Movement and Distribution of Arsenic in the Aberjona Watershed

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The distribution and movement of arsenic was investigated on the Aberjona watershed in eastern Massachusetts for the purpose of identifying where and by what processes present and past human exposures to this element could have occurred. It was found that although most of the arsenic was originally released in the headwaters of the watershed, extensive migration had occurred, and the potential for human exposure existed far from designated hazardous waste sites. Both surface water and groundwater were found to be important transport pathways; arsenic moved between these two media at several locations in the watershed, with hydrology and concomitant redox, sorption, and alkylation processes determining the observed patterns of arsenic movement. These findings demonstrate that risk assessments or remedial investigations restricted to designated sites or properties in a watershed may yield both an inaccurate picture of the overall risks presented by a chemical and a less-than-optimum focus for remedial efforts. Since total recovery of the arsenic on this watershed is probably not feasible, cost-effective management will also depend on an adequate understanding of arsenic biogeochemistry and hydrologic transport processes at the watershed scale. Because the Aberjona Watershed is typical of many urban, industrialized areas, these results suggest that the whole watershed often defines the appropriate unit for investigation of chemical contamination in the environment. — Environ Health Perspect 103(Suppl 1):35–40 (1995)

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Introduction

Investigation and cleanup of chemical wastes in the environment is traditionally site-oriented. The designation of site boundaries is helpful to the legal process of identifying potentially responsible parties (e.g., property owners and former owners) who may be liable for the costs of remediation. In some cases, contaminants are restricted in their movement to the extent that they are contained within a designated site; however, in cases where chemical migration occurs, the designation of site boundaries becomes problematic.

Substances in the environment respect few boundaries, and those that are respected are more likely to be associated with hydrologic or chemical processes (stratification, redox boundaries, etc.) than with property lines or political demarcations. Hydrologists and biogeochemists have long defined their units of investigation on the basis of such natural boundaries:

one unit, the catchment, or watershed, is prominent in studies of the movement of water and chemicals in relatively undisturbed natural systems. The watershed is defined by a boundary across which surface water (and, ideally, groundwater) does not pass. Chemicals can leave a watershed only by way of a drainage stream (within which the chemical flux can be measured) or by a transport medium other than water (e.g., by volatilization or export in biomass). This simplification is of great practical significance to the study of chemical movement and has been one key to the success of several watershed-oriented studies of natural chemical cycling (e.g., at Hubbard Brook (1)).

For similar reasons, the entire watershed is the appropriate unit in which to investigate the migration of chemical wastes. When a watershed is taken as the unit of study, it becomes more feasible to invoke the simple but powerful concept of mass balance and account for the movement and fate of an entire mass of chemical. Furthermore, watersheds and river basins not infrequently coincide with coherent units of human population, especially in municipalities that owe their early industrial development to the transportation, power, process water, and/or waste disposal provided by a river draining their watershed.

The Aberjona watershed is such a place. The present paper draws from ongoing studies of industrial chemicals and their behavior on the Aberjona watershed, an area of approximately 65 km² in eastern Massachusetts (Figure 1). Home to over 50,000 people, the Aberjona watershed has hosted industry since colonial times and was the site of suffering leather and chemical industries before the end of the twentieth century. These industries reached their height in the first third of the twentieth century, leaving a legacy of chemical waste that persists to this day. Although both organic and inorganic pollutants are of concern, the present discussion focuses on arsenic, one of the most abundant and widely distributed anthropogenic pollutants on the watershed. The chemistry of arsenic in the environment is involved; aqueous arsenic occurs in the +V, +III, and +II oxidation states, and several alkylation species may be formed (Figure 2). Arsenate (As (+V)) can be taken up by biota as a phosphate analog. Arsenite also sorbs strongly onto iron oxyhydroxides, and may thus have limited mobility in soils. Arsenite (As (+III)) is less strongly sorbed and thus more mobile in groundwater. Arsenic (As (+III)) is a gaseous species produced only in highly reducing environments.

Compounds containing arsenic have a long history of use as pesticides and for medicinal purposes (2). Arsenic is acutely toxic to humans in small amounts—a lethal dose being 70 to 170 mg (3). Epidemiologic evidence shows that some forms of arsenic are also carcinogenic (3).

Although arsenic was known to be a major contaminant in the upper reaches of
the Aberjona watershed (Figure 1), previous studies had not addressed its possible past and present mobility on the watershed, its chemical speciation, its possible human exposure routes, or its long-term fate. The present discussion is a summary of ongoing research into its watershed-wide behavior.

Materials and Methods

Detailed descriptions of most methods are given in the individual studies cited (4–6). Briefly, total arsenic concentrations in sediments were determined by wet digestion and inductively coupled plasma emission spectroscopy; arsenic in water, including speciation into arsenite (As +III), arsenate (As +V), monomethylarsonic acid (MMAs), and dimethylarsinic acid (DMAs) was accomplished by borohydride reduction to arsine or the corresponding methyl-substituted species, trapping on a cryotrap cooled with liquid nitrogen, sequential elution with helium carrier gas, and detection by atomic absorption spectrophotometry. River and shallow lake sediments were grab-sampled, while peat sediments were sampled with a piston corer (P Zebo, personal communication). Deep-lake sediments were sampled with a freeze core, wet-ashed, and analyzed by inductively coupled plasma emission spectrometry (ICP)(H. Spleithoff, personal communication). Estimates of historical source functions were based on extensive reviews of commercial records from local public libraries and towns, combined with handbook information on leather and chemical manufacturing processes of the era.

Results

Major Sources of Arsenic

Leather and chemical manufacturing industries released large quantities of metals on the Aberjona Watershed during the late nineteenth and early to mid-twentieth century (4). Aurilio (6) documents in detail the industrial processes that produced most of the arsenic-containing waste. A large source of arsenic was associated with what is now the Industriplex Superfund site (Figure 3), where in excess of a hundred metric tons of arsenic waste have been discovered. Soils at the Industriplex site have been found to contain concentrations of arsenic up to 30 g/kg (dry weight) (7). In contrast, arsenic concentrations of 0.4 to 40 mg/kg are considered typical for soils with no geologic or anthropogenic arsenic inputs (2).
ARSENIC IN THE ABERJONA WATERSHED

Although there are uncertainties associated with the reconstruction of the historical waste stream, Aurilio (6) concludes that most of the arsenic on the watershed came from the production of sulfuric acid from arsenic-rich pyrites; a conservative estimate is that over 170 tons of arsenic were released. Waste from arsenical pesticide (primarily lead arsenate) production ranks second in importance, with an estimated contribution of 35 metric tons (6).

Halls Brook Storage Area

Immediately to the south of the Industriplex site is Halls Brook Storage Area, a 9-hectare impoundment created for flood control purposes (Figure 3). The northern end of the pond is fed by small springs that flow up through fluviculm orange-red sediments. Sediments in the northern portion of the basin contain up to 9.8 g/kg As (dry weight), while a marshy area in the southern portion of the basin contains in excess of 1.3 g/kg As (5,8). Water samples taken directly above the springs at the northern end of the pond contained As concentrations as high as 80 µg/l, while water from the outlet contained a maximum of 3 µg/l of arsenic on the dates sampled (6). Arsenite (As (+III)) represented about 80% of As in water collected at the springs, while arsenate (As +V) represented on average 85% of the total As at the outlet. The major processes occurring in the basin appear to be oxidation of As (+III) to As (+V), and subsequent scavenging of As (+V) onto freshly precipitated particulate material.

The major source of As to the basin under moderate flow conditions is evidently groundwater, as shown by the clearly visible groundwater inflow and the associated high As concentrations in water at the northern end of the basin. Much of the inflowing As is stored, at least temporarily, in the sediments of the basin; however, a significant fraction (estimated to be about one-third of the input) (6) is exported downstream even during moderate flow conditions. Additional input of As to the Halls Brook Storage Area as well as enhanced export from the basin could occur via surface water during periods of high flow.

The Aberjona River

Total arsenic concentrations in the Aberjona River at a gaging site near Interstate Rt. 95, 1.2 km downstream of Halls Brook Storage Area, currently average approximately 10 µg/l; slightly more than half of the arsenic passes a 0.45-µ filter (H Solo, personal communication). The annual flux of riverborne arsenic at this location, determined on the basis of monthly measurements from February 1992 to January 1993, was 92 kg. The annual flux of arsenic at a USGS gaging station several kilometers further downstream was not distinguishable from the flux at the Rt. 95 site during this period, suggesting that the majority of arsenic in the river originates north of this site (H Solo, personal communication). Evidently, additional arsenic inputs to the river, probably inflow of arsenic-rich groundwater, supplement the contribution of Halls Brook Storage Area.

Elevated levels of arsenic are found in sediments throughout the Aberjona River (5). Although considerable spatial variability exists, concentrations of several hundred mg/kg are not unusual (Figure 4). The pattern of contamination does not seem to correlate to any probable distribution of sources; however, a strong relationship with the fineness of sediment texture and with organic matter content (parameters which themselves were highly correlated) was seen. A wetland through which the Aberjona River flows as it crosses the Wells G and H Superfund site (Figure 4) was among the areas in which relatively high arsenic concentrations were found. A vertical profile of arsenic concentration in the peat deposit of this wetland, obtained by P Zeeb (personal communication), is shown in Figure 5. Two distinct, well-defined peaks occur, the upper peak defined by a maximum arsenic concentration of more than 7 g/kg.
The Mystic Lakes
Elevated arsenic concentrations were observed in surficial sediments from both the Upper and the Lower Mystic Lakes. Sediment cores [(5); H Spliethoff, personal communication] indicated that two major episodes of arsenic deposition in the lakes had occurred (Figure 6). Lead-210 dating, although potentially influenced by the large-scale watershed disturbances associated with urbanization, is consistent with the conclusion that the earlier episode occurred during the period of maximum industrial activity in the early 1900s. Maximum arsenic concentration is approximately 2000 mg/kg (dry weight) at a depth in the sediment of 58 to 60 cm. The later episode of arsenic deposition may have occurred as recently as the 1970s. Surficial arsenic concentration is approximately 200 mg/kg, while the (presumably preindustrial) arsenic concentrations found below a depth of 90 cm are less than 10 mg/kg.

Arsenic in the Water Column
Concentrations of four arsenic species, arsenite, arsenate, MMAs, and DMAs, vary seasonally in the waters of the Upper Mystic Lake (6) (R Mason, personal communication). The arsenic concentration was found to range from approximately 1 μg/l during the colder months to approximately 1.3 μg/l during the warmer months. Arsenite accounted for approximately one-quarter of the total arsenic in the water during the colder months but increased to nearly one-half of the total between May and October in the mixed layer (epilimnion) of this dimictic lake despite the fact that the upper waters remained well oxygenated. Arsenite isotopes are shown in Figure 7. DMAs followed a temporal and spatial pattern similar to that of arsenite, reaching maximum concentrations in excess of 0.3 μg/l (as arsenic). MMAs generally followed a similar pattern, but concentrations were nearly always below 0.1 μg/l. Conversely, arsenate concentrations in the hypolimnion, which became anoxic early in the summer, actually increased during the warm months, while arsenite concentrations were lower.
than in the oxic epilimnion. This counterintuitive result is evidence that kinetic considerations govern As speciation during much of the year.

Discussion

The patterns of arsenic distribution and speciation on the Aberjona watershed show that it is necessary to consider the entire watershed to assess the behavior of this contaminant. Although most of the arsenic in the watershed is relatively immobile, the fraction that is moving is potentially significant; although much of the arsenic is behind security fencing, potential human exposures may exist at far-removed locations.

Figure 8 gives a simplified view of arsenic cycling as it is hypothesized to occur on the Aberjona watershed. Arsenic deposited near the headwaters of the river moves to the surface water system by transport in groundwater following solubilization by reduction to arsenite (almost certainly, transport by surface erosion also occurs). Arsenite from groundwater is re-oxidized and scavenged by iron oxides upon entering surface waters, and a fraction of the arsenic, predominantly as arsenic (+V), is transported downstream by the river. Deposition occurs where hydrodynamic conditions favor the settling of particulate matter; a significant fraction is deposited in wetland areas.

Upon entering the Mystic Lakes, much of the arsenic is ultimately deposited to the sediment, either by settling of particle-bound arsenic or by scavenging and subsequent settling of dissolved arsenic. Within the lake, active arsenic cycling occurs. Reduction and methylation in the upper water column, probably by phytoplankton, are especially important during the warm season. Although the lakes are sinks for arsenic, they are far from 100% efficient in this role. Preliminary evidence suggests that arsenic exported from the lakes may have been a significant source to the downstream Mystic River and even Boston Harbor.

There are numerous possibilities for past and present human exposure to arsenic on the Aberjona watershed. Before public access was limited, the original disposal sites were traversed by pedestrians and motorbike riders. Currently, direct ingestion of arsenic-contaminated sediment by children playing in the river or lakes is probably a larger concern.

Another potential route of exposure is the aquatic food chain (J Durant, personal communication). The Aberjona River and the lakes are used for recreational fishing. Although informal discussions with fishermen indicate that fish are often returned to the lake or river, some people may consume their catch. The concentrations of arsenic in the Aberjona River and the Mystic Lakes exceed ambient water quality criteria for the protection of human health from eating contaminated fish (9). Moreover, the bioconcentration of arsenic in fish has been reported in the literature (10). However, a study conducted in 1991 (11) failed to detect arsenic in any of 11 species of fish sampled from the Upper Mystic Lake. It appears that the possible concentration of arsenic in fish flesh, followed by human consumption of fish from the watershed, is a pathway that should be investigated further.

Yet another concern is that human exposure could have occurred in the past via wells G and H, formerly a major source of drinking water to residents of the city of Woburn, Massachusetts. Closed due to contamination by chlorinated solvents, the wells induce substantial recharge from the river during their operation. Dissolved or colloidal arsenic (and possibly other metals as well) may thereby have been introduced into the drinking water system. Further investigation is needed to provide definitive information on this possible exposure pathway.

In conclusion, watershed scale analysis puts the issues of management and remediation in a different perspective than does a site-oriented analysis. Given the wide dispersion of arsenic in the Aberjona watershed, the most feasible management approaches will be approaches that are oriented toward the entire watershed and selectively target the processes that most directly lead to continuing contaminant mobility and possible human exposure.

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