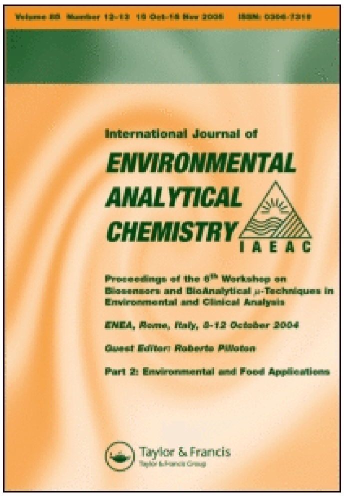

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Lake Water Acidity and the Quality of Pumped Cottage Water in Selected Areas of Northern Ontario

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Studies of the effects of standing time on the leaching of metals from the plumbing systems of cottages on three acid-rain sensitive lakes (Dickie Lake, Lake of Bays and Heeney Lake) have been carried out from August to September 1981. Passage of the lake waters through the plumbing system results in increases in pH, alkalinity and the concentrations of the metals measured: Cd, Cu, Pb and Zn. The maximum rate of leaching of metals occurred in the first 2 hours of contact time, although levels continue to rise up to 10 days. The range of leaching rates observed in (μg/l/hour) was (35–840), (14–21) and (7–254) for Cu, Pb and Zn respectively. The concentrations of Pb and Cu were closely related to the contact time and rose to or exceeded the maximum acceptable concentration "as recommended in the 1978 Canadian Drinking Water Guidelines" in the first liter of water drawn from the tap after 2 to 12 hours contact time. The maximum levels were observed in 10 day static samples where levels of 4,560 μg/l, Cu, 478 μg/l Pb, 3,610 μg/l Zn and 1.2 μg/l Cd have been recorded. These levels decreased by up to 95% in the third liter of water sampled. Concentrations of all metals in water taken after flushing of the system were all well below the

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maximum recommended limit, although still higher than those found in the corresponding lake water.

A survey of 14 cottages on Lake of Bays was also carried out during the same period. Samples of first drawn water after overnight stagnation in the plumbing system, and flushed water samples were collected at each site. Only Pb was found to be above the maximum recommended limit in the first drawn water and at only one site. The median and range (μg metal/l) for static samples collected after 4 to 12 hours stagnation time in the piping system were Cd, 0.2 (<0.1–1.0); Cu, 67 (12–442); Pb, 14 (1–53); Zn, 219 (15–935). Average concentrations of Cu and Pb in dynamic samples were 20% of those found in static samples. The concentrations of the metals were all well below recommended limits in the running water samples.

INTRODUCTION

The phenomenon of acidic precipitation, commonly known as acid rain, is acknowledged by scientists and governments to be one of the most pressing environmental issues facing widespread areas of eastern North America, western Europe and Scandinavia. Acid rain in North America is extensive and affects to varying degrees some 5×10^6 km^2 in eastern Canada and the northeastern United States.[1] Ontario government scientists claim that acid rain has acidified 140 lakes in the south-central region of Ontario and an additional 48,000 lakes are considered vulnerable to acidification.[2] This condition is predominant in many of the lakes in Canada's Precambrian Shield, in particular, the Muskoka/Haliburton, Parry Sound and Algonquin resort regions consisting of quartzite or granite based geology of limited "buffering" or neutralizing capabilities.[3] In a study by Jeffries *et al.*[4] pH values of a series of small streams in the vicinity of Dorset, Ontario, before and during run-off were compared. The pH of the lake outflows demonstrated that the surface waters, at least, of the lakes were acidified during this period of time. The lowest pH values observed, 4.1 to 5.1, are considered to be capable of causing damage to the lake ecosystem. A groundwater field survey in 1980 in the poorly buffered area of the Muskoka/Haliburton area revealed that groundwater pH values were less than 6.0 and fluctuated marginally on a seasonal basis.[6] In areas susceptible to acidification corrosion of household plumbing can occur resulting in increased levels of metals such as zinc, copper, lead and cadmium in drinking water.[7] It should be noted that the deposition of acids is not the only factor producing acidification in a lake ecosystem. Some natural processes that influence lake susceptibility to acidification are: the size and hydrological characteristics of the surrounding watershed, the nature of vegetation and soil, the nature of underlying bedrock, hydrological characteristics of the watershed, and the surrounding land use.[5] The multiplicity of interacting factors precludes the determination of the exact contribution of acid rain versus natural processes and the rate at which lakes, that are now productive, will become acidified.

General experimental studies of the effects of pH and other parameters such as alkalinity and hardness on the corrosion of pipes have been carried out by public water treatment facilities.[8, 9] These studies tend to address problems of process control in the treatment facilities and the economic impact of corrosion on the main distribution systems. High corrosion rates are generally always associated with water of low pH and low hardness.[8, 10] A simple measure of the corrosive nature of water used in such studies is the Aggressive Index (A.I.), a measure in which lower numbers indicate more corrosive waters. Very corrosive waters have an A.I. less than 10, and it is estimated that over 16% of the public water facilities in the U.S. handle water of this class.[10]

Surveys of drinking waters in Canada and the U.S. have indicated that the levels of heavy metals are generally below the recommended maximum limits.[11-14] A survey of 969 public water supply systems in the U.S. showed that 1% or less of the facilities exceeded recommended values for As, Cu, Zn, Cd and Pb.[11] In national surveys of drinking water in Canada, levels of Cd, Cr, Cu, Pb and Zn were found to be well below the WHO recommended upper limits.[13, 14] It should be noted that both of the above mentioned surveys were carried out on samples taken after flushing the water system for several minutes. It is well known that the first water drawn from the tap in the morning shows generally higher levels of a number of elements due to the increased time of contact of the water with the pipes and fixtures in the plumbing system.[13] Further research is required to delineate the effects of acid precipitation on the levels and species of metals in drinking water in Canada as related to the water source and distribution system.

The metal that has received the greatest attention by investigators has been lead.[8-19] Controlled laboratory tests on leaching of metals from pipes have not been extensive, and have focussed mainly on lead. A study on the leaching of lead from the standard 50/50 lead–tin solder used in copper plumbing was undertaken in Britain.[20] It was found that 200–300 μg of lead was released per joint in newly soldered copper pipe sections in tap water left in the pipe for 16 hours. This dropped to 10–30 μg per joint over a 4–5 week period. Samples removed from sections of pipe in an office building showed more erratic behaviour, which was ascribed to inhomogeneity in the samples. Another study on the effect of pH using a 50-year-old section of lead pipe revealed large increases in the rate of release of Pb at pH values less than 6 or greater than 8.[17] Controlled studies on the release of elements other than lead have been reported with much less frequency.[21,22] The present study was designed to investigate the effects of lake acidity on the quality of untreated drinking waters drawn from waterbodies located in the acid sensitive region of Muskoka/Haliburton. The lakes selected for the program were Lake of Bays, Dickie and Heeney lakes. Samples were collected from residential/cottage test sites at all three lakes following 0, 2, 12, 24 hours and 10 day standing periods in order to assess the degree of metal leaching (in untreated drinking water). A survey of 14 selected cottage sites in Lake of Bays area involving 37 static and dynamic sample was also undertaken.

EXPERIMENTAL

Apparatus

A Varian Techtron Model AA-475 atomic absorption spectrophotometer equipped with a deuterium background corrector for non-specific attenuation and a Perkin–Elmer Model HGA 2100 heated graphite atomizer were used for the analyses of Cd, Cu, Pb, Zn and Cr. Sample aliquots of 20 μl were delivered to the furnace by a Perkin–Elmer AS-1 autosampler and absorbances were recorded on a Datel Intersel Model DPP-Q7 printer. Pyrolytic graphite tubes were used. The optimum operating parameters are given in Table I.

A Varian Techtron AA-5 atomic absorption spectrophotometer equipped with a heated open-end quartz tube was used for the determination of As and Se by the hydride generation technique. The optimized operating conditions were given in Table II. The temperature of the tube furnace was regulated by means of a 0–

TABLE I

Optimized parameters for the determinations of Cd, Cu, Pb, Zn and Cr by graphite furnace atomic absorption spectroscopy

Parameter	Element				
	Cd	Cu	Pb	Zn	Cr
Lamp	HCL[a]				
Lamp current, mA	4	4	7	5	5
Analytical line, nm	228.8	324.7	283.3	213.9	357.9
Deuterium lamp	On				
Integration	10 s				
Mode	peak height				
Drying temp. °C	125	125	125	125	125
Time, s	30	30	30	30	30
Charring temp. °C	500	900	500	400	1000
Time, s	30	30	30	30	30
Atomization temp. °C	1900	2700	2700	2500	2700
Time, s	10	10	10	10	10
Ourge gas	argon				
Flow mode	Normal	Interrupt	Interrupt	Normal	Interrupt

[a]HCL = Hollow cathode lamp.

TABLE II

Optimized parameters for the determinations of As and Se by hydride generation

Parameter	Element	
	As	Se
Analytical line (nm)	193.7	196.0
Lamp type	HCL[a]	HCL[a]
Lamp current (mA)	7	5
Slit width (μm)	300	300
Recorder span (mv full scale)	2	2
Chart speed (cm/min)	0.5	0.5
Sample time (min)	1.0	1.0
Wash time (min)	2.0	2.0
Atomization temperature (°C)	850	850

[a]HCL = Hollow cathode lamp.

100 V Variac transformer. A Technicon autosampler, proportionating pump, and manifold were used in conjunction with a 1–10 mV variable range strip-chart recorder for automatic operation.

A Varian Techtron Model AA-5 atomic absorption spectrophotometer was used for the analyses of Ca, Mg and Zn by flame atomization.

Reagents

Stock standard solutions containing 1000 mg/l of the elements of interest were prepared by dissolving the pure metals or their salts in a slight excess of nitric acid or hydrochloric acid (Ultrex, J. T. Baker Co.). The solutions were made up to volume with high purity water which was obtained by distillation of tap water in a corning all-glass distillation system followed by passing through a mixed bed ion exchange column. Ultrex HNO_3 (J. T. Baker Co.) was used to acidify water samples and for preparation of working standard solutions. All other solutions were prepared using reagent grade chemicals.

Sampling locations

The three rented cottage sites are located on Lake of Bays, Dickie Lake and Heeney Lake. All are within an 83 kilometer radius of Lake of Bays in the Muskoka/Haliburton region. These lakes were classified by the Ministry of the Environment Acid Sensitivity Survey of Lakes in Ontario—March 1981 in the category of Lakes of "Extreme Sensitivity". Lakes in this category are of a very low alkalinity, but the pH itself is not expected to be toxic to most of the biota for the majority of the year. The pH however would almost certainly be depressed during spring snow melt and fish kills and other biological damage might occur at that time. The locations of these lakes are given in Figure 1 and locations of the three rented cottages are given in Figure 2 and Figure 3. A brief description of the plumbing system for each cottage is as follows:

i) *Lake of Bays—rented cottage 1* It consisted of 1.8 meters of copper pipe, 70.1 meters of PVC pipe with a 114 liter galvanized steel storage tank and a pump, in line, feeding the sample tap.

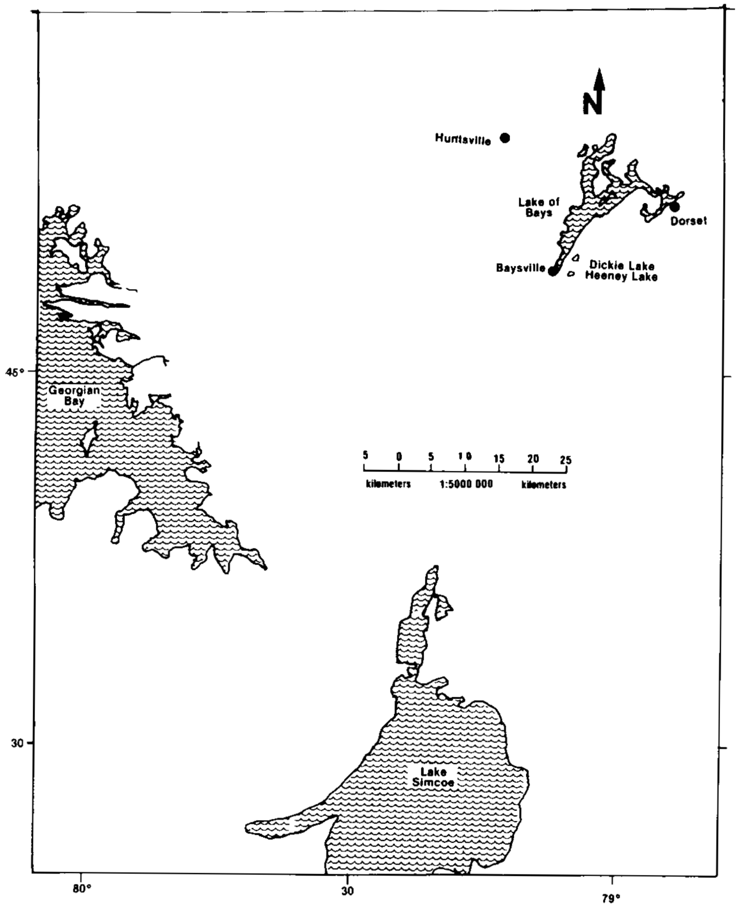

FIGURE 1 Location of lakes for the cottage study and cottage survey.

ii) *Dickie Lake—rented cottage 2* It consisted of 5.5 meters of copper pipe, 36.6 meters of PVC pipe with a pump and a 45 liter galvanized steel pressure tank feeding a 45 liter unheated glass-lined hot water tank, which fed the sample tap.

iii) *Heeney Lake—rented cottage 3* It consisted of 7.0 meters of standard copper pipe, 0.6 meters of 2.5 cm diameter copper pipe, 0.6 meters of steel pipe, part of which was rusted, 30.5 meters of PVC

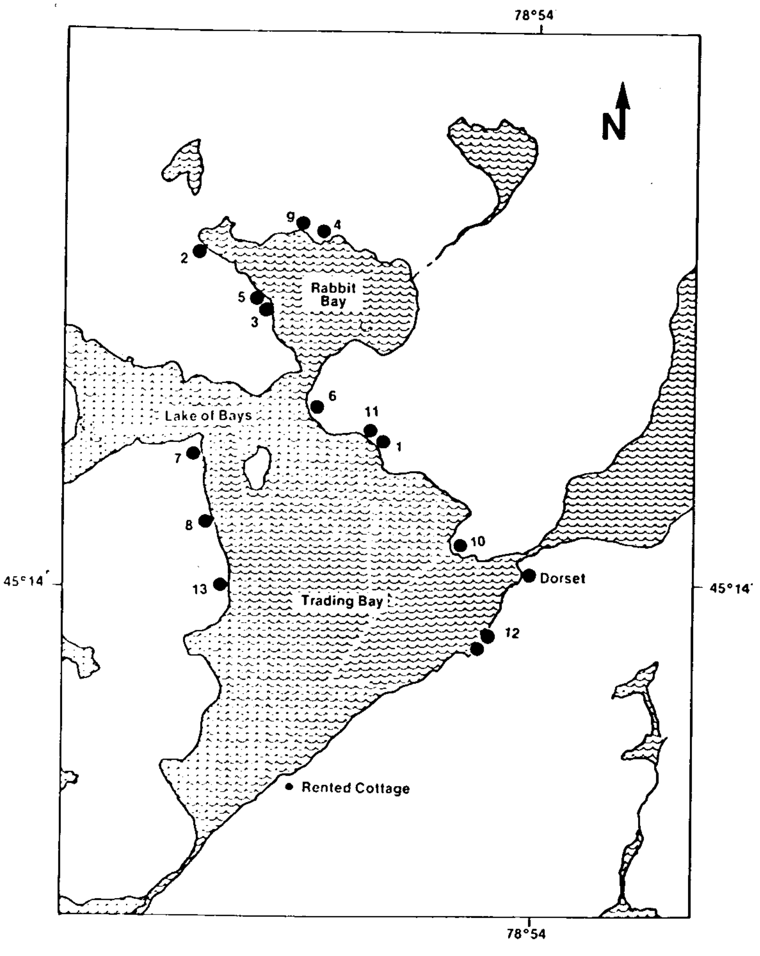

FIGURE 2. Location of cottage sites for the study and survey.

pipe with a pump and a 227 liter galvanized storage tank feeding the sample tap.

Sample collection

For time studies, 0, 2, 12 and 24 hour cold water tap samples were collected in duplicate, while 10 day samples were collected in

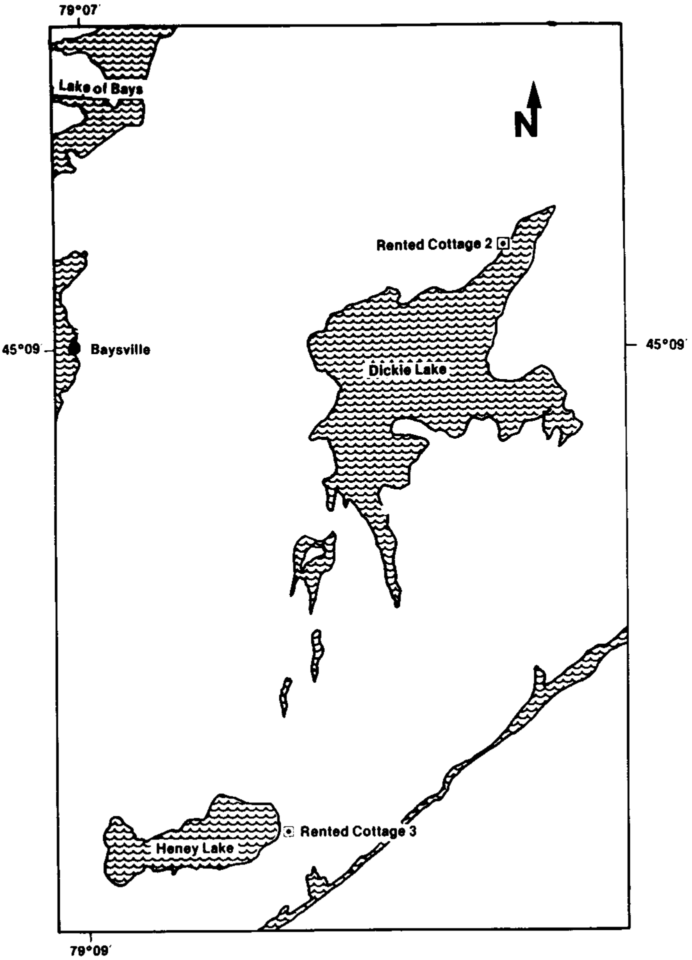

FIGURE 3. Location of cottage sites for the study and survey.

triplicate, from the three cottages. Dynamic water samples (0 hour), taken after the taps had run for 5 minutes were collected in 1000 ml sample bottles in duplicate. For static waters, in general, the taps were run for 5 minutes before they were closed and sealed for the required time. At the end of the specified time, 1000 ml samples were collected in duplicate or triplicate.

The cottage survey involved 20 static (first draw) and dynamic (running-second draw) cold water tap drinking water samples collected in duplicate 1000 ml bottles from the Lake of Bays. Then samples were split into two 500 ml bottles as soon as possible, one of which was acidified with 2 ml of HNO_3 (Ultrex). Raw water samples from three lakes were also collected in triplicate for analysis of Cd, Cu, Pb, Zn, As, Se, Cr, pH, alkalinity and hardness and stored in 1000 ml linear polyethylene (Nalgene) and 500 ml polypropylene (Nalgene) screw-cap bottles. Prior to use, the bottles were cleaned according to the procedure adopted by Meranger *et al.*[13] 1000 ml samples were then split into two 500 ml polypropylene screw-cap bottles. One was acidified with 2 ml HNO_3 (Ultrex) for metal analysis and the other remained unacidified for pH and alkalinity determinations. Only the first sample of duplicate and triplicate collections was analyzed for Cd, Cu, Pb, Zn, pH, alkalinity and hardness. All others were analyzed for Cd, Cu, Pb and Zn only. Some selected samples were analyzed for As and Cr. All samples were kept in coolers and shipped immediately for analysis.

Analytical procedures

The pH measurements were done using an Orion Research pH meter (Ionalyzer, Model 407A), equipped with a glass electrode (Fisher Scientific Ltd., No. 13-639-31) and a single junction reference electrode (Orion Research, Inc. Model 90-01). Calibration of the pH meter was performed daily using buffer solutions of pH 4, 7 and 9 prepared from Certified Buffer Tables (Perkin–Elmer Corp.) according to the manufacturers' instructions.

Alkalinity was determined by potentiometric titration using 0.002N H_2SO_4 as a titrant. The end point (pH 4.0) was located by plotting pH vs. volume of H_2SO_4 added on Gran's paper. The concentrations of Ca and Mg were determined by flame atomic absorption spectroscopy as described in Environment Canada "Analytical Methods Manual".[23] A solution of 0.2% lanthanum oxide in 0.4% HCl and 0.2% HNO_3 was added prior to the measurement to mask matrix interferences. Hardness was then calculated from the concentrations of Ca and Mg.

The concentrations of Cd, Cu, Pb, Zn and Cr in water samples were determined in most cases by graphite furnace atomic absorption spectroscopy (GFAAS). However, concentrations of Zn in most water samples except for the raw lake water samples were so high that flame atomic absorption spectroscopy was used. For GFASS determinations, the analytical procedures were based on those developed by the U.S. EPA.[24] In the analysis of Cu, Zn and Cr, direct determination was used without any treatment except for suitable dilution with 0.5% HNO_3 (Ultrex) for the high concentration samples. In the analysis of Cd and Pb, a solution of 40% $(NH_4)_2HPO_4$ or 5% $(La(NO_3)_3$, respectively, was added prior to the measurement in combination with a high charring temperature to eliminate matrix effect. The optimum operating parameters for GFAAS are given in Table I. Calibration curves for each element were prepared using standard solutions in 0.5% HNO_3 (Ultrex). Average concentrations of each element were calculated from triplicate runs discarding the outliers based on the Q-test. Concentrations of As and Se were determined by heated quartz tube atomic absorption spectroscopy. The As or Se is volatilized by converting it to the corresponding hydride by *in situ* reduction of As or Se by the acid-induced decomposition of $NaBH_4$. The method is semi-automatic and the sampling and hydride generation train is based on that of Vijan *et al.*[25] The optimized operating conditions for As and Se by the hydride generation systems are given in Table II.

Quality control

A reagent blanks and standards were run with a frequency of 10% of total analyses. Since no appropriate certified standard was available at the time of analysis, a pool solution containing low levels of the metals of interest was used.

RESULTS AND DISCUSSION

Quality assurance

Direct determination of Cd, Cu, Pb, Zn and Cr in a drinking water matrix by GFAAS can be relatively easy. The addition of $(NH_4)_2HPO_4$ and $LA(NO_3)_3$, for Cd and Pb respectively to the samples and standards prior to the measurement allowed for the selective volatilization of the matrix during the charring cycle without loss of Cd and Pb. The linear working ranges obtained under optimized conditions were as follows: 0–5 μg/l for Cd and Zn; 0–40 μg/l for As and Se; 0–50 μg/l for Cr; 0–70 μg/l for Cu; 0–100 μg/l for Pb. Detection limits of 1.0 μg/l were obtained for As, Cr, Cu, Pb and Se while values of 0.1 and 0.5 μg/l were obtained for Cd and Zn respectively.

The validity of using the direct GFAAS method for Cu, Pb, Cr, Cd and the heated quartz furnace AAS method for determining As and Se was verified by obtaining recoveries on spiked water samples. The spike levels used were 1 μg/l for Cd and 20 μg/l for Pb, Cr, As and Se. The average percentage recovery for 16 spiked water samples was 104%, 98% and 102% for Cd, Cu and Pb respectively. In the case of Cr, As and Se the average percentage recovery on three spiked samples was 90%, 97% and 91% respectively. The maximum coefficient of variation obtained based on triplicate determinations was 10%.

Data to determine the accuracy and precision of the analyses were collected by the analyses of a pool solution and by repeat determinations, respectively. Although NBS Standard Reference Material 1643a (Trace Elements in Water) was commercially available and ordered, the material did not arrive in time to use during this study. For this project, a stock solution containing 1 mg/l of Cu, Pb and Zn and 0.5 mg/l of Cd was prepared and diluted to contain the following concentrations: Cu 21.0 μg/l; Pb, 19.5 μg/l; Zn, 994 μg/l; Cd, 2.6 μg/l. This pooled solution was treated as a sample throughout all of the preparation and analysis steps for all samples to evaluate accuracy and precision. The coefficient of variation obtained was $\leqq 10\%$ in all cases and the 95% confidence limit was $\leqq 12\%$.

Cottage time study

Table III presents a comparison of analytical results between raw lake water and pumped cottage water. The low alkalinity and hardness values for all three lakes show the low buffering capacity of these lakes, and hence their susceptibility to the effects of acidic deposition. The low pH values in combination with low alkalinity render these waters aggressive and result in the corrosion of

TABLE III

Average pH, alkalinity, hardness and trace element content in raw lake water and pumped cottage water[a]

Location	Type of water[b]	pH	Alkalinity (p.p.m. CaCO)	Hardness (p.p.m. CaCO)	Ca (mg/l)	Mg (mg/l)	Cd (μg/l)	Cu (μg/l)	Pb (μg/l)	Zn (μg/l)
Lake of Bays	R	6.03	8.0	22.0	7.2	1.0	≦0.1	≦1	≦1	2
	C	6.32	7.2	21.6	7.0	1.0	≦0.1	8	4	41
Dickie Lake	R	5.57	7.3	15.5	5.2	0.6	0.1	≦1	≦1	4
	C	5.90	6.1	15.2	5.0	0.65	0.3	141	4	476
Heeney Lake	R	5.47	7.1	13.6	4.5	0.6	0.2	≦1	≦1	5
	C	5.75	5.1	13.5	4.5	0.55	0.4	45	3	759

[a] As, Se and Cr content were below the detection limit of (1 μg/l) in both types of water.

[b] R = raw lake water; C = pumped cottage water.

plumbing materials. The values measured for the lake waters are close to those previously recorded for several American cities [8,19] where elevated levels of Pb and other metals are known to be leached from domestic plumbing systems. The low concentrations of metals measured in the lake waters (at or below detection limit) indicate that very little contamination of the streams feeding the lakes occurred during this sampling period.

The analytical results of the 0, 2, 12, 24 hours and 10 day time studies of the three rented cottages are given in Tables IV–VI. The mean and range of hardness values for all dynamic and standing samples were essentially the same as the corresponding lake waters and are therefore not given in these tables. There is a trend of low alkalinity for the dynamic and short standing samples and higher for the long standing samples. While high concentrations of polyvalent anions such as phosphate, silicate and borate, interfere with alkalinity determinations[24] the concentrations of these ions are expected to be low in the lake waters, and their concentrations should also not be expected to change on contact with the plumbing systems. The increase in alkalinity can, however, be accounted for by the reduction of acid in the release of metal ions. The average change in alkalinity between the dynamic and 10 day static samples, converted to *u*eq/l, for the Lake of Bays, Dickie Lake and Heeney Lake cottages was 60, 200 and 170 respectively. The corresponding changes, in *u* eq/l, of the two metals leached in significant concentrations, Cu and Zn, are 30, 190 and 50. Other parameters that can also contribute to the changes in alkalinity, such as oxidized iron and oxidizable organic species, were not measured in this study.

The concentrations of Cu and Pb dropped significantly in the second and third liter sampling for all static samples. In some cases, decreases of up to 95% have been observed. No similar trends were observed for Cd and Zn. The relatively high levels of Cu and Pb no doubt result from the leaching of piping and solder materials as previously reported by Moore[15] while the Zn is expected to be a result of galvanized steel pressure tanks present in the water distribution system.

The rate and extent of leaching of Cu, Pb and Zn were strongly influenced by the composition of water (pH and hardness), cottage plumbing system and period of contact with the system. For a given

TABLE IV

Effect of standing time and repetitive sampling on the quality of pumped water from Lake of Bays.[a]

Standing time (hours)	Cu (μg/l)			Zn (μg/l)			Pb (μg/l)			pH	Alkalinity (mg/l CaCO$_3$)
	a	b	c	a	b	c	a	b	c	a	a
0	5	14		30	27		2	5		6.5	6.0
	5[d]	*8*		*58*	*47*		*3*[d]	*4*		*6.15*	*8.4*
2	83	17		218	234		45	11		6.65	6.0
	66	*14*		*180*	*191*		*42*	*9*		*6.65*	*6.0*
12	110	13		213	214		77	8		6.35	5.0
	116	*19*		*165*	*325*		*78*	*10*		*6.75*	*10.0*
24	196	23		223	262		103	13		6.30	10.6
	226	*25*		*275*	*566*		*108*	*15*		*6.30*	*10.0*
240	245	44	27	730	1370	918	340	55	35	6.40	10.0
	138	*35*	*34*	*800*	*977*	*996*	*191*	*58*	*54*	*6.50*	*10.4*

[a] First liter sampled.

[b] Second liter sampled.

[c] Third liter sampled.

[d] Italicized figures indicate repeat sampling from the same location following identical standing periods.

TABLE V

Effect of standing time and repetitive sampling on the quality of pumped water from Dickie Lake.[a]

Standing time (hours)	Cu (μg/l)			Zn (μg/l)			Pb (μg/l)			pH	Alkalinity (mg/l $CaCO_3$)
	a	b	c	a	b	c	a	b	c	a	a
0	105	333		560	566		4	5		6.00	7.2
	105[d]	*201*		*440*	*336*		*4*	*3*		*5.80*	*5.0*
2	1890	1620		545	371		31	9		6.40	10.0
	1680	*1460*		*465*	*316*		*33*	*8*		*6.20*	*4.0*
12	2050	1450		510	324		27	12		6.55	12.0
	2240	*1550*		*580*	*566*		*46*	*12*		*6.35*	*8.0*
24	2690	1680		1080	957		73	19		6.30	12.0
	2380	*1860*		*675*	*645*		*81*	*14*		*6.45*	*12.0*
240	4490	670	585	1760	1150	1150	115	35	30	6.20	16.0
	3750	*447*	*316*	*2000*	*1780*	*1740*	*478*	*30*	*65*	*6.20*	*16.8*
	4560	*660*	*520*	*2480*	*2210*	*2210*	*343*	*79*	*66*		

[a] First liter sampled.

[b] Second liter sampled.

[c] Third liter sampled.

[d] Italicized figures indicate repeat sampling from the same location following identical standing periods.

TABLE VI

Effect of standing time and repetitive sampling on the quality of pumped water from Heeney Lake.[a]

Standing time (hours)	Cu (μg/l)			Zn (μg/l)			Pb (μg/l)			pH	Alkalinity (mg/l $CaCO_3$)
	a	b	c	a	b	c	a	b	c	a	a
0	42	47		250	547		3	3		5.55	5.0
	46[d]	*45*		*1130*	*1110*		*3*	*2*		*5.95*	*5.2*
2	419	136		1460	1390		31	9		6.10	6.4
	479	*188*		*1250*	*1270*		*35*	*9*		*6.10*	*7.2*
12	350	119		1010	1110		30	8		6.10	6.0
	656	*194*		*1050*	*1110*		*44*	*9*		*6.35*	*6.4*
24	973	450		1200	1350		80	15		6.3	8.0
	935	*385*		*1220*	*1500*		*89*	*16*		*6.4*	*8.0*
240	2820	2320	212	2800	3300	1540	304	59	18	6.45	14.4
	1840	*1780*	*243*	*2330*	*3610*	*2210*	*236*	*80*	*25*	*6.20*	*12.8*

[a] First liter sampled.

[b] Second liter sampled.

[c] Third liter sampled.

[d] Italicized figures indicate repeat sampling from the same location following identical standing periods.

water source and cottage plumbing system, the concentration of the metals Cu, Pb and Zn leached were a function of standing time. A rapid initial leaching was observed within a 2 hour period followed by a slow rate from 2 to 24 hours. A period of almost 10 days was required to reach the equilibrium level. The corrosion of metal pipes is a complex phenomenon involving the presence of many electrode couples on the surface of the pipe.[26] Metals are oxidized at the anode and become solubilized while hydrogen ions in solution are reduced. In the presence of dissolved oxygen, no hydrogen gas is produced due to removal of reduced H^+ as water. If left undisturbed, hydrogen gas produces a protective film on the surface and reduces the rate of leaching. The substantial decreased rate of leaching observed after 2 hours standing can be ascribed to the build up of a protective film at the anode due to a decrease in the concentration of dissolved oxygen. The generally lower values for the dynamic water samples are due to the short contact time available for the electrochemical reactions to occur.

A summary of the rate of metal (Cu, Pb and Zn) leaching as a function of standing time for the three cottages studied is presented in Table VII. As can be seen from this table, the rates for Cu and Zn especially for the 0–2 hour period were very different for the three cottages studied whereas the rate for Pb was substantially lower and more uniform. Equilibrium values of metals leached in 10-day dynamic and static tests are presented in Table VIII. In general, the coefficients of variation of duplicate runs for the dynamic test were less than 10% for Cu and Pb and larger than 10% for these metals in the 10 day standing test. The coefficients of variation of duplicate runs for Zn were erratic and larger than 10% for all the dynamic and standing tests. The major source of Zn would be expected to be from the steel pressure tanks in the cottages, but the levels of Zn found showed no correlation with the size of the tanks. This result, plus the relatively large variation for the repeat tests, was probably due to variable contact time in the pressure tanks. The agreement between two tests was much better for Cu and there were substantial differences in the levels of both dynamic and standing water in the three cottages. The lowest copper level was seen in the Lake of Bays cottage which had the shortest length of copper pipe (1.8 meters) compared to Dickie and Heeney Lake cottages with 5.5 meters and 7.0 meters of copper pipe, respectively. However, the effect of length

TABLE VII

Rate of metal leaching as a function of standing time in the cottage water system

	Rate of leaching		
Standing time	Cu	Pb (μg metal/l/h)	Zn
Lake of Bays cottage			
0– 2 hours	35	21	78
2–24 hours	6	3	2
24 hours–10 days	0	1	2
Dickie Lake cottage			
0– 2 hours	840	14	7
2—24 hours	34	2	7
24 hours–10 days	8	1	7
Heeney Lake cottage			
0– 2 hours	203	15	254
2—24 hours	23	2	0
24 hours–10 days	6	1	7

TABLE VIII

Equilibrium values of metals leached in dynamic and static water samples

	Equilibrium value		
	Cu	Pb (μg metal/l)	Zn
Lake of Bays cottage			
Dynamic (0 hours)	5±0	3±0.7	44±20
Static (10 days)	192±76	266±105	765±49
Dickie Lake cottage			
Dynamic (0 hours)	105±0	4±0	500±85
Static (10 days)	4267±449	329±190	2080±367
Heeney Lake cottage			
Dynamic (0 hours)	44±3	3±0	690±622
Static (10 days)	2330±693	270±48	2565±332

of copper pipe was far from linear. The lower pH of the lake waters for the latter two cottages may also have contributed to the higher Cu concentrations but the number of sites was too small to draw a definite conclusion. Inter-cottage variation in age, source and condition of piping would also make a significant contribution to variations in the leaching rate. Although the variation in Cu concentrations in the water of the cottages, was large, levels of Pb (Table VIII) were much closer. The apparent agreement of the Pb values, despite the differences in the length of pipe and number of soldered joints, needs further investigations.

Arsenic and chromium could not be detected in 10 day static samples and lake waters (detection limit 1 μg/l). Although As and Cr are known to be present in plumbing fixtures[22] and that traces of Cr have been reported previously by Meranger *et al.*[13, 14] no evidence of leaching of these metals was found in any of the cottages sampled in this study.

Although not given in the tables the mean Cd concentrations of 0.2 ± 0.1 and 0.5 ± 0.1 μg/l found for Dickie Lake and Heeney Lake cottages respectively, were higher than the mean concentration in the corresponding raw lake waters of 0.1 and 0.2 μg/l, the Cd levels showed no correlation with standing time or the concentrations of the other elements. Cadmium was not detected in the Lake of Bays. Strain[22] has pointed out the presence of Cd as a contaminant of the zinc used to galvanize steel and Cd has been found to be leached from galvanized steel pipe.[8] The highest levels of Cd were seen in the Heeney Lake cottage which also had the highest Zn levels. This cottage had the largest galvanized steel storage tank and is the only cottage with galvanized pipe (short lengths) in the plumbing system. The main source of Cd leaching thus appeared to be the galvanized storage tank present in all these cottages.

Water survey of selected cottages

Two types of samples were collected in the early morning for comparison—a static and a dynamic sample. Static samples were first drawn waters from the sample taps and represented water with maximum contact time in the cottage plumbing system. The average length of contact time from the questionnaires filled out by the cottage owners was 9 hours. Dynamic samples were collected after flushing the taps for 5 minutes and represented waters with a minimum contact time in the cottage plumbing system. Cottages selected for this survey were those with a lake water-pressure system and copper pipe. A total of 14 cottage sites in Lake of Bays of the Muskoka/Haliburton region were sampled on Sunday, August 22, 1981. Repeat samples from five of 14 cottages were collected on Monday, August 23, 1981. At one site (No. 2) a standing sample was not collected. Thus, a total of 18 static samples and 19 dynamic samples were analyzed in the cottage water survey (Tables IX and X). A considerable decrease in concentration from the static to the dynamic samples was observed at all sites. As was seen in the cottage time study, the changes in Cd and Zn concentrations were smaller than in other metals. It should be noted that the anomalously high value for Cd in the second dynamic sample at site 1 was verified by the repeated analysis of separate aliquots from the sample container. It was also found that the low values for Cu and Pb in the first static sample for site No. 3 were the result of a mistake in the sample collection and therefore the values obtained for this site were not included when calculating the averages.

As can be seen from Table X, pH and hardness showed little variation for all samples. For some cottage sites (Nos. 6, 9 and 11), the alkalinity of the static sample was substantially higher than that of the dynamic sample, as observed in the cottage time study. However, the difference between the mean alkalinity of static and dynamic samples were not significant. The increase in alkalinity observed in the cottage study did not occur until 12–24 hours of standing time, which was longer than the average of 9 hour contact time for the cottage water survey.

Concentrations of trace metals (Cd, Cu, Pb and Zn) showed significant variation between different cottages in spite of the fact that all sites used water from the same lake (Lake of Bays) and all sites had basically all copper and/or plastic plumbing systems. The mean and median values of Cd, Cu, Pb and Zn for the whole population, static and dynamic samples are given in Table XI. In general, the mean values for all the metals were higher than the median values for all three populations. Correlation analysis indicated that the best correlations were for Cu with pH and Pb for the static samples and Pb with Zn for the dynamic samples. Cd was never found to exceed the recommended level (5 μg/l)[1] and was often

TABLE IX

Trace element content of static[a] and dynamic[b] sampling of pumped water from 14 cottages in the Lake of Bays area.

Site number	Cu, μg/l		Zn, μg/l		Pb, μg/l		Cd, μg/l	
	a	b	a	b	a	b	a	b
1	20 (44)[c]	9 (16)	298 (255)	151 (290)	5 (8)	2 (4)	0.9 (0.8)	≦0.1 (1.1)
2	— (211)	20 (12)	— (52)	40 (59)	— (10)	1 (1)	— (0.8)	0.2 (0.1)
3	23 (118)	14 (13)	38 (36)	20 (31)	2 (16)	3 (2)	0.4 (≦0.1)	0.1 (≦0.1)
4	48	38	29	43	3	1	≦0.1	≦0.1
5	179	31	62	65	2	≦1	≦0.1	≦0.1
6	442	39	15	8	4	1	≦0.1	0.2
7	120 (162)	11 (14)	368 (353)	255 (325)	46 (42)	6 (6)	0.4 (0.1)	0.4 (0.2)
8	13 (12)	3 (5)	130 (155)	123 (165)	1 (2)	≦1 (2)	0.1 (0.4)	0.1 (0.2)
9	155	8	448	50	53	4	1.0	0.2
10	21	33	403	408	6	1	0.1	0.2
11	121	77	182	225	14	15	0.2	≦0.1
12	32	25	363	425	4	3	0.3	0.2
13	85	14	353	133	20	4	0.1	0.1
14	32	3	935	485	8	3	≦0.1	≦0.1
Average	106 (107)	24 (12)	299 (203)	185 (210)	14 (16)	3 (3)	0.3 (0.5)	0.2 (0.4)

[a] Static sample obtained after 4 to 12 hours standing period.

[b] Dynamic sample obtained after flushing the taps for 5 minutes.

[c] Numbers in parentheses indicate repeat samples at the same site obtained the next day.

TABLE X

pH, alkalinity and hardness values of static[a] and dynamic[b] sampling of pumped water from 14 cottage sites in the Lake of Bays area.

Site number	pH		Alkalinity (mg $CaCO_3$/l)		Hardness (mg $CaCO_3$/l)	
	a	b	a	b	a	b
1	6.25 (6.70)	6.70 (6.50)	9 (6)[c]	11 (6)	11.1 (11.9)	11.1 (11.1)
2	— (6.40)	6.70 (6.50)	— (4)	10 (3)	— (12.7)	11.1 (11.1)
3	6.15 (6.66)	6.20 (6.50)	8 (5)	7 (5)	11.1 (11.1)	11.1 (11.1)
4	7.05	7.20	10	12	12.5	11.1
5	6.60	6.10	7	6	11.9	11.1
6	6.95	6.50	10	4	11.5	11.1
7	6.80 (6.90)	6.80 (6.70)	10 (10)	12 (8)	11.1 (11.1)	11.1 (11.1)
8	6.30 (6.20)	5.90 (6.50)	8 (14)	6.4 (4)	11.1 (11.6)	11.1 (11.1)
9	6.90	6.50	10.4	5.0	12.7	11.1
10	6.60	6.50	8.0	6.0	10.1	11.1
11	6.70	6.50	9.0	6.0	13.2	11.1
12	6.70	6.80	10.9	9.0	12.1	12.1
13	6.50	6.60	6.0	5.0	10.1	11.1
14	6.70	6.45	5.0	4.0	11.1	11.1
Average	6.7 (6.8)	6.5 (6.6)	8.6 (6.0)	7.4 (5.2)	11.5 (12.0)	11.2 (11.1)

[a] Static sample obtained after 4 to 12 hours standing period.

[b] Dynamic sample obtained after flushing the taps for 5 minutes.

[c] Numbers in parentheses indicate repeat samples at the same site obtained the next day.

TABLE XI

Average and median trace metal concentrations obtained in the cottage water survey

Type of sample		Trace element			
		Cd	Cu	Pb (μg metal/l)	Zn
Whole pop.	Mean	0.3	60	8	210
	Median	0.1	25	4	155
Static samples	Mean	0.3	102	14	249
	Median	0.2	67	7	219
Dynamic samples	Mean	0.2	20	3	174
	Median	0.1	14	2	133

below the detection limit. The concentration ranged from 0.1 to 1.0 μg/l with a mean value of 0.3 μg/l for the static samples as compared to 0.1 to 1.1 μg/l with a mean value of 0.2 μg/l for the running samples. The mean Cd level in the running samples was higher than that in the corresponding raw lake water and indicated that some contamination of the drinking water did occur. The value was higher than that reported for distributed water in a Canada-wide survey,[13,14] but was substantially below the mean value of 1.3 μg/l from a U.S. study.[19] The average enrichment factor for the standing sample as compared to the running water was only 1.5. Although significant leaching of Cu occurred, even in the dynamic samples, the concentration never exceeded the maximum recommended level of 1000 μg/l in this cottage time study. The concentrations ranged from 12 to 442 μg/l with a mean value of 102 μg/l for the static samples as compared to 3 to 77 μg/l with a mean value of 20 μg/l for the dynamic samples. The mean Cu for the dynamic samples was the same as the mean value of 20 μg/l reported by Meranger *et al.*[13] The average enrichment factor for the static sample as compared to the dynamic sample was about 5, and indicated that the Cu concentration of cottage tap waters was significantly influenced by the contact time of water with the plumbing system. Analysis of 18 standing samples for Pb showed that only sample number 9 exceeded the recommended level of 50 μg/l while two samples from site 7 were very close to the maximum acceptable level. However, analysis of 19 running samples showed that Pb concentrations were generally well below the recommended level. The concentrations ranged from 2 to 53 μg/l with a mean value of 14 μg/l for the static samples as compared to 1 to 15 μg/l with a mean value of 3 μg/l for the dynamic samples. The average enrichment factor for the static sample as compared to the dynamic samples was four-fold. As for Cd, the mean for the dynamic sample is higher than found in the Canadian surveys[13, 14] and lower than a U.S. survey.[19] Zn concentrations never exceeded the maximum acceptable level of 5000 μg/l in this cottage time study. The concentration ranged from 15 to 935 μg/l with a mean value of 249 μg/l for the static sample as compared to 8 to 485 μg/l with a mean value of 185 μg/l for the dynamic samples. The average enrichment factor for the static samples as compared to the dynamic samples was 1.3, indicating that the Zn concentration was not significantly influenced by the contact time of water with the plumbing system.

CONCLUSIONS

The results of the cottage water survey showed that the plumbing system had a reasonably consistent effect on the drinking water available from cold water taps. Alkalinity and pH of the water increased, and the metals Cd, Cu, Pb and Zn were all leached in significant amounts from the plumbing material. The concentrations of Pb and Cu in static samples are closely related to the length of contact time of the water with the metals of the plumbing system. The greatest rate of leaching occurred in the first two hours of contact, although release of the metals continued up to 10 days. The results for Zn were less consistent although similar trends are observed. For Cd, no consistent correlation with contact time was observed and, although levels of Cd were above those of the raw lake water, which contained levels up to 0.4 μg/l, the values obtained (<0.1 to 1.2) μg/l were much lower than the maximum of 5 μg/l recommended by the 1978 Canadian drinking water guidelines.[27] The above trends demonstrated that Cu and Pb were leached principally from the copper piping, whereas Zn and Cd contamination arose mainly from the galvanized steel pressure tank.

In the test cottages, Pb and Cu concentrations exceeded the recommended limit for drinking water in static samples after 12 to 14 hours contact time with the pipes. These levels were generally lower in the second liter of water sampled, although for long contact times (1 to 10 days), the recommended limit was still exceeded in the case of five samples. The results of the 14 cottage water (Table IX) survey showed good agreement with the cottage time study results. The average concentrations of Pb and Cu in dynamic samples was one-fifth of those in the static ones, whereas the decreases for Cd and Zn were only 1.5 fold. The average contact time for the static samples was 9.2 hours which was substantially less than the 12–24 hours contact time required in the cottage time study for Pb and Cu to rise above the maximum acceptable limit. The average Pb and Cd concentrations in the dynamic samples were higher than those reported for distributed water system by Meranger[13,14] for the elements in two cross-Canada surveys.

It should be pointed out that the average intake of metals from the drinking water would be between the two extremes from the static and dynamic samples. Water drawn from the tap during the day would have lower concentrations of metals than the static samples, but contact times of 1/2 to 2 hours would not be unusual, and it was shown in the cottage time study that the maximum rate of leaching occurred in this time period. The traditional grab sampling method does not provide a suitable sample for the accurate estimation of trace element intake from drinking water.[28,29] The Department of National Health and Welfare is presently developing a trace metal integrating sampler based on chelex-100 ion exchange resin concentration.[29] It is hoped that this sampling technique will provide a more realistic risk estimation by producing better exposure data.

In conclusion the present study has shown that care should be exercised when consuming water without pH from areas which are subject to relatively high acidic precipitation and have been in prolonged contact with plumbing systems. In many cases the maximum recommended levels for toxic trace elements can be exceeded within a few hours of contact with the plumbing system. The amount of leaching is no doubt enhanced by the low pH of the raw water source. Although there is no cause for immediate alarm with only one static sample barely exceeding the recommended level in the case of Pb in one cottage site it is recommended that taps be flushed prior to the consumption of water. Work is continuing to assess the impact of acidic precipitation on the overall quality of drinking water from selected areas in Canada. The following areas will be considered for future study: geographic areas which have poorly buffered lakes and streams, areas known to be in proximity of recognized pollution sources and/or long range transboundary air pollutants, areas lacking in drinking water treatment facilities, areas where water treatment facilities do not adjust pH or raw drinking water, areas with substandard lead plumbing and or high content of lead in plumbing solder.

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