CAUSES OF TEMPORAL VARIABILITY OF LEAD IN DOMESTIC PLUMBING SYSTEMS

MICHAEL R. SCHOCK
Aquatic Chemistry Section, Illinois State Water Survey, 2204 Griffith Drive, Champaign, IL 61820, U.S.A.

(Received March 1989)

Abstract. Sources of lead in drinking water are primarily lead pipe, lead/tin solder, and brass fixture materials.

Lead levels in the water depend upon many solubility factors, such as pH, concentrations of substances such as inorganic carbonate, orthophosphate, chlorine, and silicate, the temperature, the nature of the pipe surface, etc. Physical factors, time, and chemical mass transfer are significant in governing lead levels in nonequilibrium systems. The diameter and length of lead pipe is extremely important, as well as the age and chemical history of the solder and brass fixtures. Analytical variability is not particularly significant relative to between-site and within-site variability. Knowledge of temporal variability at each site is necessary to define a statistically valid monitoring program. An analysis of published data covering repetitive measurements at a given site show that the variability of lead concentration at each site tends to be characterized by the frequent occurrence of 'spikes'. Variability expressed as approximate relative standard deviations tends to be of about 50 to 75% in untreated water, regardless of the mean lead concentration. The distributions are frequently nonnormal for small numbers of samples. Monitoring programs must incorporate controls for the causes of the within-site and between-site variability into their sampling design. The determination of necessary sampling frequency, sample number, and sample volume must be made with consideration of the system variability, or the results will be unrepresentative and irreproducible.

Introduction

The promulgation of the 1986 Amendments to the Safe Drinking Water Act will soon result in the necessity for a large number of public water systems to implement monitoring programs for lead and copper to assess the effectiveness of their corrosion control treatment programs. Further, there will be a continuing interest in finding and investigating the occurrence of trace metal contamination problems, and determining the impact on human health.

Monitoring programs reporting their results in the environmental literature frequently have done so through simple averaging of samples from multiple sites. However, several of these surveys have shown the presence of seemingly random, but very high, metal concentrations in water samples. The data from both published and unpublished surveys of lead corrosion frequently present a confused picture. Sometimes, the reported lead values appear to be unrelated to any obvious water quality parameters. Often, the field data seem to contradict chemical interrelationships established by theoretical or carefully-controlled laboratory studies. Whether or not these discrepancies represent inadequacies of the equilibrium chemical speciation or mass-transport models that must be corrected is an essential issue in developing chemical treatment strategies to control lead corrosion. The defensibility...
of the establishment of drinking water standards, the ability of monitoring programs
to fulfill regulatory needs, and monitoring to provide control information for
evaluating corrosion treatment all depend upon the knowledge of what each sample
represents of actual lead exposure.

This research was undertaken to gain an understanding of chemical or physical
reasons for the observed behavior of the lead in the samples, and identify those design
factors which must be incorporated into or controlled by future lead monitoring
programs.

Factors Governing the Leaching Rate of Lead from Plumbing Materials

Lead is present in plumbing materials (pipes, goosenecks, solder, faucets, etc.) in
the form of elemental lead, Pb. In alloyed materials, such as brasses used in faucets,
the lead is interspersed throughout the alloy matrix in particle form. When the
material comes in contact with potable water, the lead becomes oxidized to the Pb(II)
valence state. Theoretically, lead can be further converted into the Pb(IV) form, in
highly oxidizing solutions such as battery acid. The formation of Pb(IV) solid species
has been occasionally observed in some studies of lead chemistry in drinking water.
The oxidation of elemental Pb to Pb(II) and possibly Pb(IV) enables the mobilization
and subsequent transport of lead into the drinking water.

Lead mobilization in drinking water

The most reactive areas of the surfaces of the plumbing materials, such as the grain
boundaries, become anodic areas where the lead is oxidized from Pb metal to Pb\(^{2+}\)
(Schock and Wagner, 1985). The cathodic areas (where some constituent oxidizing
agent of the water becomes reduced) are normally the less reactive areas, such as the
centers of the grains themselves. The corrosion, and thus, the solubilization, of lead
occurs at the anodic areas.

In potable waters, the most common oxidizing agents for lead pipe are dissolved
oxygen and various chlorine species introduced through disinfection. The oxidation
of lead depends upon the activity of the free lead ion (Pb\(^{2+}\)), the activity of dissolved
oxygen or other oxidizing agents (such as hypochlorous acid, hypochlorite ion and
chloramine species), and the pH. The reaction is enhanced by increases in the
dissolved oxygen content, by decreases in pH, and by the complexation of free lead
ion by ligands such as carbonate, hydroxide, sulfate, polyphosphate species and
chloride. A recent study by Treweek et al. (1985) indicates that under some con-
ditions, chloraminated water is more solubilizing than water with free chlorine,
although the apparent Pb corrosion rate is slower. Complexation by hydroxyl and
carbonate ions is dominant at concentrations normally present in potable waters
(Schock and Wagner, 1985). Complexation of Pb\(^{2+}\) by amine species or reaction
by-products is also possible, but has not been confirmed. The rates of overall lead
oxidation reactions, (i.e., the rates of reactions leading to dissolution, diffusion, and