

Inexplicable Arsenic: Human Dimensions of Soil, Water, Food and Microbial Resources

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Arsenicals are a double-edged sword and are used as therapeutics as well as poisons from time immemorial. Mineral arsenicals such as orpiment (As_2S_3), realgar (As_4S_4) and arsenolite (As_2O_3) have been used for therapeutic purposes, even during 200 BC in China [1]. Both the Dr. Fowler's solution and Salvarsan (arsphenamine) made the arsenic-based medication popular in the allopathic medicine before the introduction of antibiotics. But, this element is poisonous in larger doses. The lethal doses of 'Poudre de succession' (inheritance powder) of white arsenic were used even in the Roman days [2]. Since the introduction of 'Marsh test' for detecting arsenic in tissues [3], its use for human poisoning has diminished. But, several wood preservatives, herbicides and insecticides have arsenic compounds as toxins now. Health risks of these arsenic compounds are very high. Besides, millions of people are regularly exposed to arsenic through eating food grown in contaminated soils or drinking water containing high amounts of arsenic. But, the contemporary human tendency is to perceive ill effects as unconnected events. The soil and water contamination can occur either naturally or anthropogenically. The agricultural activities may have the cause-effect relationships with arsenic laden food and water. Chronic arsenic intake may be due to the cascading effects of human dimensions of soil and water resources.

The new paradigm of agriculture worldwide is to make cheaper and faster food, feed, fuel, and fiber. Intensive cultivation of food crops in about 13,056 million hectares (Mha) of land provides almost 99.7% of human food [4]. But, this agricultural intensification has also led to the depletion of topsoil, by 10-40 percent more than their replacement. Globally, agricultural activities are one of the causes of soil degradation; the extent of degradation is being observed nearly in 550 Mha. Other causes of degradation include overgrazing (680 Mha), deforestation (580 Mha), overexploitation of land for fuelwood production (137 Mha) and industry and urbanization (19.5 Mha) [5]. The loss of soil from cropland is about 1.7 billion tons annually while it takes 500 years to form an inch of it [6]. Even the agricultural extensification by bringing more land into similar intensive agricultural use may lead to further loss of soil [7].

Topsoil has much of the essential nutrients needed by plants. The fertile topsoil has on an average of 1-6 kg nitrogen, 1-3 kg phosphorus, and 2-30 kg potassium per ton. But, the eroded soil will have reduced levels of nitrogen to 0.1-0.5 kg per ton [8]. The loss of nutrients during cultivation is primarily due to leaching of mobile elements when the stratigraphic barrier of soil is disturbed for the vertical water movement of water. Increased mineral weathering and plant uptake and subsequent harvest also lead to further loss of nutrients. For optimal health, humans require at least 60 minerals and animals about 45 minerals [9]. But, most food produced from the agricultural soils has only eight minerals now. Significant reductions in the concentrations of calcium, magnesium, copper and sodium in vegetables and magnesium, iron, copper and potassium in fruits were noted between those grown in the 1930s and the 1980s [10]. The introduction of high-yielding plant cultivars was also found to result in significant inverse relationships between yield and concentrations of minerals [11]. The decline in mineral concentrations of food has been linked partly due

to the loss of topsoil and current agricultural production methods. Paradoxically, high amounts of toxic arsenic minerals that are naturally available are absorbed by plants from these soils.

Nutrient deficient soils are generally a poor medium for growing food that can keep humans healthy [12]. Fertilizers, either organic or synthetic as an external source of nutrients are used to boost agricultural productivity since long. Often, the macronutrients are supplied in the form of synthetic fertilizers, with other minerals as trace elements or contaminants. Not only for healthy human foods, but the content and composition of soil minerals is critical for the storage and turnover of soil organic carbon [13]. Now, enormous amounts of chemical fertilizers with more emphasis on macronutrients for plants are applied to increase the agricultural productivity. For the fertilizers of N, P_2O_5 , and K_2O alone, the demand is projected to be around 190,377 thousand tons by 2015 [14]. The chemical load in food from the 'cradle' of its making to the processing has become enormous with pesticides and herbicides. Even during the medieval period, natural chemical compounds such as arsenic and lead were used for the control of pests in farming. Pesticides of 40 billion US dollars are used annually for agricultural production [15]. Many of these agrochemicals have arsenic compounds as toxins or contaminants. The present-day agriculture has become a controlled system of chemical substances, especially those of fertilizers, pesticides, and herbicides. The deficiencies or toxicities of chemicals continue to be the major issue in agriculture and subsequently on human health.

For the 3.8 billion tons (3830 km^3) freshwater withdrawn annually, agriculture competes with domestic, industrial and environmental uses [16]. About 70% of this withdrawal including groundwater goes for agricultural production. Groundwater, the long-term reservoir of the natural water cycle is safer than the fresh surface water. But, several contaminants, as a result of natural processes or human activities, from the point or nonpoint sources are discharged into the surface waters. The present day agricultural fields are an important source through which fertilizers and pesticides are introduced into the water bodies. Varied sources, as well as chemical species, pollute both surface and groundwater sources. In recent times, groundwater contamination of arsenic has received global attention. Arsenopyrite, base metal sulphides, realgar and orpiment, arsenic-rich pyrite and iron oxyhydroxide contribute to the groundwater contamination.

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The oxidation of arsenic-bearing sulphides, desorption from oxides and hydroxides, reductive dissolution, evaporative concentration, leaching from sulphides by carbonate and microbial mobilization are the significant mechanisms [17]. The oxidation of pyrite and arsenopyrite can make the oxidized arsenopyrite highly soluble, making it an important mechanism of increasing arsenic concentration in the groundwater. Alternatively, the reduction of oxyhydroxides may increase the levels of arsenic in aquifers under strongly reducing condition.

More than 200 mineral species contain arsenic in the natural environment. In the air of rural areas, the arsenic concentrations are about 0.02-4 ng/m³ while they range from 3-200 ng/m³ in the urban areas [18]. The levels of arsenic in seawater are about 1-2 µg/l while those of surface freshwaters are usually below 10 µg/l. In soils, their concentrations can be about 1-40 mg/kg. Continuous cycling of different arsenic forms occurs through soil, water, and air. But, human activities such as pyrite mining, chemical intensive agriculture, coal burning and extensive withdrawal of groundwater along with geological activities contribute to the arsenic contamination of soil and water resources [19]. Soils associated with certain geological substrata (e.g., sulfide ores) and those contaminated by human activities may have arsenic up to several grams per kg. Plants in the arsenic contaminated soils accumulate them by root uptake or adsorption from the deposits on leaves. In the arsenical mine sites, some plant species can take up to the levels of 3000 mg/kg as against the general background concentrations of less than 0.7 mg/kg [20].

Arsenic is an essential trace element as it is related to the metabolism of arginine amino acid. Interestingly, humans and animals show hormesis dose-response to this element. The inorganic forms of arsenic are considered to be more harmful than the organic forms. Plaice, oysters, mussels, and prawns are some of the sea inhabitants that can accumulate 4 to 175 mg of arsenic in organic forms of arsenobetaine or sugars or polyunsaturated fatty acids per kg of their body weight. Earlier, the organic forms are considered potentially beneficial to humans. In 1944, the Food and Drug Administration of United States of America approved the use 4-hydroxy-3-nitrobenzenearsonic acid (Roxarsone) as a drug. This organic form of arsenic is used in poultry, piggery and turkey farming industries for increased growth promotion and feed efficiencies. Three other approved arsenical animal drugs include nitarsonic acid (4-Nitrophenyl) arsenic acid for controlling blackhead disease in poultry, arsanilic acid (4-aminophenylarsonic acid) for prevention of dysentery and carbarsone for the antiprotozoal treatment. With the findings of inorganic arsenic forms in tissues of animals and their accumulation in soils after the application of manures from those industries, nitarsonic acid is only marketed in the U. S. A. now [21].

Measuring the inorganic arsenic in edible plant tissues is a daunting task, especially without the sophisticated instrumentation, because of the presence of various organic and inorganic species together in these complex matrices. Low levels of inorganic arsenic (less than 10 ppb) can only be detected by the ion chromatography inductively coupled plasma mass spectrometry. The regular monitoring of arsenic concentrations in plant, animal or human tissues are near impossible due to the sophisticated and cumbersome nature of detection and quantification of inorganic arsenic species. Poisoning by arsenic may not be acute but chronic in many contaminated environments. Toxic effects of arsenic in humans may be observed slowly, from about 2 to 20 years. Many of the arsenic-contaminated sites are densely populated, and the reliance on agricultural activities including rice cultivation is

more in these areas.

Anaerobic conditions can significantly influence the bioavailability of arsenic in soils. The microorganisms are probably the first life forms to react with chemical arsenic species. Numerous bacteria and archaea can reduce arsenate [As(V)] to arsenite [As(III)] as a detoxification mechanism based on the enhanced outward mobility from the cell of As(III). The dissimilatory arsenic reducing bacteria and archaea belonging to γ -, δ -, and ϵ -Proteobacteria, low-GC Gram-positive bacteria, Thermophilic eubacteria and archaea can solubilize arsenic by reduction, after liberating through reductive dissolution of iron and manganese (oxy)hydroxides. In the opposing reaction, some microorganisms oxidize arsenite to arsenate, the less toxic form. Arsenate can be immobilized onto adsorbents such as iron and manganese (oxy) hydroxides that are found in plaques of rice roots. Heterotrophs oxidize arsenite as a detoxification reaction. This makes arsenate less likely to enter the cells while the chemolithoautotrophic arsenite oxidizers oxidize arsenite with the reduction of either oxygen or nitrate, using the energy derived to fix CO₂ in organic cellular material for growth.

Under the predominantly anaerobic conditions such as rice soils, the methylated arsenicals such as mono-methyl arsonic acid and dimethyl arsinic acid are also produced. Methanogenic archaea are capable of methylating inorganic arsenic to volatile dimethyl arsinic acid, suggesting that the coupled methane biosynthetic pathway as a mechanism for arsenic removal and detoxification. Kulp and coworkers described the anaerobic photosynthetic oxidation of As (III) instead of oxidation of water for photosynthesis [22]. The bacterium GFAJ-1, a strain of *Halomonas* isolated from Mono Lake, California was found having periplasmic phosphate-binding proteins. These proteins are capable of preferentially binding to phosphate in solutions containing 4500-fold more arsenate than phosphate [23]. Thus, these organisms have evolved resistance to arsenic in nature. The abundance of these 'microbial indicators' can show the potential presence of dangerous arsenic in soils, water, and food. The direct impact of arsenic contamination on microbial communities and structure offers opportunities to identify the hotspots of arsenic contamination. New strategies can also be formed for remediation of arsenic contaminated soils and groundwater using these microbial agents [24,25]. The microbial communities respond by the dynamic changes better than physical and chemical properties of contaminated soils or waters. Appropriate molecular methods for detecting and quantifying these microorganisms or their resistance genes can improve the cost-effectiveness and user-friendliness, relatively to the highly advanced spectrometric methods, for the toxicity assessment as well as during remediation.

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