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Article

Arsenic pollution in food and water: an overview

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Abstract

Drinking water pollution sustained by Arsenic (As) is a phenomenon mainly connected to the geological characteristics of the soil in Italy (i.e., Viberbo, Monte Amiata, basin of the Lazio volcano) as well as in the world (in Bengal in India, wells in Mongolia, in the Delta of the Red River in Vietnam and in the Chaco Pampean in Argentina, sites in Nevada and Arizona in the USA and wells at Ron Phibun in Thailand). This aspect is also joined by industrial pollution in other areas (Taranto, Gela). This results in significant negative effects from a health point of view, as As is a carcinogen (IARC group 1) and an endocrine corruptor. The Italian situation is described, characterized by the existence, in the province of Viterbo, of municipalities still involved due to levels of contamination and the situation of a large area, called the "Lazio volcanic basin" where since 2004 significant concentrations of arsenic have been reported in the past. drinking water. The construction of arsenic abatement systems or with adduction of water from other aquifers and with the strengthening of the water network has contributed to the reduction of the risk. In the municipalities with higher exposure levels (VT = As> 20μg / L) an excess of mortality was observed overall for all tumor causes. In excess, lung tumors and bladder cancer in men. In addition to an excess of mortality due to arterial hypertension, ischemic heart disease , COPD and Diabetes demonstrating the potential effects of As on the cardiovascular system. The implementation of food self-control practices on the water supply system, the training and information of citizens, the implementation wherever possible of arsenic removal systems in water (adsorption, membrane or precipitation processes), study and control of aquifers and aqueducts will constitute the fundamental prerequisites for the implementation of optimal interventions of real prevention.

Keywords: Arsenic, water, food, pollution

Introduction

Arsenic is a semi-metal with physical-chemical characteristics in-between metals and non-metals. In nature, it can be found in the form of small greyish rhomboidal concretions in Germany, France, Cornwall, Chile, Mexico and in Italy in Sarrabaus and Borgofranco d'Ivrea. It can be found in the soil, in the atmosphere, in rocks, in the water and in organisms with a mobility linked to atmospheric events, volcanic eruptions, biological activities and anthropic emissions. Arsenic toxicity increases when combined with other elements, for instance those resulting from processing of minerals containing iron, copper, and lead used to obtain trivalent oxide of arsenic and whose production amounts to 6000 t/year globally. Many of its uses are controversial due to the high level of toxicity and effects on health. For this reason, the implementation of prevention policies has become necessary.

History

Arsenic has been used since ancient times. Before Roman times, Egyptians used it as a decorative pigment whereas alchemists employed it in their attempts to create gold during the Middle Ages. In China, arsenic used to be administered as a drug for the treatment of malaria. However, due to its colorless and odorless features was considered as a perfect poison. Many scholars claimed that it was dissolved every day in food in the attempt to murder Napoleon Bonaparte. In 1780 Doctor Fowler and Doctor Pearson implemented the first arsenical solutions for the treatment of many forms of dermatosis. Until the mid90s of the 20th century, arsenic was a popular devitalizing agent used to necrotize inflamed dental pulp. Moreover, arsenic organic compounds such as sodium cacodylate and methyl arsenate were employed to cure syphilis, yawns, and trypanosomiasis. There have been proven benefits in the use of arsenic trioxide to reactivate silenced onco-suppressor genes. This was demonstrated by some studies conducted in China, in which arsenic anhydride contained in some herbs, had been used for the treatment of acute promyelocytic leukemia. This was sufficient to stimulate further investigation by the Food and Drug Administration for the treatment of relapse and refractory APL.

Arsenic in water

The OMS has sets limits to ensure drinking-water safety in specific non mandatory "guidelines" which defines the tolerable daily intake (expressed in mg/kg) that can be assumed

throughout life. The quantity has been set to a daily per capita of 2 liters for a 60kg subject, 1 liter for a 10kg child and 0,75 liter for a 5kg newborn. The OMS took into account the studies carried out by the IARC which identified the threshold concentration of genotoxic carcinogenic substances associated to an excessive risk of cancer. In 1958 the threshold was initially set to 0,20 mg/kg and was then decreased to 0,05 in 1963 and furtherly confirmed in 1984.
In 1993 and 1996 the threshold decreased to 0,01mg/dl (=10ug/l) even though the WHO estimated that this value was associated to a risk of skin cancer of 6×10^{-4}. In the European Community, the maximum limit in drinking water has been currently set to 10 micrograms/liter with possible justified derogations by the Dir. 98/83/CE and in Italy the D.Lgs. 31/2001. In Argentina, Bangladesh, Chile, China, Egypt, India, Mexico, and Taiwan the legislation set a limit to 50 micrograms/liter whereas a threshold of 25 and 7 micrograms/liter has been respectively established in Canada and Australia. It is worth noticing that in some Italian regions as well as in some Belgian, Croatian, Welsh, and Slovakian areas the 10 micrograms/liter is often exceeded. In ocean water, arsenic is present in a concentration equal to 0,3 μg/l whereas in continental waters, it varies between 0,05 and 1,00 μg/l. In natural waters, the element is present in the form of soluble oxyanion, Arsenite (III) and Arsenate (V) with concentrations of 1-10 ug/l (WHO, 2001) in uncontaminated water and 100-5000 μg/l in contaminated water. Italian scientists have conducted widespread research to investigate the presence of arsenic in the environment and particularly in the water. These studies report an accurate worldwide analysis with a particular attention to some critical areas:

- Austria: in the area of Strasseeg in Gasen, arsenic is present in the soil with a concentration of 700 to 4000 mg/kg.
- Great Britain: in the industrial areas of Devon and Cornwall the levels of arsenic in water vary between 10 and 50 μg/l.
- *France*: in the Auvergne, the level of arsenic in water is higher than 10 μg/l whereas in the areas of Allier and Puy de Dome the levels are respectively 190 μg/l and up to 27 μg/l.
- Switzerland: there are critical thermal areas in the northeast, in Giura and the Alps. The areas of Baden, Zurzach, Bad Saeckingen features levels of arsenic higher than 130 μg/l.
- Germany: in northern Bavaria the concentration in wells can reach up to 150 μg/l.
- Bangladesh: there are areas with an arsenic water concentration of up to 2500 μg/l
- India: it is characterized by areas with highly variable concentration (from 10 to 3200 μg/l)
- Taiwan: in this country concentrations reach 1820 μg/l.
- Mongolia: in some wells in the middle of the country concentrations of Arsenic peak to 2400 μg/l.
- Vietnam: in the Red River Delta area, arsenic concentration between 1 to 3050 ug/l has been measured.

- Argentina: in the region of Chaco Pampean, some wells contain up to 5300 μg/l of arsenic.
- Chile: in the mining volcanic area of Antofagasta, arsenic concentration in wells have been identified between 100 to 1000 μg/l whereas in fields and river sediments as well as in corns and potatoes cultivations, concentrations of arsenic have been measured up to 2mg/kg.
- New Zealand: high concentrations of Arsenic have been found in the volcanic area of Taupo.
- Jamaica: in the area of St. Elizabeth, concentrations of arsenic in the soil were found to be close to 400 mg/kg.
- USA: In Arizona, in alluvial basins, concentrations of arsenic were found to be up to 1300 μg/l in the waters whereas in S. Joaquin Valley in California the levels are equal to 2600 μg/l. In the area of Carson desert in Nevada, values of arsenic were found to be up to 2600 μg/l in the waters with high salt concentration. Finally in the mining area of Coeur d'Alene values of arsenic reach 5000 μg/l.
- Mexico: In the area of Lagunera, well arsenic concentration varies between 8 to 620 μg/l.
- Thailand: in the area of Ron Phibun, in proximity to tin mines, arsenic values vary between 1 to 5000 μg/l.

Legislation

The Italian National Institute of Health has defined some guidelines for the ASL (local health authority) and the local and water supply institutions particularly with regards to the permitted use of waters with a concentration of arsenic superior to 10 and 20 micrograms/liter as reported in the table below, in relation to the period in which request for exemptions from the European community are produced (**Table 1**).

Table 1 – Use limitations for different Arsenic concentration

Concentration	Use	Use limitations
>10<20 μg/L	➢ All uses for human consumption, including drinking water, private household, and food use.	➢ Hydration and food reconstitution and consumption by children (younger than three years old)
>20≤50 μg/L	➢ All operation for personal hygiene (including teeth brushing) ➢ All operation of domestic hygiene. ➢ Food preparation in which water must not be: • An important ingredient. • In contact with food for a non-relevant amount of time and must be removed from the food surface (es. washing and drying of fruits and veggies)	Drinking purposes: ➢ Cooking and food reconstitution ➢ Food preparation in which water: • is an important ingredient. • is in contact with food for prolonged time. • Food businesses

The document prepared by the Italian National Institute of health aimed to give clarification and act as a guideline to obtain a new exemption for the limit of 20 μg/l in the areas required in Italy. However, in the Official Gazette dated 17th November 2020, a new law was published regarding exemptions limited to fluoride and boron, and not including arsenic. Moreover, according to some lawmakers since the decision by the European Commission was immediately enforceable, any new exemption required would have become automatically invalid. Consequently, without the formalization of a new exemption from the European Commission, and just from 2013 at the end of a 6-year period of exemption given by the European Commission, the safe levels of arsenic should have been reduced back to 10 μg/l.

Table 2 – Limits in Arsenic concentration in water (modified by ANSA centimetri)

Arsenic concentration	Action
10 μg/l	Limit derived from EU Directive in 1998 on safety of drinking water
20 μg/l	maximum derogable limit according to WHO (for short period only)
30 μg/l	Over this limit the risk for some pathologies increases (i.e., cancer)
50 μg/l	Limit authorized in Italy by a derogation, found in some municipalities in the Lazio region

Following this, the second part of the document was unable to be used or it could have been used only to support an ASL evaluation requested by the mayors, so to allow to guarantee the hydraulic supply for a limited amount of time. The local health authority in Rome and Latina asked the mayors of the affected regions to declare water with arsenic above 10 micrograms as undrinkable and allow use only for cleaning (including tooth brushing and washing of fruits and vegetables). For further information, it is advised to consult the attached document written by the Prevention Commission of Order of Doctors in collaboration with the National Institute of Health.

Arsenic removal system in waters

The removal of arsenic from water can be carried out through different techniques depending on the concentration of arsenic and on the water volumes that need to be processed. Some techniques are based on the use of specific absorption filters which have turned out to be particularly effective regardless of the plant size. With the correct size and scale, a filtration plant can effectively solve the issue of arsenic contamination for a considerable amount of time before it becomes necessary to require the substitution of the absorption filters. The systems used for the removal are mainly adsorption based, membrane filtration, or precipitation processes. The EPA highly recommends the ion exchange on resins, adsorption on activated alumina, reverse osmosis, coagulation/filtration and softening. Other possible methods include inverse electrodialysis, oxidation/filtration. In the system adopted, pH is particularly important, and some technologies include pH correction to improve the efficiency (disinfection, solubilization, precipitation). In any case, the removal of the arsenate is easier compared to arsenite. Therefore, some systems require firstly an oxidation step followed by preliminary transformation in arsenate.

In the selection of the most effective technique, it is necessary to consider the suitability of the method in relation to many factors: water characteristics, investment cost, operation and performance, waste storage and disposal, personnel training, availability of materials and reagents, together with the evaluation of suitable techniques and technological equipment that has been internationally recognized.

For instance, natural air oxidation, which is catalyzed by bacteria, UV radiation, alkaline or strongly acid solutions, copper and activated carbon, has a low reaction rate with arsenic. The half-life of arsenite ranges between 2-5 or 4-9 days depending on the use of pure oxygen or air respectively. The arsenite chemical oxidation can be performed with hypochlorite, ozone, hydrogen peroxide (also used in the water bodies with high concentrations of iron dissolved as arsenic is also removed through ferric oxide precipitations.) However, the oxidation with up to 1mg/l of free chloride ions is rapid and highly effective. In contrast, in the USA, ozone and potassium permanganate or manganese oxide are the preferred reagents. Highly specialized personnel are needed to operate the ion exchange machines and the coagulation/filtration, microfiltration, softening processes. On the other hand, it is crucial to consider that in some plants the waste produced needs to be disposed of. This includes exhausted resins and brine with backwash water in the process of adsorption with activated alumina, exhausted minerals in case of adsorption with granular iron hydroxide. This latter is a very expensive procedure that is able to purify water with an arsenic concentration of up to 400 ug/l, but it can be carried out by low-skilled personnel. By using alumina and iron the main advantage of the adsorption process is that this can also be carried out in relatively small plants. Regarding the processes of precipitation, it generally reclaims lower concentration of arsenic from the water. The coagulation/filtration can reach up to 160 ug/l.

However, in order to undertake this procedure in a small plant, removal with iron/ manganese through oxidation/filtration is required. In the membrane process with reverse osmosis, up to 160 ug/l of arsenic concentration can be processed. In this case the personnel must have an intermediate level of specialization. Recently, the approval of simplified, portable, and low-cost technologies for arsenic removal has been object of strong debate since their efficacy needs to be fully demonstrated.

Industrial use

In some limited situations, industrial use can cause water pollution due to the contamination of groundwater. It is necessary to clarify that pure arsenic metal is used in electronics since it works as an excellent semiconductor and is added to metal alloys to improve thermal hardness and resistance (steel, brass, and lead). In the past, it was used in the pharmaceutical and agricultural field, as paint pigment (Scheele green), in the war industry as chemical agent and in the ceramics industry. Today the restrictions implemented due to its toxicity have widely limited or completely banned its use. Arsenic is still used in painting (arsenic Sulphur of yellowish color), in the tanning industry, to produce shotgun pellets and particular glasses and finally in pyrotechnics to confer green colors to fireworks.

Arsenic in the diet

Adventitious contamination and industrial pollution can increase arsenic concentration levels in food and beverages. In Great Britain in 1900, around 6000 people were poisoned by beer contaminated with arsenical pyrite. Arsenical pyrite was used to produce sulphuric acid to hydrolyse starch in the drink production process. Another serious accident occurred in Japan, where thousands of children were poisoned due to the administration of food contaminated by arsenic. Moreover, the use of pesticides containing arsenic in vineyards has led to the contamination of wine. Information about the presence of arsenic in food is quite scarce. Fish, crustaceans, and shellfish in the marine environment can contain high levels of arsenic and can significantly contribute to its daily intake. The determination of the element's concentration (expressed in mg/kg) in the edible portions of freshwater fish, trout, and marine fish has highlighted concentrations of arsenic that are low in freshwater fish (0,137) compared to the marine fish (6,22 and 3,03). The concentrations in this last species are 30 to 40 times and nearly 100 times higher compared respectively to marine fish and farmed trout (0,069). In bivalve molluscs coming from the Adriatic Sea, levels of arsenic (6,94) can be compared to those in marine fish, whereas in the gastropod and cephalopods molluscs and in crustacea the concentrations are particularly high. These results highlight how aquatic animals can accumulate arsenic without biological magnification.

The accumulation of arsenic in crustacea and shellfish can be put in relation not only with food but also with water contamination. However, similar levels have also been found in fishery product in the Adriatic Sea. The average concentrations of arsenic in a sample of fishery products (7,83 mg/kg), together with their average consumption (0,420 kg/per week in Italy) have been considered to approximately evaluate the contribution of fishery products in the consumption of arsenic. The result of this analysis shows a weekly intake equal to 3,29 mg of arsenic. The minimum tolerated dose of arsenic by an adult (60kg) is 0,882 mg. By hypothesizing in the sample considered a percentage of inorganic arsenic equal to 1%, the contribution of this food to the inorganic intake of this element amounts to 37,3%. Therefore, even if arsenic in fishery products is mainly present as organic component, the contribution through the diet could be relatively high, also given that other food sources can account for an increase of the amount a person ingests, consequently reaching the maximum level permitted by the FAO/OMS. The risk is highly increased in the case of elevated dietary consumption of fish, which is quite frequent in Italy particularly for some job categories such as fisherman and fishmongers who tend to consume higher quantities of crustaceans and shellfish compared to the average population.

Food businesses obligations

The policy based on the regulation CE n. 178/2002 establishes the food legislation's general requirements and lays down the procedures in the field of food safety. The article 2 of the regulation CE 178/2002 defines "food" also water indirectly ingested, therefore intentionally included in the food preparation process or treatment. The personnel of the food sector in compliance with the current regulation 283/62, DPR 327/80, Legislation CE 178/2002,852/2004,882/2004 from the juridical-institutional point of view, are obliged to include in the internal control plan the risk deriving from the management of the available water. The personnel are indeed the most qualified individuals to devise safe systems for food supply (including water) and to guarantee the safety of the food provided. Therefore, it is necessary that water used for the washing, preparing, producing food must be safe, in other words it must contain arsenic and fluorites respectively in the quantities of maximum 10micrograms/liters and 1,5 mg/liters. Therefore, food sector companies should guarantee internal control plan also for the hydraulic supply system. Very often due to old and obsolete plants, the internal network is not hygienically adequate due to the use of artesian wells to increase the hydraulic supply or due to the absence of aqueducts. Therefore, these are rarely controlled and not judged as drinkable water by the ASL as established by the Dlgs 31/2001.

The lack of sufficient autoregulation in this industry means that, from an administrative point of view, the use of private wells which contain unsafe levels of arsenic is questionable. Furthermore, food growing especially in areas with high arsenic concentrations should be regularly controlled, and if it is deemed to be unsafe, removed from the supply chain. In this case, it is expected that the EU will give warnings. The industry should also be aware that employees use water that is potentially high in arsenic. Considering both Annex IV of Dlgs 81/2008 and Dlgs 31/2001 together, the employer is subject to criminal liability in case of toxicity.

It is also necessary to establish an alternative water supply to use for the production, preparation, treatment of food products provided to the client. Therefore, it could be possible to:

- Use spring water or natural minerals as defined by the legislation 8 October 2011 (implementation of the directive 2009/54/CE) on the use and commercialization of mineral natural waters still traced by the production company according to the regulation CE 178/2002.
- Another option is to treat waters derived from the municipal hydraulic network with plants that comply to the indication present in the health ministry decreet n.25 7th February 2012 (G.U.n.69 del 22/3/2012), used to guarantee the compliance to the arsenic and fluorites levels delivered in water for daily use. Particularly, regular quantitative analysis must be carried out for the same parameters, in the approved laboratories for analysis of food registered in the regional directory.

Training and formation

In this field, it appears particularly clear the importance of the article 10 dlgs 31/2001 which establishes to provide mandatory information to the consumers regarding the measures adopted in case water element concentration does not corresponds to the expected values. The mayor, the ASL, related authorities and the manager of the plant according to their respective competences are responsible to provide this information. The communication must be effective and comprehensive with regards to the precautions to be adopted. According to the article 13, a further information measure elaborated from the region, is planned in the case the same region makes use of derogations. In the subparagraph 11 is established that "the population interested should be adequately informed about the derogation applied and the conditions that regulate them. Moreover, the regulation establishes that the region must provide recommendation to specific subgroup population for whom the derogation could represent a particular risk."

Effects on human health

Arsenic can be found naturally in the soil, rocks, waters, in organisms and almost in any animal and vegetal tissue. In humans, the main source of non-occupational exposure is represented by contaminated drinking water. Arsenic is harmful to health. Studies carried out in populations that experience chronic exposure to arsenic have demonstrated negative outcomes in neurological, cardiovascular, and respiratory disease, as well as diabetes, tumors, and reproductive system dysfunction. Arsenic has been classified by the *International Agency for Research on Cancer* as cancerogenic: lung, skin, bladder tumours have been associated to arsenic exposure either through inhalation or drinking water. Inorganic arsenic, both trivalent and pentavalent, is easily absorbed in the lungs and through the GI tract from food, in quantities that vary according to the chemical form in which the element is present (usually above 50% of the dose assumed). After 24 hours, the concentration in the organ usually starts decreasing because of the removal through the renal system. Whereas in the skin, increased levels are observed for several days. The accumulation can also occur in nails, hair and in small quantities in bones and muscles. Organic arsenic can pass through the placenta and induce lethal damage in the developing fetus.

On the contrary, arsenic organic compounds are generally considered absorbable in low quantities by mammals since they are rapidly eliminated through the feces and urine as well as undergoing a detoxifying hepatic biomethylation. Considering that fishery products contain arsenic in the organic form, the determination of trimethyl arsine in the urine has been proposed as a marker of the element quantities derived from the consumption of fishing products. On the other hand, hair is used particularly for forensic investigations.

As it is well known, food represents the main exposure to arsenic for the general population. The parameter most used for the arsenic risk evaluation is represented by the provisional tolerated daily intake which for the inorganic arsenic is set to 2,1 μg/Kg/die *(Joint Fao /WHO, 1989).* In the specific case of adult American population, the daily intake is estimated to be between 2 and 92 μg/die. Values higher than 515 ug/die and 174 ug/die respectively have been reported for some adult population subgroups. This data represents an important reference, particularly in the context of studies monitoring the population exposed to natural sources (contaminated water).

This with the aim to limit within a threshold, established by the international scientific community, the arsenic intake concentration in the population.

Toxicity

The oral LD5O has been estimated equal to 1-2 mg/Kg. Chronic exposition to inorganic arsenic can lead to negative outcomes that affect development of the reproductive, vascular, and hematological systems, causing specific fetal malformations such as defects of the neural tube. Arsenic exposition is a risk factor for skin tumors. An altered cognitive function has been observed in children chronically exposed to organic arsenic in Bangladesh. In case of severe intoxication due to organic arsenic, symptoms can include nausea, vomit, abdominal pain, laryngitis, or bronchitis. After an hour of exposure, possible issues in the circulatory system may also occur such as vasodilation, increased capillary permeability, diffused edema, consequent dehydration, and deadly shock.

The observed effects include blistering, peripheral sensitive and motor neuropathy, encephalopathy due to organic damage, and finally delirium and coma. Other symptoms include pancytopenia or hepatic steatosis, necrosis, or cirrhosis. In case of chronic arsenic intoxication, the most common symptoms are; hepatoxicity, hematotoxicity, neurotoxicity, muscle weakness, cutaneous irritability, white stripes on nails and palmar and plantar hyperkeratosis. Water intoxication, as observed in many developing countries, can cause cutaneous hyperpigmentation and vasculopathies in the inferior limb with non-frequent black foot gangrene cases. Chronic intoxication due to organic arsenic is indeed rare. It leads to a type of neurotoxicity due to sulfhydryl enzyme inhibition in the white and grey matter leading to organic damage.

Carcinogenicity

The International Agency for Cancer Research and the US EPA (1993), have classified inorganic arsenic as cancerogenic, including it respectively in group I and group A. The carcinogenic mechanism induced by inorganic arsenic is not well understood. However, exposition to this element can generate free radicals and other reactive species in the biological systems. Possible cancerogenic mechanisms include genotoxicity, oxidative stress, DNA repair inhibition, tumorigenesis promotion, co-carcinogenesis cellular proliferation and alterations in the signal transduction or DNA methylation.

Endocrine interferences

It has been highlighted how arsenic can act as a powerful endocrine disrupter, altering the gene regulation though the interaction with hormonal steroidal receptors [(glucocorticoids (GR), mineralocorticoids (MR) progesterone (PR) and androgens (AR)]. It has been proven that glucocorticoid metabolic alteration can negatively impact development and ultimately lead to adverse health outcomes. The endocrine disrupters play a crucial role in healthy development, in liver functioning and carcinogenesis. Daily intake of drinking water contaminated by arsenic has been associated with increased risk of hepatic cancer, therefore arsenic may be a significant risk factor in the onset of this pathology. Exposure to arsenic during fetal life (through the placental barrier) may determine gene mutations associated to severe pathologies including neurocognitive impairment, which may arise even decades after the maternal exposure to the element. Exposure to Arsenic has been commonly associated to cutaneous pathologies. Studies carried out in India, Bangladesh and Mongolia have found cutaneous lesions also in individuals exposed to concentrations of arsenic lower than 50 μg/L.

Metabolic interferences

Numerous studies have highlighted the significant association between exposition to high values of inorganic arsenic and type 2 diabetes (higher incidence and mortality for diabetes mellitus in the areas of Taiwan where the so-called black foot disease is endemic). Some studies suggest a relation dose-effect between cumulative exposition to Arsenic and diabetes prevalence even with low concentrations of arsenic in drinking water.

Findings

Lazio is among the regions with the highest level of arsenic contamination in drinking water. However, some districts are more involved than others. Viterbo province is currently raising the most concern, both for the number of municipalities involved and for the levels of contamination found. From 2004 until 2013 many areas were characterized by significant concentrations of arsenic in drinking water such as ASL RM F, ASL Latina, and finally a wide district including between 11 and 21 commons named "volcanic basin". Critical situations have arisen as private users have taken water from artesian wells, often non authorized or not reported, in which contamination by arsenic and vanadium has been found. Regular checks on this type of utilities are still complex, rare, and usually lead to emanation of trade union ordinances to ban the use of water for food reasons. For instance, in the areas of Pomezia and Ardea between 2009-2011, manganese, arsenic and fluoride have sometimes been found to be elevated and higher than the threshold levels recognized by the CEE. In some commons of the volcanic basin, relevant improvements have occurred since 2004 when levels of arsenic higher than 100mg/liters were registered. This was achieved thanks to the realization of arsenic abatement system or supply of water from other aquifers and strengthening of the hydraulic network.

Epidemiological investigations

The ASL Epidemiological Observatory has carried out a wide mortality study on a population living in 91 municipalities in Lazio. In the province of Viterbo, the municipalities have been classified according to three levels of exposition $5.2<As<10$ μg/L, $10<As<20$ μg/L, $20<As<80.4$ μg/L. Whereas the exposure in the Latina and Roma areas has respectively a different reference level: Latina $1.6<As<19.8$ μg/L – Rome $3.3<As<18.5$ μg/L. These different values were not correlated to the classification used in Viterbo. The link between arsenic exposure and the pathological risk associations was studied through a Multilevel Model with Poisson regression. The confounding variables included were tobacco individual expenses, socio-economic status and radon, relative risks (RR) and the IC 95% for pathologies associated to Arsenic. Considering as reference the population of the municipalities with the lowest levels of arsenic. The results were in accordance with the evidence available in literature. The investigation carried out in Lazio refers to areas with low to medium exposure (As<50 μg/L) whereas most studies available were carried out in areas with higher exposure (As>100 μg/L). The same results obtained in independent analysis for the provinces of Viterbo and Latina reduce the probability that some spurious results or confounding risk factors were included in the analysis. New studies with a higher level of accuracy have already been planned. The results point to an increased risk for lung and bladder tumors and for hypertension, cardiological pathologies, diabetes and BPCO. These risks were very strongly associated with the municipalities with much higher concentrations of arsenic.

In the group of municipalities situated in the province of Viterbo, in the period between 2005-2011, the average arsenic concentrations were found to be higher than 20μg/L. The incidence data seems to confirm the increased risk of ischemic damage in populations living in the areas with high exposure to arsenic. A significant increase in the number of aortocoronary by-pass surgery has been observed in the areas exposed such as Latina, Viterbo and Rome. In Amiata, in the municipality of Abbadia San Salvatore, higher than average mortality has been observed in men from causes including cancer and pneumoconiosis. Whereas women show increased rates of digestive system diseases and renal insufficiency. Analysis performed on hospitalized patients have shown a significant number of respiratory diseases in both sexes, in addition to stomach tumors and genital-urinary disease and pneumonia in men and chronic-obstructive pulmonary disease in women. In the south of Italy, theTaranto area is characterized by different industrial plants which are responsible for arsenic emissions. The national and European emission and sources inventory report has observed both a reduction of arsenic emission in water (from 1.463,7 to 655 kg/per year) and an increase in the air (from 24,1 to 186,2 kg/year) respectively in the periods between 2003-2010 and 2006-2010. The state of health of the Taranto population seems to be critically affected. The estimation of cancerogenic risk associated to inhalation of arsenic emitted by ILVA steel plants is less than 1: 100.000, even near the industrial area. Overall, 2,7% of cancerogenic risk because of inhalation is associated to Arsenic.

On the other hand, Sicily has defined the Gela district as "area at high risk of environmental crisis". Arsenic has been found in concentrations 25.000 times higher than the regulatory limits. In the soil, arsenic levels have been measured up to 1,5 times higher than the threshold contamination concentration of 20mg/kg. In the air, the average concentration of arsenic has been found to be lower than 6 ng/m3. In 2010, the refinery in Gela emitted 32 kg of arsenic and 1,52 tons in water. Mortality analysis has shown excess of deaths for all types of cancer, cardiovascular and cerebrovascular diseases in both sexes, for stomach tumors in men and for trachea, bronchi, and pulmonary cancer as well as ischemic diseases in women. In addition, the overall number of hospitalizations has risen due to an excess of all types of cancer in both sexes and for many other types of non – cancer related diseases. The type and valency of arsenic has been identified through urine analysis together with the genotypic analysis to identify functional polymorphism of genes involved in the arsenic metabolism and the evaluation of the H2AX histone phosphorylation to verify DNA damage. Finally, the analysis has also included the identification of cardiovascular risk markers such as the thickening of the carotidal intimal layer as ultrasonographic index of preclinical damage, the arterial compliance, calcium level, and the pericardium adipose tissue.

Conclusions

Arsenic is an environmental ubiquitous contaminant, and it can cause a series of pathologies which include cutaneous lesions, respiratory tract diseases (i.e., chronic bronchitis), nervous system pathologies (e.g., neuropathies, neurobehavioral disorders, memory loss, low IQ, attentional disorders), tumors (skin, lungs, bladder), effects on the reproductive system (pregnancy complications, fetal abnormalities, premature birth, low weight at birth) and cardiovascular and diabetic diseases. The identification of a chronic exposure due to contaminated waters can be carried out by analyzing arsenic forms present in the urine. This represents a useful individual monitoring system, which is often necessary for an accurate characterization of the exposure risk. Further investigations are needed in this field including more research about: organic arsenic contamination through food, more accurate information about potentially vulnerable populations, development of effective biomarkers and their validation at low doses, mechanisms of action of organic arsenic as endocrine disrupter and carcinogenic agent. It is also necessary to decrease the exposure of the population to arsenic within the limits established by international and national organizations. In this sense, if on one hand the study and control of aqueducts represents a fundamental prerequisite to carry out training and informational activities, at the same time raising awareness among employers and local administrators is necessary for future allocation of plants in areas adequately supplied so to avoid the use of private wells whose control is difficult due to the lack of regulation implementation. The system of self-control in the food industry should be integrated with water hygiene evaluations whereas the regional and local authorities should improve consumers knowledge and together with system's operators facilitate the construction and realization of reclamation and abatement work of arsenic in water. Avoiding at the same time, the possible usage of critical plants and buildings which can contribute to the spreading of toxic substances in the environment, soil, and aqueducts.

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