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Abstract In 1996 the US Geological Survey (USGS) began a national fluxbased water quality monitoring programme in the Mississippi, Columbia, Colorado, and Rio Grande basins. Suspended sediment flux estimates for periods greater than a year are generally accurate within  $\pm 15\%$ . Discharge and suspended sediment concentrations varied much more than chemical levels. Most trace element concentrations are not elevated except Zn and Hg in the Ohio River, and Ag, Cu, Pb, Zn, Cd, Cr, Co, Ba, Mo, Sb, Hg, and Fe in the upper Columbia River, which is impacted by mining waste. The majority ( $\geq 70\%$ ) of Cu, Zn, Cr, Ni, Ba, P, As, Fe, Mn, and Al are transported by suspended sediment; Sr transported seems dominated by the dissolved phase, whereas the transport of Li and TOC seem to be divided equally between both phases.

### **INTRODUCTION**

The United States Geological Survey's (USGS) National Stream Quality Accounting Network programme (NASOAN) began in 1973 with four major objectives: (a) to account for the quantity and quality of water moving within and from the USA; (b) to depict the areal variability of water quantity and quality; (c) to detect changes in water quantity and quality; and (d) to set the stage for future water quality assessments. The programme operated more-or-less continuously under these guidelines through 1995 (Ficke & Hawkinson, 1975; Office of Water Quality (OWQ), 1996). In 1994, in response to substantially diminishing resources, changes in data requirements, and to better integrate the programme with other USGS ambient waterquality monitoring programmes, NASOAN was redesigned (NASOAN\*: OWO, 1996). Initially, the new programme, which began in late 1995 (the 1996 water year), had two data objectives: to characterize large US river basins by measuring the mass flux of selected constituents at critical nodes in various systems; and 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. The selected basins were the Mississippi, Columbia, Colorado, and Rio Grande. The determination of coastal zone fluxes was dropped after the first year because of insufficient spatial and temporal coverage due to funding limitations. Based on historical data, the NASQAN\* network should account for >80% of the annual movement of water within the conterminous USA. Further, the basins represent four of the seven largest sources of suspended sediment in the conterminous USA, and

should account for the discharge of more than 260 Mt of suspended sediment to the coastal zone (Meade & Parker, 1985).

### **DESIGN CONSIDERATIONS/CAVEATS**

Each of the four NASQAN\* basin sampling designs was established with a view to understanding and evaluating the movement of water and a variety of water-qualityassociated parameters. In general, and particularly in large rivers where individual point sources (e.g. an industrial outfall) only tend to have relatively local impacts, water and dissolved constituents tend to behave conservatively; therefore, large river segments tend to be fairly 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. Further, hydrophilic substances tend to move through large basins along with the water itself. Hence, on-going sampling (i.e. Lagrangian sampling) of the same segment of water as it moves through the system will permit the delineation of concentration changes and, potentially, the physical/chemical processes acting on that substance to engender those compositional changes. Finally, the travel time for the impacted "segment" can be readily determined/predicted if the discharge or water velocity is known.

Contrariwise, suspended sediment does not behave conservatively; it moves in and out of suspension, and there are constant exchanges between the water column, the river bed, and the river 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" while the packet is transported downstream. As such, the packet rarely retains its original composition, even over relatively short distances, and travel times are difficult to predict. Thus, suspended sediment and sediment-associated chemical constituents display much more marked spatial and temporal variability than dissolved constituents (e.g. Horowitz, 1995). Hence, continued sampling of the same packet of water as it moves downstream will not readily permit the delineation of on-going particle-specific concentration changes, nor potential physical/chemical processes acting on that sediment-associated substance. 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 differences in the behaviour of 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 can and does create major network design problems, particularly when funding is limited. As an example of the impact of these differences, examine the sampling scheme for the middle/lower Mississippi River (from Thebes to St. Francisville, including the location of the Old River Control Structure, as well as the location of the Melville sampling site on the Atchafalaya River (Fig. 1).

Note that there are no mainstem sampling sites below the confluence of the Ohio and the Mississippi rivers before St. Francisville, a distance of over 1100 km.



Fig. 1 Sampling scheme for the Mississippi River basin (locations in italics are actual sampling sites, whereas those in normal type are provided for reference purposes only—see text).

Between the Ohio and Mississippi confluence and St. Francisville, the Arkansas River joins the Mississippi River, and about 25% of the Mississippi River is diverted into the Atchafalaya River at the Old River Control Structure (Fig. 1). Further, the Atchafalaya sampling site (Melville) is downstream from its confluence with the Red River. As such, the effects of suspended sediment and the sediment-associated chemical contributions from the Ohio and the Arkansas rivers on the mainstem Mississippi River cannot be readily delineated. Further, due to the location of the Melville sampling site and the lack of a sampling site at or near the Control Structure, there is no way to separate out the suspended sediment and suspended sediment-associated trace element contributions to the Atchafalaya between the Mississippi and Red rivers. Water chemists resolve this by assuming that dissolved constituents behave conservatively: thus the dissolved concentrations determined at St. Francisville are assumed to be equivalent to those in Mississippi River water diverted by the Control Structure. On the other hand, sediment chemists cannot make this assumption. In fact, substantial sediment resuspension has been observed between the Control Structure and the St. Francisville sampling site (R. H. Meade, USGS, personal communication, 1999). Thus, a comprehensive flux monitoring programme may require two separate sampling schemes, one for water and one for suspended sediment.

## ESTIMATING SUSPENDED SEDIMENT FLUXES

Although each NASQAN\* site was instrumented to determine mean daily discharge, actual water and suspended sediment samples were collected no more than 12–15 times per year (OWQ, 1996). Sampling schedules were established to try to cover >80% of the range of flows of a typical annual hydrograph; 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 would be required to produce precise and accurate flux calculations (Walling & Webb, 1981, 1988; de Vries & Klavers, 1994; Horowitz, 1995; Roberts, 1997; 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 suspended sediment concentration (de Vries & Klavers, 1994; Phillips *et al.*, 1999). No NASQAN\* sites were instrumented with either automatic sampling equipment or measuring devices; hence, the only means of estimating mean daily suspended sediment concentrations was by developing site-specific discharge-based regression equations (a rating curve).

Although there are various methods (extrapolation or interpolation plus various correction factors) of estimating suspended sediment concentration from discharge data, most are based on the determination of a log-log regression (a rating or transport curve) relating the two (e.g. Walling & Webb, 1981; de Vries & Klavers, 1994; Phillips *et al.*, 1999). The efficacy of this procedure depends on the number of paired data points available to develop the rating curve, and how well they represent the range of discharges and suspended sediment concentrations at a site (Walling & Webb, 1981; Roberts, 1997). With the exception of the Mississippi River at Thebes, which is a daily sediment station, the number of available data points from the 3-year NASQAN\* programme is not large, and ranges from a low of 10 (Rio Grande at Laredo) to a maximum of 45 (Missouri River at Hermann). Fortunately, all but one (the Colorado River above Diamond Creek) of the NASQAN\* locations were former NASQAN sites, or sites where other studies had been performed; hence, a substantial amount of historical data is available.

The procedure for developing estimates of a single daily suspended sediment concentration was the same for all 30 NASQAN\* sites. NASQAN\* and all available historical suspended sediment and discharge data for each site were combined into a single calibration set, and log transformed. A series of regression equations (e.g. linear, polynomial) were then calculated; the one with the highest  $R^2$  was selected, and a residual analysis performed. If the pattern for the residual analysis was random, then predicted daily suspended sediment concentrations were generated. In turn, these were used to calculate instantaneous daily fluxes for each set of data points; then the individual, as well as the sum of all the predicted and actual fluxes were compared for accuracy and bias (Table 1). As can occur with these types of calculations, the conversion from log space to arithmetic space may produce a negative bias; when compensation was necessary to reduce/eliminate the bias, it was done using a "smearing correction" (Duan, 1983). When no significant regression (based on the value of  $R^2$ ) could be calculated for a site-specific calibration set, mean suspended sediment concentration was used to estimate instantaneous daily fluxes. The percentage deviations (D) listed in Table 1 represent the difference between the actual, as opposed to the calculated (based on the model-derived daily suspended sediment concentrations), summed instantaneous daily fluxes for the individual calibration sets for each site. Hence, the D values provide an overall indication of error, whereas the sign provides an indication of bias. Errors using this approach usually are less than  $\pm 10\%$  for the 3-year reporting period; however, these errors increase substantially for temporal spans shorter than one year.

As a daily sediment station, the Mississippi River at Thebes provides an ideal case for examining both the nature of the errors associated with the use of the ratingcurve method of estimating suspended sediment concentrations (fluxes), as well as

Basin	Site	Flux	Pred. flux	Avg. flux	Method*	$n^{\dagger}$	D <sup>‡</sup> (%)
Mississippi	Ohio at Greenup	5.9	5.7	3.0	RMw/C	109	-3
	Ohio at Cannelton	12.1	13.3	6.6	RMw/C	116	+10
	Wabash at New Harmony	1.7	1.7	1.4	RMw/C	100	<1
	Tennessee at Paducah	0.42	0.41	0.37	RMw/C	134	-2
	Ohio near Grand Chain	25.0	23.7	17.1	RM	258	-5
	Mississippi at Clinton	2.0	2.0	1.6	RMw/C	163	<1
	Missouri near Culbertson	1.8	2.0	1.3	RMw/C	127	+11
	Yellowstone near Sydney	16.3	12.6	8.6	RM	235	-23
	Missouri at Omaha	13.3		12.3	Α	184	-8
	Mississippi at Thebes	347.4	344.4	269.6	RMw/C	1418	<1
	Missouri at Hermann	61.2	63.5	43.3	RMw/C	253	+3
	Arkansas at D. Terry Dam	2.0	1.9	0.9	RMw/C	169	-5
	Mississippi at St. Francisville	70.9	71.0	66.4	RMw/C	210	<1
	Atchafalaya at Melville	26.7	27.0	23.3	RMw/C	152	+1
Columbia	Columbia at Northport	0.26		0.23	Α	162	-12
	Columbia at Vernita	0.18		0.17	Α	116	-6
	Willamette at Portland	0.81	0.79	0.37	RM	205	-2
	Snake at Burbank	0.68	0.60	0.40	RMw/C	157	-13
	Columbia at Warrendale	1.4	1.4	1.2	RMw/C	156	<1
	Columbia near Beaver Army	2.7	2.7	1.8	RMw/C	68	<1
Colorado	Colorado near Cisco	5.5	4.4	3.6	RM	213	-20
	Green River at Green River	6.4	4.9	4.6	RM	225	-23
	San Juan near Bluff	6.8		5.8	Α	207	-15
	Colorado above Diamond Creek	0.54		0.49	Α	16	-9
	Colorado at NIB	1.0	1.2	0.50	RMw/C	122	+20
Rio Grande	Rio Grande at El Paso	0.18	0.16	0.09	RMw/C	135	-11
	Rio Grande at Foster Ranch	1.2	1.0	0.3	RM	151	-20
	Rio Grande at Laredo	0.31	0.32	0.11	RM	95	+3
	Arroyo Colorado at Harlingen	0.015	5	0.014	Α	83	-7
	Rio Grande near Brownsville	0.17	0.15	0.07	RMw/C	136	-12

Table 1 Summary of the results and associated errors for the NASQAN II suspended sediment-predictive models (fluxes are in megatonnes, Mt).

\* RM = regression model; RMw/C = regression model with "smearing" correction; A = average values.

<sup>†</sup> number of samples in the calibration set and used to estimate the error.

<sup>‡</sup> percentage deviation from the calibration set used to develop the site-specific model.

the relative errors associated with different levels of temporal resolution. Examination of a plot of the actual daily fluxes vs the calculated daily fluxes for the site indicates that the rating curve method tends to underpredict the highs and overpredict the lows (Fig. 2); thus, the method fails to encompass the complete range of variance in the daily fluxes (suspended sediment concentrations) at the site. As such, the range of errors associated with shorter timeframes are likely to be substantially larger than those associated with longer timeframes (Fig. 2). Hence, for the Mississippi River at Thebes, where three years of daily suspended sediment concentration and discharge data were used to develop the predictive model, the *D* values range from -74 to +146% for daily values, -48 to +68% for monthly values, -27 to +24% for quarterly values, -14 to +12% for annual values, and <2% for three or more years.



Fig. 2 Comparison of predicted vs measured suspended sediment fluxes for the Mississippi River at Thebes for different time scales.

The predicted annual suspended sediment flux for the 1998 water year (about 94 Mt) was generated without any 1998 suspended sediment data in the calibration set and had a D value of -6% (Horowitz *et al.*, 1999, unpublished data).

The patterns of prediction for rating curve-derived single daily suspended sediment concentrations (fluxes) displayed by the model for the Mississippi River at Thebes are mirrored by all the other models for the various NASQAN\* sampling sites. That is, all the models tend to underpredict the high and overpredict the low single daily suspended sediment concentrations at their respective sites. Also, note that the D values for sand-dominated rivers (e.g. Yellowstone River at Sydney, Colorado River near Cisco, Green River at Green River) tend to be substantially worse than those where the suspended sediment is dominated by silt- and clay-sized particles (Table 1). Thus, it would seem that the rating-curve method for predicting suspended sediment concentration is less effective for large sand-dominated rivers. However, it should be noted that because all the models for the other NASQAN\* sites are based on substantially smaller and less complete calibration sets, the Ds associated with the estimations of total fluxes for the 3-year period tend to be larger than those cited for the Thebes site (Table 1). Further, the errors associated with

temporal periods shorter than three years will be greater than those determined for the Thebes site. Obviously, based on the foregoing, it is possible to produce "reasonable" estimates of annual suspended sediment fluxes using the rating curve method, without actually obtaining daily suspended sediment concentrations. However, it should be noted that the relative success of this approach occurred because there was a substantial amount of historical data available to enhance the calibration sets. Finally, end users must determine the maximum acceptable error limits for different levels of temporal resolution. In the case of NASQAN\*, an acceptable limit seems to be quarterly flux estimates; more accurate, shorter-term estimates would require an increase in sampling frequency and/or a different approach for estimating mean daily sediment concentrations in the absence of actual measurements.

# SEDIMENT-ASSOCIATED TRACE ELEMENT CONCENTRATIONS AND FLUXES

The traditional, as well as the regulatory method of determining suspended sedimentassociated 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, 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 above, NASQAN\* adopted a different approach. Field crews collected large-volume (10-100 l) depthand width-integrated isokinetic whole-water samples. The intent was to collect sufficient volumes of whole water 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.

All attempts at developing regression models for predicting suspended sedimentassociated trace element concentrations, using either discharge or suspended sediment concentration as the independent variable, proved inadequate (based on  $R^2$ ). However, site-specific intra- and inter-annual suspended sediment-associated trace element variations were markedly less (usually no more than a factor of two) than those for either discharge or suspended sediment concentrations in all the NASQAN\* basins (Table 2). In fact, except where concentrations approach the reporting limit, the differences between site-specific inter-annual trace element means/medians typically do not exceed the errors (generally  $\pm 10\%$ ) associated with the analytical methods 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 calculating annual sediment-associated trace element fluxes, through the use of derived mean/median concentrations. Errors associated with the use of this approach ranged from <1% to as much as 75% and were determined using the same procedure

Table 2 Annual minimum, maximum, mean, and median values for discharge, suspended sediment, and sediment-associated chemical concentrations for selected NASQAN II sites.

Sample name	Water S. sed. Q				Sediment associated chemical concentrations (mg kg <sup>-1</sup> ):													Weig	Weight (%):						
	year	(mg l <sup>-1</sup> )	(m <sup>3</sup> l <sup>-1</sup> )	Cu	Pb	Zn	Cd	Cr	Co	Ni	Ba	v	Li	Be	Ρ	Sr	As	Sb	Se	Hg	Mn	Fe	Al	Ti	TOC
Mississippi R at Thebes, Illinois*	1996			16	16	16	16	14	16	14	17	17	17	17	16	16	16	16	15	10	16	16	17	17	13
Min		43	2 557	16	20	66	0.2	46	5	30	470	46	16	0.8	300	140	4.9	0.7	0.5	0.03	230	1.4	4.1	0.18	1.4
Max		1 480	17 840	43	55	150	1.4	110	14	69	910	120	48	1.7	1 600	270	12.9	4.1	2.2	0.07	1600	3.5	7.2	0.36	7.3
Mean		289	6 723	23	28	97	0.6	72	10	42	611	82	31	1.3	1 019	181	8.5	1.4	1.1	0.05	760	2.5	5.5	0.28	3.1
Median		193	4 842	22	27	90	0.5	61	10	38	600	85	30	1.5	1 000	170	8.8	1	0.9	0.05	830	2.5	5.5	0.29	2.3
	1997			15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
Min		100	3 341	14	19	69	0.3	43	7	29	290	51	19	1.0	680	150	6.8	0.9	0.6	0.01	690	1.6	4.3	0.19	1.4
Max		1 340	17 840	25	37	110	0.6	82	12	62	680	100	39	1.5	1 100	290	11.9	10	1.4	0.13	1400	3	6.5	0.36	2.2
Mean		288	7 504	19	24	89	0.5	63	10	40	576	79	30	1.3	854	207	8.8	2.9	0.9	0.04	981	2.4	5.4	0.29	1.8
Median		221	6 428	18	22	89	0.5	63	11	38	640	75	27	1.3	850	200	8.7	2	0.8	0.03	1000	2.4	5.5	0.30	1.8
	1998			17	17	17	17	17	17	17	17	17	17	17	17	17	17	16	17	13	17	17	17	17	17
Min		120	3 030	11	15	63	0.2	47	8	25	550	45	23	1.0	700	140	6.0	0.7	0.6	0.01	610	1.7	3.8	0.17	1.6
Max		1 460	17 557	27	43	130	1.2	82	15	59	700	120	41	1.6	1 100	350	13.0	6.8	1.3	0.04	1500	3.6	7.0	0.37	2.2
Mean		354	8 181	20	25	93	0.5	65	11	42	626	81	32	1.3	846	211	9.0	2.9	0.9	0.03	996	2.6	5.5	0.29	1.9
Median		279	7 504	19	26	96	0.5	64	11	38	630	82	32	1.3	880	190	9.0	1.9	0.8	0.03	980	2.6	5.5	0.31	1.9
Willamette River at Portland, Oregon	1996			11	11	11	7	5	11	5	11	11	11	11	11	11	11	11	10	10	11	11	11	11	9
Min		7	241	49	12	130	0.1	73	23	44	380	140	22	1.2	1 600	190	6.5	0.7	0.1	0.06	1400	5.2	6.2	0.59	2.7
Max		80	11 893	390	120	250	0.8	92	30	58	500	171	31	1.5	3 000	260	10.4	1.3	0.6	0.18	3400	6.1	9.0	0.75	7.1
Mean		58	1 584	88	40	161	0.4	79	26	50	438	156	25	1.4	2 136	232	8.3	0.9	0.4	0.11	2436	5.7	8.0	0.67	4.4
Median		12	968	53	31	140	0.3	79	26	47	430	160	24	1.4	2 200	240	8.2	0.8	0.4	0.1	2400	5.6	8.3	0.66	4.1
	1997			19	19	19	17	19	19	19	19	19	19	19	19	19	19	19	19	16	19	19	19	19	15
Min		5	283	14	14	38	0.1	62	23	42	93	140	20	1.1	1 200	200	6.5	0.5	0.2	0.02	1100	5.2	6.8	0.58	1.6
Max		349	8 297	69	52	170	0.6	180	29	110	760	180	160	1.6	2 600	320	10.2	2	0.5	0.16	3500	6.3	9.7	0.81	5.8
Mean		51	1 628	52	24	130	0.3	83	25	51	471	162	32	1.5	1 695	259	8.6	0.9	0.3	0.07	1947	5.8	8.6	0.69	2.8
Median		11	864	53	18	130	0.2	72	24	45	490	160	25	1.5	1 600	250	8.8	0.8	0.3	0.06	1500	5.9	8.9	0.69	2.3
	1998			20	20	20	17	20	20	20	20	20	20	20	20	20	20	20	20	14	20	20	20	20	12
Min		5	239	42	14	120	0.1	63	21	37	390	130	19	1.1	1 500	190	7.0	0.8	0.4	0.04	1300	4.7	6.4	0.51	2.7
Max		45	3 879	85	44	190	0.6	210	32	140	530	190	36	1.7	2 400	270	10.0	2	0.5	0.14	4100	6.6	9.0	0.79	4.6
Mean		16	918	62	23	146	0.4	89	26	52	465	160	29	1.4	1 850	222	8.0	1.2	0.5	0.08	2115	5.9	8.0	0.67	3.5
Median		10	702	60	23	140	0.3	81	26	46	460	155	30	1.5	1 800	220	8.0	1.2	0.5	0.08	1750	6.1	8.1	0.68	3.7

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Sample name		Sec	limer	t asso	ciated	l chen	nical	cond	centra	tions	(mg l	(g <sup>-1</sup> ):		(** *						Weig	eight (%):					
	year	(mg l <sup>-1</sup> ) (n	n <sup>3</sup> l⁻¹)	Cu	Pb	Zn	Cd	Cr	Co	Ni	Ba	v	Li	Be	P	Sr	As	Sb	Se	Hg	Mn	Fe	Al	Ti	TOC	
Green River at Green River, Utah	1996			12	11	12	11	10	12	10	13	13	13	13	12	13	13	13	13	9	13	13	13	13	9	•
Min		16	25	8	12	31	0.1	35	5	16	250	34	19	0.8	500	270	5	0.5	0.2	0.01	230	1.1	3.2	0.13	0.3	
Max		21 521	92	28	26	110	0.6	71	10	70	680	120	70	2.3	1 000	2000	11.3	21.6	1.2	0.06	490	2.9	7.2	0.35	1.7	
Mean		4 610	44	18	17	68	0.4	52	7	29	501	61	39	1.3	675	531	7.3	2.6	0.6	0.03	347	1.8	4.8	0.20	1	
Median		197	34	19	16	69	0.4	50	6	26	470	51	39	1.1	700	360	7.2	0.8	0.6	0.04	330	1.7	4.6	0.19	1.2	
	1997			13	13	13	12	13	13	13	13	13	13	13	13	13	13	13	13	9	13	13	13	13	12	
Min		82	20	7	12	34	0.1	44	5	21	390	32	16	0.8	480	260	4.1	0.4	0.2	0.01	250	1.1	3.2	0.14	0.4	2
Max		21 471	249	29	26	160	1.3	72	12	58	630	120	71	2.1	900	650	9.1	10.5	1.2	0.05	470	3.3	7.3	0.35	1.1	4
Mean		4 745	105	18	18	78	0.5	58	8	32	535	71	38	1.4	674	335	6.5	2.5	0.5	0.03	365	2.1	5.3	0.23	0.8	õ
Median		2 819	71	16	18	63	0.5	55	7	30	580	58	29	1.2	660	280	5.6	0.9	0.4	0.02	360	1.8	4.7	0.21	0.8	AN
	1998			11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	5	11	11	11	11	7	.*
Min		168	15	12	6	49	0.1	27	4	16	360	46	29	0.9	510	270	5.0	0.6	0.4	0.01	240	1.3	3.6	0.16	0.8	de
Max		2 284	182	20	34	83	0.5	130	10	75	650	70	47	1.6	800	1200	10.0	10.1	1.1	0.03	450	2.5	5.8	0.25	2	Sis
Mean		807	54	15	16	66	0.3	67	7	35	500	56	38	1.1	658	509	6.0	3.2	0.7	0.02	350	1.8	4.5	0.20	1.2	n
Median		636	33	15	16	66	0.3	58	7	29	480	53	38	1.1	660	490	6.0	1.7	0.7	0.02	340	1.8	4.2	0.20	1.2	anc
Rio Grande at Foster Ranch	1996			15	15	15	13	13	15	13	15	15	15	15	15	15	15	15 -	15	15	15	15	15	15	11	t ii
Min		21	7	7	12	33	0.1	23	3	16	120	31	28	0.6	300	370	6.4	0.6	0.4	0.03	250	0.9	3.8	0.11	0.7	npi
Max		24 300	419	19	35	120	0.6	60	11	44	360	110	69	2.5	900	1300	10.1	18.3	1.3	2.76	660	3.3	7.3	0.37	2.4	len
Mean		1 120	25	14	19	82	0.3	41	7	25	271	76	46	1.6	700	755	8.0	2.0	0.7	0.29	441	2.2	5.4	0.26	1.2	ıen
Median		274	15	15	17	92	0.3	39	9	22	300	78	41	1.6	800	600	7.9	0.8	0.7	0.06	450	2.4	5.7	0.28	0.9	utai
	1997			11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	ior
Min		70	7	12	11	64	0.2	29	6	18	240	51	35	0.9	580	420	6.9	1.0	0.5	0.02	380	1.3	2.9	0.15	0.6	1
Max		22 400	238	21	21	110	0.5	150	11	110	370	140	52	2.0	900	1100	11.6	7.1	2.2	0.05	1200	3.2	7.9	0.36	4.2	
Mean		570	23	15	16	85	0.4	53	8	31	293	89	43	1.6	763	728	8.6	2.5	0.8	0.04	565	2.4	5.9	0.28	1.5	
Median		272	15	15	17	81	0.4	41	8	24	290	87	42	1.7	780	780	8.5	1.7	0.7	0.04	450	2.5	6.1	0.29	1.1	
	1998			10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	
Min		161	5	13	13	79	0.3	37	6	16	270	83	34	1.3	590	420	7.0	0.8	0.4	0.03	320	2.2	5.4	0.25	0.6	
Max		26 000	177	17	21	100	0.4	50	11	21	390	110	46	2.0	1 200	980	11.0	1.7	1.1	0.07	560	3.3	7.5	0.38	2.1	
Mean		328	15	14	17	89	0.4	41	8	20	300	93	40	1.6	749	738	9.0	1.2	0.8	0.05	476	2.6	6.2	0.29	1.3	
Median		242	14	14	16	91	0.4	40	8	20	280	90	40	1.5	805	815	9.0	1.2	0.7	0.04	480	2.4	6.1	0.28	1.2	

\* - the numbers in the top row of each box in the chemical data section of the table for each water year refer to the number of chemical data points.

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Fig. 3 Comparison of total phosphorus and suspended organic carbon results for the Mississippi River basin sites.

employed with the suspended sediment fluxes, 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.

NASQAN\* suspended sediment-associated P and organic carbon were determined both by the traditional/regulatory paired whole-water/filtered-water approach and directly (dewatered suspended sediment). The latter method consistently generated significantly higher (by factors ranging from 1.5- to 10-fold) concentrations/fluxes (Fig. 3). The differences seem to result from a combination of sampling and analytical factors, with the latter likely to be more significant. This could be important for such issues as nutrient transport, eutrophication, algal blooms and coastal productivity.

# DISSOLVED TRACE ELEMENT CONCENTRATIONS AND FLUXES

Dissolved (filtered water-associated) trace element concentrations were determined as part of the original NASQAN programme. Unfortunately, substantial portions of these data appear to have been affected by contamination introduced during collection, processing, and chemical analysis (Shiller & Boyle, 1987; Windom *et al.*, 1991; Taylor & Shiller, 1995). As a result, NASQAN ceased collecting this type of data in 1991. On the other hand, although the majority of most trace elements are transported in association with suspended sediment, the dissolved fraction can make a substantial contribution (e.g. Horowitz, 1995). To prevent a recurrence of the problems encountered during the original NASQAN programme, NASQAN\* employed a newly designed clean protocol, as well as extensive QA/QC procedures, to ensure the integrity of the dissolved trace element data (Horowitz *et al.*, 1994). In fact, NASQAN\* may well be the first large-scale (national) programme employing such a procedure.

Filtered water-associated (dissolved) trace element concentrations were markedly lower than those determined during the original NASQAN programme. This seems due to the use of the clean protocol rather than to improvements in water quality, and produced a marked number of censored values. Censored values are an acceptable result in a standard regulatory/traditional monitoring programme because concentration, *per se*, is a major issue of concern. Unfortunately, this is not the case for a flux-based programme. As a result of all the censored data, the fluxes for filtered water-associated (dissolved) Ag, Pb, Cd, Cr, Co, V, Be, As, Sb, Hg, and Ti, as well as the total (filtered water plus suspended sediment-associated) fluxes for these constituents, could not be estimated. Hence, the trade-off for obtaining uncontaminated/accurate dissolved trace element data is either an inability to calculate fluxes at all, or the need to employ much more sensitive (expensive) analytical procedures to permit flux estimations.

# TRACE ELEMENT CONCENTRATIONS AND SUSPENDED SEDIMENT AND TRACE ELEMENT FLUXES IN THE FOUR NASQAN\* BASINS

The majority of suspended sediment-associated trace element concentrations determined under the NASQAN\* programme do not seem to be elevated, and are typical for fine-grained sediment. However, there are a limited number of exceptions. Elevated suspended sediment-associated Zn levels were detected in the Ohio River basin and elevated Hg levels were detected in the Tennessee River; the former may affect the mainstem Mississippi River, whereas the latter probably do not. Sedimentassociated concentrations of Ag, Cu, Pb, Zn, Cd, Cr, Co, Ba, Mo, Sb, Hg, and Fe are markedly elevated in the upper Columbia basin; these elevated concentrations seem to result from mining and/or mining-related activities. Consistently detectable levels of dissolved Se were found only in the Colorado River basin.

Suspended sediment, sediment-associated, total trace element, phosphorus (P), and total organic carbon (TOC) fluxes were determined for the Mississippi, Columbia, Rio Grande, and Colorado basins for the 1996, 1997, and 1998 water years. The majority ( $\geq$ 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).

Overall, annual suspended sediment fluxes in the Mississippi River basin seem somewhat low ( $\sim 17\%$ ) relative to previously published averages, but are well within the range of natural variability (Table 3). This occurred even though suspended sediment fluxes from the Ohio and Missouri rivers were above average, and probably resulted from low discharges from the Atchafalaya River and the upper part of the basin as measured at Clinton (Fig. 1, Table 3). Downstream sediment-associated trace element, P, and TOC fluxes increase in the Mississippi River; the increases are markedly greater in the upper part of the basin between Clinton and Thebes (20-fold) than in the middle and lower parts of the basin between Thebes and St. Francisville (1.5-fold) (Fig. 1). This would indicate that substantial chemical changes in the upper part of the basin are unlikely to be detected at the mouth of the river except after long periods of time.

Suspended sediment fluxes at the mouth of the Columbia River, in total for the 1996, 1997, and 1998 water years, averaged about 25% above the annual average,



Fig. 4 Partitioning of various trace elements between the filtered water and the solid phase for the Mississippi River basin.

River	Historic discharge (Mt year <sup>-1</sup> )	Current discharge (Mt year <sup>-1</sup> )
Mississippi River	210-230*	190
Missouri River	$95^{\dagger}$	107
Ohio River	40 <sup>†</sup>	46
Wabash River	$7^{\dagger}$	6.5
Tennessee River	$2^{\dagger}$	1.2
Atchafalaya River	80 <sup>†, ‡</sup>	66
Columbia	10 <sup>*</sup>	12.6
Snake River	2 <sup>§</sup>	1.7
Willamette River	$1.1^{\$}$	5.9
Rio Grande	0.7*	0.09
Colorado	0.1*	0.4
Green River	8.8 <sup>‡</sup>	8.0
San Juan River	15.4 <sup>‡</sup>	7.1

Table 3 Comparison of historic and current annual suspended sediment fluxes in the NASQAN\* basins.

\* Meade & Parker, 1985.

<sup>+</sup> Meade, 1995.

<sup>‡</sup> USGS Suspended Sediment Database.

<sup>8</sup> Haushild et al., 1966.

predominantly as a result of record discharges from the Willamette River in 1996 (1000%) and 1997 (600%) (Table 3). Despite the presence of numerous dams and impoundments, including the Grand Coulee, total net suspended sediment fluxes display a fairly simple downstream additive pattern. During this period, there was a 7.5-fold increase in suspended sediment fluxes between Vernita (about 2 Mt) and Warrendale (about 15 Mt) (Fig. 5). About 40% of this increase can be attributed to inputs from the Snake River (about 5 Mt). The remaining increases probably are attributable to inflows from the Yakima, John Day, and Deschutes River basins, especially the latter two which are heavily agricultural (cropping and particularly grazing). However, this can not be confirmed because there were no NASQAN\* sampling sites located in these sub-basins. As noted previously, the upper Columbia River is markedly impacted by mining or mining-related activities. These chemical impacts seem detectable as far downstream as Warrendale (Zn, Cd), and despite inflows from the unimpacted Snake River (Fig. 5). With the exception of the upper part of the Columbia River basin, where the results are heavily skewed by miningrelated impacts, there is a steady downstream increase in sediment-associated trace element, P, and TOC fluxes.

Annual suspended sediment fluxes at the mouth of the Rio Grande averaged only slightly above 1% of the published annual value, and were the direct result of a severe and on-going regional drought (Table 3). Despite its size, and as a result of the relatively arid conditions extant, as well as the presence of Amistad and Falcon reservoirs, responses to local tropical depressions moving inland from the Gulf of Mexico can be both extreme and highly localized (Fig. 5). For example, suspended sediment transport at Foster Ranch for the 1996, 1997, and 1998 water years was about 9 Mt. The majority of this material ( $\sim 77\%$ ) was transported in 1996 and,



Fig. 5 Sampling schemes for the Colorado, Columbia and Rio Grande basins (locations in italics are actual sampling sites, whereas those in normal type are provided for reference purposes only).

secondarily, in 1997 ( $\sim$ 19%). In 1996, two events accounted for 94% of the annual flux; between 29 August and 8 September 1996, and between 14 and 27 September 1996, 2.4 Mt and 4.1 Mt respectively, of suspended sediment transited the Foster Ranch site as a result of localized tropical depressions. However, none of this excessive transport was detected at the next downstream site (Laredo) due to the intervening presence of Amistad Reservoir (Fig. 5). A similar pattern was observed for the Laredo and Brownsville sites due to the presence of Falcon Reservoir (Fig. 5). Hence, suspended sediment fluxes were both highly localized and extremely "flashy". As a result, there were no consistent downstream trends in suspended sediment-associated nor total trace element fluxes in the Rio Grande basin.

Annual suspended sediment fluxes near the mouth of the Colorado River at the USA/Mexico border averaged about 3.5 times higher than the published average due to a surplus of water in the lower Colorado River basin in 1997 and 1998 (NIB site, Fig. 5). In fact, in terms of suspended sediment, the Colorado does not behave as a single continuous river, but as three separate ones. The upper part of the basin extends to Glen Canyon Dam, the middle part of the basin extends to Hoover Dam, and the lower part of the basin begins after Hoover Dam and extends to the end of the system (Fig. 5). Not surprisingly, suspended sediment fluxes markedly decrease

downstream in the basin. The majority (>99%) of suspended sediment derived from the upper Colorado River basin is retained in Lake Powell. Based on the current study, about 60 Mt entered Lake Powell but only 0.3 Mt emerged through the Glen Canyon Dam. This is in agreement with much prior information (Iorns *et al.*, 1964) but, based on the most current Lake Powell survey, indicates that the three upper Colorado sampling sites account for only some 35% of the suspended sediment entering the impoundment (Ferrari, 1988). The majority of suspended sediment derived from the middle part of the basin (as measured at Diamond Creek) is retained in Lake Mead (Fig. 5). Presumably, due to the presence of Glen Canyon Dam, the great majority of this material is derived from such relatively local sources as the Little Colorado, Paria, and Havasu rivers. As a result of the patterns in the upper and middle part of the basin, suspended sediment-associated, as well as total trace element fluxes decrease downstream. The differences between the upper and lower Colorado River basin typically exceed an order of magnitude, but can be as large as two orders of magnitude.

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