

Fate of Arsenicals in Different Environmental Substrates

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The current knowledge of arsenic (As) transformations in the environment, as well as some gaps in this knowledge, are reviewed. These transformations involve As chemical and biochemical transformations in air, waters, sediments, and soils. Arsenic moves in a dispersive manner through air and water and is in physical and chemical equilibrium in many substrates. It is oxidized, reduced, methylated, volatilized, incorporated into biotic tissues, excreted, adsorbed, and desorbed. Oceanic sediments become the eventual sink for As.

The rates of As movement and transformation vary with environmental conditions. Besides inorganic As, various methylated arsenicals are found naturally at environmentally sensitive equilibrium concentrations, which are probably maintained biotically.

An As-transformation model has been constructed from rate constants derived from field observations. The environmental factors affecting these rate constants are discussed.

Arsenic in Soil

Arsenic (As) is found in all environmental substrates and has recently been shown as an essential element for rats (1). Only at high exposure levels, usually industrial, has it become a human and environmental problem. Normally, As used commercially as a pesticide and a nonpoint source is not present in high enough concentrations to present serious environmental problems. However when the soil and/or environmental conditions cannot detoxify the As levels applied, soil As toxicity becomes a problem. Since most environmental contamination from point sources (i.e., smelters and coal burning electric plants) will be reduced, as stricter air pollution controls are required, this paper will be limited generally, to fate and transformations that occur agriculturally at relatively low As concentrations. These same processes, however, may also occur from point sources.

Arsenic, as a labile element, is subject to several processes in the soil. Under various conditions, it is oxidized, reduced, methylated, volatilized, adsorbed, and desorbed.

Besides smelters and coal-burning electric plants, As compounds contaminate the soil in the form of

pesticides from the burning of cotton wastes, from natural weathering processes, and in runoff from mining operations.

Of all the As sources reaching the soil, As pesticides are the most widely distributed geographically. Arsenic acid (H_3AsO_4) is applied to cotton for leaf desiccation or to vegetation as a general weed killer. Lead and calcium arsenates are insecticides used to kill leaf chewing insects. The organic arsenicals, methanearsonic acid (MAA; sodium salts MSMA and DSMA) and cacodylic acid (dimethylarsinic acid, CA) are selective and general postemergence herbicides, respectively. Arsenates are the oxidized degradation products from the organoarsenicals also, although under moderately reduced conditions (2), arsenite may be formed both biotically and abiotically. All other transformations are biotic. The arsenicals are adsorbed to amorphous iron and aluminum oxides, which coat the clay particles (3) or react with cations in the soil solution. Arsenate can also be associated with goethite particles, $HFeO_2$, (4).

The adsorption of arsenate to clay depends on soil pH, texture, Fe, Al, organic matter, and the elapsed time after exposure. As the soil's clay content increases, the As amount adsorbed increases (5). Equilibrium conditions are reached slowly with the soluble arsenate decreasing continually (6) and the Fe and Al forms stabilizing. Some As is always

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present in the soil solution and is probably the form available for biotransformation and plant uptake. Soluble As is also subject to leaching, especially in a sandy soil (5).

Arsenate can be reduced and methylated in soil (7), but this process is slow: from 10 ppm applied only 1 to 2% was volatilized as dimethylarsine [DMA; $(\text{CH}_3)_2\text{AsH}$] in 160 days.

The organoarsenical herbicides react like arsenate in soil—they are adsorbed on clay surfaces by Fe and Al oxides, leached from sandy soils, and subject to metabolism (8). Arsanilic acid, a feed additive, is also fixed to clay surfaces and metabolized to arsenate (9). The degree of fixation decreases as methyl groups are added to the As atom (6, 10).

Arsenic in Water

Inorganic As can exist in several oxidation states and forms in water (11), depending on the pH and Eh of the water. In a stratified lake, many reactions occur (Fig. 1). The adsorption of arsenate by Fe and Al oxides in sediments and formation of As_2S_3 removes As from solution and prevents large As concentrations from being present in water.

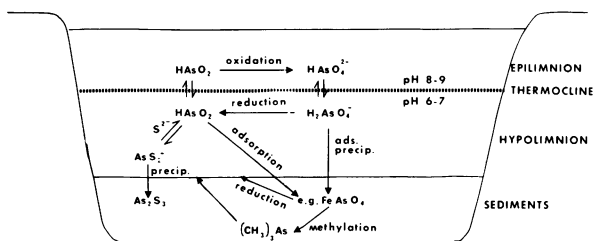


FIGURE 1. Arsenic reactions in a stratified lake [taken from Ferguson and Gavis (11)].

Concentrations in Lake Michigan water (0.5–2.3 $\mu\text{g}/\text{l}$.) are generally much less than that in its sediments (7.2–28.8 mg/kg) (12, 13). Sediments quickly remove As from streams containing high As inputs, with a resultant increase in the As concentration of sediment. The adsorption is probably associated with Fe and Al oxides, as in soils. Movement of As within the stream can be the result of dissolved load or the movement of suspended sediment (14). Formation of small amounts of volatile organo-arsines also remove As from streams.

Ferguson and Gavis (11), who estimated that the total As moved to the oceans was 30×10^6 kg/yr , saw no imminent increase in oceans levels from this input.

Arsenate is reduced to arsenite, apparently by bacteria in the marine environment. Observed ratios of arsenate to total As were about 0.8 (15,

16). Thermodynamic calculations indicated a 10^{26} : 1 ratio of $\text{As}^{(+5)}:\text{As}^{(+3)}$ in oxygenated seawater at pH 8.16 (17).

Arsenate in both fresh and salt water is metabolized to methylated compounds. Mono-, di-, and trimethylarsenicals have been isolated from both sources (16). The relative amounts of As^{+3} , As^{+5} , MAA, and CA vary, but generally As^{+5} and CA predominate. Arsenic is methylated by bacteria and fungi in water and/or sediments. Reactions of the organoarsenicals in water, however, have not been investigated. Organisms accumulate organoarsenicals, regardless of the form (18–20). Some metabolism does occur, but it may be within the host organism. Biomagnification through the food chain, however, does not occur with the arsenicals (21). Lower members of the aquatic food chain contain the highest residues.

Natural Concentrations of Total Arsenic

Most residue values have been reported only as total As. In soil, As levels normally range from 1 to 40 ppm total As (22). These values were derived from weathered parent rock material and As may have been present as arsenate or arseno-sulfides. The U. S. National Soils Monitoring Program reported As values for 12 states in the Corn Belt as ranging from 0.10 to 22.75 ppm; and averaging 2.74 (23). Residues from cropland in 43 states ranged from 0.25 to 54.17 ppm As and averaged 6.43 ppm for 1969 samples (24). However, some of these samples received As applications. In several states soil residues in untreated cropland were compared with that in cities. Five of six cities had higher soil residues (9.9 ppm) than did soils from cropland (5.2 ppm). This may be attributed to As deposition from industrial or combustion sources (24), rather than to differences in use of various arsenical pesticides.

Arsenic residues in water are generally low. Durum, Hem, and Heidel (25), who examined U. S. surface waters, reported that 79% of 727 samples examined had less than 10 μg As/l., the recommended drinking water standard; only 2% contained more than the mandatory upper limit for drinking water of 50 $\mu\text{g}/\text{l}$. By the time water is treated and distributed to the general populace, only five of 2595 systems (0.2%) exceeded the mandatory limit for As in drinking water, while five others exceeded the recommended limit (26). Concentrations of As in seawater generally range from 0.15 to 6 $\mu\text{g}/\text{l}$. with an average of about 2 $\mu\text{g}/\text{l}$. Concentrations in seawater tend to be higher at the river

outflows because of dissolved As and sediment load (11).

Sediments, even in areas with some industrial input, remain at a relatively low level. Lake Michigan contained 11 ppm As in the sediment with an estimated 145,000 kg As/yr input (12). Residues in the Puget Sound sediments, where smelter contamination was not a factor, varied from 3.2 to 15 ppm As (27), while those contaminated contained up to 10,000 ppm As, the content in slag. These background concentrations (3–11 ppm As) resemble those reported for deep sea sediments (28) and are positively correlated with organic matter (29), clay, extractable Fe and Al compounds (27), and decreasing particle size (13, 28).

Natural Concentrations of Organoarsenicals

Measurements of natural concentrations of organoarsenical compounds have suffered from lack of specific methodology necessary for speciation. Recent developments in technology have allowed speciation in a limited number of studies. Methylated arsenicals are formed naturally by various fungi (30), bacteria (31), molds (32), animals (33, 34), and aquatic organisms (16). Concentrations of the transformed arsenical are dose related in those instances where As was added to the system. Braman (16) reported natural environmental concentrations of arsenical compounds in fresh and salt water that ranged from 0.02 to 0.22 ppb for MAA, 0.15 to 1.00 ppb for CA, and 0.14 ppb for a trimethylarsenical with human urine containing 1.8 ppb MAA and 15 ppb CA. Aquatic weeds contained 10 ppb MAA and 64 to 185 ppb CA, while shrimp contained 72 ppb CA. No reports were found that described the natural levels of the organoarsenicals in the soil environment. However, a trimethyl compound was formed in a laboratory experiment (7). We might expect intuitively that low concentrations of alkylarsenicals are found under some soil conditions. We do not know if the organoarsenicals are photo-degraded in water, air, or soil surfaces.

Dimethylarsine and trimethylarsine [TMA ; $(\text{CH}_3)_3\text{As}$] were detected in air as a gas or adsorbed onto filterable particles. Outdoor levels were less than 1 ng/m^3 and averaged 0.09 ng/m^3 DMA and 0.08 ng/m^3 TMA. Indoor home levels were higher, averaging 0.10 and 0.25 ng/m^3 , respectively. Little DMA was found as a gas in greenhouses, but TMA averaged 0.21 ng/m^3 . On filterable particles, greenhouse samples ranged to 27 ng/m^3 ($\bar{x} = 8.5$) TMA, but those from home and outdoor environments remained low ($<0.5 \text{ ng}/\text{m}^3$) (35).

Transport Cycle

Cycling of As in the environment is dominated by adsorption and desorption to soils and sediments. Significant As losses from the dissolved state are due to adsorption within hours in laboratory solutions (2, 6). Sediment movement can also account for large As losses from a watershed. With a polluted watershed, large amounts of As (probably from arsenic acid wastes) were transported in the suspended state during high stream flow (14). At low flow rates, little sediment transport occurred while the water contained 15 to 59 $\mu\text{g}/\text{l}$. with a total dissolved As load of 1.8 to 3.5 kg/day . Only 0.2–0.3 kg/day was transported on suspended sediment under the same conditions. During flooding, large amounts of contaminated sediments will be moved. Nevertheless, much of the As moved to the oceans is in the dissolved state ($30 \times 10^6 \text{ kg}/\text{yr}$) (11).

At Tacoma, Washington, a smelter discharges large amounts of As_2O_3 into the air, and liquid effluent and slag into Puget Sound, where it is distributed by both wind and water. Wind movement accounts for high residues in soils and sediments on Vashon Island, because water flows away from and air moves toward the island. Sediments near the Tacoma smelter contain high levels of As (up to 10,000 ppm As). Surface seawater samples taken next to the smelter, contained a maximum 1200 ppb As. The concentration decreased very rapidly with distance to about 4 ppb within 1 mile from the smelter (36). Although the slag dumped into Puget Sound contained 1% As, this material is chemically and physically very stable in seawater and does not move from the site of deposition.

Yearly mass balance was calculated for the Puget Sound area. The inputs considered were sea and river water, precipitation, smelter effluent, Seattle sewage, and a drydock operation. Total inputs were estimated at $7.3 \pm 0.7 \times 10^8 \text{ g As}/\text{yr}$, with 5.8×10^8 from seawater through Admiralty Inlet. The As content, flowing out of the sound in surface waters, indicated that $6.3 \pm 0.6 \times 10^8 \text{ g As}/\text{yr}$ were removed. The difference, $1.0 \pm 0.9 \times 10^8 \text{ g As}/\text{yr}$, is that removed in the sediments. However, sedimentation is much less-important (14% of As input in this case) as a sink for As than that discharged through the Strait of Juan de Fuca (27).

Contamination of air from smelter stack emissions or from the burning of coal results in elevated As levels in the surrounding environment. Arsenic is returned to soil through either direct fallout as particulate matter or in precipitation. At the Tacoma smelter, an estimated $2 \times 10^8 \text{ g As}/\text{yr}$ are emitted in the stack gas (36). Total airborne losses, as As_2O_3 , from the smelting of Cu ores was esti-

mated at 48×10^8 g As/yr nationwide. Coal burning emits 6.5×10^8 g As/yr into urban air (37). As a result, large cities have higher As levels in air than do small cities or rural areas (38). New York City air contained $30 \mu\text{g}/\text{m}^3$, with rural areas having less than $10 \mu\text{g}/\text{m}^3$. The As in air reaches the soil in rain or dust, where it is adsorbed and effectively removed from the transport cycle. This results in an elevated soil residue (24). Improvements in air pollution control should decrease As air concentrations and the amount reaching the soil.

Studies of the alkylarsenicals have indicated that biotransformations do occur; however, the transport mechanisms are less clear. Alkylarsines are formed in soil (7) and possibly sediments (16), and in sewage sludge (30). Thus transport occurs in two media, air and water.

Transport of alkylarsines in air may involve only the gaseous phase or perhaps a gaseous/particulate phase. The identity of alkylarsines adsorbed to particulates is unknown. They may be the oxidized form, MAA, CA, or TMA oxide, while that in the gaseous form is the alkylarsine. However, the extent of transport of the alkylarsines in air is unknown.

Also, transport of alkylarsenicals in waters is unknown. Fresh and salt waters have been shown to contain MAA and CA at low levels (16). Aquatic organisms can accumulate the alkylarsenicals to some extent (18–21). The lower food chain organisms contained the higher As residues. Metabolism to other compounds within fish may also occur (39–41). With the organo-arsenicals, movement probably occurs both through physical transport and through uptake by aquatic organisms.

Thus, the data indicate the fluvial transport of As is appreciable in a dissipative fashion downstream from point sources and that the bottom sediment of natural aquatic systems functions as a temporary reservoir in the dispersive transport of As. Oceanic sediments are the ultimate sink for As residues.

Due to complex multimedia (sediment/soil–water–biota–air) exchange of As in the transport cycle and the natural differences between air, soil, and water systems, it is difficult to quantitate the degree of transport. We do know that As is sorbed by biota and sediments/soils, and is maintained at low concentrations in water and air. These processes of interchange are depicted in Figure 2. However, beyond intuitive reasoning, we know little of the rates of resuspension, desorption, and volatilization and the collective effects of environmental parameters controlling those rates.

Arsenic Transformations

Alkylarsines have been known environmentally, since Challenger et al. (42) identified “Gosio” gas as TMA. Gosio gas was generated by molds growing on wallpaper paste containing an As pigment. Various fungi, molds, and microorganisms can metabolize arsenate, arsenite, MSMA, and cacodylic acid to volatile arsenicals (10, 30, 31, 43–47). Usually DMA or TMA are the forms identified. Both have a “garlic” odor and sometimes appear in the air simultaneously above treated areas (16). Metabolism in soil seems to proceed through cacodylic acid to TMA oxide as evidenced by the work of Braman (16) and Woolson (7). After treating grass with CA, an initial high level of DMA in air decreased, while the level of TMA increased. The greater the degree of methylation of the As atom, the more rapid is the soil generation of alkylarsines (7).

In methylation studies, McBride and Wolfe (31) demonstrated that *Methanobacterium* strain M.o.H. reduced and methylated arsenate under anaerobic conditions to DMA. A methyl donor, methylcobolamin, was necessary. Cox and Alexander (30) isolated from sewage three fungi that produced TMA from either organic or inorganic As sources. Lakso and Peoples (33) found both inorganic and methylated As in urine when cows or dogs were fed sodium arsenate or potassium arsenite. Urine levels for both forms (methylated and nonmethylated) increased during feeding with the organic forms predominant. The excretion half-life rate was about 1.5 days. Braman and Foreback (48) also found several forms of As in human urine. The average concentration (in ppb) and percent detected were: arsenite, 1.9 and 8; arsenate, 3.9 and 17; MAA, 1.8 and 8; CA, 15.0 and 66. Total residues averaged 22.5 ppb As. They concluded that CA is a major and ubiquitous form of As in the environment, particularly in biological systems. Although MAA was found, it was generally present in smaller

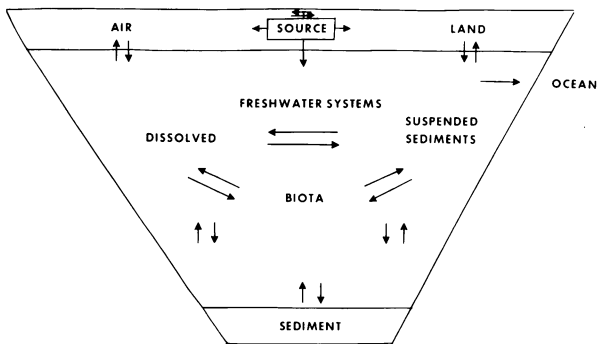


FIGURE 2. General flow processes of arsenic in the ecosystem.

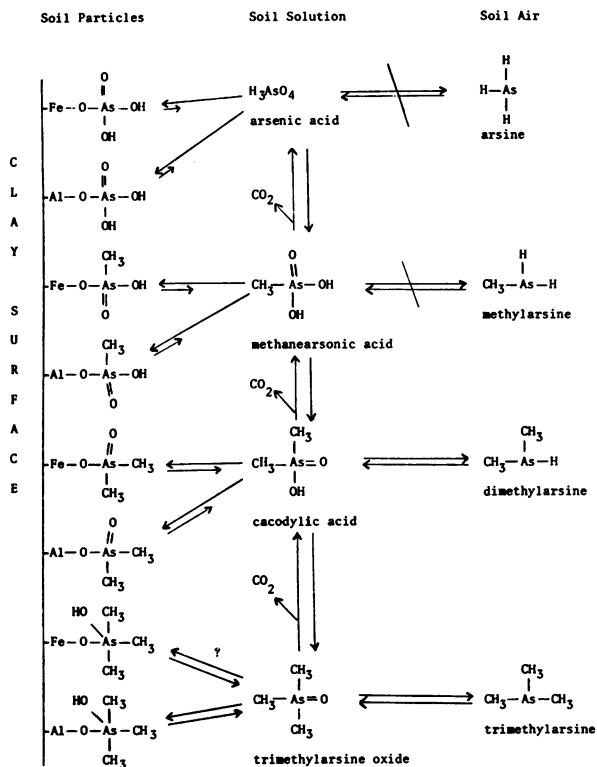


FIGURE 5. Dissolution and reactions of arsenicals within the soil environment.

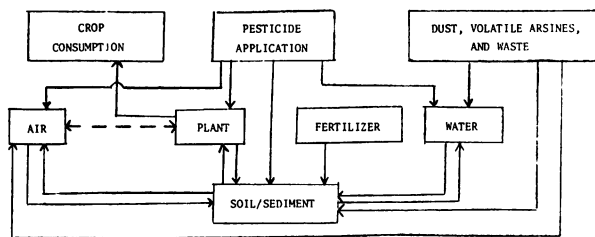


FIGURE 6. Fluxes of total arsenic in an agroecosystem [adapted from Sandberg and Allen (50)].

Rates of Transformation

Because of extreme difficulties in monitoring natural environmental systems and the lack of methodology (until recently) to distinguish between As compounds, no work has been reported on transformation rates per se under natural conditions. In a few instances, however, transfer rates can be inferred and calculated from previous experiments.

Two reactions can occur with any As compound: oxidative metabolism and reductive methylation with subsequent volatilization of the derived alkylarsine. The reactions and their rates will vary

depending on environmental conditions. Data from several researchers were used to calculate that transformed or lost (in %/day) in various substrates (Table 1). The two types of studies represented included laboratory experiments designed to isolate and identify the volatile As compounds and field experiments where the As loss was measured over time. The As loss in these field studies, however, was not limited only to volatilization by alkylarsines, but included leaching, wind-borne dust, runoff, and crop removal.

Losses from field studies where arsenite was applied ranged from 0.010 to 0.124 %/day of the total As present. The average loss was computed at 0.030 %/day. This agrees with the laboratory experimental range reported by Woolson (7) for arsenate-treated soil. The calcium arsenate loss reported by Epps and Sturgis (45) is higher than the other values reported.

Field studies with MAA averaged 0.032 %/day loss for three experiments, whereas, losses in the laboratory experiment (7) were about twice as large. Based on two studies in different parts of the country, CA loss averaged 0.034 %/day. Again, values from the laboratory study were higher.

The loss rates of MAA and CA were similar, because oxidative metabolism is quicker and after an initial period, most of the As (regardless of the starting form) is likely to be at equilibrium within any particular soil. Intuitively, the concentration at this equilibrium may vary depending on soil characteristics (pH, Fe, Al, etc.), the organic matter content, rainfall, temperature, and soil microbial population. This may explain by some soils apparently have not lost very much As after lead arsenate application, while the As content in others seemed to decrease substantially (55).

In the field studies reviewed and tabulated in Table 1, the half-life for arsenate in soil was calculated as 6.0 yr, MAA as 5.6 yr, and CA as 5.2 yr.

The loss rates increase slightly with the increased methylation of the compound, which seems reasonable since fewer methylation steps are needed in MAA and CA to reach the DMA or TMA stage where reduction and volatilization can occur. Volatilization from aquatic systems was faster than from soil, although the evolved gases have not been isolated or identified. Loss was measured as total As from the system.

The necessary experiments to verify the rates of conversion and the identity of the transformed As compounds have not yet been performed.

The transformation As in the environment consists of a series of oxidations, reductions, methylations, and volatilizations and can be depicted as in Eq. (1):

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