UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

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OFFICE OF
WATER

MEMORANDUM

SUBJECT: Recent Concerns About USGS Data for Selected Metals

FROM: James F. Pendergast, Acting Chief
Water Quality and Industrial Permits Branch (EN-336)

TO: Regional NPDES Permits Branch Chiefs (I-X)

We recently learned that the U. S. Geological Survey (USGS) historical ambient monitoring information for arsenic, boron, beryllium, cadmium, chromium, copper, lead, and zinc may be overstated and are no longer supported by USGS. For this reason, we recommend that you and the States in your Region do not use these data in establishing NPDES permit limits.

USGS recently briefed representatives of the Office of Water on the USGS ambient monitoring program. During the briefing, USGS explained that it now believes that its historical river monitoring data for the above listed eight metals are too high due to trace level contamination of the sampling and field collection apparatus.

Some investigators have started using ultra-clean samplers, filters, and containers, and have found much lower ambient concentrations for some elements than were reported in USGS reports. I have enclosed a copy of the USGS handout which compared their data for the Mississippi River to data from other investigators; this comparison shows that some ambient measurements using ultra-clean methods were considerably lower than measurements using existing methods. A critique of the USGS data was also published in the June 1991 issue of the American Chemical Society journal Environmental Science and Technology.

USGS is now working on protocols for using the newer ultra-clean methods in its sampling, and will take a closer look at its database to see if there are similar problems in lakes and with other compounds or elements.

Attachment

David Rickert USGS
December 12, 1991

CONCERNS ABOUT DISSOLVED TRACE-ELEMENT DATA

- About 15 years ago, the oceanographic community began to develop so-called ultra-clean techniques for cleaning samplers, filter apparatus, and containers for use in dissolved trace-element work. In North America, these techniques were then applied to the Great Lakes, but were not widely implemented in rivers. It is probable that most dissolved trace-element data collected on rivers before 1985 include contamination. To date, no large-scale program in the U.S. has used the ultra-clean technology.

- New research studies by USGS, university scientists, and Environment Canada suggest that most dissolved trace-element results in U.S. data bases (and throughout the world) are contaminated, primarily by sample collection and field processing activities.

- The new results (see Table 1) show that dissolved trace-element concentrations are low and in the same range in the Mississippi River, 13 east coast rivers, the St. Lawrence River, and streams of the Canadian Shield. The actual concentrations are at the parts-per-trillion (ppt or nanograms/liter) level:
  - 10's of ppt for cadmium and lead
  - High 100's ppt for zinc and copper
  - Around 1,000 ppt (1 part per billion) for nickel

- USGS evaluation of operational methods to collect trace element data included two 1990 studies: (a) a Blank Sample Study, and (b) a Mississippi River Methods Comparison Study.

- Data from the two studies were evaluated producing the following conclusions:
  1) **Noncontaminated or minimally contaminated**--barium, calcium, cobalt, lithium, magnesium, molybdenum, nickel, sodium, silicon, strontium, uranium, and vanadium.

  2) **Significantly contaminated**--arsenic, boron, beryllium, cadmium, chromium, copper, lead, and zinc. From other studies and lines of evidence, the mercury data base is known to contain contaminated results.

  3) **Signficantly different from NRP data, but the differences may result largely from filtration artifacts, rather than contamination**--alumium, iron, and manganese.

  4) **As yet undetermined**--selenium and silver.

- As a result, the USGS:
  1) Has discontinued the contaminated elements from NASQAN and Benchmark.
  2) Is developing a small capacity for ppt analyses in the National Water Quality Laboratory. (special 1,000 [illegible] room [illegible]
  3) Is evaluating sampling equipment to identify equipment adequate for ppb level work. (current equip cannot be used. some need cleaning others unrecoverable
  4) Is developing guidelines for proper quality assurance of all trace element data.
  5) Is writing protocols for ppt and ppb sample collection, processing and analysis.
  6) Is evaluating methods for collection, processing, and analysis of suspended sediment, bed sediment, and tissue.
  7) Is defining experiments to determine if analyte loss is a concern for ppt work. (does cleaning result in more solubility of instrument to absorb the traces)
  8) Will evaluate the historic database to the extent possible.

  need to look at lakes & streams

- The future may include a significantly reduced number of analyses for dissolved trace elements in operational programs.
  1) PPB
  2) PPT

REFERENCES FOR TABLE 1

Lum, K.R., Kaiser, K.L.E., and Jaskot, C., 1991, Distribution and fluxes of metals in the St. Lawrence River from the outflow of Lake Ontario to Quebec City: Aquatic Sciences, v. 53, no. 1, 19 p.

Shiller, A.M., and Boyle, E.A., 1987, Variability of dissolved trace metals in the Mississippi River: Geochimica et Cosmochimica. Acta, v. 51, p. 3273-3277.

Windom, H.L., Byrd, J.T., Smith, R.G., Jr., and Huan, F., 1991, Inadequacy of NASQAN data for assessing metal trends in the nation's rivers: Environmental Science and Technology, v. 25, no. 6, p. 1137-1142.

Table 1.--Concentrations of Dissolved Elements from Selected Investigations
[Parts per trillion (ng/L)]

Constituent	Statistics	USGS Mississippi River Methods Comparison Study: District[a] (N=9)	USGS Mississippi River Methods Comparison Study: Taylor[a] (N=10)	USGS Mississippi River Methods Comparison Study: Shiller[b] (N=9)	Mississippi River: Shiller & Boyle (N=7)	Eastern U.S. Rivers: Windom et al. (N=36)	St. Lawrence River: Lum et al. (N=52)	Streams & Lakes, Bruce Peninsula[c]: McCrea (N=33)
Cd	median	1,200	<100	14	16	-	-	<100
	mean	2,600-3,000 [d]	<100	16	13 [e]	11 [f]	17 [g]	<100
Cr	median	1,100	<200		83			<200
	mean	950-1,100 [d]	40-200 [d]		73 [e]			20-200 [d]
Cu	median	4,600	1,700	1,600	1,300	-	-	500
	mean	4,500-5,600 [d]	1,800	1,600	1,500 [e]	1,100 [f]	580 [g]	500
Ni	median	1,800	-	1,500	1,400		-	<200
	mean	1,800	-	1,700	1,400 [e]		770 [g]	100-200 [d]
Pb	median	<500	<60			-	-	<200
	mean	1,900-2,300 [d]	10-60 [d]			23 [f]	18 [g]	10-200 [d]
Zn	median	5,300	900	190	240	-	-	
	mean	6,100-6,700 [d]	980	290	200 [e]	850 [f]	550 [g]	
Al	median	-	9,800	4,500				
	mean	-	8,500	4,000				
Fe	median	24,000	-	1,700	1,700			
	mean	45,000	-	2,600	1,700 [e]			

a) Depth- and width-integrated samples. The District samples were collected and processed by District crews and analyzed at the National Water Quality Laboratory. Members of Howard Taylor's USGS National Research Program project collected, processed, and analyzed the "Taylor" samples.
b) Grab samples.
c) Whole water samples with low suspended sediment content.
d) Data base contained "less than" values. The reported mean was calculated twice, once with the "less than" value(s) set to zero and again with the "less than" values set at the reporting limit.
e) Discharge weighted means.
f) Unweighted mean of two sampling campaigns for 18 U.S. east coast rivers.
g) Estimated mean based on average concentration for each site and the number of samples at each site.