# Arsenic: it's extent of pollution and toxicosis: An animal perspective

Debashis Roy, Tapan Kumar Das<sup>1</sup>, Shalini Vaswani

Department of Animal Nutrition, Veterinary College, Pt. Deen Dayal Upadhyaya Veterinary Science University, Mathura-281001, UP, India 1.Research Associate, National Dairy Research Institute, Karnal, Haryana-132001, India Corresponding author: Tapan Kumar Das, email:tapanndri@gmail.com Received: 22-05-2012, Accepted: 18-06-2012, Published online: 30-11-2012

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### Abstract

Arsenic poisoning is now considered as one of the biggest environmental disaster and a major public health issue. Incidence of arsenicpoisoning has been reported from many parts of the world. While Bangladesh and West Bengal (India) account for the most of the incidence, occasional reports from Mexico, Taiwan and mainland China have also appeared. It is a natural metalloid found in low concentrations in virtually every part of the environment as it is used in a wide variety of industrial applications, from computers to fireworks. Ground water arsenic is the major source of poisoning in animals and human. About 80% of ingested arsenic is absorbed and metabolized in liver and then excreted through urine and faeces while upon chronic exposure, it is deposited in liver, kidney and skin. Human populations are also being exposed to this poison by consuming the milk of affected animal. Inorganic forms of arsenic are more toxic compared to organic forms. Acute toxicity is rare in nature in comparison to chronic toxicity, which is prevalent in contaminated areas. Most non-ruminants are more susceptible to intoxication than ruminants. Chronic exposure of arsenic in animals and human beings causes severe adverse effects in the form of lowered immunity, diseases and production performances.

Key words: Acute toxicity, arsenic, chronic toxicity, immunity

#### Introduction

Environmental pollution due to Arsenic (As) has gained global attention owing to its several deleterious health effects on human and animal population. The Agency for Toxic substances and Disease Registry [1] lists As among the top seven of 275 most hazardous substances in the environment. This listing is based on toxicity of substance and the potential for its exposure from air, water or soil contamination.

Among the general public, the word "arsenic" has become almost synonymous with the word "poison" [2]. Indeed, Haas [3] has suggested that As has a fairly low toxicity in comparison with some of the other metals. Furthermore, As deprivation has been associated with impaired growth and abnormal reproduction in rats, hamsters, chicks, goats, and miniature pigs [4]. The source of As in India's groundwater has eluded scientists for more than a decade after the toxin was discovered in the water supply of the Bengal delta [5]. Due to chronic exposure of As human beings including animals are exposed to its adverse effects in the form of lowered immunity, diseases and production performances. The situation worsens if nutritional status of As exposed individual is also not optimum.

#### Physical and chemical properties of As

Arsenic, a well known poisonous element is commonly used in industries of clothes, dyes, pharmaceuticals, insecticides, pesticides and wood preservatives [6]. It is considered as heavy metal due to its specific gravity higher than five (specific gravity =5.73). Its atomic number and atomic weight are 33 and 74.91, respectively. It can exist in four valency states; -3, 0, +3,and +5. It occurs in particularly two forms i.e. organic and inorganic. Inorganic As is prevalent in two forms i.e. trivalent and pentavalent. Trivalent forms are As tri- oxide, As trichloride and arsenites, whereas pentavalent forms are As pentoxide, As acids and arsenate. Major organic compounds of As are basically marine origin i.e. arsenosugars (macroalgae), arsenocholine, arsenobetaine (invertebrates and fish) and trimethylarsonium salts. In strongly reducing environments, elemental As and arsine (-3) can exist. Under moderately reducing conditions, arsenite (As (III)) is the dominant form; arsenate (As (V)) is generally the stable form in oxygenated environments. Elemental As is not soluble in water. Arsenic salts exhibit a wide range of solubility depending on pH and the ionic environment. Water soluble arsenites and arsenates are the most toxic, particularly trivalent form, while the elemental As is nontoxic, even if eaten in substantial amounts [7].

### Extent of pollution of As

Higher level of As (0.20-3.7 mg/lit of water) in ground water has posed serious threats to millions of human populations in various parts of the world especially India, China, Thailand, Bangladesh and Taiwan [8]. Several studies showed that As affected people in Bangladesh are 30-35 million [9]. Serious health hazards can be occurred due to As contaminated drinking water use after a long period of about 5- 15 years, but the duration can be even 2-5 years for high exposure of contamination [10]. Slow As poisoning observed in scalp hair samples among the As contaminated water consumers [11]. Safiuddin and Karim [12] reported that the melanosis (93.5%) and keratosis (68.3%) are the most common sufferings among the As affected people in Bangladesh. Thereafter, the seriously affected people are by arsenical (arsenite and arsenate), resulting skin cancer of about 0.8% of the total skin disease patients.

Livestock reared in and around such localities are also likely victims of such catastrophe arising from As pollution.In Indian sub continent, the ground water posses a major threat of exposing animals and human beings to toxic level of As in some geographical locations. Reports of As toxicity as an emerging epidemic appeared in the newspapers in West Bengal in the early 1970s depicting the tale of people suffering from a peculiar disease, characterized by rain drip skin pigmentation, thickening and pricking sensation of palm and feet tissues, excessive sweating, cirrhosis of liver and cancer etc.

The first report on As contamination of ground water in West Bengal appeared in 1978. A report indicated that the flood prone areas of Ganga-Meghna-Brahmaputra (GMB) covering an area of 5 lakh sq.km in Uttar Pradesh, Bihar, Jharkhand, West Bengal and Assam inhabiting 450 million people are prone to As poisoning [13].

In 50 districts of Bangladesh and 9 districts of West Bengal, India found higher level of As in ground water i.e. above WHO's recommended limit of 0.01 mg/L [14] and suffering of huge human population has been reported. A recent survey was conducted on the As concentration of drinking water from deep wells in 64 districts of Bangladesh and it was found that 54 districts were having As concentration more than 10  $\mu$ g/Lt and 43 districts had more than 50  $\mu$ g/Lt As concentration [15]. A few districts of Madhya Pradesh are reported to have As content of ground water up to 800 ppb [16]. As content in various water sources from some industrial areas in Panipat, Yamunanagar and Sonepat was reported to be higher than the WHO permissible limits [17]. In Punjab, Bathinda belt has been shown to have high As level in water [18]. High level of As in ground water of Ballia region of U.P. was found [19]As level in 45 ground water samples collected from different areas of Delhi was in range of 0.0170 to 0.1000 ppm, which is more than WHO recommended value for As in drinking water (0.01 ppm) [20]. In the country except a few samples from Faridabad industrial area, As content in all the water samples collected from all over Haryana was below maximum contamination level (MCL) of 10 ppb [21]. The same thing was also reflected in As content of all

the feeds and fodders samples from different districts of Haryana, which was in the normal range and far below the maximum dietary tolerable limit recommended by National Research Council (NRC, India) which is 50 mg/kg DM for inorganic As and 100 mg/kg DM for organic As, thereby rendering the feeds fit for animal consumption [22].

# Sources of contamination in diet of animals

Arsenic is present in more than 200 mineral species, the most common of which is arsenopyrite. There are various sources of As. Arsenic appears in the earth's crust at an average concentration of 2 to 5 mg/kg, with low levels commonly found in the air, water, and soil [23]. Ores are the most abundant source of As in nature. Most commonly As bearing ores are Niceolite, Realger, Orpiment, Lobaltile, Arsenopyrite, Tennanites. Arsenic is a major constituent of many minerals of the earth crust. Clays, phosphate rocks, sedimentary iron ores and coal are notably rich in As. The most common form of As is arsenite and arsenate compounds [24]. It can be introduced to a groundwater system through various means, including surface water and precipitation as well as anthropogenic and naturally occurring sources [25,26]. In addition to anthropogenic sources of As contamination, human activity can aggravate and accelerate the release of naturally occurring As [27, 28]. Organic As compounds usually containing carbon are mainly found in marine organisms. Industrial process, such as mining, smelting and coal-fired power plants, found as another source of environmental As [12,29,30]. Agricultural pesticides and chemicals for timber preservation also play important roles in the presence of As [31,32].

Ground water can be a major source of As, especially in the inorganic form. As concentration in unpolluted fresh waters, mainly as arsenate, generally ranges from1 to  $10 \mu g/L$ . However, As content can be much higher in waters in some geochemical environments. These include aquifers under strongly reducing condition, aquifers under oxidizing, high pH (>8) condition, areas of sulphide mineralization and mining and geothermal areas [33].

In nature, As-bearing minerals undergo oxidation and release As to water. This could be one explanation for the problems of As in the groundwater of West Bengal and Bangladesh. In these areas, the ground water usage is very high. It has been estimated that there are about 4–10 million tube wells in Bangladesh alone. The excessive withdrawal and lowering of the water table for rice irrigation and other requirements lead to the exposure and subsequent oxidation of Ascontaining pyrite in the sediment. As the water table recharges after rainfall, As leaches out of the sediment into the aquifer. However, another studies seem to favour the reduction of Fe/As oxyhydroxides as the source for As contamination in groundwater [34].

Sewage water from industries and households contain high amounts of heavy metals. When untreated

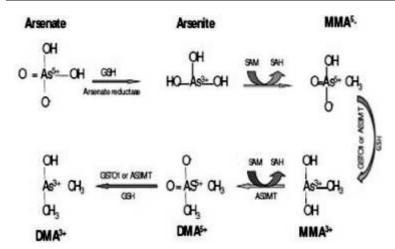


Figure-1. As metabolism showing arsenate reduction to arsenite and methylation in pentavalent forms [50]. (GSH, reduced glutathione; GSTO1, glutathione Stransferase omega-1; SAM, S-adenosylmethione; SAH, S-adenosylhomocysteine; AS3MT, As methyltransferase (Cyt 19); SAM, S-adenosylmethionine; MMA<sup>s</sup>, monomethylAs acid; MMA<sup>3</sup>, monomethylarsonous acid; DMA<sup>s</sup>, dimethylAs acid; DMA<sup>3</sup>, dimethylarsonous acid)

sewage water is used for irrigation, there is a sharp increase in the content of toxic elements in the soil. In 40 sewage irrigated vegetable farming locations of Punjab, the soil samples were found to contain potentially toxic levels of As, Cr and Pb [35]. Sewage water irrigated vegetables grown in Ferozpur district of Punjab are reported to contain high As content [36].

Fertilizer is one of the reasons of higher As content of feeds. Mono-ammonium phosphate application causes higher soil As uptake by plants with a phosphorusenhanced solid phase As release mechanism. Phosphate fertilizer application to soils containing lead arsenate pesticide residue can increase As solubility [37]. Lead smelter contributes a great amount of As in nature. Sea plants, fish products and supplemental minerals contribute towards most of the As found in animal feeds. The concentration of As has been found to range between 1 and 180 mg/kg DM for various marine micro algae and it ranges from 2 to 170 mg/kg fresh weigh in marine fish and bivalves and between 0.1 to 3 mg/kg fresh weight for fresh water fish [38].

Gallium arsenate (GaAs) is also used as a doping agent for semiconductors. Furthermore, semiconductors have been found to release As making them a possible pathway for As contamination [39].

Arsenic compounds are used in medicinal preparation. Organic Arsenical compounds like acetarsol, neoarsphenamine are used in the treatment of histomoniasis, Leishmaniasis, tryponosomiasis and sleeping sickness. Arsenical dips for sheep and cattle are usually combined with sulphur and contain about 20 per cent of soluble As and 3 per cent insoluble arsenious sulphide. As is essential constituent of many organic and inorganic coloring agents in dyeing. It is also used as discoloring agent in glass and enamel industry. The effluent from these industries may contribute Asin environment.

As levels in milk and animal tissues and recommended level of As

Based on limited data, it has been estimated that the percentage of inorganic As is about 75% in meats and dairy products, and 65% in cereals. In As polluted areas of West Bengal, high As level was reported in animal milk and tissues. In milk the average value of As was 0.08 ppm and 0.07 ppm in low As level villages (LAL) and high As level villages (HAL), respectively. As content in goat meat was 1.80 ppm (1.13 to 2.94 ppb) and 0.13 ppm (0.00- 0.31 ppb) in LAL and HAL respectively [40]. Roy *et al.* [41] reported 2-3 ppb As content in goat tissue samples collected from different districts of Haryana. Milk sample collected from different districts of Haryana were found to contain less As than the critical limit of 50 ppb [40] indicating that both cow and buffalo milk in Haryana is safe for human consumption [42].

In another study, it was reported that the As content in cattle tail hair samples from As polluted area was 0.22 to 1.22 ppm, whereas in As unpolluted area it was 0.10 to 0.73 ppm [43]. As content of cattle hair samples was 684.4 ppb, whereas in animals supplemented with 50 ppm  $As_2O_3$  contained three times higher As in hair as compared to control [44].

The maximum allowable concentration of As in drinking water were 0.05 ppm by WHO [45], which was reduced to 0.01 ppm, WHO (14). However the level recommended by FAO [46] was 0.10 ppm. For cattle, sheep, swine and poultry, the maximum tolerable dietary As level is 50 mg/kg and 100 mg/kg for inorganic and organic As, respectively [47]. Critical level of As in animal feeds (both roughage and concentrate) is reported to be 1.4 ppm, whereas for milk the critical level is 50 ppb [40].

#### Metabolism of As

Inorganic As as well as its organic metabolites are extensively absorbed (approximately 80%) and excreted in the urine. Accumulation of As in tissue is slow and occurs mainly in liver, kidney and skin. Withdrawal of exposure led to a decrease in tissue contamination [48]. The absorption and metabolism of As may be influenced by intestinal bacteria that can methylate As and metabolize methylated As [49].

Once absorbed inorganic As is transferred to various tissues including the liver and testes, where it is methylated by S-adenosyl-methionine as a methyl donor to mono methyl arsonic acid [51]. Before arsenate is methylated, it is reduced to arsenite. This reduction is facilitated by glutathione [52]. As methyl transferase, methylates arsenite to form mono methyl arsonic acid, which is then reduced to mono-methyl arsonous acid (Fig-1). This is a toxic form of As, which is then rapidly methylated by a methyltransferase to form dimethyl As acid. The formation of dimethyl arsenic acid usually is the final step of metabolism of As in most animals.

Excretion of ingested higher levels of As is rapid principally in the urine. However, high retention of As in the body was also been found in experimental group of crossbred calves given 50 ppm As (As<sub>s</sub>O<sub>3</sub>) daily upto a period of 90 days in their diet. The amount of As retained in the control and experimental group were 34.17% and 97%, respectively. The retention was further confirmed by increased levels of As in blood as well as hairs [44]. In some species, significant amounts of As are reported to be excreted through the bile in association with glutathione [52].

Arsenic in addition to its excretion via urine and faeces also secreted via milk. High As level was reported in animal milk and tissues from areas having high As content [40] with increased morbidity in all species of ruminants. Anke *et al.* [53] reported significantly lower As concentration in goat colostrum compared to goat milk (from 0.01 to 0.024 mg/kg).

# Toxicosis of As

Trivalent As (arsenite) is about 60 times more toxic than pentavalent As (arsenate). Furthermore, inorganic As is about 100 times more toxic than organic As compound [54]. Trivalent As is much more toxic than pentavalent As compounds, which may be due in part to different rates of cellular uptake. Sodium arsenite, which is more soluble than As (III) oxide, has been shown to be ten times more toxic than As (III) oxide. The toxicity of organic As compounds is inversely related to their degree of methylation. Inorganic forms are much more toxic than organic As [55]. It may be surprising to some individuals that As has a low order of toxicity, especially when it is in the pentavalent oxidation state. The lethal dose in domestic animals ranges from 1 to 25 mg/kg body weight as sodium arsenite, which is 3 to 10 fold more toxic than As trioxide [38]. Trivalent arsenical compounds combine with thiol group (SH) of lipoic acid moiety of lipothiamide phosphate, an essential in oxidative decarboxylation of pyruvic acid and - ketoglutaric acid. Arsenic also appears to exert toxic action by attachment to sulphydryl groups of protein.

# Acute toxicity

Acute toxicity of As is rare in occurrence as As poisoning is cumulative in nature. The acute toxicity of As is determined by its chemical form and oxidation state. Generally, the acute toxicity of trivalent As is greater than pentavalent As [56]. In most of the cases, death occurs prior to detection of cause and proper treatment. The signs of acute toxicity in cattle are colic pain, vomiting, diarrhea, marked depression and dermatitis usually due to increased capillary permeability and cellular necrosis.

# Chronic toxicity

Chronic toxicity of As is reported in animals from As intoxicated areas. It is mostly manifested in weight loss, capricious appetite, conjunctivitis and mucosal erythematic lesion including mouth ulceration and reduced milk yield. It is a cumulative poison having long retention time inside the body and therefore poses a threat on various physiological functions of the body. Animal exhibits signs of abdominal pain, hemorrhagic diarrhea, salivation, vomiting, constipation, anorexia, weight loss, dark urination and discrete skin eruptions [57]. Liver and kidney are the primary target organs for toxic effects of As as evidenced by clinical manifestation and biochemical alterations [58]. ATSDR [1] also reported that chronic poisoning of As includes anemia, liver and kidney damage, hyperpigmentation and keratosis. Symptoms in goat include abortion, skin problems, white and black spot in the body, sometimes diarrhea with blood, stunted growth, weakness, anorexia, dark and cloudy urine [59].

Chronic exposure to As, in addition to its general toxicity and its stimulation of many diseases, may affect lymphocyte, monocyte and macrophage activity in many mammals, resulting in immunosuppression [60]. Supplementation of As through drinking water has been found to suppress the natural, humoral and cell mediated immune response in broiler chicks [61].

# Conclusions

Arsenic, a metalloid, is ranked first in a list of 20 hazardous substances by ATSDR and United States Environmental Protection Agency. Exposures to As large enough to cause acute toxic effects would be easily recognized and the source of exposure would be found and eliminated. But the problem lies in the fact that lowdoses of As that would be too low to cause overt acute toxicity, finally be recognized after a long time with the development of toxic symptoms. This has demanded a serious effort to trace all the possible sources that cause human and animal exposure of this "king of poison". Finally, it is worth mentioning that As poisoning in humans and animals should not be considered a natural phenomenon, rather it is due to wrong policy of uncontrolled industrialization and ignorance to develop an effective water management of surface-water resources.

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