

# Developing an Empirical 90<sup>th</sup> Percentile Lead Equation for Metropolitan Boston

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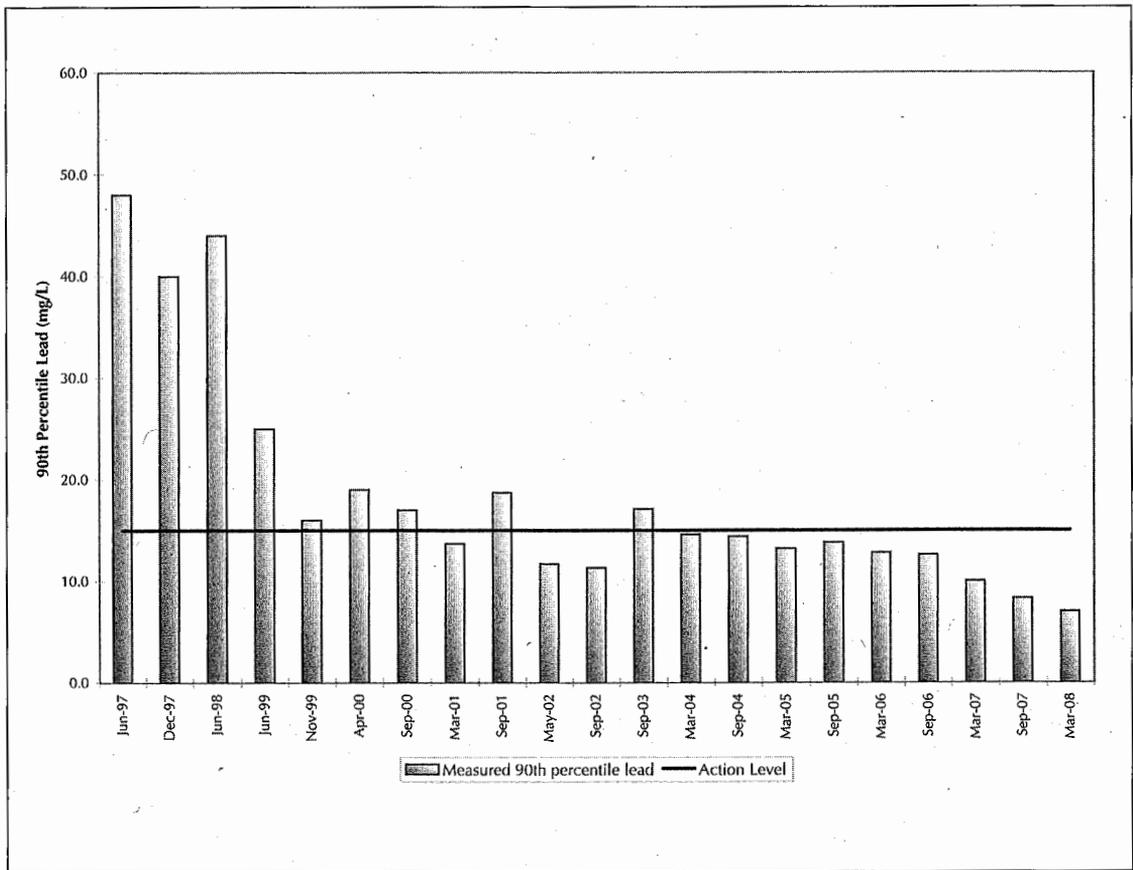
*This equation was used to guide the chemical additions needed to balance lead and disinfection by-product formation concerns, and also served as a point of discussion with regulatory agencies on setting optimum water quality parameters.*

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**T**he Massachusetts Water Resources Authority (MWRA) supplies unfiltered surface water to over two million people in the metropolitan Boston area. Source water for the MWRA comes from two reser-

voirs — the Wachusett and Quabbin. The Wachusett Reservoir watershed is smaller and does not produce enough water to meet the summer demands of metropolitan Boston. Quabbin Reservoir water is typically transferred to Wachusett Reservoir in the summer months for augmentation. This transfer also produces a side benefit in improved water quality when water yield at Wachusett is low. The major water treatment processes consist of disinfection and corrosion control. For disinfection, the MWRA practiced simple chloramination prior to 1996 and switched to chlorine followed by chloramination between 1996 and 2005. Present disinfection consists of ozone treatment followed by chloramination. For corrosion control, the MWRA started to add sodium hydroxide in the late 1970s and switched to soda ash (sodium carbonate) in 1997. Additional chemical treatment includes fluoridation. The John J. Carroll Water Treatment Plant (JJCWTP) in Marlborough, Massachusetts, came on-line in late July 2005



**FIGURE 1. MWRA compliance 90<sup>th</sup> percentile lead levels.**

and consolidated all treatment processes under one roof.

### The Lead Issue

The issue of lead in Boston tap water became widely known in the late 1970s when Karalekas *et al.* demonstrated that there were elevated levels greater than 50 micrograms per liter ( $\mu\text{g/L}$ ) (the maximum contaminant limit then) in the city's drinking water.<sup>1</sup> The Metropolitan District Commission (MDC, predecessor of MWRA) started to add caustic soda (sodium hydroxide) in the late 1970s to increase pH to address the issue. Continued concern over lead was reflected in the U.S. Department of Environmental Protection (EPA) lead and copper rule promulgated in 1991 and still in force. Compliance is now based on meeting a 90<sup>th</sup> percentile lead level of 15  $\mu\text{g/L}$ . No more than 10 percent of compliance samples

can have concentrations of lead greater than 15  $\mu\text{g/L}$  (hence, the 90<sup>th</sup> percentile lead action level of 15  $\mu\text{g/L}$ ). Non-compliance necessitates public education about the hazards of lead and may include lead pipe replacement. In 1997, the MWRA adopted the addition of soda ash (sodium carbonate) to increase alkalinity and raise pH after a series of pilot studies and expert panels. Lead levels dropped dramatically at the tap. The MWRA has consistently met the action level as a system since 2004.

Table 1 and Figure 1 summarize the compliance with 90<sup>th</sup> percentile lead levels from June 1997 to March 2008. The pH/alkalinity targets, and associated water quality data, are also presented in Table 1. Each lead sampling round involved greater than 400 samples collected during the course of a month. The average pH and alkalinity values were calculated from samples collected from about twenty-

**TABLE 1.**  
**Compliance With 90<sup>th</sup> Percentile Lead Monitoring**  
**by the MWRA (With Water Quality Information)**

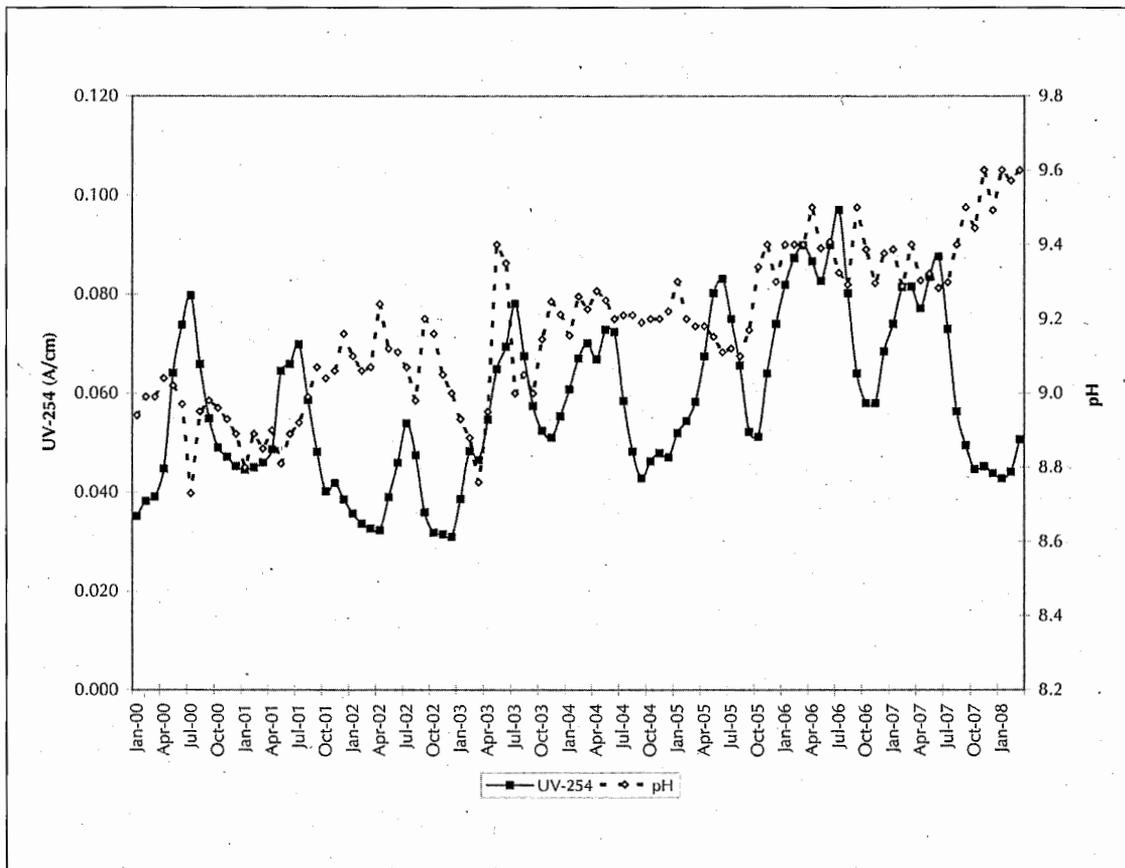
| Date    | 90 <sup>th</sup> Percentile Lead (µg/L) | Average pH | Average Alkalinity (mg/L as CaCO <sub>3</sub> ) | Raw Water UV-254 (A/cm) | Treated Water UV-254 (A/cm) | Average Temperature (°C) | Alkalinity & pH Target |
|---------|---|------------|---|-------------------------|-----------------------------|--------------------------|------------------------|
| Jun 97  | 48.0                                    | 7.9        | 31.0  | 0.092                   | 0.066                       | 16.0                     | 30/8.0                 |
| Dec 97  | 40.0                                    | 7.7        | 29.8  | 0.049                   | 0.035                       | 10.0                     | 30/8.0                 |
| Jun 98  | 44.0                                    | 7.9        | 30.5  | 0.089                   | 0.064                       | 15.9                     | 30/8.0                 |
| Jun 99  | 25.0                                    | 9.1        | 29.0  | 0.054                   | 0.039                       | 15.0                     | 30/9.0                 |
| Nov 99  | 16.0                                    | 8.8        | 28.1  | 0.037                   | 0.026                       | 15.0                     | 30/9.0                 |
| Apr 00  | 19.0                                    | 9.0        | 28.6  | 0.045                   | 0.033                       | 11.1                     | 30/9.0                 |
| Sep 00  | 17.0                                    | 9.0        | 30.0  | 0.055                   | 0.039                       | 19.6                     | 30/9.0                 |
| Mar 01  | 13.7                                    | 8.9        | 31.3  | 0.046                   | 0.032                       | 6.4                      | 30/9.0                 |
| Sep 01  | 18.7                                    | 9.1        | 29.1  | 0.048                   | 0.037                       | 16.8                     | 30/9.0                 |
| May 02  | 11.7                                    | 9.1        | 34.5  | 0.039                   | 0.028                       | 13.6                     | 35/9.1                 |
| Sep 02  | 11.3                                    | 9.2        | 34.5  | 0.036                   | 0.031                       | 20.3                     | 35/9.1                 |
| Sep 03  | 17.1                                    | 9.0        | 34.3  | 0.057                   | 0.049                       | 19.0                     | 35/9.1                 |
| Mar 04  | 14.6                                    | 9.2        | 38.5  | 0.071                   | 0.051                       | 5.9                      | 40/9.3                 |
| Sep 04  | 14.4                                    | 9.2        | 33.8  | 0.046                   | 0.033                       | 17.0                     | 40/9.3                 |
| Mar 05  | 13.2                                    | 9.2        | 38.3  | 0.060                   | 0.043                       | 8.0                      | 40/9.3                 |
| Sep 05* | 13.8                                    | 9.2        | 39.4  | 0.053                   | 0.016                       | 18.0                     | 40/9.3                 |
| Mar 06* | 12.8                                    | 9.4        | 43.3  | 0.090                   | 0.027                       | 5.7                      | 40/9.3                 |
| Sep 06* | 12.6                                    | 9.5        | 40.6  | 0.060                   | 0.021                       | 19.2                     | 40/9.3                 |
| Mar 07* | 9.5                                     | 9.4        | 38.5  | 0.082                   | 0.022                       | 6.4                      | 40/9.3                 |
| Sep 07* | 8.3                                     | 9.5        | 42.4  | 0.049                   | 0.017                       | 19.8                     | 40/9.3                 |
| Mar 08* | 7.0                                     | 9.6        | 41.7  | 0.053                   | 0.019                       | 7.7                      | 40/9.3                 |

Note: \*Ozone disinfection started in late July 2005.

seven locations (typically fire stations where there is easy access).

There is a significant relationship between pH and lead levels. However, there was not any significant correlation found between the 90<sup>th</sup> percentile lead and alkalinity based on early limited data prior to 2002. Nevertheless, the question of whether the MWRA has achieved the optimum pH and alkalinity targets requires some sort of quantification approach for both parameters. It was not

apparent what the optimum pH should be even though lead levels dropped significantly as the pH target was raised. The use of chlorine in 1996 to meet the EPA's Surface Water Treatment Rule for unfiltered systems increased the disinfection by-product (DBP) levels in the system. The MWRA was concerned with meeting the DBP requirements prior to the use of ozone. It was known that increasing pH can increase the level of total trihalomethanes (TTHMs), one of the classes



**FIGURE 2. Monthly variations in raw water UV-254 and distribution pH.**

of regulated DBPs. It was also not obvious, initially, whether alkalinity had a direct impact on lead, or whether it just provided pH stability. Increasing both pH and alkalinity also increases the likelihood of causing calcium carbonate scale formation. The Massachusetts Department of Environmental Protection (MassDEP) requires the MWRA to perform quarterly sampling of water quality parameters that will ensure that lead concentrations are being controlled. These parameters are termed optimum water quality parameters (OWQPs) and consist of twenty-seven samples. This sampling program is in addition to twice-a-year sampling for lead and copper. The OWQP parameters for the MWRA are minimum pH and alkalinity targets of 9.1 and 37 mg/L (as CaCO<sub>3</sub>), respectively, in the distribution system. These targets were derived partly from using the model equation described below.

### The Model Equation

Schock, as well as Edwards *et al.*, discussed the control of lead solubility when hydrocerrusite (a lead [II] hydroxide carbonate solid) is present.<sup>2-4</sup> If this solid exists, then the amount of soluble lead is a function of pH and carbonate ion activity (related to alkalinity). Noel and Giammar analyzed scale from lead pipes excavated from Boston and confirmed the existence of hydrocerrusite.<sup>5</sup>

In the process of trying to better quantify how changes in pH and alkalinity levels might affect lead, several linear and multi-linear regressions were performed. Performing a simple regression of lead versus pH demonstrated that pH is the most important water quality parameter, producing a coefficient of determination,  $r^2$ , of 0.87 and a standard error of 4.0 µg/L. Inclusion of raw water UV-254 absorbance, pH and alkalinity

improves the model, with  $r^2$  increasing to 0.90 and the standard error decreasing to 3.0  $\mu\text{g/L}$ . UV-254 absorbance can be considered as a surrogate measurement for natural organic matter (NOM). The UV-254 effect can be hypothesized to increase both the particulate and soluble lead levels (as discussed in a number of studies<sup>6-8</sup>). These findings could be understood as the result of forming soluble lead-NOM complexes and surface charge changes due to NOM adsorption on the lead solids. Changing surface charge on the solids can increase the amount of particulate lead. Figure 2 shows the variation of monthly UV-254 of MWRA raw water from January 2000 to March 2008, along with the distribution average pH. The fairly large variation in UV-254 is mainly due to source water changes. Transfer of Quabbin Reservoir water typically occurs during the summer and this water source has lower UV-254. It should be pointed out that UV-254 also undergoes in-reservoir decomposition due to photolysis. The UV-254 does not co-vary with distribution pH and is an independent variable.

The regression result should not be extrapolated beyond the observed ranges or a meaningless result such as a negative lead value can be the result. An alternative to multi-linear regression is to postulate a power-law relationship and use log-transformed variables. Such an empirical equation was first proposed in 2002.<sup>9,10</sup> This equation was in the form of  $\text{lead} = A(\text{UV-254})^a 10^{\text{pH}b} (\text{Alk})^c$ , where  $A$ ,  $a$ ,  $b$  and  $c$  are constants. The range in alkalinity was extremely limited prior to 2002. The present equation coefficients have been refined with more data (June 1997 to March 2008) and the regression result is:

$$\text{Log } Pb = 6.09 + 0.524 \log (\text{Raw water UV}) - 1.22 \log (\text{Alk}) - 0.26\text{pH} \quad (1)$$

where:

$Pb$  = the measured 90<sup>th</sup> percentile value in  $\mu\text{g/L}$ ;

$\text{Raw water UV}$  = the UV-254 before treatment in amperes per centimeter (A/cm); and,

$\text{Alk}$  = alkalinity in  $\text{mg/L}$  (as  $\text{CaCO}_3$ ).

The  $r^2$  for Equation 1 is 0.91 and the standard

error is 2.3  $\mu\text{g/L}$ . The log-transformed model is preferred over the linear model since it will not produce a negative value for lead. It also has the form of a pseudo-solubility product, which provides some theoretical basis.

## Extension of the Model Equation

In order to test the validity of the MWRA alkalinity-UV-pH model, it would be useful to include data from other water systems to extend the range in the raw and treated water quality parameters. In addition to published results, several utilities were contacted by phone or their consumer confidence reports (CCRs, an annual water quality report required by the EPA) were scrutinized in order to obtain the needed data. Relatively few systems measure all the necessary parameters for direct comparability.

Table 2 summarizes the data gathered from the following utilities: Cambridge, Massachusetts; Hampden Water District, Maine (a consecutive system to Bangor, Maine) and Tampa, Florida (research). Cambridge uses dissolved air flotation, ozone, filtration and chloramination for treatment. Cambridge measures all the necessary parameters for using the model and its 2004 CCR results were used for comparison. Bangor has a treatment train almost identical to the MWRA. Bangor used lime to raise pH prior to 2005 but then switched to soda ash. A sample of Bangor's treated water was measured for UV-254 in May 2006 by the MWRA. Hampden Water District receives water from Bangor with no additional treatment and reported a May 2006 90<sup>th</sup> percentile lead of 80  $\mu\text{g/L}$ . Corresponding pH and alkalinity values measured for Hampden were obtained from Torrey.<sup>11</sup> There was a noticeable drop in pH from the entry to Hampden's system and measured pH in its distribution system. This difference is most likely due to nitrification. Tang *et al.* and Vasquez *et al.* reported on lead releases from pilot plant studies using combinations of Tampa Bay, Florida, water using reverse osmosis.<sup>12,13</sup> Three of their studies that used chloramination were included in this analysis. Data from these three utilities were pooled with the MWRA data and a

**TABLE 2.**  
**Data Collected for Model Extension\***

| System   | Treated UV-254 (A/cm) | pH   | Alkalinity (mg/L as CaCO <sub>3</sub> ) | Measured 90 <sup>th</sup> Percentile Lead (µg/L) |
|--|-----------------------|------|---|--|
| Cambridge, Mass.   | 0.032                 | 9.12 | 35.0                                    | 7.0  |
| Hampden, Maine   | 0.060                 | 8.81 | 20.9                                    | 80.0   |
| Tampa Bay, Florida (Blend of Groundwater & RO Treated Water) | 0.024                 | 7.90 | 60.0                                    | 3.0  |
| Tampa Bay, Florida (Groundwater)                             | 0.060                 | 7.90 | 207.0                                   | 3.9  |
| Tampa Bay, Florida (RO Treated Water)                        | 0.028                 | 8.20 | 75.0                                    | 9.3  |

Note: \*Cambridge data collected from CCR and monthly report. Hampden data collected from personal correspondence and Tampa Bay is published information.

regression performed using the power law relationship. Calculated lead is given by the equation:

$$\text{Log Pb} = 5.23 + 0.748 \log (\text{Treated UV}) - 1.27 \log (\text{Alk}) - 0.11\text{pH} \quad (2)$$

where:

*Treated UV* = the UV-254 after treatment in A/cm.

Treated UV-254 is used because raw water UV-254 was not available. The  $r^2$  for Equation 2 is 0.74 and the standard error is 8 µg/L. Figure 3 shows the calculated lead using Equation 2 plotted against measured lead values. The agreement is not as good as hoped, but it could serve as an adequate first-order approximation. Some of the variation could be due to differences in where pH was measured; some samples were from actual at-the-tap pH sources and some samples were taken at typical distribution system locations.

## Summary

Lead in tap water is a complicated issue that

does not readily lend itself to simple and easily reached solutions. Much work remains to be done on tackling this issue. The MWRA has developed a model equation for predicting compliance based on alkalinity-UV-pH. The availability of such an equation allows for quick comparison of the efficacy of various treatment changes. For example, is it more cost effective to lower lead by raising alkalinity rather than by lowering NOM? The pH cannot be continually increased since this augmentation has to be balanced against increasing TTHM formation or calcium carbonate precipitation. There is also the likelihood of increasing lead due to hydrolysis beyond a certain pH range (theoretically 10.2). The measurement of UV-254 is relatively straightforward and could provide useful information. It is recommended that UV-254 be included with lead sampling so that site-specific relations can be derived.

*NOTE — This article represents the personal opinions of the author and not those of the Massachusetts Water Resources Authority.*

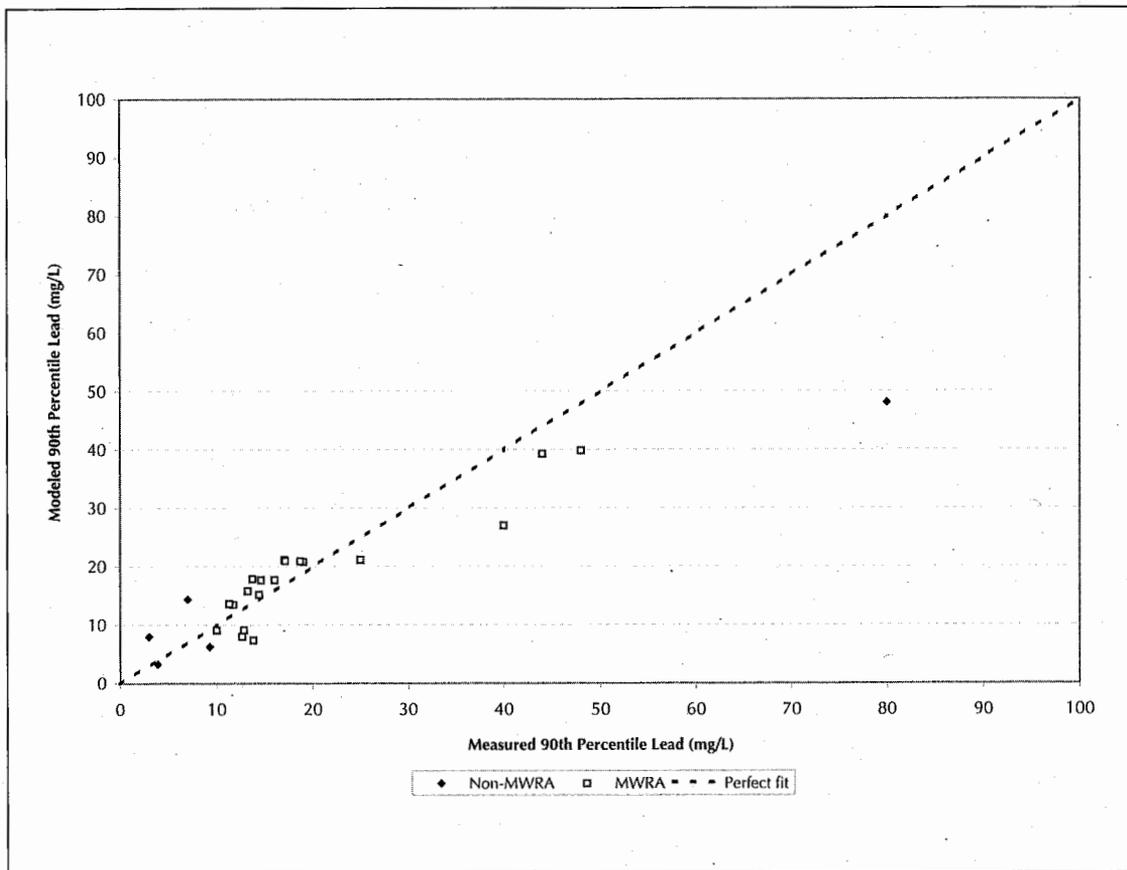


FIGURE 3. Calculated versus measured 90<sup>th</sup> percentile lead.



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