

## Measuring the benefit of orthophosphate treatment on lead in drinking water

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### ABSTRACT

Many water companies are adding low concentrations of orthophosphate to the water supply in order to reduce lead concentrations in drinking water produced from corrosion of lead service pipes. Despite the erratic nature of lead concentrations measured at customer properties it has been possible to quantify the impact of treatment on lead concentrations and thereby quantify the effectiveness of treatment at both a regional and zonal level. This showed that the treatment policy has delivered more than 90 per cent reduction in lead concentrations, and was largely in accordance with theory. Across the region, lead performance and the reduction in lead performance show significant variation. A large part of this variation can be accounted for by variations in the proportion of leaded properties supplied through lead service pipes. Analysis showed that the proportion of particulate lead has also reduced significantly over the last decade. This is attributed to improved mechanical robustness of the corrosion layer caused by changes in its physical structure. This appears to be a very slow process with a natural time-scale of years.

**Key words** | colour, drinking water, lead, orthophosphate, particulate lead, plumbosolvency control

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### INTRODUCTION

Over the last twenty years standards for lead in drinking water have fallen in response to greater awareness of its health related effects. In the EC the standard has fallen from 50 to 25  $\mu\text{g Pb/L}$ , and is set to fall again to 10  $\mu\text{g Pb/L}$ . The basis of this standard is the WHO guideline value which is based on an average weekly exposure to lead.

Water from treatment works is virtually lead free. However, when water passes through a lead service pipe, which connects a property to the water distribution system, lead is solubilised. This service pipe is made up of two segments—the communication pipe, owned by the water utility company, and the supply pipe, owned by the customer. These pipes are connected by a stopcock which is usually on or close to the property boundary. Throughout this paper properties supplied through a lead service pipe are referred to as “leaded properties” and those supplied

through other materials are referred to as “unleaded properties”.

For pipes that have been used for some years the observed lead concentration is controlled by the lead compounds which make-up the corrosion layer that forms at the metal-water interface (Paterson & O'Brien 1979; Schock 1980; Sheiham & Jackson 1981). In the late 1970s theoretical and laboratory work indicated that a potential treatment solution was the addition of orthophosphate.

Lead compliance has been a long standing issue in the north west of England (referred to as the region) where the water is supplied by United Utilities. Orthophosphate dosing was introduced in the 1990s. By 2005 treatment was applied to 98% of the region, 75% dosed at 2.0 mg P/L, 18% at 1.5 mg as P/L, 5% at 1.0 mg P/L, the rest being low or undosed (these zones were excluded from the analysis).

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The question therefore arises as to how far the theoretical model, on which the policy is based, is able to account for the actual reduction in lead concentrations.

The benefit of orthophosphate is that it produces a more insoluble corrosion compound at the lead water interface. The equilibrium solubility model predicts that lead concentrations should follow a power law dependence on orthophosphate concentration,  $P$ , viz.

$$\text{Lead Concentrations} \propto \frac{1}{P^n} \quad (1)$$

where the exponent  $n$  is a small number less than or equal to  $2/3$  depending on the compound that forms in the corrosion layer. However, other water quality factors (e.g. pH, alkalinity, organics) are also known to influence lead concentrations. Colling *et al.* (1992) showed that the effect of orthophosphate is not immediate but can take up to a month to control, particularly if the concentration of orthophosphate is low. This is believed to be due to the time required to precipitate sufficient surface area of lead phosphate to exert full control over the equilibrium concentration. In the time-scale of the analysis presented such short term changes are negligible.

An important consequence of the power law behaviour is there is a diminishing benefit of increasing orthophosphate concentrations on lead concentrations, and eventually the benefit will become small compared with uncontrolled factors (e.g. temperature).

The solubility model does not fully account for all the lead observed at customers' taps. Occasionally, high lead concentrations are observed. These are attributed to particulate lead, which arises either from small fragments sloughing off the corrosion layer or adsorption of lead onto particulate material (De Mora *et al.* 1987; Hulsmann 1990). To date the impact of orthophosphate on particulate lead has not been quantified.

One of the methods used for assessing lead at customer properties is known as random day-time sampling (RDT). This method involves randomly selecting properties and then using the first litre of water for analysis. It is important to note the sampling takes no account of whether the property is leaded or unleaded. While the RDT sampling method contributes to the wide variability observed it is only one of many factors (Cardew 2000). The multiplicity of

factors which influence the observed lead concentrations mean that the interpretation of an individual result is of limited value. However, when there are sufficient numbers of samples non-parametric statistical methods can be applied to quantify the benefit (Cardew 2003).

Over the whole region about a third of properties have lead pipe, but local studies show that there is a wide variation. The large proportion of leaded properties means that lead has been a long standing issue. In order to better assess the risk the normal regulatory sampling programme has been considerably enhanced resulting in some 14,000 lead analyses being carried out each year. This large data set provides a major opportunity to quantify the lead risk and the effectiveness of treatment. Inspection of compliance data clearly shows that substantial improvements have occurred over the ten year period in which orthophosphate dosing has been introduced (see Table 1). While this provides a measure of the regulatory risk it does not provide a quantification of the benefit which customers have received or a measure of the remaining risk as it pertains to the WHO guideline value. Also, the compliance measure does not allow comparison with theoretical models and is not a transferable model since it depends on the extent of lead in an area, as well the water quality. The aim of this paper is to show how the benefit of treatment can be quantified in a more useful way and to examine whether the benefit is in accordance with the original expectations.

## ANALYSIS

### Introduction

The distribution of lead concentrations from RDT sampling is highly non-normal and spans four orders of magnitude (see Figure 1). This distribution is made up of at least three

**Table 1** | Percentage sample compliance for regulatory samples for 1995, 2004 and 2005

Year	Standard		
	10 µg Pb/L	25 µg Pb/L	50 µg Pb/L
1995	75.12	87.60	94.99
2004	96.94	98.89	99.49
2005	98.37	99.62	99.86

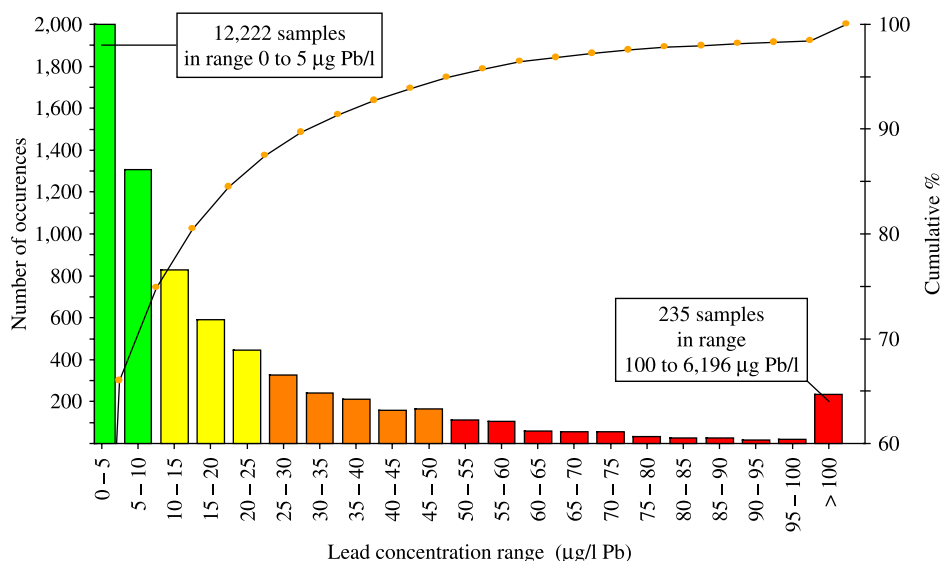


Figure 1 | Distribution of lead concentrations in 1995.

components. The large peak at low lead concentrations is a reflection of the high proportion of properties that are unleaded, and hence contribute only to the lowest concentration range. Leaded properties contribute to all ranges through three mechanisms, the dissolution of the corrosion layer, particulate lead caused by disturbance of the corrosion layer which forms between the water and the lead pipe, particulate lead caused by adsorption of soluble lead onto particulate material in the water. The last two mechanisms account for the high lead concentrations observed, and is of concern since if treatment only reduced the soluble component then particulate lead would increasingly become the dominant cause for exceedances of the standard.

The form of the distribution suggests that non-parametric methods should be used to analyse the data. Because 70% of samples are at or close to the limit of detection it is appropriate to select a higher percentile as a suitable metric to measure performance. High percentiles also seem more appropriate since they reflect the interest in samples which contribute to exceedances of the standard.

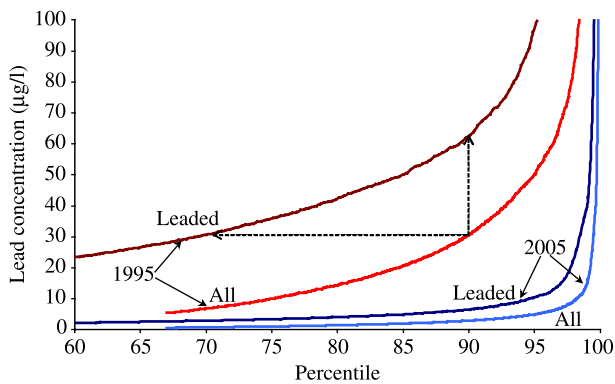
It is important to recognise that there are two lead distributions of interest. One is the distribution observed for all properties and the other is the distribution observed for leaded properties. Depending on the proportion of leaded properties in an area any percentile,  $p_{obs}$ , translates to a

different percentile for leaded only properties,  $p_{lead}$ . The former provides a measure of the regulatory risk while the latter is a measure of the customer risk if they have lead pipes. These percentiles are related by

$$1 - p_{obs} = \alpha(1 - p_{lead}) \quad (2)$$

where  $\alpha$  is the proportion of leaded properties. Thus, for example an area where a third of properties are leaded the observed 90 percentile translates to a 70 percentile for leaded properties. As expected the “true” level of non-compliance amongst leaded properties is substantially higher (see Figure 2). Unfortunately, the proportion of leaded properties in a particular area is generally unknown, and hence the “true” lead risk for customers with lead pipes in this area cannot be quantified. Consequently, comparative analysis between areas cannot be made unless the performance is benchmarked by using samples collected from a particular property location (this is referred to as fixed point sampling). Nevertheless, since the relative improvement in lead concentrations for most percentiles is the same, the relative benefit can be assessed. However, the accuracy of the measure will decrease as the proportion of leaded properties decreases.

While sources of water have not changed substantially over the last ten years, treatment has changed. As well as introducing orthophosphate dosing to deal with the lead



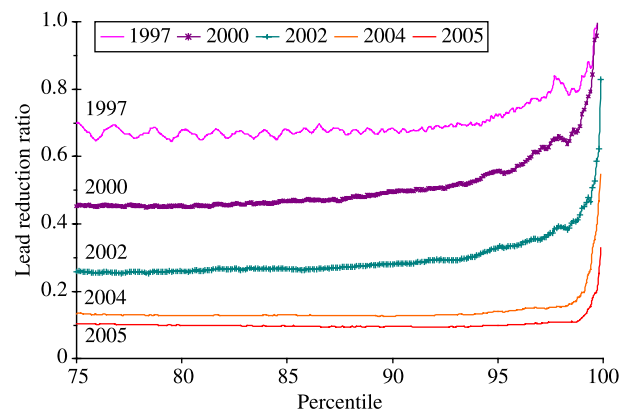
**Figure 2** | Lead concentrations corresponding to a specified percentile in 1995 and 2005 for all properties (ALL) and for leaded properties only (LEADED).

issue, the pH has been reduced to about 7.5, wherever practicable, to ensure the full benefits from orthophosphate addition. In addition, organics concentrations in the water have fallen by 75% across the region, principally due to improved treatment of surface waters.

Analysis has been carried out at three levels. Firstly, all the data has been analysed by year which removes seasonal and short term effects. Secondly, the analysis was carried out for each of the two main water quality sub-groups (surface water and ground water derived supplies). This is seen as important since the water chemistry of these supplies is significantly different, and this may have a bearing on the impact of orthophosphate. Finally, the data has been analysed at the water supply zone level.

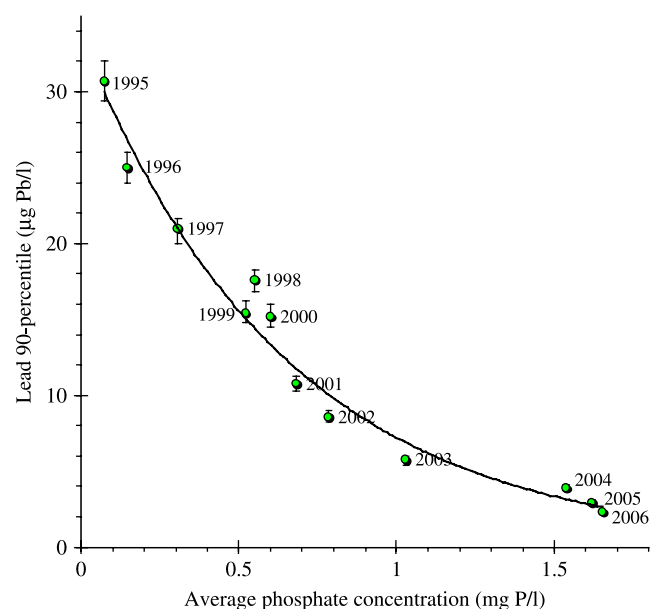
### Regional analysis

The percentiles for the distribution of lead concentrations were calculated for each year from 1995 to 2005 inclusive. The improvement in lead concentrations was then assessed for each percentile, by ratioing the percentile value in each year to that in 1995 (lead reduction ratio). This analysis finds that the reduction in lead concentrations for percentiles in the range 70 to 90 is largely a constant, as would be predicted by the solubility model. However, for percentiles above 90 percent the reduction in lead concentrations is increasingly smaller (see Figure 3). A plausible explanation for this is that above the 90-percentile a significant number of the high lead concentrations are attributable to particulate lead, which is not responding in the same way to orthophosphate as the soluble component. Interestingly,

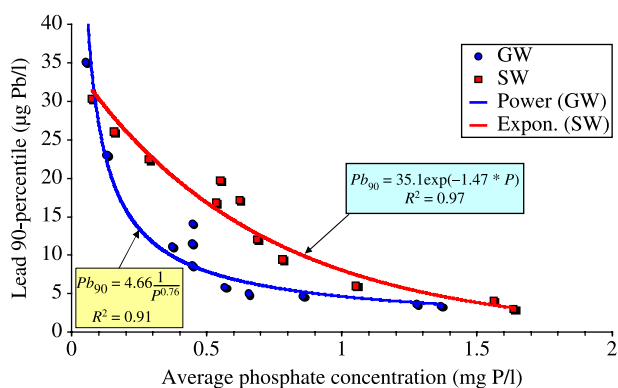


**Figure 3** | Graph of lead reduction ratio (base year 1995) versus percentile for selected years.

over the ten years the issue has shifted to higher and higher percentiles (see Figure 3). This suggests that over many years orthophosphate is reducing the proportion of material that is particulate. From Figure 3 it is clear that lead concentrations have fallen by about 90% over the last decade. From this analysis it was decided that the 90 percentile provide an appropriate metric for assessing the effectiveness of orthophosphate. A plot of the lead 90-percentile concentration versus orthophosphate confirms the expected trend of reducing lead concentrations with increasing orthophosphate concentration (see Figure 4). The graph also shows the expected diminishing return of



**Figure 4** | Graph of lead 90-percentile versus average phosphate by year.



**Figure 5** | Graph of annual lead 90-percentile versus average phosphate by year for surface waters (SW) and ground waters (GW).

increasing orthophosphate above 1.0 mg P/L. Inspection shows a small anomaly in the data associated with results from 1999 to 2000. Investigation found that this was due to deterioration in the analytical accuracy of measurements of lead concentrations during this period.

### By water type

An important question is whether the benefit obtained with orthophosphate depends on the water type. About 80% of the region's drinking water is derived from surface waters with the balance from ground waters (it should be noted that to minimise the impact of hardness most ground waters in the region are often diluted with some surface water).

The lead 90-percentile shows the same downward trend with orthophosphate concentration (see Figure 5). However, while the ground water follows the expected power law model, the surface waters appear less responsive and higher doses of orthophosphate are required to achieve the same reduction.

A possible explanation for the more gradual response observed on surface waters could be due to the heterogeneous way in which phosphate was introduced. Another contributory factor could be changes in other water quality factors. Most notably there has been a large reduction in organics as a result of investment at surface water treatment plants that may have confounded some of the benefits observed on surface waters. Average true colour, which is an indicator of organic concentrations fell by nearly 70% from 3.78 Hazen in 1995 to 1.21 Hazen in 2005 (see Table 2). The presence of organics is well known to enhance lead concentrations (Gregory 2000).

Despite these differences the reduction in lead concentrations for all water types is similar at about 90%, and it is concluded that the general action of orthophosphate on lead concentrations applies to all water types. However, for surface waters some of this benefit could be due to the large changes in organics which occurred following treatment improvements in 2003/4 (see Figure 6).

### By water supply zone

There are several factors which complicate the interpretation of the regional data. Firstly, changes in orthophosphate treatment and dose were not implemented uniformly across the region, but varied from area to area with focus on areas with the worst problem. Secondly, there were particular changes in the quality of the water from certain works which could impact on lead concentrations, e.g. reduction in colour. One way which allows us to assess the influence of these factors is to analyse over smaller areas. A natural division is water supply zones. In 2005 the distribution system was split into 261 water supply zones. These zones are monitored

**Table 2** | Water quality measured in zones for 1995 and 2005 (N.B. All potable waters includes mixed waters. These are waters of variable composition which cannot be assigned to either of the two main water sub-groups)

Measurement	Units	Surface water		Ground water		All potable water	
		1995	2005	1995	2005	1995	2005
Lead 90%ile	µg Pb/L	30.3	2.99	35.1	3.39	30.7	2.93
Orthophosphate	mg P/L	0.08	1.64	54	1.37	0.07	1.62
Calcium	mg Ca/L	41.2	41.1	119.1	125.5	51.5	47.5
Colour	Hazen	4.11	1.24	1.70	1.01	3.78	1.21
pH	–	7.95	7.31	7.41	7.22	7.88	7.30

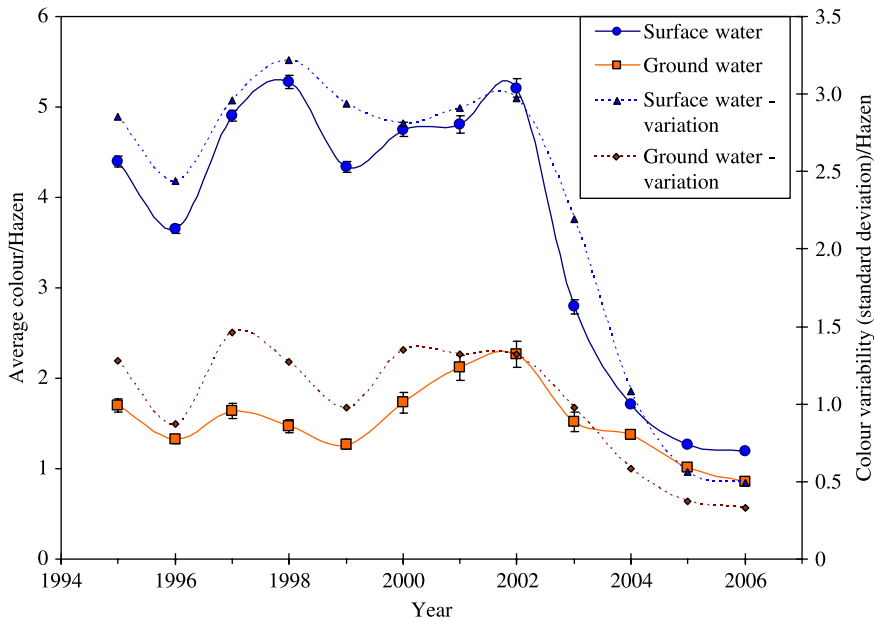


Figure 6 | Graph of true colour and true colour variability in region for 1995 to 2006.

through random sampling throughout the year determined by a regulatory requirement. In addition, because of the significant lead issue in the region there is an enhanced sampling programme resulting in about 50 samples being taken per year in most water supply zones. However, because of the high variability the confidence limits for any percentile are large, and therefore interpretation of any particular result needs to be treated with care.

In 1995 the lead 90-percentile in water supply zones ranged from 1.9 to 120.4  $\mu\text{g Pb/L}$  (Figure 7) with more than 72% of the zones having a value greater than 10  $\mu\text{g Pb/L}$ . A large percentage of this variation can be accounted by variations in the proportion of leaded properties. In 1995 the regional lead 90-percentile was 30.7  $\mu\text{g Pb/L}$  and this translates to 59.7  $\mu\text{g Pb/L}$  for an all leaded properties (only about a third of properties in region are leaded—see Figure 2). Similarly, in 2005 the regional lead 90-percentile was 2.93  $\mu\text{g Pb/L}$  which translates to 6.56  $\mu\text{g Pb/L}$  for leaded properties. These calculations indicate that variation in the fraction of leaded properties from zone to zone is capable of explaining a large amount of variation in the zonal 90-percentile. Hence the importance of quantifying the proportion of leaded properties in any zone.

One of the interesting questions is whether or not the same improvement in lead concentrations has been

observed everywhere. To explore this question the reduction of lead concentrations has been calculated for each water supply zone where orthophosphate treatment has been applied by taking the ratio of the lead 90-percentile in 2005 to the lead percentile in 1995 (lead reduction ratio). As can be seen from Figure 8 the majority of zones have similar reduction ratios close to 0.1 but there are a significant number which have not achieved this level of reduction. From the classification used in Figure 8 it is clear that small reductions are not explained by treatment

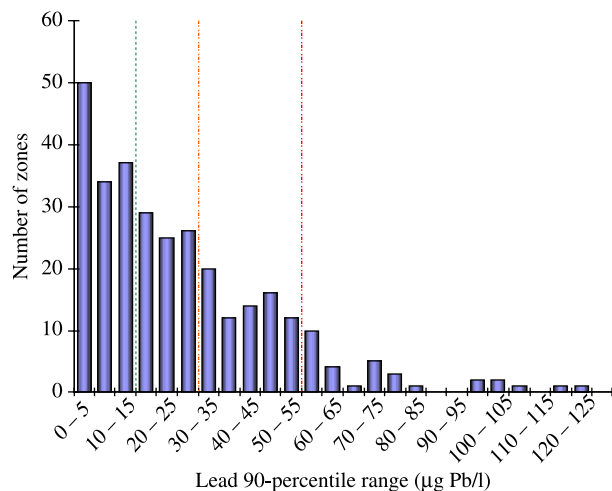
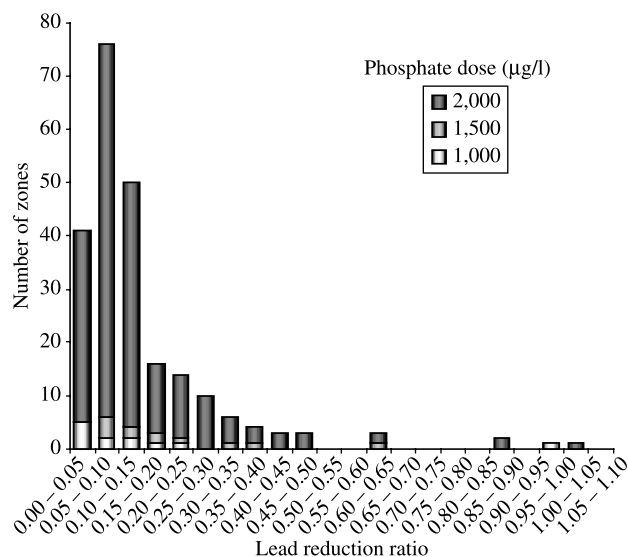


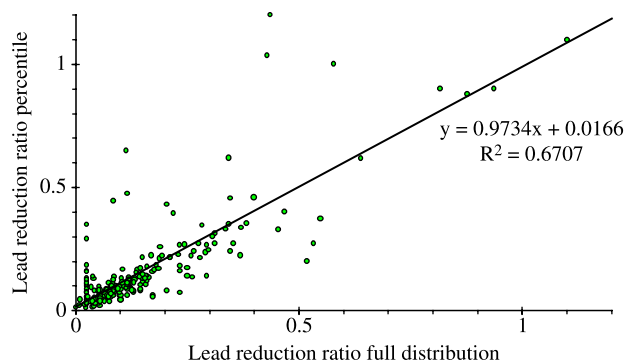
Figure 7 | Distribution of lead 90-percentile in zones in 1995.



**Figure 8** | Distribution of lead reduction ratios (2005/1995) for water supply zones.

differences. A possible explanation is the small sample size may have increased the uncertainty in the estimate of the 90-percentile and therefore in the lead reduction ratio. A non-parametric method, which uses the full distribution to determine the lead reduction factor, was developed by Cardew (2003), and as such should be a more accurate measure of the lead reduction ratio. Comparison of the two estimates show that there is good agreement between the two methods of estimation (see Figure 9), and while there are a few outliers these are not sufficient to explain the distribution shown in Figure 7.

A plot of the lead reduction ratio versus the lead 90-percentile in 1995 shows that for zones with a high 90-percentile always exhibit a large improvement, but



**Figure 9** | Graph of lead reduction achieved in water supply zones from the year 1995 to 2005 calculated using 90-percentile versus that calculated from full distribution.

zones with lower lead 90-percentile show greater spread in reductions (Figure 10). This is consistent with the view that much of the variation observed relates to the proportion of leaded properties in the zones. As the proportion of leaded properties falls then the estimated percentile will also fall. It also follows that as the proportion of leaded properties falls there is a greater relative uncertainty in the lead percentile and hence wider confidence limits on the estimated lead reduction ratio.

## DISCUSSION

The results of the previous section show that over the last decade lead concentrations have systematically fallen by about 90% as the extent and the concentration of orthophosphate dosing has increased. A large part of this gain can be attributed to the action of orthophosphate in creating a more insoluble corrosion layer. However, the data indicates that there has also been a reduction in the number of high lead concentrations observed. This is an indication that orthophosphate must also be affecting the particulate lead component. Orthophosphate might be expected to impact on lead adsorbed onto particulate material since the amount adsorbed should increase in proportion to the amount of soluble lead (Stumm & Morgan 1996). Accordingly, this contribution should largely have had the same response as soluble components. The observation is that the reduction in high lead concentrations took several years. This slow response could be explained by the time required for changes to the physical structure of the corrosion layer. This hypothesis is in keeping with the observation of Davidson *et al.* (2004) which shows the presence of lead phosphate occurs throughout the corrosion layer and not simply as a new layer forming on the outside of the original corrosion layer. More recently, Korshin *et al.* (2005) has shown natural organic material can have a profound effect on the form and type lead phases that develop.

Dose optimisation was completed at the end of 2003, and therefore expectation was that thereafter there would be no significant improvement. However, the lead 90-percentile in 2005 was nearly 25% lower than in 2004 and nearly 40% lower in 2006 (see Figure 11). A small amount of this improvement can be to a slight increase of 7.5% in

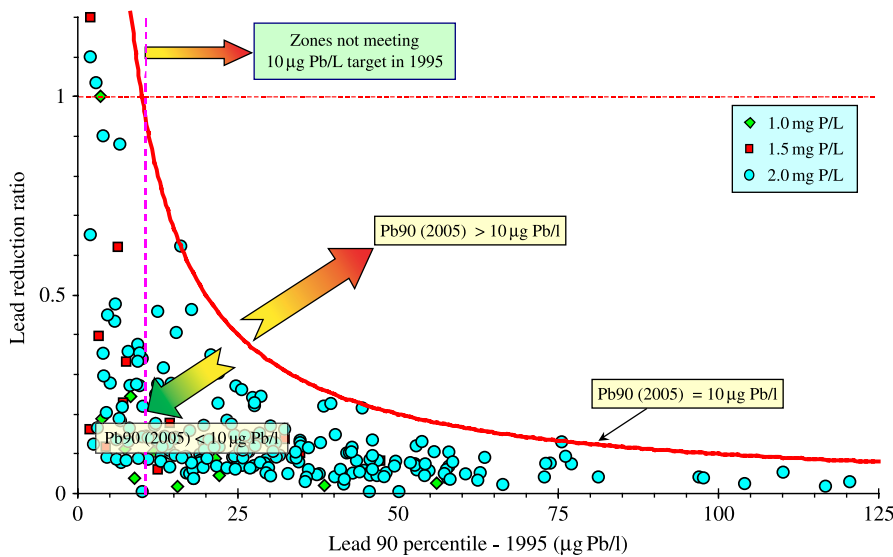


Figure 10 | Graph of lead reduction ratio (2005 to 1995) versus the lead 90-percentile in 1995 for all water supply zones.

orthophosphate concentration. The power-law model indicates that this would only account for just over 10% of the observed improvement. Since 2004 a much larger change has been in the concentration of organics. Average true colour, which provides a measure of organic content, fell from 1.63 Hazen in 2004 to 1.13 Hazen in 2006. On the basis of linearity the reduction in organics could account for a maximum of 75% of the observed reduction in lead concentrations since 2004. This issue needs further investigation since it may have significant implications for the operation of treatment processes involved in removing organics from surface waters. A third factor which might be

contributing to the improvements is a slow change in the structure of the corrosion layer. This process would be expected to develop over many years as the composition of the corrosion later transforms from lead carbonate to lead phosphate.

The analysis shows that a large part of the observed variation in lead metrics could be accounted for by regional variations in the proportion of leaded properties. It would be a useful exercise to demonstrate this. In areas with a small percentage of leaded properties the regulatory risk is low. However, RDT sampling will in such areas be an unreliable assessment tool, since sampling frequencies are too low to be representative. In such areas benchmarking performance using fixed point sampling is essential.

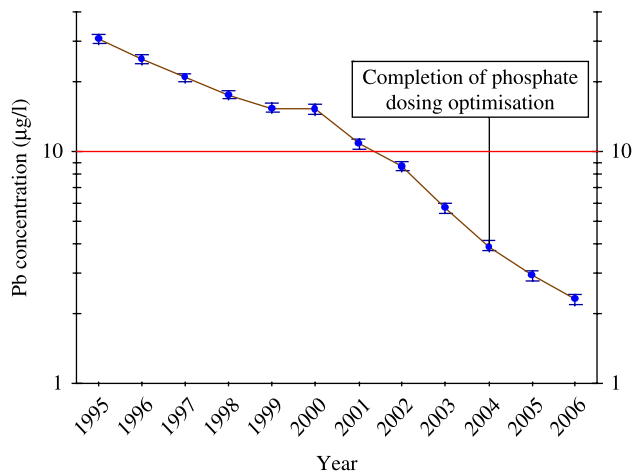


Figure 11 | Graph of lead 90-percentile by year for period 1995 to 2006.

## CONCLUSIONS

Over the last 10 years lead concentrations in the north west of England have been reduced by 90% due to treatment changes and improvements. In a large part this improvement is due to addition of orthophosphate and pH adjustment. This treatment strategy has gone a long way to meeting the revised regulatory standard of 10 µg Pb/L which applies from Dec 2013.

The dependence of lead concentrations on orthophosphate is in line with the general theoretical model and



confirms an inverse power relationship with orthophosphate. Because of the diminishing returns nature of this relationship, further increases in orthophosphate will have limited benefit.

The benefit obtained with orthophosphate appears different for surface and ground waters. Ground waters follow the expected theoretical model dependency on orthophosphate, while surface waters showed a more gradual exponential decrease with orthophosphate. This is attributed to the way in which phosphate was introduced in surface waters, and substantial changes in the organics content of the supplied water following treatment improvements. The data suggest that orthophosphate has not only reduced the soluble component but the particulate component as well. The response time of this process is much slower and appears to be measured in years.

Despite the erratic nature of lead concentrations measured in random day time samples the accumulation of data can be used to determine the lead risk on a regional and sub-regional level by using for example the lead 90-percentile. Interestingly the reduction in the lead percentiles from year to year was the same for lower percentiles, but this is increasingly not the case for percentiles above the 90-percentile. This is in keeping with lower percentiles being reflective of soluble lead, while the higher percentiles are increasingly being influenced by particulate lead.

Assessments based on the lead metric correlate well with more robust statistical measures even when applied at a water supply zone level. However, as the proportion of lead pipes, in an area, decreases the error in the metric will increase. Hence, for areas with small percentage of lead pipes a large amount of sampling will be required to ensure that the data is representative.

The lead risk for customers with lead pipe is higher than that indicated by any selected lead metric based on random day time sampling. Knowing the proportion of leaded properties in an area allows one to quantify the level of customer risk in comparison to any standard. Variation in the fraction of leaded properties can account for a large proportion of the regional variation in lead metrics. Quantifying the proportion of leaded pipes in an area is essential for comparing lead metrics between areas.

Despite orthophosphate treatment conditions being fairly static since 2004 lead concentrations have continued

to reduce. A number of possible causes have been identified of which a reduction in organic concentrations appears to be the most significant.

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