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RECEIVED
CLERK'S OFFICE

MAR 28 2002

STATE OF ILLINOIS
Pollution Control Board

March 25, 2002

Dorothy Gunn, Clerk
Illinois Pollution Control Board
100 W. Randolph Street, Suite 11-500
Chicago, Illinois 60601

P.C. #16

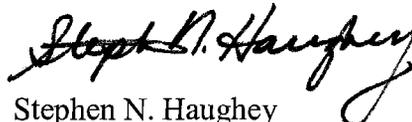
Re: R 02-011/Rulemaking/Water/Comments of DeKalb Sanitary District

Dear Ms. Dunn:

Enclosed please find for filing in the above-referenced docket the original and ten copies of the comments of DeKalb Sanitary District in support of IEPA's proposed triennial review rulemaking. Please stamp the original and all copies and return the extra copy to me in the enclosed, self-addressed, postage-prepaid envelope for our files. Thank you for your assistance in this matter. Please contact me if there are any questions about this filing.

Very truly yours,

FROST BROWN TODD LLC



Stephen N. Haughey
Outside Counsel to the District

Enclosures

cc: Marie E. Tipsord, Hearing Officer (w/encl.)
Mathew Dunn, Illinois Attorney General's Office (w/encl.)
Office of Legal Services, IDNR (w/encl.)
IEPA, Division of Legal Counsel
Service List of Participants (w/encl.)

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ORIGINAL

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BEFORE THE ILLINOIS POLLUTION CONTROL BOARD MAR 28 2002

STATE OF ILLINOIS

R 02-01 **Pollution Control Board**
(Rulemaking – Water)

In the matter of:)

WATER QUALITY TRIENNIAL REVIEW:)
Amendments to 35 Ill. Adm. Code 302.208(e)-(g),)
302.504(a), 302.575(d), 303.444, 309.141(h), and)
Proposed 35 Ill. Adm. Code 301.267, 301.313,)
301.413, 304.120, and 309.157)

***Comments Of DeKalb Sanitary District
In Support Of IEPA's Proposed
Water Quality Standards Rulemaking***

TO:

Dorothy Gunn
Clerk
Illinois Pollution Control Board
100 W. Randolph Street, Suite 11-500
Chicago, Illinois 60601

Office of Legal Services
Illinois Department of Natural Resources
524 S. Second Street
Springfield, Illinois 62701-1787

Mathew Dunn
Illinois Attorney General's Office
Environmental Control Division
James R. Thompson Center
100 W. Randolph Street
Chicago, Illinois 60601

Illinois Environmental Protection Agency
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1021 N. Grand Avenue East
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Springfield, Illinois 62794-9276

Marie E. Tipsord
Hearing Officer
Illinois Pollution Control Board
100 W. Randolph Street, Suite 11-500
Chicago, Illinois 60601

Please take notice that the DeKalb Sanitary District (hereinafter "DeKalb" or the "District") hereby offers the following comments in support of IEPA's proposed revisions to Illinois' water quality standards. The proposed revisions are part of the State's triennial review of its water quality standards as required by the federal Clean Water Act.

A. BACKGROUND.

Among the revisions proposed by the IEPA to Illinois' water quality standards and implementing rules is the proposed conversion of Illinois' water quality criteria for certain hardness-based metals, including copper, from the present total recoverable form of the metal to a dissolved form of the metal, and proposed rules establishing a procedure for developing water quality based permit limits for these metals in the federally-required total recoverable form using default or site-specific conversion factors for the proposed dissolved metals criteria. IEPA's rules presently allow the use of default or site-specific conversion factors from total recoverable to dissolved form of the metals only in the Lake Michigan basin. *See* 35 Ill. Adm. Code 309.141(h)(3). The proposed revisions would expand the use of these factors statewide. The proposed revisions are set forth in Title 35, Subtitle C, Chapter I, Parts 301, 302, 304, and 309 of the Illinois Administrative Code. The specific sections affected are 301.267, 301.313, 301.413, 302.208, 302.504, 309.141, and 309.157.

B. NATURE OF DEKALB'S INTEREST.

The DeKalb Sanitary District was incorporated in 1928. Its service area is a population of approximately 45,000 people in the City of DeKalb, the Town of Cortland, nearby Northern Illinois University, and a small group of commercial and industrial customers. The District employs 15 people. The District owns and operates a medium-sized, trickling filter, activated sludge biological publicly-owned treatment works ("POTW") that has a mean annual average daily flow of approximately 5.95 mgd and a design average daily flow capacity of 8.63 mgd.

Treated effluent from the POTW is discharged into the South Branch of the Kishwaukee River pursuant to the terms and conditions of an NPDES permit issued in 1995 by the Division of Water Pollution Control for IEPA, which permit was renewed in November 2000. The

renewal permit contains daily maximum and 30-day monthly average, water quality-based effluent limitations (“WQBELs”) for copper of 0.056 mg/l [56 parts per billion (“ppb”)] and 0.034 mg/l [34 ppb], respectively.

In early 2000 the District undertook an evaluation of the sources of copper in its collection system and determined that more than 95% of the copper coming to the POTW for treatment was from leaching of residential copper plumbing lines due in part to water softening systems used to offset exceptionally hard water found in the area. Because of the aesthetic problems associated with hard water, a substantial percentage of homes in the service area have private water softeners. These softeners tend to increase the corrosivity of the treated water during the removal of calcium, magnesium, and sodium-based minerals that contribute to the hardness of the water and its aesthetic problems. The historic use of private water softeners in the service area makes it very difficult for the District to limit copper from entering the sanitary collection system for transport to the District’s POTW.

As part of its efforts to consistently achieve its stringent copper WQBELs, the District engaged its engineering consultants to investigate the potential costs of modifying the wastewater treatment processes at the POTW to remove additional copper from the influent. The District’s engineering consultants estimated that the costs to modify the POTW in order to remove additional low ppb levels of copper from the influent would be more than \$500,000 in capital cost, with annual O&M costs of more than \$600,000.

Based on the primary source of the copper and the substantial expense to consistently remove low ppb levels of copper from the effluent produced by a conventional biological trickling filter, activated sludge plant, the District and its engineers decided, with the support of representatives for IEPA’s Division of Water Pollution Control, to submit a petition to the IPCB

for a site-specific, adjusted water quality standard for copper using U.S. EPA's dissolved metals translator guidance entitled: “The Metals Translator: Guidance for Calculating a Total Recoverable Permit Limit from a Dissolved Criterion,” EPA 823-B-96-007, June 1996 (hereinafter “U.S. EPA’s Metals Translator Guidance”). That petition was filed with the IPCB in mid August 2000, and is captioned as “*In the matter of: Petition of DeKalb Sanitary District for an Adjusted Standard from 35 Ill. Adm. Code 302.208(E)*,” Docket No. AS 01-3 (Adjusted Standard – Water).” The petition is pending before the IPCB.

The portion of IEPA’s proposed rulemaking relating to dissolved metals is premised upon the same U.S. EPA guidance document that was used by the District to support its petition for adjusted standard. If the IEPA’s proposed rulemaking is approved by the IPCB, it would moot DeKalb’s petition in that the District would no longer need to complete a formal petition process before the IPCB in order to obtain adjusted WQBELs for copper based on the total to dissolved ratio of copper in its treated effluent, but would instead, after the IPCB approves the proposed revisions, file a request with the IEPA to modify the District’s permit based on the new rules. Thus, DeKalb has a substantial interest in the outcome of the IEPA’s proposed rulemaking.

C. THE APPROVAL OF IEPA’S PROPOSED RULEMAKING IS IN THE BEST INTEREST OF ILLINOIS’ SEWER AUTHORITIES GENERALLY.

As a general rule, biological activated sludge wastewater treatment works are designed primarily to remove the conventional pollutants found in domestic sewage, *i.e.*, ammonia, organic loading in the form of CBOD, suspended solids, and fecal coliform bacteria. A well-designed and operated POTW with at least secondary treatment technology typically removes greater than 90-95% of the influent loadings for these parameters. On the other hand, biological wastewater treatment works typically remove no more than an average of 60-70% of the influent

loadings of most metals, including copper, and the removals thereof are almost exclusively through adsorption or uptake by the biomass of the metals and transfer thereof into the sludge generated at the works, rather than through direct treatment processes. See Exhibit A hereto. The District's average removal rate for copper is higher than the average at 78%, but even at that level the District has difficulty consistently meeting the current QBELs for copper in its permit.

In order to meet low ppb QBELs for metals, including copper, a POTW will typically look first to the possibility of reducing the influent loadings by imposing pretreatment limits on the largest categories of customers discharging copper into the collection system. Such step can often be successful in reducing influent copper loadings when the primary sources of copper are industrial and commercial dischargers. These sources can usually be retrofitted cost-effectively with small treatment systems such as dissolved air floatation (DAF) units, chemical addition/precipitation/settling units, and ion exchange columns. However, the area served by many POTWs, including DeKalb, often has a very small industrial and commercial base, typically contributing less than 5% of the copper influent loading to the POTW. Where the predominant source of copper is leaching from residential plumbing, enhanced by water softening units used to combat naturally occurring hard water, as is the case in DeKalb, the sewer authority cannot readily impose pretreatment limits and control systems on its local residents.

Without a readily available means to significantly reduce the influent loadings of copper, many POTWs in the same situation as DeKalb face the unpleasant alternative of incurring substantial capital expenditures and large annual O&M costs to modify existing wastewater treatment equipment in order to remove additional low ppb levels of copper from the final effluent. The District believes that such additional costs are unnecessary and unjustified to

remove such low concentrations of copper that are already well below applicable state and federal drinking water standards and that, for the reasons demonstrated below, do not present a threat to aquatic species.

D. U.S. EPA’S DISSOLVED METALS TRANSLATOR GUIDANCE OR ITS EQUIVALENT IS WIDELY ACCEPTED IN THE SCIENTIFIC COMMUNITY, HAS BEEN ADOPTED BY ALL NEIGHBORING STATES, AND CURRENTLY IS IN USE IN ILLINOIS AS PART OF THE EXISTING NPDES PERMIT RULES FOR POINT SOURCE DISCHARGES INTO THE LAKE MICHIGAN BASIN.

On October 1, 1993, U.S. EPA’s Office of Water issued a policy memorandum entitled “Office of Water Policy and Technical Guidance on Interpretation and Implementation of Aquatic Life Metals Criteria.” A copy of the policy memorandum is enclosed as Exhibit B hereto. In that policy memorandum, U.S. EPA stated as follows:

It is now the policy of the Office of Water that the use of dissolved metal to set and measure compliance with water quality standards is the recommended approach, because dissolved metal more closely approximates the bioavailable fraction of metal in the water column than does total recoverable metal. *This conclusion regarding metals bioavailability is supported by a majority of the scientific community within and outside the Agency.* One reason is that the primary mechanism for water column toxicity is adsorption at the gill surface, which requires metals to be in the dissolved form.

See Exhibit B at p.2 (emphasis added). The policy memorandum states that, although the particulate form of metals may contribute somewhat to the toxicity of metals, the toxicity of particulate metals is dramatically less than that of the dissolved form of the metal. *Id.* The policy memorandum further states that the toxicity tests used to develop metals water quality criteria (Illinois developed its state water quality criteria for metals based on the federal water quality criteria) involve the addition of simple metal salts to pure water, resulting in overly conservative water quality criteria based on the dissolved form of the metal salts in the water. *Id.*

In addition, due to the presence of significance concentrations of binding agents in

virtually all treated discharges and in most ambient waters (*e.g.*, calcium, magnesium, and sodium minerals found in hard water, and naturally occurring humic compounds found in all receiving waters), the metals in effluent discharges and in ambient waters are much less bioavailable to aquatic species than the conditions under which the applicable water quality criteria were developed. *Id.*

The policy memorandum concludes by recommending that states' water quality standards for metals be based on the dissolved criteria, and that where states' existing water quality standards are based on the dissolved form of the metal that a total recoverable to dissolved conversion factor be employed. *See* Exhibit B at p.3. The October 1993 policy memorandum was subsequently incorporated within and replaced by U.S. EPA's June 1996 Metals Translator: Guidance, a copy of which was submitted by IEPA in support of its proposed rulemaking.

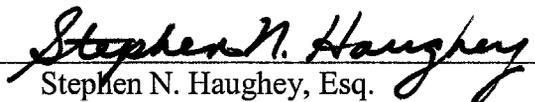
The 1996 Metals Translator Guidance or its functional equivalent has been adopted by all states that border the Great Lakes as part of the implementation of the 1995 federal Great Lakes Initiative. In Illinois, a rule permitting the use of dissolved metals translators has already been promulgated for point source discharges to streams flowing into Lake Michigan. *See* 35 Ill. Adm. Code 309.141(h)(3). ***IEPA's proposed rulemaking seeks merely to expand the use of dissolved metals translators from the Lake Michigan basin to all basins in the State of Illinois.*** Compare proposed amended 35 Ill. Adm. Code 309.141(h)(3) (deleting its limited application to the Lake Michigan basin) *with* proposed new 35 Ill. Adm. Code 309.157 (transferring its application to the general statewide NPDES rules). In other Great Lakes states, including Michigan, Wisconsin, Ohio, and New York, the use of dissolved metals translators has already been adopted for the entire state. Upon information and belief, the federal guidance or its equivalent has been adopted in many other non-Great Lakes states.

E. CONCLUSION.

The DeKalb Sanitary District strongly supports IEPA's proposed expansion of the use of default and site-specific dissolved metals translators from the Lake Michigan basin to all basins in the State of Illinois. The applicability of dissolved metals translators was developed by U.S. EPA, the agency that developed the recommended metals water quality criteria upon which Illinois has modeled its current metals water quality criteria. U.S. EPA's recommendation to the states to allow the use of such dissolved metals translators has been widely supported in the scientific community, and is already incorporated within Illinois' water quality standards, *albeit* at the present time only for permit holders discharging into the Lake Michigan basin. There is no logical reason to reject the expansion of the use of such translators to all permit holders in Illinois.

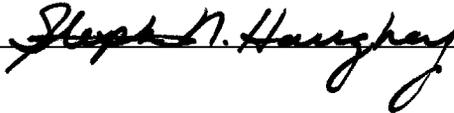
Respectfully submitted,

DEKALB SANITARY DISTRICT

By 
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Counsel to the DeKalb Sanitary District

CERTIFICATE OF SERVICE

In accordance with 35 Ill. Adm. Code 101.304 and 102.400, I hereby certify that a copy of the foregoing comments was served by first class regular U.S. mail to all participants in this proceeding, based on the current service list as of March 25, 2002 (copy attached).



SERVICE LIST OF "PARTICIPANTS" AS OF MARCH 25, 2002

Lname	fname	company	address	citystate	Zip
Callahan	Mike	Bloomington Normal Water Reclamation District	PO Box 3307	Bloomington, Illinois	61702-3307
Cox	Larry	Downers Grove Sanitary District	2710 Curtiss Street	Downers Grove, Illinois	60515
Daffield	Dennis	Department of Public Works City of Joliet	921 E. Washington Street	Joliet, Illinois	60433
Ettinger	Albert	Environmental Law & Policy Center	35 E. Wacker Drive, Suite 1300	Chicago, Illinois	60601-2110
Frede	Lisa M.	Chemical Industry Council	9801 W. Higgins Rd, Suite 515	Rosemont, Illinois	60018
Gunn	Dorothy	Clerk, Pollution Control Board	100 West Randolph, Suite 11-500	Chicago, Illinois	60601
Harrington	James T.	Ross & Hardies	150 North Michigan, Suite 2500	Chicago, Illinois	60601
Hill	Ron	Metropolitan Water Reclamation District	100 East Erie	Chicago, Illinois	60611
Hodge	Katherine	Hodge Dwyer Zeman	3150 Roland Avenue, PO Box 5776	Springfield, Illinois	62705-5776
Howard	Margaret P.	Hedinger & Howard	1225 S. Sixth Street	Springfield, Illinois	62703
Messina	Robert A.	Illinois Environmental Regulatory Group	215 East Adams Street	Springfield, Illinois	62701
Muth	Tom	Fox Metro Water Reclamation District	682 State Route 31	Oswego, Illinois	60543
Polls	Irwin	Metropolitan Water Reclamation, Dist. Of Chicago	6001 West	Cicero, Illinois	60804
Sofat	Sanjay	Illinois Environmental Protection Agency	1021 North Grand Ave. East	Springfield, Illinois	62794-9276
Tipsord	Marie	Attorney, Pollution Control Board	100 West Randolph, Suite 11-500	Chicago, Illinois	60601

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THE PHYSICO-CHEMICAL SPECIATION OF Cd, Pb, Cu, Fe AND Mn IN THE FINAL EFFLUENT OF A SEWAGE TREATMENT WORKS AND ITS IMPACT ON SPECIATION IN THE RECEIVING RIVER



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(Received July 1980)

Abstract—A scheme for the speciation of metals in freshwaters has been applied to the analysis of the final effluent from a sewage treatment plant and to the receiving river upstream and downstream of the effluent outfall. The treatment plant was selected because of the high influent and effluent concentrations of Cd. The metal speciation patterns in the effluent are interpreted primarily in terms of organic interactions, which appear to be exerting a solubilizing effect on Cd and Cu, but not on the Pb and Fe which are principally associated with the particulate size fraction ($>12 \mu\text{m}$). The influx of metals with the sewage effluent alters the speciation pattern in the river. A large part of the Cd is added to the smallest size fraction ($<0.015 \mu\text{m}$). However, the major part of each metal, with the exception of Mn, is associated with the colloidal and particulate size fractions, thus minimising the immediate toxic significance to aquatic life.

INTRODUCTION

Sewage treatment plants receive effluents from both domestic and industrial sources, as well as intermittent influxes of stormwater runoff from highways and urban areas (Harrison & Laxen, 1981; Atkins & Hawley, 1978). All three sources produce effluents contaminated with heavy metals and some part of these metals will pass through the treatment plant to be discharged to surface waters (Lester *et al.*, 1979). There is a trend towards the greater use of sewage treatment plants to treat both industrial effluents and stormwater runoff. On the one hand, this development requires a better understanding of the role of treatment processes in metal abatement (Brown & Lester, 1979), whilst on the other, it focuses attention

on the effluents from sewage treatment plants as point sources of metal pollution (Harrison & Laxen, 1981).

The efficiency with which a sewage treatment plant retains influent metals will depend upon the physico-chemical forms of the metals and their response to the physical and biological treatment processes. In all treatment plants the initial stage is primary sedimentation, whereby larger solids are allowed to settle out. This is followed by either a biological filter or activated sludge process in order to digest the organic matter, succeeded by passage through a settling (humus) tank to reduce the residual solids loading before discharge. Typical data for retention of metals during these different processes are summarised in Table 1. It would appear that actual retention varies from plant to plant and within a plant from day to day. The recent work by Stoveland *et al.* (1979a) emphasises the importance of the metal speciation, and their findings may account for some of the variability in the retention efficiencies. They found that the

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Table 1. Removal efficiency for selected metals as a function of the treatment process

Metal	Removal (%)*		
	Primary sedimentation (Lester <i>et al.</i> , 1979)	Activated sludge (Brown & Lester, 1979)	Biological filter (Stones, 1977)
Cd	72 (60-83)†	50 (11-80)‡	
Cu	70 (50-95)	71 (55-93)	59
Pb	73 (66-82)	67 (43-89)	70
Fe		86 (72-97)	62
Mn		17 (6-28)	

* The data from the different references are not strictly comparable.

† Mean and range for 4 values.

‡ Mean and range of averages from 3 to 6 different studies.

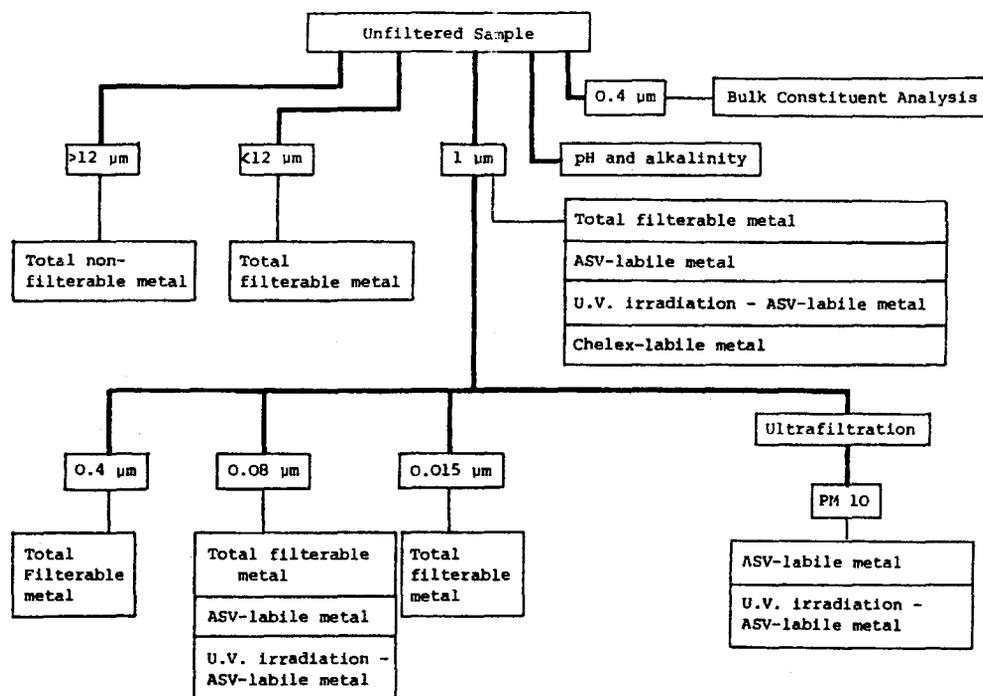


Fig. 1. Speciation scheme.

presence of the detergent builder, NTA, in the influent can reduce the efficiency of metal removal in the activated sludge process. Furthermore, they found that shock loading of NTA could mobilise some of the metals previously retained within the sludge (Stoveland *et al.*, 1979b). Such effects as these are important in relation to how much metal will find its way to the final effluent of a sewage treatment plant, but equally important, in terms of defining the impact of the discharge on the receiving water will be the speciation of the metals within the final effluent. This will determine the metal speciation in the receiving water, which in turn will determine both the immediate and potential toxic significance to aquatic life, as well as the mobility of the metals in the waterbody (Andrew *et al.*, 1977; Davies *et al.*, 1976; Waiwood & Beamish, 1978; Wagemann & Barica, 1979; Harrison & Laxen, 1980).

In spite of the now well recognised importance of defining the speciation of metals within a waterbody, in relation to both their mobility and their toxic effects, there is still considerable uncertainty as to the actual metal forms and their various interactions (Laxen & Harrison, 1977; Florence & Batley, 1980). This can be accounted for by a number of factors, including the wide range of possible physicochemical forms, the difficulty of defining the forms analytically and the low concentrations of the metals under consideration. A number of studies have examined certain aspects of metal speciation in freshwater samples (e.g. Chau & Lum-shue-chan, 1974; Beneš & Steinnes, 1975; Gardiner, 1976; Beneš *et al.*, 1979), but only one

reasonably comprehensive speciation scheme has been reported (Batley & Florence, 1976a,b). This scheme was developed principally for use with seawater samples and has unfortunately been shown to be of limited applicability to the study of most freshwaters (Laxen & Harrison, 1981a). We have however, recently developed a speciation scheme for freshwaters, based upon an initial size fractionation of the metal species, along the lines of the classification originally suggested by Stumm & Bilinski (1973) (Laxen & Harrison, 1981a) (Fig. 1).

In this paper we describe the application of our speciation scheme to the final effluent from a sewage treatment plant which uses the biological filter process, as well as to samples taken upstream and downstream of the effluent outfall. The particular sewage treatment plant examined was chosen because of the high cadmium loading in the raw sewage, a consequence of discharges from a plating works. In all, five metals were studied, Cd, Pb, Cu, Fe and Mn. The latter two were included principally because of their potential importance as metal scavengers, due to their tendency to form colloidal/particulate hydrous oxides (Stumm & Morgan, 1970; Mill, 1980), which have strong adsorption affinities for certain metals (Gadde & Laitinen, 1974).

EXPERIMENTAL

Speciation scheme

The detailed development and testing of the speciation scheme is described elsewhere (Laxen & Harrison, 1981a).

The size fractionation of the metal species was performed with Nuclepore filters of 12, 1.0, 0.4, 0.08 and 0.015 μm rated pore size in Amicon stirred cells (Model 52) and an Amicon PM10 ultrafilter (nominal molecular weight 10,000) in an Amicon Model 202 stirred cell, under nitrogen pressure. The filters and stirred cells were cleaned immediately before use with dilute HNO_3 and pre-treated with a $\text{Ca}(\text{NO}_3)_2$ solution to minimise adsorption losses. Tests showed such losses to be negligible.

Total metal concentrations were determined by flameless atomic absorption (Fe and Mn) and by ASV after u.v.-acid digestion (Cd, Pb and Cu). Non-filterable metal collected on the 12 μm filter was determined after successive HNO_3 and HClO_4 digestion. All concentrations were determined by the method of standard additions.

Further analyses were performed on certain filtrate fractions as follows: ASV-labile metal was determined at the natural pH of the sample, buffered with a $\text{CO}_2:\text{N}_2$ mixture. Analyses were performed with a hanging mercury drop electrode using a fresh drop for each deposition/stripping cycle. The metals Cd, Pb and Cu were deposited at -950 mV (vs SCE) and stripped at 5 mV s^{-1} in the differential pulse mode. The samples were titrated with a mixed metal standard to quantify the labile response and provide information on the state of metal complexation.

Chelex-labile metal was determined using Chelex-100 in the calcium form in a batch technique, 2 ml resin to 60 ml of sample for 48 h. The non-Chelex-labile metal was determined, as for total metals above, and the Chelex-labile fraction determined by difference.

Filtrates were exposed to u.v. irradiation at their natural pH for 8–12 h in quartz tubes and the ASV-labile metals then re-measured. Prior to u.v. irradiation the sample pH was adjusted to approx. pH 5.5–6 with HClO_4 to compensate for the increase in pH that occurred during irradiation. A brown precipitate was generally found after the u.v. irradiation, which is thought to be due to precipitation of organically stabilised hydrous iron oxide colloids (Laxen & Harrison, 1981a). There was a simultaneous loss of ASV-labile metal. It is thus not possible to quantify the non-labile organically bound metal fraction. The u.v. irradiation procedure does however provide qualitative information on the nature of any metal complexation (Laxen & Harrison, 1981a).

Standard methods were used to analyse the samples for their bulk constituents (*Standard Methods*, 1976). Suspended sediment concentrations refer however to material retained by a 0.4 μm Nuclepore filter. Total organic carbon was estimated from the u.v. absorbance at 254 nm on filtered samples, according to the relationship derived by Dobbs *et al.* (1972). The pH and alkalinity were measured on unfiltered portions of sample immediately on return to the laboratory, i.e. within 2–3 h of taking the sample.

Samples

The samples were collected in 5 l polythene containers pre-cleaned with 10% HNO_3 (Laxen & Harrison, 1981b) and rinsed with sample before filling. The sewage final effluent was taken from Barrowford sewage treatment plant at Nelson in Lancashire, on 18 February 1980, from the overflow of the final sedimentation (humus) tank. The flow of sewage through the treatment plant is split into two after the primary sedimentation and the sample was taken from what is known as line B. The effluent is discharged into a small river named Pendle Water. Samples were taken from this river on 4 March 1980, whilst the river flow was low following a dry spell. The samples were taken about 30 m upstream and approx. 100 m downstream of the effluent outfall at a point where mixing was complete. The flow at the downstream site was relatively turbulent in contrast to that at the upstream site.

RESULTS

Sewage effluent

The sample of final effluent was taken from a sewage treatment plant involving both primary sedimentation and secondary treatment by biological filtration. Following passage through the primary sedimentation tanks the effluent stream is split to pass through two sets of biological filters, A and B, each with their own final sedimentation (humus) tanks. The quality of the final effluent from the two streams A and B differs slightly (Table 2), due to a poorer performance of the final sedimentation tank B. The present sample was taken from this stream. It is apparent from the results in Table 2 that the sample taken for this study is representative of the final effluent from tank B (cf. pH, suspended solids, cadmium).

The speciation results for the effluent sample are presented in Table 3. A major part of the Cd (45%) is associated with the smallest size fraction (<0.015 μm) and most of this is probably both ASV and Chelex-labile. It is also apparent that some of the labile Cd must be derived from the colloidal size fraction. The ASV titration provides no indication of a residual non-labile complexation capacity for Cd, consistent with the strong labile signal in the original sample. There was no change in the stripping peak potential (E_p) following u.v. irradiation, the values remaining between -575 to -585 mV. A further feature of note is the association of a significant portion of the Cd with the 0.08–0.4 μm colloidal size fraction. This particular size fraction is also emphasised in the case of Cu and Fe but not for Pb. The Pb shows a particularly strong association with the larger size fraction material; 77% is greater than 0.4 μm , and only a small portion, 10%, is found in the smallest size fraction (<0.015 μm). There was a small ASV Pb signal at 410–430 mV in the various filtrate fractions. However, this was not quantified as there was a shift in the peak potential (E_p) during the titrations to 395–405 mV. This is indicative of a labile Pb complex in the original sample, although caution must be exercised in the interpretation of E_p shifts due to interference from organics (Brezonik *et al.*, 1976; Batley & Florence, 1976a,b), particularly in an organic-rich sewage effluent. The ASV titration curves for the three filtrate fractions (1 μm , 0.08 μm and PM10) were similar, showing a possible small residual complexation capacity for Pb (Fig. 2). However, after the addition of approx. 150 $\mu\text{g l}^{-1}$ Pb the sensitivity was progressively reduced.

The results for Cu reveal a strong association (47%) with the smallest size fraction (<0.015 μm) and much of this metal would appear to be Chelex-labile. The Cu is not, however, ASV-labile and there is a strong residual complexation capacity for the Cu, which is undiminished even in the PM10 ultrafiltrate, suggesting that ligands of relatively low molecular weight ($<10,000$ MW) are responsible for the non-labile complexation. The complexation capacity was almost

Table 2. Analyses of Barrowford sewage treatment plant effluents

Parameter	Final effluent B	Treatment plant average, Oct-Dec 1979*		
	18.2.80 10.30 h	Crude Sewage	Final Effluent A	Final Effluent B
Flow (m ³ s ⁻¹)		0.051 (0.028-0.081)†		
pH	6.9	7.0 (6.4-8.2)	6.7 (6.4-7.0)	6.8 (6.5-7.1)
Temp (°C)	7.5			
Specific conductance (μS)	510			
Suspended solids (mg l ⁻¹)	23	122 (44-224)	18 (10-29)	22 (10-34)
TOC (mg l ⁻¹)	13‡			
Alkalinity (as CaCO ₃) mg l ⁻¹	88			
Ca (mg l ⁻¹)	40			
Mg (mg l ⁻¹)	3.6			
Na (mg l ⁻¹)	4.9			
K (mg l ⁻¹)	9.1			
SO ₄ ²⁻ (mg l ⁻¹)	56			
Cl ⁻ (mg l ⁻¹)	59			
PO ₄ ³⁻ - P (mg l ⁻¹)	1.5			
NO ₃ ⁻ - N (mg l ⁻¹)		0.6 (0.2-1.8)	6.8 (2.3-14)	5.4 (2.3-11)
COD (mg l ⁻¹)		304 (106-580)	77 (43-138)	87 (37-134)
Cd (μg l ⁻¹)	139§	280 (70-1010)	80 (30-120)	110 (50-170)
Pb (μg l ⁻¹)	12	<10-100	<10-40	<10-40
Cu (μg l ⁻¹)	36	80 (10-290)	<10-50	<10-80
Fe (μg l ⁻¹)	693			
Mn (μg l ⁻¹)	77			

* North West Water Authority data, based on hourly samples, bulked for analysis, see text for difference between effluents A and B.

† Mean and range.

‡ Filtered sample.

§ Total metal concentrations.

entirely lost following u.v. irradiation providing evidence that the complexation was due to organic compounds of relatively low molecular weight.

The Fe is present principally in association with the particulate size fraction >12 μm (58%), the remainder being fairly evenly distributed among the other size fractions. Only 30 μg l⁻¹ (4%) of the Fe is found in the smallest size fraction (<0.015 μm) suggesting that it is not complexed to any significant extent with the lower molecular weight organics (less than approx. 300,000 MW). The Mn is found almost entirely (83%) in association with the smallest size fraction (<0.015 μm), but not all of this is Chelex-labile suggesting the existence of some very strong complexes.

River samples

The river samples were taken during a period of low flow, following 6 days of dry weather. Hence there was a rather small dilution capacity for the influx from the sewage treatment plant, of the order of 10-20-fold. The analyses of the two samples taken upstream and downstream of the sewage effluent outfall are shown in Table 4, together with the results from two stations operated by the North-West Water Authority (NWWA) 1.5 km upstream and downstream respectively of the Barrowford sewage treatment plant outfall. It should be noted that there is an additional effluent outfall about 500 m downstream of the sampling points used in this study, discharging

Table 3. Speciation of Cd, Pb, Cu, Fe and Mn in the sewage treatment plant final effluent. Sampled 18.2.80

Size fraction (μm)	Concentration (μg l ⁻¹)				
	Cd (%)	Pb (%)	Cu (%)	Fe (%)	Mn (%)
>12	28 (20)	6.3 (52)	11.5 (32)	405 (58)	10 (13)
1-12	5 (4)	0.4 (3)	—	58 (8)	—
0.4-1	—	2.7 (22)	—	43 (6)	—
0.08-0.4	34 (24)	1.6 (13)	5.1 (14)	101 (15)	—
0.015-0.08	10 (7)	—	2.2 (6)	56 (8)	3 (4)
<0.015	62 (45)	1.2 (10)	17.0 (47)	30 (4)	65 (83)
Sum total	139	12.2	35.8	693	77
ASV-labile*	80 (58)	NQ†	NQ		
Chelex-labile*	86 (62)	2.9 (24)	16.6 (46)	31 (4)	31 (40)

* 1 μm filtrate.

† NQ = not quantifiable.

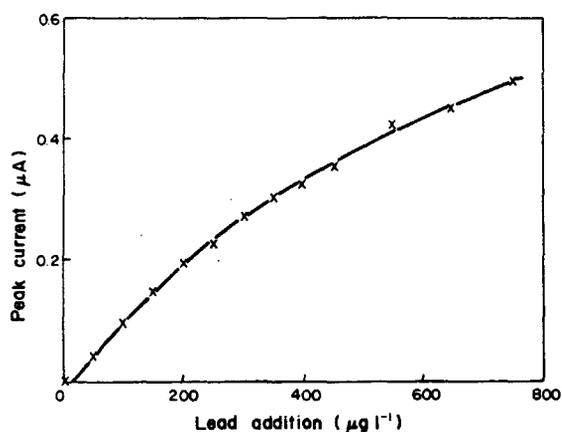


Fig. 2. ASV titration of $1 \mu\text{m}$ filtrate of the sewage effluent. Result for Pb.

effluent from the somewhat larger Nelson sewage treatment plant. This will be reflected in the analyses for the downstream NWWA sampling station (Table 4). The samples taken for this study were clearly fairly typical of the conditions found in Pendle Water. The low suspended solids concentrations are consistent with the low flow conditions, which resulted in a fairly slow moving body of water. In general terms, the water is one of moderate alkalinity and pH, with a relatively high organic loading. The influx of effluent from the Barrowford sewage treatment plant has a

marked effect on the Cd concentration in the river, increasing the total concentration from 0.3 to $9.0 \mu\text{g l}^{-1}$. There is also a significant increase in the Cu concentration. However, apart from these changes, there is not a great deal of difference between the composition of the two samples.

The speciation results for the two samples are set out in Tables 5 and 6. There is no obvious similarity in the distribution patterns of the five metals. Furthermore, there are significant differences between the metal distribution patterns above and below the outfall. Thus the speciation of each metal will be considered in turn.

Cadmium

Cd is present at a low concentration in the upstream sample and is found mostly in the $1\text{--}12 \mu\text{m}$ particulate size range (58%). A significant fraction is also associated with the smallest size fraction ($<0.015 \mu\text{m}$) and most or all of this is probably Chel-ex-labile. The ASV Cd signal in the original sample was more cathodic at -635 to -650 mV than the stripping potential developed towards the end of the titration, of -575 mV (after the addition of $160 \mu\text{g l}^{-1} \text{ Cd}$). The ASV titration also indicated a small residual complexation capacity in the $1 \mu\text{m}$ filtrate (Fig. 3) which was absent in the PM10 ultrafiltrate. The ASV labile Cd signal in the u.v. irradiated samples was constant throughout the titration between -585 and -590 mV . The ASV behaviour

Table 4. Analyses of Pendle water upstream and downstream of Barrowford sewage treatment plant outfall

Parameter	Sampled 4.3.80		Pendle water analyses, 1976-1980*	
	Upstream 10.05 h	Downstream 10.00 h	Upstream (approx. 1.5 km)	Downstream (approx. 1.5 km)
Flow ($\text{m}^3 \text{ s}^{-1}$)				3.1 (0.5-15)‡
pH	7.7	7.6	7.5 (7.0-8.4)†	7.4 (6.9-8.2)
Temp ($^{\circ}\text{C}$)	3	3		
Specific conductance (μS)	367	380		
Suspended solids (mg l^{-1})	4.6	5.4	31 (5-285)	33 (5-309)
TOC (mg l^{-1})	6.0§	6.4		
Alkalinity (as CaCO_3) (mg l^{-1})	90	91	82 (40-160)	79 (43-129)
Ca (mg l^{-1})	44	46		
Mg (mg l^{-1})	5.0	8.5		
Na (mg l^{-1})	24	26		
K (mg l^{-1})	3.6	4.1		
SO_4^{2-} (mg l^{-1})	56	51		
Cl^- (mg l^{-1})	39	34	39 (12-70)	44 (15-116)
$\text{PO}_4^{3-} - \text{P}$ (mg l^{-1})	<0.2	<0.2	0.35 (0.05-1.1)	1.1 (0.1-3.5)
$\text{NO}_3^- - \text{N}$ (mg l^{-1})			2.2 (1.1-3.8)	3.7 (1.3-6.8)
COD (mg l^{-1})			28 (13-60)	37 (18-74)
Cd ($\mu\text{g l}^{-1}$)	0.31¶	9.0		
Pb ($\mu\text{g l}^{-1}$)	1.8	2.1		
Cu ($\mu\text{g l}^{-1}$)	3.8	6.5		
Fe ($\mu\text{g l}^{-1}$)	830	841		
Mn ($\mu\text{g l}^{-1}$)	116	113		

* North West Water Authority data, 27 and 28 spot samples respectively.

† Mean and range.

‡ Flow measured 3 km downstream.

§ Filtered sample.

¶ Total metal concentrations.

Table 5. Speciation of Cd, Pb, Cu, Fe and Mn in Pendle water upstream of the sewage outfall

Size fraction (μm)	Concentration ($\mu\text{g l}^{-1}$)				
	Cd (%)	Pb (%)	Cu (%)	Fe (%)	Mn (%)
>12	0.01 (3)	0.40 (22)	0.15 (4)	59 (7)	2 (2)
1-12	0.18 (58)	0.44 (24)	0.89 (24)	235 (28)	—
0.4-1	0.02 (6)	0.08 (4)	0.28 (7)	180 (22)	2 (2)
0.08-0.4	0.02 (6)	0.53 (29)	0.71 (19)	342 (41)	4 (3)
0.015-0.08	—	0.03 (2)	0.63 (17)	—	4 (3)
<0.015	<u>0.08 (26)</u>	<u>0.32 (18)</u>	<u>1.12 (30)</u>	<u>14 (2)</u>	<u>104 (90)</u>
Sum total	0.31	1.80	3.78	830	116
ASV-labile*	NQ†	NQ	NQ		
Chelex-labile*	0.09 (29)	0.00 (0)	0.56 (15)	80 (10)	110 (95)

* 1 μm filtrate.

† NQ = not quantifiable.

suggests the presence of a labile organic complex, together with a residual non-labile complexation capacity associated with the colloidal size range.

In the downstream sample a major part of the Cd (44%) is associated with the smallest size fraction. A significant amount is also associated with the 0.015-0.08 μm colloidal size fraction, whereas this size fraction had no Cd in the upstream sample. The predominance of the 1-12 μm fraction is lost, but this is not due to a loss of Cd from this size fraction but rather to the addition of Cd to the other size fractions (Fig. 4). It is evident from Fig. 4 that the Cd influx with the sewage effluent has a major impact on the smallest size fraction. Not all of this Cd in the smallest size fraction is labile. The ASV titration of the 1 μm filtrate provides no indication of any residual complexation capacity for Cd.

Lead

In the upstream sample a smaller proportion of the Pb (18%) is found in the smallest size fraction than is the case with Cd (26%) and Cu (30%). The major

proportion of the Pb is in the particulate (46%) and the 0.08 to 0.4 μm colloidal (29%) size ranges. None of the lead appears to be Chelex-labile. There is however a small ASV-labile response at -480 to -490 mV, which is 60-70 mV more cathodic than the Pb response towards the end of the titration. The ASV titration indicates a residual complexation capacity for Pb (Fig. 5), which is largely removed by filtration through the PMIO ultrafilter.

The distribution pattern below the outfall shows an increase in the lead concentration in the colloidal size range, but significantly not in the 0.08-0.4 μm fraction which predominated in the upstream sample (Fig. 6). The Pb concentration below the outfall is only slightly increased but there is a significant shift from the 1-12 μm size fraction to the >12 μm particulates. The ASV titration revealed a similar residual complexation capacity to that in the upstream sample. There is a small amount of Chelex-labile lead (7%) in this sample, and the small ASV-labile response was only 20 mV more cathodic than the response towards the end of the titration. The lead in both upstream and downstream samples thus appears to be strongly

Table 6. Speciation of Cd, Pb, Cu, Fe and Mn in Pendle water downstream of the sewage outfall

Size fraction (μm)	Concentration ($\mu\text{g l}^{-1}$)				
	Cd (%)	Pb (%)	Cu (%)	Fe (%)	Mn (%)
>12	1.2 (13)	0.80 (37)	1.26 (19)	96 (11)	2 (2)
1-12	1.3 (14)	0.08 (4)	1.04 (16)	200 (24)	3 (3)
0.4-1	0.2 (2)	0.16 (7)	0.18 (3)	143 (17)	—
0.08-0.4	0.8 (9)	0.54 (25)	0.66 (10)	368 (44)	6 (5)
0.015-0.08	1.5 (17)	0.23 (11)	1.28 (20)	14 (2)	5 (4)
<0.015	<u>4.0 (44)</u>	<u>0.33 (15)</u>	<u>2.08 (32)</u>	<u>20 (2)</u>	<u>97 (86)</u>
Sum total	9.0	2.14	6.50	841	113
ASV-labile*	2.9 (32)	NQ†	NQ		
Chelex-labile*	3.1 (34)	0.16 (7)	0.86 (13)	91 (11)	105 (93)

* 1 μm filtrate.

† NQ = not quantifiable.

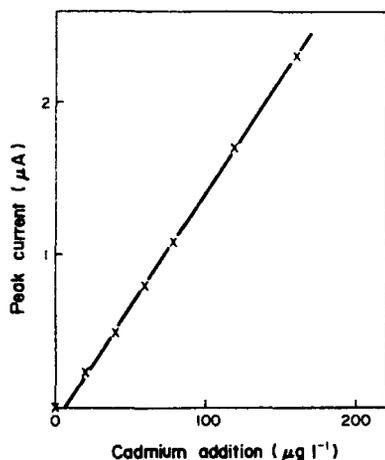


Fig. 3. ASV titration of 1 μm filtrate of the Pendle Water upstream sample. Result for Cd.

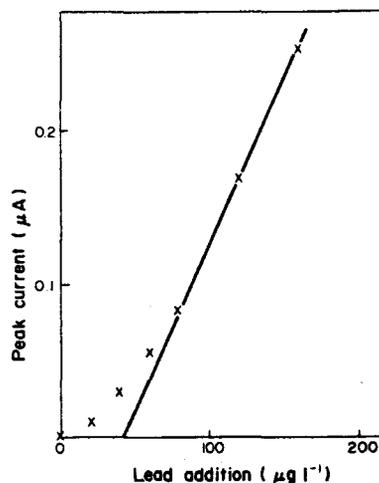


Fig. 5. ASV titration of 1 μm filtrate of the Pendle Water upstream sample. Result for Pb.

complexed and there is a residual complexation capacity associated with the colloidal size fraction.

Copper

The copper in the upstream sample is fairly evenly distributed across the size fractions. There is, however, a significant fraction (17%) associated with the 0.015–0.08 μm colloidal size range in contrast to the other metals and a fairly high proportion (30%) in the smallest size range. Not all of the Cu in this smallest size range is Chelex-labile suggesting some of the Cu to be strongly complexed. There was a significant residual complexation capacity for Cu (Fig. 7) of approx. 28 μg l⁻¹ (0.4 × 10⁻⁶ M), which was undiminished by filtration through the PMIO ultrafilter. A small ASV labile response at –135 mV may have been due to a Cu complex. This peak was 160 mV more cathodic than the Cu response after the complexation capacity

had been exceeded. The ASV behaviour following u.v. irradiation of the sample was somewhat unusual. A strong initial Cu signal in the 1 μm filtrate at +20 mV declined in size rapidly to be replaced by a peak more cathodic at approx. –60 mV. There is no immediate explanation for this behaviour.

The speciation pattern of the Cu below the outfall shows that the major addition of the Cu influx from the sewage effluent is to the smallest size fraction and to the particulate size fractions > 42 μm; although there is also a significant increase in the 0.015–0.08 μm colloidal size fraction (Fig. 8). The ASV titration indicated a similar complexation capacity to the upstream sample, of 27 μg l⁻¹ (0.4 × 10⁻⁶ M), which was also undiminished by passage through the PMIO ultrafilter. There were ASV signals, possibly due to labile Cu species at –190 mV in the 1 μm

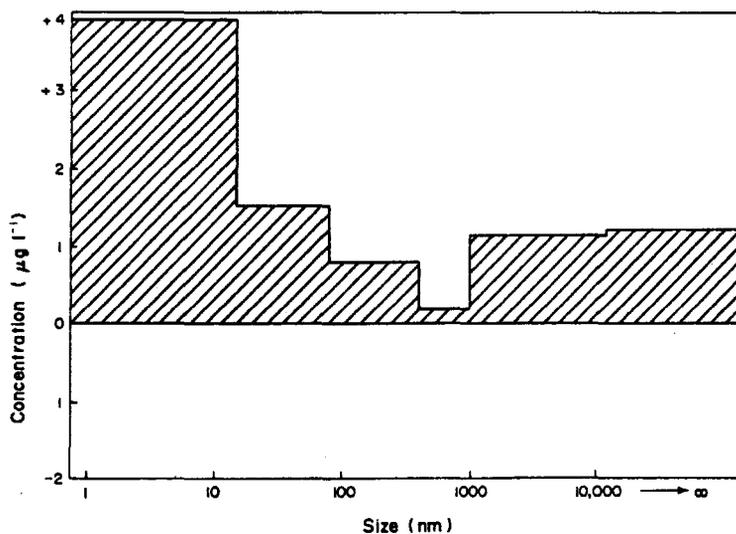


Fig. 4. Change in concentration of Cd in the different size fractions below the sewage effluent outfall.

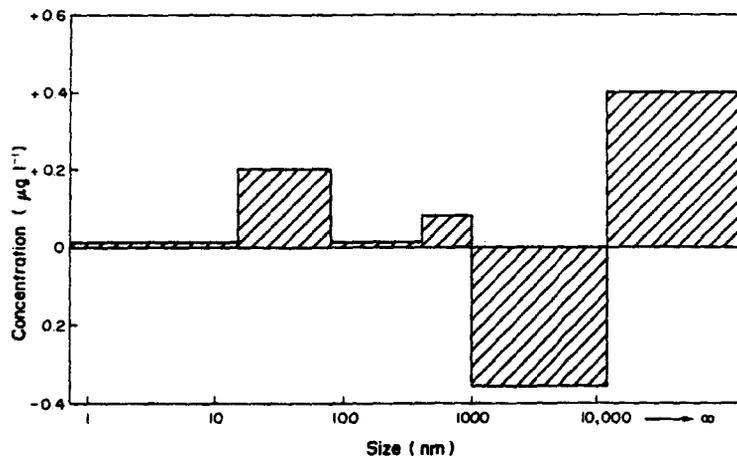


Fig. 6. Change in concentration of Pb in the different size fractions below the sewage effluent outfall.

filtrate and -250 and -150 mV in the PMIO filtrate, which would be indicative of strong complexation. (The response towards the end of the titration was at $+35$ to $+40$ mV.) These peaks were absent following u.v. irradiation.

Iron

The predominant size fraction for Fe in the upstream sample is the 0.08 – 0.4 μm colloidal size range (41%). Altogether, 98% of the Fe is in the colloidal and particulate size ranges. The Chelex-labile fraction (10%) is greater than the Fe in the smallest size fractions (2%) indicating a contribution from the colloidal size range. A similar Fe distribution is found in the downstream sample with only slight changes in the pattern (Fig. 9). There is no major addition to the total Fe burden of the river due to the effluent discharge.

Manganese

The distribution of Mn in both samples is similar, with virtually all of the metal being found in the smallest size fraction (86–90%) in a Chelex-labile form.

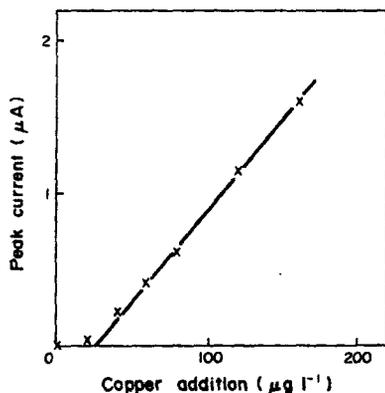


Fig. 7. ASV titration of 1 μm filtrate of the Pendle Water upstream sample. Result for Cu.

The sewage effluent has no significant impact in terms of both the total concentration and the speciation pattern.

DISCUSSION

Sewage effluent contains high concentrations of both particulate and dissolved organic matter (Hunter, 1971). It is thus reasonable initially to consider the speciation results in terms of the potential influence of organic interactions. The results for copper in the Barrowford sewage effluent provide fairly clear evidence of complexation with low molecular weight organics ($<10,000$ MW). This complexation may well account for the fairly high proportion of Cu found in the smallest size fraction (<0.015 μm) i.e. complexation with dissolved organics is exerting a solubilizing effect. Bender *et al.* (1970) found that Cu added to a secondary sewage effluent was complexed, with two distinct molecular weight fractions. Part of the Cu was associated with approx. $10,000$ MW fraction, but the major part was found in a 500 – 1000 MW fraction, which the authors ascribed to complexation with synthetic chelators. In this context, Gardiner (1976) measured concentrations of the chelating agent EDTA ranging from 0.3×10^{-6} to 4×10^{-6} M in the final effluent from several sewage treatment plants in England. The higher concentrations were associated with plants treating industrial as well as domestic effluent. Cu has a particularly strong affinity for EDTA with a stability constant of the order of 10^{18} to 10^{19} M^{-1} (Gardiner, 1976), hence Cu complexation with this chelating agent would be expected to occur if it is present in the sewage effluent. However, the results do not suggest a strong interaction between Cu and EDTA in the present sample. Under the conditions of the ASV analysis, where a plating potential of -950 mV was used for all three metals, the Cu-EDTA complex would be directly reduced (Figura & McDuffie, 1979). During the stripping the Cu originally associated with the EDTA would be revealed as

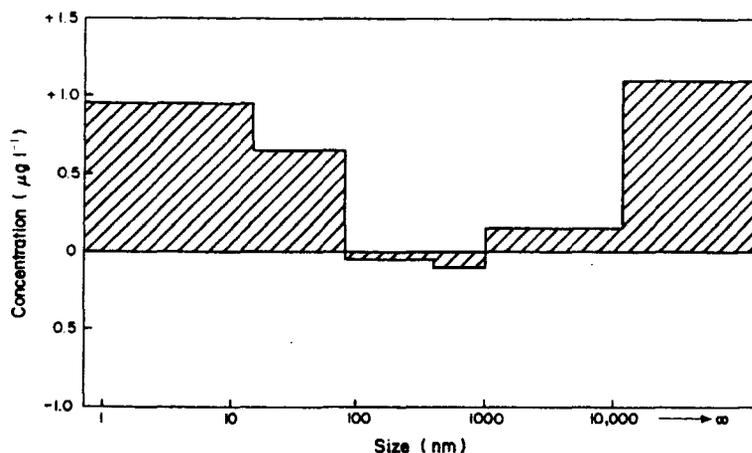


Fig. 8. Change in concentration of Cu in the different size fractions below the sewage effluent outfall.

a labile Cu peak at the potential (E_p) for uncomplexed Cu (Gardiner, 1975; Schonberger & Pickering, 1980). There is no evidence for such behaviour in the present sample. The results provide evidence of a partially labile residual complexation capacity (Fig. 10) and such ASV behaviour is more consistent with Cu complexation with humic acids. The Cu-humic acid response is partially reversible (Ernst *et al.*, 1975), hence the limited response to copper additions prior to the satisfaction of the complexation capacity. Cu complexation with humic acids also results in a cathodic shift in the stripping potential (Ernst *et al.*, 1975) as was evident during the early part of the titration of the present sample.

The precise shape of the titration response is a reflection of both the conditional formation constant of the complex and the concentration of the ligand (Shuman & Woodward, 1977). The concentration of ligand in the present sample is approx. 2×10^{-6} M, based on the inflexion in the titration curve. Comparison of the shape of the titration curve with theoretical curves presented by Shuman & Woodward (1977)

would suggest a conditional formation constant of the order of 10^6 – 10^7 M^{-1} for a 1:1 complex. Such a value is reasonable for Cu-humic acid complexation (Ernst *et al.*, 1975; Shuman & Woodward, 1977; Mantoura *et al.*, 1978). Inflexions in the titration curves for Cd and Pb, due to complexation with humic acids, are less likely to be observed as their formation constants with humic acids are lower than those of copper. Furthermore the mixed metal titration would lead to a preferential complexation of Cu at the expense of any complexation with Cd and Pb. However, a cathodic shift in the E_p would be expected and this was found in the case of Pb. There might also have been a marginal cathodic shift in the E_p of Cd of the order of 5 mV.

If humic acids are assumed to be present, then it is likely that a significant amount of the Cd in the original sample would exist as Cd-humic acid complexes, given its high concentration relative to Cu and the significant excess complexation capacity for the Cu. However, in these circumstances, the presence of the strong complex former, Cu, in the mixed metal titrant

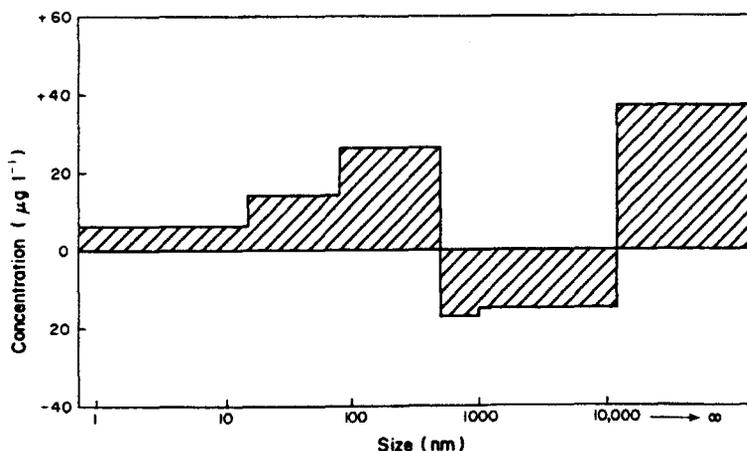


Fig. 9. Change in concentration of Fe in the different size fractions below the sewage effluent outfall.

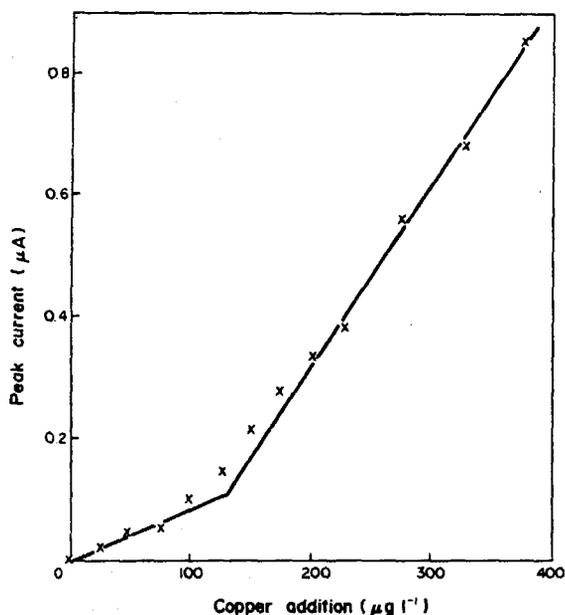


Fig. 10. ASV titration of 1 μm filtrate of the sewage effluent. Result for Cu.

might lead to the competitive displacement of Cd from complexation sites. There is indeed some evidence of such a substitution process occurring during the titration (Fig. 11). The sensitivity to added Cd is reduced once the Cu complexation capacity has been fulfilled. The initial labile Cd response may thus represent both the added Cd plus Cd released from partially labile complexation sites. It is possible therefore that humic acids are responsible for exerting a solubilizing effect on the Cd as well as the Cu, hence the high proportion of Cd in the smallest size fraction. Murray & Meinke (1974) have demonstrated a similar ability of sewage effluent to retain Cd in solution.

The residual Cu complexation capacity measured in the present sample of approx. 2×10^{-6} M, is similar to that measured by Lewin & Rowell (1973) of 1×10^{-6} M, using a similar mixed metal titration on the final effluent from the Oxford sewage treatment plant. They also found a small residual complexation capacity for Pb of 7.7×10^{-8} M, but none in the case of Cd. In the present sample there was a similar small residual complexation capacity for Pb of approx. 2×10^{-8} M, but none in the case of Cd. However, only a small part of the Pb is in the smallest size fraction (10%) suggesting that very little lead is being solubilized by low molecular weight organics and that other mechanisms are operating to preferentially associate the Pb with other size fractions. Pb has a stronger adsorption/ion exchange affinity for clays and hydrous iron oxides than either Cu or Cd (Rama-moorthy & Rust, 1978; Farrah & Pickering, 1977). Hence the different distribution pattern for Pb than Cd or Cu, in particular the emphasis on the 0.4–1 μm fraction may reflect the greater affinity of Pb for inorganic solids.

The speciation results for the sample of final effluent provide a clue to the differing efficiencies of metal removal during treatment (Table 1). Factors which retain the metals in the colloidal and soluble (<0.015 μm) size fractions will make it more likely that the metals will pass through the plant, whilst association of the metals with the particulate size fractions will ensure a greater loss of metal during the passage through the final sedimentation tank. The speciation results (Table 3) would suggest that the efficiency of removal would be in the order Fe > Pb > Cu > Cd > Mn, which bears a reasonable correspondence to the results for actual plants presented in Table 1. These are not, however, the only factors to take into account, as the removal efficiency will also depend upon the affinity of the metals for the floc in the biological filter or activated sludge plant, as they pass through the treatment works.

The metal speciation patterns in the river differ from those in the sewage effluent. A major proportion of all metals, except Mn, is found in the colloidal and particulate fractions. This is particularly evident in the case of Fe where 98% is >0.015 μm. This is probably due principally to the hydrolysis of Fe to ferric hydroxide species. X-ray diffractometry performed on the solids >0.4 μm revealed the presence of goethite (α-FeOOH), together with quartz, calcite, truscottite, kaolinite and muscovite. Amorphous iron oxide would not have shown up but may also have been present.

Gardiner (1974) has examined the association of Cd with river muds and various components thereof and concluded that the Cd is probably associated with particulate humic substances. Suzuki *et al.* (1979) have similarly suggested that Cd is probably associated with organic matter in river suspended sediments. It is thus possible that the colloidal and particulate Cd in

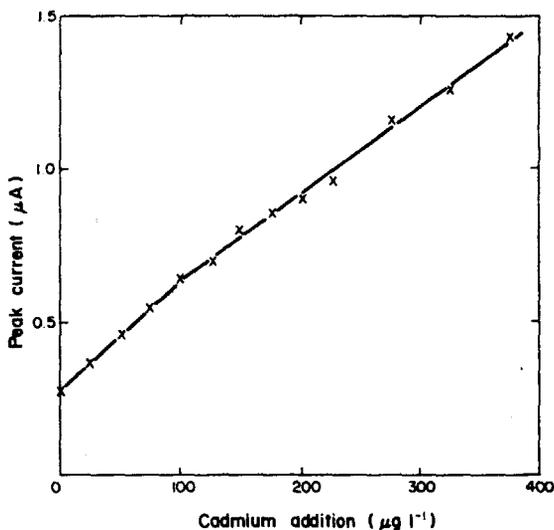


Fig. 11. ASV titration of 1 μm filtrate of the sewage effluent. Result for Cd.

Table 7. Chelex-labile metal as a proportion of total filterable (0.4 μm) metal in various freshwaters

Method	Chelex-labile metal (%)			pH	TOC (mg l^{-1})	Sample	Reference
	Pb	Cd	Cu				
Batch	0	90	23	7.7	6.0	Pendle Water (upstream)	This work
Batch	15	49	21	7.6	6.4	Pendle Water (downstream)	This work
Batch	18	33	42	7.5	6.3	River Irwell (upstream)	Laxen & Harrison (1981c)
Batch	36	43	48	7.4	6.2	River Irwell (downstream)	Laxen & Harrison (1981c)
Batch	67	94	22	7.7	24	Mordialloc Creek	Hart & Davies (1976)
Batch	55	91	58	7.1	NA*	Yarra River	Hart & Davies (1977)
Column	67	94	22	6.5	NA	Susquehanna River	Figura & McDuffie (1977)
Column	100	92	66	6.1	4.5	Woronora Reservoir	Florence (1977)
Column	78	100	49	6.1	2.7	Woronora Reservoir	Florence (1977)
Column	71	100	36	6.0	1.6	Woronora Reservoir	Florence (1977)

* NA not available.

the present samples is associated with organics. Murray & Meinke (1974) have shown that Cd adsorption onto sediments ($>0.45 \mu\text{m}$) in unpolluted river water is strongly pH dependent, increasing from 5 to 95% over the pH range 7–8. The pH of the present samples, pH 7.7 and 7.6, is commensurate with significant Cd adsorption.

Copper shows a stronger affinity for adsorption onto solids than does Cd and it also shows a strong affinity towards humic acids. Thus if Cd is associated with colloidal and particulate organics then Cu is likely to be similarly associated. There is certainly a similarity in the speciation patterns for Cd and Cu, especially in the downstream sample. Lead, on the other hand, as has already been noted, shows a stronger adsorption/ion exchange tendency towards inorganic solids, and is thus more likely to be associated with the clay minerals and hydrous ferric oxides in the samples. Adsorption or coprecipitation with hydrous ferric oxides probably does not account entirely for the Pb distribution as the Pb and Fe patterns are not wholly similar.

In terms of the biological significance, the most important metal species are likely to be those within the smallest size fraction ($<0.015 \mu\text{m}$). Complexation will generally reduce the bioavailability of the metals, thus the Chelex labile fraction is probably an even closer index of biological significance. Indeed, not all of the Pb and Cu in the smallest size fraction was Chelex-labile indicating a certain amount of strong complexation. The ASV results also indicate a significant complexation of all three metals Cd, Pb and Cu together with a residual complexation capacity, further suggesting a reduced biological significance. In Table 7 the fraction of each metal which is Chelex-labile in relation to the total metal in the fractions $<0.4 \mu\text{m}$ is compared to other reported data. The fraction of labile Cd in the upstream sample is fairly typical of the results obtained in most other studies. However, this fraction is reduced in the downstream sample. This is probably a reflection of the greater proportion of colloidal (0.015– $0.4 \mu\text{m}$) Cd in the downstream

sample, 36% as against 20%. The order of Chelex-lability of the metals in the present samples is Cd $>$ Cu $>$ Pb, which differs from the results for the River Irwell samples, where the order was Cu $>$ Cd $>$ Pb, which in turn differed from the general pattern found in other studies Cd $>$ Pb $>$ Cu. This merely reflects the high degree of variability in metal speciation, which will be highly dependent upon the composition of the particular water under study. It also warns against the use of sweeping generalisations in discussing speciation results, which refer essentially to a particular sample from a particular water body.

The source of the relatively strong complexation of the metals in Pendle Water is uncertain. In the upstream sample there was a residual complexation capacity for Cd which was associated with the colloidal size range, with a similar behaviour for Pb in both samples. The residual complexation capacity for Cu, on the other hand, was associated with the lower molecular weight material ($<10,000 \text{ MW}$) and was probably organic in nature. The existence of these residual complexation capacities in the upstream sample would suggest that addition of metals to the river would result in their uptake by the components contributing to the complexation capacity. Hence the Cd and Pb in the sewage effluent that are available for complexation would be directed towards the colloidal size range upon mixing with the river water, whilst the Cu would be taken up by the smallest size fraction. A key word here is "available". During the ASV titration the metals are added as simple inorganic labile metals, whereas the metals in the sewage effluent are being added in forms which are to a large extent already complexed. A further complication is that the ASV titration was performed on the $1 \mu\text{m}$ filtrate and hence took no account of the possible residual complexation capacity of the particulates ($>1 \mu\text{m}$). For instance Barnes *et al.* (1975) found that particulates in the 2– $16 \mu\text{m}$ size range in a lake water had a significant complexation capacity for lead (ASV titration). Nevertheless, the additions of the metals in

the sewage effluent to the different size fractions (Figs 4, 6 and 8) is in broad agreement with the identified source of complexation capacity. In particular, the lead is taken up by the colloidal size fraction, whilst little is added to the smallest size fraction. Sufficient Cd is added by the sewage works effluent to roughly equal the original residual complexation capacity hence the absence of any residual complexation capacity in the downstream sample.

There are some marked changes in the metal size distribution patterns below the outfall (Figs 4, 6, 8 and 9) which are not merely the result of the addition of the sewage effluent distribution pattern to that of the river. However, the size fractions within which there is a major increase in concentration coincide broadly with those size fractions which are emphasised in the sewage effluent. The altered metal speciation patterns below the outfall correspond with only minor changes in the bulk chemistry of the river (Table 4), further emphasising the importance of the pre-existing speciation in the effluent. The fraction of Chelex-labile metal below the outfall was not substantially altered, but in the case of Cd the absolute amount increased from 0.09 to 3.1 $\mu\text{g l}^{-1}$. In general, however, the major part of the metal additions from the effluent became associated with the colloidal and particulate size fractions; 55% for Cd, 65% for Cu and 97% for Pb. Hence a large part of each metal added to the river is unlikely to be of immediate significance, although the speciation pattern may well change downstream possibly rendering the metals more biologically available.

Acknowledgements—We thank the Ribble Division of the North West Water Authority (NWWA) for their permission to sample the Barrowford sewage effluent and for provision of analytical data for the effluent. In addition, we thank the NWWA for providing us with analytical data for Pendle Water. We also thank Mrs J. Walsh for her assistance with the major ion analyses for this study. Finally we thank the Science Research Council for their support of this project.

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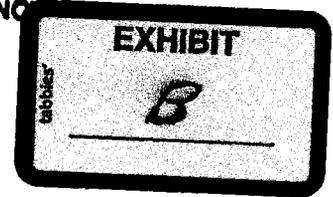
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ORIGINAL

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



OCT 1 1993

OFFICE OF
WATER

MEMORANDUM

SUBJECT: Office of Water Policy and Technical Guidance on Interpretation and Implementation of Aquatic Life Metals Criteria

FROM: Martha G. Prothro *Martha G. Prothro*
Acting Assistant Administrator for Water

TO: Water Management Division Directors
Environmental Services Division Directors
Regions I-X

Introduction

The implementation of metals criteria is complex due to the site-specific nature of metals toxicity. We have undertaken a number of activities to develop guidance in this area, notably the Interim Metals Guidance, published May 1992, and a public meeting of experts held in Annapolis, MD, in January 1993. This memorandum transmits Office of Water (OW) policy and guidance on the interpretation and implementation of aquatic life criteria for the management of metals and supplements my April 1, 1993, memorandum on the same subject. The issue covers a number of areas including the expression of aquatic life criteria; total maximum daily loads (TMDLs), permits, effluent monitoring, and compliance; and ambient monitoring. The memorandum covers each in turn. Attached to this policy memorandum are three guidance documents with additional technical details. They are: Guidance Document on Expression of Aquatic Life Criteria as Dissolved Criteria (Attachment #2), Guidance Document on Dynamic Modeling and Translators (Attachment #3), and Guidance Document on Monitoring (Attachment #4). These will be supplemented as additional data become available. (See the schedule in Attachment #1.)

Since metals toxicity is significantly affected by site-specific factors, it presents a number of programmatic challenges. Factors that must be considered in the management of metals in the aquatic environment include: toxicity specific to effluent chemistry; toxicity specific to ambient water chemistry; different patterns of toxicity for different metals; evolution of the state of the science of metals toxicity, fate, and transport; resource limitations for monitoring, analysis, implementation, and research functions; concerns regarding some of the analytical data currently on record due to possible sampling and analytical contamination; and lack of standardized protocols for clean and ultraclean metals analysis. The States have the key role in the risk management process of balancing these factors in the management of water programs. The site-specific nature of this issue could be perceived as requiring a permit-by-permit approach to implementation. However, we believe

that this guidance can be effectively implemented on a broader level, across any waters with roughly the same physical and chemical characteristics, and recommend that we work with the States with that perspective in mind.

Expression of Aquatic Life Criteria

o Dissolved vs. Total Recoverable Metal

A major issue is whether, and how, to use dissolved metal concentrations ("dissolved metal") or total recoverable metal concentrations ("total recoverable metal") in setting State water quality standards. In the past, States have used both approaches when applying the same Environmental Protection Agency (EPA) criteria numbers. Some older criteria documents may have facilitated these different approaches to interpretation of the criteria because the documents were somewhat equivocal with regards to analytical methods. The May 1992 interim guidance continued the policy that either approach was acceptable.

It is now the policy of the Office of Water that the use of dissolved metal to set and measure compliance with water quality standards is the recommended approach, because dissolved metal more closely approximates the bioavailable fraction of metal in the water column than does total recoverable metal. This conclusion regarding metals bioavailability is supported by a majority of the scientific community within and outside the Agency. One reason is that a primary mechanism for water column toxicity is adsorption at the gill surface which requires metals to be in the dissolved form.

The position that the dissolved metals approach is more accurate has been questioned because it neglects the possible toxicity of particulate metal. It is true that some studies have indicated that particulate metals appear to contribute to the toxicity of metals, perhaps because of factors such as desorption of metals at the gill surface, but these same studies indicate the toxicity of particulate metal is substantially less than that of dissolved metal.

Furthermore, any error incurred from excluding the contribution of particulate metal will generally be compensated by other factors which make criteria conservative. For example, metals in toxicity tests are added as simple salts to relatively clean water. Due to the likely presence of a significant concentration of metals binding agents in many discharges and ambient waters, metals in toxicity tests would generally be expected to be more bioavailable than metals in discharges or in ambient waters.

If total recoverable metal is used for the purpose of water quality standards, compounding of factors due to the lower bioavailability of particulate metal and lower bioavailability of metals as they are discharged may result in a conservative water quality standard. The use of dissolved metal in water quality standards gives a more accurate result. However, the majority of the participants at the Annapolis meeting felt that total recoverable measurements in ambient water had some value, and that exceedences of criteria on a total recoverable basis were an indication that metal loadings could be a stress to the ecosystem, particularly in locations other than the water column.

The reasons for the potential consideration of total recoverable measurements include risk management considerations not covered by evaluation of water column toxicity. The ambient water quality criteria are neither designed nor intended to protect sediments, or to prevent effects due to food webs containing sediment dwelling organisms. A risk manager, however, may consider sediments and food chain effects and may decide to take a conservative approach for metals, considering that metals are very persistent chemicals. This conservative approach could include the use of total recoverable metal in water quality standards. However, since consideration of sediment impacts is not incorporated into the criteria methodology, the degree of conservatism inherent in the total recoverable approach is unknown. The uncertainty of metal impacts in sediments stem from the lack of sediment criteria and an imprecise understanding of the fate and transport of metals. EPA will continue to pursue research and other activities to close these knowledge gaps.

Until the scientific uncertainties are better resolved, a range of different risk management decisions can be justified. EPA recommends that State water quality standards be based on dissolved metal. (See the paragraph below and the attached guidance for technical details on developing dissolved criteria.) EPA will also approve a State risk management decision to adopt standards based on total recoverable metal, if those standards are otherwise approvable as a matter of law.

o Dissolved Criteria

In the toxicity tests used to develop EPA metals criteria for aquatic life, some fraction of the metal is dissolved while some fraction is bound to particulate matter. The present criteria were developed using total recoverable metal measurements or measures expected to give equivalent results in toxicity tests, and are articulated as total recoverable. Therefore, in order to express the EPA criteria as dissolved, a total recoverable to dissolved correction factor must be used. Attachment #2 provides guidance for calculating EPA dissolved criteria from the published total recoverable criteria. The data expressed as percentage metal dissolved are presented as recommended values and ranges. However, the choice within ranges is a State risk management decision. We have recently supplemented the data for copper and are proceeding to further supplement the data for copper and other metals. As testing is completed, we will make this information available and this is expected to reduce the magnitude of the ranges for some of the conversion factors provided. We also strongly encourage the application of dissolved criteria across a watershed or waterbody, as technically sound and the best use of resources.

o Site-Specific Criteria Modifications

While the above methods will correct some site-specific factors affecting metals toxicity, further refinements are possible. EPA has issued guidance (Water Quality Standards Handbook, 1983; Guidelines for Deriving Numerical Aquatic Site-Specific Water Quality Criteria by Modifying National Criteria, EPA-600/3-H4-099, October 1984) for three site-specific criteria development methodologies: recalculation procedure, indicator species procedure (also known as the water-effect ratio (WER)) and resident species procedure. Only the first two of these have been widely used.

In the National Toxics Rule (57 FR 60848, December 22, 1992), EPA identified the WER as an optional method for site-specific criteria development for certain metals. EPA committed in the NTR preamble to provide guidance on determining the WER. A draft of this guidance has been circulated to the States and Regions for review and comment. As justified by water characteristics and as recommended by the WER guidance, we strongly encourage the application of the WER across a watershed or waterbody as opposed to application on a discharger by discharger basis, as technically sound and an efficient use of resources.

In order to meet current needs, but allow for changes suggested by protocol users, EPA will issue the guidance as "interim." EPA will accept WERs developed using this guidance, as well as by using other scientifically defensible protocols. OW expects the interim WER guidance will be issued in the next two months.

Total Maximum Daily Loads (TMDLs) and National Pollutant Discharge Elimination System (NPDES) Permits

o Dynamic Water Quality Modeling

Although not specifically part of the reassessment of water quality criteria for metals, dynamic or probabilistic models are another useful tool for implementing water quality criteria, especially for those criteria protecting aquatic life. These models provide another way to incorporate site-specific data. The 1991 Technical Support Document for Water Quality-based Toxics Control (TSD) (EPA/505/2-90-001) describes dynamic, as well as static (steady-state) models. Dynamic models make the best use of the specified magnitude, duration, and frequency of water quality criteria and, therefore, provide a more accurate representation of the probability that a water quality standard exceedence will occur. In contrast, steady-state models make a number of simplifying, worst case assumptions which makes them less complex and less accurate than dynamic models.

Dynamic models have received increased attention over the last few years as a result of the widespread belief that steady-state modeling is over-conservative due to environmentally conservative dilution assumptions. This belief has led to the misconception that dynamic models will always lead to less stringent regulatory controls (e.g., NPDES effluent limits) than steady-state models, which is not true in every application of dynamic models. EPA considers dynamic models to be a more accurate approach to implementing water quality criteria and continues to recommend their use. Dynamic modeling does require commitment of resources to develop appropriate data. (See Attachment #3 and the TSD for details on the use of dynamic models.)

o Dissolved-Total Metal Translators

Expressing water quality criteria as the dissolved form of a metal poses a need to be able to translate from dissolved metal to total recoverable metal for TMDLs and NPDES permits. TMDLs for metals must be able to calculate: (1) dissolved metal in order to ascertain attainment of water quality standards, and (2) total recoverable metal in order to achieve mass balance necessary for permitting purposes.

EPA's NPDES regulations require that limits of metals in permits be stated as total recoverable in most cases (see 40 CFR §122.45(c)) except when an effluent guideline specifies the limitation in another form of the metal, the approved analytical methods measure only dissolved metal, or the permit writer expresses a metals limit in another form (e.g., dissolved, valent, or total) when required to carry out provisions of the Clean Water Act. This is because the chemical conditions in ambient waters frequently differ substantially from those in the effluent, and there is no assurance that effluent particulate metal would not dissolve after discharge. The NPDES rule does not require that State water quality standards be expressed as total recoverable; rather, the rule requires permit writers to translate between different metal forms in the calculation of the permit limit so that a total recoverable limit can be established. Both the TMDL and NPDES uses of water quality criteria require the ability to translate between dissolved metal and total recoverable metal. Attachment #3 provides methods for this translation.

Guidance on Monitoring

o Use of Clean Sampling and Analytical Techniques

In assessing waterbodies to determine the potential for toxicity problems due to metals, the quality of the data used is an important issue. Metals data are used to determine attainment status for water quality standards, discern trends in water quality, estimate background loads for TMDLs, calibrate fate and transport models, estimate effluent concentrations (including effluent variability), assess permit compliance, and conduct research. The quality of trace level metal data, especially below 1 ppb, may be compromised due to contamination of samples during collection, preparation, storage, and analysis. Depending on the level of metal present, the use of "clean" and "ultraclean" techniques for sampling and analysis may be critical to accurate data for implementation of aquatic life criteria for metals.

The magnitude of the contamination problem increases as the ambient and effluent metal concentration decreases and, therefore, problems are more likely in ambient measurements. "Clean" techniques refer to those requirements (or practices for sample collection and handling) necessary to produce reliable analytical data in the part per billion (ppb) range. "Ultraclean" techniques refer to those requirements or practices necessary to produce reliable analytical data in the part per trillion (ppt) range. Because typical concentrations of metals in surface waters and effluents vary from one metal to another, the effect of contamination on the quality of metals monitoring data varies appreciably.

We plan to develop protocols on the use of clean and ultra-clean techniques and are coordinating with the United States Geological Survey (USGS) on this project, because USGS has been doing work on these techniques for some time, especially the sampling procedures. We anticipate that our draft protocols for clean techniques will be available in late calendar year 1993. The development of comparable protocols for ultra-clean techniques is underway and will be available in 1995. In developing these protocols, we will consider the costs of these techniques and will give guidance as to the situations where their use is necessary. Appendix B to the WER guidance document provides some general guidance on the use of

clean analytical techniques. (See Attachment #4.) We recommend that this guidance be used by States and Regions as an interim step, while the clean and ultra-clean protocols are being developed.

o **Use of Historical Data**

The concerns about metals sampling and analysis discussed above raise corresponding concerns about the validity of historical data. Data on effluent and ambient metal concentrations are collected by a variety of organizations including Federal agencies (e.g., EPA, USGS), State pollution control agencies and health departments, local government agencies, municipalities, industrial dischargers, researchers, and others. The data are collected for a variety of purposes as discussed above.

Concern about the reliability of the sample collection and analysis procedures is greatest where they have been used to monitor very low level metal concentrations. Specifically, studies have shown data sets with contamination problems during sample collection and laboratory analysis, that have resulted in inaccurate measurements. For example, in developing a TMDL for New York Harbor, some historical ambient data showed extensive metals problems in the harbor, while other historical ambient data showed only limited metals problems. Careful resampling and analysis in 1992/1993 showed the latter view was correct. The key to producing accurate data is appropriate quality assurance (QA) and quality control (QC) procedures. We believe that most historical data for metals, collected and analyzed with appropriate QA and QC at levels of 1 ppb or higher, are reliable. The data used in development of EPA criteria are also considered reliable, both because they meet the above test and because the toxicity test solutions are created by adding known amounts of metals.

With respect to effluent monitoring reported by an NPDES permittee, the permittee is responsible for collecting and reporting quality data on a Discharge Monitoring Report (DMR). Permitting authorities should continue to consider the information reported to be true, accurate, and complete as certified by the permittee. Where the permittee becomes aware of new information specific to the effluent discharge that questions the quality of previously submitted DMR data, the permittee must promptly submit that information to the permitting authority. The permitting authority will consider all information submitted by the permittee in determining appropriate enforcement responses to monitoring/reporting and effluent violations. (See Attachment #4 for additional details.)

Summary

The management of metals in the aquatic environment is complex. The science supporting our technical and regulatory programs is continuing to evolve, here as in all areas. The policy and guidance outlined above represent the position of OW and should be incorporated into ongoing program operations. We do not expect that ongoing operations would be delayed or deferred because of this guidance.

If you have questions concerning this guidance, please contact Jim Hanlon, Acting Director, Office of Science and Technology, at 202-260-5400. If you have questions on specific details of the guidance, please contact the appropriate OW Branch Chief. The Branch Chiefs responsible for the various areas of the water quality program are: Bob April (202-260-6322, water quality criteria), Elizabeth Fellows (202-260-7046, monitoring and data issues), Russ Kinerson (202-260-1330, modeling and translators), Don Brady (202-260-7074, Total Maximum Daily Loads), Sheila Frace (202-260-9537, permits), Dave Sabock (202-260-1315, water quality standards), Bill Telliard (202-260-7134, analytical methods) and Dave Lyons (202-260-8310, enforcement).

Attachments

TECHNICAL GUIDANCE FOR METALS

Schedule of Upcoming Guidance

Water-effect Ratio Guidance - September 1993

Draft "Clean" Analytical Methods - Spring 1994

Dissolved Criteria - currently being done; as testing is completed, we will release the updated percent dissolved data

Draft Sediment Criteria for Metals - 1994

Final Sediment Criteria for Metals - 1995

ATTACHMENT #2

**GUIDANCE DOCUMENT
ON DISSOLVED CRITERIA**
Expression of Aquatic Life Criteria
October 1993

Percent Dissolved in Aquatic Toxicity Tests on Metals

The attached table contains all the data that were found concerning the percent of the total recoverable metal that was dissolved in aquatic toxicity tests. This table is intended to contain the available data that are relevant to the conversion of EPA's aquatic life criteria for metals from a total recoverable basis to a dissolved basis. (A factor of 1.0 is used to convert aquatic life criteria for metals that are expressed on the basis of the acid-soluble measurement to criteria expressed on the basis of the total recoverable measurement.) Reports by Grunwald (1992) and Brungs et al. (1992) provided references to many of the documents in which pertinent data were found. Each document was obtained and examined to determine whether it contained useful data.

"Dissolved" is defined as metal that passes through a 0.45- μ m membrane filter. If otherwise acceptable, data that were obtained using 0.3- μ m glass fiber filters and 0.1- μ m membrane filters were used, and are identified in the table; these data did not seem to be outliers.

Data were used only if the metal was in a dissolved inorganic form when it was added to the dilution water. In addition, data were used only if they were generated in water that would have been acceptable for use as a dilution water in tests used in the derivation of water quality criteria for aquatic life; in particular, the pH had to be between 6.5 and 9.0, and the concentrations of total organic carbon (TOC) and total suspended solids (TSS) had to be below 5 mg/L. Thus most data generated using river water would not be used.

Some data were not used for other reasons. Data presented by Carroll et al. (1979) for cadmium were not used because 9 of the 36 values were above 150%. Data presented by Davies et al. (1976) for lead and Holcombe and Andrew (1978) for zinc were not used because "dissolved" was defined on the basis of polarography, rather than filtration.

Beyond this, the data were not reviewed for quality. Horowitz et al. (1992) reported that a number of aspects of the filtration procedure might affect the results. In addition, there might be concern about use of "clean techniques" and adequate QA/QC.

Each line in the table is intended to represent a separate piece of information. All of the data in the table were determined in fresh water, because no saltwater data were found. Data are becoming available for copper in salt water from the New York

Harbor study; based on the first set of tests, Hansen (1993) suggested that the average percent of the copper that is dissolved in sensitive saltwater tests is in the range of 76 to 82 percent.

A thorough investigation of the percent of total recoverable metal that is dissolved in toxicity tests might attempt to determine if the percentage is affected by test technique (static, renewal, flow-through), feeding (were the test animals fed and, if so, what food and how much), water quality characteristics (hardness, alkalinity, pH, salinity), test organisms (species, loading), etc.

The attached table also gives the freshwater criteria concentrations (CMC and CCC) because percentages for total recoverable concentrations much (e.g., more than a factor of 3) above or below the CMC and CCC are likely to be less relevant. When a criterion is expressed as a hardness equation, the range given extends from a hardness of 50 mg/L to a hardness of 200 mg/L.

The following is a summary of the available information for each metal:

Arsenic(III)

The data available indicate that the percent dissolved is about 100, but all the available data are for concentrations that are much higher than the CMC and CCC.

Cadmium

Schuytema et al. (1984) reported that "there were no real differences" between measurements of total and dissolved cadmium at concentrations of 10 to 80 ug/L (pH = 6.7 to 7.8, hardness = 25 mg/L, and alkalinity = 33 mg/L); total and dissolved concentrations were said to be "virtually equivalent".

The CMC and CCC are close together and only range from 0.66 to 8.6 ug/L. The only available data that are known to be in the range of the CMC and CCC were determined with a glass fiber filter. The percentages that are probably most relevant are 75, 92, 89, 78, and 80.

Chromium(III)

The percent dissolved decreased as the total recoverable concentration increased, even though the highest concentrations reduced the pH substantially. The percentages that are probably

most relevant to the CMC are 50-75, whereas the percentages that are probably most relevant to the CCC are 86 and 61.

Chromium(VI)

The data available indicate that the percent dissolved is about 100, but all the available data are for concentrations that are much higher than the CMC and CCC.

Copper

Howarth and Sprague (1978) reported that the total and dissolved concentrations of copper were "little different" except when the total copper concentration was above 500 ug/L at hardness = 360 mg/L and pH = 8 or 9. Chakoumakos et al. (1979) found that the percent dissolved depended more on alkalinity than on hardness, pH, or the total recoverable concentration of copper.

Chapman (1993) and Lazorchak (1987) both found that the addition of daphnid food affected the percent dissolved very little, even though Chapman used yeast-trout chow-alfalfa whereas Lazorchak used algae in most tests, but yeast-trout chow-alfalfa in some tests. Chapman (1993) found a low percent dissolved with and without food, whereas Lazorchak (1987) found a high percent dissolved with and without food. All of Lazorchak's values were in high hardness water; Chapman's one value in high hardness water was much higher than his other values.

Chapman (1993) and Lazorchak (1987) both compared the effect of food on the total recoverable LC50 with the effect of food on the dissolved LC50. Both authors found that food raised both the dissolved LC50 and the total recoverable LC50 in about the same proportion, indicating that food did not raise the total recoverable LC50 by sorbing metal onto food particles; possibly the food raised both LC50s by (a) decreasing the toxicity of dissolved metal, (b) forming nontoxic dissolved complexes with the metal, or (c) reducing uptake.

The CMC and CCC are close together and only range from 6.5 to 34 ug/L. The percentages that are probably most relevant are 74, 95, 95, 73, 57, 53, 52, 64, and 91.

Lead

The data presented in Spehar et al. (1978) were from Holcombe et al. (1976). Both Chapman (1993) and Holcombe et al. (1976) found that the percent dissolved increased as the total recoverable concentration increased. It would seem reasonable to expect more precipitate at higher total recoverable concentrations and

therefore a lower percent dissolved at higher concentrations. The increase in percent dissolved with increasing concentration might be due to a lowering of the pH as more metal is added if the stock solution was acidic.

The percentages that are probably most relevant to the CMC are 9, 18, 25, 10, 62, 68, 71, 75, 81, and 95, whereas the percentages that are probably most relevant to the CCC are 9 and 10.

Mercury

The only percentage that is available is 73, but it is for a concentration that is much higher than the CMC.

Nickel

The percentages that are probably most relevant to the CMC are 88, 93, 92, and 100, whereas the only percentage that is probably relevant to the CCC is 76.

Selenium

No data are available.

Silver

There is a CMC, but not a CCC. The percentage dissolved seems to be greatly reduced by the food used to feed daphnids, but not by the food used to feed fathead minnows. The percentages that are probably most relevant to the CMC are 41, 79, 79, 73, 91, 90, and 93.

Zinc

The CMC and CCC are close together and only range from 59 to 210 ug/L. The percentages that are probably most relevant are 31, 77, 77, 99, 94, 100, 103, and 96.

**Recommended Values (%)^A and Ranges of Measured Percent Dissolved
Considered Most Relevant in Fresh Water**

<u>Metal</u>	<u>CMC</u>		<u>CCC</u>	
	<u>Recommended Value (%)</u>	<u>(Range %)</u>	<u>Recommended Value (%)</u>	<u>(Range %)</u>
Arsenic(III)	95	100-104 ^B	95	100-104 ^B
Cadmium	85	75-92	85	75-92
Chromium(III)	85	50-75	85	61-86
Chromium(VI)	95	100 ^B	95	100 ^B
Copper	85	52-95	85	52-95
Lead	50	9-95	25	9-10
Mercury	85	73 ^B	NA ^E	NA ^E
Nickel	85	88-100	85	76
Selenium	NA ^E	NA ^C	NA ^E	NA ^C
Silver	85	41-93	YY ^D	YY ^D
Zinc	85	31-103	85	31-103

^A The recommended values are based on current knowledge and are subject to change as more data becomes available.

^B All available data are for concentrations that are much higher than the CMC.

^C NA = No data are available.

^D YY = A CCC is not available, and therefore cannot be adjusted.

^E NA = Bioaccumulative chemical and not appropriate to adjust to percent dissolved.

<u>Concn.^A</u> <u>(ug/L)</u>	<u>Percent</u> <u>Diss.^B</u>	<u>n^C</u>	<u>Species^D</u>	<u>SRF^E</u>	<u>Food</u>	<u>Hard.</u>	<u>Alk.</u>	<u>pH</u>	<u>Ref.</u>
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ARSENIC(III) (Freshwater: CCC = 190 ug/L; CMC = 360 ug/L)

600-15000	104	5	?	?	?	48	41	7.6	Lima et al. 1984
12600	100	3	FM	F	No	44	43	7.4	Spehar and Fiandt 1986

CADMIUM (Freshwater: CCC = 0.66 to 2.0 ug/L; CMC = 1.8 to 8.6 ug/L)^F

0.16	41	?	DM	R	Yes	53	46	7.6	Chapman 1993
0.28	75	?	DM	R	Yes	103	83	7.9	Chapman 1993
0.4-4.0	92 ^O	?	CS	F	No	21	19	7.1	Finlayson and Verrue 1982
13	89	3	FM	F	No	44	43	7.4	Spehar and Fiandt 1986
15-21	96	8	FM	S	No	42	31	7.5	Spehar and Carlson 1984
42	84	4	FM	S	No	45	41	7.4	Spehar and Carlson 1984
10	78	?	DM	S	No	51	38	7.5	Chapman 1993
35	77	?	DM	S	No	105	88	8.0	Chapman 1993
51	59	?	DM	S	No	209	167	8.4	Chapman 1993
6-80	80	8	?	S	No	47	44	7.5	Call et al. 1982
3-232	90 ^H	5	?	F	?	46	42	7.4	Spehar et al. 1978
450-6400	70	5	FM	F	No	202	157	7.7	Pickering and Gast 1972

CHROMIUM(III) (Freshwater: CCC = 120 to 370 ug/L; CMC = 980 to 3100 ug/L)^F

5-13	94	?	SG	F	?	25	24	7.3	Stevens and Chapman 1984
19-495	86	?	SG	F	?	25	24	7.2	Stevens and Chapman 1984
>1100	50-75	?	SG	F	No	25	24	7.0	Stevens and Chapman 1984
42	54	?	DM	R	Yes	206	166	8.2	Chapman 1993
114	61	?	DM	R	Yes	52	45	7.4	Chapman 1993
16840	26	?	DM	S	No	<51	9	6.3 ¹	Chapman 1993
26267	32	?	DM	S	No	110	9	6.7	Chapman 1993
27416	27	?	DM	S	No	96	10	6.0 ¹	Chapman 1993
58665	23	?	DM	S	No	190	25	6.2 ¹	Chapman 1993

CHROMIUM(VI) (Freshwater: CCC = 11 ug/L; CMC = 16 ug/L)

>25,000	100	1	FM,GF	F	Yes	220	214	7.6	Adelman and Smith 1976
43,300	99.5	4	FM	F	No	44	43	7.4	Spehar and Fiantdt 1986

COPPER (Freshwater: CCC = 6.5 to 21 ug/L; CMC = 9.2 to 34 ug/L)^F

10-30	74	?	CT	F	No	27	20	7.0	Chakoumakos et al. 1979
40-200	78	?	CT	F	No	154	20	6.8	Chakoumakos et al. 1979
30-100	79	?	CT	F	No	74	23	7.6	Chakoumakos et al. 1979
100-200	82	?	CT	F	No	192	72	7.0	Chakoumakos et al. 1979
20-200	86	?	CT	F	No	31	78	8.3	Chakoumakos et al. 1979
40-300	87	?	CT	F	No	83	70	7.4	Chakoumakos et al. 1979
10-80	89	?	CT	F	No	25	169	8.5	Chakoumakos et al. 1979

300-1300	92	?	CT	F	No	195	160	7.0	Chakoumakos et al. 1979
100-400	94	?	CT	F	No	70	174	8.5	Chakoumakos et al. 1979
3-4 ^J	125-167	2	CD	R	Yes	31	38	7.2	Carlson et al. 1986a,b
12-91 ^J	79-84	3	CD	R	Yes	31	38	7.2	Carlson et al. 1986a,b
18-19	95	2	DA	S	No	52	55	7.7	Carlson et al. 1986b
20 ^J	95	1	DA	R	No	31	38	7.2	Carlson et al. 1986b
50	96	2	FM	S	No	52	55	7.7	Carlson et al. 1986b
175 ^J	91	2	FM	R	No	31	38	7.2	Carlson et al. 1986b
5-52	>82 ^K	?	FM	F	Yes ^L	47	43	8.0	Lind et al. 1978
6-80	83 ^O	?	CS	F	No	21	19	7.1	Finlayson and Verrue 1982
6.7	57	?	DM	S	No	49	37	7.7	Chapman 1993
35	43	?	DM	S	Yes	48	39	7.4	Chapman 1993
13	73	?	DM	R	Yes	211	169	8.1	Chapman 1993
16	57	?	DM	R	Yes	51	44	7.6	Chapman 1993
51	39	?	DM	R	Yes	104	83	7.8	Chapman 1993
32	53	?	DM	S	No	52	45	7.8	Chapman 1993
33	52	?	DM	S	No	105	79	7.9	Chapman 1993
39	64	?	DM	S	No	106	82	8.1	Chapman 1993
25-84	96	14	FM,GM	S	No	50	40	7.0	Hammermeister et al. 1983
17	91	6	DM	S	No	52	43	7.3	Hammermeister et al. 1983
120	88	14	SG	S	No	48	47	7.3	Hammermeister et al. 1983
15-90	74	19	?	S	No	48	47	7.7	Call et al. 1982
12-162	80 ^H	?	BG	F	Yes ^L	45	43	7-8	Benoit 1975
28-58	85	6	DM	R	No	168	117	8.0	Lazorchak 1987
26-59	79	7	DM	R	Yes ^M	168	117	8.0	Lazorchak 1987
56,101	86	2	DM	R	Yes ^N	168	117	8.0	Lazorchak 1987

96	86	4	FM	F	No	44	43	7.4	Spehar and Fiandt 1986
160	94	1	FM	S	No	203	171	8.2	Geckler et al. 1976
230-3000	>69->79	?	CR	F	No	17	13	7.6	Rice and Harrison 1983

LEAD (Freshwater: CCC = 1.3 to 7.7 ug/L; CMC = 34 to 200 ug/L)^F

17	9	?	DM	R	Yes	52	47	7.6	Chapman 1993
181	18	?	DM	R	Yes	102	86	7.8	Chapman 1993
193	25	?	DM	R	Yes	151	126	8.1	Chapman 1993
612	29	?	DM	S	No	50	--	---	Chapman 1993
952	33	?	DM	S	No	100	--	---	Chapman 1993
1907	-38	?	DM	S	No	150	--	---	Chapman 1993
7-29	10	?	EZ	R	No	22	--	---	JRB Associates 1983
34	62 ^H	?	BT	F	Yes	44	43	7.2	Holcombe et al. 1976
58	68 ^H	?	BT	F	Yes	44	43	7.2	Holcombe et al. 1976
119	71 ^H	?	BT	F	Yes	44	43	7.2	Holcombe et al. 1976
235	75 ^H	?	BT	F	Yes	44	43	7.2	Holcombe et al. 1976
474	81 ^H	?	BT	F	Yes	44	43	7.2	Holcombe et al. 1976
4100	82 ^H	?	BT	F	No	44	43	7.2	Holcombe et al. 1976
2100	79	7	FM	F	No	44	43	7.4	Spehar and Fiandt 1986
220-2700	96	14	FM,GM,DM	S	No	49	44	7.2	Hammermeister et al. 1983
580	95	14	SG	S	No	51	48	7.2	Hammermeister et al. 1983

MERCURY(II) (Freshwater: CMC = 2.4 ug/L)

172	73	1	FM	F	No	44	43	7.4	Spehar and Fiandt 1986
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NICKEL (Freshwater: CCC = 88 to 280 ug/L; CMC = 790 to 2500 ug/L)^F

21	81	?	DM	R	Yes	51	49	7.4	Chapman 1993
150	76	?	DM	R	Yes	107	87	7.8	Chapman 1993
578	87	?	DM	R	Yes	205	161	8.1	Chapman 1993
645	88	?	DM	S	No	54	43	7.7	Chapman 1993
1809	93	?	DM	S	No	51	44	7.7	Chapman 1993
1940	92	?	DM	S	No	104	84	8.2	Chapman 1993
2344	100	?	DM	S	No	100	84	7.9	Chapman 1993
4000	90	?	PK	R	No	21	--	---	JRB Associates 1983

SELENIUM (FRESHWATER: CCC = 5 ug/L; CMC = 20 ug/L)

No data are available.

SILVER (Freshwater: CMC = 1.2 to 13 ug/L; a CCC is not available)

0.19	74	?	DM	S	No	47	37	7.6	Chapman 1993
9.98	13	?	DM	S	Yes	47	37	7.5	Chapman 1993
4.0	41	?	DM	S	No	36	25	7.0	Nebeker et al. 1983
4.0	11	?	DM	S	Yes	36	25	7.0	Nebeker et al. 1983
3	79	?	FM	S	No	51	49	8.1	UWS 1993
2-54	79	?	FM	S	Yes ^o	49	49	7.9	UWS 1993
2-32	73	?	FM	S	No	50	49	8.1	UWS 1993
4-32	91	?	FM	S	No	48	49	8.1	UWS 1993
5-89	90	?	FM	S	No	120	49	8.2	UWS 1993
6-401	93	?	FM	S	No	249	49	8.1	UWS 1993

ZINC (Freshwater: CCC = 59 to 190 ug/L; CMC 65 to 210 ug/L)^F

52	31	?	DM	R	Yes	211	169	8.2	Chapman 1993
62	77	?	DM	R	Yes	104	83	7.8	Chapman 1993
191	77	?	DM	R	Yes	52	47	7.5	Chapman 1993
356	74	?	DM	S	No	54	47	7.6	Chapman 1993
551	78	?	DM	S	No	105	85	8.1	Chapman 1993
741	76	?	DM	S	No	196	153	8.2	Chapman 1993
7 ¹	71-129	2	CD	R	Yes	31	38	7.2	Carlson et al. 1986b
18-273 ¹	81-107	2	CD	R	Yes	31	38	7.2	Carlson et al. 1986b
167 ¹	99	2	CD	R	No	31	38	7.2	Carlson et al. 1986b
180	94	1	CD	S	No	52	55	7.7	Carlson et al. 1986b
188-393 ¹	100	2	FM	R	No	31	38	7.2	Carlson et al. 1986b
551	100	1	FM	S	No	52	55	7.7	Carlson et al. 1986b
40-500	95 ⁰	?	CS	F	No	21	19	7.1	Finlayson and Verrue 1982
1940	100	?	AS	F	No	20	12	7.1	Sprague 1964
5520	83	?	AS	F	No	20	12	7.9	Sprague 1964
<4000	90	?	FM	F	No	204	162	7.7	Mount 1966
>4000	70	?	FM	F	No	204	162	7.7	Mount 1966
160-400	103	13	FM,GM,DM	S	No	52	43	7.5	Hammermeister et al. 1983
240	96	13	SG	S	No	49	46	7.2	Hammermeister et al. 1983

^A Total recoverable concentration.

^B Except as noted, a 0.45- μ m membrane filter was used.

C Number of paired comparisons.

D The abbreviations used are:

AS = Atlantic salmon
BT = Brook trout
CD = Ceriodaphnia dubia
CR = Crayfish
CS = Chinook salmon
CT = Cutthroat trout
DA = Daphnids

DM = Daphnia magna
EZ = Elassoma zonatum
FM = Fathead minnow
GF = Goldfish
GM = Gammarid
PK = Palaemonetes kadiakensis
SG = Salmo gairdneri

E The abbreviations used are:

S = static
R = renewal
F = flow-through

F The two numbers are for hardnesses of 50 and 200 mg/L, respectively.

G A 0.3- μ m glass fiber filter was used.

H A 0.10- μ m membrane filter was used.

I The pH was below 6.5.

J The dilution water was a clean river water with TSS and TOC below 5 mg/L.

K Only limited information is available concerning this value.

L It is assumed that the solution that was filtered was from the test chambers that contained fish and food.

M The food was algae.

N The food was yeast-trout chow-alfalfa.

O The food was frozen adult brine shrimp.

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