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Scale as a factor in designing sampling programs for determination of annual trace element fluxes

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Abstract Concentration data of suspended sediment-associated trace elements are a requisite for estimation of annual chemical fluxes. Fluvial suspended sediment and associated trace elements display marked short-term spatial and temporal variability, suggesting that determination of annual fluxes requires high frequency depth and width integrated sampling and subsequent chemical analyses. When time scales are shifted from hours or days to a year, short-term variability is less important. A 2 year study on the Arkansas River indicates that it may be possible, after detailed site characterization of mean/median sediment chemical data, to estimate annual fluxes of trace elements solely through monitoring of discharge and suspended sediment concentration.

INTRODUCTION

The role of suspended sediment in cycling trace elements in fluvial systems is well established (Forstner & Wittmann, 1981; Horowitz, 1991), but studies with the collection, processing, and subsequent chemical analyses of suspended sediment must consider problems associated with this sample medium. Of concern are spatial (especially cross-channel) and temporal variations in the distribution and concentration of suspended sediment and associated trace elements that commonly occur in fluvial systems. Temporal variability is of particular importance if a study addresses annual transport. An adage says "90% of transport occurs during 10% of the time". Fluvial transport tends to follow this maxim, albeit not to this extent. Temporal variability is important, and sampling to develop data of annual fluxes must deal with variations in suspended sediment and associated chemical concentrations under differing discharge ranges, as well as during events.

Sampling strategies and calculation methods to determine annual suspended sediment and chemical fluxes are controversial (Olive & Rieger, 1992; Ongley, 1992; Walling *et al.*, 1992; de Vries & Klavers, 1994). The load or flux of a constituent is considered a function of discharge, suspended sediment concentration, sediment-associated constituent concentration and dissolved constituent concentration. Although all four factors display spatial and/or temporal variability, the first three exhibit the most variability (Forstner & Wittmann, 1981; Horowitz *et al.*, 1990; 1992; Horowitz, 1991). For example, suspended sediment concentrations rise with increasing distance from river banks and with proximity to the bed due to increasing amounts of sand size (>63 μm) particles. These increases in sediment concentration, however, tend to be accompanied by decreases in associated trace element levels due to the grain size effect. In addition, short-term temporal variations in sediment and associated chemical loads can be extreme. For example, during a storm event as short as 40 min, suspended sediment concentrations can increase 60% or more, and associated trace element levels can rise an order of magnitude. During constant discharge, sediment concentrations vary up to 60% with or without chemical changes.

The variability described above suggests that determination of annual fluxes requires high frequency depth and width integrated sampling to delimit change in suspended sediment and associated trace element concentrations. Such programs are expensive due to logistical and analytical costs, and usually lead to under-sampling with concomitantly large flux estimation errors. For suspended sediment, inadequate data coverage has been addressed by manual collection of a single, daily, depth integrated vertical or automatic collection of a point sample. Single vertical or point samples, however, often do not reflect accurate cross-sectional suspended sediment and associated chemical concentrations (Horowitz *et al.*, 1990). This discrepancy is usually treated with a "box" equation, the calculation of a cross-sectional *vs* point sample coefficient (OWDC, 1978; Inland Waters Directorate, 1988). Box expressions relate suspended sediment concentrations under various conditions, in single point or vertical samples, to accurate cross-section concentrations from simultaneous depth and width integrated samples. Once expressions are developed, they are applied to additional single point or single vertical samples to obtain more accurate estimates of cross-section concentration data.

Until recently, the box equation was applied only to suspended sediment concentration. The method was evaluated, however, 1989 through 1991, on the Arkansas River to determine application to sediment-associated trace elements. Results indicate the procedure is applicable, but accuracy of concentrations determined in this way (±16%) is not as good as for concomitantly determined sediment concentrations (Horowitz *et al.*, 1992). Results were encouraging and associated costs were substantially reduced from those of traditional sediment sampling programs, but they were high enough to discourage widespread use of the technique.

Data from depth and width integrated samples of the Arkansas River automatic sampler experiment allow estimation of trace element fluxes over extended periods. The data sets are useful to evaluate relative importance/effects of discharge, suspended sediment concentration, and sediment-associated chemical concentrations on flux calculations. They also provide useful and less resource intensive alternatives to the automatic sampler/box equation technique for estimating annual fluxes. As an adjunct to this evaluation, the data provide information on effects of sampling frequency and on how use of mean and median values for discharge, suspended sediment, and chemistry can affect flux calculations. Results from these evaluations are reported here and details of procedures used can be found in Horowitz *et al.* (1992).

RESULTS AND DISCUSSION

For this discussion, fluxes at the site were calculated for actual sampling periods, not on an annual basis. Sampling periods were 103 days (30 samples) in 1989 and 250 days (20 samples) in 1990. Fluxes, in (metric) tons per day (t day^{-1})), for suspended sediment and suspended sediment-associated trace elements were calculated from the following equations:

$$Flux = (Q)(C)(6.94 \times 10^{-5}) \tag{1}$$

in which Q is discharge ($m^3\ s^{-1}$) and C is concentration (mg l^{-1}). Because suspended sediment concentration is in mg l^{-1}, the mass-to-mass chemical data (μg g^{-1}) are converted to mg l^{-1} by:

$$Concentration\ (\text{mg } l^{-1}) = (C_T)(SSC)/1000 \tag{2}$$

in which C_T is concentration (μg g^{-1}) and SSC is suspended sediment concentration (g l^{-1}). Once flux (t day^{-1}) was calculated, it was multiplied by days between each sample to determine flux for the period between samples. Each sample interval flux was then summed to estimate flux for the entire sampling period. There are different equations extant for calculating flux; however, the basic components of these equations are the same (Olive & Rieger, 1992; de Vries & Klavers, 1994). As such, although the estimated masses may differ depending on the selected equation, this does not substantially affect the basic conclusions that follow.

Basic data

A surprising result from the Arkansas River sampling was that suspended sediment chemical data for 1989 and 1990 were normally distributed (note the similarity between the mean and median values) and that chemical differences were mostly (with the possible exception of Zn) within the analytical error. This occurred although the sediment concentration and discharge data for both years were neither normally distributed nor similar (Table 1).

Flux calculations

Flux estimates and associated data for 1989 and 1990 on the Arkansas River are in Tables 2 and 3. In 1989, 74% of suspended sediment transport occurred during 41% of the time and 49% of the discharge; in 1990, 89% of sediment transport occurred during 16% of the time and 33% of the discharge (Table 2). These results indicate that sediment transport does not occur at a constant rate and that periods of high suspended sediment

Table 1 Minimum, maximum mean, standard deviation and median concentrations for suspended sediment from the Arkansas River in 1989 and 1990.

	1989					1990					1989/1990				
Parameter	Min.	Max.	Mean	Std. Dev.	Median	Min.	Max.	Mean	Std. Dev.	Median	Min.	Max.	Mean	Std. Dev.	Median
Days Btwn. Samples	0.5	13	3.4	3.2	2.5	0.5	39	12.4	11.4	10.5	0.5	39	7.0	8.7	3.0
Discharge (m^3S^{-1})	9.91	48.4	32.4	8.16	31.0	3.71	114	19.2	19.3	9.91	3.71	114	23.0	17.9	21.4
Sus. Sediment (mgl^{-1})	19	600	258	185	216	9	1700	464	570	111	9	1700	341	396	209
Cu (mg kg^{-1})	36	62	49	7	50	33	111	58	23	50	33	111	53	16	50
Pb (mg kg^{-1})	64	133	100	19	95	28	327	103	67	92	28	327	101	44	94
Zn (mg kg^{-1})	390	1270	780	255	780	215	1050	625	223	630	215	1270	720	252	740
Cd (mg kg^{-1})	1.7	7.6	3.9	1.6	3.7	1.0	5.0	3.3	1.3	3.4	1.0	7.6	3.7	1.5	3.7
Co (mg kg^{-1})	7	17	12	2	12	10	39	14	6.2	12	7	39	12	4	12
As (mg kg^{-1})	3.8	8.5	6.4	1.2	6.4	4.1	13.6	7.1	2.2	6.8	3.8	13.6	6.7	1.7	6.5
Sb (mg kg^{-1})	0.6	1.2	0.8	0.1	0.7	0.5	2.6	1.1	0.5	0.9	0.5	2.6	0.9	0.4	0.8
Se (mg kg^{-1})	0.3	1.7	0.7	0.3	0.6	0.4	3.0	1.3	0.8	0.8	0.3	3.0	0.9	0.6	0.7
Fe (wt. %)	2.2	4.4	3.4	0.4	3.5	2.8	4.5	3.4	0.4	3.4	2.2	4.5	3.4	0.4	3.4
Mn (wt. %)	0.08	0.17	0.13	0.02	0.13	0.08	0.27	0.14	0.05	0.13	0.08	0.27	0.13	0.04	0.13
Al (wt. %)	6.5	9.0	7.2	0.5	7.1	5.1	8.2	6.9	0.7	7.1	5.1	9.0	7.1	0.6	7.1
Ti (wt. %)	0.22	0.44	0.35	0.05	0.34	0.25	0.4	0.33	0.04	0.33	0.22	0.44	0.34	0.04	0.34

Table 2 Average daily transport (t day^{-1}) and the percent of transport for the Arkansas River in 1989 and 1990.

1989.00	103 Days																	
Sample Date	Days	Discharge $m^3 s^{-1}$	SS $t d^{-1}$	Cu $t d^{-1}$	Pb $t d^{-1}$	Zn $t d^{-1}$	Cd $t d^{-1}$	Co $t d^{-1}$	As $t d^{-1}$	Sb $t d^{-1}$	Se $t d^{-1}$	Fe $t d^{-1}$	Mn $t d^{-1}$	Al $t d^{-1}$	Ti $t d^{-1}$	% of Period Transport	% of Discharge	% of Period
5/12/89	6	143	392	0.02	0.04	0.46	0.0025	0.0047	0.0026	0.0003	0.0004	12.9	0.59	26.3	1.33	4.10	4.3	5.8
5/18/39	6	99.5	44	0.00	0.01	0.06	0.0003	0.0004	0.0003	0.0000	0.0001	1.5	0.07	3.0	0.14	0.50	3.0	5.8
5/24/89	2	66.8	642	0.04	0.08	0.77	0.0039	0.0071	0.0048	0.0005	0.0007	21.2	0.90	43.0	2.12	2.3*	2.0	1.9
5/26/89 #1	0.5	17.4	735	0.04	0.10	0.82	0.0040	0.0081	0.0053	0.0009	0.0006	25.0	1.10	49.3	2.50	0.70	0.5	0.5
5/26/89 #2	3.5	96.0	507	0.03	0.07	0.56	0.0030	0.0061	0.0037	0.0004	0.0005	17.2	0.76	36.0	1.67	3.10	2.9	3.4
5/30/89 #1	0.5	20.0	2069	0.09	0.18	1.63	0.0074	0.0207	0.0120	0.0014	0.0014	72.4	2.28	140.7	7.66	1.8*	2.9*	0.5
5/30/89 #2	0.5	20.0	2045	0.09	0.18	1.62	0.0074	0.0245	0.0123	0.0016	0.0016	73.6	2.25	141.1	7.36	1.8*	0.6	0.5
5/31/89	1	46.7	1718	0.06	0.20	1.53	0.0076	0.0172	0.0110	0.0014	0.0010	55.0	2.23	115.1	5.33	3.0*	1.4*	1.0
6/1/89	1	45.6	1519	0.07	0.20	1.38	0.0067	0.0152	0.0100	0.0011	0.0009	54.7	1.97	104.8	5.16	2.7*	1.4*	1.0
6/2/89	2	79.6	998	0.05	0.12	0.98	0.0050	0.0130	0.0072	0.0007	0.0005	36.9	1.40	69.9	3.69	3.5*	2.4*	1.9
6/4/89	2	71.4	262	0.01	0.02	0.22	0.0011	0.0029	0.0016	0.0002	0.0001	8.1	0.31	18.1	0.73	0.9	2.1	1.9
6/6/89	3	89.2	157	0.01	0.02	0.17	0.0008	0.0011	0.0012	0.0001	0.0000	5.6	0.27	11.6	0.53	0.8	2.7	2.9
6/9/89	4	133	545	0.02	0.05	0.38	0.0019	0.0071	0.0044	0.0005	0.0003	19.6	0.76	45.2	2.02	3.8	4.0	3.9
6/13/89	3	108	1036	0.04	0.09	0.67	0.0029	0.0124	0.0083	0.0008	0.0004	39.4	1.14	93.3	3.52	5.5*	3.2*	2.9
6/16/89	3	125	214	0.01	0.02	0.19	0.0010	0.0021	0.0014	0.0002	0.0001	7.9	0.28	15.8	0.73	1.1	3.8*	2.9
6/19/89	2	95.2	584	0.03	0.06	0.45	0.0024	0.0064	0.0031	0.0004	0.0002	19.9	0.76	41.5	1.99	2.1	2.9*	1.9
6/21/89	3	125	380	0.02	0.03	0.27	0.0011	0.0038	0.0021	0.0003	0.0002	11.0	0.42	28.1	1.14	2.0	3.8*	2.9
6/24/89	4	106	110	0.01	0.01	0.09	0.0004	0.0012	0.0006	0.0001	0.0001	3.5	0.12	7.8	0.34	0.8	3.2	3.9
6/28/89	8	233	60	0.00	0.01	0.05	0.0002	0.0006	0.0003	0.0000	0.0001	1.7	0.07	3.9	0.17	0.9	7.0	7.8
7/6/89	7	209	49	0.00	0.01	0.03	0.0004	0.0004	0.0002	0.0000	0.0000	1.1	0.05	3.6	0.11	0.6	6.3	6.8
7/13/89	1	42.2	1617	0.07	0.15	1.20	0.0058	0.0226	0.0137	0.0011	0.0008	63.1	1.94	116.4	6.31	2.9*	1.3*	1.0
7/14/89	3	114	1445	0.07	0.12	0.64	0.0032	0.0188	0.0080	0.0009	0.0004	50.6	1.59	107.0	5.78	7.6*	3.4*	2.9
7/17/89	7	199	350	0.02	0.03	0.21	0.0013	0.0042	0.0018	0.0002	0.0002	12.2	0.49	26.2	1.36	4.3	6.0	6.8
7/24/89	1	32.9	1472	0.08	0.13	0.62	0.0035	0.0250	0.0125	0.0010	0.0010	64.8	2.21	113.4	6.48	2.6*	1.0	1.0
7/25/89	1	38.2	1144	0.05	0.11	0.55	0.0026	0.0149	0.0063	0.0008	0.0006	41.2	1.37	90.4	4.46	2.0*	1.1	1.0
7/26/89#1	0.5	22.1	2068	0.09	0.16	0.89	0.0035	0.0310	0.0132	0.0014	0.0010	78.6	2.48	159.2	8.27	1.8*	0.7*	0.5
7/26/89#2	1.5	69.7	2036	0.09	0.16	0.90	0.0035	0.0285	0.0090	0.0012	0.0006	71.3	2.04	146.6	8.55	5.3*	2.1*	1.5
7/28/89	13	524	733	0.04	0.09	0.46	0.0019	0.0088	0.0043	0.0005	0.0003	24.9	0.95	54.2	2.93	16.8*	15.8*	12.6
8/10/89	11	312	740	0.03	0.05	0.29	0.0016	0.0074	0.0054	0.0007	0.0006	23.7	0.59	51.1	2.59	14.3*	9.4	10.7
8/21/89	2	40.5	81	0.00	0.01	0.04	0.0002	0.0010	0.0005	0.0001	0.0001	2.6	0.10	5.6	0.28	0.3	1.2	1.9
Period Avg.	3.4	32.4	551	0.03	0.05	0.37	0.0018	0.01	0.0036	0.0004	0.0003	19.1	0.66	40.3	2.0	99.9	99.9	100.0

74% of the sediment transport took place during 41% of the time.

45% of the water discharge took place during 32% of the time

74% of the sediment transport took place during 49% of the discharge

*** The % of Period of Transport and the % of Discharge marked with an asterisk (*) exceed their respective percent of the (time) Period in which they occurred.**

Table 2 continued.

1990.00	250 Days																	
Sample		Discharge	SS	Cu	Pb	Zn	Cd	Co	As	Sb	Se	Fe	Mn	Al	Ti	% of Period	% of	% of
Date	Days	$m^3 s^{-1}$	$t\,d^{-1}$	$t\,d^{-1}$	$t\,d^{-1}$	$t\,d^{-1}$	$t\,d^{-1}$	$t\,d^{-1}$	$t\,d^{-1}$	$t\,d^{-1}$	$t\,d^{-1}$	$t\,d^{-1}$	$t\,d^{-1}$	$t\,d^{-1}$	$t\,d^{-1}$	Transport	Discharge	Period
12/28/89	29	240	52	0.00	0.00	0.02	0.0001	0.0006	0.0006	0.0001	0.0001	1.8	0.05	4.3	0.18	1.0	4.7	11.6
1/25/90	25	188	7	0.00	0.00	0.01	0.0000	0.0001	0.0000	0.0000	0.0000	0.2	0.01	0.4	0.02	0.1	3.7	10.0
2/22/90	40	330	15	0.00	0.00	0.01	0.0001	0.0002	0.0001	0.0000	0.0000	0.5	0.03	0.9	0.05	0.4	6.4	16.0
4/3/90	21	169	18	0.00	0.00	0.01	0.0001	0.0002	0.0001	0.0000	0.0000	0.6	0.04	1.1	0.06	0.2	3.3	8.4
4/24/90	10	63.4	5	0.00	0.00	0.00	0.0000	0.0001	0.0000	0.0000	0.0000	0.2	0.01	0.3	0.02	0.0	1.2	4.0
5/4/90	3	49.3	152	0.01	0.01	0.12	0.0008	0.0018	0.0011	0.0002	0.0004	5.2	0.23	10.2	0.50	0.3	1.0	1.2
5/7/90	16	171	1569	0.08	0.11	0.42	0.0016	0.0267	0.0110	0.0013	0.0011	64.3	2.35	116.1	6.28	16.0*	3.3	6.4
5/23/90	3	54.3	462	0.02	0.01	0.10	0.0005	0.0060	0.0063	0.0006	0.0008	17.5	0.46	36.0	1.62	0.9	1.1	1.2
5/26/90	11	375	3569	0.15	0.34	2.77	0.0178	0.0428	0.0336	0.0029	0.0039	121.4	4.28	246.3	11.06	25.0*	7.3*	4.4
6/6/90 #1	0.5	35.8	9378	0.39	0.93	6.10	0.0375	0.1125	0.0600	0.0075	0.0066	328.2	10.32	675.2	34.70	3.0*	0.7*	0.2
6/6/90 #2	0.5	35.8	7612	0.31	1.10	6.55	0.0381	0.0913	0.0700	0.0069	0.0061	281.6	10.66	548.0	28.16	2.4*	0.7*	0.2
6/7/90	2	178	6413	0.28	0.89	5.42	0.0257	0.0770	0.0513	0.0058	0.0045	230.9	8.98	474.6	23.73	8.2*	3.5*	0.8
6/9/90	2	201	6585	0.28	0.68	4.02	0.0198	0.0724	0.0454	0.0066	0.0053	223.9	7.24	480.7	22.39	8.4*	3.9*	0.8
6/11/90	4	415	8387	0.27	0.80	4.68	0.0252	0.1006	0.0528	0.0050	0.0050	276.8	8.39	603.8	31.03	21.3*	8.1*	1.6
6/15/90	5	287	1342	0.06	0.12	0.66	0.0027	0.0134	0.0068	0.0007	0.0005	37.6	1.21	95.2	4.16	4.3*	5.6*	2.0
6/20/90	12	809	426	0.02	0.04	0.23	0.0009	0.0043	0.0022	0.0003	0.0002	11.9	0.34	30.3	1.32	3.3	15.7*	4.8
7/2/90	24	793	220	0.01	0.03	0.16	0.0009	0.0026	0.0009	0.0002	0.0001	6.2	0.24	15.8	0.62	3.4	15.4*	9.6
7/26/90	15	335	126	0.01	0.01	0.05	0.0003	0.0014	0.0007	0.0001	0.0001	3.5	0.11	8.4	0.36	1.2	6.5*	6.0
8/10/90	26	405	49	0.00	0.00	0.03	0.0001	0.0006	0.0002	0.0000	0.0000	1.6	0.07	3.3	0.16	0.8	7.9	10.4
9/5/90	1	6.51	5	0.00	0.00	0.00	0.0000	0.0002	0.0000	0.0000	0.0000	0.2	0.01	0.3	0.01	0.0	0.1	0.4
Period Avg.	12.4	19.2	629	0.03	0.06	0.38	0.0020	0.0080	0.0046	0.0005	0.0005	21.7	0.74	45.1	2.2	100.2	100.1	100.0

89% of the sediment transport took place during 16% of the time.
67% of the water discharge took place during 30% of the time.
89% of the sediment transport took place during 33% of the discharge

* The % of Period of Transport and the % of Discharge marked with an asterisk (*) exceed their respective percent of the (time) Period in which they occurred.

and associated trace element transport do not always coincide with elevated discharge. Lack of a linear relation between discharge and suspended sediment flux indicates that decisions of when to sample for annual transport should not be predicated solely on changes in discharge. Thus, a sampling program requires both systematic [with knowledge of factors controlling sediment concentration] and "event" sampling. It may be necessary, therefore, to design a sampling program around variations in sediment and trace element inputs from the different sources of water and sediment rather than on a fixed calendar scheme.

Despite differences in sampling periods, mean discharge and suspended sediment concentrations (Table 1), average daily sediment and trace element fluxes for both years were quite similar, typically within 15% (Table 2). Chemical fluxes displayed less variance than did sediment fluxes. If this were to continue after years of detailed study, sampling to determine annual flux at the site could be discontinued. That is, if average daily flux values remain constant over a few years, future flux estimates could be made mathematically (average daily flux multiplied by number of days desired). Future sampling then could be substantially curtailed and subsequent sampling and analysis would insure continued validity of the daily flux estimates.

Flux calculations for the Arkansas River show that most for 1989 are similar. The largest differences between estimates occurred when sampling was reduced 50% or when mean, not actual, values for discharge, sediment concentration and trace element concentration were used in a set of calculations (Table 3). Based on estimates for 1989, sampling interval and discharge most significantly affect flux; sediment concentration appears of secondary importance and associated chemical concentrations appear to be of tertiary importance (Table 3). Sampling interval, *per se*, is not significant, but magnitude, number, and duration of measured changes in discharge, suspended sediment and chemical concentrations that occur during the interval are important. Duration is very significant because short-term events lead to marked variations in discharge and sediment and chemical concentrations. Unless these events represent a significant portion of the annual hydrograph in terms of time, discharge or suspended sediment mass, however, they are unlikely to have much effect on the annual fluxes of sediment and associated trace elements.

Relative to 1990, flux estimates for 1989 display limited variability due probably to (a) short intervals between samples (about 3 days) and (b) a limited discharge range in 1989 of 9.9-48.4 m^3 s^{-1} (Table 1). The effect of sampling frequency on flux estimate error has a critical limit of around 3-7 days, depending on basin size and sources of water and sediment. Generally, the larger a river, longer is the acceptable sampling interval (Ongley, 1993; de Vries & Klavers, 1994). If the interval exceeds 7 days, however, the errors (standard deviation of the mean) of the flux estimates increase significantly. The differences in "acceptable" sampling intervals for different rivers is directly related to duration of an event. That is, rivers of any size display marked variations in discharge of water, sediment and chemicals. The impact of any event on annual flux estimates, however, is a function of its duration. The larger the river, the longer is the duration required to make a significant impact.

Flux estimates for 1990 display much greater variability than do those of 1989, emphasizing the importance of sampling interval and discharge (Table 3). For example, marked differences occur among fluxes calculated for the 250 day period using (a) sample time discharge to represent each individual sampling interval, (b) mean discharge

Table 3 Calculated fluxes for suspended sediment and associated trace elements (tonnes) for the Arkansas River in 1989 and 1990.

Sample Date/Type	Days	SS	Cu	Pb	Zn	Cd	Co	As	Sb	Se	Fe	Mn	Al	Ti
1989 Comp														
Total (30 Samples) w/Sample Q (1)	103	59,998	2.85	5.91	40.2	0.20	0.71	0.39	0.045	0.035	2,071	72.3	4,394	220
Total (30 Samples) w/Daily Mn Q (2)		58,998	2.80	5.81	39.6	0.20	0.70	0.38	0.044	0.034	2,035	71.1	4,318	217
Total/2 (15 Samples) w/Sample Q (3)		80,934	3.69	7.04	50.6	0.24	1.02	0.47	0.057	0.044	2,807	90.6	5,801	308
Total w/Mn.Q/period (4)*		56,767	2.69	5.55	38.0	0.19	0.67	0.37	0.042	0.033	1,962	68.0	4,149	209
Total w/Mn.Q/period/2 (15 Samples) (5)		71,196	3.24	6.20	44.8	0.21	0.89	0.42	0.051	0.040	2,469	79.7	5,102	269
Total w/Sample Q, SS w/Mn Chem/all (6)		56,767	3.01	5.73	40.9	0.21	0.68	0.38	0.051	0.051	1,930	73.8	4,030	193
Total w/Sample Q, SS w/Md Chem/all (7)		56,767	2.84	5.34	42.0	0.21	0.68	0.37	0.045	0.039	1,930	73.8	4,030	193
Total w/Sam SS, w/Mn Q & Chem/all (8)		52,709	2.79	5.32	38.0	0.20	0.63	0.35	0.047	0.047	1,792	69.0	3,742	179
Total w/Sam SS, w/Md Q & Chem/all (9)		50,539	2.53	4.75	37.4	0.19	0.61	0.33	0.040	0.035	1,718	66.0	3,588	172
Total w/Mn Q, Mn SS, Mn Chem/all (10)		74,482	3.65	7.45	58.1	0.29	0.89	0.48	0.060	0.050	2,532	96.8	5,363	261
Total w/Md Q, Md SS, Md Chem/all (11)		59,686	2.98	5.67	46.6	0.22	0.72	0.38	0.040	0.040	2,089	77.6	4,238	203
1990 Comp														
Total (20 Samples) w/Sample Q (1)	250	252,230	11.0	22.7	137	0.74	3.4	1.88	0.20	0.20	9,033	316	18,137	897
Total (20 Samples) w/Daily Mn Q (2)		214,391	9.4	19.3	113	0.59	2.9	1.56	0.17	0.17	7,686	268	15,467	769
Total/2 (10 Samples) w/Sample Q (3)		273,000	12.4	24.9	147	0.78	3.7	2.06	0.22	0.22	9,826	348	19,680	961
Total w/Mn.Q/period (4)*		157,237	6.7	15.0	94.7	0.51	2.0	1.16	0.12	0.13	5,422	186	11,270	547
Total w/Mn.Q/period/2 (10 Samples) (5)		170,549	7.6	16.9	104	0.56	2.1	1.29	0.14	0.14	5,952	209	12,257	586
Total w/Sample Q, SS w/Mn Chem/all (6)		157,237	8.3	15.9	113	0.58	1.9	1.05	0.14	0.14	5,346	204	11,164	535
Total w/Sample Q, SS w/Md Chem/all (7)		157,237	7.9	14.8	116	0.58	1.9	1.02	0.13	0.11	5,346	204	11,164	535
Total w/Sam SS, w/Mn Q & Chem/all (8)		100,031	5.3	10.1	72	0.37	1.2	0.67	0.09	0.09	3,401	130	7,102	340
Total w/Sam SS, w/Md Q & Chem/all (9)		51,715	2.6	4.9	38.3	0.19	0.6	0.34	0.04	0.04	1,758	67.0	3,672	176
Total w/Mn Q, Mn SS, Mn Chem/all (10)		192,111	11.7	20.7	126	0.66	2.8	1.43	0.22	0.26	6,838	282	13,877	664
Total w/Md Q, Md SS, Md Chem/all (11)		23,796	1.22	2.25	15.4	0.08	0.3	0.17	0.02	0.02	831	31.8	1,735	80.6

Considered the best estimate of transport for the period.

(1): Calculated assuming that the discharge (Q) and the suspended sediment and chemical concentrations determined at the time of sampling were constant for the entire sampling interval.

(2): Calculated assuming that the mean daily discharge (Q) for the day the sample was obtained as well as the suspended sediment and chemical concentrations were constant for the entire sampling interval.

(3): Calculated as in (1) but only using every other sample.

(4): Calculated using the mean discharge (Q), and assuming that the suspended sediment and chemical concentrations for the sample were constant, for the sampling interval.

(5): Calculated as in (4), but only using every other sample.

(6): Calculated using the mean discharge for the sampling interval, with the sample suspended sediment concentration, and the mean chemistry for all the Arkansas River samples (50).

(7): Calculated as in (6) but using the median chemical concentrations.

(8): Calculated using the sample suspended sediment for each interval along with the mean discharge for the year and the mean chemistry for all the Arkansas River samples (50).

(9): Calculated as in (8) but using the median discharge for the year and the median chemistry for all the samples.

(10): Calculated using mean discharge and suspended sediment concentrations for the year, and the mean chemistry for all the Arkansas River samples.

(11): Calculated as in 10 but using the median discharge and suspended sediment concentration for the year and the median chemistry for all the Arkansas River samples.

for the day of sampling to represent each interval, (c) the mean of all daily discharges to represent each interval, and (d) the mean or the median discharge for the entire sampling period to represent each of the individually summed sampling intervals. Marked differences occur if the sample number is reduced 50% (Table 3). The various estimates for both 1990 and 1989 indicate that of least significance in estimating trace element flux are actual concentrations of sediment-associated trace elements (note the differences when actual concentrations are compared to the same calculations using mean or median values) (Table 3). Although sample-specific chemical concentrations are of limited importance (Ongley, 1992), the calculations emphasize the importance of variations in discharge and suspended sediment.

Flux estimates for the Arkansas River site indicate that mean or median chemical values used with sample measurements of water and sediment discharge yield values ±20% of those from actual individual sample chemical concentrations. This range is slightly greater than for variances between actual chemical concentrations from depth and width integrated sediment-associated chemical concentrations and from site-specific box equations (±16%) (Horowitz *et al.*, 1992). If typical of most sites, the approach is a useful and less expensive alternative to box equations to estimate annual trace element fluxes; emphasis could be shifted from compositing of samples to defining and delimiting chemical variability at a site. Once appropriate mean and median chemical concentrations are developed, systematic trace element analyses of suspended sediment could be discontinued and chemical data required to estimate annual fluxes would be supplied by the mean or median determined during site characterization. Development of mean or median chemical values, however, should not preclude future analyses of some samples. Four to six samples a year, encompassing various flow or seasonal regimes, should be collected to insure continued validity of the mean/median values, much as stage/discharge relations are periodically checked and updated. Based on results of suspended sediment studies, measurements of chemical fluxes require a combination of systematic and event samples. Typically, event sampling is the more difficult owing to logistical, financial and manpower limitations. A purpose of the automatic sampler and box equation study was to deal with this problem. If the requisite chemical concentrations are obtainable from appropriate mean or median values, however, rather than by analyses of composites followed by conversion to depth and width integrated equivalents using box equations, and if discharge and sediment concentrations can be determined using automatic equipment, then costs of long term monitoring sites can be substantially reduced.

Even mean or median values for sediment-associated trace element concentrations used with automatically determined discharges and suspended sediment concentrations may not have to be continued *ad infinitum*. Average daily fluxes of suspended sediment and associated trace elements at the Arkansas River site remained within ±15% for nearly two years (Table 2). If this constancy is typical, determination of fluxes may devolve to a mathematical exercise without need to collect data or samples other than to check the continued viability of the average daily flux values.

A major conclusion drawn from the Arkansas River experiment is the need for and importance of initial site characterization prior to the inception of attempts to estimate annual fluxes of suspended sediment and associated trace element concentrations. Such site characterizations can and should entail examination of available data, as well as collection and analysis of new samples and data. Then, based on program goals and available resources, decisions regarding an appropriate sampling scheme can be made.

The start of a monitoring program to estimate annual flux of sediment and trace elements is not an end but an initiation. A monitoring program should provide for scheduled evaluations of how well goals are met; after several years at a site, an evaluation should be made that may suggest sample number reduction, an increase in time interval, etc., while changing accuracy as required. With more information and re-evaluation, operating costs should decline. Program sponsors/coordinators, however, must be prepared to invest sufficient initial resources to permit adequate site characterization and to realize future savings.

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