

BEDROCK MINERALOGY VERSUS SOIL TOTAL ARSENIC, SPECIATION AND PLANT AVAILABILITY

DEJENE AYELE¹, ABERRA MOGESSIE², KEBEDE HAILU
and WALTER KOSMUS³

¹Jimma University, College of Agriculture, P.O. Box 307, Jimma, Ethiopia;

²Institute of Mineralogy and Petrology, Karl-Franzens-University of Graz, Universitaetsplatz 2,

A-8010 Graz, Austria; ³Institute of Chemistry, Analytical Chemistry, Karl-Franzens
University of Graz, Universitaetsplatz 1, A-8010 Graz, Austria

ABSTRACT

The total arsenic content of a soil collected from Gasen (a village in SE Austria) was determined by using a Graphite Furnace Atomic Absorption Spectrometer (GF-AAS). The level determined was about 3000 mg kg⁻¹ which was extremely high. Scanning-Electron-Microprobe (SEM) analyses on underlying bedrocks confirmed that arsenic in the soil is of geogenic origin and arsenopyrite is the main mineral from which it is derived. Various other sulfide minerals were also observed to exist in contact with arsenopyrite among which pyrite and chalcopyrite are the predominant. Cyclic voltametric investigations of the Modified Carbon Paste Electrodes of pyrite and chalcopyrite indicated that, the co-existence of these minerals with arsenopyrite enhances the extent of its chemical weathering. Although such a high level of arsenic was known to exist in the soil, its phyto-availability remained comparably low. The mean value of arsenic concentration in the above-ground organs of the mixture of grasses grown on the soil was 1.7 mg kg⁻¹, which is very low relative to the high arsenic level. Results obtained from a sequential leach study revealed that the fraction of arsenic bound to the water-soluble and exchangeable phases, account for only about 0.5% of the total and the low level of arsenic in the grass mixture is partly attributed to the low level of arsenic in these phases.

INTRODUCTION

Arsenic, although known to be essential for life in small amounts (NAS, 1977), becomes toxic for plants, animals and humans when ingested in large amounts (NAS, 1977; Scott et al., 1995; Tang and Miller, 1991; Galbraith, 1995; Carbonell-Barrachina et al., 1998). Arsenic has been recognised through the years for the toxic properties of some of its compounds. The word 'arsenic' has become synonymous with 'poison'. It affects the skin, and in its most severe form causes skin cancer (Polmear, 1998). During its circulation in the environment, arsenic can reach into the human body via plant uptake from soils, by drinking arsenic contaminated surface or ground water, by dermal contact and by inhalation (Ng et al., 1998).

Arsenic in soils originates either from the weathering of underlying parent material or from anthropogenic sources such as mining activities, use of arsenical pesticides, application of fertilizers, irrigation, dust from the burning of fossil fuels, and disposal of industrial and animal waste. A wide range of arsenic content, with an average of 5-6 mg kg⁻¹, has been reported for soils that contain arsenic at concentrations that are reflective of the parent rock material from which they were formed. In the native state arsenic exists as the sulfide ores: orpiment (As₂S₃) and realgar (AsS), or the arsenides or sulfarsenides of heavy metals, especially arsenopyrite (FeAsS). The arsenic levels in soil enriched in these ores are often higher than in normal soil (Yan-Chu, 1994).

Arsenic is a characteristic element in Austrian soils (Tahlmann et al., 1989). Even though typical amounts of arsenic in natural uncontaminated soils varied from 5 to 6 mg kg⁻¹ (Bhumbla and Keefer, 1994), certain soils of the low-lying parts of the country contain higher concentrations. At Gasen (a rural area located in SE Austria) the level of arsenic in the soil is found to be exceptionally high, about 3000 mg kg⁻¹. In spite of such a high level, no toxic symptom due to arsenic is observed on plants, animals or people living in the surrounding. This paper reports results of studies carried out to understand the origin of such a high level of arsenic in the soil, its phyto-availability and form of binding in the soil.

MATERIALS AND METHODS

Sampling

The random and grid sampling techniques were respectively used for the collection of soil and plant samples.

SEM analysis

Minerals in underlying bedrocks were identified using a combination of reflected light microscopy and SEM analysis. The analysis was carried out on a JEOL-6310 SEM with an attached link energy dispersive system (EDX) and a microspec wavelength dispersive system (WDS) using 20 kV accelerating voltage and counting time of 100 sec calibrated on cobalt.

Mineralisation and arsenic determination

Soil samples were air-dried and allowed to pass through a 2-mm sieve. Arsenopyrite, pyrite and chalcopyrite minerals were pulverised in a ball-mill. Accurately weighed 0.5 g aliquot of the soil or mineral sample was transferred to a high-pressure Tetrafluormethaxil (TFM) microwave digestion vessel and mineralised by using a mixture of, 4.0 ml of sub-boiling distilled HNO₃, 1.0 ml

30% (w/w) H_2O_2 , and 2.0 ml 40% (w/w) HF in a microwave-heated closed-vessel digestion apparatus. The time-power heating programme applied is given in Table 1.

Table 1. Microwave-heated closed-vessel heating program used for the mineralization of soil and mineral samples

Step	1	2	3	4	5	6	7	8	9
Power (Watt)	250	0	250	0	450	0	600	500	vent
Time (min)	2	0.5	10	0.5	5	0.5	7	7	2

Plant samples were rinsed with Milli Q+ water, freeze dried and milled in an Ultra-Centrifugal mill. Accurately weighed 0.2 g portions of the processed plant samples were mineralised in a microwave-heated closed-vessel digestion apparatus by using 3.0 ml sub-boiling distilled HNO_3 and 0.5 ml, 9.8 M H_2O_2 . The time-power heating programme applied is given in Table 2.

Table 2. Microwave-heated closed-vessel heating program used for plant mineralization

Step	1	2	3	4	5	6	7	8	9
Power (Watt)	250	0	300	0	400	0	500	600	vent
Time (min)	2	0.5	5	0.5	10	0.5	5	4	2

Total arsenic in all samples was determined from appropriately diluted solutions of their respective digests by using a GF-AAS.

Weathering

Informations on the electrochemical weathering behaviors of arsenopyrite ($FeAsS$), pyrite (FeS_2) and chalcopyrite ($CuFeS_2$), and the influence of the co-existence of pyrite and chalcopyrite on the release of arsenic from arsenopyrite were acquired from cyclic-voltametric investigations carried out in ranges of potentials commonly encountered in soils on a Modified-Carbon-Paste-Electrode of each mineral and by determining the arsenic levels in the leachates of various combinations of pyrite and chalcopyrite with arsenopyrite.

Sequential leach speciation

The concentration of arsenic in the various fractions of the soil: water soluble, exchangeable, bound to carbonates, amorphous and crystalline Fe-oxide, organics

and sulfides, silicates and residual oxides was determined by using the schemes developed by Tessier et al. (1979) and Hall et al. (1996).

RESULTS AND DISCUSSION

Scanning Electron Microprobe (SEM) studies revealed that Arsenopyrite (FeAsS) is the most common mineral in the study area and is the main source for the soil arsenic. It occurs as a few centimeter long prismatic crystals often in paragenesis with pyrite. The arsenopyrite and pyrite structures are fractured and brecciated due to tectonic movements. The fractures are filled by other sulfide minerals among which chalcopyrite (CuFeS_2) is dominant. A representative image of the SEM analyses showing the association of arsenopyrite with pyrite and chalcopyrite is given in Figure 1.

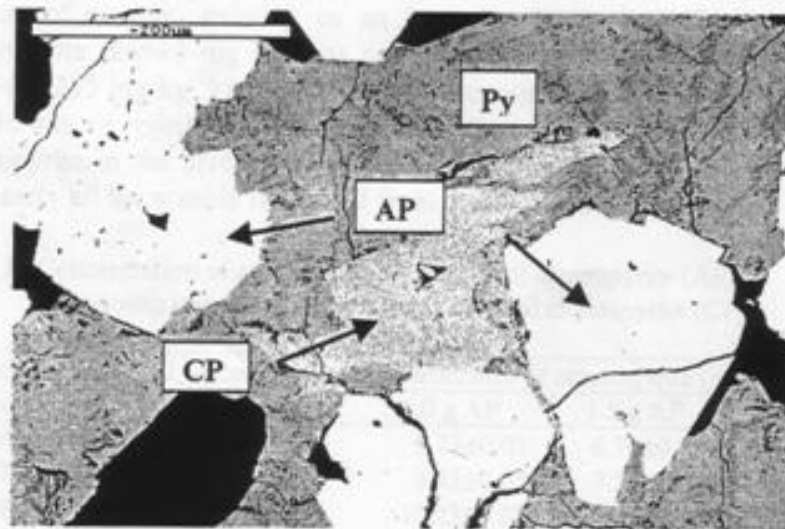


Figure 1. SEM image of arsenopyrite showing its association with pyrite and chalcopyrite. Pyrite (Py), Chalcopyrite (Cp), Arsenopyrite (Ap).

From the electrochemical and leach experiments, it seems that the release of arsenic from arsenopyrite seems to be highly influenced by the co-existence of other sulfide minerals in contact with arsenopyrite. Cyclic voltametric investigations of the minerals in the moderately acidic to moderately alkaline pH range and in the range of potentials usually encountered in soils revealed that chalcopyrite undergoes oxidation at a lower potential than arsenopyrite and pyrite to produce Cu^{2+} , Fe^{2+} , Fe^{3+} , S, SO_4^{2-} and various other oxidised forms.

Arsenopyrite on the other hand undergoes oxidation at a lower potential than pyrite to form Fe^{2+} , Fe^{3+} (or their hydroxides), H_2AsO_4^- , HAsO_4^{2-} , and SO_4^{2-} . Pyrite gets oxidised at a higher potential than chalcopyrite and arsenopyrite to form Fe^{2+} , Fe^{3+} , S, and SO_4^{2-} . Pyrite, being the most noble sulfide mineral, can influence the oxidation of arsenopyrite and chalcopyrite through galvanic coupling. Pyrite may act as the cathode and enhance the oxidation of arsenopyrite and chalcopyrite. Chalcopyrite on the other hand influences the weathering of arsenopyrite through its oxidation products. After the initial oxidation of chalcopyrite the earliest-formed free sulfuric acid and sulfates such as FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$ and CuSO_4 exert more strong oxidising effects on arsenopyrite, thus accelerating its oxidation.

Table 3 shows the level of arsenic released from one-week incubated pure arsenopyrite and arsenopyrite-pyrite or arsenopyrite-chalcopyrite mixtures. The level of arsenic in 0.5 g, 1.0 g and 1.5 g pure arsenopyrite leachates was nearly the same (about 7 mg kg^{-1}). This level was observed to increase in the leachates of the arsenopyrite-pyrite and arsenopyrite-chalcopyrite mixtures even when the quantity of arsenopyrite in the mixture is less than the pure one. The negligible amount of arsenic, existing as an impurity, in pyrite ($270 \pm 5 \text{ mg kg}^{-1}$) and chalcopyrite ($265 \pm 3 \text{ mg kg}^{-1}$) as compared to the concentration in arsenopyrite ($370900 \pm 265 \text{ mg kg}^{-1}$) indicates that the quantity of arsenic contributed from the dissolution of pyrite in the arsenopyrite-pyrite or from the dissolution of chalcopyrite in the arsenopyrite-chalcopyrite mixture leachate is also negligible and nearly all the arsenic is derived from arsenopyrite dissolution.

Table 3. Concentration of arsenic in the leachates of arsenopyrite (AP) mixed with various levels of pyrite (PR) and chalcopyrite (CP)

Quantity of PR and CP mixed with AP	Conc. of As in the leachates of arsenopyrite (mg/kg)		
	0.5 g AP	1.0 g AP	1.5 g AP
Pure AP	6.75±0.02	6.73±0.03	6.74±0.06
0.5 g PR	10.12±0.03	9.95±0.07	9.22±0.01
1.0 g PR	14.43±0.01	10.23±0.03	10.03±0.01
1.5 g PR	16.73±0.02	15.86±0.04	11.30±0.05
0.5 g CP	7.37±0.05	7.02±0.03	6.89±0.02
1.0 g CP	8.75±0.03	8.14±0.03	7.67±0.05
1.5 g CP	11.31±0.01	10.05±0.01	8.23±0.02

This indicates that chalcopyrite and pyrite, when exist in contact with arsenopyrite, are able to enhance its dissolution and thus the release of arsenic into the soil. The higher dissolution of arsenopyrite in presence of pyrite and chalcopyrite could be an electrochemical corrosion process in which dissolved species such as Fe^{3+} and Cu^{2+} get reduced at the arsenopyrite surface behaving as an anode and arsenopyrite as the cathode. In spite of the considerably high arsenic level in the soil, its phyto-availability remained comparably low. The mean

value of arsenic concentration in the above-ground organs of the grass mixtures was 1.7 mg kg^{-1} . The highest concentrations measured were in the 3 mg kg^{-1} range (terrestrial plants growing at uncontaminated sites usually contain $< 0.2 \text{ mg kg}^{-1}$ arsenic, Cullen and Reimer, 1989); where this accounted for 9% of the overall determinations. Although some plants are tolerant to higher concentrations of arsenic in the soil, normally many plants show growth disturbances if the arsenic concentration in the soil exceeds 2 mg kg^{-1} .

Total arsenic concentration in samples of four predominantly abundant plant species in the pasture was determined to see if there is species-specific accumulation or not. However, observed differences were not dramatic; *Anthoxantum odoratum*, 4 mg kg^{-1} ; *Dactylis glomerata*, 1.6 mg kg^{-1} ; *Plantago lanceolata*, 5.9 mg kg^{-1} ; *Taraxacum officinale*, 0.5 mg kg^{-1} .

Results of the sequential leach speciation experiment indicated that the concentration of arsenic in the water soluble and exchangeable fractions of the soil (which are generally considered to be the most mobile and immediately bioavailable forms) account for only about 0.5% of the total arsenic. The rest of the arsenic exists in the recalcitrant fractions. This could be a reason for the less phyto-availability of arsenic in the Gasen soil. Since arsenic phyto-availability is a result of a number of soil properties and plant species, it cannot be attributed to a single factor. The low level of arsenic in the labile fractions can not be taken as the sole factor for the less phyto-availability of arsenic in the area.

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