CHEMISTRY AND PLANT ECOLOGY OF ZINC-RICH STREAMS IN FRANCE. 2. THE PYRÉNÉES

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An account is given of the chemistry and phytobenthos of streams in the vicinity of two old lead mines in the Hautes-Pyrénées south of Lourdes. All of the nine sites studied had elevated levels of aqueous Zn, and also in most cases of Cd and Pb. There was some evidence that increasing levels of heavy metals led to a decreased flora, but 30 species were recorded at sites with $> 10 \text{ mg l}^{-1}$ Zn. The most restricted flora occurred at a site with a conspicuous white precipitate, consisting largely of anglesite; here only three species were present: *Schizothrix* sp., *Pohlia cruda*, *Solenostoma crenulatum*.

Chimie et écologie de la végétation de cours d'eau en France à fortes teneurs en zinc. 2. Les Pyrénées

La chimie et le phytobenthos ont été étudiés dans 9 stations sur les cours d'eau près de deux mines de plomb dans les Hautes-Pyrénées. A chaque station les teneurs de Zn et dans la plupart des cas de Cd et Pb, sont élevées. Une flore réduite s'est manifestée tandis que les teneurs des métaux lourds ont augmenté, et pourtant 30 espèces ont été trouvées dans les stations avec $> 10 \text{ mg l}^{-1}$ Zn. La flore la plus réduite a été trouvée à la station où il existe un précipité blanc d'anglesite; à cette station 3 espèces ont été trouvées: *Schizothrix* sp., *Pohlia cruda*, *Solenostoma crenulatum*.

INTRODUCTION

Within the Pyrenees, the Central Pyrenees is the richest in minerals and according to Charrin (1952), is also one of the richest areas in the whole of France. Apart from a few floristic records given by Whitton (1980), there are no accounts of stream phytobenthos in the mining areas, but Besch *et al.* (1972) and Backhaus (1976) have surveyed non-polluted streams in the same region. The present paper describes the chemistry and phytobenthos of two abandoned mining areas south of Lourdes.

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1. — METHODS

Samples were taken from Pierrefitte Mine on 8 April, 3 June and 7 August 1977 and 15 April, 29 June and 18 September 1978. Estaing Mine is accessible only during the summer, so samples were taken on only the June and August dates. The use of 10 m reaches and analytical methods were the same as in the previous paper. Phyto-benthos were scored on a 5-point scale on each occasion, but the data have been simplified in Table 5 to a presence/absence format. Nevertheless comments on the abundance of various species are based on the full records which are held on computer file.

FIG. 1. — Location of Estaing and Pierrefitte Mines.

2. — ENVIRONMENTAL BACKGROUND

The two mining areas are in tributary valleys of the Gave de Pau (fig. 1). One borders the Gave de Cauterets about 2 km south of Pierrefitte-Nestalas, while the other borders the Labat de Bun near Estaing.

Pierrefitte

Estaing

FIG. 2. — Schematic maps of streams at the two mines.

TABLE I. — Details of 9 sites sampled for water and phytobenthos. Codes of stream and reach are those used for records and specimens held at Durham ; terms used for substratum sizes are defined by Wentworth (1922).

site	stream- reach	grid ref.	altitude (m)	width (m)	sheet	boulder	cobble	pebble	sand	silt	main rock types	environment
<i>Pierrefitte Mine</i>												
L	3015-40	4023/750	660	0.4		80	10		10		schists	stream drains border of smelter waste tips
M	3015-44	4023/750	630	0.6	40	45	5		10		schists	downstream of entry of 3016 ; leaves mine complex here
N	3016-03	4023/750	640	0.15	40		5	40	15		smelter waste	drains from old smelter house
<i>Estaing Mine</i>												
O	3028-01	3961/740	1 500	0.25					20	80	shale	only slight flow from this adit ; sediment contains ochre
P	3014-02	3962/739	1 550	0.4		30	50	15	5		shale	much water comes from this adit, substratum coated with ochre
Q	3029-01	3963/739	1 630	0.4				5	45	50	shale	steady discharge from this adit ; sediment rich in ochre
R	3030-99	3963/739	1 630	0.35		15	15	40	30		shale	continuous but slight flow of mine tip
S	3013-05	3963/739	1 650	0.75	15	50	25	10			shale	small stream draining from base of large mine tip
T	3031-90	3950/746	985	1.5	15	40	30	10	10		shale, sandstone, well downstream of mine workings, past entry of other streams unaffected by mining schist	

2.1. — Pierrefitte Mine

The mineral veins of this derelict lead mine are associated with a host rock of low to medium grade metamorphic formations, primarily schists. The main mineral is galena, with also some sphalerite, chalcopyrite and pyrite. The extensive workings extend up to 1200 m on the slopes of Pic d'Arraille, but study was restricted to two streams associated with the lower part of the mine complex (*fig. 2*). Here large tips of waste surround an old treatment plant and smelter.

2.2. — Estaing Mine

Although the area nearby is dominated by metamorphic rocks such as schists, the mineral veins at this derelict lead mine are associated with carbonate-rich rocks and shales. The main mineral is sphalerite

FIG. 3. — Estaing Mine : view of 3013-05 ; pale cover on sheets of rock is due largely to *Plectonema*.

TABLE II. — Water chemistries of sites L-N (n = 6) and sites (n = 4); variables analyzed only once are based on 29 June 1978 survey; all elements in mg l⁻¹.

	L		M		N		O		P		Q		R		S		T	
	min	max	min	max	min	max	min	max	min	max	min	max	min	max	min	max	min	max
temperature (°C)	9.8 ± 4.2	4.0	14.0 ± 2.9	6.0	13.0 ± 1.2	8.0	11.0 ± 1.7	12.0	16.0 ± 0.5	6.0	7.0 ± 0.2	7.5	7.8 ± 0.2	6.0	6.4 ± 0.1	5.8	6.0	7.1 ± 0.08
pH (field)	6.0 ± 0.2	5.7	6.2 ± 0.3	4.7	5.6 ± 0.2	3.7	4.5 ± 0.1	7.2	7.5 ± 0.4	10.4	10.4	10.4	10.4	10.4	10.4	10.4	10.4	10.4
total alkalinity (mequiv. l ⁻¹)	0.42	0.17	0.42	0.17	0.42	0.17	0.42	0.17	0.42	0.17	0.42	0.17	0.42	0.17	0.42	0.17	0.42	0.17
Na	1.9 ± 0.2	1.61	2.1 ± 0.2	1.7	2.2 ± 0.2	1.6	1.95 ± 0.2	1.4	1.1 ± 0.2	0.86	1.34 ± 0.2	0.65	1.05 ± 0.06	0.5	0.63 ± 0.1	0.37	0.6 ± 0.2	0.46
K	0.5 ± 0.1	0.42	0.6 ± 0.1	0.5	0.9 ± 0.1	0.5	1.59 ± 0.2	1.1 ± 0.2	0.45 ± 0.2	0.30 ± 0.08	0.90 ± 0.2	0.30 ± 0.08	1.00 ± 0.2	0.88	1.06 ± 0.08	0.35	0.3 ± 0.1	0.26
Mg	3.0 ± 0.5	2.2	3.6 ± 0.9	2.25	4.6 ± 0.2	0.8	9.0 ± 1.2	3.9 ± 0.6	3.16 ± 0.4	6.1 ± 0.4	5.7 ± 0.4	4.8 ± 0.2	4.6	5.0 ± 0.2	2.2	2.76 ± 0.2	0.80	1.16 ± 0.8
Ca	11.6 ± 3.6	5.5	15.0 ± 4.5	5.0	21.4 ± 3.0	10.6	14.0 ± 2.0	40.1 ± 8.8	31.0 ± 5.5	62.5 ± 8.5	53.0 ± 8.5	73.2 ± 5.5	52.7 ± 3.6	6.6	15.0 ± 0.2	6.6	15.0 ± 0.2	14.0
Al*	0.03	2.20	0.03	2.20	0.03	2.20	0.03	2.20	0.03	2.20	0.03	2.20	0.03	2.20	0.03	2.20	0.03	2.20
NH ₄ ⁺	0.09 ± 0.03	0.055	0.14 ± 0.04	0.22	0.14 ± 0.04	0.22	0.14 ± 0.04	0.22	0.14 ± 0.04	0.22	0.14 ± 0.04	0.22	0.14 ± 0.04	0.22	0.14 ± 0.04	0.22	0.14 ± 0.04	0.22
Fe	1.1 ± 0.4	0.8	1.2 ± 0.4	0.8	1.2 ± 0.4	0.8	1.2 ± 0.4	0.8	1.2 ± 0.4	0.8	1.2 ± 0.4	0.8	1.2 ± 0.4	0.8	1.2 ± 0.4	0.8	1.2 ± 0.4	0.8
NH ₄ ⁺	0.04	0.10	0.04	0.10	0.04	0.10	0.04	0.10	0.04	0.10	0.04	0.10	0.04	0.10	0.04	0.10	0.04	0.10
Co*	0.02	0.04	0.02	0.04	0.02	0.04	0.02	0.04	0.02	0.04	0.02	0.04	0.02	0.04	0.02	0.04	0.02	0.04
Cu	0.02	0.02	0.04 ± 0.02	0.02	0.08 ± 0.2	0.07	0.18 ± 0.35	0.02	0.02 ± 0.02	0.02	0.02 ± 0.02	0.02	0.02 ± 0.02	0.02	0.02 ± 0.02	0.02	0.02 ± 0.02	0.02
Zn	0.7 ± 0.3	0.32	1.2 ± 0.3	0.3	12.0 ± 3.0	3.7	12.0 ± 3.0	48.0 ± 3.0	3.0 ± 0.2	2.75 ± 0.2	0.9 ± 0.2	0.73 ± 0.2	1.2 ± 0.2	8.5 ± 0.8	16.7 ± 0.6	3.8 ± 0.7	3.06 ± 0.4	0.4 ± 0.1
Cl	0.02	0.02	0.04 ± 0.03	0.02	0.08 ± 0.2	0.1	0.57 ± 0.02	0.02	0.02 ± 0.02	0.02	0.02 ± 0.02	0.02	0.02 ± 0.02	0.02	0.02 ± 0.02	0.02	0.02 ± 0.02	0.02
Pb	0.012	0.02	0.04 ± 0.03	0.02	0.08 ± 0.2	0.1	0.57 ± 0.02	0.02	0.02 ± 0.02	0.02	0.02 ± 0.02	0.02	0.02 ± 0.02	0.02	0.02 ± 0.02	0.02	0.02 ± 0.02	0.02
PO ₄ ³⁻	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
NH ₄ ⁺	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
NH ₄ ⁺	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Si	16.8	1.15	16.8	1.15	16.8	1.15	16.8	1.15	16.8	1.15	16.8	1.15	16.8	1.15	16.8	1.15	16.8	1.15
F	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16
Cl	1.39	1.39	1.39	1.39	1.39	1.39	1.39	1.39	1.39	1.39	1.39	1.39	1.39	1.39	1.39	1.39	1.39	1.39

TABLE III. — Element composition (μg g⁻¹) of sediments from bryophytes growing at sites M and N.

species	site	site description	pH of water at time of sampling	sediment composition											
				Na	Mg	Ca	Al	Mn	Fe	Ni	Co	Cu	Zn	Cd	Pb
<i>Solenostoma crenulatum</i>	M	attached to schist bedrock in white inorganic crust	5.4	214	730	87.7	14400	204	93500	24	24	229	8430	24.4	110000
<i>Dicranella heteromalla</i>	N	attached to cement sided channel in trapped sediment	3.7	803	3380	1810	14800	247	32200	35.3	25	232	1616	6.0	1810

associated with some galena. The mine is situated below a peak (Puyos) on the slopes of Pic de Cabalirros at 1600 m. There are several adits with extensive tips of waste rock and ore below their entrances. One of the small streams studied is shown in fig. 3; the figure illustrated by Ernst (1974, p. 86) is taken slightly further down the same stream. (This site is called Pierrefitte Mine by Ernst (1966 and 1974).)

3. — RESULTS

3.1. — Water chemistry

Sites in the area of the Pierrefitte Mine had waters with low pH values (Table II), especially site N, with a mean pH of 4.2; the levels of all heavy metals except Pb were higher than at any other site at either mine. At site L only Zn occurred at elevated levels, but concentrations of all metals increased after entry of stream 3016.

Streams in the area of the Estaing Mine showed a varied chemistry according to their source. Adit streams (sites O, P, Q) had a neutral to alkaline pH and were markedly base-rich. Streams draining from waste tips (sites R, S) had lower pH values, with low levels of total alkalinity and calcium. All of the sites had elevated levels of Zn and in some cases also Cd. The highest level of Pb recorded anywhere was at site S.

3.2. — Sediments

The composition of the sediments at sites M and N is summarized in Tables III and IV. *Solenostoma crenulatum* at M grew healthily. The very high levels of Zn and Pb found in the digest of this sediment (Table III) confirm the results of X-ray diffraction (Table IV), which show the sediment at this site to be a mixture dominated by anglesite, but including also the smelter waste product, zinc ferrite.

3.3. — Plants

The occurrence of fully submerged photosynthetic plants at the nine sites is shown in Table V. 69 species were recorded at these sites; 30 of these were recorded from sites with mean levels of $\text{Zn} > 10 \text{ mg l}^{-1}$, while 20 species were recorded from the site with the highest level of zinc (site N, $\bar{x} = 42.5 \text{ mg l}^{-1} \text{ Zn}$). The occurrence of partially submerged and bank species of bryophyte is shown in Table VI; some of these also occurred fully submerged (Table V). There were 4 liverworts and 13 mosses.

3. — DISCUSSION

Mining in the vicinity of Pierrefitte and Estaing Mines ceased in the 1960's, but the streams draining these areas still carry very high levels of zinc, cadmium and lead. The sources of the heavy metals in streams draining the Pierrefitte Mine complex are mainly from the weathering of primary minerals such as sphalerite and galena, together with secondary minerals (anglesite, zinc ferrite, zinc ferrate) associated with the large smelter waste tips. In contrast, the metals in the streams draining the Estaing Mine workings not only come from waste tips with appreciable quantities of sphalerite and galena, but also from adits which discharge groundwaters circulating in contact with old worked mineral veins of zinc and lead.

The low pH of stream 3016 at site N is due to the oxidation of sulphide minerals in the smelter waste. The resulting acid conditions would be likely to mobilise heavy metals associated with the waste, hence producing the high levels of zinc, and, to a lesser extent, copper,

TABLE IV. — Mineral composition of sediments attached to bryophytes growing at sites M and N.

species	site	composition of sediment attached to bryophyte mineral	mineralogical comments
<i>Solenostoma crenulatum</i>	M	anglesite (PbSO_4)	dominant mineral in sample; in the field forming a thick white crust covering the substratum; a common secondary lead mineral in the oxidised zone of lead deposits
		zinc ferrite (ZnFe_2O_4)	second most common mineral in this sample and one often associated with remains of smelter waste
		quartz	commonly associated gangue mineral with lead and zinc ores; also a constituent of some metamorphic rocks: could come from either source here
		amphibole	this encompasses a wide group of rock-forming silicates; probably present in this sample as a result of weathering of the schist bedrock
		chlorite	can occur as an alteration product of amphiboles and as a component of schists
<i>Dicranella heteromalla</i>	N	muscovite	from weathering of bedrock
		chlorite	from weathering of bedrock
		quartz	from weathering of bedrock

TABLE V (contd.)

cadmium and lead. The conspicuous covering of anglesite over the whole bed of stream 3015 at sites L and, in particular, M is probably due simply to decreased solubility associated with a pH rise. There was no obvious covering of anglesite at site N with its lower pH of water and the levels of heavy metals in the sediment attached to *Dicranella heteromalla* at N were in general lower than those attached to *Solenostoma crenulatum* at M.

The high levels of zinc and calcium in the water at site R and of zinc and lead at site S are probably also related to their high mobility under slightly acid conditions. In general the adit waters which had circulated over carbonate-rich rock, especially site P, carried lower levels of zinc and other heavy metals. At these sites, and again especially at P, there was a conspicuous coating of ochre (hydrated oxides of iron) covering much of the substratum. Metals such as zinc are less soluble in the alkaline, base-rich waters (Hem, 1972) and might also become bound by the insoluble iron compounds.

In general there is no pronounced increase in the number of species between stream sites in the two areas as the levels of heavy metals decrease, but rather a much more obvious change in the species composition. A somewhat similar response has been reported (Say & Whitton, 1981) from a stream draining a lead-zinc mining area in Northern England. Of the 20 species recorded at site N of the Estaing Mine, 9 were not found at any of the other sites. Three of these, *Eunotia exigua*, *Hormidium rivulare* and *Microthamnium strictissimum*, are common in highly acidic streams originating from acid mine drainages (Hargreaves, Lloyd & Whitton, 1975; Whitton & Diaz, in press); such drainages also carry high levels of heavy metals. At site N *Hormidium rivulare* was especially abundant, forming dense green tufts attached to smelter waste throughout the whole length of the stream; this was also the dominant in the stream showing a gradient of zinc studied by Say and Whitton (1981). Four diatoms, *Eunotia exigua*, *Neidium alpinum*, *Navicula sohrensensis* and *Pinnularia parva*, were also abundant or frequent at this site; the former two species were found in the study of Say and Whitton (1981) to be restricted to the highest levels of zinc.

Narrow forms of blue-green algae were frequent at two sites. *Schizothrix* sp. was the only alga accompanying the two bryophytes at M, developing in close association with the anglesite. Sheets of *Plectonema* were conspicuous at S. (The distinction into two genera is rather arbitrary; morphologically the forms from the two sites were quite similar.) Similar narrow forms of occasionally branched, sheathed Oscillatoriaceae are widespread in shallow zinc-rich waters (Whitton, 1980) and at Elvins Tailings in the Old Lead Belt of Missouri they cover extensive areas (Whitton, Gale & Wixson 1981). Besides

these blue-green algae, the zinc-rich waters of the Estaing and Pierrefitte Mines show many other similarities in species composition to the zinc-rich streams draining the Northern Pennine Orefield in England (Say, 1977 ; Say & Whitton, 1981). Frequent species in both areas include *Achnanthes minutissima*, *Caloneis bacillum*, *Pinnularia borealis*, *P. subcapitata*, *P. viridis*, *P. viridis* var. *sudetica*, *Mougeotia* sp. $\leq 8 \mu\text{m}$ and *Hormidium rivulare*. Bryophyte similarities are the presence of *Solenostoma triste*, *Pohlia nutans* and *Pohlia* sp. in seepages from the base of mine tips and that of *Cratoneuron commutatum*, *Dicranella varia* and *Philonotis fontana* in wet flushes produced by the base-rich waters of adits.

The presence of *Solenostoma crenulatum* at site M growing among almost pure anglesite and with high levels of aqueous zinc flowing past the plants indicates that this species can be strongly resistant to lead and zinc. Heavy metal resistance in this species has already been noted by Brown and House (1978), who found it growing on disturbed soil near a lead mine and on the spoil tip of a copper mine in South-West England.

The larger number of algal species at site T is probably at least in part due to the much lower levels of zinc and very much lower levels of other heavy metals. This stream is however larger than the others and so can presumably offer a wider range of microhabitats. Its species composition shows similarities with that of two alpine streams described by Backhaus (1976) in a region of the Pyrénées unaffected by mining and not far from the present study area. The Cyanophyta were in particular similar, with species of *Chamaesiphon*, such as *C. fuscus*, *C. incrustans* and *C. polonicus*, *Homoeothrix varians* and species of *Gloeocapsa* and *Phormidium* common to both studies.

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