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Syringe Filtration Methods for Examining Dissolved and Colloidal Trace Element Distributions in Remote Field Locations

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It is well-established that sampling and sample processing can easily introduce contamination into dissolved trace element samples if precautions are not taken. However, work in remote locations sometimes precludes bringing bulky clean lab equipment into the field and likewise may make timely transport of samples to the lab for processing impossible. Straightforward syringe filtration methods are described here for collecting small quantities (15 mL) of 0.45- and 0.02-μm filtered river water in an uncontaminated manner. These filtration methods take advantage of recent advances in analytical capabilities that require only small amounts of water for analysis of a suite of dissolved trace elements. Filter clogging and solute rejection artifacts appear to be minimal, although some adsorption of metals and organics does affect the first approximately 10 mL of water passing through the filters. Overall the methods are clean, easy to use, and provide reproducible representations of the dissolved and colloidal fractions of trace elements in river waters. Furthermore, sample processing materials can be prepared well in advance in a clean lab and transported cleanly and compactly to the field. Application of these methods is illustrated with data from remote locations in the Rocky Mountains and along the Yukon River. Evidence from field flow fractionation suggests that the 0.02-μm filters may provide a practical cutoff to distinguish metals associated with small inorganic and organic complexes from those associated with silicate and oxide colloids.

Introduction

Methods for obtaining reliable dissolved trace element samples from natural waters generally utilize clean labs or field-portable clean environments. These types of precautions have come about because of the realization that much of the older dissolved trace element data in the literature is incorrect due to problems of sample contamination arising during collection and filtration (e.g., refs *1*−*4*). Unfortunately, it is not always possible to bring a clean environment into remote field areas, nor is it always possible to transport samples from a remote area to a clean facility in a timely manner. For instance, recent work by this investigator at remote locations on the Yukon River in Alaska (*5*) required extended periods in the field, yet space limitations precluded bringing along a typical portable laminar flow bench. In addition, methods for obtaining information on colloidal composition are likewise frequently too cumbersome for remote locations as well as being time-consuming.

In this report clean, compact, field-portable methods for collecting samples filtered through 0.45- and 0.02-μm pore size syringe filters are examined. With this methodology, only small samples are collected (typically 15 mL). However, with the introduction of the latest generation of inductively coupled plasma-mass spectrometers (ICPMS) and microflow nebulizers, sample requirements for elemental analysis are very low: a determination of a suite of first row transition elements is frequently readily obtainable with samples of less than 1 mL (*5*). Other workers have previously used the 0.02-μm filters for examining colloidal Fe distributions in lake water (*6*) and seawater (*7*), although the properties of the filters have not been extensively examined.

In examining new methodology for clean field filtration of natural waters, there are a number of factors that need to be considered. Reproducibility and reliability as well as results comparable with other techniques are obvious issues. Additionally, field-transportable filtration techniques need to rely on materials that can be precleaned in the lab and cleanly transported and utilized in the field. The filtration techniques also need to minimize size fractionation artifacts caused by filter clogging that have been the subject of much discussion in the literature (e.g., refs *8*−*11*). And any ultrafiltration method must minimize artifacts such as solute rejection (e.g., refs *12*−*14*).

Experimental Section

Sampling. The lower Mississippi River was sampled above Baton Rouge, LA. Near-surface river water was collected in the middle of the channel using an acid-cleaned polyethylene bottle attached to a nonmetallic pole. At this location, the Mississippi River can be characterized as a high suspended load, slightly alkaline river with a typical suspended load of 200 mg/L, a pH of 7.8, and a DOC of ∼3.5 mg/L.

The Pearl River was sampled near Stennis Space Center, MS. Surface grab samples were collected off the bow of a small work boat that was headed slowly into the current. An acid-cleaned polyethylene bottle was immersed below the surface, rinsed several times, and filled by a worker wearing polyethylene gloves. The Pearl River is a near-neutral pH (∼6.5), low suspended load (<20 mg/L), “blackwater” river with DOC up to 7 mg/L. Additionally, the Pearl River has a large amount of colloidal Fe: results below indicate Fe concentrations >10 μM in the <0.45-μm filtrate but Fe drops by a factor of 5 or more in the <0.02-μm filtrate.

The Yukon River near Eagle, Stevens Village, and Pilot Station, AK, as well as two of its major tributaries (Tanana and Porcupine Rivers) were sampled six times between October 2000 and October 2001. Samples were collected in a manner similar to that described for the Pearl River. Trace element and ancillary data from this work can be found elsewhere (*15*). These sampling locations tend to be slightly alkaline (pH 7−8) and vary from low DOC (1−2 mg/L) and low suspended loads (<10 mg/L) in winter to high DOC (>10 mg/L) and high suspended loads (>500 mg/L) in spring.

The Loch Vale watershed was sampled at the outlet of Loch Vale in Rocky Mountain National Park, Colorado. The waters are near-neutral (pH ∼6.4), clear, and with generally low DOC (*16*). Samples were collected using an acid-cleaned polyethylene/polypropylene 50-mL syringe held by a worker wearing polyethylene gloves.

Cleaning and Preparation of Materials. Sample collection and storage bottles (15- and 250-mL Nalgene high-density polyethylene bottles) were cleaned by soaking in hot 1.2 M

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HCl (reagent grade) for at least 8 h with subsequent thorough rinsing with ultrapure distilled deionized water (Barnstead E-pure). All polyethylene/polypropylene 50-mL syringes (Sigma-Aldrich) were cleaned in a similar manner. Use of this type of syringe is important because the black rubber gaskets of typical plastic syringes can be a major source of contamination due to the metal oxides (especially ZnO) used as activators in the rubber vulcanization process as well as the difficulty in leaching contaminating metals from the rubber during acid cleaning.

Whatman Puradisc PP 25 mm × 0.45 μm polypropylene syringe filters were cleaned by passing 40 mL of 1.2 M HCl through them followed by a similar volume of ultrapure water. Whatman Anotop 25 mm × 0.02 μm alumina syringe filters were cleaned by passing through them 40 mL of ultrapure 0.024 M HCl (Seastar) followed by a rinse of 20 mL of ultrapure water. If the Anotop filters are not to be used immediately, it is important that clean air be passed through them after rinsing in order to thoroughly dry them. All filters used in this work were dried before use. It was found to be convenient to clean four filters at a time using a self-made acrylic vacuum manifold with Luer valves and connectors for the filters and connected to a vacuum pump. All filter cleaning was performed in a laminar flow bench. After cleaning, a syringe and filters are placed in a polyethylene glove, and then the glove and two 15-mL sample bottles are placed in a new plastic zipper bag. This bag plus a clean 250-mL raw water sample collection bottle are then placed inside another new plastic zipper bag. These “river sampling kits” are then packaged inside of a larger plastic bag for transport to the field.

Filtration Procedure. A clean 0.45-μm filter is used as a prefilter for the 0.02-μm filter. For both filter types, approximately 10−15 mL of sample is passed through the filter to waste. Another approximately 5 mL is collected to rinse the sample bottle. A final 15 mL is collected as the sample. For the 0.02-μm filters, the filtration can be slow, and thus hand fatigue in operating the syringe can be a problem. Figure 1 shows a simple nylon press and polycarbonate stand that were constructed to make the filtration procedure easier. Care should be taken not to place too much pressure on the filtration apparatus by rapid tightening of the nylon nuts on the syringe press. If a protected environment is not available in the field for the filtration process, a lightweight folding plastic enclosure can be made using narrow PVC pipe and plastic sheeting such as is readily available at most hardware stores. After filtration, sample bottles are tightly closed and placed in double plastic zipper bags for transport back to the lab.

Analysis. In the lab, samples were acidified to pH <2 using ultrapure HCl (Seastar). Typically, 70 μL of 6 M HCl was added to each 15-mL sample. Dissolved trace elements were determined using a double-focusing ICPMS (Thermo-Finnigan Element 2). A low-flow (100 μL/min) self-aspirating nebulizer (Elemental Scientific) and Teflon spray chamber were utilized. Samples were slightly diluted (approximately 30%) due to the addition of ultrapure dilute nitric acid (Seastar) with added internal standards (High Purity Standards). With this addition, samples are approximately 2 μg/L in Sc, In, and Th and 0.16 M in HNO_3. Calibrations were performed using standards made in 0.16 M nitric acid. Several samples were also calibrated by the method of additions. No significant difference was noted for the two calibration methods. Sample acidification and other preparations for analysis were carried out in a laminar flow clean bench. Detection limits were $\leq$1 pM for Cs, Re, and Tl; $\leq$5 pM for Cd, Ce, and U; $\leq$10 pM for Pb; $\leq$0.1 nM for Co Cr, Cu, Mo, Ni, Rb, and V; $\leq$1 nM for Ba, Li, Mn, Sr, and Zn; and $\leq$3 nM for Al and Fe. Relative analytical precision for samples well above the detection limit was typically $\pm$5% (1σ).

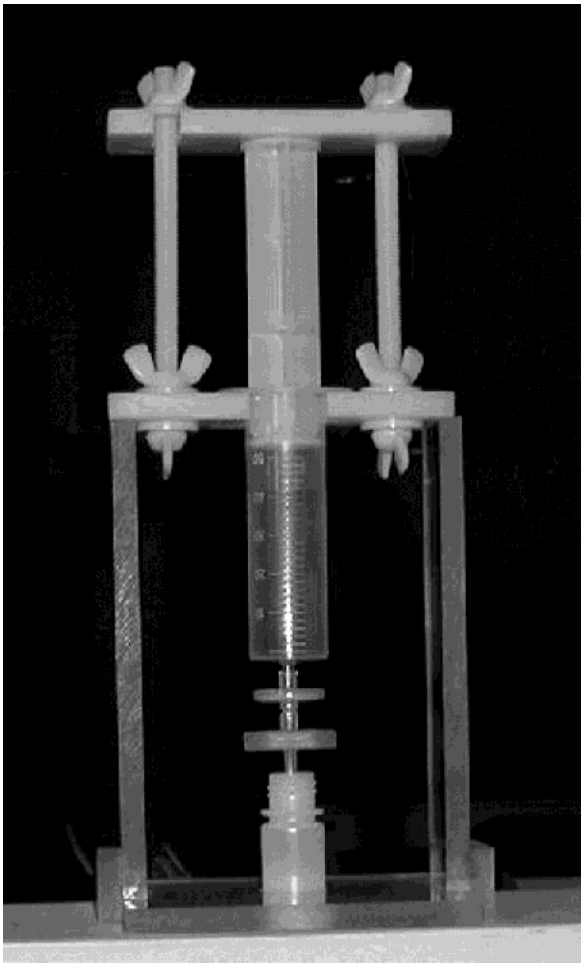

FIGURE 1. Nylon syringe press and polycarbonate stand for processing samples using a 0.02-μm Anotop filter with a 0.45-μm Puradisc prefilter.

Results and Discussion

Filter Cleaning, Reproducibility, and Storage. To examine how clean the filters were after our cleaning procedure, ultrapure 0.001 M HCl was treated as a sample with aliquots processed through several replicates of both types of filter. Thus, the first 10 mL of this weak acid passing through each filter was discarded, the next 5 mL used as a sample bottle rinse, and then finally 15 mL was collected for analysis. Elements examined included Al, Ba, Cd, Ce, Co, Cr, Cs, Cu, Fe, Li, Mn, Mo, Ni, Pb, Rb, Re, Tl, U, V, and Zn. Concentrations of these elements in the acid prior to passing through a filter were at or below our detection limits. For both types of filters, there was only one element significantly elevated in the weak acid leach after passing through the filter. Specifically, for the Anotop filters (which are made from alumina) there was an obvious Al contamination problem with concentrations in the weak acid leach of 1.3 μM; the Al concentration in the Puradisc leach was also slightly elevated at 5 nM. Concentrations of the other elements examined in the weak acid leach were not significantly different from the concentrations in the acid itself.

Filtration reproducibility was examined for Al, Ba, Cd, Ce, Co, Cr, Cs, Cu, Fe, Li, Mn, Mo, Ni, Pb, Rb, Re, Tl, U, V, and Zn using both types of filters and filtering samples of both Mississippi River and Pearl River water. Four replicates were examined for each filter and river water combination. In most cases, the relative standard deviation (RSD) was $<10\%$ for these elements. Only for Pb and Zn in Mississippi River samples filtered using 0.02-μm Anotop filters were the RSDs above 15%; however, this appeared to be due to one contaminated sample. Elimination of that one replicate resulted in RSDs for these two elements of <7% for that treatment. These RSDs are similar to our analytical precision.

Because of concern about possible corrosion of precleaned 0.02-μm Anotop filters by residual cleaning acid or water during long-term storage, a number of precleaned Anotop filters were stored for 6 months. Filters that were stored wet were found to be totally blocked. However, filters that were thoroughly dried before storage yielded generally comparable results to newly cleaned filters for both Mississippi River and Pearl River samples. Specifically, the same suite of elements determined in the previous experiments were determined in two aliquots from each river (Mississippi and Pearl Rivers) filtered through both stored and newly cleaned filters. Differences for almost all elements for these two treatments were below 10%, with the stored filters showing neither a net positive nor negative bias in concentrations. The exception to this was Al, where concentrations in aliquots passing through the stored filters were consistently several times greater than concentrations in aliquots passing through newly cleaned filters.

Sample Rinse and Filter Clogging. Rinsing of filtration apparatus with some quantity of sample is of special concern. On one hand, rinsing is thought to be useful in washing out any residual cleaning acid or water as well as in saturating any adsorption sites on the apparatus. On the other hand, rinsing with the sample begins the process of filter clogging which leads to a reduction in the effective pore size of the filter (e.g., refs *8*−*11*). This reduction in pore size, if reproducible, can still result in useful results; however, for elements with appreciable colloidal concentrations, the reduction in pore size can result in a continual decrease in concentration during the filtration process (e.g., refs *8*, *9*, and*11*). For the 0.02-μm filters, additional concerns include rejection of solutes/colloids <0.02 μm (e.g., refs *12*−*14*).

As a test for the possible rejection of small anions due to charge buildup and rejection on the 0.02-μm Anotop filters, the partitioning of Mo was examined. Because there is very little Mo in fluvial particulates (*17*) or colloids (*18*), one would expect essentially the same Mo concentration in both the <0.02- and <0.45-μm filtrates. Thirty-five samples of particle-rich waters from the Yukon River basin were analyzed for Mo in 0.45- and 0.02-μm filtered samples (*5*). The 0.02/0.45-μm concentration ratio in these samples was 1.05 ± 0.10, indicating no significant rejection of the molybdate anion. Likewise, this ratio was examined for Sr, a fairly soluble cation, in the same samples, and the 0.02/0.45 μm concentration ratio was 0.94 ± 0.08.

To further examine the effects of filter clogging, Mississippi River and Pearl River water samples were passed through both types of filters, and aliquots were collected every ~5 mL for a total of ~45 mL of sample passing through the filters. The same group of elements as examined in the experiments above was determined in each aliquot. Figure 2 summarizes some of the results. In general it is seen that for the Puradisc filters the first ~5−10 mL may be somewhat low in concentration, but subsequent aliquots show reasonably constant concentrations. For the Anotop filters, the first ~10−15 mL may be low in concentration (or in some instances may be high due to contamination washout; e.g., Zn in the Mississippi River sample), but concentrations are reasonably stable after that. For almost all of the elements examined, the mean concentration of the fourth−sixth aliquots in this experiment was within 10% of the mean concentration of the seventh−ninth aliquots. Exceptions to this were Al in the Anotop filters (where there was much scatter in the data) and a few elements that had concentrations close to their detection limits. Additionally, there was no consistent bias in comparing these aliquot averages (i.e., aliquots 4−6 were neither consistently higher nor lower in concentration than aliquots 7−9).

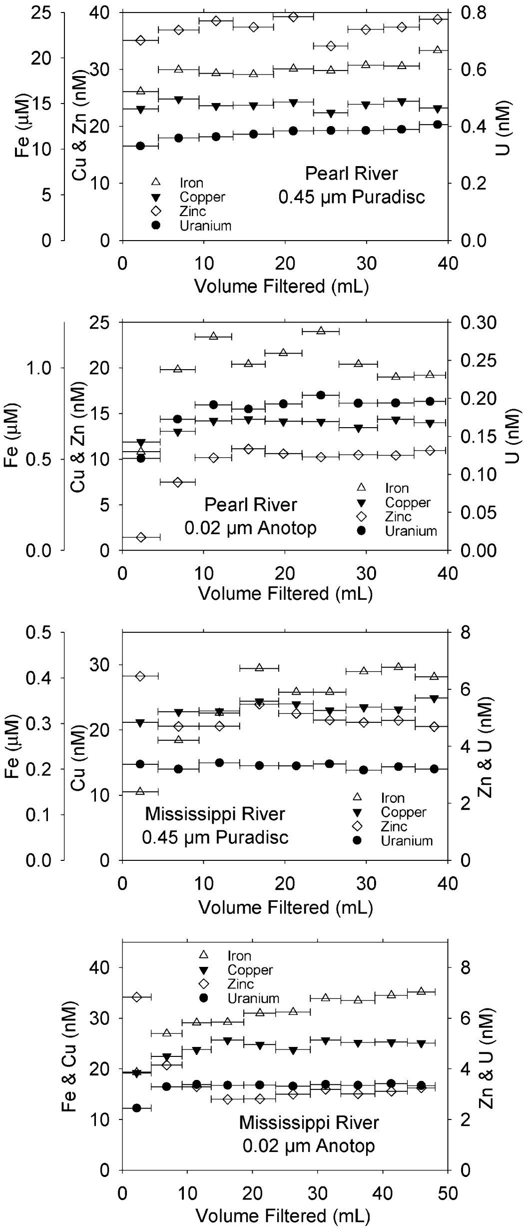

FIGURE 2. Concentration versus volume filtered for 0.45-μm Puradisc and 0.02-μm Anotop filters using Pearl River and Mississippi River water samples. Note that for the Pearl River, water samples collected on different days were used for the two experiments.

In a separate test of the 0.02-μm Anotop filters, 5-mL aliquots of sample passing through the filter were collected, and the UV absorbance at 254 nm was recorded using 1-cm quartz cuvettes. Figure 3 shows that UV absorbance increases rapidly in the first 10−15 mL, possibly due to adsorption of dissolved organic material on the filter. Subsequently, there is a very slight increase in UV absorbance that may result from permeation rejection (*14*) or breakthrough of colloidal material due to increasing pressure needed to pass material through the filter. In either case, the later increase in UV absorbance is minor, with the average absorbance of aliquots 4−6 being <5% lower than the average absorbance of aliquots 7−9.

Filter Comparison. Because variations in filters and filtration techniques may result in differing amounts of the colloidal phase being included in the "dissolved phase", it is useful to examine the comparability of results of these

TABLE 1. Comparison of Trace Element Concentrations in Filtrates Processed by Three Different Techniques[a]

	Al	Ba	Cd	Ce	Co	Cr	Cs	Cu	Fe	Li	Mn	Mo	Ni	Pb	Rb	Re	Sr	Tl	U	V	Zn
Mississippi River, 9/28/00																					
0.4-μm exhaustive	115	490	0.19	**0.035**	1.2	1.08	0.009	19	**12**	1800	**7**	33	22	**0.024**	18	0.086	2250	0.064	5.8	43	3.4
0.02-μm Anotop		490	0.19	0.009	1.2	0.98	0.009	20	6	1910	3	33	22	0.019	19	0.090	2380	0.063	5.6	52	3.5
0.45-μm Puradisc	*390*	500	0.19	***0.103***	1.2	1.08	***0.011***	19	***100***	1940	***5***	33	22	***0.048***	19	0.091	2420	0.064	5.8	46	3.6
Pearl River, 8/22/01																					
0.4-μm exhaustive	4100	220	0.12	18	8.2	8.5	**0.048**	20	**2970**	730	1520	**0.93**	23	**0.136**	40	**0.003**	245	0.059	0.32	18	50
0.02-μm Anotop		200	0.11	16	8.6	9.3	0.075	19	4740	730	1650	1.25	22	0.443	41	0.004	241	0.060	0.28	22	45
0.45-μm Puradisc	*37800*	***270***	***0.17***	***29***	***11.2***	***22.4***	***0.275***	23	***20700***	760	*1880*	*1.20*	***29***	***2.37***	46	*0.004*	267	***0.090***	***0.48***	***52***	***70***

[a] Results in nmol/L. Boldface values differ by >20% from the corresponding 0.02-μm Anotop concentration. Puradisc (0.45-μm) filtrate values in italics differ from the corresponding 0.4-μm exhaustive filtrate concentrations by >20%.

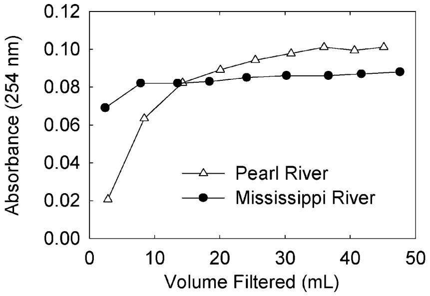

FIGURE 3. Absorbance at 254 nm (1 cm path length) vs volume filtered through 0.02-μm Anotop filters.

syringe filtration methods. In particular, previous work in our lab (e.g., ref *17*) utilized an "exhaustive filtration" method (*4*). In that technique, an acid-washed 0.4-μm polycarbonate screen-type filter is first rinsed with sample, resulting in clogging of the filter and a lower effective pore size. Table 1 shows a comparison of results from samples filtered by the syringe filtration methods as well as by exhaustive filtration. The results show that for some elements (particularly most of the alkali and alkaline earth metals) there is little difference among the filtration methods. For the more particle-reactive elements (e.g., Fe, Zn, and Pb), the 0.45-μm syringe filtered samples generally yield significantly higher concentrations than the other methods whereas the 0.4-μm exhaustive filtration and 0.02-μm syringe filters yielded more similar results. This is in accord with a previous filtration comparison that showed similar Fe results for 0.4-μm exhaustive filtration and tangential flow ultrafiltration through a 5-nm pore size membrane (*4*). Finally, it should be noted that even where there are significant differences in filtration results, the differences are generally much smaller than previously reported differences between clean sample collections and older data from national water quality programs that did not utilize clean techniques (1−4). That is, poor filtration efficiency is unlikely to account for all of the high and erratic older water quality results.

Applications. The syringe filtration methods described above have been field tested in a number of situations. The 0.45-μm Puradisc filters have been utilized in a high-resolution multi-year time series of dissolved trace elements in the Loch Vale Watershed, Colorado. Loch Vale is a seasonally snow-covered alpine/subalpine watershed (*16*), and samples were collected weekly at the outlet of a small lake. The sampling site is at an elevation of 3050 m and is approximately a 1-h hike or ski from the road. Because the people collecting the trace element samples also had many hours of other sampling work to do and did not have access to a clean lab, it would have been 1−2 d before unfiltered samples could be express delivered to our lab. Thus, this situation required use of a simple field filtration method. Figure 4 shows some of the results of this work. Dissolved Mn is observed to be comparatively high when the lake is ice-covered and then decreases rapidly when the lake opens up and becomes aerated.

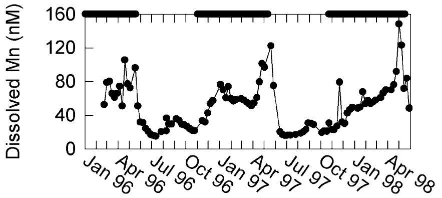

FIGURE 4. Dissolved manganese in 0.45-μm syringed filtered samples from the outlet of Loch Vale. The solid line along the top axis indicates periods of ice cover on the Loch.

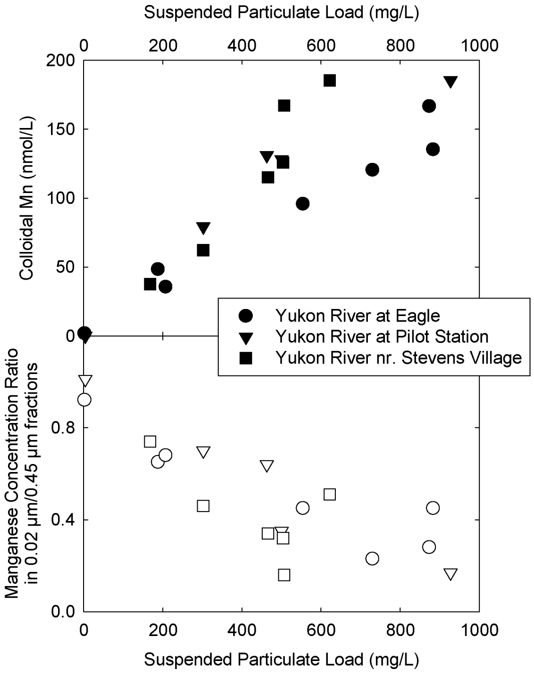

FIGURE 5. Colloidal (0.02−0.45 μm) manganese and the ratio of manganese in the 0.02-μm filtrate:0.45-μm filtrate for three locations on the Yukon River as functions of suspended particulate matter.

Both the 0.45- and 0.02-μm syringe filters are currently being used in a multi-year study of the Yukon River Basin (*15*). Here again, sampling locations are remote from laboratory facilities, only small open boats are available for the field work, and in some cases sampling crews are away from the lab for a number of days at a time. Figure 5 shows, for several locations on the Yukon River, the variation in colloidal (i.e., 0.02−0.45 μm) Mn as a function of suspended particulate material (SPM). Also shown is the ratio of Mn in the 0.02-μm filtrate to the 0.45-μm filtrate as a function of SPM. When suspended loads are low, most of the Mn is in the <0.02-μm fraction. However, the ratio decreases so that by the time suspended loads are >500 mg/L, most of the Mn is in the colloidal size range. The positive correlation between colloidal Mn and SPM in this figure is in agreement with the assumption of the colloid model frequently invoked to explain decreasing metal dissolved/solid partition coefficients with increasing SPM (i.e., the particle concentration effect; *19*, *20*).

Defining the Colloidal Phase. The IUPAC definition of a colloid refers to "molecules or polymolecular particles" having at least one dimension in the range of 1−1000 nm (*21*). In practice, recent workers have commonly defined the low end of their colloidal size range by using an ultrafiltration membrane with a molecular weight cutoff typically in the range of 1−10 kDa (*22*). A question therefore arises as to the utility of the substantially larger 20 nm cutoff of the Anotop syringe filters. In some regards, the answer to this question depends on what one is trying to accomplish with a given size separation. Indeed, the IUPAC definition notes that "The size limits given above are not rigid since they will depend to some extent on the properties under consideration." Recent flow field−flow fractionation work on colloid composition as a function of size (*18*) suggests that fluvial colloidal organic carbon is concentrated in size ranges well below 20 nm. In contrast, work with sedimentation field−flow fractionation examining fluvial particle composition in the 50−800-nm range (*23*) suggests a peak in abundance of Al, Si, and Fe around 100 nm. If both of these results are generally applicable, it would seem that a 20-nm cutoff may usefully separate metals associated with small inorganic and organic complexes from those associated with silicate and oxide colloidal particles. This may well prove as helpful to the understanding of trace element mobilization and availability as lower colloid size cutoffs.

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