

Refining a tributary monitoring program for the Great Lakes basin

I. G. DROPPA, E. D. ONGLEY & J. MARSALEK

National Water Research Institute
Burlington, Ontario, Canada, L7R 4A6

ABSTRACT There are numerous water quality and quantity programs operating within the Great Lakes Basin. While these programs are not entirely independent of each other, there are significant differences in their environmental priorities and goals. This has resulted in poor continuity of data collection, analysis, and reporting techniques between programs. Thus, integration of different data sets may result in erroneous conclusions for water resource management.

The integration of data from these many monitoring programs into a comprehensive environmental assessment framework is of great importance for the future management of the Great Lakes' water resources. This paper uses specific examples from a river in southern Ontario, Canada to discuss important fundamental scientific questions which must first be addressed, and the many field and analytical methods which must be standardized before such an integration can occur.

INTRODUCTION

Water quantity monitoring of Great Lakes' tributaries has been conducted for many decades. Sampling of water/sediment mixtures for the purpose of estimating tributary loadings of nutrients and contaminants has been occurring on a large scale for over two decades. Basin-wide assessment management programs are, however, inhibited by differences in objectives, methods, and assumptions developed by the many federal, provincial, state, and regional agencies. Institutional segregation of quality and quantity monitoring programs complicates the matter.

The many independent programs result in riverine samples being collected for different reasons with different sampler types according to different sampling designs. The accuracy of chemical loading predictions by these different monitoring programs can also be questioned because of the inherent temporal and spatial variability of suspended sediment and associated contaminant concentrations which exist within most fluvial systems. It is difficult, therefore, for managers to compare and use monitoring program data in a comprehensive ecosystem approach to lake and basin-wide management.

In this paper we examine some of the scientific and methodological problems that must be addressed by integrated tributary monitoring programs that incorporate quality and quantity objectives. Specifically, using a river in southern Ontario, Canada, we examine: sampler type; sampling and analytical strategies; temporal and spatial variability of suspended sediment and associated contaminants; and the importance of

the suspended sediment fraction for contaminant loading predictions and environmental management of the Great Lakes Basin water resources.

MATERIALS AND METHODS

Study Site

To examine the methodological issues a field site was established on the Nith River; a tributary of the Grand River in southwestern Ontario. The basin is 975 km² and is primarily agricultural land draining soils dominated by fine sand to clay particles. Samples were taken from a bridge far enough below the town of Ayr to allow for complete mixing of effluent from the sewage treatment plant. The river is approximately 25 m wide at the sampling cross-section, less than 1 m deep at base flow and has a yearly discharge range of 2 to 230 m³/sec. with a mean yearly discharge of 16 m³/sec.

Field Procedures

Five sampling procedures (depth-integrated, pump, point, grab and compositing) and four sampling apparatus were used for the collection of sediment/water mixtures. All four sampling apparatus were employed simultaneously on the Nith River at the centroid of flow on November 21, 1991.

Single Vertical Depth-Integration Single vertical depth-integrated (DI) samples were collected with a US D-77 suspended sediment sampler (Cashman, 1988) at the centroid of flow of 5 equal discharge intervals in the river cross-section. The sampler was suspended from a mobile A-reel. The sampler was lowered to the river bed and back to the surface at the same transit rate to obtain an iso-kinetic discharge weighted sample. (transit rate = 0.2 x average velocity in vertical). This procedure was repeated 2 to 4 times depending on the stream velocity in order to collect a large enough volume for analysis. Samples were collected in a churn splitter, and necessary volumes removed for chemical analysis. When only suspended sediment concentration was analyzed, the US D-77 sample bottle volume was split into three 500 ml Nalgene bottles.

Single Vertical Point Sampling Iso-kinetic point samples were collected with a US P-72 suspended sediment sampler (Cashman, 1988) suspended from an A-reel attached to a metering board. This 350 ml capacity sampler is equipped with a solenoid switch and a battery pack to remotely open and close the sampler. The sampler nozzle was placed at 0.6 of the depth and triggered to sample simultaneous with the other sampling apparatus.

Single Vertical Pump Sampling Pumped samples were collected using a 5C-MD Marsh submersible pump oriented into the direction of flow at 0.6 of the vertical depth. Samples were pumped (4 m lift) directly into three 500 ml Nalgene bottles. This type of sampling was not iso-kinetic as the pump intake velocity exceeded the river velocity.

Grab Sampling Grab samplers were collected at both river banks by consecutively dipping three 500 ml Nalgene bottles into the direction of flow.

Composite Sampling Composite samples were collected to yield the best estimate of the cross-sectional sediment concentration. This was performed iso-kinetically by using the equal-discharge-increment method. The cross-section was divided into 5 equal discharge increments (each representing 20% of the flow). Each increment was sampled at its centroid with the US D-77 DI sampler. The transit rate of the sampler varied in each increment depending on the flow velocity. Each DI sample was combined in a churn splitter and 3 replicate samples produced. The mean concentration of these samples represents our best estimate of the suspended sediment concentration.

Continuous-Flow Centrifugation In addition to the above small volume techniques, we also collected large volume, dewatered suspended sediment samples using portable continuous-flow centrifuges (Alfa Laval model WSB 103B). Water was pumped to the centrifuges by 5C-MD Marsh submersible pumps located 0.3 m below the surface of the water at the centroid of flow and oriented into the direction of flow. The centrifuges were adjusted to a flow rate of 4 l/min. for optimal efficiency. (The centrifuge sediment removal efficiency was always greater than 90%). The stainless steel centrifuge bowls were transported back to the laboratory for sediment recovery and analysis.

Field Laboratory Procedures

Sample preparation prior to submission to Environment Canada's National Water Quality Laboratory (NWQL) for total and filtered metals was performed in a field laboratory using a laminar flow hood, acid washed filtration apparatus and acid washed 0.45 µm Sartorius filters. Appropriate sample volumes were removed from the churn splitter for filtration after 1 minute of plunging. Total and filtered metals were spiked with 1 ml 50% nitric acid and transported to the NWQL.

Laboratory Procedures

Total and Filtered Metal Analysis Samples were analyzed by the NWQL using Inductively Coupled Argon Plasma (ICAP) following the methods of the NWQL Analytical Methods Manual (Environment Canada, 1979).

Metal Analysis of Suspended Sediment Total metal concentrations for the suspended sediment were analyzed by a sequential extraction procedure (Tessier *et al.*, 1979) using a Hitachi 180-80 Polarized Zeeman Atomic Absorption Spectrophotometer. ICAP and the sequential extraction technique should yield comparable total metal concentrations. This is because ICAP uses very high temperatures and the sequential extraction procedure uses increasingly stronger acids to completely digest the sediment in solution.

Suspended Sediment Concentration Analysis Suspended sediment (SS) concentration was determined by vacuum filtering through a tared 0.45 μm Millipore membrane filter.

RESULTS AND DISCUSSION

Developmental Problems for an Integrated Tributary Monitoring Program

The integration of water quality and quantity programs is difficult because of the inherent difference in the objectives of each program. Quantity programs are field oriented where samples must be representative of a particular cross-section. The emphasis of a quality program is generally oriented towards the laboratory where an accurate chemical determination from a field sample tends to be the main objective. Less importance is often placed on the field component of quality programs with the exception of an effort to minimize contamination. Nevertheless, determination of chemical presence or flux requires both approaches. There is an urgent need to address both the technical issues of sampling hardware and protocols, as well as the scientific issues surrounding the question of in-stream variability. This latter question is fundamental for the ability to simplify sampling strategies within known error limits.

Protocols for sediment data collection are well documented and have become standardized for the majority of quantity agencies (Vanoni, 1975 and Office of Water Data Coordination - Geological Survey, 1982). The strategies for chemical data collection are generally more diverse than for sediment data as the collection methodology is often different between agencies.

Currently there is a lack of SS samplers appropriate for quality sampling. There are only three samplers that are appropriate for chemical or biological sampling [US D-77, US DH-81 (Cashman, 1988), and collapsible bag sampler (Nordin *et al.*, 1983) depth-integrated samplers]. Components of these samplers exposed to the water/sediment sample are made of autoclavable, chemically inert plastic or teflon. These chemically inert samplers are, however, not functional for all river morphologies and flow conditions. Therefore, new SS samplers appropriate for organic and inorganic chemical sampling in a variety of flow conditions need to be developed to allow for representative, non-contaminated, predictions of cross-sectional chemistry.

Generally, data from quality programs are method specific; values produced from one analytical method may be different from values produced by other methods using the same sample site and medium. For example, Agemian and Chau (1976) examined 7 different extraction schemes for metals and found differences ranging over 2 orders of magnitude for some metals.

The Influence of Temporal and Spatial Variation and Sampler Type and Sampling Strategies on SS and Associated Contaminant Concentration Predictions

The accuracy of sediment and associated contaminant loading calculations is influenced by three field components; a) method of sampling, b) equipment utilized, and c) variation of sediment within the cross-section and down the river. A knowledge of how sediment and contaminants vary temporally and spatially within a river and how

methods and equipment can bias this knowledge is of importance in understanding transport and loading regimes.

Generally, dissolved contaminants are believed to be homogeneous in the cross-section provided the contaminants originate from non-point sources or sufficiently downstream from a point source to allow for mixing (Vanoni, 1975). Most water quality programs use single point sampling. However, the particulate phase of contaminant transport has inherent cross-sectional and temporal variability (Horowitz *et al.*, 1990) which makes single point sampling techniques prone to interpretive error.

Temporal variability, including hysteresis effects associated with runoff events can significantly alter loading predictions depending on the time of sampling. (Johnson, 1979 and Horowitz *et al.*, 1990). At steady base flow conditions, sediment concentrations and associated contaminant concentrations are probably stable as shown in Table 1 for two short term sampling periods on the Nith River. However, if a single sample for Fe was collected at 11:20, August 14, 1991 to represent base flow Fe concentrations, it would over-estimate the base flow contribution to Fe transport by 35%. Horowitz *et al.* (1990) have made similar observations for the Arkansas River. They found statistically significant differences in Cu, Zn, Cr, and Ni concentrations associated with the <63 μm fraction over 20 minutes sampling intervals at single verticals. Such variability illustrates the error that single sample collection techniques can impart on a sampling program.

TABLE 1 Short-term temporal variability of metal concentrations related to SS (sampled at centroid of flow).

Date	Time	Discharge ($\text{m}^3/\text{sec.}$)	SS Conc. (mg/g)	Cu (mg/l)	Fe (mg/l)	Mn (mg/l)	Zn (mg/l)
Aug 14/91	10:50	3.1	12.1	0.0007	0.2495	0.0306	0.0031
	11:00	3.1	13.9	0.0001	0.2512	0.0319	0.0028
	11:10	3.1	12.5	-ve value	0.2388	0.0309	0.0021
	11:20	3.1	12.3	0.0004	0.3598	0.0316	0.0028
	11:30	3.1	12.3	-ve value	0.2373	0.0319	0.0030
Standard Deviations		0.0	0.7	0.0003	0.0521	0.0006	0.0004
Coefficient of Var.		0.0	0.1	1.25	0.1949	0.0191	0.1472
Aug 19/91	13:00	4.0	10.5	0.0020	0.2374	0.0178	0.0026
	15:00	4.0	9.9	0.0017	0.2190	0.0177	0.0013
	17:00	4.0	10.3	0.0010	0.2077	0.0185	0.0017
	19:00	3.7	11.3	0.0014	0.2315	0.0200	0.0039
Standard Deviations		0.2	0.6	0.0004	0.0132	0.0011	0.0015
Coefficient of Var.		0.04	0.1	0.2801	0.0592	0.0574	0.4854

Note: Metal concentrations calculated using the method of differences.

Cross-sectional variability in sediment concentration and contaminant chemistry can also represent a problem for many sampling programs. Temporal and spatial variation are largely dependent on parameters such as particle size, turbulent flow conditions, seasonality of flow and channel morphology (Tywoniuk and Cashman, 1973). Table 2 gives examples of the cross-section variability of SS concentration for Big Creek (Smith, 1987) and Nith River in southwestern Ontario at various flow conditions. Big Creek demonstrates a much stronger spatial variability than does the Nith River. This is likely

due to the difference in sand-size content between the two rivers. During high flow conditions Big Creek's load may be composed of greater than 50% sand (Smith, 1987). The Nith River's SS are composed primarily of silts and clays with insignificant amounts of sand.

TABLE 2 Spatial variability of SS concentration.

River	Date	Discharge (m ³ /sec.)	SS Concentration by Vertical				
			V1	V2	V3	V4	V5
Big Ck.	Mar 04/66	12.20	330	329	326	364	342
Big Ck.	Sept 23/69	2.22	25	13	11	26	27
Big Ck.	Mar 07/73	20.50	544	347	333	382	364
Big Ck.	Feb 17/76	24.80	284	325	167	360	364
Big Ck.	Mar 22/78	49.60	177	238	225	232	78
(modified from Smith, 1987)							
Nith R.	Mar 06/91	35.40	39	39	37	37	34
Nith R.	Apr 09/91	40.60	247	241	243	241	243
Nith R.	Apr 10/91	92.20	717	735	722	722	718
Nith R.	Nov 21/91	6.70	16	19	15	14	12

TABLE 3 Spatial variability of metal concentrations related to SS.

Date	Sample Type and Location	SS Conc. (mg/l)	Cu (mg/l)	Fe (mg/l)	Mn (mg/l)	Pb (mg/l)	Zn (mg/l)
Sep 25/90	Centrifuge-29m	2.6	0.0033	0.4814	0.0524	0.0019	0.0125
	Centrifuge-33m	4.3	0.0015	0.5940	0.0498	0.0015	0.0038
Mar 28/91	DI-29m	680	0.1564	41.7296	0.4536	0.0162	0.0748
	Composite-DI-9m & 21m	680	0.1802	29.8683	0.4073	0.0183	0.1163
Apr 10/91	DI-36m	717	0.0355	31.7925	0.4051	0.0242	0.3090
	DI-33m	725	0.0159	33.0544	0.4579	0.0226	0.0955
	DI-29m	720	0.0160	32.4372	0.4008	0.0211	0.1014
	DI-25m	722	0.0161	34.6387	0.4303	0.0222	0.1126
	DI-19m	718	0.0166	34.7864	0.4215	0.0222	0.1027
Apr 17/91	Centrifuge-27m	259	0.0056	14.7304	0.1582	0.0072	0.0373
	Centrifuge-36m	254	0.0076	16.5677	0.1735	0.0064	0.0320

Note: location of samples measured from the left bank in meters.

Conventional wisdom suggests that a homogeneous mixture of fine-grained sediment within a cross-section (under a steady-state condition) will be accompanied by a homogeneous mixture of sediment associated contaminants. For the Nith River, this relationship generally holds true (Table 3). However, for rivers studied by Horowitz *et al* (1990), (Arkansas and Cowlitz Rivers) significant cross-sectional differences in SS and associated trace metal concentrations were found. Spatial differences in SS concentration were generally attributed to variations in the >63 µm fraction as the < 63

μm fraction was homogeneous in the cross-section. Despite the homogeneous nature of the $<63 \mu\text{m}$ fraction, the Cu, Cr, and Ni associated with the $<63 \mu\text{m}$ fraction exhibited significant differences in the river cross-sections.

In addition to loading inaccuracies produced by single samples at a cross-section, loading errors may be compounded by changes in the sediment and chemical characteristics of the water as it travels down stream. Chemical loadings that are extrapolated downstream from a measured section may be inaccurate due to physical, chemical and biological processing during transit (Blachford and Ongley, 1984). Processes influencing sediment-associated chemistry during transport are, however, poorly understood.

Problems of field accuracy are also associated with the sampler type or method used. We examined the influence of sediment sampler type [depth-integrated (DI), point and pump] on SS concentration prediction and the ability of a surface shoreline grab sample (a common simple sampling strategy) to predict the river mean SS concentration as determined by a composite sample for the Nith River (Table 4).

TABLE 4 Comparison of DI, pump, point and surficial shoreline grab sample SS concentrations to composite samples (November 21, 1991).

Replicate Number	Composite (mg/l)	DI (mg/l)		Pump (mg/l)		Point (mg/l)		Shoreline Grab (mg/l)	
		S-1	S-2	S-1	S-2	S-1	S-2	W-Shore S-1	E-Shore S-2
1	14.95	12.58	10.49	12.63	12.05	10.78	8.40	3.34	9.23
2	14.22	12.27	12.62	12.93	12.00			4.88	4.97
3	14.95	12.09	10.82	12.43	12.91			5.04	9.89
Mean	14.70	12.31	11.31	12.66	12.32			4.42	8.03
SD	0.42	0.24	1.15	0.25	0.51			0.94	2.67
C of V	2.85	1.99	10.15	1.99	4.13			21.20	33.24

Note: S-1 and S-2 represent samples 1 and 2 respectively
 SD represents the standard deviation
 C of V represents the coefficient of variation

All simultaneously sampled mid-river single vertical and shoreline grab sampling methods under-estimated the actual SS concentration of the composite sample. This may be attributed to some spatial variability in the distribution of the SS in the cross-section (Table 2, Nov. 21, 1991). DI and pump SS concentration estimations are similar. This is most likely due to the low SS concentration and small particle size of the suspension. The lower concentration of the point sampler as compared to the DI and pump sampler may be explained by the fact that the whole water column was not sampled as it was for the DI sampler and a smaller volume of water was sampled than from the pump sampler. The point sampler misses sampling the high turbidity zone and larger particles at the river bottom. The smaller volume of the point sampler also reduces the probability of sampling isolated larger particles. Horowitz *et al* (1990) also found significant differences in SS concentration predictions from different sampler types (point, pump, and DI). They also found significant differences in many of the sediment's metal concentration values. Variation in SS and metal concentrations was also observed for a river which possessed little or no $<63 \mu\text{m}$ material.

The surface shoreline grab samples severely under-estimate the river concentration and exhibit a high degree of variability (Table 4) due likely to the lower velocities outside of the main area of flow. Comparison of filter papers containing filtered SS indicated that shoreline samples were also visibly finer than the main channel samples.

Our results and those of Horowitz *et al* (1990) indicate that a DI composite sample is the best estimate of the cross-sectional SS and contaminant concentration. This apparent biasing of SS and contaminant loads by samplers and strategies should, however, be tested further over a larger range of flows and SS concentrations.

Unlike field programs, analytical programs generally have a high degree of accuracy. While important for scientific studies, the large imbalance between field and laboratory accuracy can create problems of inference in monitoring programs. Agencies that primarily focus on laboratory analytical accuracy may be biasing their management decisions if they do not take into account the high degree of variability of the non-analytical field component of a study (Ongley, 1991).

Dissolved and Total Water Samples vs SS Sample Analysis

Although there is a strong tendency for many priority pollutants and phosphorous to adsorb onto the surface of particulate matter, water quality monitoring programs generally analyze only for total and filtered water samples due to a lack of methodology for collecting adequate amounts of SS for chemical analysis. Chemical analyses for dissolved and total water samples are often below detection limits or significantly below sediment associated contaminant concentrations, particularly for organics and metals with low solubility in water (Ongley, 1988). For example, from 83,162 samples analyzed for pesticides and herbicides from Canadian prairie rivers, only 6% were above detection limits (Blachford and Day, 1988).

Because sediment is rarely isolated from the water column, analysts commonly used the Method of Differences (M of D) to estimate chemical concentrations associated with sediments (ie. total concentration - dissolved concentration = particulate concentration). We find, as does Horowitz (1988), that this method is inconsistent for estimating sediment-associated chemistry. Assuming that extraction procedures for water and SS can produce comparable values, the M of D is highly dependent on the concentration of SS in the total water sample. For very low SS concentrations negative values can often result because of the minimal differences in the composition of a dissolved and total water sample. At higher SS concentrations, our sediment-associated metal concentrations are almost always greater than those calculated by M of D; in some cases 50% greater than by M of D.

CONCLUSION

Tributary monitoring has evolved substantially over the last four decades from programs strictly engaged in quantity monitoring to those devoted to the physical, chemical and biological characterization of sediment and contaminants. Data produced by such programs provide environmental managers with a source of information for water quality management. The water quality and quantity data sets compiled, however, often lack continuity and compatibility as they are generally sampled, analyzed and reported

differently from one another. Traditional focus on filtered and whole water samples for chemistry has been demonstrated to under-estimate contaminant concentrations for those substances associated with the sediment phase. Sediment programs, on the other hand, may produce data which could be of considerable use in chemical transport studies if changes in sampling protocols are made to the programs.

Compounding this problem of inconsistency in data collection, analysis and reporting by different agencies, is the inherent temporal and spatial variability in SS and associated contaminants which may exist within a river cross-section and over its course of travel. This potentially high degree of variability in sediment and contaminant data in the field component of a monitoring program defeats the purpose of high resolution analytical procedures for contaminant chemistry when single samples are used for loading predictions and associated basin-wide management decisions.

Integration of quantity and quality objectives will enhance the ability to use data for management purposes. Successful integration will, however, depend on two sets of activities. One, is the resolution of fundamental scientific questions such as in-stream variance and down stream transport of cohesive sediment and associated contaminants; the second is a management exercise in standardization of field and analytical methods relative to the level of accuracy realistically required to address water quality management issues.

ACKNOWLEDGEMENTS The authors wish to thank P. Engel for his review of the manuscript and C. Jaskot, D. Blais and J. Menagon for their assistance with the field and analytical work represented in this paper.

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