HEALTH EFFECTS OF CHRONIC EXPOSURE TO ARSENIC VIA DRINKING WATER IN INNER MONGOLIA: III. NEUROLOGICAL SYMPTOMS AND PIN-PRICK MEASURES

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The purpose of this study was to assess neurological effects of chronic exposure to arsenic via drinking water. The sample consisted of 321 residents of Ba Meng, Inner Mongolia exposed to low (<21ug/L), medium(100-300ug/L), or high (430-690ug/L) concentrations of arsenic. A questionnaire was administered to assess central (CNS), peripheral (PNS), and autonomic (ANS) nerve system function. Pin-prick tests were also conducted on four limbs to assess PNS effects. Numbness was scored as follows: 1=normal, 2=end of finger/toe only, 3=whole finger/toe, 4=below wrist/ankle, 5=below elbow/knee. Group comparisons were made controlling for age and gender. No significant group difference was found in CNS symptoms (headache or dizziness, amnesia, vision, hearing or perception) except between medium and high groups in smell. On the other hand, significant group differences were observed in most PNS symptom comparisons (vibration, tactile and pain sensitivity, sense of heat-cold, and numbness). Medium and high groups also differed significantly in ANS symptoms. Pin-prick results from hands and feet indicated that numbness increased directly with arsenic concentrations in the drinking water. Significant differences in pin-prick scores were observed between the low and high, medium and high, but not low and medium exposure groups. The largest difference in pin-prick sensitivity was found between the low and high exposure groups. Consistent PNS effects were observed in questionnaire symptoms and pin-prick scores. These findings indicate peripheral sensory axonopathy resulting from arsenic exposure in drinking water.

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(This is an abstract of a proposed presentation and does not necessarily reflect EPA policy.)
HEALTH EFFECTS OF CHRONIC EXPOSURE TO ARSENIC VIA DRINKING WATER IN INNER MONGOLIA: IV. DISTRIBUTION OF ARSENIC CONCENTRATIONS IN WELLS

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In the Ba Men region of Inner Mongolia, China, a high prevalence of chronic arsenism has been reported in earlier studies. A survey of the drinking water sources was conducted in 1997 to better understand the occurrence of arsenic (As) in the drinking water. A total of 14,866 wells were analyzed for their As content. Methods used to detect As were colorimetry based on silver diethyldithiocarbamate, an adaptation of the mercury bromide stain technique, and atomic absorption spectroscopy. There was a wide range of As-concentrations (below the limit of detection to 1.2 mg/l). Elevated concentrations were related to well depth (maximum at the 15 to 25 m category), well type (most high concentrations associated with the small household pump wells) and the date the well was built (peaks from 1980-1990). Over 43,600 persons consumed water with As-concentrations above 0.01 mg/l (14,500 above 0.05 mg/l, 480 above 0.5 mg/l). There were significant differences between different counties and villages within each county. The presented database of As in wells of the Ba Men region provides a useful tool for planning future water explorations. These data were compiled into a geographic information system to provide better estimates of exposure. The database will aid in the design of upcoming epidemiological studies in the region on the human health effects of arsenic in drinking water.

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(This is an abstract of a proposed presentation and does not necessarily reflect EPA policy.)
HEALTH EFFECTS OF CHRONIC EXPOSURE TO ARSENIC VIA DRINKING WATER IN INNER MONGOLIA: V. BIOMARKER STUDIES - A PILOT STUDY

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The groundwater in Ba Men, located in Central West Inner Mongolia, China is naturally contaminated with elevated levels of arsenic and has been associated with a variety of adverse human health effects on multiple health endpoints. A pilot study was designed to (1) detect internal arsenic levels using biomarkers of exposure (urine, nail, and hair samples), (2) evaluate DNA and chromosomal damage in buccal cells and (3) evaluate relationships between exposure and effects biomarkers. Arsenic was detected in the drinking water samples of the 19 exposed subjects with a mean level of 527.5 ± 23.6 µg/l, while the 13 control subjects had a mean level of 4.4 µg/l ± 1.0 µg/l. Arsenic was detected in the urine, nail, and hair samples in the exposed group measuring 632.7 µg/l, 32.02 µg/g and 12.42 µg/g, respectively. Biomarkers of effects were examined using the micronucleus assay to detect chromosomal abnormalities and the DNA laddering assay to detect DNA fragments. Increased micronuclei frequencies and DNA fragments were found in the high-arsenic exposed group. The biological exposure markers (urine, nail, and hair samples) all statistically correlated with the water arsenic levels. The two biomarkers of effects (MN and DNA fragmentation) were statistically correlated with one another (Spearman r = 0.5238, p < 0.01). Other correlations between exposure and effects markers will be reported. The biomarker results indicate that Ba Men residents are chronically exposed to arsenic and show health effects. These biomarkers are potentially useful for assessing arsenic exposure and effects.


(This is an abstract of a proposed presentation and does not necessarily reflect EPA policy.)
HEALTH EFFECTS OF CHRONIC EXPOSURE TO ARSENIC VIA DRINKING WATER IN INNER MONGOLIA: VI. DEVELOPMENTAL EFFECTS

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Despite the large number of people exposed to drinking water arsenic (DWA) throughout their life and the large body of As literature, there are very few studies that present data on the reproductive and developmental effects of DWA in humans. Most of the studies that have looked at exposure to As and reproductive effects have investigated populations that lived near smelters and pesticide plants and were exposed to multiple agents, such as lead, mercury, and cadmium, thereby making causal inferences to As difficult. With collaborative assistance from the researchers at the Inner Mongolia Center for Endemic Disease Control and Research, researchers at the US Environmental Protection Agency have been collecting health data from the prenatal care and birth outcome records of pregnant women to determine any potential human reproductive effects of DWA. This developmental effects database consists of 27,000 pregnant women in the Ba Men region of Inner Mongolia, China, who had a pregnancy outcome between January 1, 1996 and December 31, 1999. From this database, a variety of prenatal care information is available from birth outcome data, such as birth weight and gestational age information to maternal data such as blood pressure and hypertension information. Linking this developmental effects database to the 14,866 well-water survey database will provide researchers with a valuable tool for identifying potential risks associated with exposure to drinking water arsenic and developmental effects. Overall, this study can provide new information concerning potential risks associated with exposure to DWA during pregnancy.

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DISCLAIMER: This is an abstract of a proposed presentation and does not necessarily reflect EPA policy.
ENIGMA ABOUT ARSENIC EXPOSURE IN TAIWAN

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It has been 38 years since Kao TM et al found 68 gangrene patients so-called Blackfoot Disease, at the South Western coast of Taiwan. The disease was found to be associated with chronic arsenic exposure from artesian well water. The incidence of skin cancer (Bowen's disease) was also very high in this area and apparently had significant association with long-term arsenic exposure. Besides skin cancer, the incidence of bladder and liver cancer are also significantly higher than the other areas in Taiwan. Thus, it has been speculated that chronic arsenic exposure is not only associated with Blackfoot Disease but also associated with the development of skin, bladder and liver cancer.

Hyper-pigmentation, hyper-keratosis and Bowen’s disease are manifested by chronic arsenic intoxication. Although both peripheral vascular disease and skin manifestation occurred on the same patient were quite often in this endemic area, the etiology of these two diseases might be different. Blackfoot disease is a disease of peripheral vascular disease of the extremities, usually symptom started to appear from the hand in the old days. These days the symptom was different, started from foot and leg and usually seen in old individuals. Patients with age less than 40 years were very rare. Furthermore, the main pathological changes are sclerosis or even calcification of the artery in the lower extremities with increase of age. Thus, instead of describing Blackfoot Disease, cancer of skin, bladder and liver in this area as chronic arsenic intoxication, it is necessary to further re-explore the possible roles of chronic arsenic exposure on the pathogenesis of peripheral blood vessels and cancer of skin, bladder and liver.

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ESTIMATION OF DIETARY INTAKE OF INORGANIC ARSENIC IN CHILDREN.

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Arsenic is a natural component of our environment, and is known to be ubiquitous in soils and in the diet. Accurate dietary intake estimates for inorganic arsenic are needed to establish background levels of exposure to inorganic arsenic. Previous investigations have estimated dietary intake in adults ranging from 1 to 20 μg/day with an average of 3.2 μg/day, based on a comprehensive market basket survey in which 40 commodities anticipated to provide at least 90 percent of dietary inorganic arsenic intake were analyzed for inorganic arsenic content (Schoof et al. 1999a,b). Four samples of each commodity were collected. Total arsenic was analyzed using an NaOH digestion and inductively coupled plasma-mass spectrometry. Separate aliquots were analyzed for arsenic species using an HCl digestion and hydride atomic absorption spectroscopy (Schoof et al. 1999a). In addition, intake in the USA was previously estimated using a more limited number of foods analyzed for inorganic arsenic (Yost et al. 1998), to derive an estimate of 9.4 μg/day in children and 12.7 μg/day for an adult. Estimates subsequently derived based on grouped FDA total arsenic intake estimates for years 1982 through 1990 indicated dietary intake of inorganic arsenic of estimates of inorganic arsenic ranging from 3-4 to 8.5 μg/day for infants (age six months) and 3.9 to 7.2 μg/day for toddlers (two years old) were derived. Current FDA datasets will be applied to derive updated intake estimates and to better map foods sampled for inorganic arsenic into the FDA food categories.
DERMAL PENETRATION OF ARSENIC IN CONTAMINATED WATER\textsuperscript{1}

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**ABSTRACT**

Potable use of arsenic contaminated groundwater is causing health problems in Bangladesh, China, and India. Non-potable uses of arsenic contaminated groundwater including clothes or dish washing, bathing, and crop irrigation are also occurring and may be contributing to toxicity via dermal exposure. One of the functions of skin is to prevent exogenous substances such as arsenic from entering the body. The stratum corneum, the principal penetration barrier, is not an absolute barrier. Research has indicated that polar substances such as metal ions can penetrate through the stratum corneum via an intercellular route and through sebaceous and sweat glands, and hair follicles. Factors affecting dermal absorption include degree of dermal hydration, arsenic species and concentration in water, ambient temperature, and frequency and duration of exposure. Although dermal irritation and contact sensitization can result from exposures to metals such as arsenic, chromium, cobalt, copper, nickel, and palladium, there is little information concerning adverse systemic health effects resulting from dermal absorption of these metals. Analysis of currently available data, however, indicates that there are exposure scenarios where dermal exposure to arsenic may represent a health threat. For example, rice is a major crop in many Asian countries. Many of the wells used to irrigate rice fields contain elevated levels of arsenic. Since rice cultivation involves protracted contact with water, people involved in rice cultivation are likely to have enhanced dermal arsenic uptake.

\textsuperscript{1} The opinions expressed in this manuscript are those of the authors and do not necessarily reflect the opinions or policies of NIEHS, ATSDR, or U.S. EPA.

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POTENTIAL EXPOSURE TO ARSENIC (AS) THROUGH DERMAL PENETRATION


Drinking water contaminated with As has caused or is causing health problems in Taiwan, Mexico, South America, Bangladesh, China, and India. However, exposure to As in water may occur by other routes. Non-potable uses of arsenic contaminated groundwater include washing clothes or dishes, bathing, and farming. Could these uses contribute to As exposure and toxicity via dermal penetration? One major skin function is to prevent exogenous substances from entering the body. The stratum corneum, the principal penetration barrier, however, is not an absolute barrier. Research has indicated that polar substances such as metal ions can penetrate through the stratum corneum via an intercellular route and through sebaceous and sweat glands, and hair follicles. Factors affecting skin penetration of metals include degree of dermal hydration, As species and concentration in water, ambient temperature, and frequency and duration of exposure. Although dermal irritation and contact sensitization can result from exposures to metals such as As, chromium, cobalt, copper, nickel, and palladium, there is little information concerning adverse systemic health effects resulting from dermal absorption of metals. Analysis of currently available data, however, suggests that there are exposure scenarios where dermal exposure to As poses a health threat. For example, rice is a major crop in several Asian countries. Since many of the wells used to irrigate rice fields contain elevated levels of As and rice cultivation involves protracted contact with water which causes hydration of the skin, people involved in rice cultivation may have an enhanced dermal arsenic uptake. Could this additional exposure to arsenic have contributed to the high incidence of Blackfoot Disease in SW Taiwan?

1 The opinions expressed in this manuscript are those of the authors and do not necessarily reflect the opinions or policies of NIEHS, ATSDR, NC State University or U.S. EPA.

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CHILDREN’S EXPOSURE TO METALS FROM CCA-TREATED WOOD: FACTORS IN ASSESSING INADVERTENT INGESTION EXPOSURES

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Various studies funded by government agencies, industries, and public interest groups have attempted to evaluate the potential exposures to arsenic and other metals from inadvertent ingestion of residues on the hands of children playing on structures constructed of CCA-treated wood. A comparison of exposure assessments conducted to date indicates that there is no standard method for assessing risk for this novel exposure scenario, and the different approaches that have been tried have produced widely diverse conclusions regarding the potential for exposure. The discrepancies among the assessments are not limited to differences in input values for the various exposure parameters, but also include the manner in which each exposure pathway should be assessed, and which parameters need to be defined within the exposure assessment.

This paper will present the current state of knowledge regarding the transfer of metals from residues on wood surfaces to hands, and the different methods that have been employed to estimate the hand-to-mouth transfer of residues. We will explore the implications of using behavioral data (i.e., observations of mouthing frequency in children) versus empirical data (i.e., measurements of hand soil loading and soil ingestion rates) to estimate the amount of skin surface area mouthed and thereby the amount of arsenic residue ingested. Our results indicate that only a fraction of the metals present in residues on wood are transferred to the skin surface, and that use of behavioral data on hand-to-mouth behavior, which lack an empirical basis for amounts ingested, may result in significant overestimates of exposure.

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SAMPLE PREPARATION, EXTRACTION EFFICIENCY, AND SPECIATION OF SIX ARSENIC SPECIES PRESENT IN FOOD COMPOSITES

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The toxicity of arsenic species depends on its chemical form in which inorganic forms, arsenite (As III) and arsenate (As V) are the most toxic and the arsenic metabolites: mono methylarsonic acid (MMA) and dimethyl arsinic acid (DMA) are less toxic. Arsenocholine (AsC) and arsenobetaine (AsB) are the most prevalent organo-arsenic species in dietary origin (mainly seafoods), and are non-toxic. Sample preparation procedures must be developed in which arsenic compounds are extracted at high efficiency from various food composites without compromising the integrity of the individual species. The chromatographic method should include separation of the aforementioned six arsenic species in a single run in a reasonable amount of time (<30 min). The detection method (inductively coupled plasma - mass spectrometric detection (ICP-MS)) should allow one to accurately quantitate all species at low levels.

The optimized method included lyophilization of food followed by pre-washing with acetone and extraction by sonication with 50/50 methanol/water. Six arsenic species were then separated and quantitated using an ammonium carbonate buffer system by ion-exchange chromatography (IC) coupled to ICP-MS.

The developed method was successfully applied to archived food samples from the National Human Exposure Assessment Survey (NHEXAS).

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DEVELOPMENT OF A SPACE TIME INFORMATION SYSTEM FOR ESTIMATING ARSENIC EXPOSURE FROM DRINKING WATER

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The focus of this project is the accurate characterization of exposure to low-to-moderate levels of naturally-occurring arsenic in drinking water in Michigan. Reported arsenic concentrations in well waters in the study area range from 1 to 1310 mg/L, with most common levels being 5-50 mg/L. Enhancing past arsenic exposure models, construction of the arsenic exposure scenarios includes a geostatistical groundwater model and spatio-temporal analyses. The spatio-temporal analyses address the spatial and temporal variation in both arsenic concentration and daily activity patterns.

To account for these different types of spatial and temporal variability, the project consists of three main components: personal interview, measurement of arsenic in drinking water, and the construction of exposure scenarios. Subjects will be long-term residents of eleven counties in Michigan with highest levels of arsenic in their groundwater and part of a case-control study, designed to evaluate the association between arsenic exposure and bladder cancer. Structured personal interviews will be administered to obtain information on exposure and health outcomes. A geostatistical groundwater model is being developed to predict water concentrations at past workplaces and past residences. Exposure scenarios will be generated using information provided in the interview, the measured arsenic concentration, the geostatistical groundwater model, and exposure factors.

Current efforts by the U.S. EPA. to reduce the maximum contaminant level for arsenic in drinking water have been bedeviled by contradictory and unvalidated predictions of the risks of chronic exposure to low levels (< 100 mg/L) of arsenic in water. This study is designed to shed some light on the dose-response relations for exposure of the U.S. population to arsenic concentrations in the 5-100 mg/L range where little information currently exists.

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MICHIGAN'S RESPONSE TO NATURALLY OCCURRING INORGANIC ARSENIC IN THE GROUNDWATER OF A NINE-COUNTY AREA OF EAST-CENTRAL AND SOUTHEASTERN LOWER MICHIGAN

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Naturally occurring arsenic is found in groundwater of nine contiguous Michigan counties. Sampling of 300 private wells revealed 57 with arsenic levels of \( \geq 50 \) ppb (range 31-335 ppb, median 75 ppb). A 1981 pilot clinical investigation including 221 participants from 60 households measured arsenic exposure in well water, water consumption, and urinary excretion. Relationships between exposure and physiological/clinical variables were evaluated. Participants completed a 24-hour urine screen, clinical exam, electrocardiogram, blood tests, and questionnaire. Serum calcium and blood urea nitrogen levels were positively correlated with well water arsenic; arsenic consumption and urine arsenic excretion were positively associated with history of Herpes zoster (shingles).

A population based study analyzed risk factor and outcome data from 317,919 electronic birth certificates from 1989 through 1998. Mean arsenic values were calculated for minor civil divisions within nine counties, using 16,259 water samples tested for arsenic. Maternal arsenic exposure, with values ranging from nondetectable to 30 ppb, was not associated with the prevalence of low birthweight, preterm birth, or small size for gestational age.

A standardized mortality ratio (SMR) analysis compared 1979 through 1997 Michigan Resident Death Files data from 33 underlying causes potentially associated with arsenic exposure in the nine counties with corresponding mortality data from Michigan. Two counties had average arsenic concentrations above 10 ppb. One had significantly positive SMRs for all malignant neoplasms combined and ischemic heart disease; the other had significantly positive SMRs for diabetes mellitus and kidney disease. Both counties had significantly positive SMRs for cerebrovascular disease.

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INCORPORATING ARSENIC BIOAVAILABILITY RESULTS INTO HUMAN HEALTH EXPOSURE MODELLING

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The detection of elevated levels of arsenic in soil, both due to the underlying geology and as a result of anthropogenic activities, is common in the UK. Background arsenic levels in many parts of the country exceed the recently published UK Soil Guideline Value for the protection of human health from chronic long-term exposure to arsenic in soil.

It is common practice in assessing exposure to human health to take a cautious approach and assume that arsenic in the soil is 100% bioavailable to the human receptor. However, the measured bioaccessibility of naturally occurring arsenic in soil via the ingestion route of entry to the human receptor has been found to be significantly lower.

A UK based human health risk assessment tool, the SNIFFER Framework for Deriving Numeric Targets to Minimise the Adverse Human Health Effects of Long-term Exposure to Contaminants in Soil allows the risk assessor to incorporate site specific arsenic bioaccessibility results into the soil ingestion pathway of the exposure assessment. In many land uses, including the residential scenario, soil ingestion is a key exposure pathway and will drive the risk assessment. The SNIFFER Framework also allows site specific measurements of arsenic uptake by home grown vegetables to be accommodated in the setting of site specific assessment criteria.

Utilising arsenic bioavailability results in this way has been found to result in an increase in the site specific assessment criterion and provides evidence that natural soils at sites in many parts of the UK are safe for residential land use.

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MONITORING OF ARSENIC EXPOSURE WITH SPECIATED URINARY INORGANIC ARSENIC METABOLITES FOR ION IMPLANTER MAINTENANCE ENGINEERS

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For the wafer fabrication in semiconductor industry, the maintenance engineers are potentially exposed to hazards during their work of disassembling machine compartments for clean-up. One special concern is arsenic or arsenic compounds in working environment. The present study analyzed speciated urinary inorganic arsenic metabolites of the maintenance engineers with HPLC-HG-AAS to study the potential arsenic exposure during their maintenance work. Totally, from 6 wafer fabrication facilities, 30 maintenance engineers were recruited as exposed group, so were the another 12 office-based engineers serving as control group. First morning voided urine samples of each study subject were collected for 7 consecutive days. Results show the levels of total urinary inorganic arsenic metabolites for exposed group were 1.7 ± 0.4 µg/L, 1.4 ± 0.1 µg/L, 6.2 ± 0.7 µg/L, 20.2 ± 4.1 µg/L, 29.5 ± 7.2 µg/L for As³⁺, As⁵⁺, monomethylarsonic acid, dimethylarsinic acid and total inorganic arsenic, respectively. Both concentration of monomethylarsonic acid and its proportion among various urinary inorganic arsenic metabolites showed significantly ascending trend among control group, engineers without preventative maintenance work prior to their urine sampling, and those with such work prior to sampling (p<0.005, and p<0.0005, respectively). It was also suggested that, at low level occupational arsenic exposure, the concentration of total urinary inorganic arsenic metabolites might be misleading due to the confounding effect of arsenosugars coming from seafood. Nevertheless, speciation of urinary arsenic species is good and appropriate in such case to use the proportion change of monomethylarsonic acid as an indicator for the verification of arsenic exposure.

Keywords: Arsenic, Urine, Speciation, Monomethylarsionic acid, Ion Implanter, Preventative Maintenance.

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ARSENIC CONTAMINATION IN THE RIO LOA (ANTOFAGASTA, NORTHERN CHILE)


The Loa and its main tributaries (Salado and San Salvador provide water both to the cities and to the mining activity in the region. They also support limited agriculture around a few small villages. Water and sediment samples were taken at strategic points along the River Loa and its major tributaries. The water in the whole basin is heavily contaminated by arsenic and boron, with values up to 300 and 80 times higher than the respective guidelines suggested by the WHO for drinking water. The contamination is more marked along the tributary, the River Salado, and in the medium and lower course of the Loa, where the contamination derived from the Salado is increased by interaction with sedimentary rocks, contaminated sediments, lack of dilution, and strong evaporation. Sediments from the Rio Loa have arsenic concentration in the range 400-11300 mg/kg and the arsenic is predominantly bound to Fe-Mn oxy-hydroxides as adsorbed species. This adsorbed arsenic does not seem to be readily mobile, unless significant changes in Eh-pH conditions take place in the environment. The main arsenic source is natural and the mining activity is a possible, but less likely source.
ENVIRONMENTAL CONTAMINATION OF ARSENIC AND OTHER HEAVY METALS IN THE VICINITY OF THE ABANDONED DONGIL MINE IN KOREA

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In order to assess the level of heavy metal contamination and their behavior in the soil-water system of the abandoned mine area, soil, mine, surface and groundwater samples collected in the vicinity of Dongil mine (Au-Ag-Cu-Zn) were analyze. The soil and tailing samples digested in 0.1 N HCl and aqua regia and water samples were analyzed for As, Cd, Cu, Pb and Zn by ICP-AES. Mean concentrations of As and other heavy metals in tailings digested in aqua regia 8970 mg As kg\(^{-1}\), 7 mg Cd kg\(^{-1}\), 8 mg Cr kg\(^{-1}\), 7806 mg Cu kg\(^{-1}\), 5070 Pb mg kg\(^{-1}\) and 1130 mg Zn kg\(^{-1}\). The levels of heavy metal contamination in soils are higher than normal soil concentration. Especially, arsenic(37 mg kg\(^{-1}\)) and Cu(130 mg kg\(^{-1}\)) showed more enriched level than the permissible level. Mean concentrations of As and other heavy metals are highly elevated in the farmland soils than paddy soils in the Dongil mine area. All the results obtained suggest that the mine tailings can be principle point-sources of heavy metals, and As derives from the sulfide gangue minerals such as arsenopyrite can be a characteristic pollutant in Au-Ag mining areas. The pH values of the mine and surface water from the Dongil mine creek were higher compared with those of groundwater. The surface and mine water are characterized by higher concentration of As, Cu, Cd, Mn, Zn, Ba and Fe than groundwater. The maximum concentration of As is shown 0.52 mg l\(^{-1}\) in mine water. In particular, the SO\(_4\) concentration in the mine water is 114 mg l\(^{-1}\). This is abruptly increase in surface water and then detected 253 mg l\(^{-1}\) in the ground water, which is used by drinking water in this area and this level of SO\(_4\) is higher than permissible concentration for drinking water in Korea. The main pollution sources of water system in this area are also suggested as tailings and mine waste materials, which have to be reclaimed.
ARSENIC OCCURRENCE, AND ITS POTENTIAL HEALTH HAZARDS IN THE STATE OF MINAS GERAIS, BRAZIL

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Minas Gerais state is one of the richest mineral-bearing regions in Brazil. Apart from extensive iron ores, hydromothermal gold mineralization can be found in Archean greenstone belt formations. Since the end of the 17th century a total gold production must have exceeded 1300 t. There are four main gold deposits where gold is associated with sulfides. The principal sulfides are pyrrhotite, arsenopyrite, pyrite and chalcopyrite.

The arsenic present in rocks and ores oxidizes due to weathering and part of the arsenic is naturally liberated into the environment. However, human activities related to mining, enhanced in several times the mobilization of arsenic into the environment. The tailings deposits produced in the past, were discharged directly into the drainage until 1980’s. The amount of arsenic which entered the drainage systems must have exceeded 390,000 t in the whole region.

Soils and sediments locally present unusual arsenic anomalies (median concentrations > 100 mg/kg) and wide ranges (<20 to > 2000 mg/kg) even in densely populated areas. These anomalies can be related to geological structures, and, the additional dissipation due to centuries of mining and smelting activities.

To assess the potential health risk to local populations a human biomonitoring was started with children. The study aim to find out to which extent arsenic was being transported into the human body. The results of the first sampling campaign showed that twenty per cent of the total sample population had elevated As concentrations, where adverse health effects cannot be excluded on a long-term basis. However, there is no evidence yet for major concern. Solutions have been found to minimize the As-load in densely populated areas.

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COMPARISON OF APPROACHES FOR QUANTIFYING INCIDENTAL INGESTION OF ARSENIC FROM TREATED WOOD AND OTHER MATERIALS


Potential health risks associated with arsenic originating in wood treated with chromated copper arsenate (CCA) have been the subject of extensive regulatory, scientific, and public attention. A critical parameter for quantifying such risks is the amount of dislodgeable arsenic complex from treated wood surfaces that may be incidentally ingested. In the absence of direct studies, two general approaches have been used to estimate this parameter. In the hand transfer efficiency (HTE) factor approach, empirical data from studies of incidental soil ingestion are used to estimate the fraction of the material on the hands that is ingested during a given exposure period. Based on currently available information, the best estimate of this parameter for young children is 0.25 handloads/day, with a reasonable range of 0.07-1.0. The HTE factor is combined with estimates of dislodgeable arsenic complex adherence onto hands to estimate dislodgeable arsenic complex intake. Reflecting current approaches for researching exposures to pesticide residues, a mechanistic approach has also been suggested. This approach combines measurements of components of the incidental ingestion process (e.g., surface-to-skin transfer factors and mouthing activity observations obtained from videotape studies) to yield overall estimates of intake. Currently, the scientific foundation of this approach is limited because many of the component steps are poorly characterized. Until better mechanistic information is developed, the empirical approach is likely to more reliably represent exposure. For either approach, parameter assumptions should be benchmarked against available empirical data to ensure that the derived exposure estimates are in a realistic range.

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TOXICITY DUE TO ARSENIC (AS) EXPOSURE FROM USE OF HERBAL MEDICINES AND TEAS

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Herbal medicines and teas have been routinely used in Asian cultures for several millennia. In recent years, such usage has spread and there has been an upsurge in the use of these remedies in Western Countries. The use of some of these compounds may be of concern for two major reasons. There is a general belief among many users that compounds of “natural origin are safe.” and though many are innocuous, some contain toxic moieties. Use of many herbal preparations have been reported to cause medical problems after use. Several of the preparations contain one or more chemicals such as steroids, alkaloids or heavy metals, including As. In addition, the concentrations of As, and other metals or harmful substances, in some preparations are not trivial. For example, in two Indian ethnic preparations, the As trioxide level ranged from 90 to 105 mg/package. One patient who ingested two packages/day displayed arsenical neuropathy. Since the lethal dose of As trioxide has been estimated to be approximately 2-fold higher than the ingested amounts, acute poisoning is a real possibility. In other cases, chronic use could lead to the appearance of diseases, such as bladder and lung cancers. In Singapore, 74 patients who took herbal preparations were treated for As poisoning. Many of the cases were the result of an asthmatic pill called “Sin Lak” which contained 1.2% arsenic sulfide (12,000 ppm). The most common symptoms in this series were dermatitis (91%), neuropathology (51%), gastroenteritis (23%), hematological conditions (23%), renal abnormalities (19%) and internal malignancies (5%). In 35 of the patients (17 acute and 18 chronic), chelation therapy with dimercaprol (BAL or British AntiLewisite) had to be instituted. Thus, it is important to understand that some herbal preparations may be dangerous.

1 The opinions expressed in this manuscript are those of the authors and do not necessarily reflect the opinions or policies of ATSDR, NIEHS, or U.S. EPA.

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ARE CITY WATER PIPES A FUTURE SOURCE OF ARSENIC CONTAMINATION

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Analyses of corrosion/scale deposits from Albuquerque, New Mexico water distribution pipes indicate substantial amounts of pipe-associated arsenic. Although the concentration of arsenic in the distribution water is low (<5 ug/L), the concentration of arsenic in the corrosion and scale deposits exceed 100 ug/Kg (20 times the concentration found in the distribution water). Initial analysis using scanning electron microscopy and x-ray diffraction shows that the principal phases present are magnetite>chlorite and quartz. Limonite-colored stains on sample surfaces suggest the presence of this material, though it is not abundant enough to be detected by X-ray diffraction. It is likely that much of the arsenic present in the samples is sorbed onto this minor component.

This paper will report on arsenic distribution in the pipes at different locations throughout the Albuquerque water distribution network. The mechanism of sorption of the arsenic to the corrosion and scale-forming passive layer(s) will be addressed. This study will also report on laboratory scale experiments designed to anticipate potential arsenic mobilization due to front-end removal of arsenic from the source water.

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TAP WATER VS. BOTTLED WATER: A COMPARISON OF PUBLIC RISKS IN THE CONTEXT OF THE NEW ARSENIC STANDARD

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The new drinking water standard for arsenic will place an enormous financial burden on small water utilities which rely upon high arsenic ground water as their source of supply. When presented with the costs of treatment, local officials frequently ask whether it would be cheaper to provide bottled water to the community. However, there are identifiable physical risks associated with delivery and home use of bottled water. This paper presents an analysis of the two most significant risks associated with bottled water: transportation and injuries to the consumers. The additional physical risk of bottled water delivery and consumer handling is compared to the risk of drinking water containing low concentrations of arsenic.

The principal transportation risks are due to bottled water delivery and to additional trips by consumers to the store. Transportation risks in an urban environment are similar to those from garbage pickup and would result in approximately 0.2 additional fatalities per 10^7 people over 70 years. The NIOSH lifting equation was used to estimate an approximate four-fold increased risk of in-home physical injuries from trip and fall accidents caused by lifting and carrying bottled water containers through the house. National trip and fall accident rates were then used to calculate that the lifetime risk of a fatal trip and fall accident caused by carrying bottled water is approximately double the risk of drinking water containing arsenic at 20 ug/L. This analysis demonstrates the need to consider secondary impacts of new regulations.

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RE-EXAMINATION OF THE PROPOSED ARSENIC DRINKING WATER REGULATIONS

ARSENIC IN A DEER MICE (*PEROMYSCUS MANICULATUS*) FOOD CHAIN

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A field-based ecological risk assessment of a short terrestrial food chain, comprised of deer mice (*Peromyscus maniculatus*), plant and soil/tailings samples, was carried out on mine contaminated soils. The average arsenic concentration in soils from trapping locations was 1630±1200 ppm. When soils were subjected to a simulated gastric fluid extraction (GFE) only 2% of the arsenic was found to be bioavailable. The predominant form of arsenic in the GFE was arsenate (As (V)). Deer mice edible plants were collected from the trapping locations and had a mean arsenic concentration of 25±21 ppm. The predominant arsenic species detected in plants (methanol/water extraction) were arsenate As (V) and arsenite As (III).

Arsenic concentrations ranged between non-detectable to 72 ppm (median 2.7) in deer mice tissues, with concentrations decreasing in the following order: stomach contents>skin (fur)>carcass>liver>kidney. As (III) and DMA were the predominant forms of arsenic in the tissues, with lesser amounts of arsenate and MMA also detected. This suggests that there is significant biotransformation of arsenic occurring in deer mice: i.e. the ingestion of predominantly As (V) and conversion to As (III) and DMA.

An estimated daily intake (EDI) of 37 µg arsenic / kg body weight / day was calculated for mice using average total arsenic concentrations in soil, water and plants. However, incorporation of the 2 % arsenic soil bioavailability factor results in a two and a half fold decrease in the EDI (14 µg/kg body weight/day). Therefore, ecological risk models that use total arsenic concentrations may overestimate risk posed to small mammals.

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ESTIMATES OF DIETARY INORGANIC ARSENIC INTAKE FROM SEAFOOD OVERSTATE DIETARY ARSENIC INTAKE

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Seafood contributes the greatest fraction of total arsenic (As$_{tot}$) to the diet; however, only a small portion of seafood arsenic is the more toxic inorganic arsenic (As$_i$). Due to the expense and difficulty of analyzing As$_i$ concentrations in fish, most available fish data are for As$_{tot}$ only.

Dietary intake estimates for As$_i$ in fish are frequently made by assuming that a certain fraction of the As$_{tot}$ reported in the fish is As$_i$. For example, NRC (1999) assumed that 10% of seafood As is inorganic. Several recent studies suggest that the NRC (1999) assumption may be too high. Donohue and Abernathy (1999) reviewed the literature and concluded that As$_i$ in seafood seldom exceeds 4% of As$_{tot}$. A market basket survey by Schoof, et al. (1999) reports data for seafood that suggest that As$_i$ is less than 1% of As$_{tot}$ in saltwater. If the NRC (1999) estimate is revised assuming that 1% of seafood As$_{tot}$ is inorganic, the resulting daily dietary As$_i$ intake falls by approximately 45% to approximately 4 µg/day for adults 25 to 45 years old, and is much more consistent with the estimate of 3.2 µg/day derived from the Schoof et al. (1999) market basket survey.

For freshwater finfish, As$_{tot}$ concentrations appear to vary by species, but As$_i$ concentrations were still consistently low. The implications of these findings for risk assessment of As in fish in surface water and the derivation of ambient water quality criteria for As will be explored.

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BIOACCUMULATION OF ARSENIC IN FISH AND AQUATIC FOOD WEBS IN THE VICTORIAN GOLDFIELDS

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In Australia, in the state of Victoria, in particular, arsenic (As) is naturally associated with gold bearing rocks. Historically, gold mining has brought large amounts of As to the surface in the process of extracting gold from the mined material. It has been estimated that 30,000 tonnes of As were brought to the surface in just the Ballarat goldfields alone. Subsequent erosion has redistributed the As laden material across the landscape. As a result, there are abnormally high levels of As in a number of streams and rivers in gold mining areas. The proposed research is to investigate As bioaccumulation in aquatic biota particularly fish, and to identify pathways of movement of this element through aquatic ecosystems. We have formulated postulates that are guiding our research design. Specifically, we have made theoretical links between the following factors and the likelihood of As exposure and accumulation: wide ranging versus sedentary behaviour (e.g., trout and native eel vs. river Blackfish), sediment interaction (e.g., Yabbies and European carp vs. Galaxids), trophic level (e.g., Tench vs. Redfin) and dietary preference (e.g., consumers of benthic vs. pelagic invertebrates). Over the next two years a combination of field and laboratory procedures will be directed at exploring these postulates.

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ARSENIC AND HEAVY METAL CONTAMINATION OF RICE, PULSES AND VEGETABLES GROWN IN SAMTA VILLAGE, BANGLADESH

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Drinking of arsenic contaminated well water has become a serious threat to the health of many millions in Bangladesh. However, the implications of contamination of agricultural soils from long-term irrigation with arsenic contaminated groundwater for phyto-accumulation in food crops, and thence dietary exposure to arsenic, and other metals, has not been assessed previously in Bangladesh. Various vegetables, rice, pulses and the grass pea were sampled in Samta village in the Jessore district of Bangladesh and screened for As, Cd, Cu, Pb and Zn by inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS). These local food products are the basis of human nutrition in this region and of great relevance to human health. In general, the data show the potential for some vegetables to accumulate heavy metals with concentrations of Pb greater than Cd. The concentrations of As and Cd were higher in vegetables than in rice and pulses. Rice, pulses and vegetables contained higher concentrations of Zn and Cu. The concentration of Pb was higher in rice than in pulses and vegetables. However some vegetables such as Bottle Gourd leaf, Ghotkol, Taro, Eddoe and Elephant Foot had much higher concentrations of Pb. Other leafy and root vegetables, contained higher concentrations of Zn and Cu. Considering an average daily intake of only 260 g rice per person per day, rice grown at Samta had increased Pb and As, but only the Pb is at concentrations which would be a health hazard for human consumption.

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INFLUENCE OF SOIL TYPE ON ARSENIC BIOAVAILABILITY AND ITS CONSEQUENCES FOR HUMAN HEALTH RISK ASSESSMENT

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Yellowknife, Canada has an extensive soil arsenic contaminant problem as a result of 60 years of gold mining activity. One hundred soil samples, representative of arsenic contaminated areas, were selected to determine their potential risk to Yellowknife residents. Soils were grouped by location and characterized by total organic carbon content (TOC) into four types; rock (<4 % TOC, 2000 ± 2100 ppm arsenic), tailings (<7 % TOC, 2900 ± 1300 ppm arsenic), mine site organic (>10 % TOC, 820 ± 1100 ppm arsenic), and city organic (>8 % TOC, 110 ± 92 ppm arsenic).

Samples were subjected to an in vitro gastric fluid extraction (GFE), to simulate potential human bioavailability. It was determined that soil type, not total arsenic concentration, strongly influences potential arsenic bioavailability. Only 3.2 ± 2.4 % and 2.6 ± 1.8 % of the arsenic in the rock and tailings samples was extracted using GFE, while 24 ± 14 % and 21 ± 9.0 % was extracted in the mine site organic and city organic samples. Significantly more arsenic was extracted in the organic soils than in the rock and tailings samples for both percent and total arsenic extracted using GFE (ANOVA, p<0.001). The predominant form of arsenic in the extracts was arsenate.

Although there was significantly higher total concentration of arsenic in rock and tailings (ANOVA, p<0.007), on average they pose less risk to human health than arsenic in the organic samples. These results clearly demonstrate that the use of total arsenic is no longer prudent in human health risk assessment.

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SURVEY OF ARSENIC, ZINC AND SELENIUM IN FOOD COMPOSITES AND DRINKING WATER AND ESTIMATION OF DIETARY INTAKE BY THE VILLAGERS FROM AN ARSENIC-AFFECTED AREA OF WEST BENGAL, INDIA

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Abstract

An investigation of arsenic, zinc and selenium in food composites and drinking water, collected from 34 families and estimation of daily dietary intake are carried out in the arsenic-affected areas of Murshidabad district, West Bengal, India where arsenic-contaminated groundwater (mean: 0.11 mg/l, n=34) is the main source for drinking. The shallow big diameter tubewells, installed for agricultural irrigation contain high arsenic (mean: 0.094 mg/l, n=10). So a part of arsenic could be expected in the food chain, cultivated in these areas. Most of the individual food composites contain a considerable amount of arsenic. The mean arsenic levels in food categories are vegetables (50.22 and 56.23 µg/kg), cereals and bakery goods (165.64 and 181.73 µg/kg) and spices (115.49 and 207.6 µg/kg) for Jalangi and Domkal block respectively. For zinc and selenium, the observed mean concentration values are mostly in good agreement with the reported values. The provisional tolerable daily intake (PTWI) of inorganic arsenic (µg/kg body weight/day) is: for adult male (12.0 and 9.6), adult female (14.1 and 11.3) and children (15.6 and 12.3) respectively (according to FAO/WHO report, the value is 2.1 µg/kg body weight/day). According to WHO, 1.0 µg/day of inorganic arsenic may give rise to skin lesions within a few years. The daily dietary intake of zinc is low (for adult male: 12.57 and 14.53 mg/day and children: 7.11 and 8.21 mg/day), compared to the recommended value (15 and 10 mg/day respectively). The daily dietary intake of selenium (µg/kg body weight/day) is in lower side for the children (1.12 and 1.38) and comparable for the adult male (0.86 and 1.07), compared to the recommended value (1.7 and 0.9 µg/kg body weight/day for infants and adult male respectively).

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THE PRIMARY REPORT ON THE ARSENIDE CONTENT OF DRINKING WATER IN SERIOUS PREVALENCE COUNTIES OF ENDEMIC FLUOROSIS IN CHINA MAINLAND

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Chronic arsenism caused by drinking water with high arsenide level due to special geographic situation has become a serious public health problem in some countries, especially in south-east Asia in the world. At present, drinking water type endemic arsenism has been found in six provinces and 30 counties in China land. In the course of analyzing the prevalence areas distribution of endemic arsenism, some experts found that endemic arsenism areas and endemic fluorosis areas co-existed each other. In order to study the co-existing relation between endemic arsenism and fluorosis areas, and the arsenide content of drinking water in fluorosis areas, we investigated the environmental arsenide and fluoride content of drinking water in serious prevalent counties of 11 provinces (regions). This paper only primarily reported the investigation results about the arsenide content of drinking water in 6 provinces.

Investigated provinces included Heilongjing, Gansu, Henan, Anhui, Jiangsu, Qinghai, etc. In each province, three serious prevalent counties were chosen and stratified sampling in mild, moderate, serious areas and non-prevalent areas was used to randomly choose in proportion of population, in each prevalence area 5~10 wells water were sampled, according to the state standard to determine the arsenide and fluoride content in water. All the samples were determined by province-level laboratory with quality control. 959 water samples were determined and 22 wells were beyond the state standard(>0.05mg/L). The arsenide content in water less than 0.01mg/L was 596(80.54%), 0.01~0.03mg/L was 93(12.72%) 0.03~0.05mg/L was 17(2.33%), respectively. In the over-standard wells, 20 wells whose arsenide content waved around 0.05~0.15mg/L and only 2 wells whose arsenide content was more than 0.30mg/L. We found that the water fluoride content had a trend of rising when water arsenide content was high. The correlation was significant (|r| =0.867, P<0.01), (r_{0.01(9)}=0.785), but the wells whose fluoride content were over-standard(>1.0mg/L), the arsenide content may be not high, even the fluoride content was up to over 5.0mg/L, the arsenide content was also very low.

The investigation results showed that over-standard wells of water arsenide content in fluorosis areas was about 2% in China, and the over-standard range was small and most of them were less than 0.20mg/L. The arsenide content in water was high (>0.05mg/L), the fluoride content had a rising trend, but when fluoride was over-standard(>1.0 mg/L), arsenide was not high for certain.

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ARSENIC SPECIATION IN HUMAN URINE AND SERUM AFTER INGESTION OF CHINESE SEAWEED

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An experiment is in progress that deals with the speciation of arsenic in urine and serum after ingestion of 20 g (dry mass) of the Chinese seaweed laminaria. Seaweed contains mg/kg amounts of arsenosugars. Arsenosugars are considered to be non-toxic, although the detailed metabolism has yet to be unraveled. Most studies conducted so far have used HPLC for the separation of the arsenosugars in combination with an element selective detector such as inductively coupled plasma mass spectrometry. This study applies HPLC with dual-line detection of element and molecule: hydride generation atomic fluorescence spectrometry of the element, preceded by on-line UV digestion of the arsenic compounds, and electrospray mass spectrometry for molecular and structural information. Preliminary investigations showed a peak in urinary DMA and MMA concentrations as well as several unknown As-compounds in the course of the 120 h following ingestion. In the ongoing study five male and five females are given a portion of laminaria. Blood is drawn twice within the next 24 hours after ingestion and all urine fractions are collected. Total arsenic is measured to obtain time related excretion patterns and allow mass balance. Elemental and molecular/structural information about the arsenic metabolites in serum and urine will be presented.

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ARSENIC SPECIATION IN INFANT FOOD USING IC-ICP-MS

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Health risks associated with dietary arsenic intake may be different for infants and adults. Seafood is a major contributor to arsenic intake for adults while terrestrial-based foods are the primary source for infants. The results from the FDA Total Diet Study show that products such as rice cereal and mixed rice cereal products contribute as much as 31% of the total arsenic intake for infants. Studies conducted in our laboratory have shown that total arsenic levels in several rice-based infant cereal products ranged from 0.06 to 0.32 mg kg\(^{-1}\) with inorganic arsenic and DMA being the major species detected. The speciation method developed for arsenic in rice products includes sample treatment with 2M trifluoroacetic acid and speciation analysis by ion chromatography coupled to inductively coupled plasma mass spectrometry (IC-ICP-MS). The speciation method provides good mass balance between the sum of the arsenic species determined and total arsenic determined in acid-digested samples. Results using this method will be presented for additional infant food products including infant formula, fruit juices, strained fruits and vegetables. This presentation will also include modifications to the original method given the variety and number of ingredients present in these infant food products.

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INVESTIGATION OF ARSENIC RELEASING FROM SOLID PHASE INTO WATER IN THE EARTH’S CRUST

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Arsenic in water resources, both in surface water and in ground water were found in many places in the world. In Vietnam (in 1991, Mr. Nguyen Van Cang) the contents of arsenic were very high in some springs of Ma river. Recently some researchers from Centre of Environmental Chemistry and Faculty of Chemistry, Hanoi University of Science, investigated the pollution by heavy metal in groundwater in Hanoi and found that there was an arsenic contamination with significant levels in some tube-wells and household drilled wells.

The above mentioned findings urged us to an important task to investigate a possible mechanism to explain the arsenic-releasing into water. This mechanism will help to identify a correlation of the solid phase of mineral compounds and accumulants in the earth’s crust in investigated regions with liquid phase of surface water and existing ground water.

Under the shown model, in the created anoxic conditions in some water aquifers and in non-anoxic conditions, there was studied the arsenic-releasing mechanism from different solid forms such as the precipitations of arsenate, arsenide and arsenopyrite. The presence of arsenate, Fe, Mn and organic mud deposits and other similar components such as groundwater environment, the release of Fe(II), Mn(II) and arsenic was investigated. The obtained results showed that in anoxic conditions, Mn(II) was released first and then Fe(II) and arsenic were released simultaneously. That confirmed the theory that arsenic in the accumulated alluvial aquifer is the consequence of the adsorption-coagulation of arsenic(V) on particel iron hydroxide and clays.

The study of the arsenic-releasing process from arsenide and arsenopyrite mineral compounds rich in oxygen and water reflected the mechanism of oxidization of iron sulfide accompanied by phenomena of the oxidization of arsenide to form arsenite and arsenate. These compounds easily combined with metal ions and adsorbed on the newly formed iron hydroxide(III). However, some parts were released into water, especially at the low pH values. These results contributed to explaining the reasons causing the high arsenic contents in water in some springs of the Ma River upstream crossing across the regions rich arsenopyrite minerals, mainly gold deposits.

Based on the above research results, it was a help to identify the correlation of soil and rock components or sediments with the possibility of arsenic contamination in water resources in surrounding areas.

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AN INTERVENTION TRAIL TO ASSESS THE CONTRIBUTION OF FOOD CHAIN TO TOTAL ARSENIC EXPOSURE

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There is concern that food irrigated with arsenic contaminated water has the potential to significantly increase arsenic exposure in humans. A randomized placebo-controlled intervention trial was conducted in a village of Jessore district, Bangladesh to determine if food irrigated with arsenic contaminated ground water significantly adds to total arsenic exposure. Sixty eligible participants were randomly allocated to either the intervention (30) or control group (30). The intervention consisted of the provision of food (rice, dal and vegetables) that was irrigated with arsenic free water. The control group was provided with food that was grown locally, irrigated with arsenic contaminated water. Pre and post interventional urine samples were collected and analyzed for total and inorganic arsenic (sum of As(III), As(V), DMA and MMA) over three consecutive days.

No significant differences were observed between the intervention and control groups for either (1) pre intervention urinary total arsenic concentration ($p = 0.72$), and inorganic arsenic concentration ($p = 0.51$), or (2) Post intervention urinary total arsenic concentration ($p = 0.93$), and inorganic arsenic concentration ($p = 0.91$), all adjusted for creatinine. Similarly, there was no significant within-individual difference between pre and post intervention urinary arsenic concentrations among the intervention group.

Possible explanations for these findings include the usual and the intervention foods not differing in arsenic concentration because of low uptake of arsenic from contaminated water, non-compliance, and food preparation increasing contamination in unexposed food. Our findings suggest that food irrigated with arsenic contaminated water is unlikely to add significantly to total arsenic exposure among Bangladeshis.

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