Arsenic: is it worth monitoring in the Mediterranean Sea?

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Arsenic (As) is a widely distributed element in the marine environment. Its sources are both natural (e.g. geothermal activity) and anthropogenic (e.g. industrial processing of phosphate rocks, bauxite and non-ferrous metals such as Cu, Zn, Pb, Au, Co, and fossil-fuel burning). Arsenic is also present in a wide variety of compounds used in pesticides, fertilisers, food additives, paints, glass, alloys, medicines, electronic components and wood preservatives.

Annual world production of arsenic reaches about 30,000 tons. Most of which is eventually released into the marine environment through runoff from land and river basins, as well as via air deposition (Phillips, 1990; Neff, 1997). Atmospheric inputs apparently contribute little to the global arsenic budget of the ocean. Major sources of arsenic in surface waters of the ocean are riverine inputs and upwelling of deep ocean water enriched in arsenic. Hence, the contribution of human activities to the arsenic budget may be important in estuaries and coastal waters.

The general concern regarding arsenic in the environment is mainly due to the widely-held view that it is highly toxic. Indeed, arsenic has historically been considered by the public as the archetype poison and is represented as such in many novels and plays.

During the last decades, a substantial body of evidence has shown that arsenic may cause severe poisoning (arsenicosis) leading to cardiac and neurological disturbances, skin, liver and lung cancers, and eventually death. Exposure of large human population to drinking water containing excessive concentrations of arsenic does occur in many countries of the world (e.g., Smedley and Kinniburgh, 2002; Visoottiviseth *et al*., 2002; Farias *et al*., 2003). This issue is of particular concern in poor regions of the world with limited access to drinking water such as Bangladesh or West Bengal where 40 millions people are drinking arsenic-contaminated water. In Southern Thailand, it has been shown that waste piles from tin-mining contain very high concentrations of arsenic as arsenopyrite. Leaching from these piles is contaminating local soil and groundwater serving as a water source for the local population, exposing in only the Ron Phibun District more than 30,000 people to chronic arsenic poisoning, with more than 1,000 cases of severe arsenicosis observed in 1996 (Visoottiviseth *et al*., 2002).

From the literature related to mammals, it is now well known that arsenic can compete with inorganic phosphate during the phosphorylation of adenosine diphosphate (ADP) to adenosine tri-phosphate (ATP), leading to uncoupling of oxidative phosphorylation, mitochondrial impairment and inhibition of energy metabolism. More recently embryotoxicity and genotoxicity

have also been reported for arsenic-containing compounds, with effects involving e.g. oxidative DNA damage, DNA protein crosslinks and inhibition of DNA-repair enzymes (see e.g., Fattorini and Regoli, 2004).

Although toxicity mechanisms of arsenic in marine organisms are much less documented than in terrestrial mammals, the bioaccumulation potential and the sensitivity of these organisms towards arsenic are well known.

Chemical speciation of arsenic in aquatic environments is the most important factor determining the accumulation of the element by biota and its toxicity. Indeed, arsenic toxicity is strictly related to its chemical form. Inorganic arsenite, As(III), and arsenate, As(V), are the most toxic species; methylated compounds such as methylarsonate, dimethylarsinate, trimethylarsine oxide and tetramethylarsonium are considered as moderately toxic, whereas complex organic compounds including arsenobetaine, arsenocholine and arsenosugars are considered non-toxic to living organisms (Figure 1) (e.g., Ellwood and Maher, 2002; 2003).

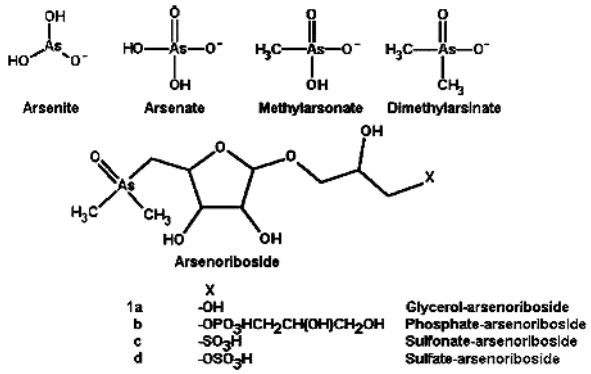

Fig. 1. Structure of some arsenic compounds found in the environment (from Tukai *et al.,* 2002).

In the marine environment, inorganic forms of arsenic predominate in seawater and sediments, whilst it is generally reported that marine organisms bioaccumulate the element mainly as organic, non-toxic compounds. Several authors have suggested that these organic forms would be the final products of detoxification processes of bioaccumulated arsenic (e.g., Phillips, 1990; Francesconi *et al*., 1998). However, important variation in concentrations and distribution of chemical forms of arsenic can be observed in marine organisms, often reflecting their trophic position or their ability to biotransform arsenic (Wrench *et al*., 1979; Fattorini *et al*., 2006).

Quantitatively, the most important routes of exposure of humans to arsenic are represented by inhalation of industrial dusts (particularly those from nonferrous metal smelters and coal-fired and geothermal plants) and consumption of drinking water and food, particularly seafood which is well documented to dominate total arsenic intake by humans (e.g., Phillips, 1990; Neff, 1997). The maximum acceptable human intake of arsenic in food has been set by the World Health Organisation as 2 $\mu g\ kg^{-1}$ body weight d^{-1} (equivalent to 160 $\mu g\ d^{-1}$ in a 80-kg person) (WHO, 1984). Nevertheless, since arsenic in seafood is present mainly as organic forms which are relatively non-toxic compared to inorganic arsenic and easily eliminated (short residence time), the risk associated with seafood consumption is generally considered as relatively low.

However, contrasting with the general trend of arsenic occurring in marine organisms mainly as organic arsenic, there is now a body of evidence showing that different organisms are able to accumulate arsenic up to unusual, very high levels and/or as the more toxic forms (e.g., Fattorini *et al*., 2005). This is for example the case for several polychaetes, such as the cirratulid *Tharyx marioni* which displays extremely high body concentrations of total arsenic (2,000 $\mu g\ g^{-1}$ dry wt; Gibbs *et al*., 1983) or *Arenicola marina* which accumulates arsenic predominantly (80%) as arsenate (Geiszinger *et al*., 2002). Elevated levels of arsenic (> 1,000 $\mu g\ g^{-1}$ dry wt), mostly present as dimethyl-arsinate, have been detected in the branchial crown of the Mediterranean fan

worm *Sabella spallanzanii*, suggesting an antipredatory role for this relatively toxic arsenic compound (Fattorini and Regoli, 2004). Recent experiments also revealed the capability of this polychaete to produce this molecule through both methylation and de-methylation reactions (Notti *et al*., in press).

Similar observations have been reported in macroalgae. Some taxa such as the *Sargassum* sp. are known to contain high percentages (> 75%) of inorganic arsenic (e.g., Phillips, 1990).

More recently, very high arsenic concentrations (500 μg g^{-1}dry wt) were monitored in muscles of edible fish from the Bay of Cienfuegos, Cuba (Fattorini *et al*., 2004). These levels were recorded a few weeks after this semi-enclosed bay experienced an episode of acute arsenic contamination in December 2001 due to the accidental release of 3.7 tons of arsenic (as arsenate oxides) from a local nitrogen fertilizer factory situated near Cienfuegos City (150,000 inhabitants) (Figure 2). Since marine organisms are an important component of the diet of the population of Cienfuegos Bay (up to 116 kg fish yr^{-1} $person^{-1}$), local fisheries were rapidly prohibited by the governmental authorities and restored only when acceptable arsenic levels were again reported for seafood and fish. Although high arsenic concentrations could have been expected in this particular situation, the most noteworthy observation concerned the arsenic speciation found in certain edible fish studied (*viz*. *Caranx latus*, *Lutjanus synagris*). In fact, the proportion of inorganic arsenic in the fish reached 98% of the total arsenic load (Fattorini *et al*., 2004) which would result locally in a daily consumption of inorganic arsenic > 400 μg d^{-1} $adult^{-1}$, *viz*. more than twice the maximum permissible daily intake recommended by the World Health Organisation.

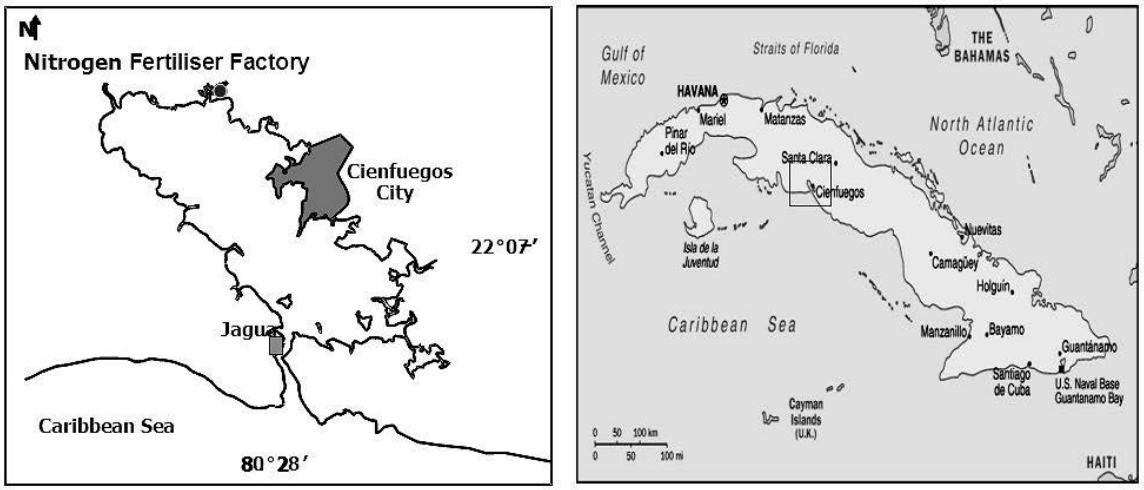

Fig. 2. Cienfuegos Bay, Cuba and location of the nitrogen factory responsible for the As spill in December 2001.

Environmental conditions and/or anthropogenic contamination are known to interfere with bioavailability of arsenic, and potentially influence the relative amounts of toxic forms in tissues of exposed organisms (e.g., Fattorini *et al*., 2004). For instance it is well known that an increase in N:P ratio in seawater greatly enhances the bioavailability of arsenic to phytoplankton (see e.g., Phillips, 1990). This in turn may lead to enhanced trophic transfer of arsenic to filter-feeders and their predators, and possibly to humans consuming the latter. For example, populations of the edible clam *Gafrarium tumidum* inhabiting non-contaminated areas of the New Caledonia lagoon are typically characterized by very high concentrations of total arsenic, up to 450 μg g^{-1} dry wt, (Hédouin and Warnau, unpublished). These levels were by far higher than those recorded in individuals from moderate to highly contaminated zones and are attributed to the influence of nitrogen inputs in coastal seawater due to terrestrial leaching of fertilisers used for local agriculture.

Overall, due to the complex biogeochemistry of arsenic and the related implications for its bioavailability and toxicity to seafood, fish and their human consumers, it is important to monitor

levels of arsenic in the coastal marine environment. It is particularly important to discriminate between toxic and non-toxic chemical species of this element.

The different factors that can affect contamination levels and speciation of arsenic (natural and anthropogenic sources, water oligotrophy) and its toxicity discussed above are all occurring within the Mediterranean basin (e.g., non-ferrous mining industries widely distributed along the Mediterranean coastline, bauxite processing in South of France, geothermal activity in the Bay of Naples and in Sicily, phosphate rock processing along north African coasts, cyclic eutrophication of coastal waters due to summer tourism, etc.). Therefore, as shown in the examples above, these factors (and their interactions) could result in environmental levels and/or speciation of arsenic which differ locally from the typically harmless, expected ones. At present, these possibilities can not be disregarded since field data for arsenic in the Mediterranean Sea are missing for numerous areas, especially those along the southern and eastern coasts.

Although the Mediterranean coastline is composed of contrasting regions with important cultural, political and regulatory differences, it is nevertheless characterized by a relative geographical homogeneity regarding the use of the coastal zone. Indeed, the tourism-related economy, welfare and fisheries of human populations living around the Mediterranean rely substantially on the quality of Mediterranean waters. Hence, it is of prime concern to survey and ensure the quality of the Mediterranean coastal waters, and monitoring the levels of key contaminants including arsenic in seafood is therefore needed as well as requested by the regulatory bodies.

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