

Sources of Trace Metal Contamination Artifacts during Collection, Handling, and Analysis of Freshwaters

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Clean techniques are necessary for reliable measurement of trace metals in freshwaters at ambient, though not necessarily regulatory concentrations. Conventional sample handling methods were compared to clean techniques for 35 individual steps used in protocols for analysis of filtrate and filter-retained forms of Ag, Cd, Cu, and Pb. Approximately two-thirds of all steps contributed statistically significant amounts of contamination in the measurement of dissolved and particulate Cd, Cu, and Pb. Average contamination for a single contributing step was 300%, 141%, and 200% for the three metals, respectively (where 100% represents no added contamination). Relative Cu contamination tended to be lower, partly because real levels in water are higher for this metal. Contamination generally was not a problem for Ag, when it was present in water at higher than background levels. With that exception, it does not seem possible to abridge clean technique protocols, even when measuring trace metals in polluted freshwaters where levels are moderately high. Our expectation is that most other metals (e.g., Zn, Cr, or Ni) will have contamination behavior that is similar to common Cd, Cu, and Pb, rather than the rare metal Ag.

Heavy metals are among the most toxic and persistent pollutants in freshwater systems. Many research and monitoring efforts have been conducted to determine sources, transport, and fate of these metals in the aquatic environment. However, recent studies have shown that contamination artifacts have seriously compromised the reliability of many past and current analyses,¹ and in some cases, metals have been measured at 100 times their true concentration.² These induced errors are of great concern since artifact-free data are necessary to detect trends and to identify processes that control the transport and fate of toxic heavy metals. In addition, without accurate and reliable data, it is impossible to accurately monitor the effect of costly regulations aimed at reducing metal emissions. To avoid these problems, and to enhance the quality of trace metal data, laboratories are putting substantial effort into improving protocols for sample collection, handling, and analysis.³ This greater level of effort devoted to clean methods is costly in both money and time.

The problems caused by contamination when measuring trace metals were first brought to the attention of the scientific community by Patterson in his investigations of stable lead isotopes in the 1960s and 1970s.⁴ Largely through his influence, clean methods became part of the standard operating procedures used by chemical oceanographers starting in the mid-1970s.^{5,6} Freshwater chemists were slow to adopt these same techniques, with the notable exception of the long series of investigations on lead cycling by Patterson and co-workers.^{7–11}

With few exceptions,^{12–15} limnologists have begun to use clean techniques only in the last three or four years. This was spurred, in part, by oceanographers who began to study freshwater systems such as the Mississippi River,^{16–18} Great Lakes,¹⁹ and Amazon River.²⁰ The result of this activity has been to cast serious doubt on earlier routine measurements. Thus, Flegal and Coale²¹ have questioned surveys of lead in surface waters,^{22,23} and Windom et al.² disputed the reliability of the United States Geological Survey (USGS) National Stream Quality Accounting Network. Ahlers et al.⁴ and Benoit²⁴ implied that most previously reported results may be in error because of failure to follow appropriate clean protocols. A parallel can be drawn with chemical oceanography, where virtually all uncensored (i.e., other than nondetects) trace metal data from before about 1975 are considered invalid. The persistence of limnologists in the use of inadequate clean methods for 15 years after oceanographers had changed their protocols may

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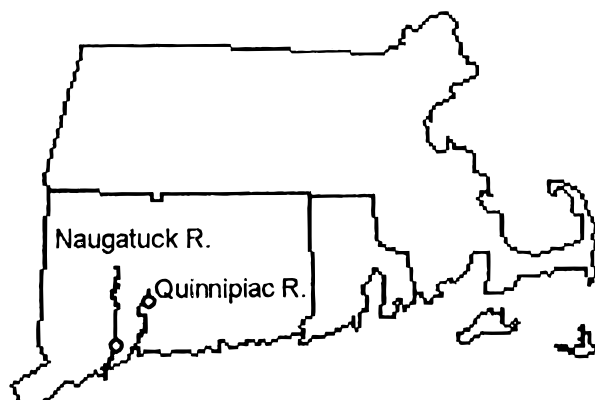


Figure 1. Map showing location of sampling sites in Connecticut.

be attributable to a belief that natural and anthropogenic sources in the terrestrial environment are great enough to maintain metals in freshwater at levels too high for contamination to have a significant influence. However, all studies to date conducted using clean methods indicate that metal levels in water are typically well below the detection limits of outdated routine methods.

The current strategy for eliminating contamination artifacts is to apply extraordinary measures during all stages of the sampling/analysis sequence, from cleaning sampling containers and collecting samples to handling them in the laboratory and conducting instrumental analyses. It seemed likely that contamination is introduced selectively at individual stages of this sequence, and that only a few steps contribute the bulk of the contamination. Furthermore, different metals are probably added at different points in the sequence. Selective application of clean methods at these trouble points might yield much higher data quality for substantially reduced effort. The current study was designed to evaluate and quantify sources of Pb, Cd, Cu, and Ag contamination in the sampling/analysis sequence. Detailed knowledge of the sources of contamination in heavy metal analysis could be used to help streamline the required clean protocols and provide for the most efficient use of limited analytical resources.

EXPERIMENTAL SECTION

Sampling Sites. The study was conducted on samples collected from streams (rather than synthetic laboratory solutions) in an effort to duplicate real world conditions, including a complex sample matrix. Samples were collected from two Connecticut sites: an unnamed tributary of the Quinnipiac River ~10 km downstream from its headwaters and the Naugatuck River just south of Seymour, CT (Figure 1). The Quinnipiac tributary was chosen because it was previously measured to have moderately low levels of trace metals (Rozan and Benoit, unpublished data). These low levels were expected to facilitate detection of the potentially subtle contamination artifacts anticipated from many of the treatments used in this study. For comparison, one sampling trip was made to an industrialized stretch of the Naugatuck River which has higher concentrations of metals, especially Ag.

Clean Techniques. This project compared a clean method (the control) to modified methods (treatments) that substituted "conventional" steps at different stages during the preparation, sampling, handling, and analysis of Pb, Cd, Cu, and Ag in freshwater. The control method employed state-of-the-art clean techniques throughout the entire procedure. Benoit²⁴ gave a

complete description of the clean methods used in this study, which can be summarized by three guiding principles: (1) water samples contact only surfaces composed of materials that are intrinsically low in trace metals and that have been extensively acid-cleaned in a filtered air environment, (2) samples are collected and transported taking extraordinary care to avoid contamination from field personnel or their gear, and (3) all other sample handling, preparation, and analysis steps take place in a filtered air environment (class 100 clean room) and using ultrapure reagents. Filtrate samples were concentrated by a subboiling evaporation procedure,⁴ except when low-flow conditions resulted in high-salt backgrounds. In those unusual cases, metals were extracted into chloroform containing the chelating agents APDC and DDDC before back extraction into a small volume of 2% HNO₃.²⁵ Both concentration methods had greater than 95% recoveries for Pb, Cd, and Cu when used with standard reference water SLRS-3 (National Research Council of Canada) and 93% recoveries for internally spiked Ag. After preconcentration, metals were measured by graphite furnace atomic absorption spectrometry (GFAAS), using a Perkin-Elmer Model 3300 instrument. This analytical method provided detection limits (IUPAC definition) on preconcentrated samples of 1 ppt for Ag, 2 ppt for cadmium, 4 ppt for Pb, and 100 ppt for Cu. Lower detection limits are possible with these methods, but the attained values were adequate for the samples tested.

Conventional Trace Metal Methods. The conventional experimental manipulations used in this study were similar to methods formerly recommended for the National Stream Quality Accounting Network.²⁶ These involve conventional acid washing, sample processing in the field and in a standard laboratory, use of reagent grade acids, and exposure of samples to unfiltered air. Each of the alternative steps listed in Chart 1 was substituted in the control protocol to quantify the contamination it contributes to the sampling/analysis sequence. Other than the single substituted "conventional" step, all other stages of each analysis followed the clean control method. Acid rinsing, as listed in Chart 1, consisted of rinsing the sample containers and filter holders three times with 2% trace metal grade HNO₃ from a low-density polyethylene squeeze bottle, followed by rinsing three times with distilled deionized water.

Three separate samples were collected for each treatment to provide information on the variability of introduced contamination artifacts. Contamination variability may be slightly overestimated since real fluctuations in the stream may also have occurred over the several minutes that the triplicate samples were collected, though these variations are expected to have been small. Triplicate control samples were collected using the complete clean protocol for each day of sampling. Except in cases where filter type was varied as an experimental variable, for each treatment 100 mL of river water was passed through 0.4 μ m Nuclepore screen-type filters by means of peristaltic pumping in the field to discriminate filter-retained (particulate) and filtrate (dissolved) fractions. (Durapore- and MF-type filters were used as alternatives in step 6 of Chart 1.) When they are not overloaded, screen-type filters are known to more accurately discriminate particle size

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Chart 1

1. sample containers
 - (a) high density polyethylene
 - (b) polypropylene
2. container cleaning procedure
 - (a) single acid bath (33% HCl) in HEPA fume hood
 - (b) single acid bath (33% HCl) in conventional fume hood
 - (c) no cleaning
 - (d) acid rinse (2% HNO₃)
 - (e) precleaned bottles (available commercially from I-Chem)
3. bottle storage
 - (a) bottles stored empty (without 0.03 N HNO₃ solution)
4. sample transport
 - (a) bottles transported without double bags
 - (b) filter holders transported without double bags
5. sample collection
 - (a) without clean room gloves
 - (b) without precautions concerning wind and current direction
6. filtration procedure
 - (a) non-acid-cleaned filter membranes
 - (b) filter holders cleaned by acid rinse (2% HNO₃)
 - (c) filter holders cleaned by single acid bath (33% HCl) in conventional fume hood
 - (d) filter membranes changed in the field
 - (e) conventional depth type 47 mm diameter Millipore MF polycarbonate filter membranes (Catalog No. HWAG 047 00)
 - (f) 47 mm diameter Millipore Durapore filter membranes (Catalog No. HVL P 047 00)
7. sample preservation
 - (a) reagent grade acid
 - (b) preacidification of sample by adding ultrapure HNO₃ to the bottle prior to sample collection
 - (c) acidification in conventional laboratory
8. sample preconcentration
 - (a) evaporation in glassware
 - (b) evaporation in conventional fume hood
 - (c) evaporation with reagent grade acid

distributions.²⁷⁻²⁹ In particular, they more reliably exclude passage of colloids so they tend to yield lower levels of filtrate metals than do depth-type filters.³⁰ Because of this difference, the measured contamination values for the alternative filtration steps are upper limits since filtrate metal levels may also include artifact metals associated with additional colloids that pass through depth-type filters but not the Nuclepore screen-type filter used as our standard.

A field blank (consisting of preanalyzed distilled water) and a pH-neutralized SLRS-3 standard reference water sample were "collected" in the field each day of sampling according to the complete clean protocol and were used to monitor contamination and metal recovery.

RESULTS AND DISCUSSION

Mean heavy metal concentrations in the two streams are shown for each sampling date in Table 1. Levels were nearly all below 1 µg/L, typical of sites affected mainly by regional atmospheric deposition. Substantial variability from day to day is linked to changes in ancillary biogeochemical parameters like suspended particulate matter (SPM), dissolved organic carbon (DOC), and total discharge (Rozan and Benoit, in preparation). Means of results from triplicate treatments are normalized to the corresponding control values and expressed as percentages in Table 2. In this table, 100% represents a treatment that is identical to

its respective control. Thus, a value of 200% indicates a measured value that is 2 times the actual concentration. A different subset of treatments was tested on each of the sampling dates, which are indicated in the last column of Table 2. Because the true concentration in the river varied from day to day, a given percentage contamination does not correspond to a fixed absolute value, but these can be calculated by comparison of Tables 1 and 2.

No Ag data are shown for the Quinnipiac since concentrations were always near the detection limit (~1 ng/L). However, contamination comparisons including Ag were made on several treatments for samples from the Naugatuck River, where Ag levels were higher.

Most treatments resulted in increased metal concentrations compared to the control (Table 2). It is likely, considering the random nature of contamination, and the small number of samples used to evaluate each step, that virtually none of the alternative treatments could be used reliably on a consistent basis. The relative magnitudes of these artifacts are the result of two main factors: (1) the true concentration of the metal in the water column and (2) the likelihood of contamination by metals that are present in the environment. As a percentage of the control sample, metal contamination generally followed the order Cd > Pb > Cu. This sequence seemed to result from the inverse of the absolute concentrations of metals in the water, Cu > Pb > Cd. There is a higher relative amount of contamination for metals with lower concentrations. This trend is also evident when two rivers are compared. Relative contamination levels are generally lower for the Naugatuck than for the Quinnipiac (Table 2). Again, this is a function of the amount of metal originally present in the water.

The second point concerns the abundance of metals that is available in the environment to cause contamination. Pb, Cd, and Cu all have relatively high contamination potentials since they all are abundantly present as pollutants in reservoirs such as soils, atmospheric aerosols, reagents, and laboratory dust. These three can be contrasted with a metal like Ag, which is a scarce pollutant. To some extent the two factors tend to counteract each other. Elevated levels of environmental pollution contribute to higher concentrations both in streams and in the surrounding environments that are likely to contribute to sample artifacts.

Treatment samples had higher absolute measured concentrations than controls, and they also showed much lower precision (as quantified by RSDs; Table 3). Relatively large variability of treatments can be attributed to several factors. First, there is real variation in the streamwater. However, real stream variability contributes equally to the SD of treatments (Table 3) and controls (Table 4). Although this natural variability may complicate interpretation of the data, sampling from a natural stream assures that the tested water has geochemical characteristics typical of the real world. Second, because the metal concentrations in the stream are so low, artifacts amounting to a few nanograms per liter will have a relatively large effect on the outcome of the analyses. This can be seen by comparing the relative percent standard deviations (% RSD) for the controls from the two sites (Table 4). The % RSD values for the Quinnipiac are all greater than the values for the Naugatuck, which has much higher metal concentrations. (Quinnipiac data in Table 4 represent the mean of the five RSDs calculated from triplicate samples for each of the sampling dates.) Third, and perhaps most importantly,

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Table 1. Mean Control Values

river	date	Pb (ng/L)		Ag (ng/L)		Cd (ng/L)		Cu (ng/L)		SPM (mg/L)
		Diss.	Part.	Diss.	Part.	Diss.	Part.	Diss.	Part.	
Quinnipiac	9/29/94	39	190	<1	<1	19	5	830	110	5.2
	10/13/94	81	440	<1	<1	41	29	580	280	8.9
	10/29/94	25	86	<1	1	14	5	360	57	2.3
	11/20/94	8	79	<1	3	20	5	250	48	2.3
	12/3/94	48	140	<1	1	18	6	380	35	2.1
Naugatuck	7/29/95	660	1300	22	33	100	36	6300	2100	3.4

Table 2. Comparison of Individual Conventional Steps To Control Protocol

	% of control values								
	Pb		Cd		Cu		Ag		
treatment	Diss.	Part.	Diss.	Part.	Diss.	Part.	Diss.	Part.	treatment date
Quinnipiac River									
bottles									
high-density polyethylene	205	n/a ^a	316	n/a	132	n/a			9/29/94
polypropylene	210	n/a	310	n/a	127	n/a			9/29/94
single acid bath	107	n/a	233	n/a	143	n/a			12/3/94
cleaned in conventional lab	287	n/a	175	n/a	110	n/a			11/20/94
acid rinsed only	218	n/a	394	n/a	111	n/a			9/29/94
noncleaned	248	n/a	1560	n/a	124	n/a			9/29/94
commercially cleaned (I-Chem)	285	n/a	125	n/a	104	n/a			11/20/94
stored empty	374	n/a	740	n/a	180	n/a			10/29/94
filtration									
noncleaned filters	204	114	114	200	106	231			10/29/94
holders cleaned in conventional lab	250	114	101	101	99	112			11/20/94
acid-rinsed holders	102	102	126	102	124	109			10/13/94
filters changed in the field	220	105	273	154	123	113			12/03/94
Millipore Durapore	98	104	96	123	95	129			10/29/94
Millipore MF (polycarbonate)	162	115	115	94	135	120			11/20/94
sample collection									
filters transported without bag	184	133	164	180	132	110			10/29/94
no gloves worn	292	160	292	240	114	152			12/3/94
sample preservation									
acidified with reagent grade acid	105	105	124	110	100	110			11/20/94
preacidified bottles	118	n/a	134	n/a	108	n/a			12/3/94
acidified in conventional lab	252	118	150	140	102	128			10/29/94
sample preconcentration									
in glassware	106	182	325	262	124	106			12/3/94
in conventional fume hood	152	138	166	241	154	324			10/13/94
with reagent grade acid	132	107	307	479	100	110			10/29/94
Naugatuck River									
filtration									
noncleaned filters	121	105	99	98	104	167	114	113	
acid-rinsed holders	110	156	101	94	99	149	86	181	
filters changed in the field	127	104	101	103	256	106	109	98	
sample preconcentration									
in glassware	116	107	148	143	113	111	205	334	
with reagent grade acid	98	126	148	89	109	121	127	101	

^a n/a, not applicable.

contamination is by nature highly variable. For example, the amount of contamination incurred by loading and unloading filter membranes into and out of filter holders in the field instead of preloading them in a laminar flow bench in a cleanroom will be largely dependent on wind conditions and airborne particles, whose composition and abundance can change on a very short time scale.

Lead. Most of the treatments tested in this study caused significant lead contamination. Treatments that resulted in significant lead contamination were highly variable, with some replicates showing little or no contamination and others exceeding 300% of levels measured using the complete clean protocol.

Several steps appeared to contribute low or even negligible levels of contamination artifacts, at least in the few samples we tested. First, using only a single acid bath and even merely acid-rinsing filter holders appeared to be sufficient to maintain low levels of Pb contamination. However, these steps need to be taken with caution. The single acid bath used was routinely monitored for Pb and Cd and was changed when levels reach 8 $\mu\text{g/L}$ Pb or 2 $\mu\text{g/L}$ Cd. In addition, Teflon filter holders were used that had been exhaustively cleaned on many previous occasions and they were rinsed in a class 100 clean room with trace metal grade acid. A second low-contamination alternative—acidification with reagent grade acid—only caused a slight increase in Pb levels. This

Table 3. Reproducibility of Individual Conventional Steps (Quinnipiac River)

treatment	% of sample values					
	Pb		Cd		Cu	
	Diss.	Part.	Diss.	Part.	Diss.	Part.
bottles						
high-density polyethylene	19	n/a ^a	29	n/a	12	n/a
polypropylene	12	n/a	46	n/a	13	n/a
single acid bath	16	n/a	45	n/a	14	n/a
cleaned in conventional lab	30	n/a	11	n/a	15	n/a
acid rinsed only	22	n/a	40	n/a	23	n/a
noncleaned	11	n/a	65	n/a	28	n/a
commercially cleaned (I-Chem)	20	n/a	16	n/a	8	n/a
stored empty	20	n/a	91	n/a	63	n/a
filtration						
noncleaned filters	6	37	12	10	5	43
holders cleaned in conventional lab	25	9	5	5	10	35
acid-rinsed holders	8	6	17	25	7	50
filters changed in the field	5	17	17	18	29	26
Millipore Durapore	9	6	17	27	12	11
Millipore MF (polycarbonate)	31	20	35	33	30	32
sample collection						
filters transported without bag	30	14	20	67	33	34
no gloves worn	19	21	10	8	22	7
sample preservation						
acidified with reagent grade acid	15	14	22	55	100	110
preacidified bottles	28	n/a	80	n/a	71	n/a
acidified in conventional lab	14	6	14	43	7	26
sample preconcentration						
in glassware	8	27	13	28	50	66
in conventional fume hood	41	6	23	36	10	30
with reagent grade acid	16	8	25	65	8	33

^a n/a, not applicable.

Table 4. Reproducibility of Controls

river	% of control values							
	Pb		Cd		Cu		Ag	
	Diss.	Part.	Diss.	Part.	Diss.	Part.	Diss.	Part.
Quinnipiac	22	11	26	21	6	10	n/a ^a	n/a
Naugatuck	11	6	9	6	5	8	9	9

^a n/a, not applicable.

probably results from comparatively low levels of metal in the acid and the small volume being used for preservation (2 mL of HNO₃/L). Furthermore, different batches of acid contain very different levels of contaminant metals. Moreover, there is no assurance that artifacts would remain consistently low for a given step when repeated in other laboratories. Researchers are cautioned to evaluate carefully any protocol step in their own laboratory before substituting a conventional for a clean method. It is also advisable to run blanks whenever a new batch of acid, filters, etc., is used.

While the amount of artifact contamination introduced by any individual conventional step might be tolerable, the total contributed by all steps is unacceptably large. For example, the average combination of conventional steps in Table 2 would cause dissolved Pb levels to be over 1 order of magnitude greater than the true value, assuming contamination from all steps is simply additive. This large error occurs even though dissolved Pb in the Quinnipiac is already high compared to many sites. Actual analysis by conventional techniques would include more than the sum of contaminants added by the individual treatments tested, since they do not encompass the entirety of the collection/treatment/analysis sequence.

Cadmium. Cadmium contamination artifacts were significant in the same number of treatment steps (23/35) as were lead artifacts (24/35). Significant is defined arbitrarily here as any step whose difference from 100% was greater than the RSD listed in Table 4 for the sum of all control steps for the given metal. Treatments that showed significant Cd contamination resulted in higher average contamination levels than were documented for Pb (Cd 300%, *N* = 23; Pb 200%, *N* = 24). (Averaging all steps, including noncontributing ones, the values are slightly lower: Cd 250%; Pb 170%.)

Copper. Copper contamination was significantly different from controls for the same number of treatments (23/35) but in general represented a smaller percentage of the control values than did contamination by the other metals (average 141%, *N* = 23). This is due to Cu's high aqueous concentrations, which help mute the effect of the comparatively small amounts of contamination introduced by the treatments. Nevertheless, the sum of all contaminant-contributing steps would cause errors of *factors* of 4 and 5 times for dissolved and particulate Cu, respectively.

Silver. Silver contamination artifacts in the Naugatuck were significant in only one replicate in the glass evaporative concentration step. Still, the full range of sampling and analytical steps was not tested for this metal, and the untested steps may introduce significant artifacts. Nevertheless, Quinnipiac River data not shown in Table 2 indicate that the sum of Ag contamination artifacts is routinely near our detection limit of 1 ng/L. These findings suggest that the potential contamination levels for silver are very low for virtually all of the treatments used in this study. Some of the precautions that are necessary for the measurement of more abundant metals, such as lead and cadmium, may not be necessary for the measurement of silver at contaminated sites.

CONCLUSIONS

Contamination at the nanogram or low-microgram per liter levels may not be important if the only goal is to test compliance with regulations whose limits are substantially higher than 1 $\mu\text{g/L}$ (e.g., Pb in drinking water is limited to 15 $\mu\text{g/L}$). However, it may not be possible to document trends, or to investigate processes that control transport and fate, unless reliable measurements can be made at true ambient concentrations, which are typically much less than 1 $\mu\text{g/L}$. For this reason, clean protocol steps cannot be confidently replaced with any of the alternative steps tested in this investigation if the goal is to determine absolute levels of lead, cadmium, or copper in water samples. Contrary to

our expectation, it does not seem possible to design streamlined clean protocols for measurement of these metals in water samples, even in polluted water bodies.

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