# REMOTE MOUNTAIN LAKES AS INDICATORS OF DIFFUSE ACIDIC AND ORGANIC POLLUTION IN THE IBERIAN PENINSULA (AL:PE 2 STUDIES)

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ABSTRACT. In the framework of the AL:PE 2 project, studies on acidification and organic pollution in mountain lakes have been conducted in several ranges in the Iberian peninsula: Pyrenees (Northeastern Spain), Sierra de Gredos (Central Spain), Sierra Nevada (Southern Spain) and Serra da Estrela (Central Portugal). These studies focused on water and sediment chemistry and organisms (benthic diatoms, zooplankton, aquatic macroinvertebrates, and fish) as indicators of acidification. Organic micropollutants (PAH, PCB, DDE, hexachlorobenzene and others) in lake sediments and fish have been studied as tracers of atmospheric pollution. The Iberian peninsula lakes do not show severe anthropogenic acidification. pH values are in the range of sensitive lakes, but the levels of acidic pollutants are low. The status of the organisms surveyed agreed with this diagnosis. Pyrenean lakes showed the highest fluxes of organic pollutants related to fossil fuel combustion., higher pollution-induced versus natural acidity ratios, and modeled alkalinity and pH declines.

## 1. Introduction

Remote lakes are good indicators of change in the regional and global environment because of the lack of local impacts. Furthermore, arctic-alpine lakes are generally on catchments that are mainly composed of igneous rocks, and are thus sensitive to acidification and chemical pollution. Lake districts on crystalline bedrocks are found in all continents, and may be used as a world-wide network for monitoring global diffuse pollution. One of the main aims of the AL:PE 2 project (Acidification of mountain lakes: palaeolimnology and ecology. Remote lakes as indicators of air pollution and climate change) was to use a set of alpine lakes from various European regions as indicators of pollution (Wathne 1992). The interest of the Iberian peninsula is related to its geographic position, at the southwestern limit of the high deposition of pollutants from Central Europe. In this paper we present the extent of diffuse atmospheric chemical pollution over the Iberian Peninsula using several mountain lakes as sentinel ecosystems. Our studies focused on the water and sediment chemical pollution (both acidic and organic), the composition of the populations of benthic diatoms, zooplankton, aquatic macroinvertebrates, and fish, and the accumulation of organic pollutants in fish.

## 2. Study sites and methods

The main physiographic and climatic characteristics of the lakes studied are given in Table I. Lakes on the main ranges of the Iberian Peninsula were selected according to the criteria of being adequate sensors of atmospheric pollution, although the selection was conditioned by the characteristics of the lakes in each range. In the Pyrenees (Northeastern Spain), Sierra de Gre-

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TABLE I

Situation and main physiographic and climatic features of the studied lakes. * In 1993 and 1994 maximum depth was 7 m and lake area 1.12 ha due to low precipitation.

| Lake | latitude | longitude | altitude (m.a.s.l.) | metres above timberline | watershed area (ha) | lake area (ha) | max. depth (m) | precip. volume (mm) | ice free period | summer temp (°C) epi..- hypo. | bedrock |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Aguiló | 42°43'N | 1°20'E | 2210 | 400 | 88 | 3.5 | 25 | 1300 | June-Oct | 14 - 10 | grano-dirorite |
| Redó | 42°38'N | 0°46'E | 2240 | 400 | 155 | 24 | 73 | 1300 | June-Dec | 14 - 4 | grano-diorite |
| Escura | 40°21'N | 7°38'W | 1680 | 100 | 5 | 0.2 | 12 | 1800 | - | 20 - 19 | monzo-nitic granite |
| Cimera | 40°16'N | 4°37'W | 2140 | 350 | 85 | 4.5 | 9 | 1300 | June-Oct. | 19 - 19 | adame-llitic granite |
| Caldera | 37°03'N | 3°20'W | 3050 | 1200 | 18 | 2.3* | 11* | 700 | June-Oct. | 17 - 17 | micha-schists marbles |

dos (Central Spain) and Serra da Estrela (Central Portugal) lakes are sensitive to acidic deposition. In contrast, all lakes in Sierra Nevada (Southern Spain) are well buffered, but the remoteness of the lake chosen (La Caldera) makes it adequate to trace the extent of diffuse organic pollution. In the Pyrenees, where lakes are much more abundant, two lakes were chosen; one very sensitive to acidic pollution (Lake Aguiló) and one approaching the most extended chemical composition in the lake district (Lake Redó) (Catalan *et al.* 1993). Lake Cimera was chosen in Sierra de Gredos, and Lake Escura in Serra da Estrela.

The sampling program for the AL:PE 2 project consisted of a preliminary survey of lakes during the summer of 1993 and regular visits during the autumn overturn in 1993 and 1994. The methods used in this study are those established for the AL:PE 1 project (Wathne *et al.* 1995), except for the organic micropollutant analysis which has been introduced in the AL:PE 2. A brief description of these methods follows. Water chemistry: surface water samples were analyzed using standard procedures for conductivity, alkalinity, pH, $NH_4^+$, $NO_2^-$, $NO_3^-$, $Cl^-$, $SO_4^{2-}$, $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$ and TP. Organic pollutants: the fish tissues (muscle) extracted in a Soxhlet apparatus. The sediments were Soxhlet extracted and fractionated into chlorinated and aromatic hydrocarbons. The fish extracts and chlorinated fractions were cleaned up with sulphuric acid. The analysis was performed by gas chromatography using electron capture and mass spectrometric detection. Diatoms: diatom epilithon was removed from stones from shoreline at 40-50 cm water depth. Preparation and counting followed standard procedures (Battarbee 1986). Zooplankton: samples consisted of quantitative vertical hauls (200 µm mesh size net), and also on qualitative (40 µm) hauls. In addition, qualitative (100 µm) samples we-

TABLE II

Solute concentrations and anion ratios for the lakes studied. Data are the mean of 1993-94 autumn overturn samplings

| Lake | cond. | pH | alk | $NH_4^+$ | $NO_3^-$ | $Cl^-$ | $SO_4^{2-}$ | $Na^+$ | $K^+$ | $Ca^{2+}$ | Mg | TP | $\frac{S+N}{Alk}$ | $\frac{S}{Cl}$ | $\frac{N}{Cl}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | µScm⁻ | | µeq l⁻¹ | | | | | | | | | µM | | | |
| Aguiló | 5.9 | 5.94 | 14 | 0.5 | 3 | 4 | 13 | 9 | 2 | 20 | 11 | 0.16 | 1.1 | 3.2 | 0.7 |
| Redó | 12.1 | 6.50 | 43 | 0.8 | 12 | 6 | 27 | 9 | 2 | 73 | 13 | 0.16 | 0.9 | 4.5 | 2.0 |
| Escura | 11.6 | 5.36 | -3 | 0.5 | 0 | 34 | 18 | 30 | 4 | 12 | 20 | 0.26 | 18.0 | 0.5 | 0.0 |
| Cimera | 7.3 | 6.30 | 37 | 0.3 | 0.1 | 9 | 18 | 12 | 2 | 30 | 14 | 0.22 | 0.5 | 2.0 | 0.1 |
| Caldera | 32.0 | 7.70 | 227 | 3.7 | 3 | 18 | 22 | 38 | 9 | 248 | 41 | 0.41 | 0.1 | 1.2 | 0.2 |

re taken from the littoral. Aquatic macroinvertebrates: three surface sediment samples were taken with an Ekmann grab or a corer in the deepest point. For littoral sampling we used the “kick“ method. Fish: Fish were collected using a series of eight different mesh-size bottom gillnets.

## 3. Results and discussion

### 3.1 ACIDIC POLLUTION

The data on water chemistry of the Iberian lakes (Table II) revealed that they were not acidified. The geology determined, within the narrow range of variation, the main differences in water chemistry. The lowest pH was found in Escura, but the ionic composition showed that acidity was due to the low base-cation supply from the rock rather than to pollution. Together with Aguiló, it was the most sensitive. The high $Ca^{2+}$ in La Caldera made it far less sensitive to acidification. La Caldera and Escura, which lie in ranges that are closer to the sea, showed higher concentration of $Cl^-$ and $Na^+$. $SO_4^{2-}$ was in a similar concentration in all lakes, and $NO_3^-$ were found in appreciable amounts only in the Pyrenean lakes and La Caldera.

Though the two Pyrenean lakes are not acidified, a certain degree of acidic pollution may be inferred. Absolute values of $SO_4^{2-}$ were similar in all lakes, but limnological processes such as overall lakewater dilution by meltwater during the thaw, or evaporation may affect the absolute concentration. We therefore used ion ratios to examinate the relative importance of acid pollutants on the chemistry of each lake. We used the $(SO_4^{2-}+NO_3^-)$/alkalinity ratio as an indicator of the impact of pollutants in relation to the buffering capacity, and the $SO_4^{2-}/Cl^-$ and $NO_3^-/Cl^-$ ratios as indicators of: a) the relative proportion of pollution versus natural acidity; and b) the acidic pollutants enrichment of the wet air masses which originate precipitation.

We found that the $(SO_4^{2-}+NO_3^-)$/alkalinity ratio was markedly higher in Redó and Aguiló than in Cimera and La Caldera. Lagoa Escura is a special case, for most of acidity is caused by the high $Cl^-$ content. Escura had the lowest values for the $SO_4^{2-}/Cl^-$ and $NO_3^-/Cl^-$ ratios. Lakes in the Pyrenees exhibited the highest values, which agree with the values found in precipitation: $SO_4^{2-}/Cl^-$ was 2.1 and 4.1 for the areas of Aguiló and Redó respectively, and $NO_3^-/Cl^-$ was 0.71 and 1.64, respectively (Camarero and Catalan 1993). Despite pollutant concentrations were lower in Aguiló, $SO_4^{2-}/Cl^-$ and $NO_3^-/Cl^-$ ratios in lakewater agreed with those in precipitation, suggesting that they represent the character and composition of precipitation on each area better than absolute concentrations. Modelling of the lake response to current deposition suggested that an average alkalinity loss of 34 $\mu eq\ l^{-1}$ has occurred in the Pyrenees since the start of acidification (Camarero *et al.* 1995). A reconstruction of pH from diatom remains in sediments showed a pH decrease from 6.57 to 6.32 in Lake Redó since 1960 (N. Cameron pers. com.). Though such slight changes inferred from chemical and diatom modelling must be taken with caution, they suggest an initial shift towards acidification.

### 3.2 ORGANIC POLLUTION

Hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB), polychlorobiphenyls (PCBs) and DDTs were determined in the muscle tissue of several fishes per lake (Table III). The results showed an East-to-West gradient of pollution in which the fishes from Redó have higher conc-

TABLE III

Main organic contaminants in the lakes from the Iberian Peninsula selected for study. The sedimentary concentrations of total organic carbon (TOC) and some natural products (*n*-alkanes and perylene) are given for reference.

| | Aguiló | Redó | Cimera | Escura | Caldera |
|---|---|---|---|---|---|
| SEDIMENT | | | | | |
| TOC (mg $g^{-1}$) | 130 | 41 | 33 | 110 | 23 |
| ALKANES (mg $g^{-1}$) | 360 (4.0)[a] | 110 (1.4) | 45 (1.5) | 190 (3.2) | 16 (0.41) |
| PAH tot. (ng $g^{-1}$) | 7000 (77) | 610 (7.6) | 230 (7.6) | 775 (14) | 180 (4.52) |
| RETENE (ng $g^{-1}$) | 1.7 (0.019) | 1.8 (0.023) | 0.17 (0.006) | 1.02 (0.017) | 0.86 (0.022) |
| PERYLENE (ng $g^{-1}$) | 208 | 4.3 | 32 | 15 | 2.4 |
| S-PAH (ng $g^{-1}$) | 186 (2.0) | 8.7 (0.11) | 2.9 (0.10) | 11 (0.19) | 3.9 (0.10) |
| HCB (ng $g^{-1}$) | 1.1 (0.012) | 0.90 (0.011) | 0.44 (0.015) | 0.95 (0.016) | 6.30 (0.016) |
| pp'-DDE (ng $g^{-1}$) | 5.2 (0.06) | 9.9 (0.12) | 4.9 (0.16) | 2.3 (0.04) | 5.3 (0.13) |
| PCBs (ng $g^{-1}$) | 6.7 (0.07) | 14 (0.17) | 0.08 (0.003) | 0.55 (0.01) | 4.7 (0.12) |
| ORGANISMS | | Brown trout n=5 | Brook trout n=5 | Rainbow trout n=3 | |
| LIPIDS (%) | | 3.1-7.7 [5.3][b] | 0.9-1.1 [1.0] | 1.3-2.0 [1.6] | |
| HCHs (ng $g^{-1}$ ww) | | 5-14 [9.5] | 0.11-0.17 [13.5] | 0.05-0.07 [0.75] | |
| DDTs (ng $g^{-1}$ ww) | | 16-35 [25] | 7.1-25 [14] | 0.65-0.89 [0.75] | |
| HCB (ng $g^{-1}$ ww) | | 1.1-2.4 [1.65] | 0.17-0.46 [0.29] | 0.017-0.032 [0.024] | |
| PCBs (ng $g^{-1}$ ww) | | 7.8-10 [9.9] | 2.0-4.9 [3.7] | 0.90-1.9 [1.8] | |

a: Fluxes in mg or ng $cm^{-2}$ $year^{-1}$ .b: average concentrations

entration and those from Escura have the lowest. This gradient was observed for all the compounds, and involves important concentration differences from lake to lake. The sedimentary flux values were more uniform than the concentrations in fishes, particularly in the case of HCB. The concentrations in the fishes were related to the standing stock of pollutants in the water column, and the accumulation in the tissues is related with the bioconcentration factor. Conversely, the deposition fluxes in the sediments are related with the settling mechanisms in the lake. Furthermore, the two types of samples correspond to different time scales. In any case, the East-to-West pollution gradient was not observed when comparing the sedimentary deposition fluxes of the chlorinated contaminants. Thus, Cimera, Redo and Escura were the sites showing a higher concentration of DDTs, PCBs and HCB, respectively (Table III). In principle, these sedimentary data did not show any uniform geographic trend as in the case of the fish samples. Nevertheless, Lake Redo showed the highest fluxes of PCBs and retene, which corresponds to industrial and pyrolytic (forest fires) inputs. Retene also exhibits a high flux in Caldera suggesting that most of polycyclic aromatic hydrocarbons (PAH) in this lake originated from forest fires. Conversely, the high PAH deposition flux in Aguiló and Cimera corresponds to a high deposition flux of petrogenic compounds (S-PAH) suggesting an origin related with fossil fuel combustion.

## 3.3 ORGANISMS AS INDICATORS OF POLLUTION

The epilithic diatom flora was dominated by species of the genus *Achnanthes*. *A. minutissima* Kutz, a circumneutral species common in lake communities prior to acidification events (Charles *et al.* 1989) was found in the lakes with pH > 6.0 (La Caldera, Redó, Cimera). In the

TABLE IV
Shannon-Weaver diversity index and acid status of the macroinvertebrate communities

| | Aguiló | Redó | Escura | Cimera | Caldera |
|---|---|---|---|---|---|
| Profundal benthos diversity | 1.58 | 1.55 | 2.42 | - | 2.13 |
| Littoral benthos diversity | 2.49 | 3.31 | 2.15 | 4.10 | 1.95 |
| no. of sensitive species (pH > 5.5) | 3 | 4 | 0 | 0 | 2 |
| no. of intermediate species (4.7 < pH < 5.5) | 4 | 3 | 2 | 1 | 0 |
| no. of tolerant species (pH < 4.7) | 9 | 15 | 4 | 5 | 0 |
| no. of species of unknown sensitivity | 28 | 13 | 27 | 18 | 8 |

lakes with pH < 6.0 (Aguiló, Escura) the acidophilic *A. marginulata* Grun was dominant. Nevertheless, the two lakes had a rich diatom flora, in particular Escura. We interprete this as an indication of that its acidity stems from natural (sea salt) acidity and not recent air pollution. A higher productivity contributed also to the specific richness. La Caldera had the most deviating diatom community, with *Cymbella aspera* Grun, and *Nitzschia sp.* in abundance, as expected because of its remarkably high pH, Ca and alkalinity.

Zooplankton communities were composed of a low number of species, typical for cold, oligotrophic lakes. The species recorded were of little indicator value with regard to acidity, because most of them are tolerant species to incipient pollution. Rotifers dominated in Redó, Aguiló, and Cimera, and crustaceans were distributed according to the characteristics of lake size, altitude, and trophic status (Miracle 1978). No clear relationship with the presence or absence of fishes appeared.

In the five lakes studied we identified a total number of 146 species of macroinvertebrates, 98 if we exclude those found at the outlets and inlets. The invertebrate fauna recorded in those high mountain lakes consisted mainly of cold stenothermal species, common in oligotrophic or ultra-oligotrophic mountain lakes and streams. Most of the species have Central and Southern Europe distribution, but we also found some relict boreoalpine species, Pyrenean endemic species, and some vicarians of species from central and northern lakes.The species found in Escura are known not to inhabit only high mountain environments, and the high densities found indicated a higher nutrient load. Using the community classification dessigned by Raddum and col. (Wathne et al., 1995), the two Pyrenean lakes and La Caldera do not seem to be affected by acidification, because of the presence of several very sensitive species (Table IV). In Escura and Cimera, sensitive species were not found, but because of the diversity and the presence of a number of species with unknown sensitivity this result must be interpreted with reserve. Most data on effects of acidification on lake benthos refer to studies in nordic countries based on sub-alpine and lowland watersheds, excluding many taxa found in southern mountain regions (Raddum *et al.* 1988). As a consequence, our sampling sites can be misclassified when applying those acidification indexes, since important indicative species may be absent due to altitudinal or biogeographical factors rather than acidification..

As for the fish, the rainbow trout *Oncorhynchus mykiss* (Walbaum) was the only species captured in Escura, the brown trout *Salmo trutta* (L.) the only one from Redó, and the brook trout *Salvelinus fontinalis* (Mitchell) from Lake Cimera. No fish was captured in Aguiló or La Caldera. The fish populations are supported by means of periodical restoking in the three lakes but spawning may take place, although we have no direct evidence. All populations were in good physiological condition, and they did not present symptoms of acid toxicity.

## 4. Conclusion

The Iberian peninsula lakes did not show severe anthropogenic acidification. pH values were in the range of sensitive lakes, but the levels of acidic pollutants were low. Nevertheless, the two lakes in the Pyrenees presented traces of a diffuse pollution higher than in southern locations. The Pyrenean lakes showed the highest fluxes of organic micropollutants related to fossil fuel combustion, and the higher pollution-induced versus natural acidity ratios. Although the absolute acid pollutant levels were of the same order than in the rest of lakes, the ion ratios adequately reflected the composition of regional precipitation, which has been shown to present a slight but significant level of pollution in earlier studies. The alkalinity and pH declines detected by biogeochemical modelling and diatom-based pH reconstruction in Pyrenean lakes also suggested an early acidification.The lowest pH found in Escura is attributable to the low cation supply rather than to input of pollutants.

The status of the organisms surveyed partly agreed with this diagnosis. In general, acidity had little effect on biota, but certain contradictory results arised when each group was examined separately in some detail. The diatom species that appeared in Iberian lakes correspond to lakes in an intermediate to low position in the acidity ranking of other European lakes. Zooplankton showed a biogeographical distribution responding to the typical high mountain environmental conditions, and not to the influence of acidity. Acid sensitive species were lacking in the macroinvertebrate inventories of Escura and Cimera, but there was in all lakes a high number of species of unknown sensitivity. There is therefore a lack of background information to interpret the invertebrate distribution. In the case of lakes supporting fish populations, these have been introduced, but they were in good physiological condition.

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