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Influence of Acid Rain Upon Water Plumbosolvency

by Michael R. Moore*

The West of Scotland has had particular problems in the past associated with soft acidic water supplies and uptake of lead from domestic plumbing systems by such water. As a consequence of this, health problems related to overexposure to lead have been identified. The current debate on acidification of ground waters by acid rain is therefore particularly pertinent to this area. Studies have shown that even a modest decrease in pH will result in very substantial increase in plumbosolvency. This was found to be of particular importance in the city of Glasgow and town of Ayr, where prior to water treatment, pH values were 6.3 and 5.4, respectively, and where, consequentially, large numbers of homes did not comply with lead in water standards. Closed-loop lime-dosing systems were introduced in both Glasgow and Ayr to increase the pH with immediate decrease in the lead content of the water and, subsequently, blood lead concentrations of the subjects living in these areas. Such closed-loop systems will compensate for any acidity in water supplies, whether of natural origin or originating from acid rain precipitation. However, when such treatment has not been applied, any increase in water acidity due to acid rain will worsen a situation which is, in many cases, already unacceptable.

Introduction

Water for human consumption suffers enormously from having to pass through distribution systems (*1*). Although most reservoir supplies of water throughout the world have modest concentrations of lead in them (*2*), these concentrations frequently rise, sometimes very steeply, after passing through distribution systems. The principal determinant of such rise would appear to be water acidity. The lead content of water supplies rises dramatically where soft acidic waters pass through lead plumbing systems (*3–5*). It is not essential that the plumbing system be made exclusively of lead, since lead solder used in the jointing of copper systems will also provide a source of contamination (*6–10*). Uptake from plastic pipes has also been experienced where lead stearate was used as filler in the plastic (*11*), although this problem is a minor one compared to that of metal pipes (*12*). A number of other factors will also contribute to the uptake of lead and other metals into the water. Where the water stands for any length of time in the distribution system concentrations tend to be higher than when water flow in the system is continuous. But even where continuous flow is found, lead concentrations can frequently be unsatisfactory where pH is low and temperature high (*13–17*). The reasons for fall in pH in water supplies have generally been accounted as natural in the past. At the end of the 18th century, spring water was considered to be particularly likely to be associated with lead poisoning. This was indubitably due to the acidity of the water (*18*). Poisoning occurred in towns in Yorkshire because of peat-related rise in acidity, water being collected from moorland sources (*19*). Another interesting instance of increased acidity was associated with an episode of lead poisoning following the removal of Louis Phillip and his family to Claremont in England in 1848. The estate there had been supplied with water for 37 years from a spring through a lead pipe which was 2 miles long. No problems were experienced by the local population prior to 1848 but, about that time, the spring, previously open to the air, had been enclosed by an iron dome which allowed accumulation of natural carbon dioxide gas from the spring with consequent increases in water acidity and hence plumbosolvency (*4*). The present investigation aims at investigating whether or not pH changes associated with acid rain could consequentially increase plumbosolvency and thereby present a hazard to subjects utilizing such water supplies.

Materials and Methods

Blood and water samples in these studies were obtained over the period 1976–1983 from human subjects and from their homes in the area served by Strathclyde

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Water Board. Two towns in particular were investigated: Ayr and Glasgow. In these, as well as measurement of blood lead concentration, extensive surveys were made of the water lead distribution in the homes of the subjects.

Groups Studied

In these studies, relatively young women were chosen who had recently borne children, as being sufficiently homogenous in age and physiological status. They also represented the whole range of social classes found typically in the social setting of the West of Scotland. In Glasgow, two different but representative groups of women were examined in the postnatal wards of a large general hospital. The first group was examined in the autumn and winter of 1977 and consisted of 236 women, while the second group consisted of 475 mothers examined in 1980. In Ayr on the Clyde coast, the initial group studied was of 114 mothers with children under the age of 5, examined in the months of January, February, and March, 1981. In the second phase of the study carried out in the same months of 1983, 96 of these mothers were re-examined together with a further 25 mothers in the same category, who lived in homes which had water lead concentrations less than 10 μg/L.

Blood and Water Lead Measurements

Blood lead measurement was carried out by electrothermal atomic absorption spectrophotometry, initially on a Perkin-Elmer Model 306 instrument with heated graphite atomizer 72 and deuterium background correction, but subsequently on a Perkin-Elmer 703 with HGA500 and AS1 Autosampler, again with background correction. The programs for both were similar. Blood was diluted 1 to 5 with 0.1% v/v Triton X-100 (Rohm and Haas) solution prepared with doubly distilled water. A 20 μL portion of this solution was injected directly into the furnace which dried the sample at 100°C for 20 sec, ashed at 450°C for a further 20 sec, and atomized at peak temperature 2040°C (HGA72) and 2500°C (HGA500) for 4 sec to complete the analysis (*20*). Measurements of absorption were taken at the lead line of 217.0 nm. Checks on accuracy and precision were made by participation in Quality Control Schemes and by a 10% exchange of samples with other accredited laboratories. In the Ayr studies, samples were analyzed independently by three different laboratories. Water lead analysis was carried out by flame atomic absorption spectrophotometry by the methods given by the Water Research Centre (*21*).

Sampling

Blood samples were taken from the women by venepuncture and the blood collected in EDTA tubes, which had been batch checked for lead contamination. Water samples were collected by mothers from their kettles, and cold water taps in the kitchen. In Ayr, kettle water samples and composite samples of cold water were collected into acid-washed polyethylene bottles by Water Board officials.

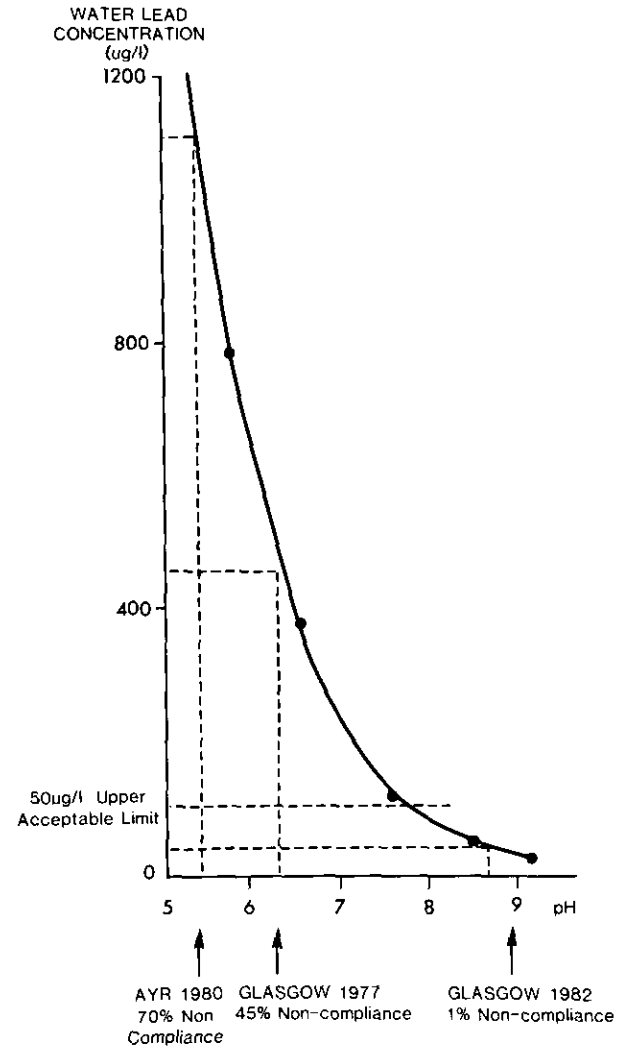

FIGURE 1. *Relationship between pH and plumbosolvency. Uptake of lead from distilled water, corrected for pH, was measured after 1 hr of standing in 1 m of old 1/2-in. diameter lead piping.*

Results

From the inception of these studies, it was obvious that the major contributor to uptake of lead from water was the acidity of the water. The graph of water pH against plumbosolvency emphasizes this (Fig. 1). The normal range of drinking water pH lies between 6 and 9 but, as is shown by the studies in Ayr, values can lie well below this. The lowest value seen in these studies was 4.5. Speciation of the lead salts contained in the interior of lead pipes suggests that this is primarily carbonate acidity although there is evidence of other salts being present.

The generally unsatisfactory nature of the water supplies in the two towns studied, as evidenced not only

by the excess of water lead found in numerous homes, but also by the proportion of mothers studied in these houses who had blood lead concentrations which were considerably greater than normal acceptable limits for such a population (<30 μg/dL) but also because of the number of subjects lying much higher than the geometric mean (Table 1).

Treatment of the water supplies to raise pH had an immediate beneficial effect upon plumbosolvency in both towns. In subsequent examination of groups of mothers a parallel change was observed in the decrease in blood lead concentrations. The relationship between water pH and plumbosolvency based on the percentage of samples complying with a limit of 100 μg/L of lead in water is shown in Figure 2. This is virtually a linear relationship which implies that any decrease in pH will inevitably result in an increase in the number of noncomplying households. This situation would be more than proportionately worse if a standard of 50 μg/L were applied, as is due to take place in July 1985 in the United Kingdom and as already applies in the USA.

During distribution of water treated with lime, there is a time and distance increment in acidity as the water "ages." This means that in areas distal to the treatment works, pH had fallen sufficiently to increase plumbosolvency. Following calculations by the Water Research Centre, orthophosphate (2 mg/L) was added to a service reservoir for such an area. When equilibrium had been attained an improvement in the plumbosolvency was seen. Where previously there was mean water lead of 244 μg/L, values fell to a mean of 21 μg/L, and no samples were found to be greater than 100 μg/L lead.

The improvement in blood lead concentrations following these pH changes have been documented previously (Fig. 3) (*22,23*). In both Glasgow and Ayr there was a highly significant fall in geometric mean blood lead (Table 1). From the information available from these studies the relationship between blood lead and water was found to be curvilinear with blood lead varying with the cube root of the water lead concentrations [Eq. (1)]:

$$\text{Blood lead} = 5.6 + 2.6\,(\text{water lead})^{0.33} \qquad (1)$$

where blood lead concentrations are in μg/dL and water lead concentrations taken from the kitchen kettle are in μg/L. The coefficient of correlation for this equation is 0.81. More significantly, where water lead concentrations of less than 50 μg/L were regressed against their blood lead concentrations, the relationship still held. Thus this nonlinear relationship between blood and water lead holds down to very low concentration of water lead. The point of noncontribution of water lead to blood lead at the axis, 5.6 μg/dL, corresponds extremely well with experimental data.

Discussion

In the geographical and sociological context of the West of Scotland, the problems of plumbosolvency have been compounded by a number of factors. Foremost among these is the extensive use of lead in plumbing systems. Until 1967, lead was still used as a link between the cast-iron main and the domestic supply in the house. In addition to this, there was frequent use of lead-lined tanks for domestic water storage. Such lead-lined tanks increased lead uptake, not only through provision of large surface areas of lead for contact with water, but also because of the enhanced absorption of carbon dioxide from the atmosphere to lower the water pH. In both of the towns examined in these studies, prior to water treatment procedures being applied, a very high percentage of households did not comply with the current EEC limits of lead and water of 100 μg/L. Ayr, with the more acidic water, had the greater percentage of noncompliance, but even in Glasgow with the median pH of 6.3 the compliance level was less than 50%.

It is difficult to approportion the weighting of the difference factors contributing to such plumbosolvency. However, of temperature, hardness, and acidity, the principal factor in lead uptake would certainly seem to be acidity. The source of such acidity in the water supplies examined is unclear. Speciation studies show that in the water in Glasgow there is a high percentage of anodic stripping voltammetry labile lead with 71% associated with the colloidal size fraction, and that little lead is in ionic form (*24*). This is not consistent with water acidity due to nitrogen or sulfur acids, but does not exclude the probability that these will contribute to the overall water plumbosolvency.

The improvement achieved by stabilization of water pH was remarkable, and with a pH of 7.8, Glasgow water provided an 80% compliance with statutory lim-

Table 1. Percentage compliance of blood and water lead with given limits of concentrations (blood leads were measured in mothers whose children were <5 yr).

		Water		Blood		
City	Year	pH	(<100 μg/L)	Geometric mean	(>30 μg/dL)	(>35 μg/dL)
Glasgow	1976	6.3	45	14.5	14	6
	1980 (lime = 4 ppm)	7.8	83	8.1	1	0
	1982 (lime = 5 ppm)	9.0	99	—	—	—
	1982 (phosphate)	9.0	97	—	—	—
Ayr	1980	5.4	28	20.5	22	13
	1983	8.6	95	9.5	0	0

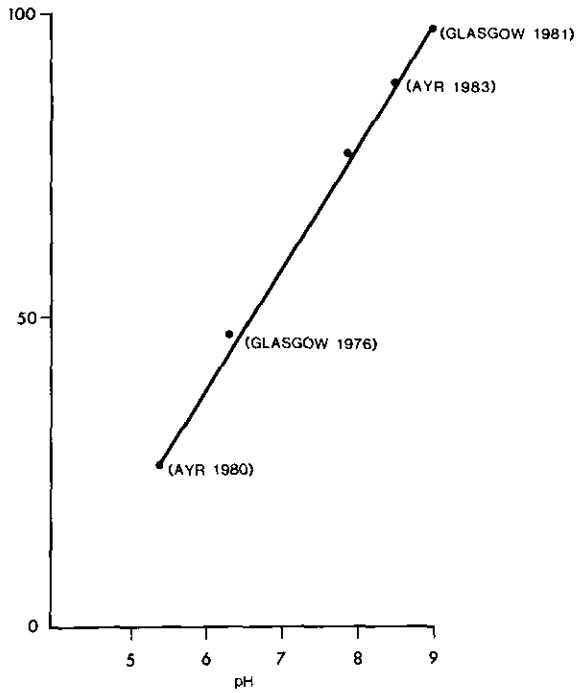

FIGURE 2. *Percentages of samples from Glasgow and Ayr complying* with the standard of 100 μg/L.

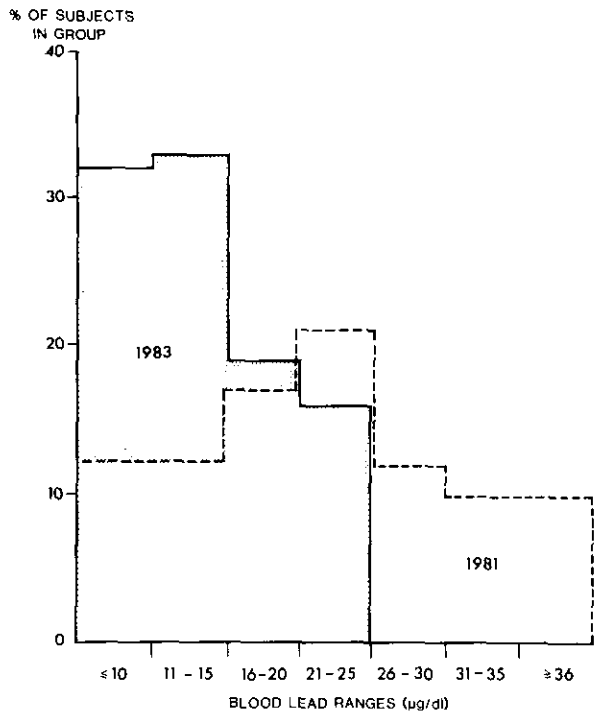

FIGURE 3. Range of maternal blood lead concentrations in 66 mothers in Ayr in 1981 and 1983. The results for 1983 are shown by the solid line.

its. This pH was achieved through the use of a closed loop of automatic lime-dosing system (*25*). Another technique that could have been used was that applied to Boston, through additions of sodium hydoxide (*26*). In the aging of waters during distribution, pH tends to fall. Thus in areas distal to the treatment works, values fell below 7 with consequent enhancement of plumbosolvency. This was controlled in Glasgow by increasing the quantity of lime addition to take the initial pH to values of around 9. This expedient was not, however, sufficient to guarantee a pH control in the most distal part of the system. Experiments suggested that buffering of the water supply might be sufficient to maintain its pH. In consequence, phosphate was added to the water supply in these areas with highly effective improvements in pH maintenance and consequent plumbosolvency. The benefits of such treatment are clearly shown by the large population decrease in blood leads both in Glasgow and in Ayr (*22,27*). The opinion has been expressed that the type of improvement in blood lead seen in these studies might in part be ascribed to the increases in the quantity of calcium in the water (*28*). This would seem unlikely. It is true that increased dietary calcium will diminish alimentary lead absorption in rats (*23*), but is has been clearly shown that even massive supplementation of diet with 2 g/day of calcium glycerophosphate will only produce a very limited amelioration of lead absorption in humans (*29*). It would therefore be naive to think that lime additions of between 4 and 6 mg/L to water would make any appreciable difference to the subjects using the water.

Based on the cube root relationship when water lead concentrations lie at the level of 100 μg/L, more than half of the total oral ingested lead comes from water. Such exposure is not exclusively from water itself, but is also associated with absorption of lead from water on to food during the cooking process (*30–32*). In these circumstances, the net burden of lead intake is excessive with little margin of safety in current dietary lead concentrations (*33*). It is possible to use these data to estimate the level of water lead exposure consistent with maintaining the requirements of the European Community Reference Level for lead in blood, which in part states that: "not more than 10% of a population should exceed a blood level concentration of 30 μg/dL" (*34*). It is not appropriate to extrapolate this value directly into the graph relating blood lead to water lead since it is a percentile standard. To do this it is necessary to separate the different components of variation between blood lead and water lead. If this is done on the 90 percentile basis, one finds that the standard of 100 μg/L does not ensure compliance with this blood standard, but that a water lead standard of 50 μg/L would allow compliance but with only a very small margin of safety (*35*).

The Commission of the European Communities' limits on lead in water are calculated on the principle that tap water should provide less than 10% of the overall daily exposure to lead. This aim may not be achieved at a standard of 50 μg/L. However, it is clear that, where water pH is maintained at values greater than 8, plumbosolvency is minimized. There is, however, still some

uptake of lead into water, especially where plumbing systems comprise of or contain extensive quantities of this metal. The nonlinear association between lead in water supplies and lead in blood guarantees an increasing enhancement of lead exposure abatement as concentrations fall. This is evident even at the lowest levels of exposure (*35,36*). It is also true that circumstances arise where pH values tend to fall as occurs during acid rain precipitation when increasing quantities of neutralizing material would be required to stabilize pH at a satisfactory level. It is always a bad principle to require additions of substances to water supplies to guarantee their safety. This has become especially evident in respect of the heroic levels of chorination required in some circumstances for bacteriological safety. This is disadvantageous since such additions may have to be discontinued for a number of reasons such as an industrial dispute. The abatement of lead exposure from water supplies has clearly been successfully achieved in the West of Scotland through chemical treatment of water supplies. It would, however, be misguided to believe that this form of chemical treatment represents any form of permanent solution to the problem. The reasons for this are clear. Firstly, there are properties amongst those examined in these studies in which the chemical treatment has been insufficient to bring down the values below the reference level of 100 μg/L, and for reference levels of 50 μg/L proportionately more of the properties would fail to comply with this requirement. Any increase in acidity would further exacerbate this situation. Secondly, should there be any interruption in water treatment, the situation would rapidly revert to that before treatment, that is low pH and high plumbosolvency. It is for this reason that acidification of water supplies and its effect upon plumbosolvency must be of considerable concern.

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