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Potential Impact of Acid Precipitation on Arsenic and Selenium

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The potential impact of acidic precipitation on the environmental mobility of the metalloids arsenic (As) and selenium (Se) has not been given much attention and is poorly understood. As with other elements, the interest here is the potential effect of environmental acidification on environmental behavior in ways that are relevant to human exposure to these metalloids. Available information on acid precipitation and the environmental behavior of these metalloids do, however, permit some preliminary conclusions to be drawn.

Both As and Se appear to be mobilized from household plumbing into tap water by the corrosive action of soft, mildly acidic water, while surface water catchment systems in areas impacted by acidic deposition may contain elevated soluble As levels.

Acidification of aquatic ecosystems that are drinking water sources may pose the prospect of enhanced release of As from sediment to water as well as reduction in water levels of Se. Acidification of ground waters, where As appears to be especially mobile, is of particular concern in this regard.

The potential impact of acidic deposition on As and Se in soils cannot readily be assessed with respect to human exposure, but it would appear that the behavior of these metalloids in poorly buffered, poorly immobilizing soils, e.g., sandy soils of low metal hydrous oxide content, would be most affected. The effect is opposite for the two elements; lowered pH would appear to enhance As mobility and to reduce Se availability.

Altered acidity of both soil and aquatic systems poses a risk for altered biotransformation processes involving both As and Se, thereby affecting the relative amounts of different chemical forms varying in their toxicity to humans as well as influencing biogeochemical cycling.

Introduction

Unlike the case for certain metal ions such as aluminum, lead, and mercury, the potential human health impact of acidic precipitation on the metalloids arsenic and selenium has been virtually ignored and is poorly understood. There are several reasons for this. The relevant data base is widely dispersed through diverse specialty literature, making it difficult to assemble a coherent rationale for human health concerns. Second, there are analytical methodology problems associated with these elements, particularly speciation methodology for specific chemical forms. Inability to assess the relative amounts of the varying forms in environmental media means overlooking the multiple ways in which environmental acidification may affect their environmental behavior.

That said, there are a number of concerns associated with these metalloids and their relationship to acid precipitation:

(1) Both arsenic (As) and selenium (Se) in certain of their forms are recognized human toxicants.
(2) These metalloids are, or can be, significant environmental pollutants.
(3) Major anthropogenic sources of these elements are the same as those held by many to be associated with the genesis of the acid precipitation problem: coal combustion and various metallurgical operations. Therefore, the two problems are intertwined, particularly in a localized context.
(4) Both As and Se enter complex geochemical and biogeochemical cycling/transformation processes, the relative expression of which determines overall environmental cycling and human exposure.
(5) Environmental acidification has the potential for interacting with these processes in a multiplicity of ways.

As with other environmental agents, there are some specific questions which help frame the issue of acid precipitation and its potential impact on the health aspects of As and Se. How does the phenomenon of environmental acidification, anthropogenic and otherwise, affect the levels of these metalloids in those media which also serve as human exposure pathways, e.g., drinking

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water, food groups, etc.? How does environmental acidification alter the relative amounts of the various chemical forms of As and Se, which differ in toxicity, in environmental media? With As, for example, toxicity decreases in the order: H_3AsO_3> H_3AsO_4> CH_3–As–O_3H_2> $(CH_3)_2$-As-O_2H≥ "biological As." Modest changes in levels of very toxic forms might be of more concern than larger changes in forms having rather low toxicity. For selenium, viewed as a human essential element in the context of nutrition rather than toxicology, does environmental acidification potentially alter eventual nutritional status through alterations in levels of dietary intakes?

Interrelationships of Arsenic and Environmental Acidification

The conclusions which may be drawn from available information having a bearing on the potential impact of environmental acidification in general, and acidic precipitation in particular, on arsenic in various environmental compartments range from some rather clear problems of arsenic in drinking water distribution systems to more generalized implications of the metalloid's behavior in certain ecosystems.

A number of factors, both physicochemical and biological, influence the behavior of As (and Se) in various environmental media. Central to the operation of many of these factors is the relative acidity of the medium. Hence, concern about the interaction of arsenic and environmental acidification does have theoretical underpinnings.

One relationship of interest is that of the redox potential and pH for various inorganic arsenicals (*1*), in the form of the redox-potential/pH stability diagram as depicted in Figure 1. The arsenicals indicated in the various compartments or domains correspond to the most stable form, while boundary lines correspond to equal concentrations of the two specific forms. For example, inspection of Figure 1 indicates that at moderate positive potential, 100 to 200 mV, decrease in the pH increasingly favors the trivalent over the pentavalent arsenical.

Figure 1 portrays thermodynamic stability for systems in equilibrium and does not readily permit assessment of the kinetics of interconversion from one form to another in response to changes in acidity or potential. For example, the favored form of inorganic As in aerated soils at neutral pH would be pentavalent arsenate. It has been noted, however, that trivalent arsenite added to such soils is only very slowly oxidized to the favored form in the absence of microbial action (*2*). Hence, both thermodynamic and kinetic aspects of acid-associated behavior of these species must be considered.

In addition to physicochemical factors, a reasonably well established data base now exists to show that a number of biotransformations involving arsenicals occur in aquatic and terrestrial ecosystems (*3–5*). These biotransformations are mediated by microbiota and higher level organisms, systems which are sensitive to media acidity. More detailed discussion of this aspect of the issue is given below.

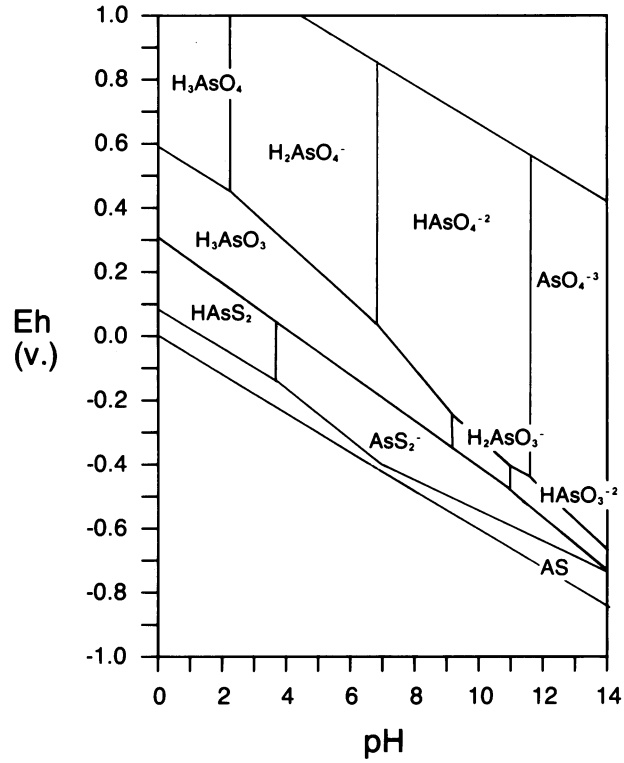

FIGURE 1. Redox potential–pH stability diagram for various inorganic arsenicals. Adapted from Bahn (*1*) and Ferguson and Gavis (*17*).

Atmospheric Transformations of Arsenic

Effects of acidity on arsenic transformations first appear in the major conduit for movement of anthropogenic arsenic to other environmental compartments, the atmosphere.

Pyrogenetic release of arsenic during coal combustion and metallurgical operations such as copper smelting involves emission of trivalent arsenic oxide, either as the dimeric vapor or the particulate form (*6*). With time, vapor increasingly reverts to particulate form. The trivalent form undergoes, to some extent, oxidation to the pentavalent oxide in the atmosphere (*7*).

Existing data strongly indicate that airborne arsenic in the less soluble and less bioavailable particulate forms would undergo hydrolytic solubilization to the corresponding oxy acids in the presence of acidic atmospheric moisture. Dreesen and co-workers (*8*) have demonstrated, for example, that arsenic in coal-fired power plant fly ash is inert to leaching by water or alkaline solutions, but is readily extracted by dilute acid solutions. Crecelius (*9*) observed that arsenic in the fine dusts from copper smelter fallout was readily soluble in weakly acidic (pH 5.5) laboratory water, with ca. 80%

dissolution over a period of several hours.

Given this indirect evidence for airborne As lability toward acidic media, we might expect that a considerable fraction of arsenic in acidic rainfall would be in soluble, bioavailable form. In an area known to have acid precipitation (*10*), Crecelius (*9*) noted that significant amounts of rain water arsenic were present in soluble form. In a comprehensive survey of surface water catchment systems scattered throughout Arizona and of the type presently used for livestock water but having potential use as household water sources, Frasier (*11*) reported that As was the sole element in catchment water which was consistently elevated to potentially toxic levels. This investigator was able to determine that the atmosphere was the sole source of the metalloid, via both wet and dry deposition. Although the emission source was not studied, it is probably related to various copper smelter operations in the state.

It is important to note that, for all practical purposes, the existence of elevated As levels in the atmosphere would be invariably linked to the presence of acidic precipitation, predictable in terms of commonality of source (as noted earlier) and demonstrated by the reported high correlation between atmospheric As (and Se) and atmospheric sulfur dioxide (*12*). As a consequence, sizable fractions of the As content in precipitation would always be in soluble, bioavailable form.

In terms of human exposure, the above discussion indicates a potential As exposure risk for use of surface water/cistern collection systems as drinking water sources, particularly in areas having both elevated atmospheric As levels and an acid precipitation problem. Furthermore, atmospheric As entering such systems would be in the relatively more toxic inorganic oxyarsenical forms.

Potential Interrelationships of As in Drinking Water Systems/Sources and Acid Precipitation

In addition to any relatively direct impact of atmospheric acidity on As in surface water catchment systems, it is also useful to consider water acidity as it potentially relates to As in conventional household distribution systems and sources: reservoirs, lakes, rivers, streams, and groundwaters.

Arsenic in Tap Water. In a recent large-scale survey of first-draw household tap water involving 3000 samples from as many households, Strain and co-workers (*13*) reported that ca. 10%, or 300, of such water samples contained As at levels exceeding the EPA standard of 50 μg As/L. As many of these samples also showed elevations in those elements—cadmium, copper, lead—commonly associated with the corrosive action of soft water, it is likely that a similar process is occurring with the mobilization of the metalloid. These investigators tested various components of ordinary household plumbing and found that joint solder consisting of 95:5 tin–antimony alloy produced a concentration of 203 μg As/L in contact with soft water over a rather short period of time (*14*). Joint solder of this composition appears to be in increasing use as an alternative to the common 50:50 tin-lead solder, presumably as a means of minimizing lead leaching.

An earlier U.S. public drinking water survey in 1969, summarized by McCabe et al. (*15*), showed a much lower rate of exceeding the standard, 0.2%, compared to the 10% figure of Strain and co-workers (*13*). The reasons for this 50-fold difference in the two surveys probably include differences in both survey design and analytical methodology. The 1969 survey was designed to reflect the diversity of drinking water sources in the U.S. and included a large number of well water sites. By contrast, the survey of Strain et al. (*13*) may well have involved primarily surface supplies. According to data of McCabe et al. (*15*), the detection limit for As in the 1969 survey was ca. 30 μg As/L at best, which is already close to the standard limit. Hence, a significant number of false negatives may have been obtained. Other differences may include the relative use of tin–antimony-based plumbing solder in households surveyed in the two reports. Finally, there is the probability that the frequency of soft water use differed in the two studies. Allied to this factor is the question of whether the difference reflects alterations in the relative acidity of water supplies over the time period between the two surveys. It would be difficult to sort out this possibility from the others noted above.

The impact of acid precipitation on household plumbing corrosibility with attendant mobilization of As and other elements is of concern to the extent that it would materially contribute to overall acidity of water supplies entering corrosible plumbing systems. At present, it is not possible to quantitate such contributions.

Arsenic in Surface Water Systems. The behavior of As in fresh water is dominated by the sediment compartment. Sediments constitute the major sink for As in many aquatic ecosystems, being capable of sequestering relatively large amounts of the element in areas of significant contamination (*16*). While different components of sediments participate in the immobilization of arsenic species, the major role appears to be played by hydrous oxides of such metals as iron, aluminum, and manganese as well as surface sites on clay particles containing these elements (*9,17*). Of particular relevance to the discussion is the fact that the relative efficacy of As binding to these components is a function of pH, redox potential, and species of arsenic (*18–20*).

In addition to the above diagenetic characteristics of As in sediments, there are the biotransformational processes which have been described for As in sediments. In circumstances where there is heavy sediment contamination by As or microbiotic stresses, it appears that inorganic As can undergo biomethylation to methylated forms (*21*). Conversely, sediments contaminated with certain organoarsenicals, particularly monomethyl arsonic and cacodylic acids, have been reported to undergo oxidative demethylation (*22*). Recently, it has been noted that fresh water green algae also are capable of

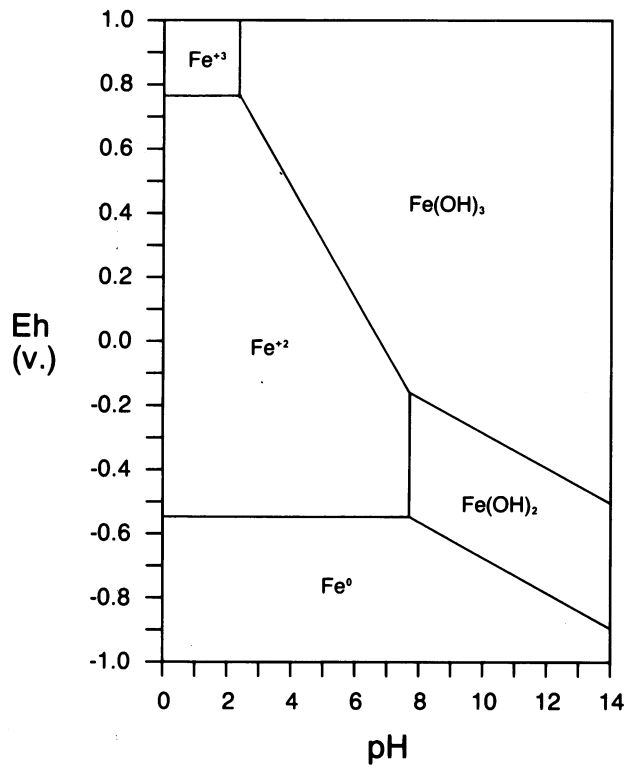

FIGURE 2. Redox potential–pH stability diagram for various iron species. From Khourey et al. (*24*).

bio-methylating inorganic arsenic (*23*).

The interaction of As and metal hydrous oxides can be exemplified by the redox potential–pH stability diagram for various species of iron as shown in Figure 2. The compartment or domain in the diagram indicated as "am- $Fe(OH)_3$" refers to the insoluble amorphous ferric hydroxide, which actually exists in the form of a hydrous oxide polymer. It is this region of potential and pH, therefore, where As binding to this particular metal species would be maximal. With reduction in potential or pH, the hydrous oxide is thermodynamically less stable, with an associated reduced binding efficiency for arsenicals (*24*).

Experimental data support the assumptions that the relative acidity of the aquatic environment governs binding processes in sediments and that the degree of binding is a function of the chemical form of arsenic.

In a detailed study of the behavior of As at rather elevated levels in lake, river, and estuarine dredge sediments, Brannon and co-workers (*22*) found that long-term arsenic release from sediments is directly proportional to the elutriate rate but is inversely related to pH, according to Eq. (1):

$$\text{As release (mg)} = 2.1414 + 6.161(\text{Elutriate rate, mg}) - 0.312\ \text{pH} \quad (1)$$

In this study, the elutriate rate was 0.008 to 0.086 mg.

Various investigations have demonstrated that decreasing pH lessens immobilization of both arsenate and arsenite by metal hydrous oxides, with the relative change being greater for arsenite (*18–20,25–27*). Furthermore, trivalent As appears to be more mobile in sediments at a given pH than is the pentavalent form (*20*). Germane to the discussion is the comprehensive survey of Singh and Subramanian (*28*) of metal/metalloid scavenging by iron and manganese hydrous oxides. In their review is a plot of system pH versus soluble Fe concentration as reported by various investigators for field surveys of different bodies of fresh waters. At a pH of ca. 7 and above, there is a minimum in soluble Fe level, while at pH 5 to 6, there is a moderate increase. Below a pH of 5, there is a huge increase. These data suggest that lowering of pH, leading to increasing dissolution of iron (III) hydrous oxide, is one explanation for soluble iron increase. It also implies, referring to the stability diagram in Figure 2, that increasing acidity would lessen As immobilization.

One factor of concern in this regard is the postdepositional diagenetic phenomenon whereby iron, manganese, and arsenic are all found to remain concentrated in the surficial layer of sediment (*9,29*), where the acidity of the water column would have the greatest impact. The basis for this behavior resides in the fact that, as a given surface layer of sediment containing iron (III) and manganese (IV) oxides is buried over time, the micro environment becomes anoxic, and these metals are reduced to soluble forms with degradation of the hydrous oxides. These solubilized metals then percolate back to the sediment surface, where the oxidizing environment regenerates the hydrous oxide. Apparently, arsenic species are borne along with the migrating reduced elements.

The relationships of aquatic acidity and various microbiota which participate in arsenical biotransformations may also be of some concern. As noted earlier, such biota induce biomethylation, oxidation–reduction, and demethylation. Studies have indicated that sediment/water column bacteria have lowered activity with increasing acidity, and that the reduction is further enhanced in the presence of such heavy metals as mercury and lead, elements which are also altered with aquatic acidification (*30,31*).

In the studies of acidifying lakes reported by Rao and Dutka (*32*), it was observed that diverse classes of bacterial populations are reduced an order of magnitude compared to control lakes. Sulfate-reducing bacteria, in particular, are almost obliterated. Since As is immobilized in anoxic sediments as the sulfide (Fig. 1), this adverse impact on sulfate-reducing bacteria may affect this metalloid's behavior. In acidifying lakes, furthermore, waters of pH < 6 are associated with reduced green algal populations, biota which are also involved in the biotransformation of inorganic As to less toxic organoarsenical forms (*33*).

The extent to which aquatic acidification has any long-term impact on the variety or mass of diverse biota determines the potential for altered biotransformational processes and the relative distribution of different ar-

senicals in water systems. At present, the extent of such changes in levels of arsenicals differing as to form and attributable to aquatic acidification remains undefined.

Arsenic in Groundwater

Groundwaters as sources of drinking water for human populations are also of concern in terms of the impact of acidification on the behavior of As. Arsenic is present in, or can enter, ground waters by either natural processes or leaching from As-contaminated sites, As herbicides used on poorly retaining soils, waste disposal, etc.

Groundwaters that feed lakes and streams consist of oxic (recharge), neutral (redox potential ca. 0), or anoxic zones. It is to be expected, therefore, that different regions of ground water, varying in pH and/or redox potential, would also differ in the behavior of arsenicals contained in these regions. Khoury and co-workers (*24*) have discussed the potential public health problems of As in groundwaters in terms of both pH and redox potential alterations, particularly enhancement of the metalloid's mobility in response to such alterations. Reduction in redox potential or pH would have the net effect of enhancing the levels of As in groundwaters.

Gulens et al. (*34*) have documented that the groundwater mobility of trivalent As from anthropogenic sources in the Perch Lake Basin, Ontario, is considerable in the neutral and even anoxic zones of groundwater systems. The effect of increased acidity would be to enhance such mobility even further (*22*), allowing levels of As in waters to rise and posing some increased exposure risk where groundwaters are used as potable water sources and have some degree of As contamination.

The discussion is given added impetus by the fact that groundwaters in various areas of the world, particularly in European locales also impacted by acidic precipitation, are undergoing detectable acidification (*33,35*). Such a phenomenon, given the above discussion, would increase the risk for As mobilization into such waters.

Arsenic in Soils

The behavior of various arsenicals, particularly the inorganic and methylated forms, in soils is a function of soil type, metal colloid content, redox potential/acidity, relative phosphate content, the chemical form of arsenical, and microbiotic populations (*36*). The metalloid can be mobilized from and through soils by such factors as volatilization due to biotransformation, leaching downward, uptake by plant species, and runoff processes (*36*).

Aerated soils favor the presence of inorganic arsenic in the pentavalent state, while soils of low redox potential, i.e., flooded zones, favor the trivalent species. The relative immobilization of inorganic arsenic and those organoarsenicals used as biocides in soil zones appears to be a function of metal (iron and aluminum) hydrous oxide content (*36*).

Dry deposition processes result in the deposition of particulate arsenic oxide onto soil surfaces (*6*). Given the earlier discussion concerning atmospheric transformation of particulate As to soluble forms with acidic atmospheric moisture, the potential exists for acidic deposition to also solubilize particulate As on soil surfaces. In fact, enhanced solubilization by acidic deposition has been documented for particulate cadmium and other metal oxides in brown earth and sandy loam soils (*37*). The net effect is to increase the bioavailability of the metalloid to plants, soil microbiota, etc.

The degree to which increasing acidity of precipitation may affect As mobility in soils cannot be well delineated at present. For one thing, there is a relatively sparse data base concerning the mobility of As in soils as a function of pH. Existing information indicates that few soil types have been surveyed in any systematic way and the pH range surveyed has been rather narrow (*38*). Comparatively speaking, existing data would suggest that sandy soils with relatively low metal hydrous oxide content and limited buffering capacity would be most vulnerable to some net pH change in at least upper soil regions with long-term acidic deposition through precipitation (*38,39*).

Various soil organisms, as indicated earlier, are involved in the mobility of As in terrestrial ecosystems, specifically the oxidation of inorganic arsenic, some level of biomethylation and oxidative demethylation to inorganic forms (*36*). A number of studies have attempted to simulate the impact of acidic precipitation on biotic populations in soil systems, with results showing a mixed picture (*40–42*). In some cases, there is limited impact; in other cases, there are demonstrable alterations in microbiotic activity. The relative persistence of these effects, however, remains to be demonstrated.

Potential Impact of Acidic Precipitation on Selenium

The impact of environmental acidification on the behavior of selenium species in ways relevant to human exposure is even less well understood than it is for arsenic. This is due in large part to the fact that the full geochemical/biogeochemical cycling processes of the metalloid remain to be fully delineated. The information available still raises some points of concern to this topic.

Atmospheric Transformations of Selenium

As is the case with arsenic, emissions from coal combustion and metallurgical processes are major atmospheric sources of the selenium (*12,43*). There is, therefore, the parallel question as to what effects there are on atmospheric Se, in terms of bioavailability, in the presence of acidic atmospheric moisture. Dreesen et al. (*8*) have shown that particulate Se in coal-fired power plant fly ash is readily solubilized by dilute acid solu-

tions, while leaching is minimal in water or alkaline media. By inference, it is likely that atmospheric Se particulate can be readily solubilized to more bioavailable selenite by acidic atmospheric moisture. Support for such a transformation can be found in the report of Suzuki et al. (*44*), who noted that chemical speciation studies of Se in rain water and aerosol in the Tokyo area showed that 50 to 90% of rainwater Se was in the form of soluble selenite with the balance as inert zero-valent Se species, and that 50 to 60% of aerosol Se was the soluble selenite form, the balance being the zero-valent form. A precise assessment of the degree of post-emission generation of the zero-valent form of the metalloid, probably through redox reaction with sulfur dioxide (*43*), is complicated by the fact that some fraction of the stack emissions of Se is already zero-valent, ca. 20%, based on data of Andren et al. (*43*).

Selenium in Tap Water

In the survey of Strain et al. (*13*) noted earlier, 3000 first-draw water samples showed that ca. 18% of the samples, or ca. 540 samples, had Se content exceeding the EPA standard of 10 μg Se/L, with the highest measured level being 450 μg Se/L. As noted in the discussion on arsenic, these same samples showed elevations in elements associated with corrosion of household plumbing by soft, acidic water. Hence, both Se and As are elements which appear to be among those mobilized from plumbing to water by such action.

Selenium and Acidity in Aquatic Ecosystems

Available information on the behavior of Se in the sediment and water column components of fresh water ecosystems is rather limited.

Studies by Schindler et al. (*45*) and Jackson and coworkers (*46*) indicate that experimental acidification of fresh water lakes is associated with enhanced movement of Se from water to the organic components of sediment, leading to increase in sediment levels and concomitant reduction in water levels of the element. This behavior is the opposite of what appears to occur in the response of As to such alterations.

Inorganic and organic Se compounds undergo microbial transformations in fresh water sediments mainly to dimethylselenide (*47*), such transformations being a factor in the metalloid's cycling. At present, it is not possible to assess the specific impact of acidification on Se biotransformations. In one report (*48*), it was observed that the relative biomethylation rate of inorganic Se by microbiota in sediments is directly proportional to pH. One cannot determine whether this is an effect of lowered biological activity *per se* or a reflection of reduced availability of the Se substrate to biotransformation because of increased sedimentary sequestration (*45,46*). As noted earlier, aquatic microbial populations can be affected to some degree in lakes undergoing acidification, at least in the short term.

Interactive Relationship of Selenium and Mercury

One aspect of the impact of acidification on aquatic ecosystems is the associated increase of neurotoxic monomethylmercury in higher trophic species, particularly predatory fish such as pike (*49*). Since it is also widely recognized that Se significantly alters methylmercury toxicokinetics and toxicity in various organisms (*50*), the question arises as to any potential impact of environmental acidification on Se–Hg relationships in aquatic ecosystems.

Several studies indicate that there is an inverse relationship between the Hg content of lake fish and Se levels in these waters, as well as an inverse relationship to fish tissue Hg/Se ratios (*51,52*). Of particular interest are the observations of Turner and Swick (*52*). Using experimental enclosure studies where Se and Hg availability to the aquatic populations were varied, they found that predatory fish Hg content decreases as food chain Se is experimentally increased. Furthermore, this response is also seen in intermediate members of the food chain. Food web Se is directly proportional to water Se level. Since others have noted that water Se levels decrease with acidification (*45,46*), there is the potential for reduced Se availability in altering Hg uptake in fish and other organisms.

Selenium in Soils

In contrast to the case of arsenic, it would appear that pH changes in soils affect Se by reducing mobility of the metalloid with increase in acidity.

Geering et al. (*53*) carried out a systematic study of the behavior of selenite in different soil types as a function of pH. These workers found that increased acidity enhanced Se (IV) binding to ferric hydrous oxide, a major immobilizing agent for the metalloid in soils. Furthermore, an increased reduction of tetravalent selenite to the zero-valent form was seen. The net effect of both these changes would appear to be reduction of Se availability to plants.

Increasing soil acidity reduces the rate of biotransformation of selenium compounds to dimethylselenide (*54,55*), which has the result of also reducing movement of soil Se to plants by foliar uptake of the volatile dimethylselenide, a process which appears to be a major route by which plants assimilate selenium (*56*).

The degree of disturbance of normal Se behavior in soils due to long-term acidic deposition on soils cannot be adequately assessed at present. Such potential impact, however, would appear to be greatest in poorly buffered soils which are marginal at best in Se content and those species, e.g., metal hydrous oxides, which serve to retain the metalloid. For example, sandy soils low in Se and iron hydrous oxide content are known to produce crops low in Se (*57*). Extended acidic deposition on such poorly buffered soil would appear to have a relatively more pronounced effect in terms of further reducing Se bioavailability to plants (*39,58*).

Summary and Overview

The available information on linkage of potential impacts of acidic precipitation to the environmental behavior of As and Se, in ways relevant to human exposure, permit some preliminary conclusions. Such conclusions range from some rather clear concerns, on the one hand, to more generalized statements as to the relationships of these metalloids in environmental media to media acidity, whether the acidity is anthropogenic or natural in origin.

Mobilization of both As and Se from household plumbing into first-draw tap water via the corrosive action of soft, acidic water appears to occur at a significant frequency, based on one large survey. Hence, these elements should be added to the list of those which undergo such mobilization. Available data do not permit determinations as to the actual chemical forms of As and Se which are so mobilized, but it can be said that they would probably be the relatively more toxic inorganic oxyarsenical forms. Acidic precipitation is of concern in this context to the extent that it is or would be a contributor to the maintenance of public surface or groundwater supplies entering systems at pH levels where metallosolvency is a problem.

Similarly, available data do make a circumstantial case for risk of As exposure with surface water catchment systems serving as drinking water sources in areas impacted simultaneously by acidic precipitation and emissions of these metalloids. The concern here is not only As exposure, *per se*, but exposure to the metalloids in highly bioavailable form and forms having relatively higher toxicity.

The behavior of As and Se in aquatic ecosystems which can serve as public water supplies, with respect to acidity, appears to be different for the two metalloids. With As, the impact of acidification would appear to be mobilization from sediment to water, with increased human exposure risk; with Se, such a change has the effect of reducing water levels and increasing sediment Se content.

One study indicates that diverse dredge sediments containing As show an inverse relationship between pH and release of the metalloid. Other evidence exists to show that certain metal hydrous oxides, e.g., those of iron (III) and manganese (IV), are effective scavengers of As and other elements and thereby contribute to As sequestration in sediments even at rather high loadings, and that those binding species become increasingly less stable with increasing media acidity, posing the potential for enhanced release of As to the water column.

Although the behavior of Se species in fresh water ecosystems has not been well studied, information exists to indicate that aquatic acidification is associated with enhanced movement of Se from water to sediment.

Of relevance to these observations on Se partitioning is how water Se changes would relate to the known observation that aquatic acidification leads to an increase of methylmercury content of fish in acidifying lakes. Experimental enclosure studies show that Se levels in water affect Se content of the food web, and that food chain Se inversely affects the Hg content of higher trophic levels. Studies have demonstrated that a key factor in increased methylmercury content of fish in acidifying systems is the enhanced formation of bioavailable monomethylmercury from volatile, nonavailable dimethylmercury via enhanced acid-mediated demethylation of the latter. A second factor is the reduced biomass attending acidification, thereby reducing any *de facto* "dilution" effect which would normally operate. These factors, however, do not in any way rule out an additional effect of altered Se bioavailability.

The problem of As in groundwaters is of particular concern. The metalloid appears to be particularly mobile in ground water regions, such that increased acidity would probably have a proportionately greater effect than it might have in surface aquatic systems. Furthermore, ground waters appear to be acidifying in certain regions of the world, particularly those impacted by acidic precipitation. Added to any concerns here is the increasing practice of land spreading of various As-containing wastes with the potential for groundwater contamination.

The relationships of As and Se in soils to alterations in soil acidity have not been as well studied as their potential implications for human exposure might support.

In many soils, As in various chemical forms appears to be effectively immobilized by clays and metal hydrous oxides. A number of these soils would also appear to offer adequate buffering to acidic deposition, resulting in a limited impact on altered As mobility.

Other soils, however, which have poor buffering capacity and little metal hydrous oxide content, would appear to be most vulnerable to the long-term impact of acidic deposition. In these soils, there would be a greater possibility of As leaching downward (to groundwaters) and being more readily available for uptake by food crops.

Available data indicate that As and Se in soils respond in opposite ways as a function of pH. Moderate experimental increase in acidity of certain soil types actually increase Se immobilization by metal hydrous oxides and also enhances reduction of selenite to zero-valent form. Lowered pH reduces the generation of volatile dimethylselenide in soils via microbial action, with the effect of lowering the assimilation of Se by plants (through foliar uptake of the dimethylselenide). All of these alterations have the effect of reducing Se bioavailability to plant life.

While such responses might be viewed as a desirable reduction in potential exposure to the element in areas having excessive Se in soils, there is little practical consequence to areas having seleniferous soils. Such soils are quite alkaline, and their high buffering capacity would presumably minimize any impact of acid deposition. Of more concern would be the potential impact of acid precipitation on agronomic soils having marginal Se content and also having poor buffering capacity. In these cases Se bioavailability to food crops is reduced

even further, with Se content of food crops being further lowered.

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