# ARSENIC, NITRATE, AND PERCHLORATE IN WATER – DANGERS, DISTRIBUTION, AND REMOVAL

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While it is generally recognized that there is a considerable amount of water on the Earth, most of it is unavailable to us.   Only about 2.5% is fresh water, and a considerable fraction of that is inaccessible in the form of ice or stored in deep groundwater (1).   The flows of water present an even more sobering picture because the amount of water stored in all the rivers of the world is thought to be 2,000 km$^3$, whereas annual withdrawal of water amounts to about 3,800 km$^3$/year (1).   Water availability may be better expressed as annual discharge, 45,500 km$^3$/year, that flows through various rivers of the seven continents to the ocean (1).  Although the quantity of water is surely important, the quality of water is no less so, and  this paper is concerned with the impacts of  three groups of species, arsenic, nitrate, and perchlorate.

## Arsenic Species

Arsenic species in groundwater have become a major worldwide problem, owing to  their  carcinogenic and other toxic properties.  Relatively high concentrations have been reported in such countries as Argentina, Bangladesh, India, Japan, Mexico, Mongolia, Taiwan, Philippines,  and the Peoples Republic of China (2-4). The Bangladesh situation is especially bad because of the very high concentrations of arsenic in the groundwater. Unfortunately, about 97% of the population drank tube well water (from hand-pump shallow wells), and nearly 85 million persons are at risk from poisoning from arsenic-contaminated water (5).

The symptoms of those adversely affected are serious:  skin lesions, hyperkeratosis, melanosis, skin cancer, cancer of internal organs, and "black-foot" disease (6). In addition, serious respiratory effects can result from long-term ingestion of arsenic (7).  According to one source (6),  contamination of groundwater by arsenic in Bangladesh is "the largest mass poisoning of a population in history" (6).  The main source of drinking water in that country, especially in the rural areas, is shallow tube wells (< 150 m deep), and this is a source of tragic irony.  Bangladesh authorities tried to prevent waterborne diseases by shifting the drinking water supply from surface water to tube wells, but many of the six to ten million drinking water wells contain high concentrations of arsenic (8).  According to a British Geological Survey study of 2,200 tube wells from eastern, southern, and western Bangladesh, about 21 million persons were drinking water with arsenic concentrations above the maximum allowable concentration of 50 ppb (50 µg/kg) set as the Bangladesh standard (9). As a consequence, widespread arsenicosis occurred with the possibility of enhanced cancer rates (10).

Several technologies have been presented for removal of arsenic from drinking water.  These include precipitation/coprecipitation, adsorption, lime softening, ion exchange, and membrane filtration.  Precipitation requires addition of an agent to produce an insoluble solid. Coprecipitation removes substances in dissolved or a colloidal state through flocculation and coagulation. Chemicals used (based on known solubilities) might

include ferric salts, ferric hydroxide, alum, ammonium sulfate, calcium hydroxide, and copper sulfate (11).

Precipitation and coprecipitation are widely used techniques, but there are challenges for arsenic removal. The problem is species-related: the presence of arsenite decreases the effectiveness of arsenic removal, and some oxidation scheme must be incorporated into the overall process (12). In addition, ortho arsenic acid, $H_3AsO_4$ is a stronger acid ($K_{a1}$ = 2.5 x $10^{-4}$) than meta arsenous acid, $HAsO_2$, ($K_{a1}$ = 6 x $10^{-10}$) (13).    This means that at pH 7, all of the ortho arsenate is ionized, 50% as $H_2AsO_4^-$ and 50% as $HAsO_4^=$.   In contrast, at the same pH, nearly all of the As (III) species would be present as the unionized acid, so removal of both species as precipitates would require pH adjustment.

A second problem with Bangladesh, and perhaps other locations,  is cost.  For rural areas where the problem is acute, the poverty level is such that a technique must be exceptionally cheap. A new approach developed at Lawrence Berkeley National Laboratory may well overcome both problems (14).   The process involves coal-ash particles (1-10 μ) coated with ferric hydroxide. When arsenic-contaminated water interacted with the composite, ferric arsenate precipitated.  Presumably, in very small villages, individuals would use a filter in the form of a pouch containing the composite, and water from a contaminated well could be passed through the filter into a suitable container. Laboratory samples with 2,400 ppb could be reduced to an arsenic level of 6-8 ppb.  No comment was made about the presence of arsenite.

While the problems of Bangladesh drinking water have been well documented, suppliers of drinking water in the United States face problems as well.  The new standard for arsenic in drinking water (10 ppb) for the United States was scheduled to begin January 23, 2006, a notable decrease from 50 ppb.   It is estimated that some 4,000 water systems will be required to reduce arsenic levels in their water supplies, and of these 97% are small utilities (15). Presumably the cheapest method of treating arsenic-laden well water is dilution with arsenic- free water, but that may not be a viable option if all the wells in the area have unacceptably high levels. Accordingly, when the standard was 50 ppb, only 0.51% of all community water systems in the United State were above the standard; with the new standard, about an estimated 6.187 % (3,034) of such systems were over the allowed level (16). Examination of the data more closely indicated that about 97% of the systems affected obtained their water supplies from groundwater with the arsenic in the As(III) form, which would be more carcinogenic and more difficult to treat. About 60% of the affected systems were in the "Very Small Water Systems" category providing water to fewer than 500 persons (16).

The size of the water system affects the increase in annual mean household cost for meeting the 10 ppb standard. (Table)

| Table.   Annual mean household cost for attaining 10 ppb As standard (16) | | | | |
|---|---|---|---|---|
| Utility size, Number of homes | <100 | 101-500 | 501-1000 | 10,000 50,000 |
| Cost, $ | 358 | 246 | 98 | 23 |

More than one mechanism is envisioned for the availability of arsenic in ground water in Bangladesh and perhaps elsewhere.  The problem has been most thoroughly considered for Bangladesh because of the extremely serious nature of the contamination. One positive aspect is that the problem seemingly is not due to point-source pollution caused by humans, although that might lead to an easier treatment.  For example, McArthur and co-workers (17) dismissed the possibility that competitive exchange of phosphorus in fertilizer contributes to arsenic availability.  One mechanism of contamination proposed by them is the release of arsenic sorbed onto hydrous iron oxides, FeOOH, where it is microbially reduced (17, 18).  They assert that the most intense reduction and thus the greatest source of arsenic pollution arises from microbial fermentation of buried peat.  A human component is involved, however, in  that microbial fermentation of organic waste from latrines could also reduce the hydrous iron (III) oxide.  Sources other than peat lack the abundance or reactivity to generate the severe effects noted but could account for low-level contamination (<50 ppb).

Another mechanism addresses the mobilization in terms of which species of hydrous iron (III) oxide is involved:  oxidation of pyrite versus oxyhydroxide reduction (4). Those that favor pyrite oxidation believe the arsenic contamination is anthropogenic and can be related to excessive groundwater withdrawal (4).  These authors suggested that a study by the British Geological Survey was flawed and rejected the pyrite oxidation hypothesis.

The authors (4) criticized errors in the estimates of the percent of wells that were polluted.

A third mechanism involves inflow of organic carbon, which in combination with groundwater removal had drawn water from a depth where the arsenic level was a maximum (19). The combination of the two processes meant that so-called young carbon had driven recent biochemical events. Further studies indicate that field injection of molasses, nitrate, and low-arsenic water could rapidly mobilize arsenic. This raised issues of the proximity of irrigation wells to tube wells used for drinking water (19).

The US EPA Office of Research and Development has supported a four-system testing program at 40 sites in 20 states (15). The technology systems tested were coagulation-filtration, iron removal, anion exchange, and adsorption (seven media). Presumably the results of the field tests will be available in due course as will the US EPA decision.

We believe a system we have described involving an iron (III) derivative of an IMLIG (immobilized ligand), a polyethyleneamine that is chemically attached to high-surface silica, Octolig®-21/Fe(III) composite, merits consideration as a removal material on a larger scale (20). The basic IMLIG, Octolig®-21, has been used in large-scale applications in the United States and Europe for removing heavy metals (21). Converting this IMLIG to the iron (III) composite (Ferrilig) was surely a facile synthesis (21), and the resulting composite could reduce 300 ppb As (150 ppb As as arsenite and 150 ppb As as arsenate) to 3 ppb or less by column chromatography (4.5 cm id, 1780 mL of Ferrilig). The removal of arsenic in the field could be accomplished by using pre-packaged Octolig®-21/Fe(III) composite. We recognize that additional research would be needed to test what would be a suitable container: A tube? A cloth or cloth-like material used in a similar manner as suggested by Binns (14)? In addition, it would be necessary to evaluate the economics and efficacy and the inevitable differences of various matrices.

## Nitrate

Nitrate is thought to be the world's most common contaminant of groundwater aquifers (22), and about 42% of the US population depends upon groundwater as its source of drinking water supply (23 ).

The contamination is use-based. For example, total nitrogen in streams and nitrate in groundwater are highest in agricultural areas, according to Ward and co-workers (24), followed by urban areas and areas of mixed land use. This variation is a consequence of the alteration of the nitrogen cycle by human activity, especially over the last fifty years, leading to a significant accumulation of nitrate ions in the sources for drinking water (24). For example, human production of nitrogen currently exceeds fixed nitrogen from natural sources by some 30% (25), whereas according to Lambert and Driscoll (26), prior to 1950, human input was a small fraction of natural sources. Major input associated with human activities is due to the use of fertilizer, followed by animal and human wastes, nitrogen oxides (automobiles, trucks, buses and utilities), and leguminous crops that fix nitrogen (25).

The problem with the build up of nitrate is a consequence of the chemistry of nitrogen. Ward and co-workers (24) noted that nitrate is not taken up by plants nor by denitrifying bacteria and migrates to streams and ground waters. Under reducing conditions, nitrate can be transformed to molecular nitrogen by denitrifying organisms under oxygen-poor conditions, a significant feature of the nitrogen budget in the ocean (27). And various sources of nitrogen can be transformed to nitrate by bacterial nitrification, by hydrolysis, and mineralization in oxygen-rich conditions of soil and water.

The maximum concentration level (MCL) mandated by the US EPA for nitrate in drinking water is 10 ppm (mg/L) nitrate-nitrogen ($NO_3$-N) or 44 mg/L as nitrate (24). The World Health Organization requires a slightly higher standard, 11 ppm $NO_3$-N or 50 ppm as nitrate (28).

The standards are provided out of concern to protect infants from "blue baby syndrome" or methemoglobinemia (24). Ingested nitrate is reduced to nitrite, which can bind to hemoglobin to form methemoglobin. Elevated levels of this substance exceeding 10% lead to the condition of methemoglobinemia, as the oxygen-carrying capacity of blood is affected, resulting in a change from a rosy complexion to the so-called "blue-baby syndrome" (24). The susceptibility of infants arises from a dual characteristic: a greater capacity to reduce nitrate to nitrite and their lower levels of a critical enzyme that converts methemoglobin back to hemoglobin (24). Nitrate can have an adverse effect on the thyroid gland, and signs of increased thyroid volumes and thyroid disorders were reported for 10-13-year-old school children in the city of Kosice, Poland (29). The children lived in a high nitrate area located in agricultural lowland with a high nitrate drinking water (51-274 ppm) supplied from shallow wells.

How widespread the contamination is depends upon the source; but one system in Florida has been well studied:  nitrate contamination of spring waters in the Suwannee River Basin in northern Florida.  There are some unique problems here, including agricultural factors.  When the Lake Okeechobee Technical Advisory Committee reviewed the contamination of Lake Okeechobee, a major source recognized was waste from dairy cattle, and a solution was a buy-out scheme: dairy farmers were paid to take their cows elsewhere, and  a number were taken to the Suwanee River basin where presumably land was cheaper   The amount of nitrogen from dairy cattle represents a small component of the total nitrogen available in the system, and only a slight impact of dairy cows seems to have been observed over the years (30, 31).

Nitrate is of potential concern because it is a precursor to *N*-nitroso compounds, a group of genotoxic substances that can be animal carcinogens (24).  While nitrate ion is a relatively inert ion that is nonmetabolizable by human enzymes, nitrate-reducing bacteria can reduce nitrate to nitrite. Under the acidic conditions of the stomach, highly reactive species are formed that can react with secondary and tertiary amines to produce the *N*-nitroso amines (33).  R. S. Braman, for example, found an association between nitrosamines in urine and bladder cancer (32).  The relationship between intake of nitrate in drinking water and urinary nitrosamines has not been established, however (24).

Other cancer effects associated with nitrate in drinking water have been considered in various studies. Pancreatic cancer showed no significant associations with quartile populations having average nitrate intake or years of exposure (34); the conclusions were similar for colorectal cancer, except for slightly elevated risks for certain subgroups, e.g., those with above-medial meat intake (35).  Ward and co-workers (36) reported dietary nitrate was associated with increased glioma (brain cancer) risk, but did not find an association with drinking water nitrate intake.

Probably adverse effects associated with drinking-water nitrates are, as noted, "the result of a complex interaction of the amount of nitrate ingested, the concomitant ingestion of nitrosating cofactors and precursors, and medical conditions of the host that may increase nitrosation" (24).

The possible association between childhood Type 1 insulin-dependent diabetes mellitus and nitrate intake has been considered in several investigations(37).  One such study covered over 1,000 cases of Type 1 diabetes in children (0-14 years old) out of over 2.8 million children (37), and the authors concluded there was no convincing evidence that drinking water at current levels in the Netherlands  was a risk factor for this disorder.

Certain areas of the world have significantly high nitrate levels in drinking water.  One of these is northern Punjab, Pakistan, where 16, 40, 67, and 70% of the samples in  four separate districts exceeded WHO and US EPA drinking water nitrate levels (38).  The authors of the study note that septic tanks, soaking pits, and solid waste dumps are common in these districts, but also excessive use of nitrate fertilizers can be a factor because of leachates from these sources combined with intensive agricultural production.   High concentrations of nitrate in shallow aquifers can also be found in  other areas of intense agriculture (Belgium, France, Germany, US Midwest, United Kingdom),as well as in near-desert regions, sites of  heavy stresses on the water resources (39).  Namibia, for example, has recorded 16 times the recommended limit of 50 mg $NO_3$/L (39).

It would be unwise to focus solely on one species in a source of water, a lake, for example.  Senn and Hemond (40) noted the positive effects of nitrate in an urban lake (Upper Mystic Lake in Massachusetts), where they demonstrated that nitrate controlled iron speciation by oxidizing iron (II) to iron (III) to produce particles that tended to remove arsenic (V) species, also  favored in the presence of sufficient nitrate ion. Thus, nitrate levels in this eutrophic lake, and perhaps many others, affected the speciation of a truly undesirable element and probably limited the recycling of arsenic to produce more soluble, more toxic species of arsenic (III).

The "Eliminate Project," whose goal is zero effluent nitrate, is in progress (39).  Some 40 selected sites in the UK have used specially developed  nitrate-selective ion-exchange resins.  Though the drinking water is very good, the resulting effluent (brine with high nitrate concentrations) constitutes a significant disposal challenge. The Eliminate Project is an effort to develop an electrochemical means of converting the nitrate-containing brine effluent to nitrogen gas and reuse the ion-exchange regenerate (39).

One good example of this type of approach is the removal and destruction of nitrate by using water-compliant selective materials such as Purolite's A520E or Rohm & Haas' Amberlite PWA 555.  These materials are regenerated with a concentration brine to regenerate the ion-exchange materials.  Then the brine solution is

sent to an electrochemical cell (EDA's SERIX-systems) to produce molecular nitrogen and water (41).

## Perchlorates

The problem of perchlorate contamination may be widespread.  US EPA identified perchlorate users and manufacturers in 44 states and releases in 18 states and came to the conclusion that perchlorate affected the drinking water of 15 million persons in the United States (42).  Perchlorates represent a comparatively recently recognized danger as a water contaminant, primarily since World War II because of the use of ammonium perchlorate as a rocket propellant.  Some lesser problems associated with fertilizer application have been suspected because perchlorate can be a natural contaminant of Chilean saltpeter (43), and there is a possibility of naturally occurring perchlorates in Texas (44).

The concern for perchlorate in water supplies arises from three factors:  the effect on the thyroid, high solubility of most perchlorates, and, curiously enough, improvement in the assay for perchlorate.  Most commonly used perchlorates are quite soluble, so that if there is contamination through careless applications of ammonium perchlorate, the material is likely to spread and contaminate ground water.  In 1997, moreover, the assay sensitivity for perchlorate in water was enhanced from 0.4 mg /L (400 ppb) to 4 μg/L (ppb) by means of a new ion chromatography method  so that lower levels of perchlorate could be detected.

Presumably because of releases of ammonium perchlorate by defense contractors, military operations, and aerospace programs and enhanced analytical sensitivity, perchlorate has been found in drinking water throughout the southwestern United States (45).  Public water supplies in Southern California had detectable perchlorate ion levels (5-8 ppb), and those in southern Nevada were at 5-25 ppb (46).  The US EPA has recommended a provisional cleanup level for this pollutant in the range of 4-18 ppb (47).

On the other hand, industrial usage of ammonium perchlorate was not the only cause of perchlorate contamination of water supplies, as a thorough study of the Texas Southern High Plains aquifer system revealed (44). Among a total of 254 wells in nine counties over an area of about 24,000 km$^2$, 70% had detectable perchlorate (>0.5 ppb), 35% had concentration of 4 ppb or greater (44).  Several possibilities were proposed: (1) a natural mineralogical contaminant, (2) agricultural fertilizers

contaminated with perchlorate, (3) in situ generation of perchlorate by redox reactions, or (4) some combination of these factors, not yet fully understood (44).

Perchlorate in drinking water is a risk for public health because of the effect on the thyroid gland.  During the past 55 years, potassium perchlorate has been used to treat hyperthyroidism (46).  More generally, perchlorate is a competitive inhibitor of iodide uptake. At current therapeutic levels or lower, pharmacological effects of perchlorate are ascribed to inhibition of the sodium-iodide symporter  (NIS)  on the thyroid follicular cell membrane. Levels of interest are those at which thyroid levels may be reduced or TSH levels increase, and such exposure may begin at the 35-100 mg/day range.  The level at which perchlorate starts to affect iodine uptake in humans may occur at about 1 mg/d.  The ions can affect production of metabolic hormones by the thyroid gland (43, 47), which would affect development; also, perchlorate ions can even induce thyroid gland tumors.

The concern over the possibility of cancer occurring as a result of drinking water contaminated with ammonium perchlorate has arisen.   One study (48) examined the number of observed cancers versus those expected for a California community (1988-1998). No significant differences were observed between observed and expected for all cancers, for thyroid cancer, or for 11 other types of cancer,  and fewer cases than expected were reported for lung and bronchus and the colon and rectum.  But more cases than expected were observed for uterine cancer and skin melanoma.

Perchlorate ion is difficult to remove from water. Because it is a very soluble ion (2.09 kg/L) (49), there is no obvious technology for its removal (47). For example, while some anion-exchange resins may remove perchlorate, they remove all other anions first, and the final product water is too corrosive for use without restoration of hardness (47). Use of zerovalent metals may successfully remediate chlorinated aliphatic compounds (e.g., trichloroethylene), but they are ineffective for perchlorate (47).

Bioremediation of perchlorate-contaminated water has potential (45, 50), as bacteria capable of such degradation are widely distributed in nature in concentrations ranging from one to thousands per gram of water or wastewater, sediment, or soil (51, 52 ).  And it may well be that bioremediation will be the penultimate solution to this challenging problem.  At present, though, Logan (47) suggested that new ion-exchange systems capable of selectively removing perchlorate would be the best

solution for small amounts of contaminated water.  One such system is Purolite A-530E bifunctionalized resin, which offers a high selectivity for perchlorate (53). Biodegradation has been successful even in 11% brine solutions, and biodegradation may ultimately be the most cost-effective system for treating "wide-spread contamination of drinking water" (47).  The problem of perchlorate contamination is one that is likely to persist, given the contamination of aquifers, a common source of drinking water.

The ultimate answer to perchlorate contamination and related problems may be wisdom of use and disposal.

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## FUTURE ACS MEETINGS

April 6-10, **2008**—New Orleans, LA

August 17-21, **2008**—Philadelphia, PA

March 22-26, **2009**—Salt Lake City, UT

August 16-20, **2009**—Washington, DC

March 21-25, **2010**—San Francisco, CA

August 22-26, **2010**—Boston, MA

March 27-31, **2011**—Anaheim, CA

## WEBSITES

**HIST:**  http://www.scs.uiuc.edu/~mainzv/HIST

**CHEMICAL HERITAGE:**  http://www.chemheritage.org

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