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Selected Total and Labile Metal Measurements in the Columbia River Water and Its Complexing Capacities for Those Metals

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INTRODUCTION

The transport, deposition, toxicity, and ultimte fate of metal in natural waters are controlled by mechanisms that determine the distribution of the chemical forms of the metal. Complexation and adsorption of naturally occurring dissolved and particulate material plays a major role in controlling this distribution of chemical forms. A number of substances found in natural waters are known to form complexes with metals, including organics such as humic and fulvic acids, amino acids, synthetic organics, and inorganics (carbonate sulfates, hydroxide ions) and suspended sediment. Each of these mechanisms contributes to the total complexing of a natural water system.

Purpose and Scope

The purpose of this study is to determine the total and labile forms of copper, zinc, lead, and cadmium in the Columbia River and the complexing capacity of the river water for these metals (over a 12-month period). Labile metal is used to describe any ionized metal ions or easily ionizable metal ions bound to carbonate, hydroxide or phosphate ligands.

Analysis of total metals will be performed by graphite furnace atomic absorption spectroscopy and the complexing capacity will be determined by polarography, utilizing differential pulse anodic stripping voltammetry (DPASV). DPASV is a two-step technique in which the first step consists of the electrolytic deposition of a chemical species onto an inert electrode surface at a constant potential. The pre-concentration step can involve either an anodic or cathodic process. The most common use of stripping voltammetry involves a cathodic process in which metal ionic species is reduced from the solution onto a mercury electrode, resulting in the formation of an amalgram. The second step consists of the application of a voltage scan to the electrode which causes an electrolytic dissolution, or stripping, of the various species in the amalgram or film back into solution at characteristic potentials. Stable metal complexes are not reduced at the electrode under normal DPASV operating conditions. Unbound or labile metals can be electrochemically reduced, and during the stripping process produce measurable currents at the characteristic potentials.

By making successive spikes of a known concentration of metal to a natural water sample, and measuring the amount of current generated by any reducible metal remaining in the sample after complexation, a relationship can be established. The point at which successive addition of metal in the sample generates a linear response with respect to current, can be considered the complexing capacity.

MATERIALS AND METHODS

Columbia River Collection Site Protocol

Water samples were collected monthly from an aluminum boat at RM366 which is located upstream from the intake of the Washington Nuclear Plant #1 and #4 at RM 351. A two-liter sample was taken for metal binding studies. The two-liter bottle was rinsed three times with river water before filling by submerging the bottle 18 inches beneath the surface of the river. A subsample was taken from this container for total metal analysis. The 100-ml bottle used for the total metal sample contained 0.5 ml Ultrex nitric acid as a preservative. The samples were stored in a chest of ice from the time of collection until they were placed in a refrigerator in our laboratory at the University of Washington in Seattle. Temperature and pH were recorded at the time of water collection.

Metal Complexing Analysis

The binding studies were done by differential pulse anodic stripping voltametry. A modification of the method first described by Chau[1] was followed using a Princeton Applied Research Model 374 polarograph and Model 303 static mercury drop electrode. All glassware was soaked in reagent grade nitric acid overnight and rinsed repeatedly with de-ionized water. Triple distilled mercury from Bethlehem Apparatus Company was used in the polarograph. Ultra pure nitrogen was used to purge samples of oxygen.

The supporting electrolyte used was ammonium acetate. The electrolyte was treated with Chelex 100 to lower the level of metalic impurities. The pH was adjusted to that measured at the collection site with ammonium hydroxide. Isothermal distillation was used to purify the ammonium hydroxide. The nitrogen used to purge the sample of oxygen was passed through a solution of the electrolyte before flushing the polarograph cell. The volume of sample tested in the cell was 10 ml. This contained 200 µl of a 3-Molar solution of the supporting electrolyte.

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[1] Chau, Y, K., R. Gachter, and K. Lum-Shu-Chan. 1974. J. Res. Bd. Can. 31:1515-1519.

Certified atomic absorption standards were used in making a stock solution containing 10 mg/l of Zn, Cd, Pb, Cu each. The pH of the stock solution was adjusted to ambient river water. For determination of complexing capacities, four metals were added at once and measured on a single scan so that the results would reflect binding in the river water when an effluent containing all 4 metals was seen.

Within 24 hr after receiving the sample, standard curves were prepared using the river water. A de-ionized curve was also prepared to determine background currents and measure any binding by the electrolyte or adsorption of metal by the test cell. These standards were prepared in 4-oz polyethylene bottles and stored in a shaker in a refrigerator at the temperature recorded when the sample was collected. After two hours the two standard curves were scanned with the polarograph starting with the lowest concentration. The glass test cells used were stored in a dilute ultrex nitric acid solution and rinsed at least five times with de-ionized water before use and between standards. The metal additions were made with Gilson automatic pipets using disposable tips also rinsed with dilute nitric acid. The set of standards, five to eight bottles, were stored between sampling periods with the standard solutions in them. This was also done with the river water complexing sample bottle to condition it and minimize metal adsorption. This procedure was introduced as a result of the inconsistent data obtained during transport of metals to the lab resulting from loss of metal to the walls of the polyethylene container (<u>see</u> Table 1).

Standard Polarograph Conditions

The standard conditions for the polarograph used throughout the binding study were as follows:

1. Analytical Technique	Differential Pulse Anode Stripping
2. Initial Potential	-1.25 volts
3. Final Potential	+0.10 volts
4. Deposition Time	100 seconds
5. Scan Rate	Fast
6. Replications	One
7. Sensitivity	Medium
8. N_2 Purge	10 min
9. Drop Size	Medium

An instrument comparison of medium and high sensitivity settings were made using the above binding protocol. Zinc current reading went off scale with 30 ppb concentration when high sensitivity was used. Current readings for standard additions were essentially the same for both sensitivity settings.

Labile and complexed metals were determined by comparing the X axis intercepts for the two curves and calculated by linear regression, least squares fit, analysis on the current measurements. Typical plots for x axis intercepts are seen in Figs. A and B. The blank intercept values are given in Table 2. These blank values are given in terms of metal concentrations which are added or subtracted from the calculated BC. In other words, if the deionized blank calculates to be a negative number, then the deionized blank number is added to the observed river BC number. If the ionized blank number calculates to be positive, then it is subtracted from the observed river BC number.

The Model 374 polarograph is equipped with a blank subtract feature which was not used because it is ineffective unless the peaks are produced at the same potential voltages on each scan. Voltage shifts did occur, negating the use of this feature. Another alternative to the de-ionized blank is to obtain an estimate of the background current by watching both the voltage and current digital displays during a scan and recording the current at a voltage at which one would expect to see a standard addition peak. If labile metal is present, it is not possible to separate background current from that which is produced by the metal. Hence, the deionized blank method was used in this study.

A complexing kinetics study on the Chehalis River has shown that metals are bound more quickly than can be ascertained by polarography. A 10-ppb standard was made up in the Columbia River water. This standard was scanned after the 10-min purge and again after 1 and 2 hr. No significant drop in currents was observed (see Table). The last two samples were analyzed without the 2-hr holding, and as a result allowed use of a spike to single river sample with increasing amounts of a concentrated standard solution, instead of making several separate river spike solutions. This resulted in a decreased error caused by carryover and subsample differences. The total volume for the standard spike was 70 μl in the 10-ml sample thus introducing only a 0.7% error. Also, the concentration of standards in the standard additions were lowered in order to reduce the error in the low level binding that was measured. This method, we feel, would be a better choice in future measurements since it reduces handling error of individual samples and produces better complexing data.

Total Metals

The sample bottles for total metal analysis were soaked in 4 N reagent grade nitric acid for at least 24 hr. After soaking, the bottles were rinsed with dilute Ultrex nitric acid and de-ionized water. To prevent loss of metals to walls of the containers and preserve the sample Ultrex nitric acid was added to the bottles before taking them to Richland for the sample collection.

All glassware used for metal analysis was soaked in reagent grade nitric acid and rinsed with de-ionized water. The conductivity of the de-ionized water in our laboratory is tested periodically with a Lab-Line Lectro MHO-meter. The conductivity ranges from 0.1 to 0.5 μmhos.

Seven concentrations for each standard curve were prepared using Fisher certified atomic absorption standards. These standards were checked against EPA quality control standards. Sample spikes were done to test for chemical or matrix interferences. None were observed for the Columbia River samples. The standards were prepared in 0.5% Ultrex nitric acid solution.

The first three samples for total metals were analyzed with a Perkin Elmer Model 380 atomic absorption spectrophotometer and a Perkin Elmer Model 2100 graphite furnace. Samples #4 and #5 were analzed with a

Perkin Elmer Model 380 spectrophotometer and a Model 4000 graphite furnace. The heating programs for the graphite furnace analysis were taken from the Environmental Protection Agency Manual of Methods for Chemical Analysis of Water and Wastes, March 1979. Samples #6 through #12 were analyzed with a Hitachi Model 180-70 Zeeman effect spectrophotometer. For these samples we used pre-programmed Hitachi heating programs. There was no significant difference between the Hitachi and EPA heating programs (see Table 3).

RESULTS AND DISCUSSION

Precision and Accuracy Results

Some differences were observed in the total metal analysis results reported by AM-Test and the results we were getting for samples taken at the same time and location on the Columbia River. However, on October 6, 1980, a single sample was split for analysis by both laboratories. Results for this sample were in good agreement (see Table 4).

Several quality control (QC) tests were made in order to confirm our atomic absorption spectrophotometry (AAS) measurements. Table 5 represents a typical check of our AAS using EPA quality control standards. This is a confirming test since EPA standards are quite reliable. A second QC test was performed on the AAS to test the accuracy of the measurement at 10 ppb concentrations or less on the metals of interest. The results of this test are shown in Table 6.

Experiments were performed to establish confidence in the polarographic measurements. First, the effects of varying the deposition potential on the copper measurement was demonstrated in Figure C and Table 7. The current increases with increasing cathodic deposition by potentially 1.4 volts over the range tested, however, the actual peak potential for copper changed by only 4 millivolts, from -0.146 volts to -0.150 volts at potential scan from -0.3 to -0.150 at deposition potential of -1.2 volts.

The decrease in current reading with increasing deposition potential is generally linear up to about -0.4 volts with a dramatic change occurring at -0.3 volts.

Complexing Capacity Results

Table 8 is the result of ten separate blank solutions measurements from a single river sample. The variability is high between readings in the zinc measurement which partially results from a decreasing background current reading occurring just before the zinc potential. The copper and lead changes are less dramatic than that for zinc.

Table 9 is the peak potential current readings obtained on seven separate 50 ppb standard solutions of Zn^{++}, Cd^{++}, Pb^{++} and Cu^{++}. A percent coefficient of variation of 10% is considered good on the polarograph and this data falls well within that range. The same standard repeated eight times also lies well within the 10% range (see Table 10).

Also the repeatability of a river blank read 7 times (see Table 11) falls within the 10% range with the exception of zinc. The zinc variability could be due to the fact that the deposition potential and the peak potential for zinc are at too close a proximity to one another, i.e., -1.2 volt depositions and -1.10 volt peak potential. Separating these two potentials is also limited by the scanning range of the Model 374 polarograph. In order to obtain the 4 metals on one scan the range has to be from -1.20 to +0.100 which approaches the maximum scanning potential of the instrument.

Table 12 demonstrates the stability of a low level standard addition spike to a river sample. Over a period of two hours with four readings the change in peak currents are negligible.

Tables 13 and 14 are experiments to illustrate the repeability of binding capacity (BC) data. Table 13 shows the results of 3 separate binding capacities performed on river sample #4. The calculated BC's are seen at the bottom of the table with the standard deviations.

Table 14 is the result of a binding-capacity done with triplicate readings. The correlation coefficient for each metal is good and offers a high degree of confidence in binding capacities performed with low standard additions of metal rather than higher ones as recommended in the method of Chau's.

Binding Capacity Data

Table 15 (four pages) is the raw complexing capacity data requested on the twelve Columbia River samples. It is from these data that the binding capacities seen in Table 16 are calculated. In the samples containing little or no binding for Zn, Cd, Pb, and Cu, it would be interesting to compare the calcium, magnesium, and other divalent cations of these samples with those in which binding occurred. (A discussion of calcium and magnesium effects will follow later.) Table 17 of the labile metal measurements indicates little or no labile metals present in the Columbia River water. Except for an occasional high zinc reading and some additional information obtained on sample #12 (to be discussed later), the table is unremarkable.

Table #18 is the physical-chemical information obtained on the twelve samples at the sampling site.

Discussion of Binding Phenomenon

In past discussions the value of the deionized water binding curve was questionable, however the dionized water blank offers a reasonable way of determining the contribution of the buffer and background current to the measurement. This type of information is invaluable for understanding the contribution to the river blank readings by the ambient bound metal and the buffer. You may note the discrepancy between assumed metal concentrations obtained from the polarograph and graphed intercepts in Table 2 and the actual total metals by AAS in Table 3. It is particularly noticeable in the copper and zinc measurements. This discrepancy is one of the more vulnerable aspects of the binding capacity measurements as well as in the general use of the polarograph for metal studies. Experience has shown that these high blank figures may arise from metals in the buffer, or aging reference electrodes, and probably least of all from uncleaned cells. The blank contribution could also arise from organics in the water such as humics and fulvics as well as those of anthropogenic origin. Some investigators feel that these substances produce a contribution manifested by increased resistance for the electric current in the water.

If actual total metals are to be determined via the polarograph the water sample would have to be digested and then measured at a ph of 2-3. Therefore, one should not compare total metals via AAS with current readings on the polarograph at assumed blank potentials for the same ambient water sample.

Additional Information on Metal Binding in Columbia River Water

In Table 16 it was noted that little or no binding was measurable in samples 10, 11, and 12. A question was posed as to what effect increasing calcium, magnesium or some other divalent cation would have on the BC of the metals being studied.

Three experiments were done in an attempt to determine the effects of calcium and magnesium on copper binding. A solution of de-ionized water and humic acid (Aldrich Chemical Co.) at 10 mg/l and electrolyte was spiked with 50 ppb copper. The polarograph was set up as for previous complexing tests. Calcium and magnesium were added, separately and combined, to the humic acid and copper solution. When calcium alone was added the current produced by copper rose from 1,343 n-amps for no calcium to 1,584 n-amps at 30 ppm calcium, indicating only a marginal effect of competition with the copper (see Table 19). However, when magnesium was added the current rose from 897 n-amps to 1,168 n-amps at 6 ppm magnesium. The current produced after the addition of calcium and magnesium rose from 967 n-amps with no addition to 1,459 n-amps at 6 ppm magnesium and 30 ppm calcium. It appears that these cations do compete with copper for binding sites on humic acid (see Table 19).

Two experiments were done with humic acid and Columbia River water. In one of these tests, Columbia River water plus 10 ppm humic acid were tested for copper binding. The results showed 2.5 ppb binding. The complexing capacity for 10 ppm humic acid in de-ionized water under the same conditions was 30 ppb. In the second of these experiments, Columbia River water was spiked with 50 ppb copper. Humic acid was added in increasing concentrations and the current was measured after each addition (see Fig. D). The current produced with no humic acid was 1,516 n-amps. After adding 40 ppm humic acid the current dropped to 813 n-amps. This indicates that 40 mg/l of standard humic acid was required to bind about 25 ppb copper in Columbia River water (see Table 20).

CONCLUDING REMARKS

Binding capacity of the Columbia River water for the metals Zn, Pb, Cd, and Cu is a highly variable phenomenon which of course depends upon the variable chemistry of a highly complex river system. The drainage into this river system from the agricultural areas must exert a sizeable influence upon the binding by natural ligans in the water. Binding capacities in a simple river system is at best very complex in itself, but when the added unknowns of anthropogenic origin such as pesticides, fertilizer, and concentration of the salts during warm weather periods are added to a river system such as the Columbia, the problem becomes very complex.

Time did not allow for a more complete examination of the effects of the cations calcium and magnesium. However, it did open the door to understanding some of the possible causitive factors in the low binding capacities measured in the samples.

Table 1. Loss of metal to container walls.

		Parts per billion		
			Found	
Date		Added	FS-R*	FS-D**
7-8-80	#1			
Cu		20	16	17
Zn		50	33	33
Pb		50	13	17
Cd		10	9	10
Ni		20	--	--
8-4-80	#2			
Cu		10	7	9
Zn		25	24	28
Pb		25	8	28
Cd		5	3	5.5
Ni		10	37	9
9-8-80	#3			
Cu		10	7	10
Zn		25	19	19
Pb		25	10	19
Cd		5	1.6	1.7
Ni		10	--	--
10-6-80	#4			
Cu		10	7.4	10
Zn		25	24	25
Pb		25	9	22
Cd		10	--	--
Ni		10	12	11
#5 added				
Cu	5			
Zn	10			
Pb	5			
Cd	5			
11-3-80				
Cu		5	3.2	< 1.0
Zn		10	11.2	< 2.5
Cd		5	--	--
Pb		5	< 0.5	< 0.5

*FS-R = Field Spiked River Water

**FS-D = Field Spiked Deionized Water

Table 2. Columbia River complexing capacity blank data (in ppb). These values include background current contributed by the buffer, ambient metals, and unknown constituents in the river water. Blank is from a deionized curve x intercept calculated the same way binding is calculated. Negative numbers indicate binding for de-ion curve.

Sample	Zn	Cd	Pb	Cu
1	4.8	-5.0	0.2	1.6
2	5.6	0.5	3.6	4.7
3	2.8	0.2	5.0	0.4
4	0.3	0.9	-2.7	5.0
5	4.5	-2.6	4.3	3.1
6	-2.7	2.3	-7.7	-6.8
7	2.4	1.6	-4.9	6.7
8	4.0	-0.6	5.0	8.4
9	6.0	2.1	6.8	9.8
10	4.8	0.8	3.8	14.2
11	6.5	1.1	3.0	3.1
12	1.9	0.4	1.4	5.6

Table 3. Total ambient metal results by Graphite AAS (in μg/L).

Sample	Date	Zinc	Cadmium	Lead	Copper	Nickel
1	7-8	11	0.2	3	4	<5
2	8-4	12	<0.2	9	3	<5
3	9-8	12	0.2	3	<1	<5
4	10-6	8	0.4	5	1	<5
5	11-3	6.5	<0.2	<0.5	1.0	<5
6	12-1	6.6	<0.2	<0.5	<1.0	<5
7	1-14	28	0.3	<0.5	0.8	<5
8	2-9	21	0.2	<0.5	<0.5	<5
9	3-2	18	<0.2	1	0.4	<5
10	4-6	27	0.2	2.9	2.0	<5
11	5-6	36	0.2	<2.0	<2.5	<2.5
12	6-3	24	<0.2	<2.0	2.9	<2.5

Table 4. Total metals analysis results for a sample of Columbia River water that was split, October 6, 1980, and analyzed by AM Test Laboratories and Fisheries Research Institute.

	Parts per billion				
	Cd	Cu	Pb	Ni	Zn
AM Test	0.3	3	3	2	7
FRI	0.4	1	5	< 5	8

Table 5. EPA quality control standards for total metals results in ppb.

	EPA	Found
Zinc	17.4	17.5
Copper	2.0	3.1
Nickel	15.2	15.2
Cadmium	1.5	1.2
Lead	7.0	6.8

Table 6. Coefficient of variation in total metal measurement from seven measurements.

	%	Concentration ppb
Zinc	7.6	10
Copper	1.1	5
Nickel	10.5	10
Cadmium	9.9	1
Lead	6.8	5

Table 7. Comparison of currents produced by different deposition potentials for copper. The copper level is 80 ppb in deionized water plus electrolyte. The peak potential ranged between -0.146 V and -0.150 V.

Deposition potential (volts)	Current produced (Na)
-0.30	3055
-0.35	3574
-0.40	3735
-0.45	3845
-0.50	3903
-0.55	3913
-0.60	3925
-0.65	4020
-0.70	3990
-0.75	4000
-0.80	4020
-0.85	4100
-0.90	4210
-0.95	4270
-1.00	4330
-1.10	4390
-1.20	4430

Table 8. Test 2: Ten separate blank solutions

	Zn	Cd	Pb	Cu
1	115	N.P.	75	272
2	78	N.P.	83	238
3	N.P.	N.P.	87	212
4	369	N.P.	N.P.	229
5	271	N.P.	65	229
6	117	N.P.	62	160
7	162	N.P.	63	167
8	137	N.P.	58	-
9	146	N.P.	61	292
10	291	N.P.	61	250
$\bar{x}$	187		68	228
s	99		10.6	43.6
n	9	-	9	9

N.P. = No observable peaks.

Table 9. Polarograph precision data. Current data for seven different 50 ppb standards, in nanoamps.

	Zn	Cd	Pb	Cu
1	5270	3004	1630	2727
2	5790	3400	1899	2867
3	5990	3178	1755	2883
4	5740	3280	1656	2834
5	6270	2825	1768	3028
6	5020	3341	1517	2561
7	5810	3443	1881	2950
$\bar{x}$	5699	3210	1729	2836
s	424	225	138.0	153
%	7.4	7.0	7.98	5.4

Table 10. Current data for precision test of polarograph 50 ppb standard. Repeated 8 times, in nanoamps.

	Zn	Cd	Pb	Cu
1	9760	4010	3528	4460
2	10600	4010	3486	3820
3	10280	4170	3430	3732
4	9980	4160	3222	3960
5	10140	4340	3148	3598
6	9850	4310	2956	3542
7	9680	4370	2831	3530
8	9310	4370	2686	3483
$\bar{x}$	9938	4218	3160	3766
s	403	152	315	325
%	4.05	3.60	9.97	8.63

Table 11. Current data for a river blank repeated seven times, in nanoamps.

	Zn	Cd	Pb	Cu
1	2123	90	114	300
2	2662	119	140	345
3	2666	115	130	325
4	2268	110	123	312
5	2784	105	127	285
6	2775	102	120	299
7	2807	100	115	295
$\bar{x}$	2584	106	124	309
s	274	9.8	9.1	20.5
%	10.6	9.2	7.4	6.6

Table 12. Columbia River water was spiked with 10 ppb of the four metals of interest and scanned four times over a period of two hours, in nanoamps.

Time (min)	Zn	Cd	Pb	Cu
10	2095	638	378	420
30	2081	659	357	444
60	2105	655	392	427
120	2159	667	350	428

Table 13. Columbia River complexing data repeatability on river sample #4, in nanoamps.

Standards added in µg/L	Zn		Cd	Pb	Cu
(A) #4					
10	673	2	82	75	85
50	4160	10	552	841	1243
100	10820	20	1380	2497	3145
150	18110	30	2125	4200	5030
200	21060	40	2586	5700	6860
300	34860	60	4450	10370	12780
(B) #4					
10	286	2	30	240	151
50	4400	10	575	1235	1100
100	10720	20	1248	2793	3349
150	17990	30	1977	4790	6710
200	20250	40	2330	6170	10000
300	35040	60	4070	11600	23280
(C) #4					
10	660	2	88	115	49
50	4600	10	575	1093	1066
100	9020	20	1107	2355	2875
150	15370	30	1649	4220	6100
200	22910	40	2583	7060	12360
300	36030	60	4120	11170	26270
(A)	9.0		1.0	21	27
(B)	10.0		1.0	19	29
(C)	15.0		2.0	21	50
$\bar{x}$	11.3		1.3	20.3	35
s	3.2		0.6	1.15	12.7
%	28.4		44.4	5.7	36.4

Table 14. Columbia #11 binding capacity data triplicate runs, in nanoamps.

ppb	$\bar{x}$	Zinc	$\bar{x}$	Cadmium	$\bar{x}$	Lead	$\bar{x}$	Copper
0		188		–		–		–
	191	187		–		–		–
		198		–		–		–
10		402		558		306		375
	409	412	565	574	286	286	381	384
		414		562		266		383
20		668		1198		522		612
	664	660	1224	1216	492	480	602	599
		665		1257		475		596
30		1040		1697		699		810
	1055	1056	1704	1667	691	680	789	770
		1070		1747		694		786
40		1413		2123		895		949
	1377	1361	2156	2159	882	877	952	957
		1357		2186		874		950
50		1595		2745		1115		1124
	1570	1565	2748	2729	1093	1100	1129	1133
		1551		2769		1065		1130
60		1739		3140		1243		1292
	1730	1729	3276	3301	1272	1271	1325	1322
		1721		3388		1301		1360
Volts		-1.134		-.714		-.565		-.216
x		-6.6		-1.65		-4.73		-11.7
r^2		0.987		0.998		1.000		0.998

Table 15. Columbia River complexing data, in nano-amps.

Standards in µg/L added to #	Zn	Pb	Cu	Cd
#1				
10	--	--	--	428
50	514	497	1427	2048
150	2934	2603	6540	9020
300	7070	7100	13750	18780
450	9260	10280	19780	24760
600	12990	9100[a]	19856[a]	22510[a]
#2				
10	223	--	240	417
50	2794	643	1983	2923
100	4760	1398	4420	4730
150	8190	2682	8630	10810
200	14220	4100	14360	14600
300	21540	5910	17740	18300
#3				
10	783	110	364	
50	1024	464	--	
100	12380	2200	2577	
150	17730	3688	6350	
200	22650	5410	9420	
300	32010	8680	13980	
2				143
10				650
20				1715
30				2411
40				3066
60				4700
#5				
10	1650	225	624	646
50	6010	1221	1872	3309
100	9430	2307	3174	5360
150	14400	3903	5070	8230
200	20860	5890	7650	12180
300	30860	9210	13720	18230
#6				
10	744	102	206	364
50	3490	895	1181	2010
100	6540	1956	2177	4260
150	11400	3726	3583	7670
200	16360	5660	5610	10940
300	22840	8330	8220	16380

Table 15, cont'd

Standards in µg/L added to #	Zn	Pb	Cu	Cd
#7				
25	812	318	492	
50	1417	936	1097	
100	2991	2392	2594	
150	3389	2941	3254	
200	5100	3908	4370	
250	7570	5990	5980	
5				361
10				556
20				1140
30				1351
40				1612
50				2462
#8				
25	4160	263	--	
50	6980	669	827	
100	12420	1845	2163	
150	17630	3531	3557	
200	21980	5210	4830	
250	26210[b]	6940	6080	
300	31340[b]	7620	6870	
5				292
10				597
20				1257
30				1881
40				2475
50				3048
60				3211[b]
#9				
25	5040	715	694	
50	6340	1402	1193	
75	10380	2422	2309	
100	11030	2921	2697	
125	13650	4130	3831	
150	15790	4390	3790	
200	24160	6920	5380	
5				386
10				622
15				1051
20				1180
25				1502
30				1760
40				2693

Table 15, cont'd

Standards in µg/L added to #	Zn	Pb	Cu	Cd
#10				
25	4290	670	792	
50	4760	977	1103	
75	8110	2079	2336	
100	11390	2303	3228	
125	10850[b]	2408	3970	
150	10870[b]	3417	4380	
200	19280	5150	2916[b]	
5				452
10				668
15				1138
20				1317
25				1349
30				1840
40				2777
#11				
0	188	--	--	--
	187	--	--	--
	198	--	--	--
$(\bar{x})$	(191)			
10	402	306	375	558
	412	286	384	574
	414	266	383	562
$(\bar{x})$	(409)	(286)	(381)	(565)
20	668	522	612	1198
	660	480	599	1216
	665	475	596	1257
$(\bar{x})$	(665)	(492)	(602)	(1224)
30	1040	699	810	1697
	1056	680	770	1667
	1070	694	786	1747
$(\bar{x})$	(1055)	(691)	(789)	(1704)
40	1413	895	949	2123
	1361	877	957	2159
	1357	874	950	2186
$(\bar{x})$	(1377)	(882)	(952)	(2156)

Table 15, cont'd

Standards in µg/L added to #	Zn	Pb	Cu	Cd
50	1595	1115	1124	2745
	1565	1100	1133	2729
	1551	1065	1130	2769
($\bar{x}$)	(1570)	(1093)	(1129)	(2748)
60	1739	1243	1292	3140
	1729	1271	1322	3301
	1721	1301	1360	3388
($\bar{x}$)	(1730)	(1272)	(1325)	(3276)
#12				
0	399	--	--	88
10	1466	292	461	684
20	2286	429	644	1313
30	3054	563	827	1810
40	4140	784	1085	2650
50	4700	902	1254	3249
60	5560	1064	1450	3816
70	6170	1274	1662	4390

[a] Not used in calculation.

[b] Problems with the mercury electrode for this sample.

Table 16. Binding in excess of ambient metal present in sample (in μg/L).

Sample and date		Zn	Cd	Pb	Cu
1	7-8-80	21	< 1	33	10
2	8-4-80	25	4	29	18
3	9-8-80	12	< 1	28	20
4	10-6-80	11	1.0	20	28
5	11-3-80	2	< 1	18	18
6	12-1-80	2	15	10	4
7	1-14-81	9	< 1	7	8
8	2-9-81	< 1	< 1	29	19
9	3-2-81	< 1	1.0	13	10
10	4-6-81	< 1	< 1	8	17
11	5-6-81	< 1	< 1	< 1	< 1
12	6-3-81	< 1	< 1	< 1	< 1

Table 17. Ambient labile metals (in μg/L).
(< indicates metals are bound.)

Sample	Zn	Cd	Pb	Cu
1	< 1	0.2	< 1	< 1
2	< 1	< 1	< 1	< 1
3	< 1	< 1	< 1	< 1
4	< 1	< 1	< 1	< 1
5	< 1		< 1	< 1
6	< 1	< 1	< 1	< 1
7	< 1	1.0	< 1	< 1
8	14	< 1	< 1	< 1
9	8	< 1	< 1	< 1
10	11	< 1	< 1	< 1
11	< 1	1.0	2	8
12	5	1.0	5.2	7

Table 18. Temperature and pH data.

Sample	Date	Temp. °C	pH
#1	7-8-80	16.2	8.13
#2	8-4-80	18.6	8.16
#3	9-4-80	18.8	8.10
#4	10-6-80	17.4	8.15
#5	11-3-80	13.5	8.10
#6	12-1-80	8.0	7.50
#7	1-14-81	6.0	7.60
#8	2-9-81	4.0	7.35
#9	3-2-81	3.6	7.40
#10	4-6-81	4.0	8.00
#11	5-4-81	9.6	8.50
#12	6-1-81	11.5	8.00

Table 19. Tests for calcium and magnesium on copper and zinc binding by humic acid. Titration of a 10 ppm humic acid in distilled water with a solution of 1000 ppm calcium. Polarograph set up conditions as for complexing studies. The humic acid solution contains 50 ppb copper.

Calcium (ppm)	Current (Na)	Mg (ppm)	Na
0	1343	0	897
2	1398	0.50	892
5	1184	1.00	813
10	1458	2.00	1052
15	1502	4.00	1102
20	1495	6.00	1168
30	1584		
Calcium and magnesium combined*			
0		0	967
5		1	1147
10		2	1248
15		3	1225
20		4	1389
30		6	1459

---

*As concentrations of Ca and Mg increase, the copper may be displaced with a resultant increase in current due to the free copper.

Table 20. Columbia River humic acid binding sample #12, 6-3-81. A 10 ppm humic acid solution in Columbia River water is spiked with a 10 ppm copper standard, pH 7.6. Conditions as for previous complexing tests.

Copper (ppb)	Current (Na)
0	275
10	400
20	748
40	1250
60	1720
80	2079
100	2726

Binding = 2.5 ppb Cu. Binding for 10 ppm humic in deionized water is about 30 ppb Cu.

Columbia River spiked with 50 ppb Cu with additions of humic acid (1,000 ppm concentrate)

Humic acid (ppm)	Current (Na)
0	1516
1	--
2	1508
4	1713
8	1346
12	1195
20	1034
30	919
40	813

High concentrations of humic are required to reduce labile copper, possibly because of competition from Ca and Mg.

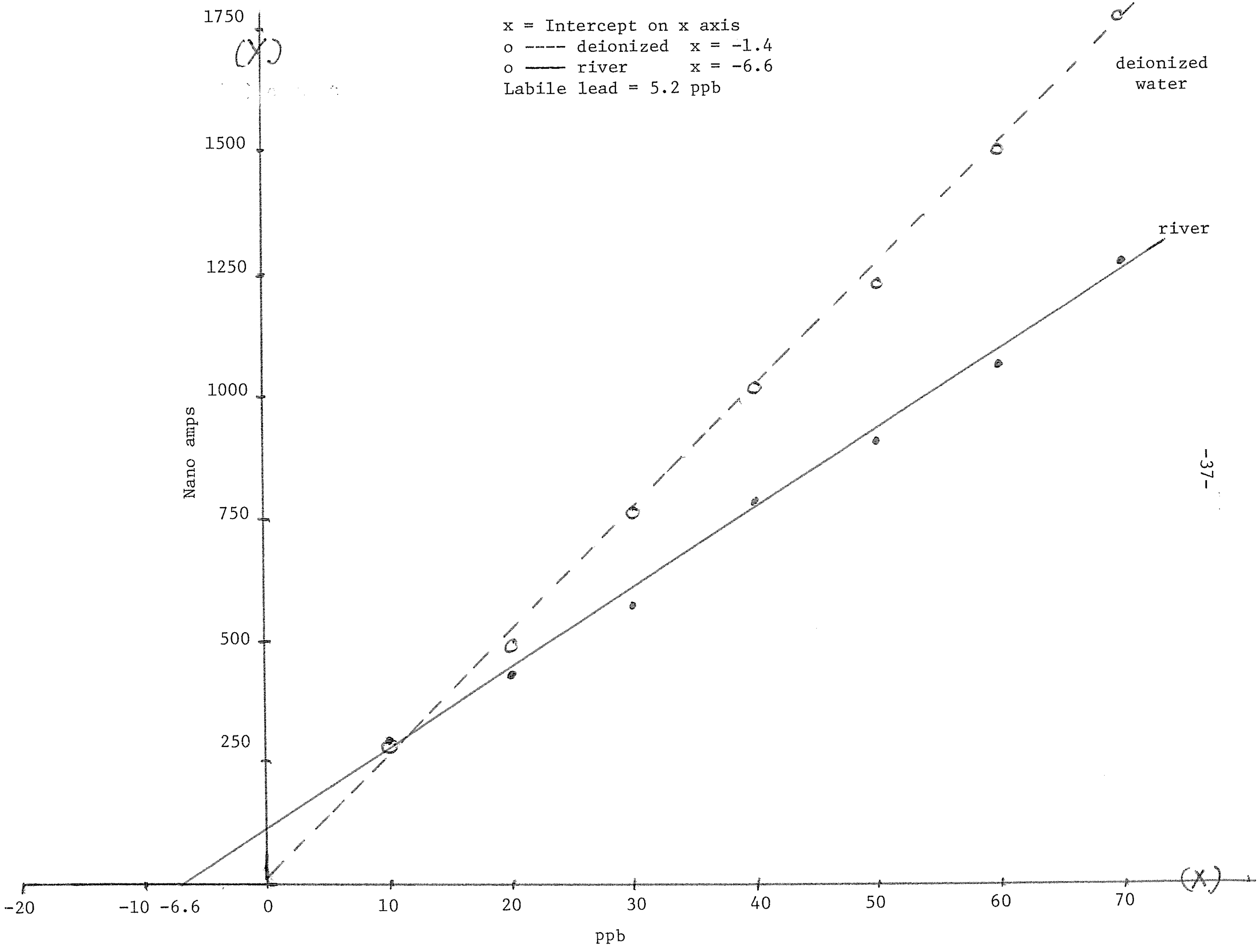

Fig. A. Labile lead in Columbia River Sample # 2.

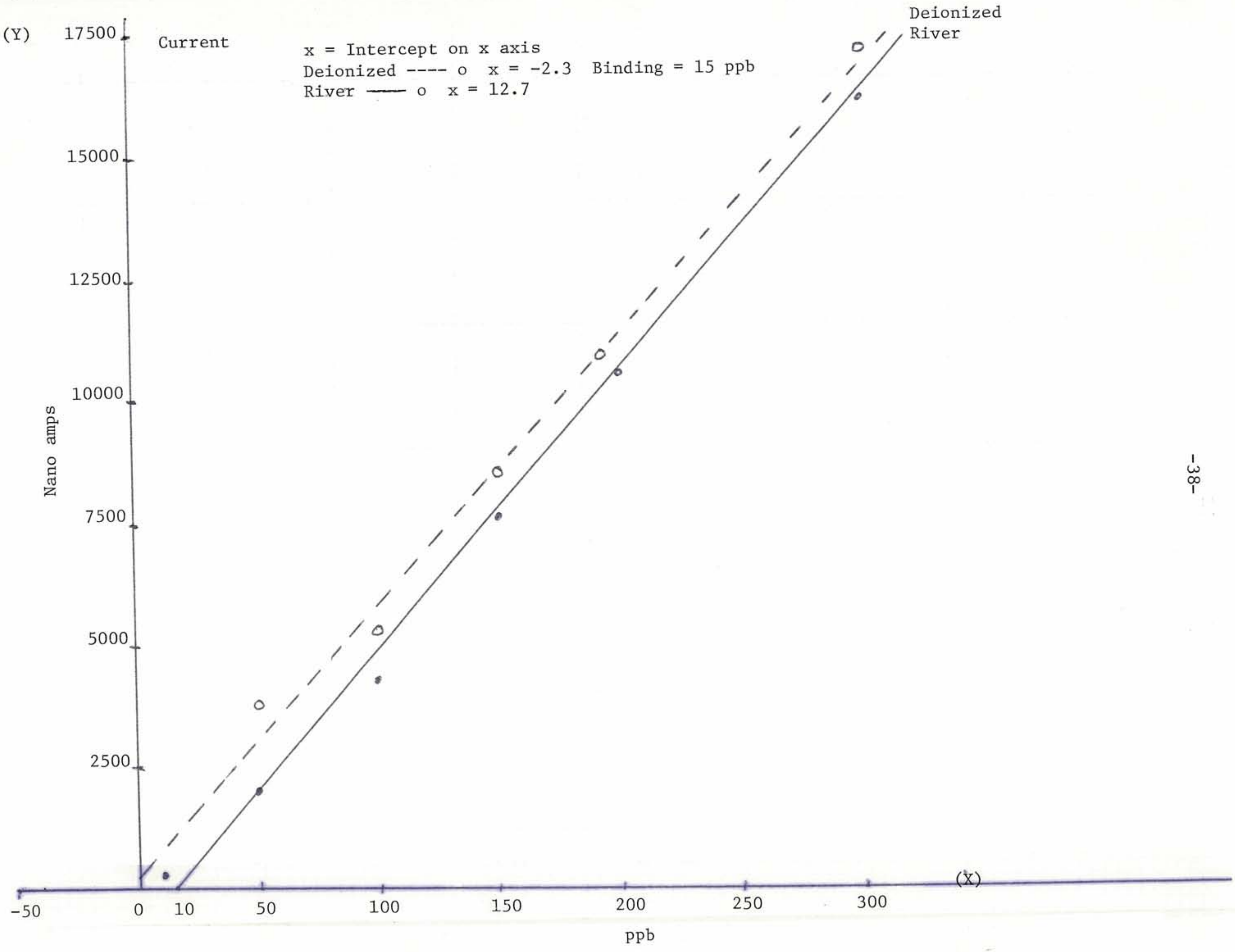

Fig. B. Cadmium binding in Columbia River Sample No. 6.

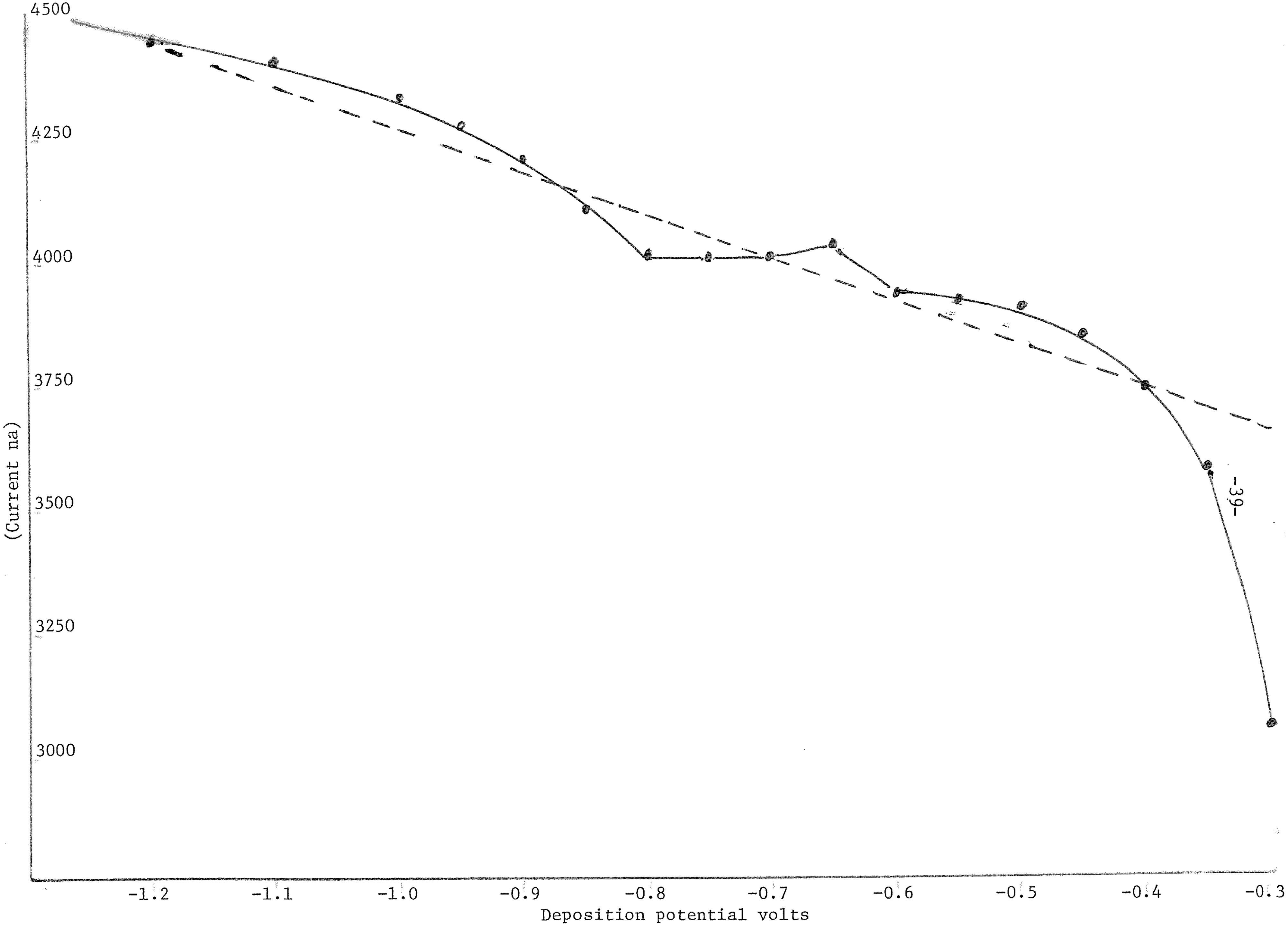

Fig. C. Copper deposition potential vs. current output with 80 ppb standard.

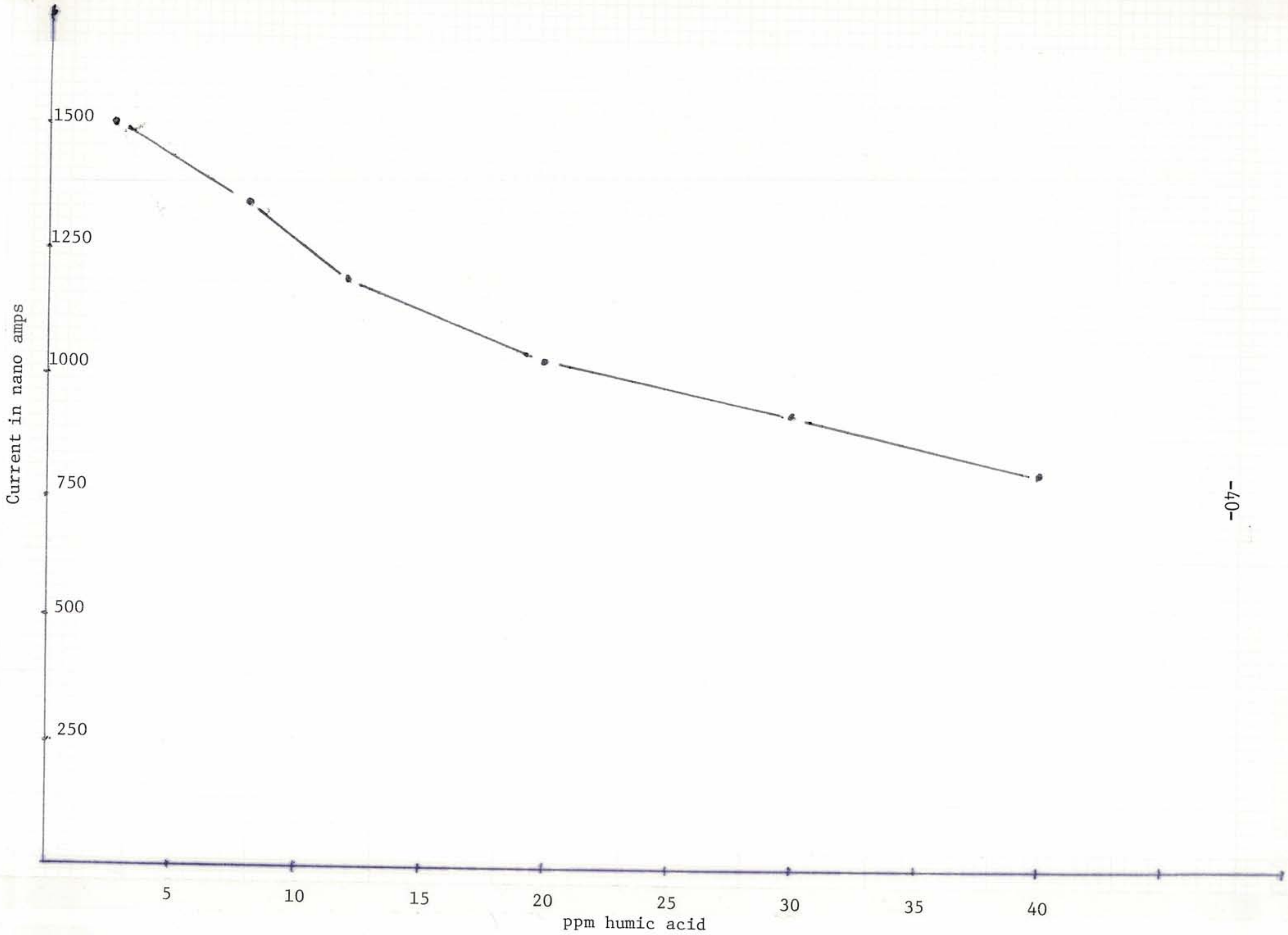

Fig. D. Columbia River plus 50 ppb copper-humic acid additions.