INLAND WATERS BRANCH

DEPARTMENT OF THE ENVIRONMENT

Heavy Metal Concentrations in Ottawa River and Rideau River Sediments

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ABSTRACT

Sediment samples were collected at two or three mile intervals along the Ottawa River from Ottawa to Thurso, and along the Rideau River from Smith Falls to Ottawa from July 19 to 24, 1971. Using atomic absorption spectrophotometry the sediments were analyzed for lead, mercury, zinc, copper, nickel, cobalt, iron, manganese, and chromium. Some of the high concentrations of heavy metals found in the sediments of these rivers appear to be from pollution by municipal and industrial wastewater discharges and waste disposal practices.

HEAVY METAL CONCENTRATIONS IN OTTAWA RIVER AND RIDEAU RIVER SEDIMENTS

B.G. Oliver and J. Kinrade

INTRODUCTION

Little data are available on heavy metal concentrations in Ottawa and Rideau River sediments. Although press coverage of pollution of the rivers has been extensive, most analyses to date have consisted of coliform counts on the water itself. A study of heavy metal concentrations in the sediments should reveal the extent population and industries have been responsible for these "hidden" pollutants. Of course not all heavy metals are dangerous, but above a certain threshold value many are toxic [1]. Since metals such as mercury and lead have long residence times and are biologically magnified, heavy metal pollution could have a serious lasting effect on the ecology of the rivers.

EXPERIMENTAL

Sampling

Sediment samples were collected at two or three mile intervals along the Ottawa River from Ottawa to Thurso, and along the Rideau River from Smith Falls to Ottawa during the period July 19 to 24, 1971. The sampling stations were labelled 1 to 20 for the Ottawa River and A to Z for the Rideau River (Figs. 1 and 2). At each sampling station three samples were taken – one sample about 10 yards from each bank and one in the centre of the river. On the Ottawa River, the first sample at each station was obtained on the Quebec side, the second in the centre, and the third on the Ontario side. For example, at Station 6, Sample No. 6-1 was taken on the Quebec side, Sample No. 6-2 in the centre, and Sample No. 6-3 on the Ontario side. For Rideau River stations, the first sample was obtained close to the east bank, the second in the centre, and the third close to the west bank. Where the channel alignement is essentially east-west, the first sample was taken near the south bank and the third sample near the north bank. In some sampling locations it was not possible to obtain three samples because the bottom was rocky.

The samples were collected by Lane-type sediment sampler (Fig. 3). After the sampling jar was placed in the holder, the sampler was lowered and dredged along the bottom for about 5 to 10 yards. After the supernatant liquid was drained, the sample was transferred to a storage jar which contained 5 ml of 4 M nitric acid. The acid was used to prevent vaporization and surface absorption of the heavy metals on the jar.

There are three main sources of error in the sediment sampling: (1) nonhomogeneous sampling areas; (2) varying amounts of organic matter in the sediments; and (3) natural mineral deposits (containing the metals of interest) close to the sampling site. The first two effects were minimized by stirring the sample to make it as homogeneous as possible and by physically removing organic matter, such as wood chips or shells, before the analysis. Although the overall effect of these three variables on the results appears small, this can be determined precisely only by means of a more extensive sediment sampling program.

Analysis

A portion of the sediment sample was spread out on a 100 × 10 mm petri dish and air dried for 4 days. A representative part of each sample was finely ground. One gram was accurately weighed and digested in a 60 ml acid solution of 4.0 M $HNO_3 \cdot$ 0.7 M HCl for 2 hours at 70-90°C. This partial extraction technique is 75-100% effective depending on the metal. The efficiency is high enough for our requirements and the method is preferred to a complete HF extraction because it is less hazardous. After cooling, 50 ml of the supernatant liquid was filtered off and diluted to 100 ml with distilled water.

The solutions were analyzed for lead, mercury, zinc, copper, nickel, cobalt, iron, manganese, and chromium using a Perkin-Elmer Model 403 Atomic Absorption Spectrophotometer. The instrument parameters for the elements are tabulated in Table 1. No spectral interferences are reported in the procedure manual [2] for these elements. Proper standards were prepared with acid and metal

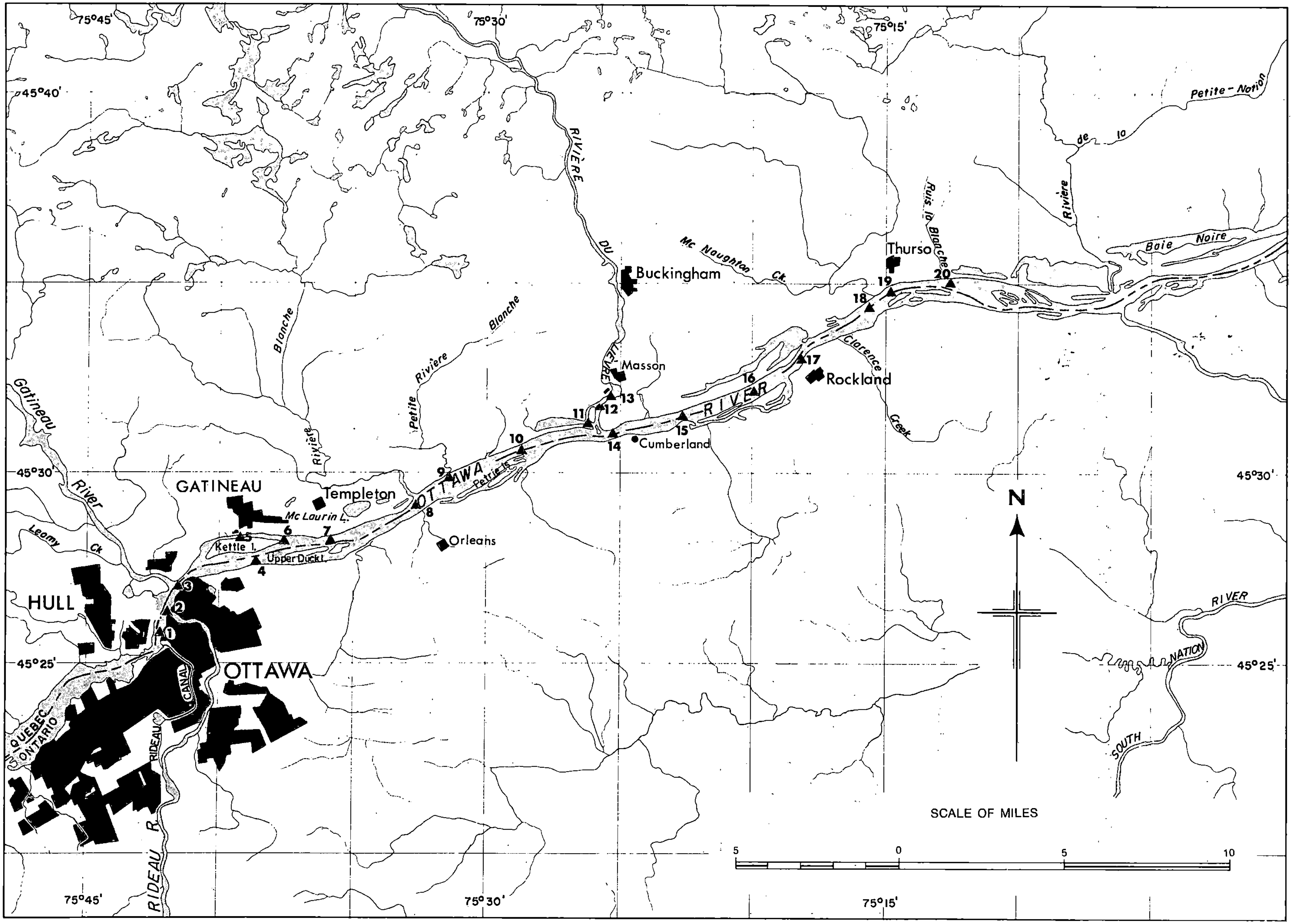

Figure 1. Sampling locations on the Ottawa River.

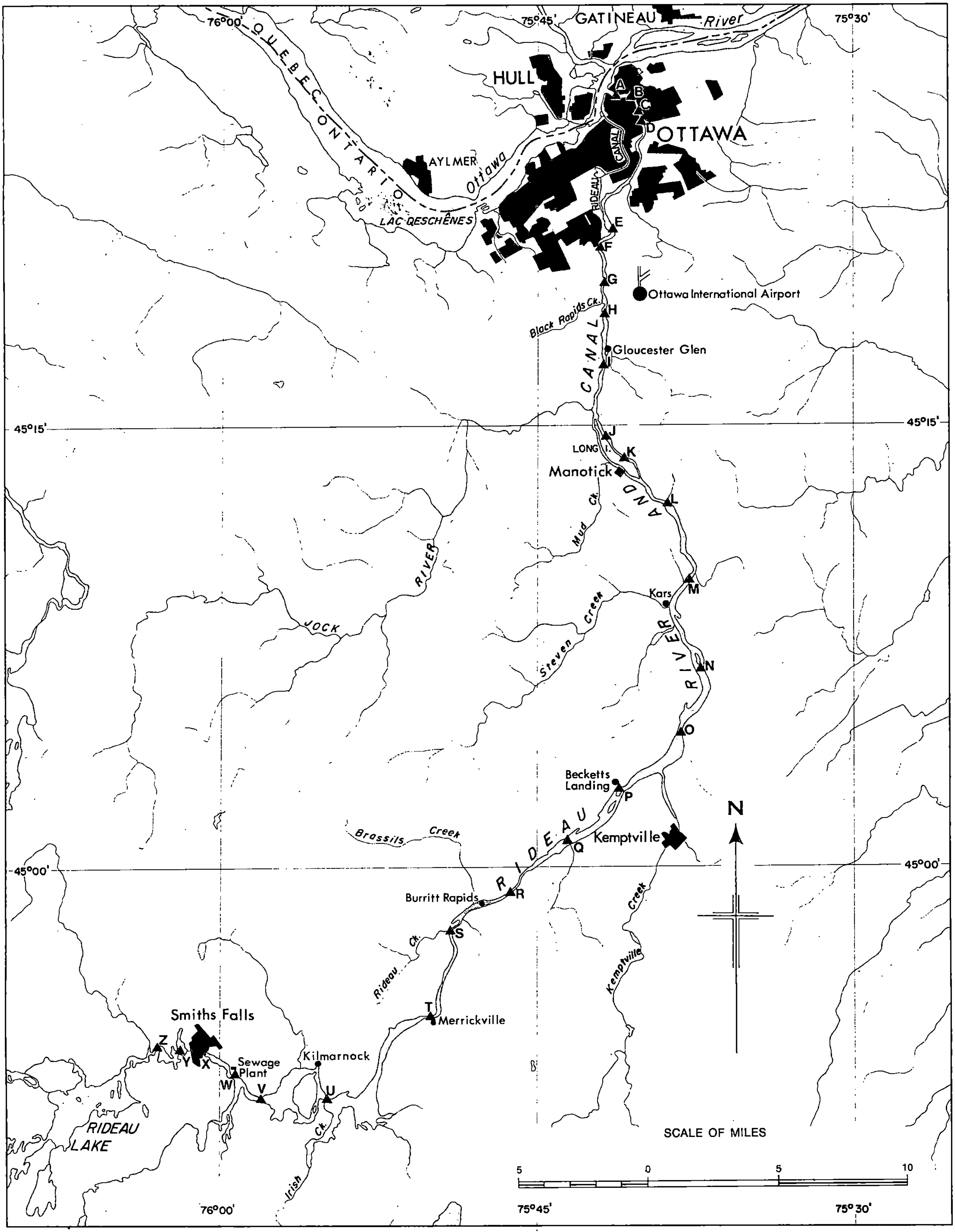

Figure 2. Sampling locations on the Rideau River.

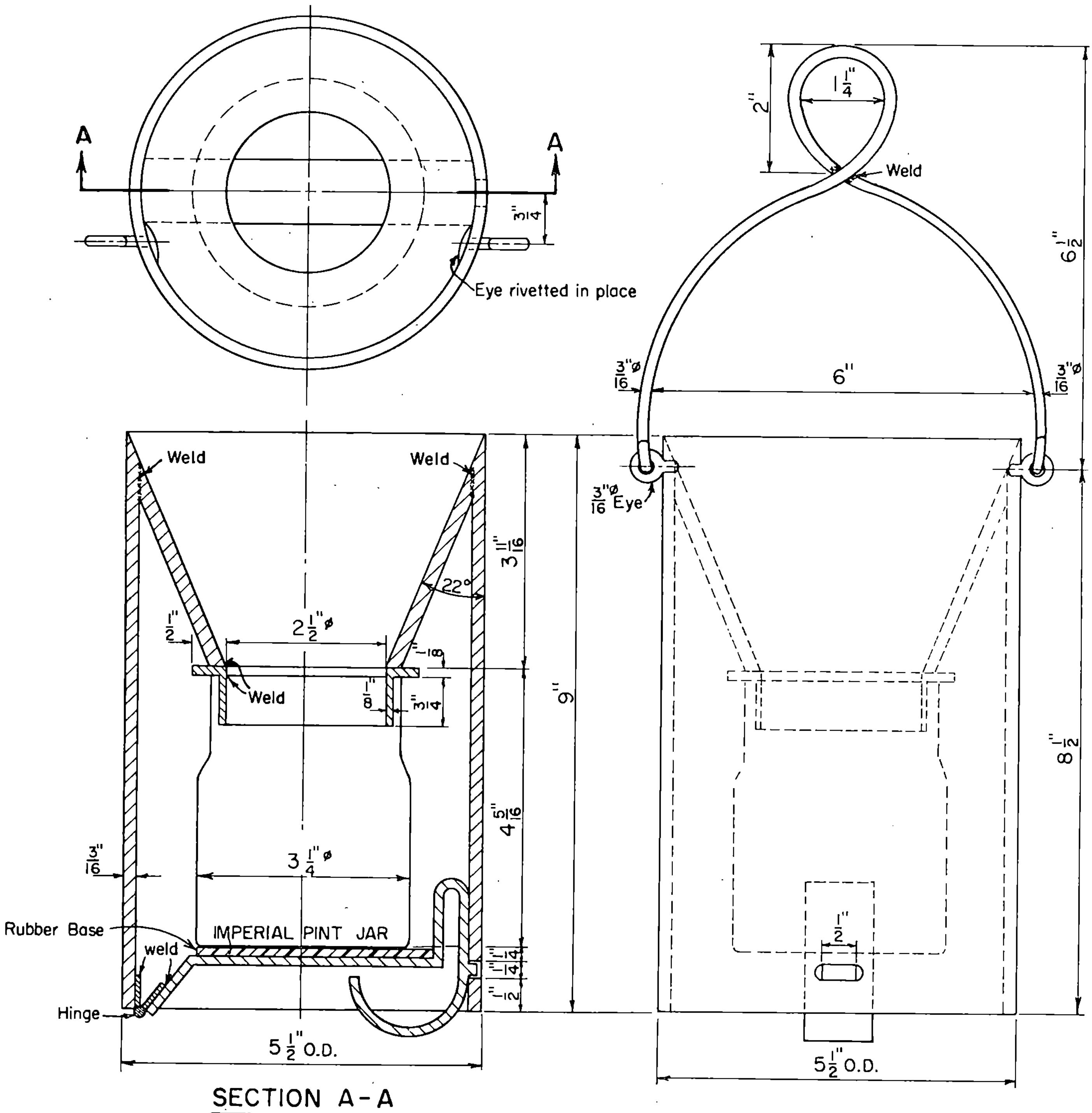

Figure 3. Lane sediment sampler.

concentrations approximately the same as the samples. These standards were analyzed both at the beginning and the end of each run to insure that the instrument was performing reproducibly. All samples were aspirated into the single-slot burner flame of the spectrometer using acetylene as the fuel and air as the oxidant. The concentration was then determined by comparing the absorbance of each metal solution with the standards.

Table 1. Atomic Absorption Spectrophotometer Instrument Parameters

Element	Lamp	Wavelength setting (mμ)	Slit width (A)	Type of flame
Pb	Pb	283	4	oxidizing
Hg	Hg	254	5	none
Zn	Zn	214	5	oxidizing
Cu	Fe-Cu-Co-Mn-Cr-Ni	325	4	oxidizing
Ni	"	232	3	oxidizing
Co	"	241	3	oxidizing
Fe	"	248	3	oxidizing
Mn	"	279	4	oxidizing
Cr	"	358	3	reducing

As conventional atomic absorption techniques are not sensitive enough to measure the concentration of mercury in the sediments, a flameless method [3] was used for this metal. A systematic diagram of the mercury apparatus is shown in Figure 4. The apparatus consists of an air pump, a reaction vessel with aerator (a gas washing bottle with a gas dispersion tube), a drying tube of $CaSO_4$, and a Pyrex absorption cell with quartz windows mounted in the spectrometer between a mercury hollow-cathode lamp and the monochromator. The detailed procedure was as follows. A 25-ml aliquot of the sample extract was pipetted into a test tube and 1 ml of 6% w/v $KMnO_4$, added to oxidize the organics in the solution. After allowing the solution to stand overnight, the excess permanganate was removed with 5 ml of 20% hydroxylamine sulphate.

The sample was then transferred to the reaction vessel where the mercury was reduced to its elemental form with 1.5 ml of 20% w/v $SnCl_2$ (in conc. HCl), and quickly aerated out of the solution and into the absorption cell with a stream of air. The sample's absorption of 254 mμ light was measured and recorded on a Perkin Elmer Model 165 Recorder. The concentration of mercury in the sample was calculated by comparing this reading with the absorption of 25 ml of mercury standards at 1 ppb, 5 ppb, 10 ppb, or 20 ppb Hg.

RESULTS AND DISCUSSION

Tables II(a) and II(b) show the results of the analyses of Ottawa River and Rideau River sediments of lead, mercury, zinc, copper, nickel, cobalt, iron, manganese, and chromium. All concentrations are presented in micrograms per gram of dry weight sediment (ppm). A description of the type of sediment is included in Column 2 of the tables. The designation of particle sizes is as follows:

(i) clay < 1/256 mm,
(ii) silt 1/256 mm to 1/16 mm,
(iii) fine 1/16 mm to 1/2 mm,
(iv) medium 1/2 mm to 2 mm,
(v) coarse > 2 mm.

Particle size is important because a fine sediment will have a larger surface area and thus should have an absorption capacity higher than that of coarse samples. The average metal concentration in ppm of the samples defined as silt (S) is: Pb 33, Hg 0.22, Zn 88, Cu 25, Ni 29, Co 15, Fe 17440, Mn 189, Cr 27; whereas, the average metal concentration of the samples defined as medium-size mineral sands (M.M.S.) is: Pb 5, Hg 0.15, Zn 24, Cu 9, Ni 10, Co 6, Fe 4300, Mn 63, Cr 9. As expected, considerably more metal is present in the finer samples. The difference is so pronounced that it is imperative to estimate or measure the particle size of the sample before analysis. This effect is probably the major reason for the large discrepancies sometimes observed in the analysis of a number of sediment samples obtained from the same location in a river. It may be necessary to separate the sediemnt into specific size fractions before analysis to assure that highly reproducible results will be obtained from a given location.

The mean background concentrations of the heavy metals in the river sediments are shown in Table III, together with the precision of the analysis at this mean concentration and the lowest detectable metal concentration in the sediment. It should be noted that the markedly high erratic values of more than 5 times the background are excluded from this average. Any result which is more than 3 times the background is termed "anomalous". The sediment samples which have been classified as "anomalous" are tabulated in Table IV.

Samples 4-3, 8-3, 12-1, 14-3, and 18-3, which have been described as clays, are high in three or more heavy metals. The large surface area in these fine samples (<1/256 mm) leads to physical or chemical adsorption and contributes to the enhancement of heavy metal concentrations in these sediments. Many of the other anomalous readings are extremely high and are definitely not due to the particle size of the sample. The sediments collected near three paper mills on the Ottawa River had mercury concentrations of 1.89, 1.99, and 2.64 ppm, respectively. The background concentration for mercury in Ottawa River sediments was only 0.28 ppm. Methoxyethylmercuric acetate was formerly used in significant quantities by the pulp and

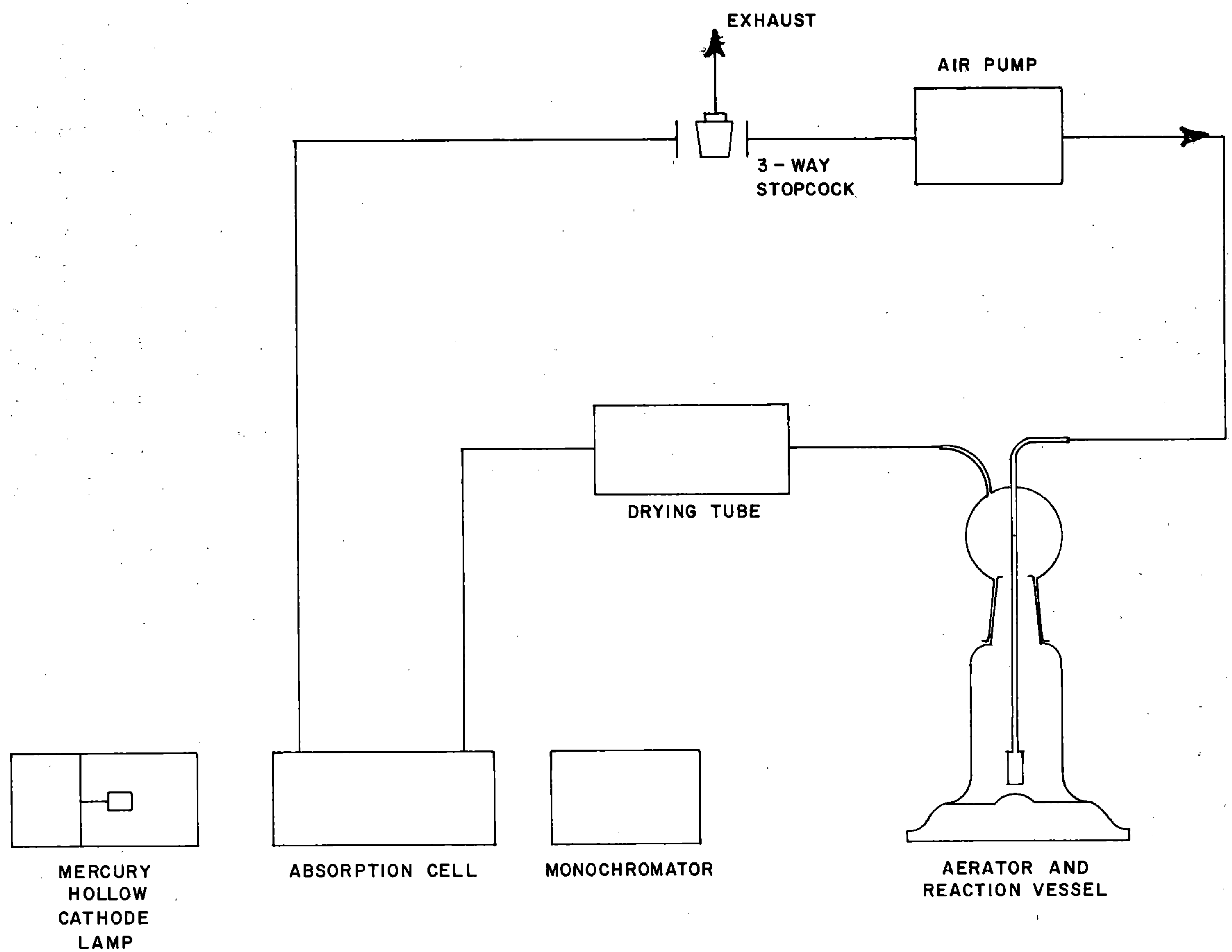

Figure 4. Mercury analysis apparatus.

TABLE II CHEMICAL ANALYSES OF OTTAWA AND RIDEAU RIVER SEDIMENTS

(a) Ottawa River Sediments

Sample Number	Sample Description*	CONCENTRATION IN PPM								
		Pb	Hg	Zn	Cu	Ni	Co	Fe	Mn	Cr
1-1	Mx.M.S.O.	216	1.89	144	41	14	7	9240	38	13
2-1	S.O.	84	0.74	115	118	25	8	5060	29	25
2-3	M.M.S.	72	0.85	149	41	28	10	7680	76	20
3-1	C.M.S.	12	0.27	23	12	3	6	3850	75	8
4-1	F.M.S.	18	0.18	24	11	9	4	2180	29	7
4-2	M.M.S.	12	0.16	25	12	8	6	3070	32	7
4-3	C.	42	0.34	143	55	75	33	30000	567	72
5-1	O.	36	0.42	46	38	11	12	4040	470	20
5-2	M.M.S.	6	0.09	24	11	9	5	2060	28	8
5-3	F.M.S.	6	0.20	24	11	9	6	3120	29	10
6-1	F.M.S.O.	42	1.99	244	74	23	9	8040	131	22
6-2	F.M.S.O.	18	0.25	50	13	14	7	4990	47	13
6-3	F.M.S.O.	24	0.41	76	25	20	9	6600	80	18
7-1	F.M.S.	0	0.53	38	25	10	7	3410	42	10
7-3	F.M.S.O.	12	0.21	78	22	15	9	6480	77	17
8-1	F.M.S.	24	0.24	19	11	9	7	2090	18	8
8-2	C.M.S.	18	0.23	30	11	14	4	4920	48	8
8-3	C.	60	0.42	187	54	67	18	27120	400	74
9-1	S.O.	24	0.47	103	35	33	15	9840	131	31
10-1	S.O.	12	0.34	52	37	37	13	6360	110	31
10-2	C.M.S.	18	0.23	20	10	8	4	3980	25	8
10-3	S.	30	0.37	83	17	18	9	9000	78	17
11-1	S.O.	36	0.44	193	54	22	12	7920	93	32
12-1	C.	36	0.14	187	54	72	31	28560	328	79
12-2	M.M.S.	0	0.10	18	8	3	4	2050	21	6
12-3	M.M.S.	12	0.27	18	8	11	5	2400	40	8
13-1	Mx.O.	222	2.64	140	56	16	8	6600	34	17
13-2	Mx.M.S.	18	0.39	18	22	14	7	7920	53	8
14-1	S.O.	0	0.41	48	19	16	5	5760	63	16
14-2	M.M.S.	12	0.21	22	8	11	1	3340	22	8
14-3	C.	30	0.30	139	52	76	29	28800	583	77
15-1	M.M.S.S.O.	30	0.29	60	18	17	9	6600	76	18
15-2	M.M.S.	12	0.13	47	8	10	2	2590	15	5
15-3	M.M.S.S.O.	36	0.14	79	24	26	13	8640	174	32
16-1	F.M.S.S.O.	18	0.16	48	13	25	12	4760	49	14
16-2	M.M.S.	0	0.10	26	8	8	7	3340	25	8
16-3	S.	54	0.20	148	35	35	15	21000	178	37
17-1	S.O.	48	0.18	125	37	26	17	15600	122	30
17-2	F.M.S.O.	36	0.10	65	12	16	10	7800	63	14
17-3	S.O.	18	0.06	67	25	14	10	7560	214	15
18-1	M.M.S.	0	0.04	23	7	8	2	2780	21	5
18-2	M.M.S.S.O.	18	0.05	74	18	17	7	6600	60	13
18-3	C.O.	84	0.36	264	55	48	23	30840	294	52
19-1	F.Q.S.	0	0.09	41	14	11	14	8640	78	18
19-3	S.O.	42	0.32	174	31	28	16	16080	142	28
20-1	S.O.	12	0.18	106	25	18	13	11400	102	23
20-2	M.M.S.S.O.	6	0.12	20	11	13	8	2860	22	7
20-3	S.O.	84	0.72	200	52	44	21	28200	215	53

(b) Rideau River Sediments

Sample Number	Sample Description	Pb	Hg	Zn	Cu	Ni	Co	Fe	Mn	Cr
A-1	Mx.M.S.	42	0.25	48	16	15	9	6960	136	9
A-3	Mx.M.S.	78	0.28	56	14	14	9	6360	110	8
B-1	Mx.M.S.	54	0.27	62	28	20	16	21600	141	23
C-2	S.O.	180	0.20	90	29	29	11	16440	206	30
C-3	C.M.S.	60	0.22	290	20	24	18	10080	218	13
D-1	S.O.	336	0.44	224	42	35	18	25800	297	48
D-2	S.O.	1344	0.17	64	24	32	18	27600	285	14
E-1	F.M.S.S.	12	0.17	46	18	18	10	14640	211	22
E-2	F.M.S.O.	0	0.17	61	11	11	8	6120	116	15
E-3	F.M.S.O.	12	0.13	38	20	16	8	7080	128	13
F-1	F.M.S.	30	0.22	53	19	18	10	10200	156	18
F-2	M.M.S.	6	0.13	26	10	9	10	6000	111	9
F-3	M.M.S.	0	0.23	20	11	13	9	4920	86	11
G-1	F.M.S.	0	0.98	17	11	6	7	3550	74	5
G-2	M.M.S.	6	0.20	14	10	13	9	3360	103	6
G-3	F.M.S.	12	0.19	18	12	11	8	5400	90	8
H-1	S.	36	0.19	78	19	24	16	18000	300	17
H-2	M.M.S.	0	0.99	30	12	20	12	6240	242	7
H-3	S.	12	0.19	104	17	26	13	15600	178	29
I-1	S.	0	0.21	61	18	24	17	18000	321	29
I-2	M.M.S.	0	0.11	16	8	10	8	4360	141	8
I-3	S.O.	12	0.15	77	20	27	16	18120	306	25
J-1	S.O.	78	0.25	109	30	40	22	32640	535	39
J-2	S.	72	0.37	83	30	40	16	22800	286	30
K-1	S.O.	48	0.22	96	23	26	16	22560	416	27
K-3	S.O.	60	0.39	91	29	27	16	19800	652	24
L-1	S.	18	0.11	108	26	43	21	29160	357	42
L-2	M.M.S.S.	18	0.11	35	11	16	9	9000	105	15
L-3	S.O.	42	0.09	74	18	20	9	15600	278	22
M-1	S.O.	18	0.08	66	20	24	20	14640	272	23
M-2	M.M.S.S.	12	0.05	41	7	11	14	5520	131	8
M-3	S.	60	0.14	121	30	36	20	25200	283	33
N-1	S.O.	48	0.12	115	28	31	21	23640	386	29
N-2	S.	18	0.12	59	29	22	15	12360	164	21
N-3	S.O.	48	0.10	121	26	27	16	20760	370	25
O-1	F.M.S.O.	18	0.35	49	19	14	13	8640	162	15
O-2	S.	30	0.28	97	37	28	12	11160	100	25
O-3	S.O.	72	0.11	100	26	32	15	15960	440	26
P-1	S.	24	0.21	31	19	19	10	9600	105	19
P-2	F.M.S.O.	42	0.11	108	32	32	20	24000	331	35
P-3	S.O.	30	0.09	54	22	18	14	10680	145	25
Q-1	S.O.	60	0.09	130	28	27	14	18120	267	24
Q-2	S.O.	30	0.09	97	20	22	12	15960	750	24
Q-3	S.O.	42	0.14	112	25	41	15	16440	372	25
R-1	S.O.	48	0.07	78	17	18	12	9000	297	18
R-2	Mx.M.S.	12	0.06	18	7	13	10	2880	75	6
R-3	Mx.M.S.	30	0.09	113	18	28	20	27840	297	33
S-2	Mx.M.S.	24	0.08	46	12	18	9	9600	144	17
S-3	S.O.	48	0.10	116	31	28	15	17160	411	26

(b) Rideau River Sediments

Sample Number	Sample Description	Pb	Hg	Zn	Cu	Ni	Co	Fe	Mn	Cr
T-1	S.O.	84	0.25	203	41	13	6	9240	405	34
T-2	S.O.	48	0.13	89	65	19	14	9000	162	25
T-3	M.M.S.S.	24	0.06	86	60	27	12	9600	189	17
U-1	S.O.	36	0.17	154	36	35	14	15000	275	27
U-2	S.O.	48	0.31	60	44	24	12	7680	107	30
U-3	S.O.	66	0.18	150	34	33	18	13200	454	30
V-1	S.O.	168	0.32	220	55	35	15	15600	700	44
V-2	M.Q.S.S.	48	0.13	34	8	7	5	1840	49	7
V-3	S.O.	174	0.34	324	56	41	15	10440	200	44
W-1	C.M.S.	42	0.13	76	24	31	17	15600	119	24
W-3	S.O.	390	2.32	846	236	71	13	6240	62	128
X-1	F.M.S.O.	174	0.17	130	92	16	8	7320	237	17
X-2	C.M.S.	42	0.11	247	18	23	14	9000	249	12
Y-1	M.M.S.S.	24	0.05	14	7	5	2	1560	53	4
Y-2	M.Q.S.O.	36	0.08	36	12	14	7	4490	237	10
Y-3	S.O.	54	0.16	77	20	18	12	6360	341	14
Z-1	F.Q.S.	18	0.13	17	8	7	5	2330	60	8
Z-2	F.M.S.	18	0.09	20	12	11	7	3580	94	9
Z-3	S.O.	36	0.18	92	24	20	12	7800	295	21

***Key to symbols:**
C – clay
S – silt
F.M.S., M.M.S., C.M.S., Mx.M.S. – fine, medium, coarse, mixed grained mineral sand
F.Q.S., M.Q.S. – fine and medium grained quartz sand
O – organic matter
Note: A second "S" in the dêsignation means the sediment contained some silt. An "O" at the end of the designation means the sediment contained some organic matter. For example: M.M.S.S.O. is a medium grained mineral sand with some silt and organic matter.

Table III. Mean Background Concentration of Heavy Metals in Ottawa River and Rideau River Sediments

Heavy metal	Mean background concentration in Ottawa River Sediments (ppm)	Mean background concentration in Rideau River Sediments (ppm)	Precision at mean concentration	Lowest detectable concentration (ppm)
Pb	26	42	±20%	6
Hg	0.28	0.20	± 3%	0.01
Zn	84	86	± 1%	1
Cu	28	24	± 4%	1
Ni	22	23	± 5%	1
Co	11	13	±10%	1
Fe	9200	12700	± 2%	5
Mn	118	241	± 1%	1
Cr	22	21	± 5%	1

Table IV. Anomalous Samples

Heavy metal	Sample number
Pb	1-1, 2-1, 13-1, 18-3, 20-3, C-2, D-1, D-2, V-1, V-3, V-3, W-3, X-1
Hg	1-1, 2-3, 6-1, 13-1, G-1, H-2, W-3
Zn	18-3, C-3, V-3, W-3
Cu	2-1, W-3, X-1
Ni	4-3, 8-3, 12-1, 14-3, W-3
Co	
Fe	4-3, 12-1, 14-3, 18-3, 20-3
Mn	4-3, 5-1, 8-3, 14-3, Q2
Cr	4-3, 8-3, 12-1, 14-3, W-3

paper industry as a slimicide to inhibit the growth of fungus during the manufacture of pulp and paper [4], but the use of mercury was discontinued by the industry in the spring of 1971. The persistence of mercury in the sediments at such high concentrations indicates that its half-life must be fairly long. Continued sampling of sediments in the vicinity of the pulp and paper plants would be useful in assessing the long-term effects of mercury on the environment.

Sediment samples taken close to a sewage treatment plant were found to be concentrated in several heavy metals. The concentration of Pb was 390 ppm, Hg 2.32 ppm, Zn 846 ppm, Cu 236 ppm, Ni 71 ppm, Cu 128 ppm. We consider that the source of these metals may well be industrial, with industries using the municipal sewage system to dispose of their waste water.

Another part on the Rideau River which caused concern was the reach through the City of Ottawa. At Stations D-1 and D-2 the lead concentrations were 336 and 1344 ppm, respectively, and just downstream at site C-2 the lead concentration was 180 ppm. The City of Ottawa formerly used a location on the river near the Mann Avenue – Range Road intersection as a snow dump in the winter. This location is almost precisely where samples D-1 and D-2 were collected, so it would seem that the high concentration of lead in the sediments is a direct result of dumping snow, probably containing lead from automobile exhausts, into the river. This practice was discontinued in late 1971 when the Ontario Water Resources Commission requested a 100-foot buffer zone between snow dumps and water courses. The reasons for the other high anomalous readings are not as clear, and further study is needed in the locations where they were collected.

The dissimilarity between the background levels of some of the metals in the two rivers requires some comment. The differences in the mercury and lead levels in the two rivers may be due in part to the pulp and paper industries on the Ottawa River and the snow dumping operations on the Rideau even though extremely high readings near these sources were excluded from the average. Another contributing factor to the higher lead levels in the Rideau sediments could be the larger number of motor boats using this shallower, slower flowing river. These craft add lead to the water in the form of leaded gasolines. Ruttner [5] has stated that the sediments of eutrophic waters act to enrich iron and manganese because of complexation between the organic material and these metals. The higher organic content of the sediments in the Rideau River may therefore contribute to the higher background concentrations of iron and manganese in this river. The background concentrations of zinc, copper, nickel, cobalt, and chromium are about the same in the two rivers.

A few general observations about the condition of the two rivers is in order. Raw sewage almost covers the surface of the Ottawa River and the discharge from industries along the river is foul. By comparison with the Ottawa River, the surface condition of the Rideau River appears to be fairly clean, but there is undoubtedly a vegetation problem, especially near sewage outfalls.

Regular sediment, water, and core sampling, especially in the areas where high metal concentrations were obtained, would be useful in following any seasonal or annual changes in sediment metal concentrations that may be occurring. A more extensive sampling program, especially in the Ottawa River, would help in obtaining more accurate background levels for the various metals in the river and in ascertaining the effects of natural heavy metal sources such as mineral deposits on the ecology of the river.

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