

Unusual aspects of Arsenic distribution, in the area of the industrial district of Scarlino (Tuscany): problems connected with sulfuric acid production from pyrite

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Abstract

The problem of Arsenic pollution, in the area of an industrial plant for the production of sulfuric acid from pyrite combustion, was studied. The plant is located in a former wetland, close to the sea, in the county of Scarlino, southwest of Tuscany.

The main Arsenic source was suspected to be the enormous stocks (1500000 tons) of hematite dust, residue of the pyrite combustion, and the stock of fine particles of pyrite, that were disposed on the soil, close to the plant, without control.

The presence of both continuous phreatic and artesian aquifers in the contaminated area, enhance the health risk for the population resident in the district.

Analytical data obtained at different depth were collected for Arsenic and other metals and compared with the historical records of the area.

Core samples collected in the area, showed a non-regular distribution of Arsenic, regarding both the depth and the distance from the plant.

Concerning the vertical distribution, the clay-rich soil, shows that Arsenic concentration reach the maximum peak at different depth from surface, with variable trends.

Horizontal distribution, shows a quite regular decreasing in the As concentration going far from the plant, but with the presence of hot spot at the distance of 4-6 km from the industry, where the As level were found very high (As>600mg/kg).

In order to understand this behavior, an analysis of chemical data for As and other toxicologically important metals, was proposed.

1 Introduction

Arsenic is a naturally occurring element, with an average abundance that ranges from 1 to 10 mg/kg (dried soil) in the earth crust^{1,2} ranking as the 20th abundant element. It is naturally associated with igneous and sedimentary rocks, particularly with sulfidic ores. In a growing number of cases the concentration of this metalloid has been found much higher than average all around the world, and most of the time these anomalies were due to anthropogenic activities. On the other hand, natural phenomena such as weathering, biological activity and volcanic activity, are also responsible for the emission of arsenic into environment, and its redistribution on earth's surface. The presence of As in the environment at high levels combined with its well-known toxicity has generated a large public concern and a widespread interest in the scientific community and government agencies for health and environment. Beside its acute toxicity, that is observable at relatively high concentration, recent researches have demonstrated that chronic exposure to low concentration of As, increase significantly the risk of skin and internal cancer.

In fact, despite its relative rarity, Arsenic appears in the first position in the USA CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act) National Priorities List (NPL), compiled by ATSDR (Agency for Toxic Substance and Disease Registry) and EPA, in which are posed the most significant potential threat to human health due to their known or suspected toxicity and potential for human exposure.

There is a general agreement that the most anthropogenic input is due to industrial operation (smelting, pesticide production and use, pyrite ores processing, dumping of hazardous substance and fossil fuels combustion) even if still debated is the extent to which man's activities contribute to the overall arsenic cycle. In many cases soil and sediments contamination results the first evidence of the occurred Arsenic pollution.

In order to understand the diffusion routes of Arsenic in the environment and its biogeochemical cycle, a large number publication on its chemistry in soil and ground water have been produced. Recently it became clear that mobility, toxicity and bioavailability of Arsenic is strictly depending on its chemical form or "species" and that the chemistry of this metalloid is strongly affected by the redox condition of the medium in which it is present. In particular it is known that reduced inorganic Arsenic, arsenite (As⁺³) is more toxic and more mobile than Arsenate species (As⁺⁵), and that Arseno-organic compound are the less toxic (usually are produced as detoxifying species by living organisms)^{3,4,5}.

It is well known that wetlands are now considered fundamental for an incredible number of living organisms, and that these delicate ecosystems need a correct management. On the other side, in the past, all around the world, wetlands were mostly seen as areas sequestered to the human productive use, and have been used as repositories for sewage sludge, industrial wastes and mine wastes⁶.

The aim of the present project is to start the study of a site, the Scarlino Plan, located in the south west of Tuscany, in which the soil presents high level of

Arsenic. In this area, a partially filled wetland, close to the sea, in the 1962 was installed a powerful plant for sulfuric acid production from pyrite combustion, using the ores found in the mine-field (Colline Metallifere), far about 15 km west from this site.

This site presents some interesting features that could help to understand the general mechanisms of Arsenic diffusion. Consequently, this could help to discern between different hypothesis about high Arsenic levels in the Scarlino plan, which potentially has been directly and/or indirectly impacted, by pyrite processing wastes and/or by the long distance transportation of As-rich sediments from the minefield, respectively.

The re-use of these polluted area, both for industrial and residential scope is considered as a priority for the local administration. Consequently, understanding and solving the problem of the wide Arsenic dispersion is fundamental for a correct and safe remediation.

2 History of the site

In Figure 1 is reported the map of the area, from which is possible to observe the position of the industry in respect to the other natural and anthropic structure of the Scarlino plan.



Figure 1: Topographic map of the Scarlino plan and its relation with Tuscany and Italy.

Letters show the main, natural and anthropic, structures of the area:

A) Pyrite cinders waste stock (hematite); B,C) Fine pyrite particle and Pyrite enrichment sludge stocks; D) Sulfuric Acid plant area; E) Titanium dioxide plant area (Huntsmann-Tioxide); F) Former pyrite cinders waste stock; G) residual wetland. The two watercourse are the Pecora river (H) and the Canale Allacciante (K). The town of Follonica is visible on the left. The medieval town of Scarlino is outside the map. The area comprises between the red curves presents average As concentration > 100 ppm.

It is important to note that the sulfuric acid plant have been located in a former wetland. This wetland was submitted to a gradual and partial filling starting from 1830. A residual pond is still present in the terminal part of the area, close to the sea. The engineering project for filling was completed with the construction of a channel, called “Canale Allacciante”, that was collecting the water of creeks coming from south and the partial canalization of the Pecora River coming from north. These two watercourses delimitate the area, which has been found polluted with arsenic. Letters A, B, and C show the storage areas for the sulfuric acid process wastes. Letter E shows a former waste storage that now is remedied. The whole area present a groundwater stream, that flows at variable dept, from 1 m under the surface just in the coincidence of the plant and the waste stocks, to some meters going far from the industrial site. This groundwater is resident in sand lenses that are present in the soil, which is mainly formed by clay mineral.

The main waste stock (A) is formed by about 2×10^6 metric tons of hematite cinder, coming from pyrite combustion. This enormous amount of material has been disposed on the ground without any protection. Moreover, this mass subsides of at least 6 m under the previous ground level and the groundwater soaks it completely. From analysis performed by current owner of the plant, the Nuova Solmine Company, results that average As concentration in this material is 450 ppm. This means that the As contained in the cumulus is about 900 kg. Fine Particle of Pyrite (FPP), contained in the milling dusts and in the ores-enrichment sludge, constitutes the other two stocks of residues wastes (B,C). These wastes were also disposed on the ground without any protection for the groundwater.

2 Experimental

Cores of native soil were collected in a 9 km² of country area, around the Sulfuric Acid Plant (SAP). Cores of waste were collected in different point of the waste stocks. The cores dimension, length and diameter, were 6 m and 10 cm respectively. Total As, Pb and Zn concentrations were determined on dried soil or waste samples, collected at different depth of the cores. Samples were homogenized and digested with nitric acid, by graphite furnace – atomic absorption spectroscopy (GF-AAS). Technicians of the chemical laboratory of the Nuova Solmine Company, which is the owner of the SAP, conducted both sampling and measurements^{7,8}. In this paper, for our convenience, we reported the As concentration in ppm units, where ppm is corresponding to mg/kg of dried material.

3 Results and Discussion

3.1 Horizontal profile for As, Pb, and Zn

In Figures 2A and 2B are reported the minimum and maximum concentration of Arsenic, registered in the soil cores respectively, as a function of the distance

from the plant. It is possible to observe that in both cases, on the average, As concentration was higher in the neighbourhood of the plant and lower far from the plant. The only exception regards a point located at about 3.5 km from the plant.

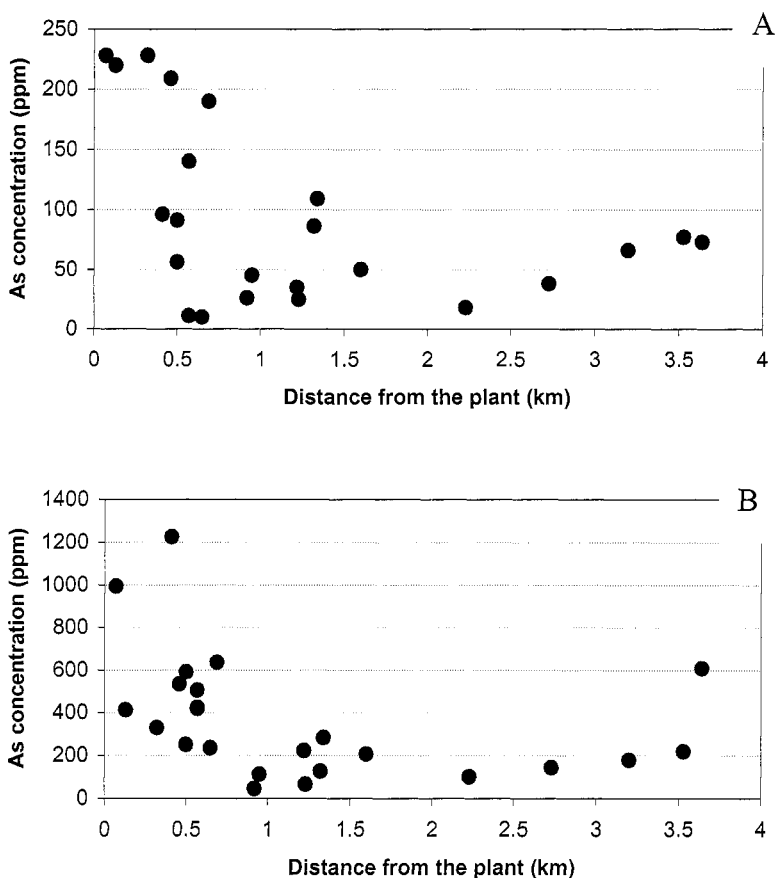


Figure 2: Two-dimensional plots obtained reporting the As concentration in respect to the actual distance from the plant. The abscissa values were reported regardless the geographical coordinates. A: maximum As level in soil cores; B) minimum As level in soil cores

This kind of behavior is compatible with a diffusion of the element from the Arsenic source that can be identified with the three production waste stocks located in close proximity of the plant. Three different diffusion routes can be hypothesized: 1) waterborne transportation of ionic forms of As by the groundwater; 2) airborne transportation of As_2O_3 containing cinders; 3) mechanical dispersion of hematite cinders for country roads sanding.

The first route is probably the most important. In fact, the freatic groundwater directly absorbs both the Hematite and FPP stocks at about 1.5 m of depth. Under anaerobic conditions, the As could become more soluble as arsenite and migrate. The migration stops when different redox and/or mineralogical conditions occur and As can be adsorbed again on the clay mineral surface.

This hypothesis is confirmed by the fact that groundwater, sampled in correspondence of the waste stocks contains high As concentration (up to 1200 ppb). Moreover, high As values were recently found in the water of wells that are about 400m far from the stocks.

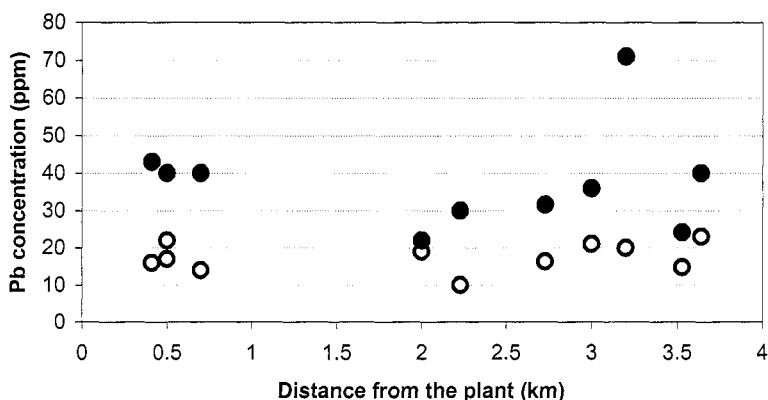


Figure 3: Two-dimensional plots obtained reporting the Pb concentration in respect to the actual distance from the plant. The abscissa values were reported regardless the geographical coordinates. Empty circles indicates the minimum Pb level in soil cores; Filled circles indicates the maximum Pb level in soil cores.

In order to compare the behavior of Arsenic with other inorganic pollutants, for the present discussion we will take in account the levels of Zinc and Lead. In the case of these last metals, the behavior appears completely different. In fact as it is shown in Figure 3, the Pb concentration in the soil, remains almost constant with the increasing distance from the plant. Also the Zinc concentration does not vary significantly, between points located in the proximity of the plant and points located far from the plant (Figure 4). This strongly suggests that the mobility of Arsenic is much higher in respect to other metals. These data confirm the findings of other authors in analogous cases.

As reported elsewhere by Marchettini et al.⁹, these data also confirm the fact that the Arsenic anomaly was probably due only to the dispersion of the metalloid in the environmental matrix from the pollution sources, which are represented by the piles of waste coming from sulfuric acid production by pyrite ores.

Unfortunately from available data, the actual mechanisms for As pollution in the Scarlino plan are not completely understood, and a deeper investigation

about different aspects of its diffusion is needed. In particular, a more accurate sampling of the soil should be conducted, in order to improve the statistical significance of the data.

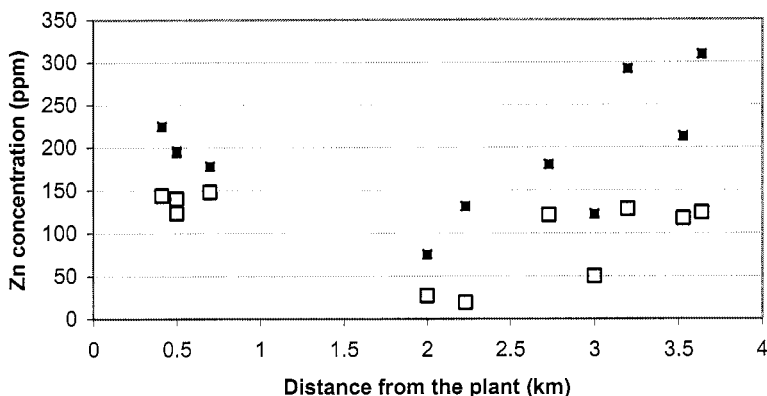


Figure 4: Two-dimensional plots obtained reporting the Zn concentration in respect to the actual distance from the plant. The abscissa values were reported regardless the geographical coordinates. Empty squares indicates the minimum Zn level in soil cores; Filled squares indicates the maximum Zn level in soil cores

3.2 Vertical profile of Arsenic, Zinc and Lead

The analysis of the vertical profile of concentrations, also, reveals a different trend for Arsenic in respect to Zinc and Lead.

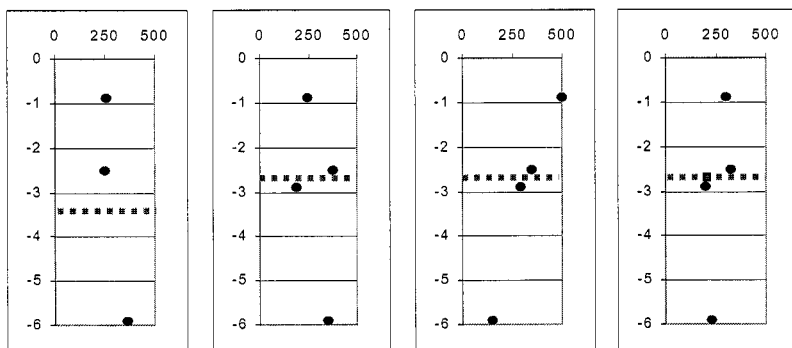


Figure 5: Depth profile for Arsenic. Cores were collected in four different points of the waste stock of fine pyrite particle. This kind of waste was derived from the milling plant. The red horizontal bar indicate the thickness of the waste stock in the sampling point. Below this line native soil was collected.

In Figure 5 the concentration of Arsenic at different depth is reported. It is possible to observe that the level of this metalloid does not decrease significantly below the limit of the waste pile. It is evident from the figure that high As values can be found also in the native soil under the pyrite waste.

It is also important to note that the values found for Arsenic in the native soil are well above the limits considered by the Italian law, which are 10 ppm and 50 ppm for residential (RD) and industrial (ID) destination of the site respectively.

On the contrary, the concentration of Lead and Zinc drop suddenly to very low values just at the interface waste/soil and remain low in the deeper layer (Figure 6A and 6B). The concentration of Lead and Zinc, in the soil collected under the FPP waste, was comparable with the natural background of the unpolluted soil. This means that migration of the two metals is blocked. The vertical profiles, reported in this work, reflect the higher ability of Arsenic to diffuse in different environmental matrix. This mobility is particularly high in reduced environment, in which the Arsenite form, which is also the most toxic, is prevalent.

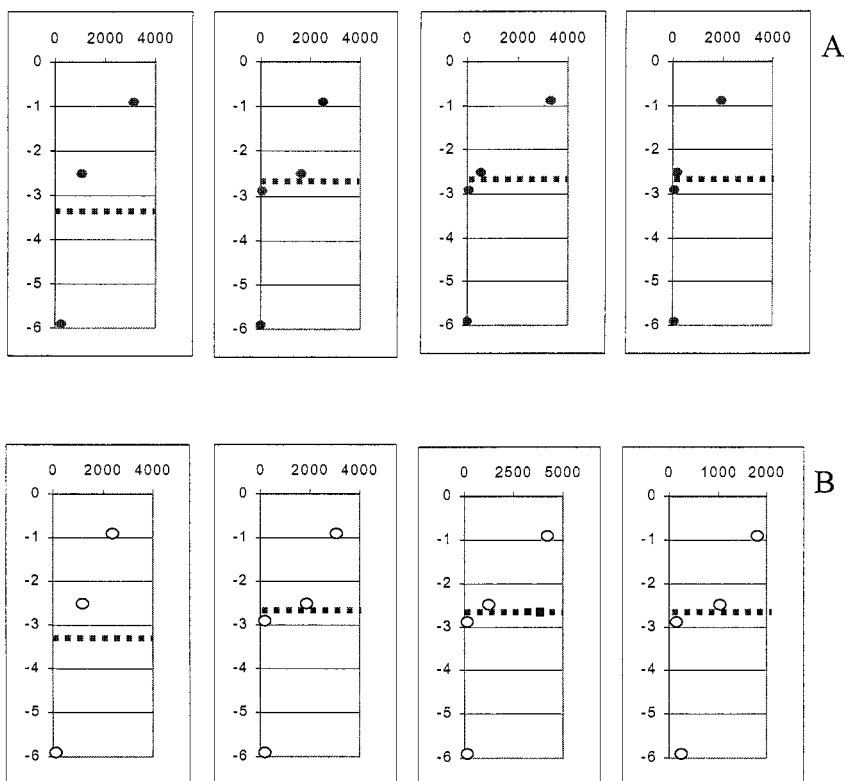


Figure 6: A) Depth profile for Lead. B) Depth profile for Zinc. Analysis was conducted on the same samples which were used for As measurements. The red horizontal bar indicate the thickness of the waste stock in the sampling point. Below this line native soil was collected.

In the case of Lead and Zinc the threshold concentration in the soil considered by the Italian law are the following: Pb, 100 ppm (RD) and 1000 ppm (ID); Zn, 150 ppm (RD) and 1500 (ID). In both cases, the actual concentration found in the soil under the waste area is well below the two limits.

These, analytical evidences, suggest that the remediation project of the site and the subsequent use that is considered for the site, must accurately take in account the different behavior of the various pollutant. For example, in the Scarlino case, the sole removal of the pyrite processing waste, could give a safe remediation for Zinc and Lead, but not for Arsenic, which migrated across wider areas.

Conclusion

Industrial area presenting high Arsenic and heavy metals concentration, presents some peculiar features that have to be accurately taken in account, for the remediation projects and for the subsequent re-use of the sites. In particular, the analysis of the data suggests that Arsenic migrates across wider areas with respect to the area of the waste site, and this could lead to only partial remediation of the sites. In these cases a risk analysis must be conducted, in order to evaluate the impact of residual pollutant concentration on the resident population and/or the environment.

From available data, the actual mechanisms for As pollution in the Scarlino plan cannot completely be understood, and a deeper investigation about different aspects of its diffusion is needed. In particular, a more accurate sampling of the soil should be conducted, in order to improve the statistical significance of the data. At the same time a higher number of measures for each core sample, together with As speciation and an accurate mineralogical study of the soil extracted, will better account for the basis of the vertical distribution of Arsenic. Moreover a microbiological study, in order to understand how the mobilization occurs, should be conducted.

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