Circular 2

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THE EFFECT OF CERTAIN ILLINOIS WATERS ON LEAD

THE EFFECT OF CERTAIN ILLINOIS WATERS ON LEAD[1]

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The question of the solubility of lead in water and its toxicity is by no means new. Although lead poisoning from water supplies is not restricted to any definite locality, most of the cases cited in the literature have been from supplies characterized by low mineral content. Since the water supplies in Illinois have relatively high mineral content, cases of lead poisoning here are uncommon. Our interest in this subject has been recently aroused by the appearance of a peculiar case in Champaign, diagnosed by physicians at Mayo Brothers' clinic, as lead poisoning. The patient had some of the characteristic symptoms of lead poisoning and was found to be excreting approximately 0.1 mgm. of lead per day. After all possible sources of lead aside from the water supply were supposed to have been thoroughly examined, an analysis of the water supply for lead was requested. The result showed 0.08 p.p.m. of lead present. From information which we have obtained there appeared to be some lead pipe between the city main and the tap in the patient's house.

Cases are on record of waters which contain lead as pumped from the ground, but the chief source of lead in water is from lead pipes which have been used for carrying water for centuries. Records at Rome indicate that lead pipes were installed there about 20 A. D. and have been in use since that time. From a table recently compiled by Donaldson (2) it appears that lead pipes are in use all over the United States. Lead poisoning must be considered a possibility wherever lead pipes are used, although certain factors to be mentioned later make it highly improbable in many instances.

One of the first clear cut cases of lead poisoning cited in the literature is that of Louis Phillipe who settled with his family at Claremont, England (3) in 1848. The water was brought from a spring two miles distant through lead pipe. For thirty-three years the

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water was used with no ill effects but when the spring was covered in such a way as to prevent the escape of carbon dioxide, 34 per cent of the users of this water were poisoned. Hamilton (4) cites the case of the poisoning of nuns in a convent near Lyons which was discovered by Lacour after three of the nuns had died and when twelve were still living but still seriously affected. For ten years the nuns had been drinking a water containing 2.7 mgm. of lead per liter. Since 1870 many cases of lead poisoning have been found in New England (5). Best known are those in Massachusetts, particularly that of the Lowell outbreak in which 41 cases were reported. Cases of lead poisoning at Milford, Fairhaven, Kingston, Norwood, Gilbertsville, New Bradford, and Hopedale, Mass., Atlantic City, N. J., and cases in Rhode Island, and New Hampshire may be mentioned.

TABLE 1

Alloioable limits of lead in water

DATE	AUTHOR	LEAD
		p. p. m.
1886	Watkins (1)	1.7
1895	Whitelegge (21)	1.0
1910	Gartner and Telekey (3)	1.0
1917	Barbour {32)	0.5
1923	Howard (6)	0.5
1925*	Thresh (34)	0.5
1920*	Weston (2)	0.1
1924	Whipple (7)	0.1
1925	Manual A. W. W. A. (8)	0.1

* Thresh and Weston cite many other authors. Limits vary from trace to 1.43.

In the above cases it appears that different amounts of lead in the waters were responsible for the poisoning. With nearly every report of a case of lead poisoning one finds a different figure given for the maximum amount of lead allowable in a water supply. Table 1 gives a list of some of the allowable limits cited with the author and date at which the statement was made. From the variations in the table it is not at all suprising that lead pipes are often accused of being responsible for lead poisoning. Many authors believe that any detectable trace of lead in a water supply should be looked upon with suspicion, while others point out that many water supplies always contain some lead.

As individuals vary greatly in their susceptibility to lead poisoning it will be very difficult to give a limit which will be satisfactory. Thresh cites one case of lead poisoning where only 0.0466 p.p.m. of lead was found in the water. He questioned the validity of this case as it was lower than any other figure which he had. The sample submitted for analysis may or may not have been a fair sample of the supply. Whipple summarized the information regarding limits quite well when he stated that ten to twenty years ago he would have placed the limit at 0.3 to 0.5 p.p.m. while now he places it at 0.1 p.p.m.

TABLE 2

Causes of lead erosion	*Causes of lead solvency*
Low alkalinity $<$ 15 p.p.m.	Free carbon dioxide
	Humic, and peaty acids
High dissolved oxygen	Mineral acids
Salts-NaCl, etc.	

TABLE 3

Water causing solution of lead

SOURCE OF SUPPLY	HARDNESS	ALKALINITY	CARBON DIOXIDE
	p. p. m.	*p. p. m.*	*p. p. m.*
Cook well at Lowell	55	33	45
42 wells (Thresh)	7.3-90	0-75	1.0-5.5
Milford-Hopedale	24	27	1.4
Canal Zone		0.6-4.2	

As there is such a variation of opinion as to the limit, considerable weight should be given to the figure of 0.1 p.p.m. given in the Manual of Water Works Practice (8).

The important factors causing the solution of lead appear to be high carbon dioxide, organic acids, oxygen, low alkalinity and possibly nitrates, nitrites, and chlorides (1, 6, 10, 11, 12, 13, 14, 15, 16, 18, 19, 20, 5, 2, 21, 22, 23, 24, 25, 26, 27, 28, 30, 31, 32, 33). The actions of water on lead according to Weston (3) can be classified into two groups (a) plumbo-solvency which is the true solution of lead and which usually takes place in the presence of carbon dioxide and other acids, and (b) erosive action caused by slightly alkaline waters containing dissolved oxygen.

Donaldson (2) agreeing with Weston defines erosion or "lead rusting" as the term used to describe the action of neutral or slightly alkaline oxygenated waters on lead. Solvency or plumbo-solvency is used to described the action on lead of highly carbonated acid waters, which may or may not contain oxygen. Baylis (33) thinks that the compound formed in the presence of much carbon dioxide may be a basic carbonate of lead $Pb_3(OH)_2(CO_3)_2$. Table 2 summarizes the important causes of lead erosion and plumbo-solvency.

The hardness, alkalinity and CO_2 of some waters known to have caused lead poisoning are given in table 3.

TABLE 4

Public ground water supplies in Illinois and their residues

NUMBER OF SUPPLIES	RESIDUE
	p. p. m.
0	0-100
0	100-200
35	200-300
111	300-400
68	400-500
62	500-600
35	600-700
29	700-800
16	800-900
11	900-1,000
41	1,000-1,500
27	1,500-2,000
24	Over 2,000

In order to show the differences between the supplies noted in table 3 and Illinois supplies, a number of ground waters analyzed by the State Water Survey are listed against the residue in p.p.m. One notes from table 4 that there is not a ground water supply in Illinois which has been listed in State Water Survey Bull. 21 (35) which has a residue of less than 200 p.p.m.

Most Illinois waters are so highly mineralized that an analyst has considerable difficulty in separating the trace of lead present from the large amount of residue obtained on evaporation.

ANALYTICAL DETERMINATION OF LEAD

Several different methods have been used in determining lead in water. H. Pick (36) removed minute quantities of lead by adsorption on asbestos. The asbestos was filtered off, and the lead dissolved and determined. B. Avery (37) and others concentrated the water to a small volume, precipitated the lead as the sulfide, dissolved this in nitric acid, precipitated the lead as the sulfate, dissolved this in ammonium acetate and finally precipitated it in Nessler tubes as the sulfide. Another method was that of spectroscopic analysis as suggested by Lewis (38). He claimed that this method could be used to determine traces of lead in water. His method was tried out in this work and was found to be unsatisfactory. To determine successfully very small quantities of lead in water, large amounts of the water must be evaporated. In a region like this where the waters have, for the most part, comparatively high residues, one is forced to handle rather large quantities of material and this is mechanically almost impossible. Another difficulty with the method is that iron, which is nearly always present in greater quantities than the lead, gives a multitude of fines in the spectroscope which makes it quite difficult to detect the line produced by lead. The lead line persists only a short time and photographic plates are almost essential to detect it.

For the most part colorimetric methods have been used in the determination of lead in which the lead is precipitated as the sulfide and compared to standards. Different modifications of this general method have been used. Von C. Reese (39) and Drost devised a modification to take care of error introduced into the general method by organic matter. They used a sample of water in question, from which all lead has been removed for making up standards. According to Thresh (29) the presence of traces of copper such as are likely to be present in distilled and in many natural waters often interferes with the colorimetric determination of lead as the sulfide. He recommended the addition of 2 cc. of the following solution before the addition of the hydrogen sulfide: 30 cc. British Pharmacopoeia acetic acid, 70 cc. copper free distilled water and 0.1 gram "gold leaf" gelatin.

The method for determining lead in this work was that given in Standard Methods of Water Analysis (17). It consists essentially in concentrating the sample, precipitation as the sulfide, solution in nitric acid, precipitation as the sulfate in 50 per cent alcohol, solution in ammonium acetate, treatment with hydrogen sulfide and comparison with standards containing known amounts of lead. This method was designed for use in determining lead in low residue waters and so has' its objection when used on high residue Illinois waters. However, it appears to be the best method available at the present time.

EFFECT OF ILLINOIS WATERS ON LEAD

Using the method just outlined, analyses of water were made from the sources shown in table 5. There appears to be some solution of lead from a water such as the Champaign-Urbana water.

A brief investigation of waters of equivalent alkalinity to Champaign-Urbana water but containing varying concentrations of NaCl was made. NaCl was used because statements were found in the literature regarding its producing increased corrosion and because the chloride content of some Illinois waters is high. Chlorides could not be used to explain the solubility of lead in Champaign-Urbana water as there are only 4 p.p.m. of chloride present. Carbon dioxide (about 30 p.p.m.) and oxygen are probably the important factors here. Table 6 summarizes the result of this investigation. A white precipitate showed definitely in samples III and IV within twenty-four hours, II showed a slight precipitate in forty-eight hours. At the close of the experiment, six weeks later, samples II, III, IV, showed a turbidity of over 100 when thoroughly shaken. I, Ia never showed more than a trace of corrosion on the plate.

TABLE 5

Lead in water

SOURCE	LEAD
	p. p. m.
Patient's home	0.08
Patient's home	0.08
House next door	0.03
Tap A	0.05
Tap B.*	0.09
University tap	0.02
Distilled water	0.01
Pontiac, Ill. †	0.027

* 125 feet lead pipe connection.

† Surface supply. Raw water.

From these experiments it appears that sodium chloride is of importance in the corrosion of lead, but of little importance in the solution of lead.

So little is known regarding the solution of lead in Illinois waters that it was decided to place strips of lead in samples of water obtained from several city supplies. The strips were weighed, and then hung in bottles by string, and the bottles stoppered and sealed with paraffin. At the end of two weeks the samples were analyzed for lead in solution and the.strips of lead were cleaned and re-weighed.

TABLE 6

Effect of varying the concentration of sodium chloride on the solubility of lead

	LEAD AT END OF SIX WEEKS		Distilled water	Solution $NaHCO_3$ AS $CaCO_2$	NaCl
	Suspension	Solution			
	p.p.m.	*p.p.m.*	*cc.*	*p.p.m.*	*p.p.m.*
I	0	0.3	1,000	400	0
I a	70	0.08	1,000	400	500
II	340	1.0	1,000	400	2,000.
III	630	0.16	1,000	400	5,000
IV	510	0.45	1,000	400	10,000

Each bottle contained a strip of lead ⅛ by 1 by 6 inches.

TABLE 7

Solution of lead in Illinois waters

SAMPLE	HARDNESS	ALKALINITY	CHLORIDE	RESIDUE	LEAD SOLUTION	LOSS OF WEIGHT OF LEAD STRIPS
	p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*mgm.*
Decatur	121	160	2	302	0.11	58.8
Cedar Point	222	150	295	1,009	0.025	46.2
Stronghurst	1,100	216	259	2,971	0.23	16.0
Danforth	156	290	530	1,374	0.2	88.7
Chenoa	240	304	550	1,276	0.5	66.0
Norris	110	542	1,010	2,743	0.43	25.8
Mt. Sterling	725	379	1,310	4,076	0.2	31.4

Table 7 gives the results of the analyses together with the alkalinity, hardness, residue and chlorides of seven samples of water.

From the data in table 7 it appears that there is no direct correlation between hardness, alkalinity, chlorides, residue and the effect of these waters on lead. We have noted that such erosion as takes place stops in a few days and if the strips which have been placed in the waters listed in table 7 and allowed to stand for two weeks are placed in fresh samples of similar waters, the corrosion is negligible; indicating that these waters form protective coatings.

Studies on the prevention of corrosion of lead as cited in the literature indicate that one could expect little corrosion of lead by hard waters. The report of D. H. Stacks on "The Effect of Artesian Water upon Galvanized Steel Pipes" read before this organization in 1913 is the only authentic report of metal poisoning from water reported in this State of which we are aware. These cases were supposed to be due to zinc poisoning and all trouble ceased with elimination of the galvanized pipe.

PREVENTION OF LEAD CORROSION

The methods for preventing corrosion of lead have been studied for a long time and appear to be well known. Watkins (1) cites the inhibiting effect of silicates in the Mississippi river water on the solubility of lead. Clark (22) states that increase in hardness or addition of sodium silicates prevent the action of water on lead. Whipple (28) states that three-quarters of the water supplies in New England have a hardness of less than 20 p.p.m. The addition of lime to decrease the carbon dioxide content and increase the hardness of the waters prevents their action on lead. At Lowell, Mass., (32) it was found that aeration of the water to decrease the carbon dioxide from 45 to 3.3 p.p.m. reduced the lead content of the water to less than 0.5 p.p.m. At Deventer (9) it was found that the lead content of the water increased after the installation of an iron removal plant. Addition of lime lowered the lead content of the water from 0.6 to 0.2 p.p.m. Bunker (31) working with waters in the canal zone found that he must keep the alkalinity above 2.4 p.p.m. with that water to prevent over 0.1 p.p.m. of lead from going into solution. Addition of lime to the Birmingham (10) supply prevented trouble from lead poisoning. Thresh (26, 27) states that alkali silicates are several times more powerful than silicic acid in preventing solution of lead in water. Donaldson (23) cites a case in South Carolina in which soda ash was added to the supply to prevent corrosion. The addition of soda ash neutralizes acidity due to carbon dioxide and does not harden the water. At Keighley, England (9) sodium carbonate was added to the water before filtration to prevent plumbo-solvency. Baylis (33) states that the pH of 7.0 to 9.5 is least inducive to lead corrosion.

Whether any of our Illinois waters which may be softened and recarbonated will dissolve appreciable quantities of lead is yet to be known.

SUMMARY

The quantity of lead found in the Champaign-Urbana water was less than the allowable limit given in the Manual of Water Works Practice and also less than the quantity usually associated with lead poisoning. If poisoned from the water supply the individual poisoned by the Champaign-Urbana water must have been extremely sensitive to traces of lead.

The erosion of lead in waters containing $NaHC0_3$ alkalinity of 400 p.p.m. and varying NaCl content was found to increase with increase in the concentration of NaCl.

Analyses of average Illinois waters in which strips of lead were placed indicates that a protective layer soon forms which practically eliminates further corrosion of lead.

The procedure given in the Standard Methods of Water Analyses for the analysis of lead is not satisfactory for high residue waters.

It is to be predicted or at least to be hoped that, in the future, experiments on the solubility of lead, copper, and zinc in many different water supplies will be made, and that these experiments will be carried out in closed systems under conditions so that the factors of carbon dioxide and oxygen may be carefully controlled.

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