mean daily discharge, but water and suspended sediment samples were collected no more than 12 to 15 times per year (OWQ, 1996). Sampling schedules were established to try to cover >80% of the typical range of annual flows at each site; however, sampling tended to be biased in favour of non-baseflow periods. As a result of the limited physical sampling programme, and the perception that at least a mean daily suspended sediment concentration (SSC) would be required to produce reasonable flux estimates (Walling & Webb, 1981, 1988; de Vries & Klavers, 1994; Horowitz, 1995; Phillips *et al.*, 1999), each site either had to be instrumented with some type of automatic sampling/measuring device (Horowitz, 1995), or a site-specific discharge-based regression equation had to be developed for predicting SSC (de Vries & Klavers, 1994; Phillips *et al.*, 1999). As no revised NASQAN site was instrumented with automatic sampling equipment or measuring devices, the only means of estimating mean-daily SSC was by developing site-specific discharge-based regression equations (rating curves).

ESTIMATING SUSPENDED SEDIMENT FLUXES AND ASSOCIATED ERRORS

For more than sixty years, in the absence of actual continuous or near-continuous SSC data, hydrologists have used rating (sediment transport) curves to estimate (predict) SSCs for flux calculations. Although there are more than 20 methods for developing rating curves, the most common is a power function (regression) that relates SSC to water discharge, with the discharge measurement constituting the independent variable (e.g. Phillips, *et al.*, 1999; Asselman, 2000). This requires the log-transformation of SSC and discharge data prior to the analysis. Comparisons of actual and predicted SSC, partially as a result of scatter about the regression line, as well as the conversion of results from log-space to arithmetic-space, indicate that rating curves can substantially underpredict actual concentrations (Walling & Webb, 1988; Asselman, 2000). To compensate, various method modifications have been applied; these include dividing the SSC–discharge data into seasonal or hydrological groupings, developing various correction factors, or using nonlinear regression equations (Duan, 1983; Ferguson, 1986; Walling & Webb, 1988; de Vries & Klavers, 1994; Phillips *et al.*, 1999; Asselman, 2000).

Within NASQAN, the Mississippi River at Thebes site is unique because it constitutes the only long-term, ongoing, daily SSC-measuring site in the network. As such, the data from this site are uniquely suited to evaluating such issues as sampling frequency, temporal resolution, and flux calculation/estimation errors. All calculations used in these evaluations are based on a 20-year data set covering water years (October–September) spanning 1981 to 2000.

The first evaluation entailed an examination of the temporal resolution, and associated errors, of estimated suspended sediment fluxes at the Thebes site covering the first 5 years (1996–2000) of the revised NASQAN programme. The actual flux for that 5-year period was 414 Mt (mega tonnes), whereas the predicted flux, using daily values was 404 Mt, a 3% underestimate. Despite this close agreement for the entire 5-year period, maximum errors in daily estimates of SSC ranged from –76% to +205%. The 5-year suspended sediment flux estimate using the approximately monthly NASQAN samples was 439 Mt, a 6% overestimate. The various errors associated with different levels of temporal resolution also were calculated for the same 5-year period; the errors tend to decline with increasing temporal resolution (Table 1). This accrues because the rating-curve approach underestimates highs and overestimates lows. Hence, the longer the period of interest, the greater the chance for the over- and underestimates to balance.

Table 1 Various levels of temporal resolution and their associated errors for the Mississippi River at the Thebes site for the five-year period 1996–2000.

Temporal Resolution	Maximum underestimate (relative %)	Maximum overestimate (relative %)	Average absolute error (relative %)
Daily	–76	205	26
Weekly	–63	157	24
Monthly	–43	58	19
Quarterly	–33	21	13
Yearly	–12	8	8

The effect of sampling frequency on the accuracy and associated errors of 5-year suspended sediment flux estimates also was investigated as part of the same evaluation. This entailed using the daily SSC values for the Thebes site and calculating a large number of rating curves to predict daily SSC values assuming different levels of sampling intensity.

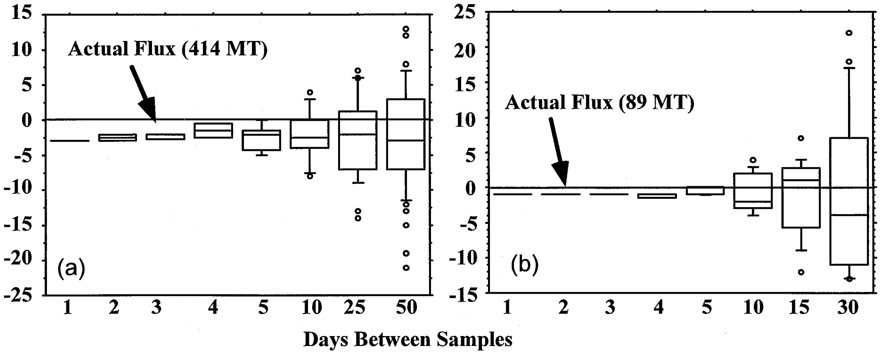

Fig. 1 Effect of sampling frequency on the errors associated with the estimation of suspended sediment fluxes over a 5-year (1996–2000 WY) period (a), and for a 1-year (1995 WY) period (b), for the Mississippi River at Thebes site.

The sampling frequencies evaluated in this way corresponded to: (a) once a day; (b) once every other day; (c) once every 3 days; (d) once every 4 days; (e) once every 5 days (weekly); (f) once every 10 days, (g) once every 25 days (monthly); and (h) once every 50 days (every other month). Not surprisingly the accuracy of the 5-year estimates decreased, and the size and range of the associated errors increased with decreasing sampling frequency (Fig. 1(a)). Interestingly, there was little difference between sampling frequencies ranging from 1- to 5-days. On the other hand, estimation errors from sampling frequencies on the order of once every two months (once every 50 days) were little compromized, and tended to fall within a range of ±20%. As the calculations were based solely on calendar distributions, they probably represent the maximum error likely to occur with this level of sampling frequency (Fig. 1(a)). If the same level of sampling (once every 50 days) were hydrologically distributed such as to encompass some 80 to 85% of the typical range of site-specific discharge, the associated estimation errors likely would be substantially less (e.g. Horowitz, 1995). The effect of sampling frequency on the accuracy and associated errors of annual suspended sediment flux estimates also were investigated concurrently (Fig. 1(b)). These evaluations covered high, median, and low flux years. The sampling frequencies evaluated in this way corresponded to: (a) once a day; (b) once every other day; (c) once every 3 days; (d) once every 4 days; (e) once every 5 days (weekly); (f) once every 10 days, (g) once every 15 days (fortnightly); and once every 30 days (every month). Note that as with the 5-year study, there is little difference between 1- and 5-day sampling. Further, even collecting a sample as infrequently as once a month only produced errors on the order of ±20%, regardless of the flow conditions (high, low, median). The same caveats apply to the annual study as to the 5-year study, hence, hydrologically-based sampling, as opposed to calendar-based sampling, is likely to produce substantially more accurate estimates.

The actual 20-year suspended sediment flux for the Thebes site for the period 1981 to 2000 was 2100 Mt. A single rating curve, using the entire 20-year data set, yielded an estimate of 2000 Mt, representing an error of <1%. This is a fairly standard approach for generating site-specific rating curves where long-term data are available, and is based on the assumption that all the data from the site are part of the same statistical population. Note that the annual errors associated with this single rating-curve approach can be significant (Fig. 2(a)). However, when individual annual rating curves are calculated for the same

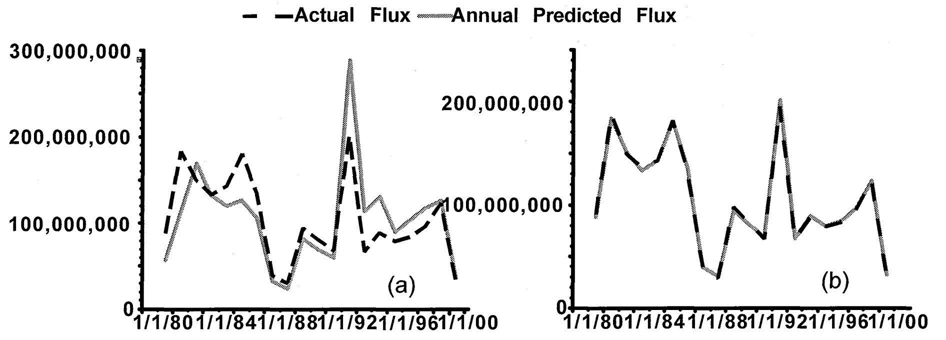

Fig. 2 Comparisons of annual fluxes calculated by using a 20-year rating curve (a), and by calculating individual annual rating curves (b), at the Mississippi River Thebes site for the period 1981–2000.

20-year period, it is apparent that the data are not part of the same statistical population. Some curves are linear whereas others are nonlinear (both concave and convex). Interestingly, the sum of the annual fluxes for the 20-year period now is 2100 Mt; however, the individual annual estimates are significantly closer to the actual fluxes (Fig. 2(b)). Hence, although the estimate of total flux does not substantially improve through the use of annual rating curves as opposed to a single rating curve, better annual estimates within the 20-year period can be obtained if individual calculations are used.

SEDIMENT-ASSOCIATED TRACE ELEMENT AND NUTRIENT FLUXES

The traditional, as well as the regulatory method of determining suspended sediment-associated trace element concentrations entails the collection and analysis of filtered (dissolved) and unfiltered (whole water) sample pairs, with subsequent subtraction of the associated concentrations of the former from the latter (Office of Water Data Coordination (OWDC), 1978, 1982). This approach is problematic because: (a) it does not provide total concentrations (with "total" being defined as ≥95% of the constituent concentration present); (b) the small sample masses typically collected can be affected by inhomogeneities; and (c) the small sample masses, combined with the dilution effects of the associated water in whole-water samples, can lead to analytical detection limit problems (e.g. Horowitz, 1995). Based on the foregoing, the revised NASQAN programme adopted a different approach. Large-volume (10 to 100 l), depth- and width-integrated isokinetic whole-water samples are collected such that aggregate suspended sediment masses would be between 1.00 and 1.25 g. All the large-volume whole-water samples were shipped to a central location (Atlanta, Georgia) for dewatering by flow-through centrifugation, and subsequent total trace element analysis.

Predicting suspended sediment-associated trace element concentrations using either discharge or SSC as the independent variable proved inadequate. However, site-specific intra- and interannual suspended sediment-associated trace element variations were markedly less (usually no more than a factor of two) than those for either discharge or SSC in all the NASQAN basins (Table 2). In fact, except where concentrations approach the reporting limit, the differences between site-specific interannual trace element means/medians typically do not exceed the errors (generally ±10%) associated with the analytical methods

Table 2 Annual mean and median values for discharge (Q), suspended sediment (S. Sed.), and sediment associated chemical concentrations for selected NASQAN sites (n is number of data points).

Site	Water Year	S. Sed. (mg kg^{-1})	Q (m^3 s^{-1})	Cu (mg kg^{-1})	Pb	Zn	Cd	P	As	Hg	Mn	Fe (wt. %)	Al	TOC
Mississippi River at Thebes, Illinois														
n	1996			16	16	16	16	16	16	10	16	16.0	17	13.0
Mean		289	6 723	23	28	97	0.6	1 000	8.5	0.05	760	2.5	5.5	3.1
Median		193	4 842	22	27	90	0.5	1 000	8.5	0.05	830	2.5	5.5	2.3
n	1997			15	15	15	15	15	15	15	15	15	15	15
Mean		288	7 504	19	24	89	0.5	850	8.8	0.04	980	2.4	5.4	1.8
Median	1998	221	6 428	18	22	89	0.5	850	8.7	0.03	1 000	2.4	5.5	1.8
n				17	17	17	17	17	17	13	17	17	17	17
Mean		354	8 181	20	25	93	0.5	850	9.0	0.03	1 000	2.6	5.5	1.9
Median		279	7 504	19	26	96	0.5	880	9.0	0.03	980	2.6	5.5	1.9
Willamette River at Portland, Oregon														
n				11	11	17	11	11	10	11	11	11	11	9
Mean	1996	58	1 584	88	40	160	0.4	2 100	8.3	0.11	2 400	5.7	8.0	4.4
Median		12	968	53	31	140	0.3	2 100	8.2	0.10	2 400	5.6	8.3	4.1
n				19	19	19	17	19	19	16	19	19	19	15
Mean	1997	51	1 628	52	24	130	0.3	1 700	8.6	0.07	1 900	5.8	8.6	2.8
Median		11	864	53	18	130	0.2	1 600	8.8	0.06	1 500	5.9	8.9	2.3
n				20	20	20	17	20	20	14	20	20	20	12
Mean	98	16	918	62	23	150	0.4	1 800	8.0	0.08	2 100	5.9	8.0	3.5
Median		10	702	60	23	140	0.3	1 800	8.0	0.08	1 800	6.1	8.1	3.7
Green River at Green River, Utah														
n				12	11	12	11	12	13	9	13	13	13	9
Mean	96	4 610	44	18	17	68	0.4	680	7.3	0.03	350	1.8	4.8	1.0
Median		197	34	19	16	69	0.4	700	7.2	0.04	330	1.7	4.6	1.2
n				13	13	13	12	13	13	9	13	13	13	12
Mean	97	2 745	105	18	18	78	0.5	670	6.5	0.03	360	2.1	5.3	0.8
Median		2 819	71	16	18	63	0.5	660	5.6	0.02	360	1.8	4.7	0.8
n				11	11	11	11	11	11	5	11	11	11	7
Mean	98	807	54	15	16	66	0.3	660	6.0	0.02	350	1.8	4.5	1.2
Median		636	33	15	16	66	0.3	660	6.0	0.02	340	1.8	4.2	1.2
Rio Grande at Foster Ranch, Texas														
n				15	15	15	13	15	15	15	15	15	15	11
Mean	96	1 120	25	14	19	82	0.3	700	8.0	0.29	440	2.2	5.4	1.2
Median		274	15	15	17	92	0.3	800	7.9	0.06	450	2.4	5.7	0.9
n				11	11	11	11	11	11	11	11	11	11	11
Mean	97	570	23	15	16	85	0.4	760	8.6	0.04	560	2.4	5.9	1.5
Median		272	15	15	17	81	0.4	780	8.5	0.04	450	2.5	6.1	1.1
n				10	10	10	10	10	10	10	10	10	10	10
Mean	98	328	15	14	17	89	0.4	750	9.0	0.05	480	2.6	6.2	1.3
Median		242	14	14	16	91	0.4	800	9.0	0.04	480	2.4	6.1	1.2

used to determine them (Table 2). With the failure of the regression model approach, this relative lack of variability provided one of the few means of estimating annual sediment-associated trace element fluxes, through the use of derived mean/median concentrations. Potential errors associated with the use of this approach ranged from <1% to as much as 75% and were determined by comparing the differences between the actual as opposed to the calculated (based on the selected mean/median concentrations) summed instantaneous daily fluxes for actual NASQAN samples.

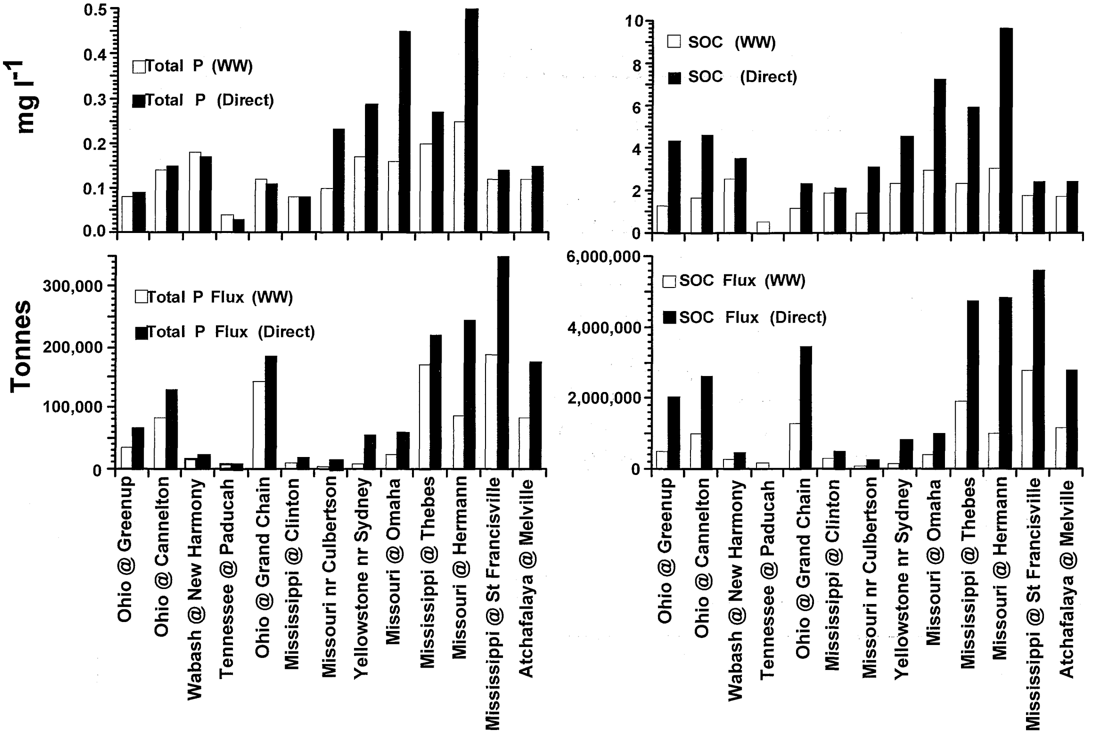

Fig. 3 A comparison of suspended sediment-associated average total phosphorus and organic carbon concentrations and cumulative (1996–1998 Water Years) suspended sediment-associated fluxes for the Mississippi River Basin sites indicating the general pattern of underestimates associated with the traditional/regulatory paired whole-water/filtered water approach, relative to direct determinations made on dewatered suspended sediment.

As part of the revised NASQAN program, suspended sediment-associated P as well as organic carbon (SOC) were determined both by the traditional/regulatory paired whole-water/filtered-water approach, and directly on dewatered suspended sediment. The latter method consistently generated significantly higher (by factors ranging from 1.5- to 10-fold) concentrations/fluxes for both constituents (Fig. 3). The apparent underestimates associated with the traditional/regulatory paired whole-water/filtered-water approach seem to result from a combination of sampling and analytical factors, with the latter likely to be more significant. These consistent underestimates may be important factors when addressing such issues as nutrient transport, eutrophication, algal blooms, and coastal/estuarine productivity.

The determination of suspended sediment, as well as total trace element, total phosphorus (P), and total organic carbon (TOC) fluxes is one of the major goals of the revised NASQAN programme. Unfortunately, as a result of a large number of censored (less than the detection limit) dissolved concentrations, total fluxes for a number of constituents (e.g. Ag, Pb, Cd, Cr, Co, V, Be, As, Sb and Hg) could not be estimated. The majority (≥70%) of the Cu, Zn, Cr, Ni, Ba, P, As, Fe, Mn and Al are transported in association with suspended sediment; Sr transport seems dominated by the dissolved phase, whereas the transport of Li and TOC seem to be divided equally between both phases (Fig. 4).

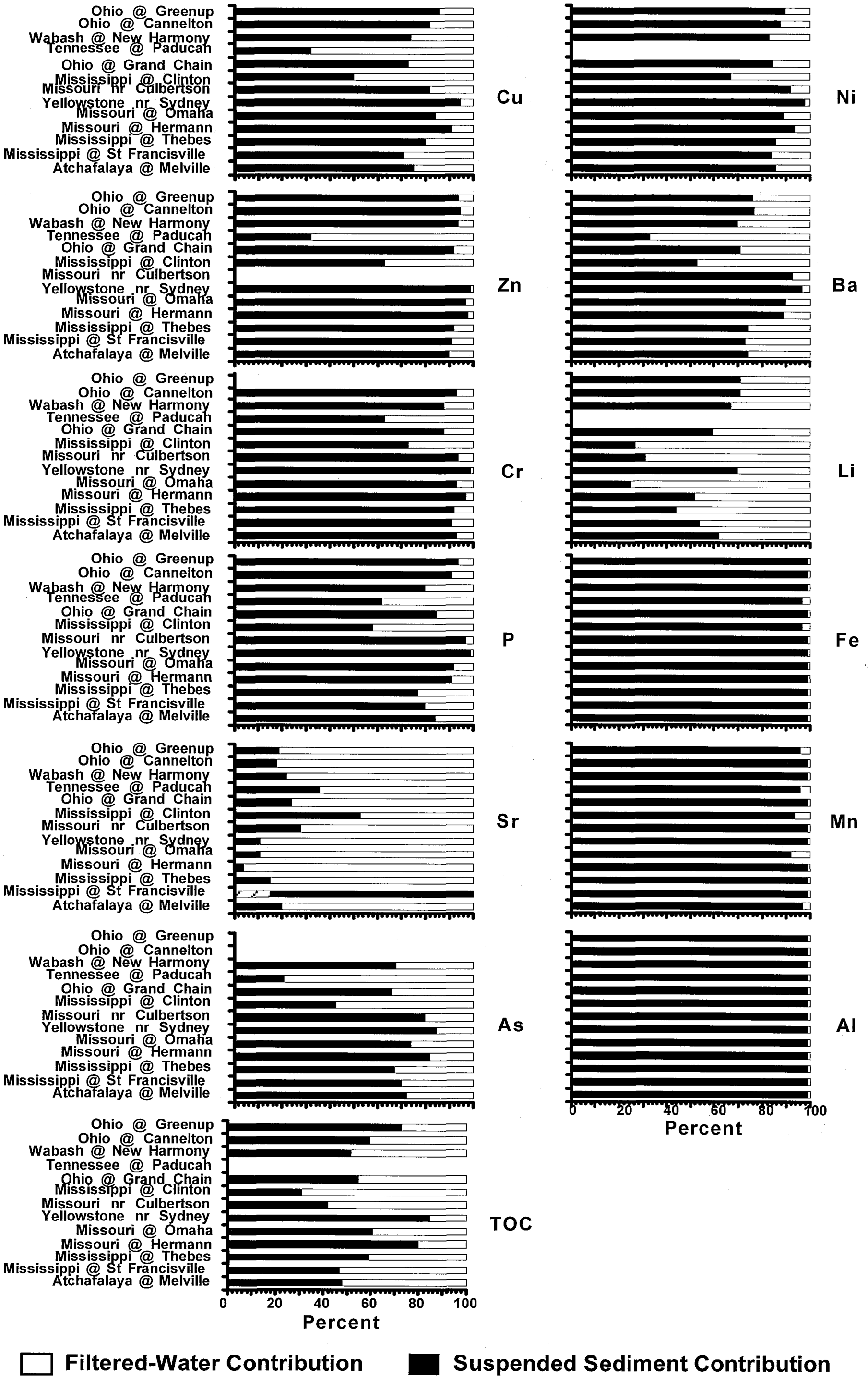

Fig. 4 Partitioning of various trace elements and nutrients between the dissolved (filtered water) and solid phases for the sites in the Mississippi River Basin.

CONCLUSIONS

(a) In large river basins, water and dissolved constituents tend to behave conservatively, whereas suspended sediment and solid phase-associated constituents tend to behave non-conservatively; therefore, different sampling schemes may be required for each type of media to adequately monitor suspended sediment, trace element, and nutrient fluxes.

(b) It appears that at least for large rivers, sediment rating curves can be used to generate reasonably accurate (≤15–20%) suspended sediment flux estimates for quarterly timeframes or greater.

(c) Sampling frequencies can exercise a substantial impact on the accuracy of sediment rating curve-generated flux estimates; however, good estimates (errors of ≤±20%) can be obtained from relatively infrequent samples. This is especially true if the samples are collected on a hydrological as opposed to a calendar-basis; good 5-year flux estimates appear to require as few as six samples per year, whereas good annual estimates appear to require as few as 12 samples per year.

(d) Site-specific intra- and interannual variations in suspended sediment associated-trace element concentrations tended to be much smaller (usually less than a factor of two) than those for discharge or SSC (typically more than an order of magnitude). As there are no strong interrelations between discharge or SSC, and suspended sediment-associated trace element chemistry, the use of site-specific mean/median concentrations provides one of the only means of estimating annual sediment-associated trace element and nutrient fluxes.

(e) The concentrations, and hence the annual fluxes, for suspended sediment-associated P and organic carbon, determined from the direct analyses of dewatered suspended sediment samples were markedly higher than those determined using the more traditional/regulatory paired whole-water/filtered-water approach; this could be important for such issues as eutrophication, algal blooms, and coastal productivity.

(f) At least in the NASQAN basins, the majority (typically ≥70%) of Cu, Zn, Cr, Ni, Ba, P, As, Fe, Mn and Al are transported in association with suspended sediment; in contrast, Sr fluxes seem to be dominated by the dissolved fraction, whereas the transport of Li and TOC appear to be divided about equally between both phases.

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