Ecosystems health and geochemistry: concepts and methods applied to abandoned mine sites

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ABSTRACT

This study is based on the premise that the good health of an ecosystem is essential for its sustainable development, introducing a new terminology for understanding pollution. Thus, the health of ecosystems is defined as an emerging science, or systemic approach, to prevent, diagnose and predict management features and establish relationships between the health of ecosystems and humans. It is within this framework that our experimental study was conducted on three sites situated in abandoned mines in the central Iberian Peninsula. The ecosystems present are mainly those of grazing pastures although cereals are also cultivated. In each of these settings, we find that soils contain more than one heavy metal in their top layers, particularly Cu, Zn, Pb and Cd. This pollution is punctate and affects both the plant populations of the sites and their consumers, with the possible transfer of pollutants to the river or groundwater systems, depending on the type of soil and geomorphological factors. We describe the protocol used to evaluate the health status of these ecosystems in terms of effects involving the geochemistry of the heavy metals they contain.

Keywords: heavy metals, pastures, punctate pollution.

INTRODUCTION: ECOSYSTEMS HEALTH IN THE CONTEXT OF SUSTAINABLE DEVELOPMENT

Thirty years ago, research into geochemistry and health commenced as one of the lines of Unesco's MAB (Man and Biosphere) programme (1978). However, we feel that in relation to ecosystems health, this line of research is practically new.

This study was not envisaged to only explore the response of plants to heavy metals (Barceló and Poschenrieder, 1992; Liphadzi and Kirkham, 2006), but to also address the so-called "ecodiseases" that heavy metals cause (Pérez, 2001). Many authors claim that there is currently a "silent pandemic" due to environmental pollutants, whose effects on persons are real yet difficult to measure (Ortega et al., 2005).

Here, we present the results obtained concerning pollution transfer via the food chain, along with a summary of related possible ecodiseases and a proposed protocol for assessing this type of issue for use on abandoned mine areas.

MATERIALS AND METHODS

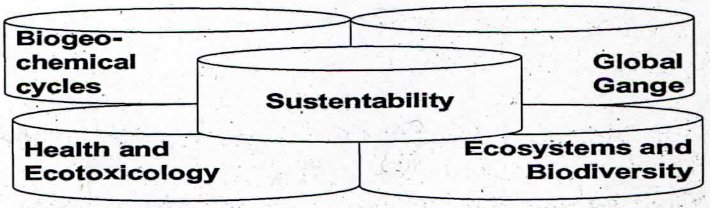
a) Study sites

Scenario 1: Garganta de los Montes. "Fernandito" is a copper mine in the Sierra de Guadarrama (Garganta de los Montes, Madrid) abandoned some 40 years ago, whose current landfill covers around 3500 m^3. The soils of the zone lie at heights of 1180 to 1200 m and have been classified by the FAO as humic and distric Cambisols. Given that the mine's main mineral is chalcopyrite, some of its Cu forms are due to its presence as mineral sulphur (Encabo et al., 1997). The main metals found are Cu, Zn, Cd and Pb.

Scenario 2: Guajaraz. This site includes the silver mine "La Económica" close to the Guajaraz River (Toledo, Spain). The site comprises the two geological domains: the migmatite domain of Toledo (in the N), mainly composed of homogenous granitoids and migmatites, and the Montes de Toledo domain (mainly in the S), harbouring Palaeozoic deposits of granitic influence. According to the FAO, the soils of the region are mainly distric Leptosols, although distric Cambisols close to the river and a poorly developed rendzic Leptosol also appear.

The orography of the mine site is flat with heights of 660 to 750 m. The mine was worked to a depth of 150 m and was exploited until 1990. Its landfills have volumes of around 25000 m^3. Pb and Zn appear at greatest concentrations in soils and alluvions.

Figure 1



The site contains poor pastures, characteristic of this semiarid region. There are no trees, only shrub vegetation, and most of the land is used to cultivate cereals.

Scenario 3: Navas del Rey. The old "La Asturiana" barium mine situated north of the village Navas del Rey (SW Madrid province). It is one of the many mines existing in the Central System, north of Madrid exploited during the XIXth and XXth centuries. The legacy left behind by these mines is a series of dispersed landfills that act as a fairly unknown constant source of pollution. The mine was used to extract barite as ore until 1945. It occurs at the contact between a granite massif and the Escorial-Villa del Prado metamorphic complex (Peinado, 1970). Generically speaking, it is a biotite granite with feldspar phenocrystals. Barite sulphate appears in quartz seams at the highest altitudes, which appear tortuous and irregular and extend in depth and length up to a thickness of 1 m alongside bands of kaolin and clay that attain a thickness of 15 cm. The barite seams have associated sulphides, mainly zinc blende, calcopyrite and galena (Gutierrez et al., 1986). Besides the metals in the paragenesis (Pb, Zn, Cu, Ba and Fe), Cd is commonly found although in scarce quantities from isomorphic replacements in blende rich in galena and calcopyrite. The open mine was a 20 m–long, 2.5 m–wide and 2 m–high trench in the granite itself exploited through a well deeper than 30 m. Until the 1980s, medium-sized landfills were derived from the main well and its channels. From a perspective of landscape, the La Asturiana mine and its surroundings occupy a plain crossed by a stream. This promotes the dispersion of mine tailings through the actions of water and wind that interrupt natural cycles. The abundance of sulphides may have resulted in the dissemination of heavy metals via the drainage network (Gutierrez-Maroto et al., 1989).

b) Sampling and chemical analyses

The soils and plants of the mine sites were sampled by stratifying according to affected landfills and ecosystems. At each established sampling point, a mean soil sample was collected at random from the topsoil layer (0-10 cm) using a hoe. At the Garganta site, 38 sampling points were established in the mine area and adjacent zones. Total and bioavailable elements in the soil and plants were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES). For soil determinations, the samples were ground in an agate mortar and acid digests prepared using a 4:1 mixture of HNO3 and HClO4. Soil analyses (pH, OM, total N and soil anions) were performed according to Hernández and Pastor (1989). Metals were determined after grinding the soil in an agate mortar by X-ray fluorescence (XRF), plasma emission spectroscopy (PES) and through the action of acid using a 4:1 mixture of HNO_3 and $HClO_4$. Available metals were determined by the acetate-EDTA method (Lakanen and Ervio, 1971). Log-transformed data were analysed by calculating Pearson correlation coefficients (using SPSS 13.0 software).

RESULTS AND DISCUSSION

The Garganta site is crossed by a droving route. Its pastures, which are mainly grazed by cattle, show the most polluted soils of the entire mine site (Table 1). Plant cover is generally high (95% in pastures), and lower in the landfills (40% at the base) (Table 2). Of 32 pasture species examined (above-ground parts), all showed notable levels of Cu; half showed Ni; 14 species Cd; 10 species Cr and three Pb. Most species exhibited more than two heavy metals. Thus, although plant diversity is reduced by soil pollution, the behaviour of these grassland species is generally tolerant towards these metals with the consequent repercussions on the food chain. The distribution of metals in the superficial layer of soils from other two scenarios, neither is homogeneous (Table 3 and 4). Table 5 show 22 plant species that grow on Site 1 of the "La Económica" mine whit high concentrations of Zn, Pb and Cd.

Sites						
Garganta Mine	Zn	Cu	Pb	Ni	As	Cd
Reference Soil	103	46,5	99	8,0	-	<3
1	157	180	108	11,5	-	<3
2	110	135	70	8,5	-	<3
3 Refuse dump	147	150	107	10,5	23	<3
3	150	185	104	11,5	-	<3
4 Ash-trees plantation-a)	166	325	120	12,5	45	<3
5	204	845	190	18,0	-	10,5
6 Ash-trees plantation-b)	133	680	199	21,5	42	<3
7 Wet grassland 200m	118	770	135	15,0	21	<3
8 Wet grassland 430m	166	910	133	12,5	30	<3
9	133	225	136	16,0	-	7,5
10	246	3500	181	14,0	-	8,5
11 Wet grassland 420m	478	1950	123	13,0	-	18
12	149	295	118	17,5	-	<3
13	159	750	145	16,5	-	4
14	95	55	118	13,5	-	<3
15	70	30	134	15,0	-	<3
16 Wet grassland	361	1000	120	15,0	-	11,5
17 Wet grassland	202	1800	160	25,5	-	3,5
18	134	950	162	17,5	-	3,5
19	139	1000	165	14,0	-	<3
20	104	680	97	19,5		<3
21	100	385	115	14,0		<3

Table 1. Heavy metal levels on the "Fernandito" Mine area grasslands.

Logically, there are also differences between the values of total metals and available ones (see Table 6). Nevertheless, enough correlations have been observed between metal levels in the superficial layer of the soils analyzed and diverse biodiversity parameters related with plant communities growing there. In the Table 7 can are shown a results for the scenario 3.

Botanical Family (Species No.)	Site 3	Site 4	Site 7	Site 11
Grasses	8	6	2	2
Legumes	2	7	3	2
Composites	6	6	2	0
Others	14	9	4	3
Total	30	28	11	7
Plant cover %	60	95	57	100

Table 2. Number of species of main botanical families found in inventories carried out in plant communities on the location of the "Fernandito" mine (Garganta de los Montes, Madrid).

Sites	Zn	Cu	Pb	Cd
1	5095	85	3855	37
2	2865	50	2430	11
3	835	19	1420	0
4	2940	46	2250	15
5	2290	22	1635	0
6	820	13	1205	0
7	1490	10	180	0
8	1005	20	1845	0
9	1585	23	1770	0
10	855	17	1220	0
Ref. Level	**200**	**50**	**50**	**1**

Table 3. Levels of heavy metals in different areas of the location of the "La Economica" mine (Guajaraz).

Descriptors	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5	Soil 6	Soil 7	Soil 8	Soil 9 (C)
Zn XRF	796	469	134	223	191	169	106	104	55
Zn PES	771	237	96	158	133	104	72	75	37
Zn L&E	198	46	14	7.1	13	14	2.5	2.4	0.2
Pb XRF	618	75	290	80	92	89	57	67	29
Pb PES	105	2.4	249	115	91	13	111	122	11
Pb L&E	52	0.7	82	12	20	0.0	0.0	0.0	0.0
Cu XRF	215	47	35	55	43	48	19.7	21	25
Cu PES	170	26	14	33	18	26	5.0	4.6	12
Cu L&E	100	3.3	2.3	2.3	3.3	3.3	1.4	0.7	1.0
Cd XRF	17	2.7	1.1	0.3	1.1	2.4	0.0	0.0	0.0
Cd PES	5.5	1.4	1.1	0.7	0.7	1.1	0.0	0.0	0.0
Cd L&E	2.5	0.3	0.0	0.0	0.0	0.3	0.0	0.0	0.0
Ba XRF	74676	1140	1501	1608	1737	1193	673	686	602

Table 4. Levels of heavy metals (ppm) in different soils of the "La Asturiana" mine.

(C) Control Soil; XRF, X-ray fluorescence; PES, plasma emission spectroscopy; L&E: Lakanen and Ervio method.

Metals can be absorbed by plants or may be lost by leaching at greater soil depths and eventually reach groundwater sources. Moreover, soil erosion may determine that metals reach surface water courses. The importance of the different routes of transfer of these elements to other compartments of the food chains varies according to the metal, species present, or the use of the pasture land (plants consumed in situ by livestock or collected for forage or preparing feeds). Several studies have shown that animals reflect the concentrations of toxic elements when they graze on plants growing in polluted soils (Ronneau and Cara, 1984, Morcombe et al., 1994, Petersson et al., 1997). This highlights the need to control metal levels in terrestrial ecosystems. The FAO (2000), established threshold limits for Pb and Cd that were later adopted by the USA. It is generally admitted that Cd is highly toxic; Cu and Pb are considered toxic although the latter is moderately toxic for plants and highly toxic for animals; and Ni, Zn and Cr add to the list of metals causing toxicity. However, the knowledge we have of these issues is still scarce (Hapke, 1996), especially related to wild plant species. Ecotoxicological data on pastures are also scant.

Descriptors	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5	Soil 6	Soil 7	Soil 8	Soil 9
Species No.	13.7	16.3	15.3	27.0	19.7	17.0	17.3	17.3	25.3
Plant cover %	40.3	47.7	64.5	59.7	127.8	46.2	51.2	41.8	84.0

Table 4. Biodiversity and plant cover mean values of plant communities (750 cm^2 plots) in the location of "La Asturiana" mine.

Species	
Agrostis castellana	*Dactylis glomerata*
Elysum granatense	*Diplotaxis catholica*
Andriala integrifolia	*Hirschfeldia incana*
Asparagus sp	*Melica cilliata*
Bellardia trixago	*Mentha rotundifolia*
Bromus rubens	*Plantago lagopus*
Cardus tenuiflorus	*Rumex bucephalophorus*
Cardus sp.	*Spergularia rubra*
Centaurea mellitensis	*Stipa sp.*
Chondrilla juncea	*Thymus zigis*
Crepis vesicaria	*Trifolium gemellum*

Table 5. Plant species growing in the site 1 of "La Económica" mine.

Specific heavy metals should be monitored since the results obtained for each of the mines indicate that they could pass to the food chain, from plants to herbivores, and to the humans that consume these animals (Hapke, 1976, 1991).

A pursuit will be made of concrete heavy metals that according to the obtained results for each one of the mines, can reach the trophic chain, from the plants to the herbivores and human populations that feed of them (Hapke, 1976).

Total Metals	Al	Fe	Mn	Zn	Cu	Cd	Ni	Pb
Scenario 1	28407	16100	515	190	1120	4,5	15,1	47,2
Scenario 2	25097	22600	1190	4675	404	25,4	29,9	6925
Available Metals								
Scenario 1	0,42	7,2	9,5	5,7	71,4	0,56	0,13	1,1
Scenario 2	0,12	6,4	7,4	129,2	34,7	0,98	0,36	137,6

Table 6. Total and available metals (ppm) in two soils of 1 and 2 Scenarios.

Metals	Species No.	Leguminosae No.	Compositae No.	Plant cover %
Zn XRF	- 0.430 (*)	- 0.182	- 0.349 (R)	- 0.349 (R)
Zn PES	- 0.448 (*)	- 0.294	- 0.295 r	- 0.328 (R)
Zn L&E	- 0.557 (**)	- 0.210	- 0.431 (*)	- 0.301
Pb XRF	- 0.600 (**)	- 0.427 (*)	- 0.323 (R)	- 0.275
Pb PES	- 0.113	- 0.262	0.032	- 0.069
Pb L&E	- 0.213	- 0.113	- 0.191	- 0.227
Cu XRF	- 0.313 (R)	- 0.224	- 0.139	- 0.226
Cu PES	- 0.241	- 0.120	- 0.117	- 0.181
Cu L&E	- 0.435 (*)	- 0.362 (R)	- 0.166	- 0.274
Cd XRF	- 0.533 (**)	- 0.326 (R)	- 0.284	- 0.313 (R)
Cd PES	- 0.348 (R)	- 0.209	- 0.229	- 0.272
Cd L&E	- 0.412 (*)	- 0.424 (*)	- 0.049	- 0.299
Cr XRF	- 0.332 (R)	- 0.371 (R)	- 0.047	0.201
Ni PES	- 0.289	- 0.134	- 0.089	- 0.171
Ba XRF	- 0.389 (*)	- 0.387 (*)	- 0.113	- 0.214

Table 7. Correlations between several biodiversity markers and plant cover for the plant communities and pseudototal (2) and bioavailable metal contents of the soils from the abandoned barium mine site.

*** significant at the level 0.001; ** significant at the level 0.01;
* significant at the level 0.05; R reliable at the 90% significance level

In the following section, using the terminology employed by Pérez (2001) we discuss the "ecodiseases" caused by metals that were found to be most closely related to the geochemistry of the soils examined.

Cadmium in nature, is found associated with other elements, especially Zn, Pb and Cu. It is among the most toxic elements, passing through plants to the food chain. Cd is a cumulative metal. In plants, Cd has effects on chlorophyll function (wilting, necrosis, leaf chlorosis), inhibiting photosynthesis and carbon dioxide fixing, which leads to the short-term death of species. In agricultural practice in this region, P fertilizers are used, and although it is known that these reduce the bioavailability of heavy metals, this is not true for Cd. Moreover, plants take up this metal more when the soil Zn content is low (Liphadzi and Kirkhan, 2006).
The toxic effects of Cd are much worse in plants and herbivores, with no Cd-related ecodiseases in carnivores detected to date. In humans, Cd can persist in the body and accumulate after many years of exposure to low levels. Eating foods containing Cd severely irritates the stomach, leading to vomiting and diarrhea. Its build-up in the body can cause damage to the kidneys, lungs and bones (Hapke, 1991).

Lead is a significant toxic element owing to its dispersion in nature. Pb is mainly generated during soil degradation and weathering of mineral deposits, although the most notable Pb pollution is provoked by anthropogenic actions. Transport of soil Pb to groundwater depends on the type of Pb compound and the characteristics of the soil. Plants may absorb this metal relatively easily and mainly store it in the roots. Thus, the risk of Pb poisoning is particularly evident when it affects certain bulbs, beetroot, potatoes, onions etc. Some animals have a special capacity to accumulate Pb with no detectable effects including the earthworm. This determines that the current use of this species, for instance, to prepare feeds in fish and poultry farms, is a dangerous practice.
Both in humans and animals, chronic Pb poisoning manifests as a reduction in body growth (reduced height). As an ecopathogen, its effects on both the peripheral (extensor muscle damage, sensory disorders, increased pain sensitivity) and central nervous system, (mainly memory loss and encephalopathy), particularly in children, are well known. However, this heavy metal may affect almost every organ of the body (especially the kidneys and male reproductive system).

Zinc is an essential micronutrient, considered non-dangerous, although it may become toxic; its toxicity may increase in the presence of arsenic, lead and cadmium. On the contrary to other heavy metals, Zn is usually gradually lost throughout the food chain. Its toxic effects on plants include chlorosis, which can in turn cause deficiencies in Mg or Fe, essential nutrients for all organisms.

Copper is another essential trace element well known for its toxic effects on beans and legumes in general. Its detrimental effects include cytoplasm membrane damage in plant and animal cells. According to the literature, Cu has been recently the most widely investigated metal in relation to its toxic effects on legumes (Bunzl et al., 2001; Cuypers et al., 2005). A study by Hernández et al. (2006) demonstrated high Cu levels in the fruits of cultivated legumes. The Zn contents of these fruits were also high, and the dry weight of the plant reduced. This latter finding has also been reported by Miyazawa et al. (2002). According to Adriano (2001), a Cu level of 2 to 250 ppm can be toxic for cultivated plants and given that, along with Zn, this nutrient is supplied in the diet by legumes, levels reached in their fruits could provoke toxic effects.

Manganese toxicity is due to its absorption by plants in soils of low pH containing Al (Hernández, 1986 and 1987). Although the soils of the present study area are basic, their Al contents are high such that we propose further work should be conducted on the possible toxic effects of both these metals.

The water-soluble components of **Cr VI** are highly toxic. Chromium tends to accumulate in roots, although toxic effects on the respiratory tract have been reported (INERIS, 2004), since this metal builds-up in the food chain.

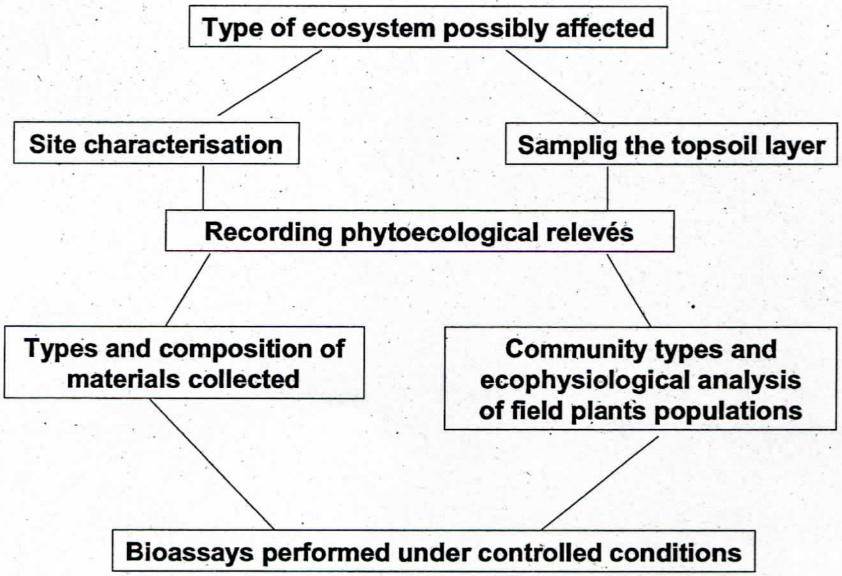


Figure2. Protocol

Nickel, which is produced by the build-up of urea in legumes, may be toxic at plant levels above 10 ppm. Ni inhibits meristem cell division and limits the spreading of roots (Liphadzi & Kirkhan, 2006).

Arsenic is used in pesticides and slowly accumulates since although highly absorbed it is excreted in the urine. In conditions of humidity, moulds in soil convert As into highly toxic gasses. According to the EPA (USA Environmental Protection Agency), the dangers of As for humans may be linked to waters and fish but rarely to soils or to domestic animal excretory products. Although most plants tend to exclude As from their above-ground mass, they accumulate the metal in their roots (Landis & Ming-HoYu, 1999). The ecodisease due to this metal produces vomiting, abdominal pain and even death. Epidemiological evidence for its carcinogenicity has been obtained in experimental animals (lung tumours produced by inorganic As compounds).
Lastly, in the figure 2, is shown the protocol that has been deduced as important to carry out the study of the relationship between the geochemistry and the health of ecosystems.

CONCLUSIVE ASPECTS

The diagnosis of soil pollution in relation to the most commonly used remediation methods is an innovative way of tackling this problem. To this end, the theoretical framework of Ecosystems Health has been instrumental, since this area is presently emerging as a new language for general discourse on pollution. For example, the use of the term stressor for a pollutant implies the study of behavior responses in living organisms (at different levels of organization, from the cell to ecosystem) both in terms of impacts (toxicity) and tolerance towards the pollutant (their adaptation).

We focused on the autotrophic component of the affected ecosystems for several reasons: toxicity tests could be used to examine the physiological and behavioral responses of organisms (mortality, injury, metabolic changes) as well as population (population density, risk of extinction) or community (structure, diversity, biomass, nutrient flow changes) variables. The build-up of a heavy metal in the above-ground part of a plant (phytoaccumulation) consumed by herbivores is also detrimental for health, due to transfer to the trophic network. Root systems may play a role in phytostabilizing heavy metals and in preventing them from passing to deeper soil layers. Finally, given the erosion problems of fine materials in landfills and waste tip slopes, vegetation helps avoid the movement of topsoil layer pollutants to other ecosystems.

The methodological approaches validated by results obtained over the last twenty years can be summarized as: studies of polluted sites based on phytoecological sampling, analysis of soil chemical and physical properties, georeferencing of the heavy metals they contain for further sampling in areas showing the highest levels, collecting and chemically analyzing plants at these sites, and the use of soils with their seed banks to perform experiments on microcosms in controlled conditions. The idea is to use a combination of field and laboratory methods that simulate real scenarios in which soil pollution occurs.

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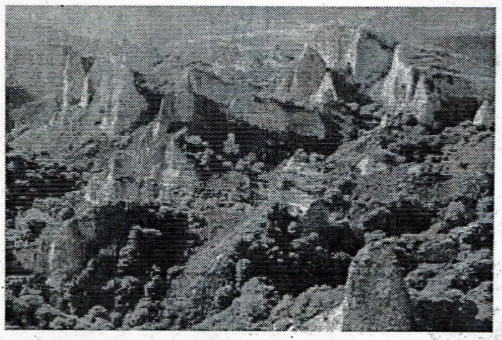
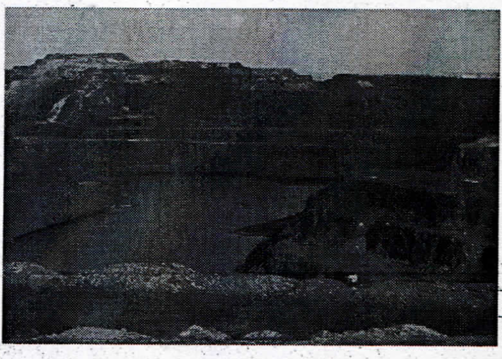
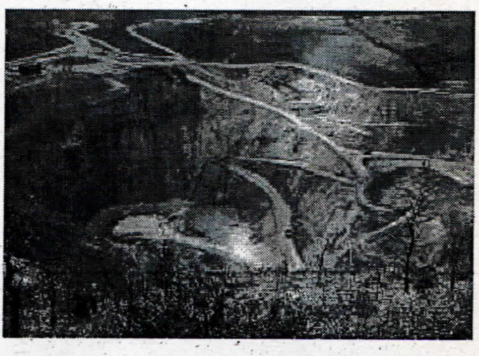

Extended Abstracts

Jointly organized by the Department of Exploration and Mining of the University of Oviedo (Spain), the Geological and Mining Institute of Spain (IGME) and the Association of Applied Geochemists.

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