High soil as level in the area of a plant for pyrite processing: natural anomaly vs pollution hypothesis

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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. Horizontal distribution, shows a 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>600 mg kg^{-1}). Other irregularities in the vertical distribution of As concentration in the clay-rich soil, were found.

This induced some chemists and geologists to propose the hypothesis of Natural origin of Arsenic anomalies, due by the fact that the site under study is down stream to a large area that is characterized by large metal mineralizations.

On the other hand, several facts induced to think that hematite dusts that are residue of the pyrite combustion, and the stock of fine pyrite particles that have been disposed on the soil close to the plant, without control, are the major responsible for the widespread pollution.

Analytical and hydrological data, were collected and geo-chemical map were produced in order to verify which one of these two hypothesis was corrected.

Keywords: arsenic pollution, pyrite processing, wetland, anaerobic soil

Introduction

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 wastes (Masscheleyn *et al.,* 1992).

In the present case the wetland of Scarlino, a medieval town, located in the south west of Tuscany, Italy, were partially filled in subsequent stages starting from 1830. In 1962, in this area was located a big plant for the production of sulfuric acid from pyrite combustion (SAP), and since that time, the waste of the process have been stored in the ground without any form of control or protection. The pyrite ores were produced in a minefield of the inner lands (Colline Metallifere) that are located about 20 km east of the site.

In the last 20 years it has been clear that a large area around the industrial site was strongly contaminated by Arsenic compounds (Aquater, 1985; Nuova Solmine, 1997). This finding was not surprising taking into account that about $2x10^6$ metric tons of hematite cinders (HC) are still disposed in the ground. Considering an average concentration of about 450 mg kg^{-1} of Arsenic, the total mass of this metalloid, potentially available for diffusion in the environment, is of about 900 metric tons. Moreover other stocks of sulfuric acid production wastes are also disposed in the ground (see below).

The unusual aspect of the Arsenic contamination of this industrial site concerns both its horizontal and vertical distribution in the soil. In fact, despite the fact that generally the Arsenic concentration decreases, with the increasing distance from the plant, some remote sample shows high concentration, and the vertical profile of the As level is very different from point to point.

These features induced some geologists and chemists to formulate the hypothesis of the natural occurring As contamination (Nuova Solmine, 1999; ARPAT, 2001). This hypothesis was based on the idea that, in the past, the river coming from the mining district, upstream the industrial site, transported contaminated sediments which contributed to form the present alluvial Scarlino plan (SP).

On the other hand, recently, several evidences show that as mobility in the soil can be very high in the appropriate redox conditions (Aurilio *et al*., 1994). In anoxic systems, such as wetlands, redox-sensitive elements such as Fe, influence As and other contaminant cycles, and this behavior is fundamental in the present case of hematite dust wastes (Stumm and Sulzberg, 1992). The presence of continuous freatic aquifers at an average dept of 1.5 m, in the area can be the key point for understanding the diffusion of the contaminants, but other diffusion routes must be considered.

It is also important to note that, beside mobility, also bioavailability and toxicity of As are strictly depending from its oxidation state. For example the less toxic arsenate is frequently found under oxic condition, whereas arsenite, that is more toxic and mobile, and arsenic sulfides occur under anoxic conditions (Cullen and Reimer, 1989; Smith *et al*., 1998).

In this paper an analysis of as concentration data, in the soil surrounding the SAP, was conducted, in order to understand the possible mechanisms of pollution in the area by this metalloid. 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.

Materials and methods

Cores were collected in a 9 km^2 of country area, around the SAP. The cores dimensions, length and diameter, were 6 m and 10 cm respectively. Total As concentration was determined on dried soil samples, that were homogenized and digested with nitric acid and sulfuric 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. Iso-concentration map was obtained by Surfer 7.0 package (Golden Software, Inc.), using the kriging method for data interpolation. In this paper, for our convenience, we reported the As concentration in mg kg^{-1} units, where mg kg^{-1} is corresponding to mg/kg of dried material.

Results and discussion

Study 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. 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” (CA), that was collecting the water of creeks coming from south and the partial canalization of the Pecora river (PR) 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 $2x10^6$ 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 mg kg^{-1}. 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.

The main watercourse in the area is the Pecora River (PR), which flows in the Tyrrhenian sea after a course of 26 km, with approximate direction East-West. In its first tract, the river flows through a mineralized area called the “Colline Metallifere” (Metal Hills). Here, since a long time (Etruscan age and Medieval age), metal ores were extracted.

As reported above, before the 1860 the Pecora river was flooding in the Scarlino lake, a wetland that was partially filled by the alluvial sediments of both the PR itself and of the southern artificial channel (CA).

The hypothesis of the natural occurrence of As pollution in the area derives from this type of filling. In fact, it is supposed that subsequent floods of the PR could stratify Arsenic rich sediments, coming from the mineralized district.

Vertical Distribution of Arsenic

The analysis of the vertical distribution of the As in the soil is very interesting for the irregular profile that it assume at different distances form the industrial site. For this analysis, 6 m cores were collected and the concentration of As was measured at different depth (0.1 m, 2.90 m and 5.9 m). In some cases measurement occurred every 1 m of depth (0.1 m, 1.90 m, 2.90 m, 3.90 m, 4.90 m, 5.9 m).

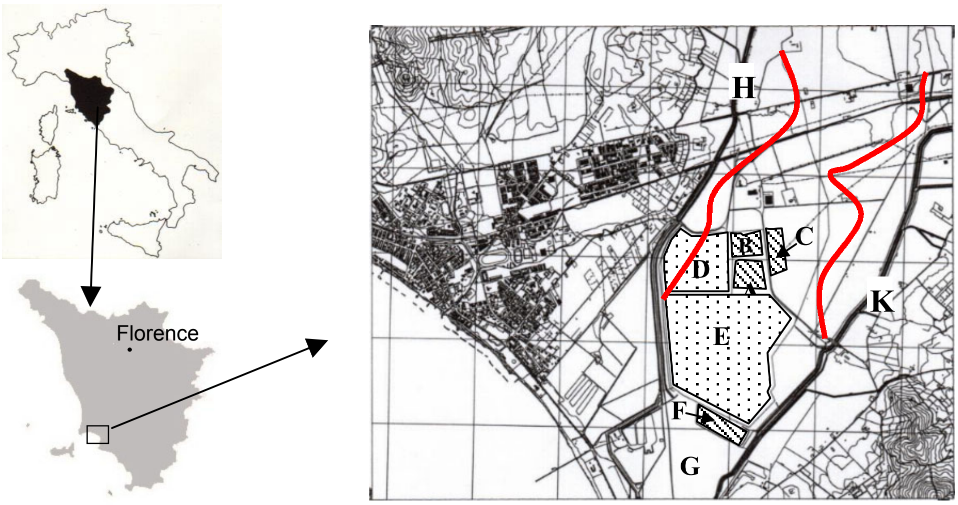

Figure 1 Topographic map of the Scarlino plan and its relation with Tuscany and Italy. Letters show the main, natural and anthropic, structures of the area. A) Pyrite cinders waste stock (hematite); B, C) Fine pyrite particle and Pyrite enrichment sludge stocks; D) Sulfuric Acid plant area; E) Titanium 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 mg kg^{-1}.

From Figure 2 it is possible to observe the non-homogeneous profile of As concentration from different samples. In some cases the maximum concentration was recorded on the surface, in other cases the As peak occurs at various depth. These different findings were not easily interpretable, without considering high As mobility and different absorption/desorption properties of Arsenic in correspondence of different soils and their microenvironment.

As reported in other well studied sites (Ahmann *et al.,* 1997; Aurilio *et al.,* 1995) the mobilization of As at the sulfuric waste storage occurs in anoxic condition with the participation of microbial activity. In this case the importance of ground water in the early diffusion of As is also known.

Horizontal Distribution of Arsenic

In Figure 3 are reported the iso-concentration contours for As, together with the 26 sampling points recorded in at different distances from the sulfuric acid plant. From the location of the points, it is not possible to individuate a pre-arranged grid, or a particular sampling strategy. This was also due to the fact that sampling was conducted in two different periods. However, sampling points were sufficiently distributed in the area of interest.

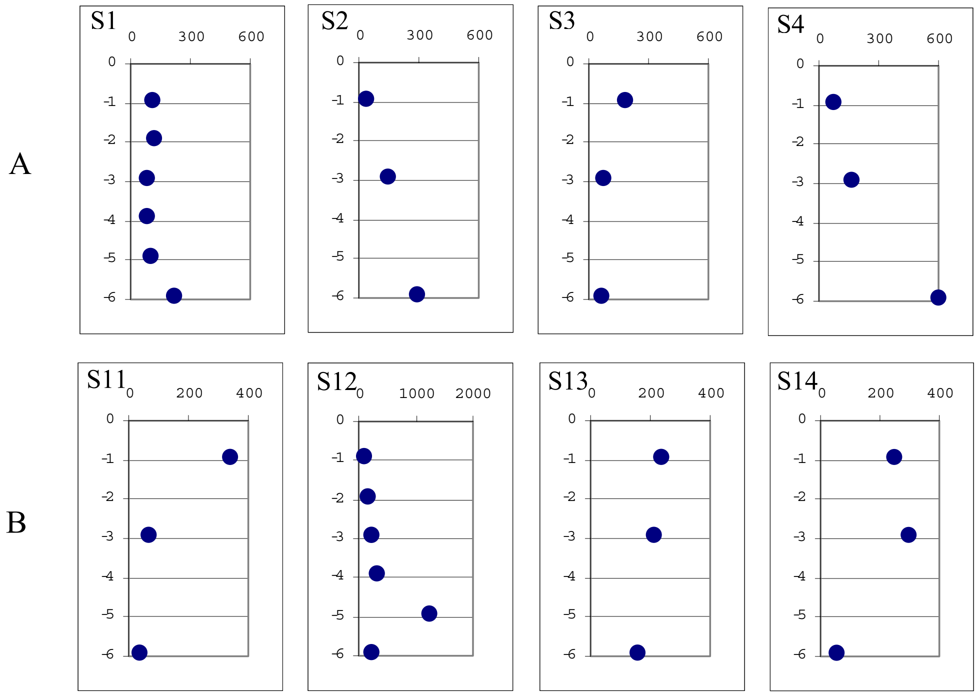

Figure 2 Vertical profile of the As concentration in the soil cores sampled in the Scarlino plan. Group A (S1, S2, S3, S4) concern samples collected in an area about 3 km far from the SAP (north). Group B (S11, S12, S13, S14) concern samples collected in proximity of the SAP. All the samples, except S2, are located inside the area with average As level >100 mg kg^{-1}.

Using these data, we can compare the hypothesis of a natural occurring As pollution (NOAP), with the other one in which As migration from the waste stocks (AMWS) is consider.

In the NOAP hypothesis, it was considered the average value of the vertical distribution of As for each sampling point. This kind of analysis induced to individuate a sinuous area, in between the PR and CA, in which the average As concentration was higher than 100 mg kg^{-1}. The location of the high level of As, could correspond to the ancient bed of the PR, consequently it was conceivable that As-rich sediments transported during flooding, from the mining district, was accumulated in the former wetland. This point of view is also used to explain the vertical distribution of As and the high level of As in point S4.

However, other evidences cannot fit with this kind of analysis. In fact, from other studies (Protano *et al.,* 1999), it is evident that the metal and metalloid concentration in the PR sediments is uniformly decreasing in the last 10 km of the course. Moreover in the upstream tract, closer to the plant, the As concentration is similar to the natural background of the Tuscany for alluvial basin (7-11 mg kg^{-1}). This means that now, As is not involved in a long distance transportation with sediments by the surface watercourse. Considering the geological time, it is difficult to think that present PR sediments should strongly differ from the ones of the 19th Century. Consequently, there is a very low possibility that high As concentration should be due to the filling of wetland by material accumulated during the PR floods.

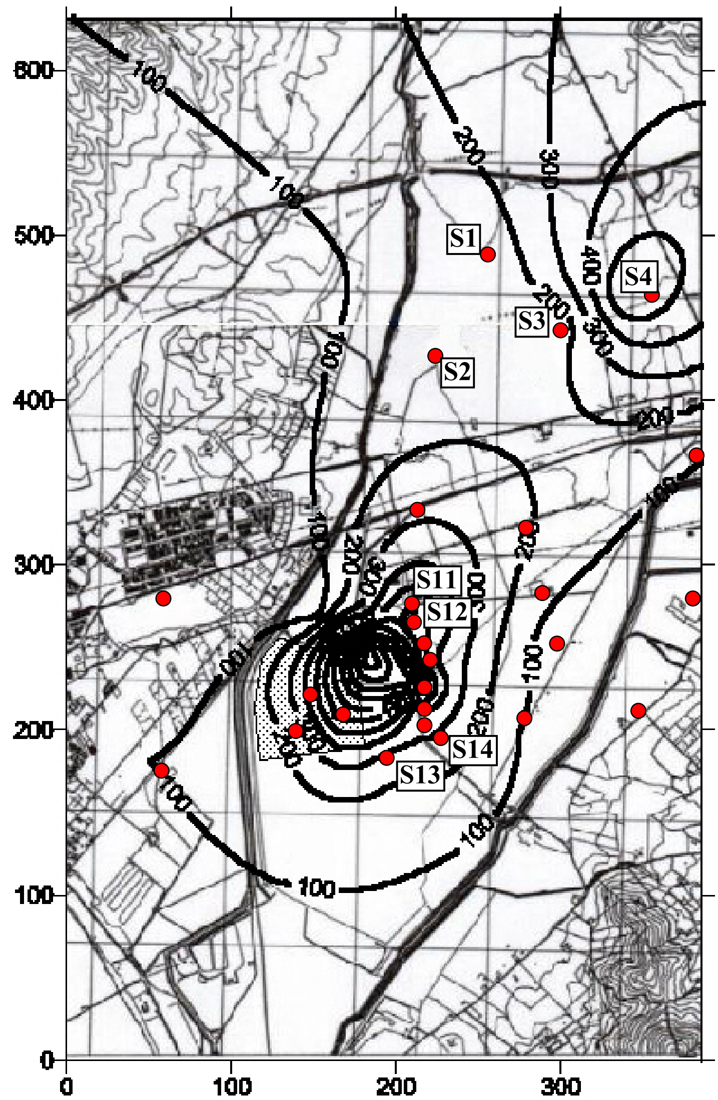

Figure 3 Contour plot of the As concentration, obtained using the maximum As value recorded in the 6 m cores. The isopleths are superposed to the topographic map of the Scarlino plan. Red circles represent the sampling points. Labeled are the points discussed in Figure 2.

Another evidence that contradicts the NOAP hypothesis concerns the concentration of As in the marine sediments. In fact, in the tract of sea in correspondence of the PR mouth, low As levels were found, both in surface and in depth layers (Leoni and Sartori, 1997). This confirms the scarce transport of the metalloid by the PR.

These two evidences can be combined with the observation of the contour map that can be drawn by using As data obtained from the core samples Figure 2. In this case, the iso-concentration curves were drawn using the maximum As level found in the cores, independently by the depth at which it was recorded.

It is easy to understand that the highest concentrations recorded in the soil were found exactly in the SAP area and that As level decreased regularly going far from the plant. The only exception was the, already mentioned point S4, for which the anomalous As level was 609 mg kg^{-1} at 5.9 m of depth. In light of these data it is obvious that the NOAP hypothesis became quite weak. In fact it is unlikely that the PR sediments concentrated As just under the plant and in the proximity of the waste piles.

The As pollution in the Scarlino plan is, therefore, more probably due to the industrial activity of sulfuric acid production. The dispersion of the metalloid in the soil probably started by the waste stocks (cinders of pyrite combustion, FPP and sludge) that were disposed in the ground without protection. 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 soaks both the Hematite and FPP stocks at about 1.5 m of depth, and here in anaerobic condition, the As could become more soluble like arsenite and migrates. The migration stops when different redox and/or mineralogical condition occurs 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 400 m far from the stocks.

Conclusion

On the basis of the reported data, the hypothesis of natural occurring high level of As in the Scarlino plan, has to be considered highly improbable. Therefore, we conclude that the dispersion of the metalloid in the environment is only due to sulfuric acid production from pyrite ores processing. Unfortunately from available data, the actual mechanisms for As pollution in the Scarlino plan is 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 statistic meaning 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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