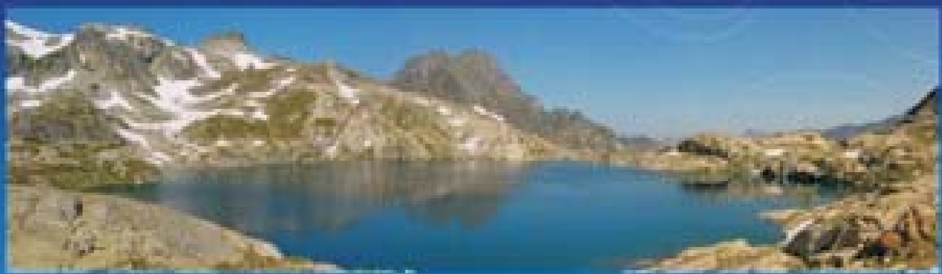

Landscape Ecology and Geochemistry of High Altitude Lakes | DG Zaharescu | PhD Dissertation

Landscape Ecology and Geochemistry of High Altitude Lakes

– Insight from the Central Pyrenees –

Dragos G. Zaharescu

2010

Thesis submitted to Vigo University for the degree of Doctor of Philosophy

Doctor Europaeus Honour

UNIVERSITY OF VIGO

UNIVERSITY OF KINGSTON

Landscape Ecology and Geochemistry of High Altitude Lakes

– Insight from the Central Pyrenees –

FRONT COVER
Pyrenees view on background (courtesy of pasarlascanutas.com) with Micoulaou lake (2333m a.s.l.) in Azun valley, France, geological map of central Pyrenees, *Eriophorum angustifolium* sedge, dry Bubal reservoir, plot of rain days at Bubal and an example of R code.

BACK COVER
Arras pond (2070m a.s.l.), Cauterets valley and
Lake Arrémoulit (2285), Ossau valley, Pyrénées National Park.

UNIVERSITY OF VIGO

Kingston University London

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PhD Dissertation

Doctor Europaeus Honour

2010

This thesis is based on a collaborative PhD research project jointly supported by:

Animal anatomy Lab, Faculty of Biological Sciences, Vigo University, Spain and
School of Geography, Geology and the Environment, Kingston University London, UK

UNIVERSITY OF VIGO

Kingston University London

Dissertation presented at Faculty of Biological Sciences, Vigo University for the approval of the University Committee on Postgraduate Studies in fulfillment of the criteria for the degree of Doctor of Philosophy, *Doctor Europaeus* Honour.

I certify that I have read the dissertation titled: Landscape Ecology and Geochemistry of High Altitude Lakes; Insight from the Central Pyrenees , and that, in my opinion it fulfils the scope and quality criteria for the degree of Doctor of Philosophy.

Professor Antonio Palanca Soler, Animal Ecology and Biology Department, Vigo University (Supervisor)

I certify that I have read the dissertation titled: Landscape Ecology and Geochemistry of High Altitude Lakes; Insight from the Central Pyrenees, and that, in my opinion it fulfils the scope and quality criteria for the degree of Doctor of Philosophy.

PSHooda

Professor Peter S. Hooda, School of Geography, Geology and the Environment, Kingston University, London (Supervisor)

June 30, 2010

Landscape Ecology and Geochemistry of High Altitude Lakes
- Insight from the Central Pyrenees -

Abstract

High elevation lakes are promising sentinels of global environmental changes. Yet many of the fundamental processes at these sites are still poorly understood. In this thesis I examined how environmental factors shape ecotope and ecosystem development at high altitude lakes and identified potential environmental hazard sources from the local geology. The study area spans a roughly 80 km E-W linear gradient in the central Pyrenees and is characterised by a high lake density. Data were collected during several field surveys and included a complex pool of landscape, ecological, geochemical and climate variables which helped answer fundamental questions regarding ecological and geochemical processes at high elevation lakes.

I found that ecotope development at high altitude waterbodies is largely driven by a particular combination of hydrological, geo-morphological and topographical forces. This can be interpreted as major evidence of postglacial landscape evolution which created different physical niches for biota setting. Complex interactions among these factors were found to shape the riparian vegetation structure and determined their species co-occurrence patterns. Major littoral zoobenthic communities showed significant sensitivity to external ecotope factors such as topography formation (through its effects on catchment type, shore and catchment snow coverage and connectivity with other lakes) and hydrodynamics (waterbody size, type and discharge of input/output), as well as to the riparian vegetation structure. These communities formed eurytopic associations, i.e. associations present in a variety of habitats.

Both riparian and littoral ecosystems also responded considerably to large scale gradients such as altitude, latitude and longitude, possibly a condition of major climates converging in the Central Pyrenees. Generally altitude waterbodies are poor in nutrient resources. The present results showed that their riparian and littoral ecosystems have a high capacity to reflect a particular set of attributes from the surrounding terrestrial system.

Relatively high levels of trace metals were found in the sediment and water of Respomuso lake catchment, at the contact zone between granite and metamorphosed sedimentary bedrock. The origin of these metals was the metal-rich geology. The sediment-bound trace metals constitute a considerable metal burden in the catchment, with the concentrations of As, Cd and Ni exceeding the sediment quality guidelines for the protection of aquatic life. With respect to arsenic - a highly toxic element of concern, the results revealed a relatively high degree of natural enrichment in the sediments, due to mobilisation from source areas upstream which are dominated by quartzite and slate elements. The arsenic concentrations in the water also exceeded the guideline value for the protection of aquatic biota at a number of sites. The findings indicate that this most likely resulted from its higher mobility from the sediments or surrounding metal-rich bedrock under the oxic condition of the streams. This is a significant result as these concentrations may increase if the environmental/climate conditions change.

Nonetheless, one of the most significant findings resulted from the paleogeochemical analysis of a sediment core. The results uncovered the potential of climate change, particularly the elevation of the freezing line, a general increase in the frequency of drier periods and a

reduction of snow cover in the last three decades to enhance trace metals mobilisation from mountain exposed topography. Among the metals, arsenic and nickel, two hazardous elements, crossed their safe concentrations for the protection of aquatic life in the sediments deposited in recent years, pointing out to a potential threat to the wider environment. While this finding may raise as many questions as it answers, no doubt it has the potential to open a new direction in the challenging field of climate change research. These achievements have potential implications for the use of mountain waterbodies as sensors and integrators in the global monitoring of the environment.

Keywords: high altitude lakes, ecology, geochemistry, climate change

Aknowledgements

The research presented in this dissertation has been carried out at the department of Animal Biology and Ecology, Vigo University, Spain and the School of Geography, Geology and the Environment, Kingston University, London, UK. The path towards this thesis spans several years of work in an interdisciplinary environment.

In this effort I have been fortunate to interact with a number of people who have been involved in the development of the research presented in this thesis. I am deeply thankful to all those who helped find solutions to the problems raised in this work, and whose names are mentioned in the subsequent chapters.

Special gratitude goes to my enthusiastic supervisors Antonio Palanca-Soler and Peter S. Hooda who have provided the stimulating and critical setting while allowing to develop my own ideas; all these were vital for the completion of this study.

I am deeply grateful to Carmen Burghelea with whom I shared most of the hypotheses and headaches together with long hours of work pretty much along the whole trajectory of this research.

Finally I express my appreciation to Richard Lester from Birmingham University, UK with whom I shared many exciting moments during the mountain campaigns and subsequent visits we had made each other. Richard sadly passed away in April 2006 but he left behind great memorable moments and a valuable scientific legacy.

Sometimes I worked in large teams, others independently. All these helped distillate the ideas exposed herein.

List of chapters

1

HIGH ALTITUDE LAKES

A geomorphic legacy from glacial times

The global importance of mountain regions has been increasing in recent years especially as hotspots of biodiversity, resources for human populations and reliable sensors of global environmental changes (GLOCHAMORE, 2006). Although they occupy 24% of the Earth's land surface, mountain areas directly and indirectly provide resources for more than half of the humanity, including water, energy, wood, minerals and recreation (Price, 2004).

Geomorphically, mountain landscapes are the product of a dynamic interplay between endogenic constructive forces, i.e. agradation (e.g. tectonism and vulcanism) and external degradation processes, e.g. hydrological erosion (including glaciations) and weathering (Thornbury, 1969). In general, the major features of present mountain landscapes are the result of latest Pleistocenic glaciations which have carved the mountain surface at global scale (Fig. 1.1). For example it has been reported that more than 24 million km^2 of Tibetan plateau (representing ca. 80% of its surface) has been affected by the last glaciations (Kuhle, 1998). Its effects extended far beyond the areas covered by ice, and influenced the global radiation balance further aiding to an existing cooling (Kuhle, 1998). After the last glacial retreat (roughly 10000 years ago), the action of fluvial, climate and other weathering forces during the modern Holocene contributed to the creation of lower resolution land forms, e.g. variability within catchments, lakes and stream networks, and added a characteristic aspect to the present landscape.

In mountain regions erosional (degradation) glacial topography generally prevails over the depositional one. As a result, cirques, U, V and hanging valleys are typical erosional formations of mountains (Fig. 1.1). Cirques are amphitheatre-like glacial basins frequently found at mountain valley heads, which are not always directly connected with the valleys (Fig. 1.1D). A cirque has generally three distinct features: a headwall, notably vertical, which is usually depleted of slope debris due to previous glacier transport, a central bowl-shape depression which extends from the header to a rocky threshold which marks the side at which the glacier flowed away from the cirque. As a consequence glacier cirques are common places where water accumulates forming lakes, ponds and aquifers (Fig. 1.1D). Cirques can be circular, subcircular and composed (a more advanced stage), according to the variability in the local structure, lithology and age. Glacial valleys/channels originate either in cirques or at a lower step. The difference commonly lies in the size of the flowing glacial tongue which determined whether a valley is V- or U-shape. A special type of glacial channel is the hanging valley. This is formed when a tributary glacier flowed into a glacier of larger volume and resulted in differences in level and depth between the two valleys (Fig. 1.1C). The tributaries in the hanging valley usually form cascades when they flow into the major valley. Major depositional land forms left behind by glaciations are the moraines. These can be terminal, lateral and basal depending upon whether deposition took place at the end of, at the lateral of, or beneath the glacier stream (Thornbury, 1969).

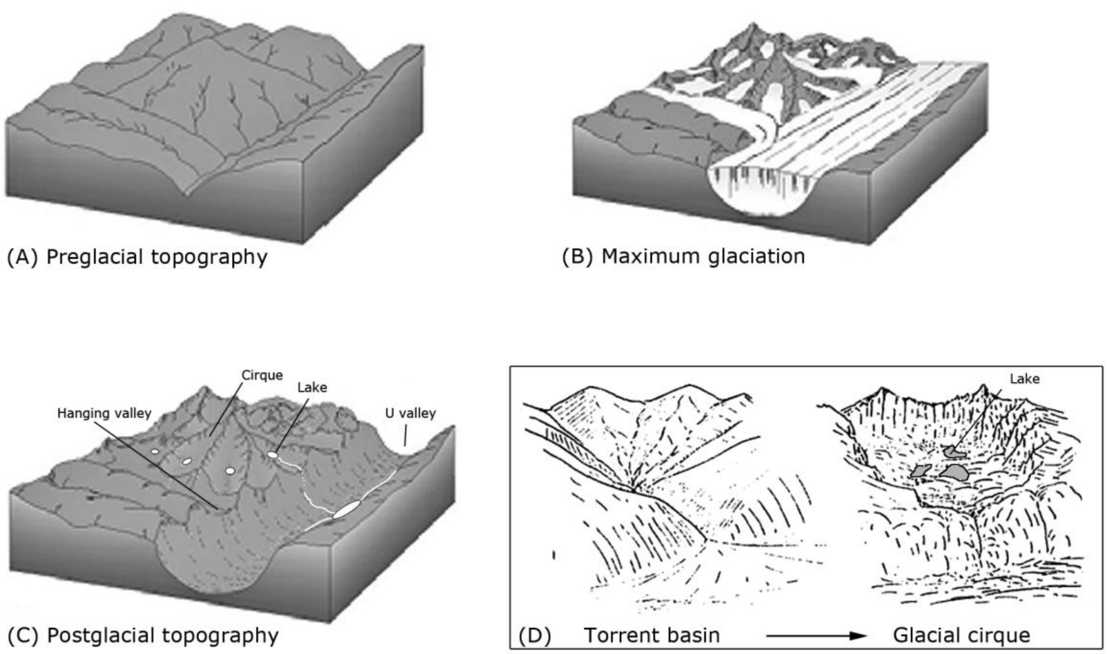

Fig. 1.1 Role of mountain glaciations in landscape modelling and glacial lakes formation (A to C; after Draper, 2010); D - detailed depiction of cirque formation from torrent basin (after Martonne, 1948).

Glacial lakes, either extinct or extant, are common elements of the mountain landscape. In general it is safe to assume that the latest glaciation cycle was responsible for the formation of more mountain lakes than all other geomorphological causes together (Thornbury, 1969). The present condition of a lake is thus generally an evolutionary consequence triggered back in glacial times. The most common types of glacial origin lakes are: basins carved in cirques' bedrock and upon the treads of glacial steps; basins formed behind the terminal or lateral moraines; basins formed by the damming of a tributary valley by sediments left from the retreat of the glacier in the main valley; and basins formed behind rock bars in the valleys floor (Thornbury, 1969; Goude, 2004). These relatively small lake bodies are ephemeral formations which finally evolve into lacustrine plains at a pace largely depending on the sedimentation/ erosional rhythms in their local topography.

Ecosystem development

While at large temporal scale glacial lake landscapes are modelled by very dynamic processes, at smaller scales these geomorphic modifiers are slow enough to allow stable ecosystem development. Biotic adaptation, evolution and persistence through time in these environments generally depend on a fragile equilibrium between slowly changing environmental forces and stable seasonal fluctuations that allow species to adapt gradually. In this scenario, major mobile geomorphic agents such as running water (including runoff), springs, glaciers and the flow inside the lotic system (waves and currents) have the potential to shape the settlement of biotic communities in altitude waterbodies. Other factors such as climate (temperature, precipitations and wind), local morphology, and variability in the bedrock geochemistry (minerals, major and trace element contents), which interact with major geomorphic processes, are expected to shape the structure and functioning of ecosystems. For instance, climatological variations such as the type and intensity of precipitation, daily temperature variation, frequency of 0ºC temperatures and the duration of freezing (e.g. Keller et al., 2005), as well as variation in these factors with slope orientation and altitude, can affect the distribution of plant cover over localized areas (e.g. Baker, 1989). Moreover, bedrock geochemistry is supposedly a major factor influencing lake invertebrate communities in these landscapes.

Mountain landscapes contain hotspots of biodiversity, often coinciding with centres of cultural diversity (Price, 2004). A major threat to aquatic ecosystems in mountainous landscapes has emerged in the recent Anthropocene, as a result of human impacts on both land and atmosphere. These range from fish introductions into high altitude lakes (Schilling et al., 2009), rising temperatures and extreme events such as flooding due to global climate change (Schindler et al., 1996; Primicerio et al., 2007; Russell, 2009), to acidification and long-range transport and deposition of pollutants from industrial activities (Camarero, 1994). The great capacity of mountain lakes to store signals of environmental change globally has promoted them as sensitive sentinels of environmental changes (Williamson, 2009). As a result aquatic ecosystem function and the effects of climate change have become primary research goals under the UNESCO mountain research agenda (GLOCHAMORE, 2006).

Research goals

Previous research on alpine waterbodies has addressed questions such as biotic structure and function (Lencioni, 2004; Nieto-Román, 2007; Oertli et al., 2008; Kernan et al., 2009), biological quality assessment (Borderelle et al., 2005), biological and chemical dynamics and stratification within the water column (Macek et al., 2009; Lüthy et al., 2000), trace metal aerial deposition (Lavilla et al., 2006) and, sensitivity to acidification and climate change (Camarero, 1994; Vilanova et al., 2001; Williamson, 2009). Despite the ecological and geochemical importance of alpine lakes and their high sensitivity to environmental variability, the complexity of their unique ecosystem formation and the hazards they may experience are still to be fully appreciated.

The overall objectives of the work presented herein were to unveil patterns in ecotopic and ecosystem development of altitude lakes at the appropriate catchment scale, and to assess potential hazards affecting these environments. I address these objectives in a case area comprising a significant number of waterbodies in the central Pyrenees.

Thesis outline

This work is structured in two major parts, each consisting of three chapters. Each chapter is written as stand-alone manuscript and some repetition may occur in the information presented. The first part describes the regional ecotopic and ecosystem structuring of 354 lentic waterbodies from the central French Pyrenees. This is developed in three chapters: first, I examine the ecotope formation at high elevation lakes. Second, I assess the role of external (geoposition and catchment) and in-lake (sediment and water physico-chemistry) factors in riparian vegetation species structuring; and, third, I discuss the sensitivity of major littoral macrozoobenthos groups to external and internal factors, including geolocation, catchment factors, riparian macrophytes and vertebrate predation.

In the second part environmental hazards are discussed in three chapters. First, a case of natural trace elements distribution and levels in the sediment and water is assessed from a whole catchment perspective. Second, I discuss arsenic source and mobilization within and from an altitude catchment. Third, the role of climate change on arsenic and other trace elements behaviour is examined using a sedimentary record from a mountain reservoir, i.e. Bubal, Tena Valley (Spain).

Finally, in the last chapter I integrated all the findings from the previous chapters and combine all the results into a general Summary and Perspectives.

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PART I

Ecosystem structure of high altitude lakes

Lake Gentau

Eriophorum angustifolium

Limnephilidae trichopters

2

The architecture for ecotope formation at high altitude lakes

Abstract

The ecotope is the physical setting in which an ecosystem commonly occurs. Understanding how landscape components shape ecotope development not only can shed light on the processes involved in biota settling but can also help develop conservation strategies based on natural laws. This study assessed the degree of influence a number of landscape factors have on altitude lake ecotope development at the catchment and larger geographical scales. This provided a conceptual mechanism of lacustrine ecotope development and classification.

This study was conducted in the axial Pyrenees and included most of the lakes/ponds (n=354) within the boundaries of Pyrénées National Park, a highly protected and undisturbed area. The influence of landscape components on lake ecotope development was assessed by multivariate analyses of a large number of landscape variables. The relationships and interdependencies between the various variables were evaluated by means of principal component analysis (PCA) and categorical principal component analysis (CATPCA). The behaviour of main driving components along broad geographical settings was tested using regression analysis.

The PCA revealed three major composite factors that can account for most of the variability in lake ecotope development. In order of their contribution they were: (i) hydrodynamics (type and discharge of tributary/output, and waterbody size), (ii) bedrock geo/morphology (geology, shore slope, % vegetated slope/shore, fractal order and the presence of aquatic vegetation) and, (iii) topography (presence of snow deposits at shore level and in the near catchment, catchment type and visible connectivity with other lakes). Of these, bedrock geo/morphology and topography showed significant variations along altitudinal and latitudinal gradients in terms of their influence on ecotope development. An analysis of related categories forming each major factor by CATPCA allowed a classification (typification) of water-bodies according to their similarities. This is interpreted as the result of landscape evolution in the Holocene, following the glaciers' retreat 11 000 years ago. Here I also propose a conceptual model of lake ecotopes at high altitudes, that integrates physical, geological and climatic processes. This model can be further used in both research and management of high altitude lakes. This is important as ecological studies often require diverse and well-defined habitat units where processes are to be studied. Such an ecotope-based classification could also improve policies on water-bodies and their landscape conservation.

Keywords: altitude lakes, ecotope, landscape, processes, lake classification, Pyrenees, PCA, CATPCA

1. Introduction

High altitude lakes are pristine ecosystems which are under increasing attention worldwide due to their role as hotspots of biodiversity (Gopal et al., 2001), repository of long-range transported pollutants (Andrea et al., 2007) and global warming (Williamson et al., 2009). Moreover, they are sources of genetic variation and evolutionary challenges at species distributional boundaries. Of more than 300 million lakes on the Earth's surface, a great number occur at mid-to-high altitudes (Downing et al., 2006). Therefore high altitude lakes offer a unique setting to study the physical environment involved in their ecosystem development.

Generally, lake ecosystems are sustained/shaped by a physical template (spatial eco-space) that includes climate, geomorphology and the surrounding land cover. Understanding how changes in the physical environment influence ecosystems is generally difficult due to the heterogeneity of landscape and the many direct and indirect linkages between landscape features and processes, especially at the broad scale. Abiotic factors, such as water resilience and cycling, primary productivity and nutrient cycling are key to characterising aquatic ecotopes, and they shape community/ ecosystem development (Van der Molen et al., 2003).

The key concept of this work is the lake/pond and its surrounding landscape as a structural and functional unit, termed here "ecotope". Our judgement follows the principles of landscape ecology that divide a landscape into fundamental and holistic units, named "patches". Landscape patches are unique combinations of hierarchically organised abiotic conditions that interact at multiple spatial scales and shape the biotic communities (Forman, 1995). Forbes (1887) also pointed out that a typical pond is "a self-contained system, a world within itself". The terrestrial component surrounding a lake/pond represents the landscape features that dictate the inflow of sediments, nutrients and other chemicals which ultimately determine the ecotope-biota interrelationships.

General trends in fauna and flora species and their functional composition can be predicted by ecotope features (e.g. Della Bella et al., 2005, Mazerolle et al., 2005; Goebel et al., 2006), in other words geology, geomorphology, waterbody size and slope, and land cover. It is noteworthy that species richness in relation to environmental constraints of distinct lake and mountain-top habitats (e.g. Vuilleumier, 1970; Barbour and Brown, 1974; Brown and Dismore, 1988) has been widely discussed and tested in the conceptual framework of Equilibrium Theory of Island Biogeography. The theory predicts species structure at equilibrium, in a suitable habitat, being a function of habitat/ecotope isolation, size and composition (MacArthur and Wilson 1963; MacArthur and Wilson 2001). Lakes/ponds ecotopes therefore can be assumed to support a particular type of vegetation and fauna which result from a particular succession/evolution over time. However, little is known of lacustrine ecotope development at high altitudes, due to a number of constraints, including the difficulty of sampling large and rough terrain and the short period of time the landscape features are visible. At the same time, there is a growing need in ecology to better understand how heterogeneity within a system affects current and future ecological dynamics.

The concept of ecotope and its functioning has been studied mainly in lowland terrestrial ecosystems, whilst its application to high altitude water-bodies is yet to be fully appreciated. Furthermore, it is fundamental to understand the link between biotic and abiotic processes and the uncertainty often associated with scaling up of these intrinsically linked landscape processes. The strong E-W orientation of the Pyrenees chain of mountains, together with contrasting blocks of different bedrock geology provide sharp contrasts in climate and biogeography. This along with the relatively high density of lakes makes form an ideal setting to disentangle usually complex ecotope processes into simple structures at high altitudes.

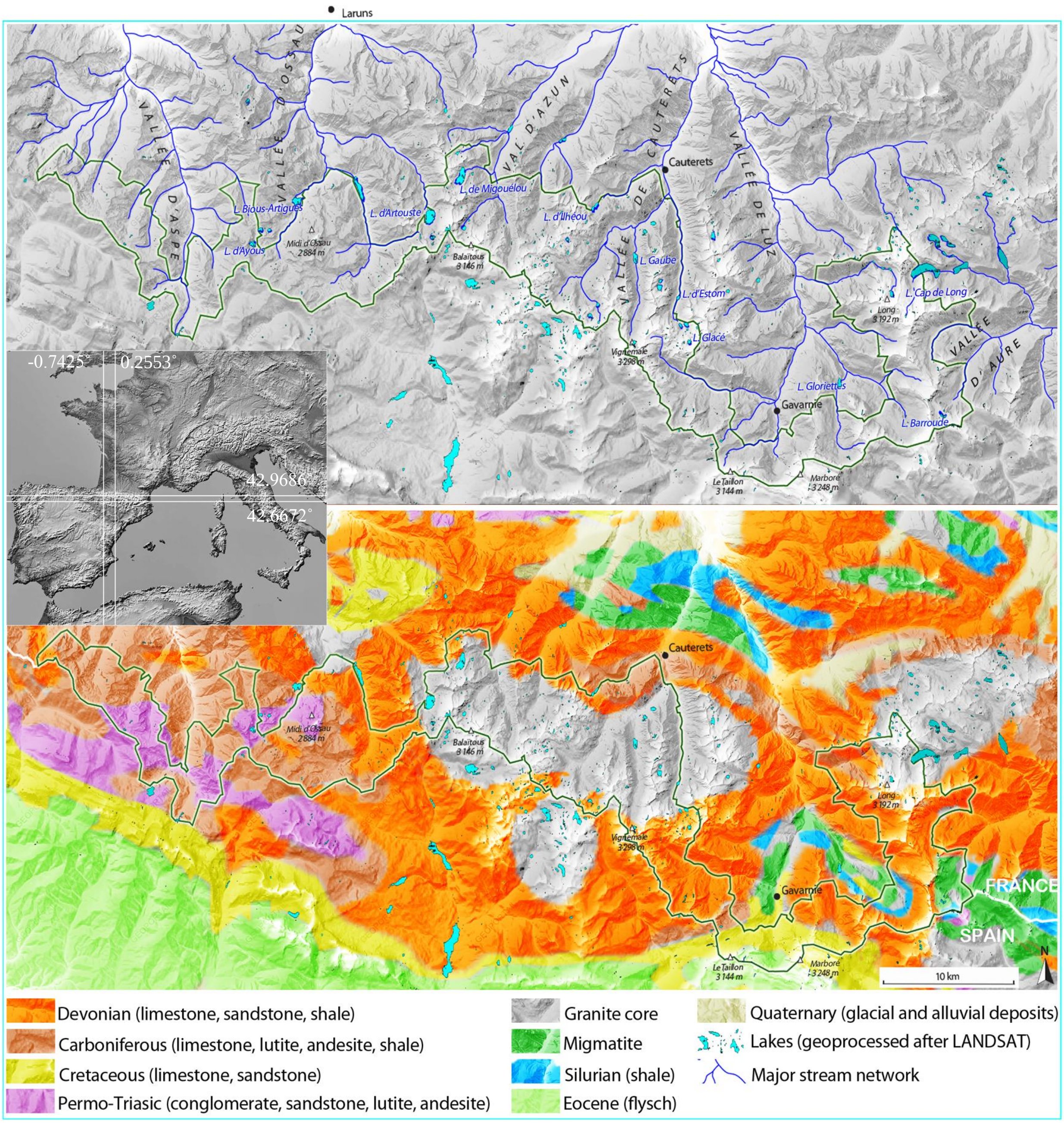

Fig. 2.1 Study area (axial Pyrénées National Park, outlined in dark green) together with major hydrological and geological formations on digital elevation model. Lake representations are after LANDSAT imagery; inset radar map is after JPL (2000); Pyrenees digital elevation model is after Geoportail (http://www.geoportail.fr/); geological representation is after SGN (1996).

The main aim of the work presented herein was to determine the degree of influence a number of landscape variables have on altitude lake/pond ecotope development. We also theorize that lakes ecotopes are not formed randomly. Rather, the lake's physical condition is a geomorphic inheritance left by the retreat of the glaciers 11 000 years ago. The work stems from a large number of locations within the axial Pyrenees, which comprises practically the full range of glacial-origin lake environments. A second emphasis was placed on defining a number of reference (model) lacustrine ecotopes based on their landscape similarities. We finally propose a conceptual model of lacustrine ecotopes at high altitudes, integrating physical, geological and climatic processes that shape the formation of ecotopes and habitats.

2. Study area

The Pyrenees are an E-W mountain range which extends over roughly 430 km from the Atlantic to the Mediterranean Sea and separate the Iberian Peninsula from the rest of continental Europe. The area under study extends over about 80 km in the axial part of Pyrénées National Park (Atlantic Pyrenees), France (Fig. 2.1). This area, under reinforced protection, is restricted to recreational hiking, angling, and seasonal grazing of livestock. Due to their location the majority of waterbodies could be considered to reflect most of the natural ecotope processes.

2.1 Geology

Bedrock geology is marked by the outcrop of Cauterets-Panticosa igneous (granitic) batholith in the central part, massively flanked by metasedimentary (shale) and sedimentary (limestone) materials (Fig. 2.1). The abundance of granite, which is particularly resistant to erosion, gives the region a characteristic steep-sloping aspect. The contact zone between Cauterets granitic outcrop and the low-grade Cambrian-Carboniferous metamorphic material yields ore deposits, some of which have been exploited for metalliferous mining in the past (Paegelow, 2008). Mineral springs are abundant in this area, particularly the hot springs at the contact of granite with the stratified rocks.

2.2 Climatology

The main air masses are from the W - NW, bringing precipitation (i.e. rain, snow and moist air) mainly from the Atlantic and the Bay of Biscay (oceanic-suboceanic climate; MATE, 2002). This leads to a marked contrast between different sections/valleys of the region with glacial formations being present mainly on the N-oriented slopes of the western and the central parts of the range. Some of the glaciers are still active and are the source of major torrents. Precipitation averages 100-160cm year^{-1} in the area while mean annual temperature is 13-14°C (0°C isotherm oscillating between 1200m in January- 3300m in July/August). Tree line varies between 2000-2500m a.s.l. The snow cover above 2000m settles down in November and starts to break up in April. The glacier forming line is relatively high, ranging between 2500 to 3200m a.s.l. (Kessler and Chambraud, 1990).

2.3 Hydrology

There are more than 400 lakes and ponds within the boundaries of The Pyrénées National Park. The great majority of the lakes are of post-glacial origin and they are generally formed at the head of the valleys, in the axial part of the mountain range. At global scale they are relatively small water-bodies, like >90% of the lakes on the Earth's surface (Downing et al., 2006). A large number of mountain torrents (>210), locally called *gaves*, drain the lake catchments, and give a generally dendritic structure to the hydrological network (Fig. 2.1). These 'gaves' are used to subdivide the area in six major units: Aspe, Ossau, Azun, Cauterets, Luz and Aure (Fig. 2.1 and Appendix 1). A number of lakes in the major valleys were transformed into reservoirs and are used to generate hydroelectricity and supply water to human populations further downstream (MATE, 2002).

3. Methodology

A total of 354 lakes/ponds in the axial region of Pyrénées National Park was surveyed during the month of July in 2000, 2001 and 2002. The sampling was aimed to represent the majority of mountain lakes in the area. The survey of lakes was undertaken in an east-westward direction to minimize the possible bias induced by a generally late snow thaw in the western side. Appendix 1 lists the name and location of the surveyed water-bodies. At each location a number of major landscape factors considered to influence ecotope/habitat processes were visually approximated and scored according to dominant units. A detailed description of the variables surveyed is presented in Table 2.1. Lakes' size/type categories were estimated from their surface area. This was calculated as the surface of an ellipse whose major and minor diameters were measured in the field. A digital laser telemeter was used for this purpose. Furthermore, a portable GPS device helped record the geo-position coordinates, i.e. latitude, longitude and altitude, at each location.

Principal Component Analysis (PCA) was the statistical approach used to reduce the landscape variables to a small number of composite variables (factors) that represent the major environmental trends/ processes in the dataset. PCA is suitable for multivariate data which find non-correlated sets (principal components) of linearly related variables. Also, PCA is a relatively robust tool for datasets which are not normally distributed. A Varimax rotation was applied to the extracted axes (components) in order to maximize the captured variance. Any considered variable was excluded if the model was not improved by its inclusion in a principal component (Table 2.1).

To help identify ecotope units, the interaction between variable categories of each extracted PC and projected variables' vectors on lakes ordination space were evaluated. A categorical principal component analysis (CATPCA) was applied in this case. CATPCA is a nonparametric approach appropriate to find relationships between variables which span over multiple scales (e.g. numerical, categorical and nominal). Despite its potential for environmental studies, its use has been, however limited (Burghelea et al., 2010). Moreover, as an exploratory technique, CATPCA may be influenced by the sample characteristics. For this, the stability of CATPCA results from our data (the degree of sensitivity to changes in the data) has been tested by bootstrap procedure. It implied 1000 sets of bootstrap samples with replacement being taken randomly from the original dataset and repeating CATPCA on each set. This procedure determined the constancy of assignment (correlation) of the variables to the component vectors and produced 90% confidence regions of component loadings. If the results provided by CATPCA are stable, we expect narrow confidence ellipses.

Simple regression analysis was used to determine the behaviour of catchment-scale ecotope properties along large scale geographical gradients. The variables were summarised as regression factor scores of the extracted principal components (PCs) before being used as response variables to geographical predictors in the regression analysis. Statistical treatment of the data was

Table 2.1: Description of geographical and ecological variables used in the analysis of 354 altitude lakes from central Pyrenees

Parameter	Values
Latitude^{+}	Geographic coordinates
Longitude^{+}	Geographic coordinates
Altitude^{+}	Meters a.s.l.
Catchment type^{+++}	Plain, U shape valley, slope, mountain pass, V shape valley, head of glacial valley
Main geology^{+++}	Conglomerate-sandstone-claystone, limestone (+sandstone-marlstone-schist enclaves), schist (+andesite-sandstone-claystone and granite-limestone), granite (+schist)
Size^{++}	Pool (<315±333m^2), pond (1566±1985m^2), small lake (9157±10267m^2), medium size lake (41127±31820m^2), large lake (91441±37307m^2)
Fractal order^{++}	1-4 scale
Visible connectivity with other^{+++}	Absent, surrounded by another lake, with another one, in chain
Nature of water input^{+++}	Meteoric, spring, stream/waterfall
Tributary discharge^{++}	Absent, low discharge, medium discharge, high discharge
Nature of water output^{+++}	Absent, temporary, surface-small, surface-medium, surface-large, subterranean, dam output
Aquatic vegetation^{++}	Absent, Absent but water flooding the grassland, scarce, abundant
% grass covered shore	Categorized numeric
% grass covered slopes	Categorized numeric
Slope of lake perimeter^{++}	Plain, plain in alternation with medium slopes, medium slopes, steep in alternation with medium/plain, steep in >50% of perimeter
Shore snow coverage^{++}	Absent, <10%, 10-50%, >50%, into the water
Snow deposits in the catchment^{++}	Absent, very scarce, scarce, abundant, very abundant
*Shape of lake/pond^{+++}	Circular, elliptic, elongate, irregular, triangular, rectangular, in 8, boomerang
*Modifications in lake's shape^{++}	Absent, one input/output stream, various input/output streams
*Colour^{+++}	Blue-grey, opaline blue, opaline white, turquoise green
*Water level marks^{++}	Absent, < 50cm, > 50cm
*Damming^{++}	Absent, small dam, big dam
*Shore vegetation coverage^{++}	Most of it, partially, scarce
*Shore coverage^{+++}	Scarce vegetal cover (>50% cliffs, >50% slope drift, cliffs+slope drift, bedrock, bedrock+slope drift, bedrock+dispersed rocks, big granite blocks), medium vegetal cover (bedrock+grass patches, grassland+rocks, grassland+slope drift+rock blocks, cliffs+slope drift+ grassland, slope drift+grassland+scrubs, forest+cliffs+slope drift+grassland area) and dominant vegetal cover (>50% grassland, >50% scrubland, grassland+scrubs+forest, grassland+dispersed rocks, grassland+scrubs+rocks, grassland+bedrock+rocks, sheep field)
*Coverage of near catchment^{+++}	Scarce vegetal cover (>50% cliffs, >50% slope drift, cliffs and slope drift), medium vegetal cover (cliffs with slope drift and vegetated patches, grassland with scrubs and rocks, grassland with cliffs and slope drift, cliffs with slope drift, grass patches, scrubs and forest) and dominant vegetal cover (>50% grass land, grassland and scrubs, forest with grass land and scrubs)

Variables are: $^{+}$ numerical, $^{++}$ categorical and $^{+++}$ nominal. Variables preceded by superscript (*) did not contribute to PCA and were removed from analyses.

conducted in PASW (former SPSS) for Windows. Bootstrap procedure was computed with macro file Categories CATPCA Bootstrap for PASW developed by Linting et al. (2007; available online at http://www.spss.com/devcentral/).

4. Results and discussion

The surveyed Pyrenean water-bodies spanned from 1161 to 2747 m a.s.l. Figure 2.2 displays the exploratory statistics of the assessed landscape variables. As can be observed from this figure most of the water-bodies can be included into pond and small lake categories. These water-bodies are mostly located on relatively flat surfaces at the head of glacial valleys; they have granite dominant bedrock, and a great number are connected in chain with other lakes within their area. Likewise, the typical altitude lakes in the central Pyrenees have feebly developed riparian zones (as shown by a high frequency of lakes with low fractal order, Fig. 2.2), which corresponds to a relatively young age on a lake evolutionary time scale. Aquatic vegetation was largely absent at the time of sampling. Regarding the hydrological dynamics most of the lakes/ponds are fed by precipitation or small surface streams of very low discharge, which is typical of high altitudes. Accordingly, a great number of them have visibly absent or small outputs. Water flowing from springs, on the other hand, seems to have very little importance in their hydrodynamics. Shore/slopes vegetation coverage for most of the water-bodies was < 10%, and relatively mixed snow coverage was recorded in their near-catchment during the month of surveying, i.e. July.

4.1 Processes shaping ecotope development

The interaction between climate and geomorphology can potentially shape the formation of an ecotope at high altitude. To examine the influence of landscape components on the structure of lake ecotopes at catchment-scale, a principal component analysis (PCA) of all assessed variables (Table 2.1) was carried out. This reduced the variables to a limited number of key components which can explain the main environmental processes. Three components accounted for more than 58% of the total variance in the lakes characteristics (Fig. 2.3). The first extracted component (PC1) accounted for 21.3% of the variation (Fig. 2.3). It, i.e. PC1 (interpreted hereafter as hydrodynamics), indicates a strong association between waterbody size and lake hydrology (type and volume of water input/output). This is important as wetland macrophyte and invertebrate richness are likely to vary with the size of a lake/pond (Biggs et al., 2005; Oertli et al., 2002), a core idea in the “ecological theory of island biogeography” (MacArthur and Wilson, 1963, 2001).

The second component (PC2, explaining additional 19.2% of total variance) had high loadings for the variables that would be determined by the main bedrock geology/ geomorphology, i.e. geology, shore sloping, % of slope/shore covered by grass, fractal order and the presence of aquatic vegetation (Fig. 2.3). Geerling et al. (2006) have shown that ecotope composition (i.e. riparian surface, vegetation coverage and composition) can change during rejuvenating hydro-geomorphological processes of rivers, i.e., meander progression, meander interruption and channel shift. Likewise, substrate geology and slope are recognised physical factors that can influence the characteristics of a lake

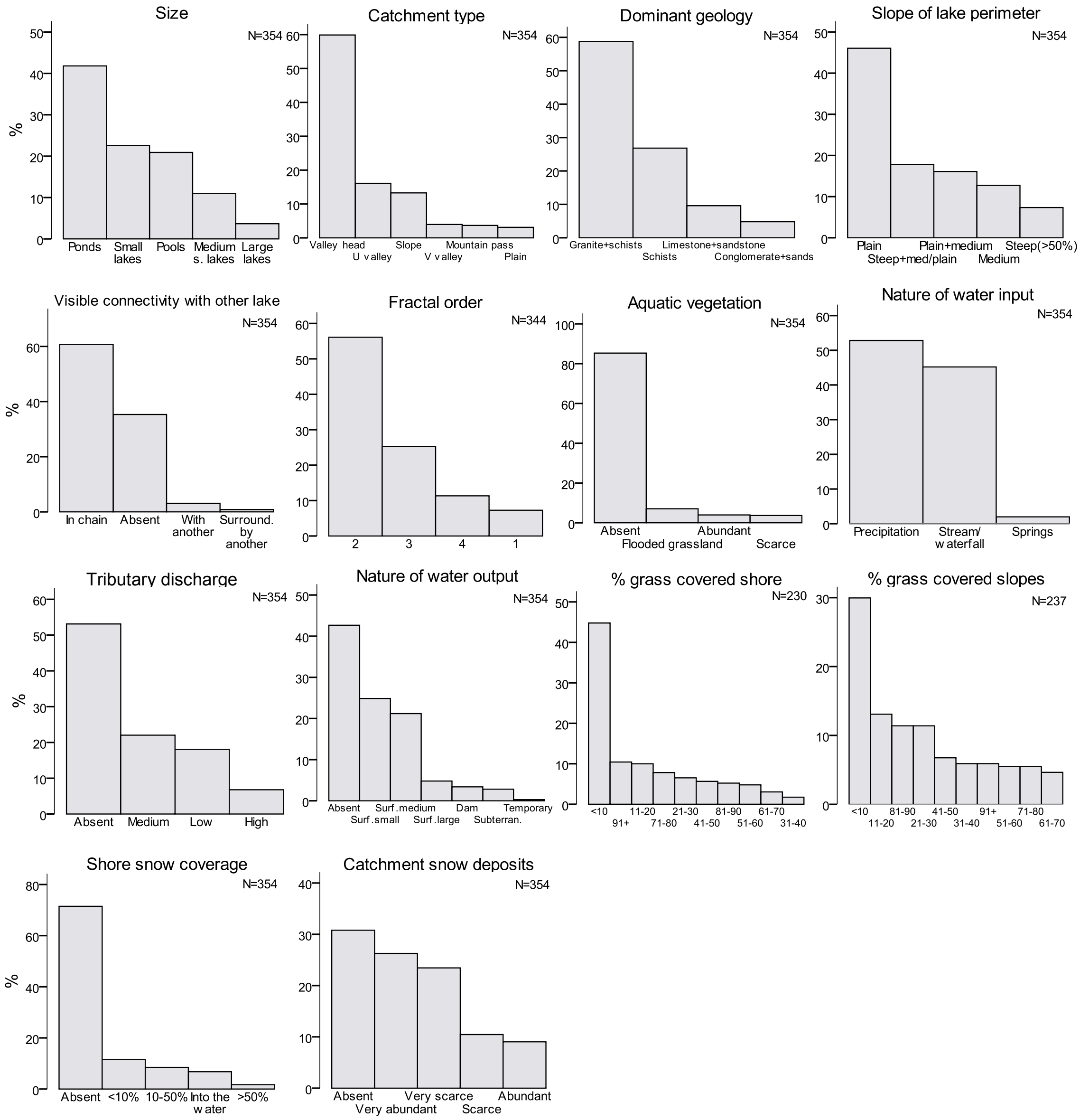

Fig. 2.2 Plots showing the frequency distribution (%) of sampled landscape variables at 354 altitude lakes/ponds locations from the Central Pyrenees.

through their effects on hydraulics, weathering and nutrient cycling processes which together shape its biological structure (EC, 2000; Kamenik et al., 2001). It seems therefore that geo-morphology is a second major driver of an altitude lake ecotope development and can influence not only the topographically-related high energy processes, such as slope erosion and runoff, but also the riparian development, its vegetation coverage and the development of aquatic vegetation. Lake shores vegetation coverage is a crucial ecotope factor in high

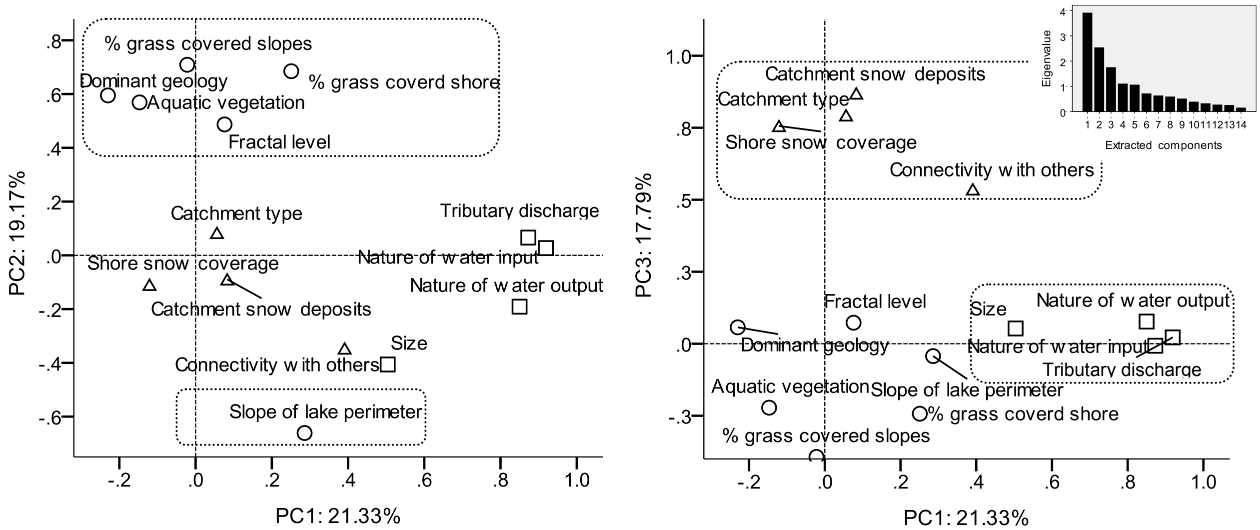

Fig. 2.3 Plots showing the relationship between landscape variables as they project on the principal components 1-2 and 1-3 of principal component analysis (PCA). Variables clustering with the PCs are enclosed. Figure symbols represent the variables with high loading on: (□) PC1, (○) PC2 and (Δ) PC3. These variables are from a sample pool of 354 altitude waterbodies (lakes, ponds and pools) from the central Pyrenees. Rotation method: Varimax with Kaiser normalization. Kaiser-Meyer-Olkin measure of sampling adequacy= 0.72 Bartlett's test of sphericity: approx. χ^2= 1398.2 (P<0.001). Inset plot shows the number of extracted components.

altitude waterbodies which has been found to control nutrient cycling in a lake and therefore its biotic composition (Kopáček et al., 2000).

Finally, the third PC axis accounted for 17.8% of the variability in the lakes characteristics. The variables grouped under PC3 were: presence of snow deposits at shore level and in the near catchment, catchment type and visible connectivity with other lakes, together being interpreted as topographical formation (Fig. 2.3). The PC3 findings suggest that topography can also have significant control on ecotopic processes by its influence on important factors such as habitat connectivity and habitat snow coverage, the latter being important in shaping land-water processes during the large periods a mountain lake catchment is snow-covered (Edwards et al., 2007).

Indeed, the patterns of snow distribution in rugged alpine terrain are the most visible consequence of topography and its interaction with climatic variables like precipitation, solar radiation and wind (Körner, 1992; Gottfried et al., 1999; Körner, 1999). The seasonal cycles of snow accumulation and ablation as well as snow coverage can have a crucial influence on high altitudes ecosystem composition at a variety of scales, with species capable of coping with the environmental conditions/stresses becoming more abundant (Walker et al., 1993; Keller et al., 2005). Habitat connectivity, on the other hand, is an important factor in maintaining the integrity of metapopulations of plant (Biggs et al., 2005) and animal (Richards-Zawacki, 2009) species, with species assemblages likely to be richer in areas that facilitate propagule dispersal and colonisation. This is a second important aspect of "island biogeography" theory (MacArthur and Wilson, 1963) which predicts an increase in species number with a decrease in remoteness of an island ecotope.

4.2 The interaction between landscape factors drive ecotope forms

In this study lake ecotope types are quantified as major composite units, rather than species-specific habitats. They are meant to represent the overall environment, as an integration of climate, hydrology, topography and bedrock geology, together underpinning ecotope functioning (Sales, 2007). Thus abiotic components in a given ecotope together will sustain a certain type of biotic community, depending upon the extent and degree of synergy between the components involved.

To classify the water-bodies into qualitative units (ecotopes) we studied the interaction between the variable categories of the three principal driving forces previously discussed, i.e. hydrodynamics (PC1), geo/morphology (PC2) and topographical formation (PC3). The plot of variables on these factors yielded a considerable degree of stability, as shown by relatively narrow 90% confidence ellipses of the bootstrap component loadings (Appendix 2). We can therefore confidently use CATPCA to uncover relationships between variable vectors.

As displayed in Figure 2.4A the interaction between hydrodynamics variables (PC1) shows that small water-bodies such as pools and ponds are fed principally by meteoric water, e.g. snow and rain, and such water-bodies either lack or have temporary tributaries/effluents. They would represent a first lake ecotope category. A second category is represented by small and medium-size lakes. They are characterized by various forms of water input, e.g. springs and streams/waterfalls of low to high discharge which is also associated to a diverse output nature, e.g. surface and subterranean (Fig. 2.4A). On the other side, large lakes plot further apart and are represented by dam lakes (Fig. 2.4A). The CATPCA also shows the cross-point where major lake properties change, with variable vectors plotting onto two well defined water-body clusters; first cluster, pools and ponds of low water turnover, plotting on the negative side of the first dimension, and second cluster, represented by small to large lakes of relatively large tributary/effluent, which plot on the positive side in the ordination space (Fig. 2.4B). This is an important finding since water-bodies which receive significant runoff can have different biotic composition when compared with the mainly rain-fed ones, as they will receive more nutrients from the catchment (Kamenik et al., 2001; EC, 2000). For example Saros et al. (2005), Robinson and Kawecka (2005) and Magnuson et al. (2000) provide illustrative cases of how nutrient availability/ drainage type can shape phytoplankton, crayfish and fish development in oligotrophic alpine lakes. A conceptualization of this composite ecotope factor, i.e.hydrodynamics, is presented in Fig. 2.6. This figure shows differences in precipitation amount received by two slopes of a mountain wall as a result of Foehn cloud formation, which is typical to high altitudes. This is characterised by a sharp drop in air moisture and an elevation of the cloud as it meets dry, warm air masses from the opposite slopes. This is a typical phenomenon found along the wet Atlantic- dry Mediterranean climate gradient (N-S) in the Pyrenees.

The plot of interaction between PC2 variables, representing geo/morphological processes, shows that landscape categories such as limestone/sandstone/conglomerates associate with lakes surrounded by relatively

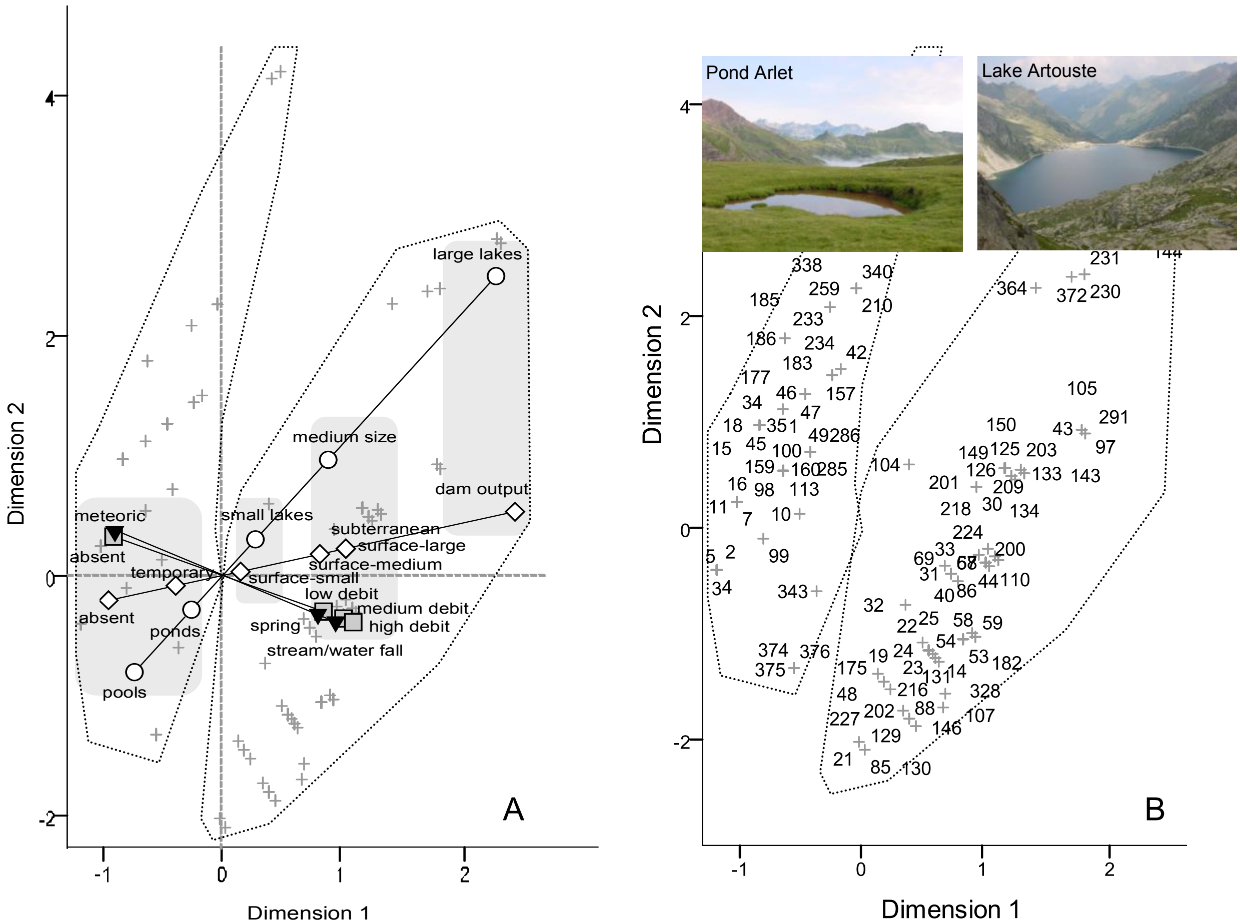

Fig. 2.4 (A) Interaction between categorical variables of the first principal component (i.e. hydrodynamics- Fig. 2.2) of PCA and their projection on lake ordination space. Interacting categories are enclosed in grey. The association between variables and lakes is enclosed in dashed polygons (lake identities are illustrated in B) and shows the point where lakes' proprieties change. Figure legend: ○, water-body size; ◇, nature of water output; ▢, tributary discharge; ▼nature of water input. N=354 water-bodies. Inset pictures are examples of lakes conforming with the characteristics of the two lake clusters. Lake identities are presented in Appendix I.

flat topography, >50% grass covered shore/slopes, a highly developed riparian zone and the presence of aquatic vegetation (Fig. 2.5A).

On the other hand granite-schist bedrock plot together with medium to steep lake shore slopes, <20% grass covered shore/slopes, a poorly developed riparian zone and lack of aquatic vegetation. These two lake categories, i.e. formed on limestone and granite bedrocks, point out to a spatial segregation of lake ecotopes according to the two main geomorphological units in the Pyrenees. That is, the Paleozoic-Mezozoic sedimentary/ limestone bedrock and the granitic outcrops which can influence biota composition at these sites. The plotting of the surveyed sites, however, did not form well-defined clusters, suggesting rather transient ecotope differences between the two main categories (Fig. 2.5B), possibly owing to the influence of mixed geological materials in them. A simplified concept of this composite factor influence on ecotope development is presented in Fig. 2.6. Such influence of contrasting substratum geologies, i.e.

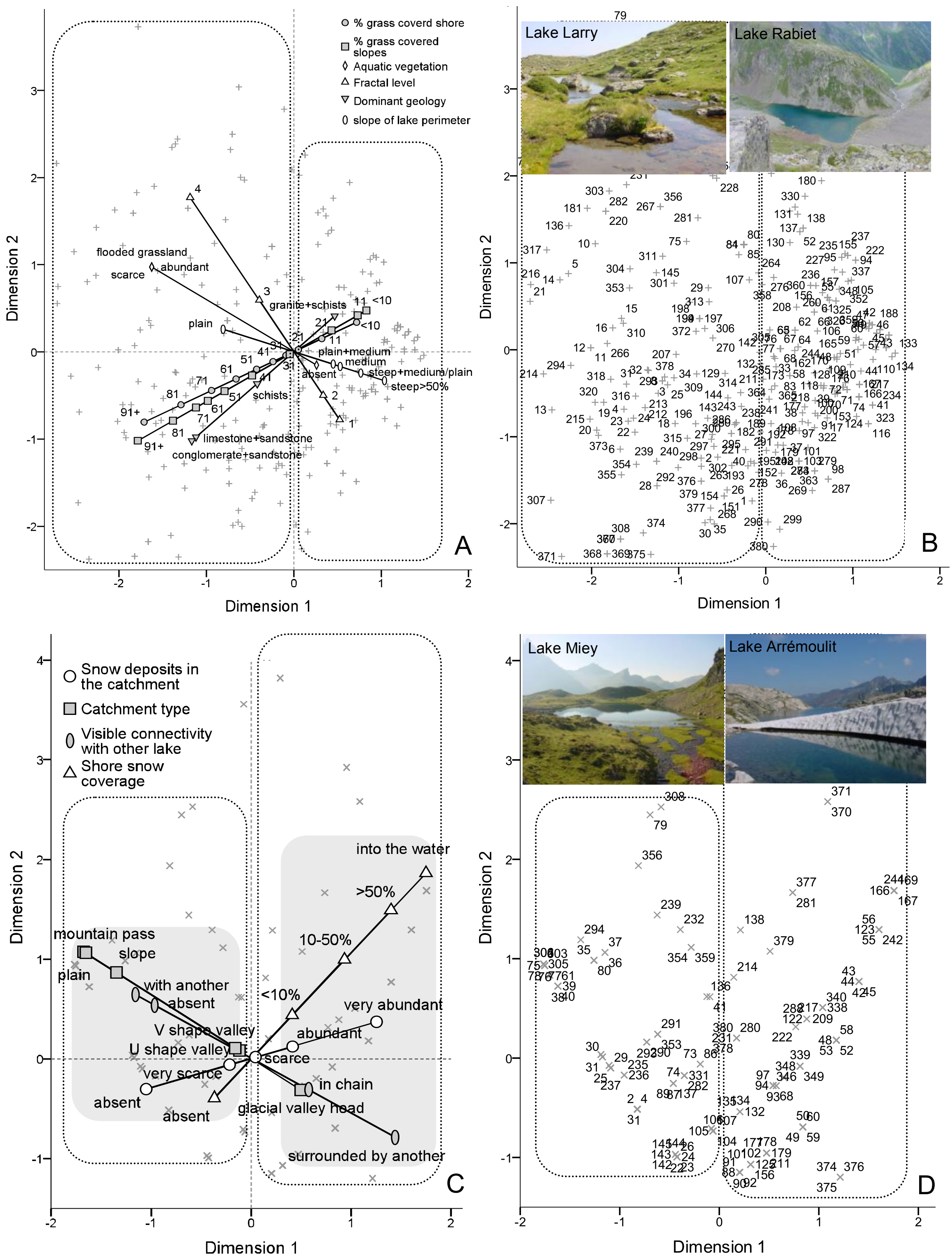

Fig. 2.5 (A) Interaction between categorical variables of the second principal component of PCA (i.e. geomorphology; Fig. 2.2) and their projection on lakes (detailed in B). N=237. (C) Nonlinear relationship between categorical variables of the third principal component, i.e. topographical formation, and their projection on lakes (labelled in D). N=354 water bodies.

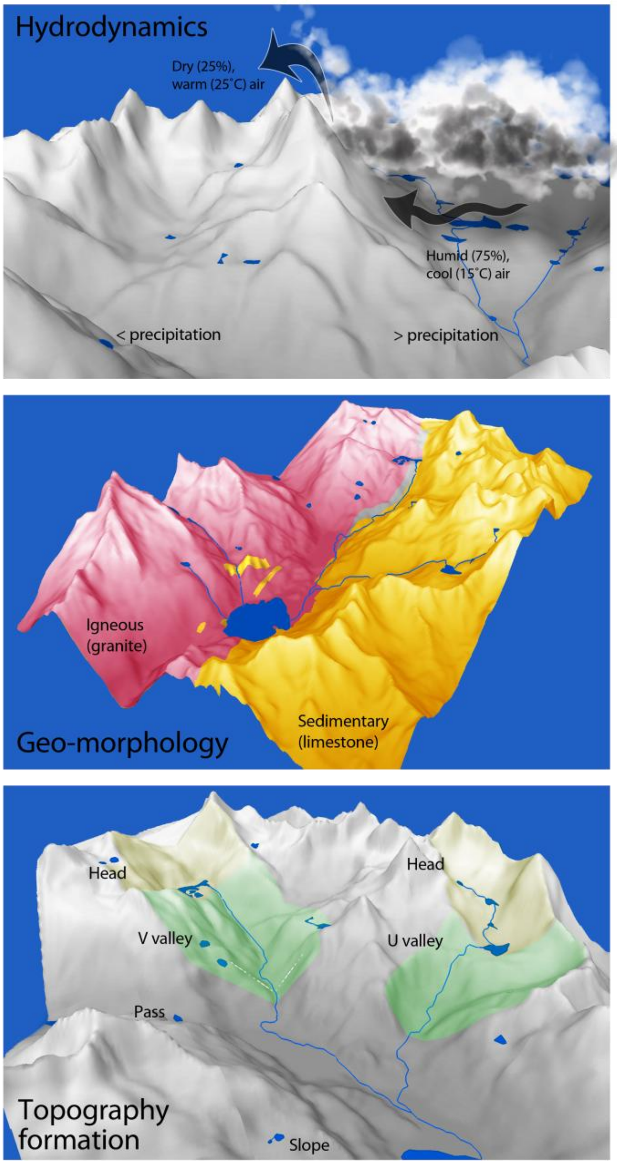

Fig. 2.6 Conceptualization of lake ecotope development at high altitudes and its principal drivers, i.e. hydrodynamics, geo-morphology and topography. A digital elevation model of upper Tena Valley, central Pyrenees was used for this representation to show the complexity of the alpine terrain. A hydrodynamic gradient is represented here with a typical mountain Foehn cloud which leaves the precipitation charge on one slope, then it is dispersed as it comes in contact with warm, dry air masses on the opposite slopes. Colours in geo-morphology and topography models represent geological materials and glacial valley sections, respectively.

limestone and siliceous, on zoobenthos assemblages has been clearly exemplified by Borderelle et al. (2005).

An analysis of the third composite factor, i.e. topographical formation (PC3; Fig. 2.5C and D) reveals two major ecotope forms. On one hand, there are lakes at the head of glacial valleys, which are generally either interconnected in chain with other lakes or in a basin surrounded by a major lake and have a high proportion of snow deposits on their shores/near-catchment. Secondly, there are lakes on plain terrains/slopes/mountain passes and V/U shaped valleys which are generally isolated or connected to a neighbouring lake and have very scarce or no summer snow cover in their surroundings (Fig. 2.5C). The geomorphic processes induced by the last glaciations are likely the main drivers of this factor and their location/connectivity in the landscape. For example, differences in biota templates in different geomorphic settings have been found for the Northern Highland Lake District, Wisconsin, U.S.A (Rieira et al., 2000). We conceptualise this composite factor in Fig. 2.6. This figure shows in a simplified way that different topographical forms/glacial formations determine different lake assemblages/forms. A digital elevation model of upper Tena Valley from central Pyrenees was used for this modelling.

Size and geology are central factors for lake typology differentiation, as stated under the European Community Water Framework Directive (EC, 2000). They are also recognised as driving reference ecological conditions for biotic populations (EC, 2000). While catchment type has been largely neglected from such legislation, our results suggest that it, i.e. topography, can be an important constraint on ecotope development and should be considered for further study.

4.3 Behaviour of ecotope parameters along large geographical gradients

The effects of altitude, latitude and longitude are potentially important large geophysical factors to follow when determining lake characteristics as they are known drivers of biological populations change (EC, 2000). An analysis of the behaviour of the three landscape-scale composite factors, i.e. hydrodynamics (PC1), geo-morphology (PC2) and topographical formation (PC3) along altitudinal, latitudinal and longitudinal (continentality) gradients (Table 2.2) identifies elevation as a primary gradient explaining lake ecotopes development, with local effects of the variables associated with topography, i.e. PC3 (Fig. 2.7A). Altitude is a geographical constraint with known influences on catchment development through its main effects on glacial processes such as cirque and valley formation. This can influence water and nutrient cycling and photosynthesis, and can lead to biota compositional differences along aquatic gradients at high altitudes. Examples of altitudinal effect on biota composition have been reported for various taxa, including zoobenthos, macrophyte and amphibian species (Hinden et al., 2005). The authors reported a general decrease in family/species richness with increasing waterbody elevation.

Latitude was the second most important broad-scale gradient for lake ecotope variation, with local effects of variables related to bedrock geo-morphology (regression factor score of the second PC) (Fig. 2.7B). Latitude apparently also had a broad effect on the variables associated to lake hydrodynamics, as shown by its relatively weak, but significant relationship with PC1 regression score (Spearman ρ=0.26; Table 2.2). The association of latitude to geological constraints may unveil a major N-S geomorphological gradient involved in lakes

Table 2.2: Relationship (Spearman rank correlation coefficients) between geo-position variables and summarised landscape variables (i.e. regression factor scores of principal components) resulting from PCA. They represent: PC1, hydrodynamics; PC2, geo-morphology and, PC3, topographical formation. Variables summarised by these composite factors are presented in Fig. 2.2

	Hydro-dynamics	Geo-morphology	Topographical formation
Altitude	-0.11	-0.31**	0.64**
Latitude	0.26**	-0.40**	-0.15*
Longitude	0.07	0.05	0.17**

**, correlation is significant at the 0.01 level (2-tailed).
*, correlation is significant at the 0.05 level (2-tailed).
N(number of cases)=234.

ecotope development across the mountain range. However the variation in lake hydrodynamics across latitude could be explained by the rates at which the catchments are fed by the dominant Atlantic air masses/cyclones (i.e. N-S direction), which lose moisture as they advance toward the (drier) axial part of the mountain range.

Conclusions

Hydrodynamics, geo/morphology and topographical formation were the main composite drivers of altitude lakes/ponds ecotope development in the central Pyrenees. They divided the water-bodies into a number of ecotope units, which are characterised by particular landscape parameters. These units are intended to represent distinctive abiotic settings for flora and fauna communities at these altitudes. Furthermore, the identified factors/processes appear to follow major geographical gradients, of which altitude and latitude are the most relevant. Physical, chemical and biological processes are all

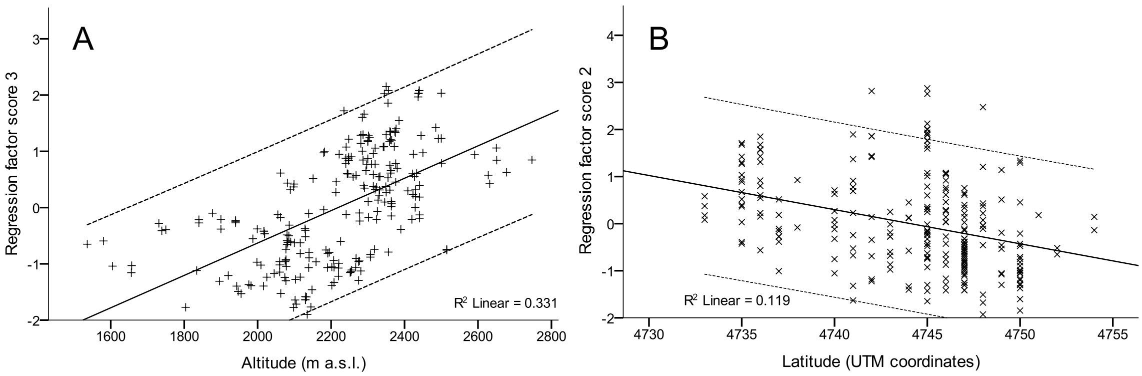

Fig. 2.7 (A) Relationship (linear) between topographical formation (i.e. regression factor scores of PC 3: catchment type, connectivity with other lakes, catchment and shore snow coverage – see Fig. 2.2) and altitudinal gradient. Slope equation is: y= 0.0029 × x – 6.3451. (B) Relationship between geo-morphology (i.e. regression factor scores of PC 2: dominant bedrock geology, % grass covered slopes, % grass covered shore, aquatic vegetation and fractal development) and latitude. Slope equation is: y= –1.6403 × x + 4744.0970. Confidence intervals (95%) are dashed.

expected to change with both altitude and latitude. We interpret this as major evidence of landscape evolution in the postglacial period (Holocene) starting 11 000 years ago, which created these physical conditions for biota settings.

As broad-scale geographical and landscape processes have been found to have primary influence on altitude lakes ecotope development, this could be a common feature in other similar mountain ranges. We also provide a conceptualisation of lake ecotopes driven by hydrodynamics, geo/morphology and topographical formation. Our conceptualised template for ecotope development could provide a basis for hypothesis testing and experimentation in further studies. Likewise this study has the advantage that it provides an objective background for decision makers and conservationists which lack a proper representation of physical settings, shaping biological communities at high altitudes.

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APPENDIX 1

Water-bodies of central Pyrenees (The Pyrénées National Park) used in the present study. Altitude is in m a.s.l.; latitude and longitude are in geographic coordinates. Main valleys, locally called *gaves*, give the structure of the region

Lake no.	Sampling year	Name	Main valley	Altitude	Latitude	Longitude
1	2002	Lake Arlet	Aspe	1987	42.4955	-0.3735
2	2002	Pond Arlet 1	Aspe	1999	42.4955	-0.3735
3	2002	Pond Arlet 2	Aspe	1999	42.4955	-0.3735
4	2002	Pond Lurbe 1	Aspe	1900	42.4955	-0.3651
5	2002	Pond Lurbe 2	Aspe	1900	42.4955	-0.3651
6	2002	Pond Lurbe 4	Aspe	1900	42.4955	-0.3651
7	2002	Pond Lurbe 5	Aspe	1880	42.4955	-0.3651
8	2002	Pond Lurbe 3	Aspe	1990	42.4955	-0.3651
9	2002	Pond Caillaous	Aspe	1877	42.4954	-0.3607
10	2002	Pond Caillaous 1	Aspe	1877	42.4954	-0.3607
11	2002	Lake Gourgue	Aspe	1840	42.4954	-0.3607
12	2002	Pond Gourgue 1	Aspe	1840	42.4954	-0.3607
13	2002	Pond Gourgue 2	Aspe	1840	42.4954	-0.3607
14	2002	Lake Banasse 1	Aspe	1940	42.4954	-0.3607
15	2002	Lake Banasse 2	Aspe	1940	42.4954	-0.3607
16	2002	Lake Banasse 3	Aspe	1940	42.4954	-0.3607
17	2001	Lake Berseau	Ossau	2082	42.4959	-0.3015
18	2001	Lake Berseau 1	Ossau	2080	42.4959	-0.3015
19	2001	Lake Berseau 2	Ossau	2100	42.4959	-0.3015
20	2001	Pond Berseau 1	Ossau	2085	42.4959	-0.3015
21	2001	Pond Berseau 2	Ossau	2086	42.4959	-0.3015
22	2001	Lake Larry 1	Ossau	2077	42.5018	-0.3014
23	2001	Lake Larry 2	Ossau	2077	42.5018	-0.3014
24	2001	Lake Larry 3	Ossau	2077	42.5018	-0.3014
25	2001	Lake Larry 4	Ossau	2077	42.5018	-0.3014
26	2001	Lake Ayous 1	Ossau	2060	42.5018	-0.2929
27	2001	Lake Ayous 2	Ossau	2060	42.5018	-0.2929
28	2001	Lake Ayous 3	Ossau	2060	42.5018	-0.2929
29	2001	Lake Gentau 1	Ossau	1982	42.5018	-0.2929
30	2001	Lake Gentau	Ossau	1947	42.5018	-0.2929
31	2001	Lake Miey	Ossau	1920	42.5018	-0.2929
32	2001	Lake Roumassot	Ossau	1845	42.5018	-0.2929
33	2001	Lake Castérau	Ossau	1943	42.4945	-0.2931
34	2001	Lake Paradis	Ossau	1976	42.4945	-0.2931
35	2001	Lake Peyreget	Ossau	2074	42.4942	-0.2719
36	2001	Lake Peyreget 3	Ossau	2159	42.4941	-0.2635
37	2001	Pond Peyreget	Ossau	2180	42.4941	-0.2635
38	2001	Lake Col de Peyreget 1	Ossau	2220	42.4941	-0.2635
39	2001	Lake Col de Peyreget 2	Ossau	2208	42.4941	-0.2635
40	2001	Lake Pombie	Ossau	2025	42.4941	-0.2635
41	2001	Lake Artouste	Ossau	1989	42.5110	-0.2039
42	2001	Lake Arrémoulit Supérieur	Ossau	2281	42.5005	-0.1957
43	2001	Lake Arrémoulit	Ossau	2285	42.5037	-0.1956
44	2001	Lake Arrémoulit (bellow dam)	Ossau	2255	42.5037	-0.1956

45	2001	Lake Palas	Ossau	2359	42.5037	-0.1956
46	2001	Lake Palas 1	Ossau	2365	42.5037	-0.1956
47	2001	Lake Palas 2	Ossau	2362	42.5037	-0.1956
48	2001	Lake Arrémoulit Superior 1	Ossau	2300	42.5037	-0.1956
49	2001	Lake Arrémoulit Superior 2	Ossau	2295	42.5037	-0.1956
50	2001	Lake Arrémoulit Superior 3	Ossau	2297	42.5037	-0.1956
51	2001	Lake Arrémoulit Superior 4	Ossau	2300	42.5037	-0.1956
52	2001	Lake Arrémoulit Superior 5	Ossau	2300	42.5037	-0.1956
53	2001	Lake Arrémoulit Superior 6	Ossau	2305	42.5037	-0.1956
54	2001	Lake Arrémoulit Superior 6A	Ossau	2305	42.5037	-0.1956
55	2001	Lake Arrémoulit Superior 7	Ossau	2290	42.5037	-0.1956
56	2001	Lake Arrémoulit Superior 8	Ossau	2285	42.5037	-0.1956
57	2001	Lake Arrémoulit Inférieur	Ossau	2241	42.5037	-0.1956
58	2001	Lake Arrémoulit Inferior 1	Ossau	2248	42.5037	-0.1956
59	2001	Lake Arrémoulit Inferior 2	Ossau	2246	42.5037	-0.1956
60	2001	Lake Arrémoulit Inferior 3	Ossau	2244	42.5037	-0.1956
61	2001	Lake Arrémoulit Inferior 4	Ossau	2256	42.5037	-0.1956
62	2001	Lake Arrémoulit Inferior 5A	Ossau	2254	42.5037	-0.1956
63	2001	Lake Arrémoulit Inferior 5B	Ossau	2254	42.5037	-0.1956
64	2001	Lake Arrémoulit Inferior 5C	Ossau	2254	42.5037	-0.1956
65	2001	Lake Arrémoulit Inferior 5D	Ossau	2254	42.5037	-0.1956
66	2001	Lake Arrémoulit Inferior 6	Ossau	2252	42.5037	-0.1956
67	2001	Lake Arrémoulit Inferior 7	Ossau	2248	42.5037	-0.1956
68	2001	Lake Arrémoulit Inferior 8	Ossau	2100	42.5037	-0.1956
69	2002	Lake Carnau 1	Ossau	2208	42.5213	-0.1908
70	2002	Lake Carnau 2	Ossau	2202	42.5213	-0.1908
71	2002	Lake Carnau 3A	Ossau	2202	42.5213	-0.1908
72	2002	Lake Carnau 3B	Ossau	2202	42.5213	-0.1908
73	2000 (74/2002)	Lake Migouélou	Azun	2278	42.5212	-0.1824
75	2000	Pond Migouélou_1	Azun	2420	42.5212	-0.1824
76	2000	Pond Migouélou_2	Azun	2420	42.5212	-0.1824
77	2000	Pond Migouélou_3	Azun	2420	42.5212	-0.1824
78	2000	Pond Migouélou_4	Azun	2420	42.5212	-0.1824
79	2000	Pond Migouélou_5	Azun	2420	42.5212	-0.1824
80	2000	Pond Migouélou_6	Azun	2420	42.5212	-0.1824
81	2000	Pond Migouélou_7	Azun	2420	42.5212	-0.1824
82	2000	Pond Migouélou_8	Azun	2420	42.5212	-0.1824
83	2000	Pond Migouélou_9	Azun	2420	42.5212	-0.1824
84	2000	Pond Migouélou_10	Azun	2420	42.5212	-0.1824
85	2000	Pond Migouélou_11	Azun	2420	42.5212	-0.1824
86	2000 (87/2002)	Lake Amont Migouélou	Azun	2301	42.5003	-0.1829
88	2002	Pond Amont Migouélou_1	Azun	2301	42.5003	-0.1829
89	2002	Pond Amont Migouélou_2	Azun	2301	42.5003	-0.1829
90	2002	Lake Les Lacarrats_1	Azun	2441	42.5212	-0.1824
91	2002	Lake Les Lacarrats_2	Azun	2441	42.5212	-0.1824
92	2002	Lake Les Lacarrats_3	Azun	2429	42.5212	-0.1824
93	2002	Lake Les Lacarrats_4	Azun	2430	42.5212	-0.1824
94	2002	Lake Les Lacarrats_5	Azun	2430	42.5212	-0.1824
95	2002	Lake Les Lacarrats_6	Azun	2441	42.5212	-0.1824
96	2002	Pond Les Lacarrats_6	Azun	2441	42.5212	-0.1824
97	2000	Lake Pouey Laun	Azun	2346	42.5316	-0.1737
98	2000	Lake Pic de Hautafulhe	Azun	2361	42.5316	-0.1737
99	2000	Pond Puey Laun	Azun	2350	42.5316	-0.1737
100	2000	Lake Amount Puey Laun	Azun	2355	42.5316	-0.1737

101	2000	Pond above Puey Laun 1	Azun	2354	42.5316	-0.1737
102	2000	Pond above Puey Laun 2	Azun	2353	42.5316	-0.1737
103	2000	Pond above Puey Laun 3	Azun	2352	42.5316	-0.1737
104	2000	Pond down Migouélou	Azun	2226	42.5243	-0.1738
105	2000	Lake Lassiédouat	Azun	2202	42.5211	-0.1740
106	2000	Pond Lassiédouat-1	Azun	2356	42.5211	-0.1740
107	2000	Pond Lassiédouat-2	Azun	2356	42.5211	-0.1740
108	2000	Lake Lassiédouat 1	Azun	2220	42.5211	-0.1740
109	2000	Lake Lassiédouat 2	Azun	2268	42.5211	-0.1740
110	2000	Lake Lassiédouat 3	Azun	2267	42.5211	-0.1740
111	2000	Pond Lasiedouat 3a	Azun	2267	42.5211	-0.1740
112	2000	Pond Lasiedouat 3b	Azun	2267	42.5211	-0.1740
113	2000	Lake Tramasaygues Supérieur 1	Azun	2277	42.5211	-0.1740
114	2000	Lake Tramasaygues Supérieur 2	Azun	2277	42.5211	-0.1740
115	2000	Lake Tramasaygues Supérieur 3	Azun	2277	42.5211	-0.1740
116	2000	Lake Tramasaygues Supérieur 4	Azun	2277	42.5211	-0.1740
117	2000	Lake Tramasaygues Supérieur 5	Azun	2277	42.5211	-0.1740
118	2000	Pond Touest	Azun	2016	42.5210	-0.1656
119	2000	Lake Touest	Azun	1955	42.5210	-0.1656
120	2001	Lake Micoulaou 1	Azun	2302	42.5034	-0.1744
121	2000	Lake Micoulaou 2	Azun	2333	42.5001	-0.1745
122	2000 (123/2001)	Lake Micoulaou 3	Azun	2362	42.5001	-0.1745
124	2001	Lake Micoulaou 4	Azun	2375	42.5001	-0.1745
125	2001 (126/2000)	Lake Batcrabère Supérieur	Azun	2180	42.5034	-0.1744
127	2001	Lake Batcrabère Supérieur 1	Azun	2182	42.5034	-0.1744
128	2001	Lake Batcrabére Milieu	Azun	2130	42.5034	-0.1744
129	2001	Pond Batcrabére Milieu 1	Azun	2130	42.5106	-0.1743
130	2000	Pond Batcrabére Milieu 2	Azun	2140	42.5034	-0.1744
131	2000	Lake above Batcrabére Milieu	Azun	2140	42.5034	-0.1744
132	2001	Lake bellow Batcrabére Milieu	Azun	2129	42.5034	-0.1744
133	2001 (134/2000)	Lake Batcrabère Inférieur	Azun	2116	42.5106	-0.1743
135	2001	Lake Batcrabère Inférieur 1	Azun	2116	42.5106	-0.1743
136	2001	Pond next to Larribet Refuge	Azun	2055	42.5106	-0.1743
137	2001 (138/2000)	Pond Pabat	Azun	2062	42.5106	-0.1743
139	2001	Lake La Claou Supérieur	Azun	1750	42.5210	-0.1656
140	2001 (141/2000)	Lake La Claou	Azun	1739	42.5210	-0.1656
142	2001	Lake Doumblas	Azun	1580	42.5209	-0.1612
143	2000	Lake Suyen	Azun	1536	42.5137	-0.1613
144	2000	Lake Tech	Azun	1207	42.5417	-0.1522
145	2001	Pond Pluviometre	Azun	1731	42.5135	-0.1529
146	2000	Pond Labassa	Azun	1750	42.5135	-0.1529
147	2000 (148/2001)	Lake Remoulis Inférieur	Azun	2017	42.5031	-0.1532
149	2000 (150/2001)	Lake Remoulis Supérieur	Azun	2019	42.5031	-0.1532
151	2000 (152/2001)	Pond Casteric	Azun	2080	42.4958	-0.1533
153	2000 (154/2001)	Pond Toue	Azun	2090	42.4958	-0.1533
155	2000	Pond Chemin du Portet de Heche	Azun	2380	42.4926	-0.1535
156	2000	Lake Houns De Heche Inférieur	Azun	2213	42.4957	-0.1449
157	2000	Lake Houns De Heche Supérieur	Azun	2214	42.4957	-0.1449
158	2000	Pond Liantran 2	Azun	1824	42.4957	-0.1449
159	2000	Pond Liantran 1	Azun	1824	42.4957	-0.1449
160	2000	Pond Liantran 3	Azun	1824	42.4957	-0.1449
161	2000	Pond Liantran 4	Azun	1824	42.4957	-0.1449
162	2000	Pond Plaa de Prat 1	Azun	1657	42.5133	-0.1401
163	2000	Pond Plaa de Prat 2	Azun	1657	42.5133	-0.1401

164	2000	Lake Prat	Azun	1656	42.5133	-0.1401
165	2000	Lake Langle	Azun	1605	42.5133	-0.1401
166	2001	Lake Col de Cambalés	Cauterets	2582	42.4925	-0.1451
167	2001	Lake Crete Du Cambalés	Cauterets	2440	42.4925	-0.1451
168	2001	Lake Peyregnets de Cambalés Grand	Cauterets	2492	42.4925	-0.1451
169	2001	Lake Peyregnets de Cambalés Petit	Cauterets	2453	42.4925	-0.1451
170	2001	Lake Cambalés 2	Cauterets	2424	42.4924	-0.1407
171	2001	Pond Cambalés 2	Cauterets	2424	42.4924	-0.1407
172	2001	Pond Cambalés Grand	Cauterets	2380	42.4924	-0.1407
173	2001	Pond Cambalés Grand 1	Cauterets	2386	42.4924	-0.1407
174	2001	Pond Cambalés Grand 2	Cauterets	2390	42.4924	-0.1407
175	2001	Pond Cambalés Grand 3	Cauterets	2441	42.4924	-0.1407
176	2001	Lake Cambalés Grand	Cauterets	2342	42.4924	-0.1407
177	2000	Lake Fache Supérieur	Cauterets	2427	42.4819	-0.1410
178	2000	Lake Fache Inférieur	Cauterets	2332	42.4819	-0.1410
179	2000	Lake Sentier Fache	Cauterets	2291	42.4850	-0.1324
180	2001	Pond Opale	Cauterets	2222	42.4923	-0.1323
181	2001	Pond Opale 1	Cauterets	2248	42.4923	-0.1323
182	2001	Pond Opale 2	Cauterets	2260	42.4923	-0.1323
183	2000 (184/2001)	Lake Opale Petit Inférieur	Cauterets	2287	42.4923	-0.1323
185	2000 (186/2001)	Lake Opale Supérieur	Cauterets	2320	42.4923	-0.1323
187	2001	Pond Petit Laquet	Cauterets	2360	42.4923	-0.1323
188	2001	Lake Petit Laquet	Cauterets	2350	42.4923	-0.1323
189	2001	Lake Costalade Supérieur	Cauterets	2320	42.4923	-0.1323
190	2001	Pond Cambalés	Cauterets	2315	42.4923	-0.1323
191	2001	Lake Costalade Inférieur	Cauterets	2310	42.4923	-0.1323
192	2000	Lake Staing	Azun	1161	42.5413	-0.1226
193	2000	Lake Long	Azun	2326	42.5059	-0.1235
194	2000	Pond Long 1	Azun	2350	42.5059	-0.1235
195	2000	Pond Long 2	Azun	2360	42.5059	-0.1235
196	2000	Pond Long 3	Azun	2365	42.5059	-0.1235
197	2000	Pond Pic Arrouy	Azun	2370	42.5059	-0.1235
198	2000	Pond Pic Arrouy 1	Azun	2370	42.5059	-0.1235
199	2000	Lake Pic Arrouy	Azun	2376	42.5059	-0.1235
200	2000	Lake Nère de Arrouy	Azun	2241	42.5131	-0.1233
201	2002	Lake Nère de Bassia	Cauterets	2309	42.5026	-0.1236
202	2002	Pond Nére	Cauterets	2400	42.5026	-0.1236
203	2002	Lake Pourtet	Cauterets	2420	42.5026	-0.1236
204	2002	Lake Pourtet 1	Cauterets	2307	42.5025	-0.1152
205	2002	Lake Pourtet 2	Cauterets	2307	42.5025	-0.1152
206	2000 (207/2002)	Lake Embarrat 2	Cauterets	2139	42.5025	-0.1152
208	2002	Lake Embarrat 1	Cauterets	2078	42.5024	-0.1108
209	2001	Lake Badéte	Cauterets	2344	42.5024	-0.1108
210	2001	Lake Col d'Arratille	Cauterets	2501	42.4709	-0.1033
211	2001	Pond Arratille 1	Cauterets	2363	42.4741	-0.1031
212	2001	Pond Arratille 2	Cauterets	2330	42.4741	-0.1031
213	2001	Pond Arratille 3	Cauterets	2315	42.4741	-0.1031
214	2001	Pond Arratille 4	Cauterets	2289	42.4741	-0.1031
215	2001	Pond Arratille 5	Cauterets	2315	42.4741	-0.1031
216	2001	Pond Arratille 6	Cauterets	2268	42.4741	-0.1031
217	2001	Lake Arratille	Cauterets	2247	42.4741	-0.1031
218	2000	Lake Ilhéou	Cauterets	1998	42.5128	-0.1021
219	2000	Lake Noir d'Ilheou 1	Cauterets	1896	42.5200	-0.1020
220	2000	Pond Arras	Cauterets	2070	42.5233	-0.1018

221	2000	Pond Col d’Ilhéou	Cauterets	2242	42.5234	-0.1102
222	2002	Lake Chabarrou Supérieur	Cauterets	2422	42.4813	-0.0946
223	2002	Pond Chabarrou Supérieur	Cauterets	2400	42.4813	-0.0946
224	2002	Lake Chabarrou	Cauterets	2302	42.4812	-0.0902
225	2002	Lake Chabarrou Inférieur	Cauterets	2390	42.4812	-0.0902
226	2002	Pond Chabarrou 1	Cauterets	2364	42.4812	-0.0902
227	2002	Pond Chabarrou 2	Cauterets	2364	42.4812	-0.0902
228	2002	Pond Chabarrou 3	Cauterets	2364	42.4812	-0.0902
229	2002	Pond Chabarrou 4	Cauterets	2364	42.4812	-0.0902
230	2002	Lake Gaube	Cauterets	1725	42.4949	-0.0858
231	2001	Oulettes. glacier runoff	Cauterets	2151	42.4707	-0.0905
232	2001	Pond Arraillé Inférieur	Cauterets	2441	42.4706	-0.0821
233	2001	Lake Arraillé Milieu	Cauterets	2450	42.4706	-0.0821
234	2001	Lake Arraillé Supérieur	Cauterets	2485	42.4706	-0.0821
235	2002	Lake Estibe Aute 1	Cauterets	2515	42.4737	-0.0736
236	2002	Lake Estibe Aute 2	Cauterets	2515	42.4737	-0.0736
237	2002	Lake Estibe Aute 3	Cauterets	2515	42.4737	-0.0736
238	2001	Pond Baysselance	Luz	2555	42.4632	-0.0739
239	2001	Pond Baysselance 2	Luz	2378	42.4632	-0.0739
240	2001	Pond Baysselance 1	Luz	2236	42.4632	-0.0739
241	2001	Pond Montferrat	Luz	2207	42.4455	-0.0743
242	2001	Lake Montferrat	Luz	2374	42.4455	-0.0743
243	2001	Pond Montferrat 1	Luz	2372	42.4455	-0.0743
244	2001	Pond Montferrat 2	Luz	2440	42.4455	-0.0743
245	2001	Lake Montferrat 1	Luz	2438	42.4455	-0.0743
246	2001	Lake Montferrat 3	Luz	2438	42.4455	-0.0743
247	2001	Lake Montferrat 4	Luz	2437	42.4455	-0.0743
248	2001	Lake Montferrat 5	Luz	2437	42.4455	-0.0743
249	2001	Lake Montferrat 6	Luz	2440	42.4455	-0.0743
250	2001	Lake Montferrat 7	Luz	2440	42.4455	-0.0743
251	2001	Lake Montferrat 8	Luz	2440	42.4455	-0.0743
252	2002	Lake Estibet d'Estom	Cauterets	2470	42.4809	-0.0734
253	2002	Lake Estibet d'Estom 2	Cauterets	2464	42.4809	-0.0734
254	2002	Pond Estibet d'Estom	Cauterets	2464	42.4809	-0.0734
255	2002	Lake Estibe Aute Inférieur	Cauterets	2324	42.4842	-0.0733
256	2002	Pond Estibe Aute Supérieur	Cauterets	2324	42.4842	-0.0733
257	2002	Lake Estibe Aute Milieu	Cauterets	2324	42.4842	-0.0733
258	2002	Pond Estibe Aute Milieu	Cauterets	2324	42.4842	-0.0733
259	2002	Lake Estibe Aute Supérieur	Cauterets	2328	42.4842	-0.0733
260	2002	Pond Estibe Aute Supérieur	Cauterets	2328	42.4842	-0.0733
261	2002	Pond Estibe Aute Supérieur 1	Cauterets	2331	42.4842	-0.0733
262	2002	Pond Estibe Aute Supérieur 2	Cauterets	2331	42.4842	-0.0733
263	2001	Lake Estom	Cauterets	1804	42.4808	-0.0650
264	2001 (265/2002)	Pond Sentier d’Estom 1	Cauterets	2235	42.4703	-0.0653
266	2001 (267/2002)	Pond Sentier d’Estom 2	Cauterets	2240	42.4703	-0.0653
268	2001 (269/2002)	Pond Sentier d’Estom 3	Cauterets	2240	42.4703	-0.0653
270	2001 (271/2002)	Pond Sentier d’Estom 4	Cauterets	2248	42.4703	-0.0653
272	2001 (273/2002)	Lake Labas	Cauterets	2281	42.4702	-0.0609
274	2001 (275/2002)	Lake Oulettes d'Estom	Cauterets	2360	42.4702	-0.0609
276	2001 (277/2002)	Lake Couy	Cauterets	2445	42.4702	-0.0609
278	2001 (279/2002	Lake Turon Couy	Cauterets	2485	42.4630	-0.0611
280	2002	Pons Turon Couy 1	Cauterets	2487	42.4630	-0.0611
281	2001 (282/2002)	Pond Turon Couy 2	Cauterets	2492	42.4630	-0.0611
283	2001 (284/2002)	Lake Couy Supérieur	Cauterets	2500	42.4630	-0.0611

285	2001 (286/2002)	Pond Couy Supérieur	Cauterets	2500	42.4630	-0.0611
287	2001 (288/2002)	Lake Glace	Cauterets	2678	42.4630	-0.0611
289	2002	Lake Petit Lac Du Col	Cauterets	2650	42.4630	-0.0611
290	2002	Lake Gentianes	Luz	2642	42.4630	-0.0611
291	2001	Lake Ossue	Luz	1834	42.4525	-0.0614
292	2002	Lake Cardal	Luz	2221	42.4348	-0.0618
293	2002	Pond Col de la Bernatoire	Luz	2045	42.4348	-0.0618
294	2002	Pond Col de la Bernatoire 1	Luz	2393	42.4316	-0.0620
295	2001	Lake Especiérès	Luz	2195	42.4240	-0.0409
296	2001	Lake Especiérès Infèrieur	Luz	2186	42.4240	-0.0409
297	2001	Pond Plaiteau de Saint André	Luz	2075	42.4239	-0.0326
298	2001	Ponds Labas Blanc	Luz	2009	42.4239	-0.0326
299	2002	Lake Gloriettes	Luz	1668	42.4513	0.0149
300	2002	Laquet de Bassia	Luz	2275	42.4613	0.0448
301	2001	Pond Bassia 1	Luz	2277	42.4613	0.0448
302	2002	Pond Bassia 2	Luz	2275	42.4613	0.0448
303	2002	Pond Le Cot 1	Luz	2063	42.4402	0.0525
304	2002	Pond Le Cot 2	Luz	2130	42.4402	0.0525
305	2002	Pond Le Cot 3	Luz	2130	42.4402	0.0525
306	2002	Pond Le Cot 4	Luz	2130	42.4402	0.0525
307	2001	Pond Serre Longue	Luz	2190	42.4330	0.0523
308	2001	Pond Esbarris	Luz	2139	42.4329	0.0607
309	2001	Lake Aires Supérieur	Luz	2089	42.4329	0.0607
310	2001	Lake Aires Inférieur 1	Luz	2081	42.4329	0.0607
311	2001	Lake Aires Inférieur 2	Luz	2081	42.4329	0.0607
312	2001	Lake Comble 2	Luz	2099	42.4327	0.0651
313	2001	Lake Comble 1	Luz	2098	42.4327	0.0651
314	2001	Lake Troumouse 1	Luz	2098	42.4329	0.0607
315	2001	Pond Troumouse 1	Luz	2105	42.4329	0.0607
316	2001	Pond Troumouse 2	Luz	2102	42.4329	0.0607
317	2001	Pond Troumouse 3	Luz	2133	42.4329	0.0607
318	2001	Lake Troumouse 2	Luz	2135	42.4329	0.0607
319	2001	Lake Troumouse3	Luz	2145	42.4329	0.0607
320	2001	Lake Troumouse 4	Luz	2148	42.4329	0.0607
321	2002	Lake Pourtet	Luz	2411	42.4959	0.0459
322	2002	Lake Rabiet	Luz	2191	42.4927	0.0457
323	2002	Lake Couvela det Mey	Luz	2273	42.4855	0.0456
324	2002	Lake Bugarret	Luz	2281	42.4853	0.0540
325	2002	Lake Glere	Luz	2103	42.5103	0.0546
326	2002	Lake Coume Escuree	Luz	2150	42.5103	0.0546
327	2002	Lake Mourele	Luz	2297	42.5031	0.0544
328	2002	Pond Mourele	Luz	2340	42.5031	0.0544
329	2002	Lake Mail	Luz	2350	42.5031	0.0544
330	2002	Lake Oueil Nègre	Luz	2349	42.5031	0.0544
331	2002	Pond Mail 1	Luz	2652	42.5031	0.0544
332	2002	Pond Mail 2	Luz	2652	42.5031	0.0544
333	2002	Pond Mail 3	Luz	2652	42.5031	0.0544
334	2002	Pond Mail 4	Luz	2652	42.5031	0.0544
335	2002	Lake La Manche	Luz	2351	42.5031	0.0544
336	2002	Lake Estelat Inférieur	Luz	2399	42.4958	0.0543
337	2002	Lake Estelat Supérieur	Luz	2423	42.4958	0.0543
338	2002	Lake Glacé de Maniportet	Luz	2747	42.4926	0.0541
339	2002	Pond Maniportet	Luz	2720	42.4926	0.0541
340	2002	Lake Bleu De Maniportet	Luz	2651	42.4958	0.0543

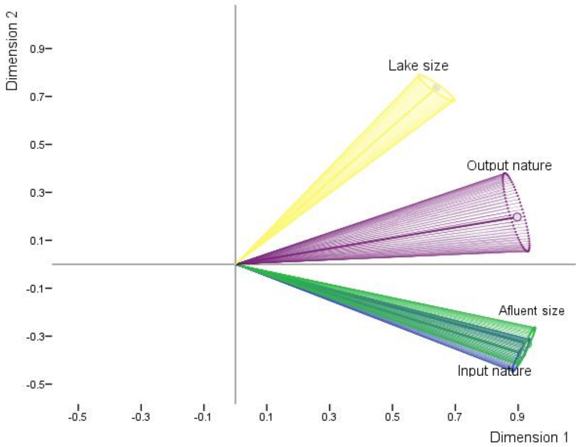
341	2002	Pond Bleu De Maniportet 1	Luz	2651	42.4958	0.0543
342	2002	Pond Bleu De Maniportet 2	Luz	2651	42.4958	0.0543
343	2002	Lake Maniportet Infèrieur	Luz	2650	42.4958	0.0543
344	2002	Pond Bleu	Luz	2665	42.4957	0.0627
345	2002	Lake Vert Maniportet Long	Luz	2632	42.4957	0.0627
346	2002	Lake Vert Maniportet Rond	Luz	2626	42.4957	0.0627
347	2002	Pond Vert Maniportet Rond	Luz	2628	42.4957	0.0627
348	2002	Lake Vert Inférieur	Luz	2465	42.4957	0.0627
349	2002	Pond Vert Inférieur 1	Luz	2465	42.4957	0.0627
350	2002	Pond Vert Inférieur 2	Luz	2465	42.4957	0.0627
351	2002	Lake Breche 2	Luz	2433	42.4957	0.0627
352	2002	Lake Breche 1	Luz	2409	42.4957	0.0627
353	2001	Pond Aguilous	Luz	2318	42.4506	0.0612
354	2001	Pond Aguilous 1	Luz	2240	42.4506	0.0612
355	2001	Pond Agulious 2	Luz	2255	42.4506	0.0612
356	2002	Runoff Cap de Long 3	Aure	2602	42.4746	0.0704
357	2002	Pond Cap de Long 2	Aure	2591	42.4819	0.0706
358	2002	Pond Cap de Long 1	Aure	2179	42.4851	0.0707
359	2002	Lake Cap de Long	Aure	2160	42.4851	0.0707
360	2002	Pond Neuvelle reserve	Aure	2471	42.5101	0.0714
361	2002	Lake Aubert	Aure	2154	42.5101	0.0714
362	2002	Lake Aumar	Aure	2193	42.5101	0.0714
363	2001	Lake Badet	Aure	2084	42.4536	0.0742
364	2001	Pond Barroude 6	Aure	2345	42.4326	0.0735
365	2001	Pond Barroude 5	Aure	2350	42.4326	0.0735
366	2001	Pond Barroude 4	Aure	2356	42.4326	0.0735
367	2001	Pond Barroude 3	Aure	2374	42.4326	0.0735
368	2001	Pond Barroude 2	Aure	2375	42.4326	0.0735
369	2001	Pond Barroude 1	Aure	2376	42.4325	0.0819
370	2001	Pond Barroude	Aure	2385	42.4325	0.0819
371	2001	Pond Barraode refuge	Aure	2377	42.4325	0.0819
372	2001	Lake Barroude Grand	Aure	2355	42.4325	0.0819
373	2001	Lake Barroude Petit	Aure	2377	42.4325	0.0819
374	2001	Pond Barroude Petit 1	Aure	2377	42.4325	0.0819
375	2001	Pond Barroude Petit 2	Aure	2377	42.4325	0.0819
376	2001	Pond Barroude Petit 3	Aure	2377	42.4325	0.0819
377	2001	Pond Barroude Grand 1	Aure	2458	42.4325	0.0819
378	2001	Pond Barroude Grand 2	Aure	2458	42.4325	0.0819
379	2001	Pond Barroude Grand 3	Aure	2458	42.4325	0.0819
380	2001	Pond Barroude Grand 4	Aure	2440	42.4325	0.0819

Note: some of nameless lakes/ponds were given the name of the adjacent area. Largest lake in an area bears no suffix.

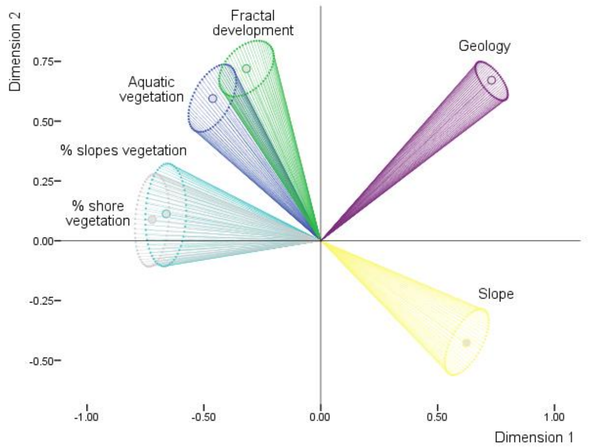
APPENDIX 2

Plots showing the stability of CATPCA results (i.e. variables loading on first 2 extracted dimensions), for hydrodynamics, geo-morphology and topography factors (as summarized by PCA), as resulting from Bootstrap procedure. Component loadings are displayed together with 90% confidence intervals. The procedure shows a generally good level of stability, as illustrated by generally narrow confidence intervals

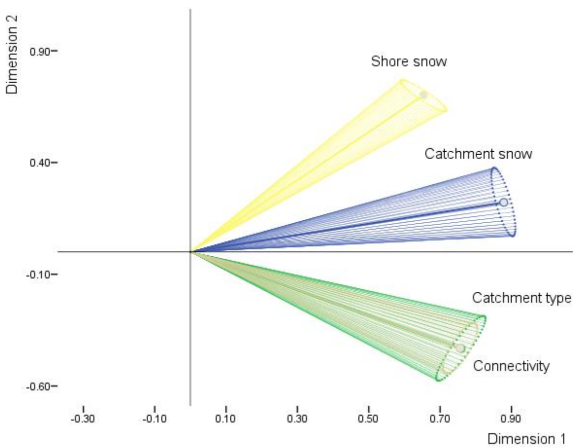
HYDRODYNAMICS



GEO-MORPHOLOGY



TOPOGRAPHY FORMATION



3

An ecotope perspective of riparian vegetation at high altitude lakes

Abstract

Riparian ecotones are the transitional surfaces between the aquatic and terrestrial systems and hold particular biota communities. At high altitude waterbodies riparian ecosystem development is generally controlled by challenging landscape, climate and local environmental conditions. Here I used the logic of fuzzy set ordination (FSO) and multidimensional FSO (MFSO) to test the degree of influence a number of composite catchment, geolocation and local geochemistry factors have on riparian vegetation structure in a case area comprising 189 protected glacial origin lakes and ponds in the Pyrénées National Park, France. The multivariate assessment included vegetation species composition together with a number of composite catchment (hydrodynamics, geo-morphology and topography) and local (sediment nutrients, major and trace element contents and water pH, conductivity and major elements) scale factors, and geolocation (altitude, latitude and longitude). A second objective was to test for riparian vegetation associations and their ecotope preferences.

Complex interactions among hydrodynamics, topography and geo-morphology appear to significantly control the riparian vegetation structure of Pyrenean lakes. This catchment scale variability in vegetation composition changed considerably along latitudinal and altitudinal gradients, possibly reflecting a N-S transition between the large paneuropean climatic zones Continental, Atlantic, Mediterranean and Alpine. At local scale, sediment Mg and Pb contents and water Mn and Fe contents showed significant relationships with the vegetation variability, there possibly being secondary effects from bedrock geology and hydrological fluctuations in the riparian zone.

Indicator species analysis identified four riparian communities which represented different lakes categories. They were communities with preferences for (a) damp ecotones, (b) snow beds-Si bedrock, (c) wet heath, and (d) one group was possibly indicative of calcareous substratum. Boxplot distribution analysis helped identify ecotope preferences for these communities. The findings have implications for the understanding of riparian vegetation structuring at high altitude waterbodies and its potential sensitivity to environmental changes.

Keywords: altitude lakes, riparian vegetation, landscape, Pyrenees, PCA, (Multidimensional) Fuzzy Set Ordination, PGMA clustering, Indicator Species Analysis

1. Introduction

High elevation lakes are sensitive ecosystems of clear water and low nutrient/ mineral input, placed in harsh environmental settings (Williamson et al., 2009).

Most of these are remnants of the latest glaciations; they have evolved throughout the modern Holocene, and are commonly formed at valley heads. The complex landscape texture, a legacy from the glacial times, controls the inputs and outputs of water and nutrients from a given basin. These, in turn, are the primary drivers which control the chemical composition of altitude waterbodies. Moreover, tight interactions between landscape morphology, bedrock geochemistry and climate are responsible for the settlement and functioning of unique plant and animal communities inhabiting altitude lakes, giving them a high ecological value (Kernan et al., 2009).

Geomorphic surfaces, together with altitude and other large-scale variables, provide a physical template (i.e. ecotope) for the development of aquatic ecosystems and the associated bordering area, called riparian ecotone. At the interface between terrestrial and aquatic environments, riparian zones bring together contrasting gradients of environmental factors, ecological processes, and plant communities (Gregory et al., 1991). The riparian zones are usually the most productive in a mountain landscape and hold a disproportionately high diversity of life forms compared to the surrounding ecosystems.

The geographical relationships between vegetation and ecotope can result in similarities among the distribution patterns of species, i.e. species sharing similar environments, with gradual species substitution along large continuum gradients (Austin and Smith, 1989; Hengeveld, 1990). Baroni-Urbani et al. (1978) introduced the term “chorotype” to define a pool of species with significantly similar distribution patterns, which are different from those of other associations. A chorotype has two components: the area occupied by any given community and the biotic element, being the association of species with similar distributions. Technically, when chorotypes (association membership) for some species cannot be established significantly, they can be assumed to follow continuum distributions (Báez et al., 2005). At high altitudes, however, the rough nature of the terrain, the limitations which arise from particularly severe alpine restrictions (low temperatures, abrasion by snow/ice) together with the insularity of lentic environments may lead to a natural fragmentation of this continuum into pools of species locked to local resource gradients. Species composition and gene flow in these communities are expected to be largely limited by the degree of connectivity between waterbodies. Since these systems appear somewhat isolated from one another and because resources are often extremely limiting, the question of how existing communities are actually structured and interact with the surfaces they inhabit remains largely unknown.

Research on the ecotope influence on riparian development and functioning has often been approached from studies conducted at low altitudes which generally regarded the physical alterations that hydrological or habitat disturbance caused to riparian communities at the local scale (e.g. Merritt et al., 2010). Moreover, an important goal in environmental science is to assess coexistent species’ response to environmental change in highly sensitive areas. It is therefore fundamental to determine the role ecotope processes have on riparian vegetation communities around high altitude lakes, a subject little understood, especially over large areas.

The objectives of the study presented herein were therefore:

(a) To determine the degree of influence a number of ecotope factors have on riparian vegetation composition, from different perspectives, i.e. geolocation, catchment and local geochemistry. For this I used the logic of (Multidimensional) Fuzzy Set Ordination. This is an attractive approach for ecological questions due to its power in addressing nonlinear and complex relationships as well as its freedom from restrictive assumptions.

(b) A secondary objective was to ascertain potential riparian vegetation associations and the degree of their ecotope and lake preferences. To answer these questions a case area which contains a large range of waterbodies in a protected region of the Central Pyrenees was chosen.

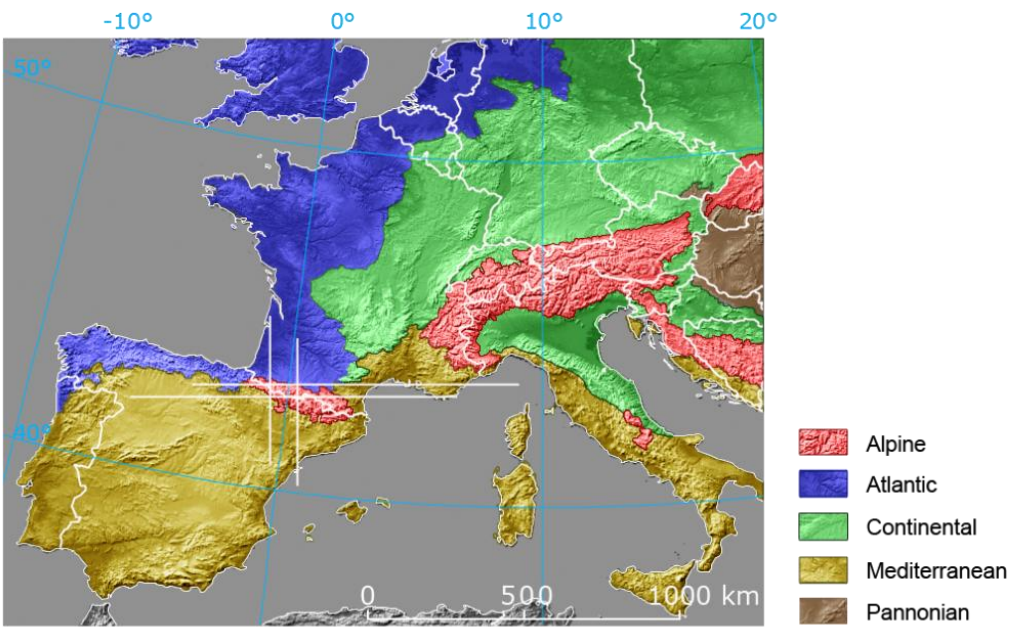


Fig. 3.1 Location of study area (delimited in white) in the axial Pyrenees, together with the biogeorgaphical regions of W Europe (after EEA, 2001). Country boundaries are in white.

2. The case area

The lakes under study extend from -0˚37’35” to 0˚08’19” E and 42˚43’25”-42˚49’55” N in the axial region of the central Pyrenees (see Chapter 2). This area is under the protection of the Pyrénées National Park.

Hydrology of the region is broadly shaped by Atlantic influences which feed the >400 lakes and ponds of this lake district. Most of the lakes are the remnants of glaciers retreat 11000 years ago and they are in different stages of lake evolution. A great number of the lakes is drained by torrents which converge into major valleys, though isolated waterbodies are not rare. Some of the big lakes were transformed into reservoirs and are used for hydropower and as freshwater reserves of high quality. A detailed depiction of the area is presented in Chapter 2.

Ecologically, the region bears the imprint of four large biogeographical influences of Europe which shape the biotic composition, i.e. Atlantic with Continental remnants from the north, Mediterranean from the south and local alpine influence (EEA, 2009; Fig. 3.1). This leads to a rich biodiversity (generally greater than in the Alpine arch) and a relatively high proportion of endemic plant species (± 11.8%) above the tree line (Gómez et al., 2003). Thus, by their relatively simple E-W geographical gradient but contrasting geoclimatic features, the Pyrenees chain is an adequate setting for empirical analyses of riparian plant communities and associated ecological processes in the mountain environment.

3. Methodology

3.1. Sampling strategy

A total number of 189 altitude lakes and ponds, ranging from 1161 to 2747m a.s.l. were visited during the months of July 2000, 2001 and 2002. The sampling strategy was designed to cover the great majority of waterbodies in the region in a minimum period, so as to capture the ecotope processes and the riparian vegetation coverage at similar phenological stages in the summer season.

Each lake was characterised according to riparian vegetation composition and a range of environmental attributes. Information on the type of species present around each waterbody was collected in the field using Grey-Wilson and Blamey (1979), Fitter et al. (1984) and García-Rollán (1985) keys. Certain species needed to be collected and transported in a portable herbarium to the laboratory for complete identification. They were thereupon identified using Flora Europea (available online at: http://rbg-web2.rbge.org.uk/FE/fe.html).

At each location a number of hydrological (tributary discharge, nature and size of water input/output), geomorphological (bedrock geology, % slope of lake perimeter, fractal order, % shore/slopes covered by meadow and aquatic vegetation) and topographical (catchment type, catchment/shore snow coverage and connectivity with other lake/s) attributes were visually inspected and scored according to dominant units. Their detailed description is presented in Chapter 2. Geolocation, i.e. altitude, latitude and longitude, was recorded at each lake using a portable GPS device.

To test for relationships between lake chemistry and riparian vegetation composition, <2cm depth littoral sediments and water ±5m off the littoral (for small waterbodies, the distance was less) were sampled using clean procedures. The sediments comprised fragmented rocks, coarse sands and fine materials. As the chemical composition of the finer sediment fraction is the most likely to relate to riparian vegetation, sampling deliberately targeted this fraction. To assure sample homogeneity each sample comprised >5 randomly selected subsamples. All sediment and water samples were kept at <4˚ C until laboratory analysis.

Water pH and conductivity were recorded at the surface and bottom of the lake at each location from samples taken with a Teflon bottom water sampler. Portable pH/conductivity probes were used in this case.

3.2. Sample preparation for trace, major and nutrient element analyses

The sediment samples were dried at 40 °C for 2 days and sieved through a 0.1mm sieve. Trace and major element contents were characterised by X-ray fluorescence spectrometry (XRF). A portion of 5g sample was prepared as lithium tetraborate melt for the determination of trace (As, Ba, Co, Cr, Cu, Ni, Pb, Mn, Rb, Sr, Zn and V) and major (Al, Ca, Cl, Fe, K, Mg, Na, P, S, Si and Ti) elements. Results are expressed in mg kg^{-1} and % mass-mass, respectively for trace and major elemenets. Fusions were performed in Pt–Au crucibles. Calibration and quality control analyses were carried out using replicated certified reference materials from National Research Council of Canada, NRCC (SO-3, SO-4, HISS-1, MESS-3 and PACS-2, soils and sediments) and from South Africa Bureau of Standards, SACCRM (SARM 52, stream sediment). Additionally, a given sample was analysed several times during the analysis run. The analysis was highly reliable, with the recovery figures for the reference materials being within an acceptable range for all major elements (±10%). Percent coefficient of variability (%CV) between replicates was <5% and % relative standard deviation, RSD (1σ) between measurements of the same sample <2%.

Total C and N contents were simultaniously detemined by flash combusting 5 mg dried sediments in a Carlo Erba 1108 elemental analyser following standard operating procedure (Verardo et al., 1990).

Water samples were prepared for analysis by filtering through 0.45 μm cellulose nitrate membrane followed by acidification to 2% with ultrapure Merck nitric acid. The acidified samples were analysed for Cu, Li, Mn, Ni, Pb, Rb, Se and Sr by inductively coupled (argon) plasma – mass spectrometry (ICP-MS), and for Al, B, Ba, Ca, Fe, Ga, K, Mg and Na by inductively coupled plasma - optical emission spectrometer (ICP-OES) using standard ICP-MS/OES operating conditions. The analyses followed standard procedures and QA/QC protocols.

3.3. Statistical procedures

Principal component analysis to summarise ecotope factors

Principal component analysis (PCA) was used to reduce the multiple environmental variables to a limited number of composite factors (principal components; PCs) that represent the major ecotope processes being investigated (Table 3.1). This was performed by summarising the variables into regression factor scores of the principal components (Varimax rotation) which were used as explanatory composite factors in further analysis. The analysis was produced in PASW (former SPSS) statistical package.

(Multidimensional) Fuzzy Set Ordination to identify riparian vegetation constrains

To understand the relationship between vegetation composition/incidence and environmental gradients we used fuzzy set ordination (FSO) followed by a forward stepwise multidimensional FSO (MFSO), both run on a distance matrix of species incidence data.

Fuzzy set ordination (FSO), introduced by Roberts (1986) is a heuristic alternative to traditional ordination methods, e.g. CCA and RDA. Unlike classical set theory based on linear algebra, where elements (cases) are either in or out of a given set (i.e. 0 or 1), in FSO cases are assigned partial membership (fuzzy) values ranging from 0 to 1 that denote their membership in a set (Roberts, 2008). Likewise, species responses to environmental factors are generally not limited to a certain function; they can be, for example, nonlinear or discontinuous. FSO, therefore, is a generalized technique (Roberts, 1986) that overcomes this problem and includes the types of ordination that ecologists are more familiar with, such as direct gradient analysis (Whittaker, 1967) and environmental scalars ordination (Loucks, 1962). Thus, in fuzzy logic applications the results can facilitate the expression of rules and processes.

Technically, a distance matrix of species incidence was first calculated. For the binary data used herein we used Sørensen similarity index, as suggested by Boyce and Ellison (2001). This gave a measure of similarity between sites based solely on biota composition. This was followed by one-dimensional FSO, taking distance matrices as response variables and the environmental variables as explanatory variables. FSO also requires that the environmental variables be as much uncorrelated as possible (Boyce, 2008). A number of landscape variables showed strong correlation. Their summarised version, i.e. the PC' regression factor scores from prior PCA (Table 3.1), were therefore used as explanatory variables in FSO. By default the principal components of PCA computed with Varimax rotation are uncorrelated, therefore suitable for this approach.

A multidimensional FSO (MFSO) was run on the best subset of variables (highest correlation with the distance matrix at >95% efficiency; Table 3.3) selected from the individual FSO and allowed multidimensional interpretability of the results. Statistically in MFSO, first, a FSO is performed on the variable that accounts for most of the variation. Then, the residuals from that fuzzy ordination are used with the next most important variable, and the process is repeated until no more variables are left. Therefore unlike classical ordination methods used in ecology, e.g. Canonical Correspondence Analysis (CCA) and distance-based redundancy analysis (DB-RDA), in MFSO each variable selected by the model can be considered as an independent axis, and only the fraction of axis membership values which is uncorrelated with previous axes is included into the model (Roberts, 2009a). Moreover, MFSO is expected to perform better than the other methods on more complex datasets, and it is insensitive to rare species and noise in environmental factors (Roberts, 2009a).

The effect magnitude of each variable on species composition is assessed visually by the relative scatter attributable to that variable, and can be numerically assessed by the increment in correlation attributable to that variable (Roberts, 2009a). In FSO/MFSO, if an axis is influential in determining the distribution of vegetation, then one should be able to estimate the values of that variable based on species composition (Roberts, 2009b). Following MFSO, a “step-across” function was used to eliminate distortions in the ordination space (Boyce and Ellison, 2001).

The significance of the matrix correlation coefficient between environmental variables and species composition was established by permuting the rows and columns of one of the matrices 1000 times in both, FSO and MFSO, recalculating the correlation coefficient and comparing the observed matrix correlation coefficient with the distribution of values obtained via permutation.

FSO and MFSO were computed with FSO (Roberts, 2007a) and LabDSV (Roberts, 2007b) packages, while the step-across function was computed with VEGAN package (Oksanen et al., 2009), R statistical language and environment.

Probability classification analysis to identify chorotypes

The riparian vegetation composition (species incidence) was analysed for species association into chorotypes, i.e. species with significant co-occurrence patterns. These communities were constructed following a multi-step approach. First, the sites/lakes were clustered into typologies on the basis of shared species. For this a cluster procedure (Pair-Group Method using the Arithmetic Averages (PGMA) using flexible linkage parameter, parameter= 0.6) was computed on the Sørensen distance matrix of species incidence (Fig. 3.6). This allowed selecting the most appropriate clustering for dendrogram nodes cut. Plotting cluster results in discriminating space showed a good clustering (Fig. 3.6).

The selected clusters of lakes were subsequently assigned code numbers into a new categorical variable. This variable was used as grouping variable in Indicator Species Analysis (Dufrene and Legendre, 1997) to determine plant species with significant affinity to the lake categories, i.e. species of similar ecological preferences. Indicator species can be defined as the most characteristic species of each lake type, being found mostly in that group and present in the riparian zone of the majority of lakes of that type (Dufrene and Legendre, 1997). The higher the indicator value is, the higher is the species affinity to a lake type. Furthermore, ecotope selectivity of the resulting vegetation groups was tested by box-plotting them against environmental gradients. Sørensen similarity matrix was computed with ADE4 (“dist.binary” function; Thioulouse et al., 1997), cluster and boxplot analyses with CLUSTER (“agnes” and “boxplot” functions, respectively; Kaufman and Rousseeuw, 1990), Discriminant Analysis with FPC (“plotcluster” function; Hennig, 2005) and Indicator Species Analysis with LabDSV (“duleg” function; Dufrene and Legendre, 1997) packages for R statistical language (R Core Development Team, 2005); available online at http://cran.r-project.org/.

4. Results and discussion

4.1 Summarising large ecotope variables

Biotic structure at high altitude waterbodies is generally controlled via complex ecotope factors and geographical gradients which can characterize major driving forces. To better understand this complexity we reduced the catchment-scale variables to main drivers by principal component analysis (PCA). The first three extracted components accounted for more than 58% of the total variance in lake characteristics (Table 3.1).

The first principal component (PC1) was interpreted as hydrodynamics and accounted for tributary nature and discharge, water output and waterbody size (Table 3.1). The second component (PC2) would characterize the main bedrock geo-morphology, i.e. geology, shore sloping, % of slope/shore covered by meadow, fractal order/riparian development and the presence of aquatic vegetation. The third PC would represent topography, i.e. catchment type, visible connectivity with other lakes, and catchment and shore snow deposits. A detailed description of these factors is presented in Chapter 2. The three composite factors were therefore regarded as major drivers of the lake ecotopes development. They ought to be summarised as PC regression factor scores, in order to use them

Table 3.1: Association of landscape variables characterising the Pyrenees lakes into three composite factors. Variables are displayed in the order of correlation with the principal components (PC). Highest correlation of a variable with any of the components is in bold. This helped interpret PC1 as hydrodynamics, PC2 as geo-morphology and PC3 as topography

	Principal component		
	PC 1	PC 2	PC 3
Tributary discharge	**0.92**	0.04	0.02
Nature of tributary	**0.90**	0.02	0.01
Nature of water output	**0.87**	-0.17	0.07
Waterbody size	**0.52**	-0.38	0.05
% meadow covered slopes	-0.07	**0.72**	-0.37
% meadow covered shore	0.21	**0.68**	-0.24
Slope of lake perimeter	0.30	**-0.67**	-0.03
Geology	-0.23	**0.60**	0.07
Aquatic vegetation	-0.16	**0.58**	-0.22
Fractal order	0.07	**0.50**	0.08
Catchment snow deposits	0.09	-0.10	**0.86**
Catchment type	0.05	0.07	**0.79**
Shore snow coverage	-0.11	-0.11	**0.75**
Connectivity with others	0.39	-0.36	**0.52**
Total Eigenvalue (rotated)	3.07	2.69	2.46
% of variance explained	21.96	19.24	17.59
Cumulative %	21.96	41.20	**58.79**

Rotation method: Varimax with Kaiser normalization. Kaiser-Meyer-Olkin measure of sampling adequacy= 0.73. Bartlett's test of sphericity: approx. χ^2= 1456.9 ($P<0.001$).

as predictors of vegetation composition in further analysis.

4.2 Response of riparian vegetation to environmental gradients by means of FSO-MFSO

As an initial step in the evaluation of environmental influence on vegetation variability all environmental factors, i.e. geoposition, landscape, and sediment and water chemistry variables, were screened independently with a single-dimensional FSO. Table 3.2 gives the observed correlations between the factors and apparent factors (ordination location) predicted by vegetation,

Table 3.2: One-dimensional fuzzy relationship of riparian vegetation species composition with environmental factors in the central Pyrenees. Factor superscripts represent: (a) geoposition, (b) landscape (detailed in Table 3.1), (c) sediment chemistry, and (d) water chemistry variables. Correlations between factors and apparent factors (as predicted by vegetation) are listed in descending order. Factors with correlations >0.3 (in bold) were retained for further MFSO analysis. *P* represents the probability after 1000 permutations

Variable	*r* (Pearson)	*P*	Variable *(continued)*	*r* (Pearson)	*P*
[a]Altitude	**0.855**	0.001	[c]Sediment Sr	-0.005	0.545
[a]Latitude	**0.695**	0.001	[c]Sediment Na	-0.020	0.439
[a]Longitude	**0.636**	0.001	[c]Sediment Ti	-0.107	0.540
[b]Topography (PC3)	**0.644**	0.001	[c]Sediment Rb	-0.164	0.624
[b]Geo-morphology (PC2)	**0.603**	0.001	[c]Sediment Al	-0.443	0.900
[b]Hydrodynamics (PC1)	**0.442**	0.001	[d]Water Mn	**0.751**	0.001
[c]Sediment Mg	**0.712**	0.001	[d]Water Fe	**0.730**	0.001
[c]Sediment Pb	**0.515**	0.003	[d]Conductivity (surface)	**0.584**	0.001
[c]Sediment Ca	**0.510**	0.004	[d]Conductivity (bottom)	0.545	0.001
[c]Sediment Cu	**0.501**	0.007	[d]WaterAl	**0.531**	0.014
[c]Sediment Co	**0.497**	0.006	[d]Water Cu	**0.465**	0.009
[c]Sediment Ba	**0.484**	0.007	[d]pH (bottom)	**0.307**	0.002
[c]Sediment Ni	**0.432**	0.018	[d]pH(surface)	0.257	0.002
[c]Sediment Mn	**0.405**	0.024	[d]Water K	0.254	0.108
[c]Sediment Fe	**0.362**	0.037	[d]Water Na	0.204	0.170
[c]Sediment Zn	**0.361**	0.033	[d]Water B	0.177	0.089
[c]Sediment C	**0.351**	0.032	[d]Water Pb	0.130	0.272
[c]Sediment Si	**0.337**	0.046	[d]Water Ba	0.108	0.248
[c]Sediment N	**0.324**	0.036	[d]Water Sr	0.088	0.293
[c]Sediment Cr	**0.309**	0.069	[d]Water Se	0.057	0.340
[c]Sediment V	0.210	0.130	[d]Water Ni	-0.010	0.482
[c]C/N	0.114	0.145	[d]Water Ga	-0.020	0.445
[c]Sediment S	0.112	0.249	[d]Water Li	-0.030	0.462
[c]Sediment As	0.110	0.298	[d]Water Mg	-0.101	0.590
[c]Sediment K	0.029	0.342	[d]Water Ca	-0.234	0.746
[c]Sediment P	0.013	0.394	[d]Water Rb	-0.350	0.841
[c]Sediment Cl	-0.001	0.418			

Measurement units: altitude in m a.s.l., latitude and longitude in UTM; sediment Mg, Ca, Fe, C, Si, N, S, K, P, Cl, Na, Ti and Al in % mass-mass, sediment Pb, Cu, Co, Ba, Ni, Mn, Zn, Cr, V, As, Sr and Rb in mg kg^{-1}; water conductivity in µS cm^{-1}; and water trace and major elements in mg l^{-1}.

and the estimated probabilities resulting from 1000 permutations. Each FSO is an estimate of the environmental characteristics we would expect for a site based on its vegetation composition. The correlations of the actual factor values and their fuzzy set μ values ranged from 0.86 (for altitude) to 0.31 (for pH) for a number of factors which were retained for further analysis (Table 3.2 and Figs. 3.2-3.5). Generally, the strongest signal came from the geoposition variables, followed by a number of sediment, water and landscape variables (Table 3.2 and Figs. 3.2-3.5). Clearly altitude from the geoposition variables set appeared to exert a large influence on the variation in vegetation composition topography formation (PC3), geo-morphology (PC2) and hydrodynamics (PC1) in the landscape variables set, Mg in sediment chemistry set and Mn and Fe in water chemistry variables set (Table 3.2). A multidimensional FSO (MFSO) would however help to better quantify the effect size of environmental factors on riparian vegetation variability.

Response to geolocation

Employing the forward stepwise procedure of MFSO, all environmental factors retained from FSO were tested in turn within each set, i.e. geoposition, landscape, sediment chemistry and water chemistry. Table 3.3 lists the significant axes/factors in order of the correlations obtained with the apparent factors as predicted by riparian vegetation, along with their significance. MFSO on geolocation variables gives a two dimensional solution, with altitude and latitude, in order (cumulative r =0.65; Fig 3.2 and Table 3.3). It shows that riparian plant composition can be confidently predicted by altitude and latitude. The first factor, altitude, is an expected classical constraint of vegetation composition, and it is

Table 3.3: Participation of each factor (as independent axis) in the multidimensional fuzzy set ordination (MFSO) of vegetation data on geoposition, landscape, sediment chemistry and water chemistry variables for the central Pyrenees. Figures for geoposition, landscape characteristics and water chemistry result from MFO with step-across improvement. γ (gamma)= a vector of the fraction of variance for an axis that is independent of all previous axes. Axes are listed in the order of their implication into the model. Axes superscripts represent: (a) geoposition, (b) landscape (detailed in Table 3.1), (c) sediment chemistry, and (d) water chemistry. Axes with highest influence in the ordination and their contributed correlations are in bold

Axis	Cumulative *r*	Increment *r*	*P*-value	γ
[a]Altitude	0.46	**0.46**	0.002	1.00
[a]Latitude	0.65	**0.19**	0.001	0.97
[a]Longitude	0.66	0.01	0.740	0.06
[b]Topography (PC3)	0.43	**0.43**	0.026	1.00
[b]Geo-morphology (PC2)	0.52	**0.09**	0.325	0.54
[b]Hydrodynamics (PC1)	0.64	**0.12**	0.001	0.97
[c]Mg	0.49	**0.49**	0.270	1.00
[c]Pb	0.74	**0.25**	0.044	0.49
[c]Ca	0.74	0.01	0.057	0.09
[c]Cu	0.75	0.01	0.035	0.05
[c]Co	0.76	0.01	0.025	0.05
[c]Ba	0.75	-0.01	0.142	0.06
[c]Ni	0.75	-0.004	0.157	0.02
[c]Mn	0.75	-0.001	0.135	0.02
[c]Fe	0.75	0.002	0.096	0.02
[c]Zn	0.75	-0.001	0.118	0.01
[c]C	0.74	-0.01	0.334	0.09
[c]Si	0.74	0.00	0.180	0.004
[c]N	0.74	0.00	0.164	0.01
[d]Mn	0.56	**0.56**	0.281	1.00
[d]Fe	0.73	**0.17**	0.384	0.22
[d]Conductivity	0.71	-0.03	0.406	0.06
[d]Al	0.71	0.002	0.177	0.03
[d]Cu	0.71	0.003	0.182	0.09
[d]pH (bottom)	0.71	-0.01	0.297	0.13

Due to the high-dimensional variability of the dissimilarity matrix, the correlation probability for the one-dimensional solution sometimes has low significance, but it is still valid. Altitude is in m a.s.l., latitude and longitude in UTM; sediment Mg, Ca, Fe, C, Si and N in % mass-mass, sediment Pb, Cu, Co, Ba, Ni, Mn, Zn and Rb in mg kg^{-1}; water conductivity in μS cm^{-1}; and water Mn, Fe, Al and Cu in mg l^{-1}.

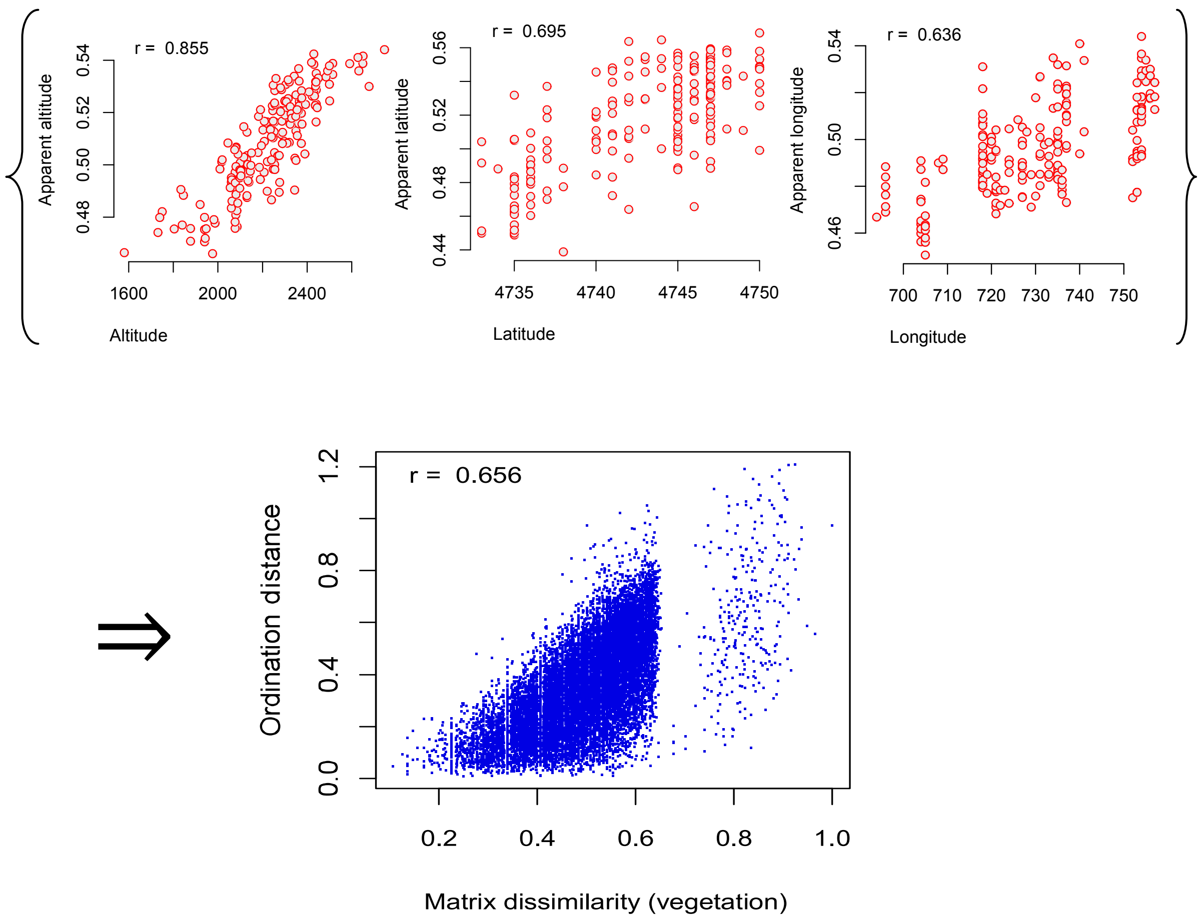


Fig. 3.2 Fuzzy set ordination (FSO) of riparian vegetation structure (computed with Sørensen similarity index of species incidence data) on geolocation variables, i.e. altitude (m a.s.l.), latitude (UTM) and longitude (UTM), and their interaction in a multidimensional FSO (MFSO) with step-across improvement. Variables are input in the MFSO model in the order of decreasing Pearson fuzzy correlation with the dissimilarity matrix of species composition. Number of permutations = 1000. Note that not all FSO variables contribute substantially to the total variance captured by MFSO (see Table 3.3).

an associate to the alpine climate gradient. As far as latitude is concerned, Pyrenees are an E-W chain and the study area covers a relatively narrow latitudinal gradient. Yet this area shares four main biogeographic influences of Europe: Atlantic and Continental remnants from north, Mediteranean from south, with local alpine climate (EEA, 2009; Fig. 3.1). The predicted latitudinal influence on vegetation composition could therefore unveil a transitional N-S gradient between these macroregions. The longitude, though it shows an individual relationship with vegetation variability (Fig 3.2), does not seem to contribute significantly to the multivariate solution (Table 3.3).

Response to landscape composite factors

MFSO on composite landscape variables gave a three-dimensional solution, with topography (PC3), hydrodynamics (PC1) and geo-morphology (PC2), in order (cumulative r =0.64; Table 3.3 and Fig. 3.3) correlating to the vegetation species structure. The first composite axis, i.e. topography, shows that collectively catchment type, with local effects from snow cover and lake connectivity (Table 3.1), had strong influence on riparian vegetation community variability. Glaciological formations (e.g. head of glacial valley, U and V shape valleys, mountain pass and slopes; Chapter 2) left behind by the last glaciations that shaped the landscape at macroscale are topographical factors likely to trigger different microclimates and shape the vegetation settlement. Topography has been shown to control terrestrial vegetation through its effect on snow coverage in alpine regions (Keller et al., 2005), which is a visible consequence of topography interaction with climatic variables like radiation, precipitation

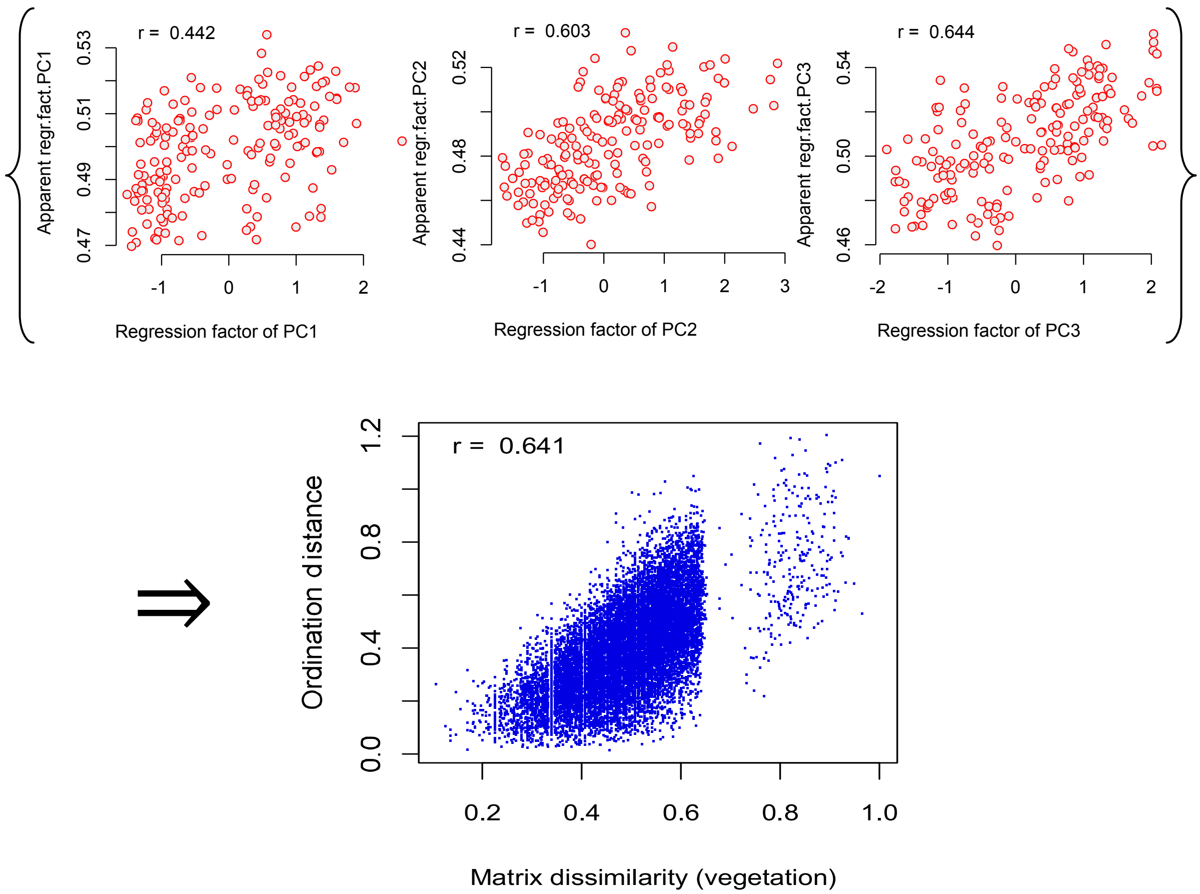


Fig. 3.3 Fuzzy set ordination (FSO) of riparian vegetation composition and the summarised components from principal component analysis run on landscape variables, i.e. hydrodynamics (PC1), geo-morphology (PC2) and topography (PC3), together with their interaction in multidimensional FSO (MFSO) with step-across improvement. Number of permutations for both FSO and MFSO = 1000. The variables associated to the principal components are presented in Table 3.1.

and wind (Körner, 1999). This is supported by the PCA association of topographical variation with the distribution of snow deposits, a direct consequence of slope orientation (Table 3.1). For instance at the head of glacial valleys snow would generally last longer around the lakes, thus creating wetter conditions from thaw water than on mountain slopes or mountain passes, where the soil would be drier, with earlier light available for plant development. Consequently, these contrasting conditions would allow the colonisation of different sets of species. Water connectivity can also shape and maintain the structure of certain riparian communities via its important role in propagule dispersion and colonisation. Therefore, it seems that topography is a major factor in determining the vegetation composition of alpine riparian zones.

The second landscape axis/factor, i.e. hydrodynamics, shows that the nature and discharge of the tributaries, with associated effects from waterbody size and nature of output (Table 3.1), added to the variance of the previous axis and also contributed significantly to riparian vegetation variability (Table 3.3 and Fig. 3.3). The importance of nature and discharge of tributaries as controlling factors in an altitude lake/riparian ecotope can be explained by their role as determinants of the nutrient and other chemical loads, of the nature of sediment being mobilised from the drainage basin; all these having the potential to influence riparian vegetation development. The size of a lake is also an important factor, which has been shown to affect benthic colonisation under the Equilibrium Theory of Island Biogeography applied to altitude lakes (Oertli et al., 2002). It seems from our results that this factor (hydrodynamics) affects the riparian vegetation variability, with medium-to-large lakes which are fed largely by surface water (Table 3.1) holding significantly different vegetation communities in comparison to the smaller and shallower ones (e.g. ponds), which are fed directly by precipitation.

The effect of the main bedrock geology with secondary effects of shore sloping, vegetation coverage and shore development (fractal level)(PC2), representing the third landscape axis, also seems to contribute significantly to the variability of riparian vegetation (Table 3.3 and Fig. 3.3). Generally, geology has been reported to influence the establishment of vegetation, especially by its role in determining niche/habitat formation and general habitat/soil chemistry (Kovalchik and Chitwood, 1990). The bedrock of the study region is largely marked by two contrasting geological features: an igneous core (granite) in its central part, which is flanked by sedimentary/metasedimentary materials, e.g. limestone (Chapter 2). This would have acted through the creation of niche gradients/differences that contributed to the variability in species composition observed. For example granitic geomorphology, which is more resistant to weathering would imprint a poor chemistry on the lake environment, a slopy less developed riparian zone (lower fractal order), with unstable terrain (loose rocks) which will hold low vegetation coverage (Table 3.1; Chapter 2). Conversely, lakes on more reactive materials such as limestone would sustain different vegetation composition, due not only to a more basic/chemically rich environment but also to a higher development of riparian zones (higher fractal order), a more stable terrain (less accentuated slopes) which would also sustain more vegetation coverage (Table 3.1; Chapter 2).

The strong implication of topography, hydrodynamics and geo-morphology in riparian vegetation variability also supports the concept outlined previously (Chapter 2) which predicted a major influence of these ecotope factors on lake ecosystem formation at high altitude.

Relationship with sediment chemistry

As Lewin and Macklin (1987) pointed out, the chemistry (e.g. nutrients, major and trace element contents) of high altitude water bodies is tightly linked to the lithology of their catchment, i.e. the geological structure, the mineralogical/chemical composition of the rocks, the proportions of rock types and the weathering resistance. Therefore we would expect the riparian vegetation structure to respond to the general chemistry of the catchment, including that of the water-bodies' sediment and water, especially owing to their close interactions. The MFSO of riparian vegetation and contents of nutrients, major and trace elements in the sediments resulted in a bi-dimensional solution with sediment Mg and Pb contents (cumulative r =0.74; Table 3.3, Fig. 3.4) able to reliably predict the vegetation composition. Magnesium, as part of chlorophyll, is an essential macronutrient for the photosynthesis in green plants and it is also essential in activating many enzymes needed for growth. Soils developed on basic bedrock such as basalt and limestone generally contain higher levels of Mg (~0.3-2.9%) than those developed on granite or sandstone (~0.01-0.3%) (Beeson, 1959). The Mg axis can therefore be interpreted as a secondary effect of substratum geology, which seems to control Mg availability around the Pyrenean altitude lakes.

The influence of Pb on vegetation composition in a natural landscape is not totally clear. Lead uptake in plants has been reported as being positively correlated with mycorrhizal colonization under low soil metal concentrations (Wong et al., 2007). One possible explanation is that the relationship of vegetation structure with sediment Pb content would reflect the distribution of plants that use mycorrhizae, eg. species from the Fabaceae family. As vegetation is generally highly sensitive to Pb in the environment (Kabata-Pendias and Pendias, 2001), the results could also highlight a change in vegetation composition along a rather natural Pb stress gradient, particularly in areas where Pb in bedrock minerals is at higher concentrations, e.g., in metamorphic areas at the contact zone of sedimentary strata with the granitic batholiths, as reported near the area (Catalan et al., 2006; Zaharescu et al., 2009). Nonetheless this is an interesting finding that requires further inquiry.

Although other elements/nutrients present in the samples are also essential to plants it appears that it is the contents of Mg and Pb, possibly in their bioavailable forms that play an important role in influencing species composition at these altitudes. The low effect of C, N and other elements on vegetation structure is possibly because they are either in insufficient amounts to make an impact or their importance is similar among the plant species, i.e. being in similar amounts they have not been picked up by (M)FSO. Further study is however required to ascertain why there is this influence from Mg and Pb on vegetation at these high altitude lakes and not for other nutrients/elements.

Relationship with water chemistry

The MFSO of riparian vegetation composition and selected water chemistry variables, i.e. pH, conductivity, Al, Fe, Mn and Cu contents, also resulted in a bi-dimensional solution with water Mn and Fe as the major influential axes (cumulative r =0.73) (Table 3.3 and Fig. 3.5). Fe and Mn are important elements in plant physiology.

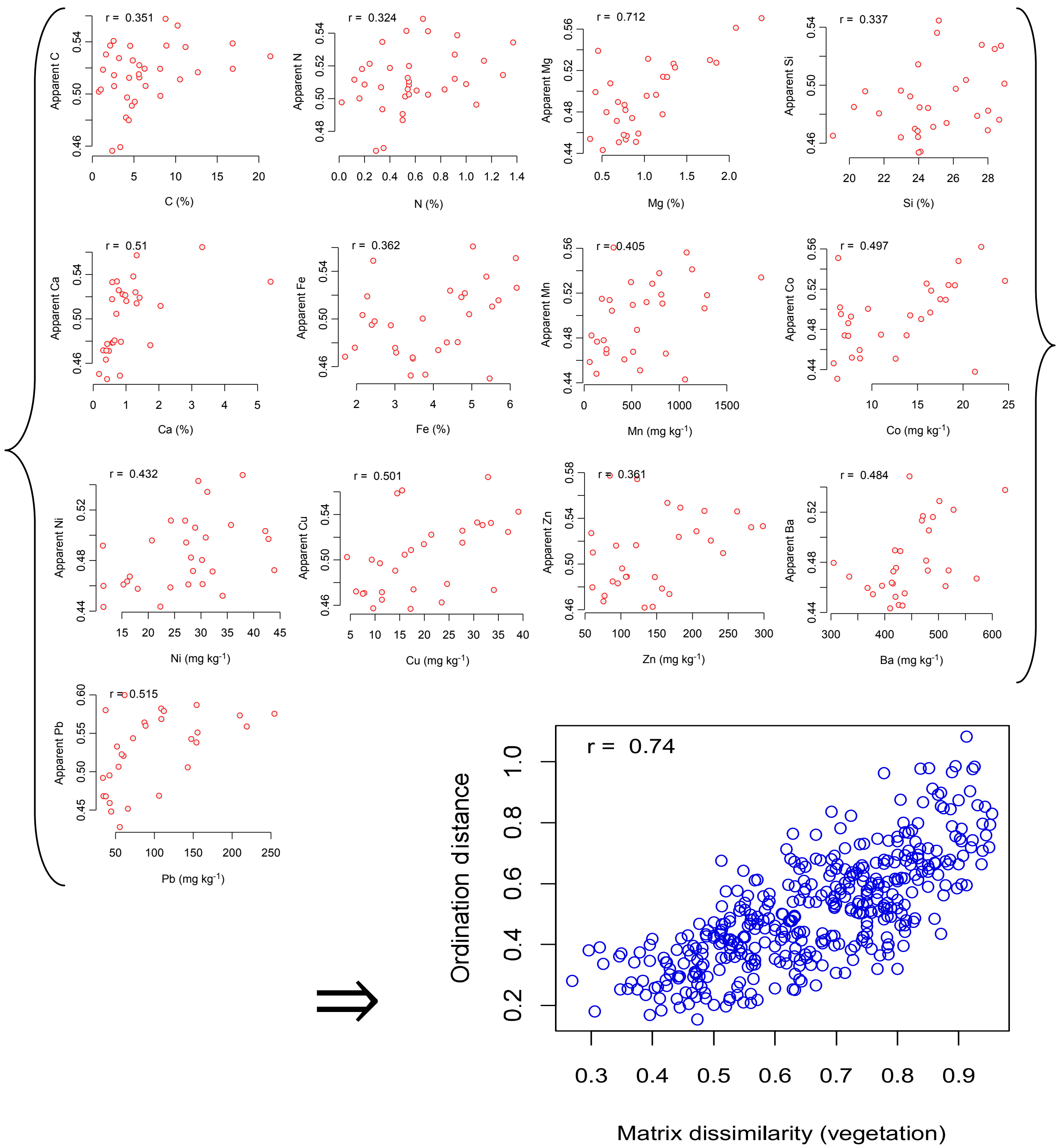


Fig. 3.4 Relationship of lake-bed sediment chemistry with vegetation composition as given by FSO and MFSO. Number of permutations = 1000. FSO variables that contribute substantially to the total variance captured by MFSO are presented in Table 3.3.

Besides, they are also major players of reduction-oxidation processes in soils/ sediments, being mobilised especially during flooding (Alam and Azmi, 1989). Varying water table condition is expected to modify the flooding effects (solubility) of Fe and Mn and, consequently, the uptake of these elements by plants (Alam, 1999). For example, in water-saturated environments, reduction prevails and plant performance can be influenced not only by preventing macro and micronutrient (e.g. Mg, Ca and Fe) uptake but also by restricting root development (Couto et al., 1983). Differential responses of plant species to the build-up of soluble Fe and Mn have been suggested as the potential factors in species ecology and habitat distribution (Alam, 1999). Similar differential response of plant families to different redox conditions has also been reported for a variety

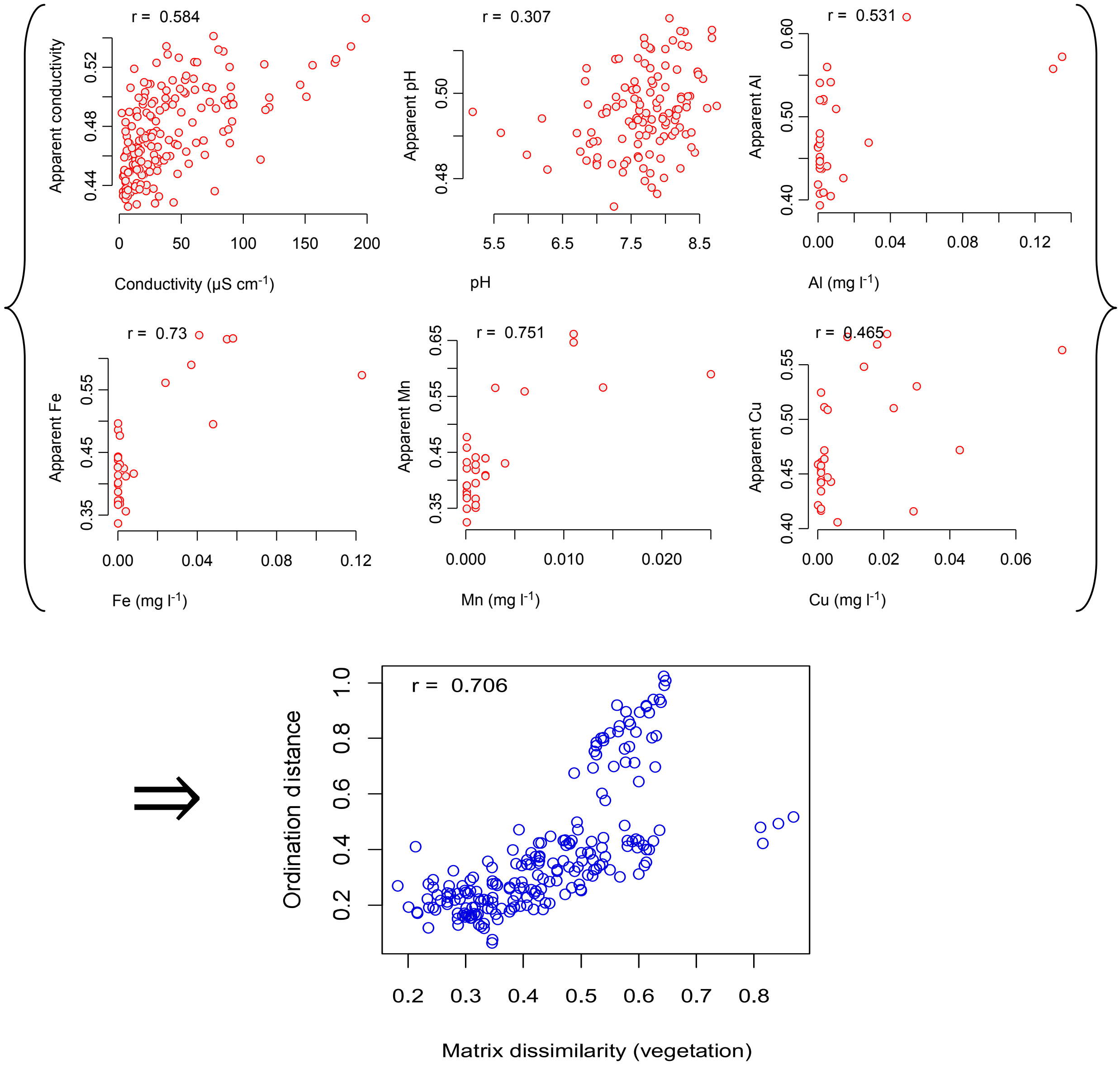


Fig. 3.5 Relationship between water chemistry and vegetation composition as given by FSO and MFSO with step-across improvement. Number of permutations = 1000. FSO variables contributing significantly to MFSO are in Table 3.3.

of species including grasses, legumes (Couto et al., 1983) and trees (Good and Patrick, 1987).

Variation in flooding of riparian zones by lake water and significant variations in the moisture of riparian zones is a common aspect at high altitude waterbodies and it is regulated by the thaw of snow deposits in the catchment during the aestival season and by the frequency and volume of summer storms. The variability of plant composition along Mn and Fe gradients as shown by our results could therefore be explained by differences in the flooding/moisture capacity of riparian zones (a secondary effect of topography; Chapter 2 and Table 3.1), with relatively higher moisture of ecotopes at the head of glacial valleys and a lower one of those on the slopes/mountain pass (Chapter 2). Water pH, conductivity and the contents of the other major and trace elements appeared to have little contribution to the multivariate solution. This is possibly because these varied within small ranges, hence becoming common factors.

4.3 Species co-occurrence and their ecotope preferences

The geographical interaction of riparian biota and ecotope attributes at high altitudes may structure certain riparian groups into pools of species which are dependent on local resources (i.e., sharing similar resources). Such grouping may be restricted by the degree of connectivity between lakes; conversely, other species would follow continuum distributions. To identify riparian vegetation groups with clear similar ecological preferences cluster and Indicator Species Analysis was applied to the species occurrence data.

Results of the Pair-Group Method using the Arithmetic Averages (PGMA) procedure for flexible linkage parameter =0.6 show a relatively good clustering structure (agglomerative coefficient = 59%), easily delimited, that allowed to represent the 189 high Pyrenees lakes into 4 well-defined types (Fig. 3.6). Of the total of 168 plant species recorded in the lakes riparian zone (Appendix), Indicator Species Analysis found 79 species being associated into 4 communities (chorologies) which represent the 4 lake typologies (Table 3.4). The identified co-occurring species span a wide range of habitat moisture, from typically aquatic/amphibian species, e.g. *Ranunculus aquatilis* and *Callitriche palustris*, to species growing in damp environments or near the snow beds (e.g. *Saxifraga stellaris* and *Bartsia alpina*) and in drier condition/rock surfaces, e.g. *Hutchinsia alpina.* This clearly shows a wide range of ecotope conditions in the riparian zone at these altitudes.

Table 3.4 shows the species with significant co-preference for the lake sets and their probability of group membership. As shown by this analysis (Table 3.4) the association of plant species to lake types A, B and D (Fig. 3.6) yielded a high degree of confidence. The riparian species characteristic of site/lake type A mostly comprise hygrophilous species of damp ecotopes such as bog-associated species with *Sparganium angustifolium*, *Ranunculus aquatilis*, *Chara foetida*, *Sphagnum* moss, *Selaginell*a fern, Cyperaceae (*Carex echinata*) and Juncaceae (*Juncus articulatus*) sedges and rushes, and other small plants of damp/wet substrata (e.g. *Caltha palustris* and *Sanguisorba officinalis*). Associated to these species are also a limited number of plants of drier/stony habitats, e.g. the cosmopolite *Bellis perenis,* the nitrogen fixing *Trifolium repens* and the endemic *Merendera pyrenaica*. The associated species tolerate a wide gradient of bedrock chemistry, from acidophiles (*Sphagnum sp.)* to neutrophiles (*Trifolium repens*) and basophiles

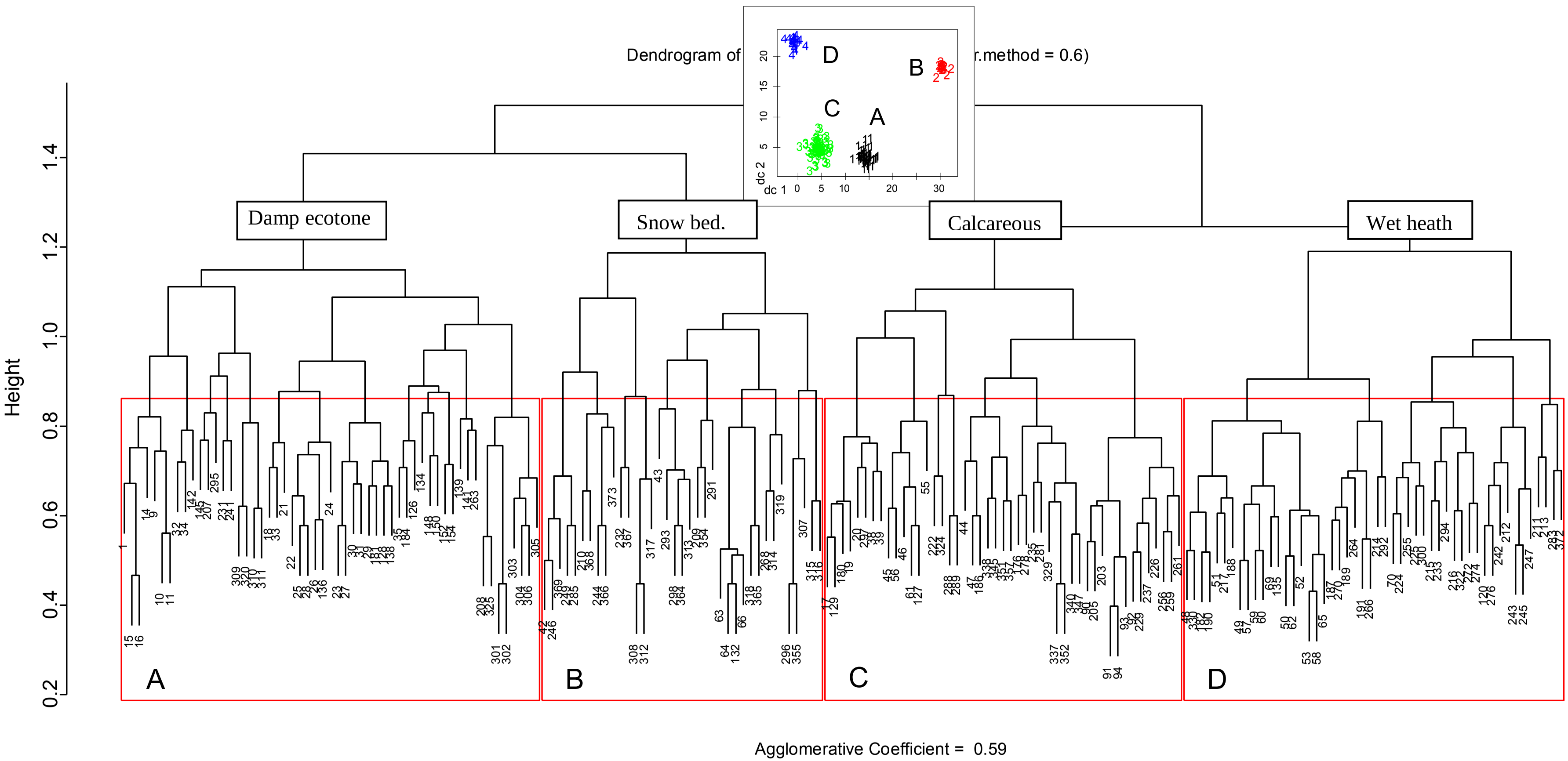


Fig. 3.6 Dendrogram showing major lakes typologies based on their similarities in riparian vegetation composition (shared species). This is a pair-group average method (PGMA) hierarchical cluster analysis (flexible linkage, parameter=0.6) on Sørensen similarity matrix of riparian vegetation data (presence-absence). A plot of cluster solutions in discriminating space (inset) shows an effective clustering. Ecotope characteristics are approximated from Indicator Species Analysis. Number of cases/variables used by the analysis =189 lakes /166 plant species. Plot numbers identify lakes (detailed in Chapter #2).

(*Polygala alpina*). This heterogeneous association seems therefore to be resulted from a combination of different habitat types along the shore of these lakes. It also appears to reflect an uneven landscape composition in the catchment of certain high altitude lakes.

The second riparian association, representing lake type B (Fig. 3.6), comprises a high proportion of species with affinity to snow bed and a short growing season, like *Saxifraga stellaris, Veronica alpina, Sibbaldia procumbens*, the herbaceous shrub *Salix herbacea*, and the fern *Cryptogramma crispa* (Table 3.4). Most of these species are generally silicophilous, tolerating poor substrate, of different textures, i.e. scree/rocky, grassland and damp soil. With the same group also clusters the endemic grass *Festuca eskia*.

Riparian species associated with lake type D (Fig. 3.6) comprises wet heath species of Ericaceae shrubs (*Vaccinium uliginosum, Vaccinium myrtillus, Calluna vulgaris*) accompanied by snow bed species, e.g. *Primula integrifolia, Soldanella alpina* and *Bartsia alpina* (Table 3.4). Associated are also the sedge *Trichophorum cespitosum* and *Luzula alpinopilosa* rush together with other smaller plants, the majority with affinity with moist substratum (e.g. *Pinguicula vulgaris* and *Homogyne alpine*). In small number are species of drier habitat, e.g. *Gentiana lutea, Hutchinsia alpina* and *Phyteuma orbiculare*, and the nitrogen fixing *Trifolium alpinum*. This community grows well on both, poor siliceous or calcareous substrata.

There is also a slight possibility for a number of species to associate with lake cluster C (Fig. 3.6) but their membership involves a relatively high degree of chance ($p<0.25$; Table 3.4). These are species of moist to dry calcareous banks, which come in association with *Rumex crispus*. Given its relatively weak probability of group membership it is safe to assume that this association is not very common. The rest of the species had no association to any of the groups, which implies they largely follow continuous/even patterns of distribution (Báez et al., 2005).

While the identified riparian communities incorporate a number of species from major alpine terrestrial groups (Gruber, 1992; Grey-Wilson and Blamey, 1995; Minot et. al, 2007), it is clear from our results that most of the co-occurring species tolerate the wet condition of waterbody banks, which indicates a tight relationship with the riparian zone. However, the relatively broad habitat range the riparian associations spanned over means they are eurytopic communities, i.e. complex communities with large niche breadth, present in a variety of habitats. This condition presumably allowed them establishing in the riparian zones of these high altitude lakes. The complex habitat/ecotope distribution may also explain the relatively low (but significant) indicator values (<0.5) obtained for the plant associations (Table 3.4). However, the ecological interest of these communities resides, in that they are indicators of peculiar ecological conditions present in the riparian zone, although it seems not all species may always be present (Dufrene and Legendre, 1997).

While the great majority of sampled waterbodies can be considered as insular ecotopes which harbour certain plant communities, their vegetation composition may also change along input/output streams. Further study is therefore needed to fully understand how species communities from lakes' riparian zones change along stream ecotones at high altitudes, whether they are sources of propagule dispersal/colonisation, and how this contributed to the dynamics of these communities over time.

Table 3.4: Fidelity of riparian plant species to the lake typologies resulting from cluster analysis, as given by Indicator Species Analysis. A species was classified into a group for which its indicator value of group membership was highest and significant, i.e. strong preference. As can be noticed, cluster C has been computed with a relatively low significance. These species associations have the distribution pattern of the cluster they represent, while species that were not associated to any of the clusters are thought to have relatively continuum distributions

Cluster A, p<0.05		Cluster D, p<0.05	
Species	Indicator value	Species	Indicator value
Potentilla erecta	0.47	*Pinguicula vulgaris*	0.42
Caltha palustris	0.42	*Gentiana acaulis*	0.40
Parnassia palustris	0.36	*Rhododendron ferrugineum*	0.35
Thymus serpyllum	0.25	*Primula integrifolia*	0.30
Trifolium repens	0.23	*Vaccinium uliginosum*	0.30
Hieracium pilosella	0.20	*Trichophorum cespitosum*	0.29
Campanula rotundifolia	0.19	*Calluna vulgaris*	0.26
Sphagnum sp.	0.19	*Silene acaulis*	0.26
Bellis perennis	0.18	*Trifolium alpinum*	0.25
Alchemilla vulgaris s.l.	0.17	*Homogyne alpina*	0.25
Sparganium angustifolium	0.15	*Soldanella alpina*	0.22
Carex echinata	0.14	*Geum montanum*	0.21
Juncus filiformis	0.13	*Vaccinium myrtillus*	0.21
Anthoxanthum odoratum	0.13	*Hutchinsia alpina*	0.20
Carex nigra	0.13	*Armeria maritima alpina*	0.19
Cardamine raphanifolia	0.11	*Phyteuma orbiculare*	0.18
Merendera pyrenaica	0.11	*Bartsia alpina*	0.17
Prunella vulgaris	0.11	*Viola palustris*	0.17
Juncus articulatus	0.11	*Geranium cinereum*	0.14
Leontodon autumnalis	0.10	*Luzula alpinopilosa*	0.12
Ranunculus aquatilis	0.10	*Lotus alpinus*	0.11
Selaginella selaginoides	0.09	*Pedicularis mixta etc*	0.10
Polygala alpina	0.09	*Thalictrum alpinum*	0.10
Carex flava	0.09	*Saxifraga aizoides*	0.09
Polygonum viviparum	0.08	*Gentiana lutea*	0.06
Carum carvi	0.07		
Galium verum	0.07		
Luzula desvauxii	0.07		
Ranunculus reptans	0.07		
Sanguisorba officinalis	0.07		
Deschampsia cespitosa	0.06		
Chara foetida	0.05		

Cluster B, p<0.05		Cluster C, p<0.25	
Species	Indicator value	Species	Indicator value
Gnaphalium supinum	0.51	*Rumex crispus*	0.04
Cryptogramma crispa	0.47	*Carex flacca*	0.03
Leucanthemopsis alpina	0.34	*Cochlearia officinalis*	0.03
Epilobium alsinifolium etc	0.28	*Leontopodium alpinum*	0.03
Sibbaldia procumbens	0.25	*Oxytropis campestris*	0.03
Kobresia myosuroides	0.23	*Veronica officinalis*	0.03
Veronica alpina	0.22	*Callitriche palustris*	0.02
Jasione montana	0.21		
Galium pyrenaicum	0.19		
Poa annua etc	0.17		
Doronicum austriacum	0.16		
Saxifraga stellaris	0.14		
Festuca eskia	0.12		
Meum athamanticum	0.10		
Salix herbacea	0.10		

166 riparian plant species from 189 water bodies were used by the analysis.

4.4 Settlement of riparian communities along geolocation and ecotope gradients

Earlier Indicator species analysis showed the main riparian communities with common patterns of distribution. The results of this analysis also suggested that associated species share common ecotope requirements. To better understand the distribution of these groups along ecotope factors a box plot distribution of riparian community/lake associations along geoposition and composite catchment gradients was carried out.

Overall, the riparian phyto-communities appeared to react considerably (i.e. are sensitive) to ecotope gradients (Fig. 3.7). Vertical altitude gradient, with its main effect on temperature, appears to have an

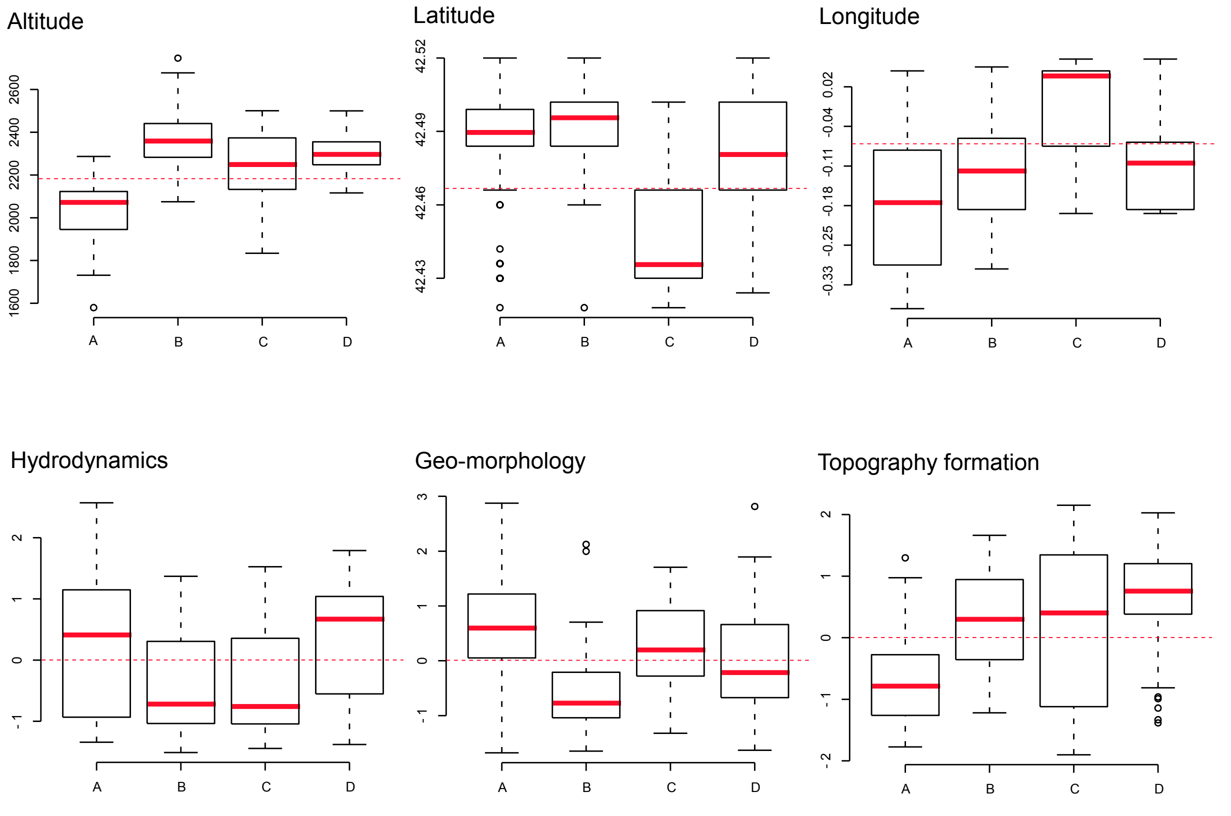


Fig. 3.7 Boxplots showing changes in the distribution of 4 indicator plant communities along geolocation, i.e. altitude (m a.s.l.), latitude (degrees N) and longitude (degrees, + for E), and composite catchment (hydrodynamics, geo-morphology and topography formation; Table 3.1) gradients. Hydrodynamics (i.e. lake and tributary size, and nature of input/output) range roughly from lower (-) values for small waterbodies fed largely by precipitation to higher values (+) for large lakes fed by stream water; geo-morphology (i.e. geology, slope, % meadow covered slopes/shore, fractal development and aquatic vegetation) ranges from granite/schist dominating the substratum for its – values, to limestone/conglomerates for the + ones; while topography formation (i.e. catchment type, snow deposits and lakes connectivity) ranges from valley floor/plains for low values to valley heads for the high, + ones (detailed in Chapter 2). The solid horizontal bar in boxplots represents the median values, and the box extends from the first quartile (25%) to the third quartile (75%); the whiskers extend to the 5th and 95th percentiles, with outliers shown as open dots. Horizontal dashed line helps in visualising major differences.

important influence on community distribution with group A showing preference for relatively lower altitudes (median ~2100 m a.s.l.), group B for highest ones (median ~2400 m a.s.l.) while cluster D was least variable with respect to this factor (Fig. 3.7). This is consistent with our previous results from indicator species analysis and shows that riparian community A, identified as preferring damp ecotones, is to be found at relatively low altitudes while communities with snow bed species, i.e. B and D would prefer colder environments of higher altitude.

Apparently horizontal latitude and longitude gradients also appear to have important effects on cluster distribution with group C distributed at lower latitudes and higher longitudes than the other groups (Fig. 3.7). This means a southern and eastern distribution in the study area.

Of the composite catchment factors, hydrodynamics was least influential on vegetation communities' variability. However, a measurement of groups' central tendencies (i.e. median; Fig. 3.7) suggests that riparian groups B and C seem to prefer relatively small waterbodies with low hydrodynamics, i.e. fed mainly by precipitation, while A and D tend to establish around larger lakes with relatively more input/output dischareg, i.e. fed by stream water.

Riparian phyto – communities' preference for certain geo-morphological substrata appears to be significant. Group B shows relatively good preference for granite materials, steep slope, poor bank vegetation coverage and low shore fractal development (Table 3.1 and Fig. 3.7). Conversely, group A spans over a wide bedrock geology, but with a relatively high content of calcareous and schist materials, weak slopes, better vegetation coverage and more developed shore line. Groups C and D tolerate a relatively wide bedrock geo-morphology, however, group C has a slight preference for calcareous bedrock while group D has one for a relatively more acidic bedrock (Fig. 3.7).

Topography formation also seems to induce a visually significant source of variability in riparian plant communities. Thus, clusters A, B and D are the most divergent, with the former (i.e. the community of damp substratum) establishing mainly on valley floors/slopes, with low summer snow coverage while the latter ones (i.e. snow bed, A; and wet heath, B associated species) visually characterise the waterbodies at the head of glacial valley, with relatively consistent presence of snow coverage throughout the summer and a high level of connectivity between waterbodies. There is also some evidence to suggest that group C might prefer valley heads, however its species can be found in a wide range of topographical features.

To summarise, indicator species and boxplot distribution analyses suggested that high altitude riparian communities in the central Pyrenees are shaped by a number of common factors. Species community A would prefer lakes of damp riparian areas on the floor/slope of glacial valleys, at comparatively low altitudes, with relatively high water turnover and complex bedrock geology (sedimentary/ metasedimentary substratum). Riparian community B, with a high proportion of snow bed species, would in turn prefer higher altitude waterbodies, relatively low water turnover (i.e. mainly fed by precipitation), high topography (e.g. head of glacial valleys and mountain passes); with a substratum dominated by granitic materials and their weathering byproducts. Less resilient riparian association C would span a relatively wide altitude range. They would establish in the area of small lakes/ponds of relatively low input/output but on a wide range of topographical formations, e.g. from valley floors to valley heads. Riparian community D had the narrowest altitudinal gradient. It distributed over a relatively wide range of lake hydrological conditions but showed a slight preference for larger lakes with high water turnover, most of them at catchments heads.

Although riparian vegetation associations tended to cluster at certain ecotope gradient levels, it is clear from our results that the factors controlling the establishment of these associations are very complex in the mountain orography and that none of them are the sole determinants of communities' formation. Rather, a complex pool of microclimatic/ orographic environments is responsible for the observed relationships of species clusters.

Conclusions

Results of FSO and MFSO show that local scale (sediment and water chemistry), catchment scale (composite ladscape) and geolocation ecotope gradients exert significant influences on riparian vegetation composition at high altitude lakes.

As the results suggest, glaciological formations left behind by the latest Holocene glaciations, with their main effects on snow coverage and lake connectivity, appear to be important in determining vegetation composition of alpine riparian ecotones. Added to this, hydrodynamics, with nested contribution from input size, waterbody size and nature of input/output also contributed significantly to riparian vegetation composition variability, an argument in the favour of an Equilibrium Theory of Island Biogeography applied to the riparian zone of altitude lakes. This should predict an influence of lake size on riparian vegetation composition. The third catchment scale composite factor, i.e. geo-morphology, with nested effects from geology, sloping, vegetation coverage and shore fractal development also seems to contribute significantly to the prediction of riparian vegetation variability. This is likely a reflection of the two major geological units of the central Pyrenees, i.e. igneous cores (granite) flanked by metasedimentary and sedimentary materials, which may have acted through the creation of niche gradients.

At local scale, variations in sediment Mg and Pb and water Mn and Fe contents appear to relate significantly with the composition of riparian vegetation. This may be a secondary effect from bedrock geology together with fluctuations in moisture/flooding of riparian ecotones, common to alpine areas. To which extent these elements are related/released from different geological formations or under different environment conditions remain however remain open questions.

(M)FSO results on riparian vegetation variability along geolocation gradients showed altitude and latitude as the major large-scale predictors of species composition. The influence of altitude is not surprising as it is a classical reflection of the climate/temperature gradient. However, the predicted latitudinal influence can be the reflection of a transitional N-S gradient between the four large biogeographic macroregions with influence in this area, i.e. Atlantic and Continental from the North, Mediterranean from South, and the local alpine gradient.

Flexible hierarchical PGMA clustering of site similarities based on shared species in combination with indicator species analysis and box plot distributions allowed establishing clearly defined and second-order nested site groups, while identifying indicator species in the form of riparian vegetation communities and their complex ecotope requirements. These communities have a relatively large amplitude breadth (eurytopic), which is determined by the surrounding ecotope, and show a certain degree of variability in their composition. The particular riparian ecotopes, with complex banks structure in terms of geology, roughness/topography and temporary flooding, allowed the establishment of species from both wet/damp and dry habitats. These eurytopic communities are responsible for the similarities between lake ecotones and contributed to the specificity of site/lake typologies.

The results show that the riparian phyto-communities also bear the influence of major terrestrial alpine groups (e.g. snow bed community, scree community, heath community). Yet they have a composition of species closely tied to the aquatic environment. It remains to be tested how the composition of these waterbody-related associations change along stream courses downstream/upstream and how these influence the vegetation colonisation and structuring.

All in all, the results illustrate the potential of riparian vegetation to reflect the complexity of riparian ecotopes. They also show the capacity of physical environment, i.e. ecotope, as a combination of complex driving factors (geographical, landscape and local) to shape the riparian plants composition and discriminate nuclei of plant communities at high altitude lakes. This has implications on appropriately recognising the sensitivity of altitude waterbody riparian zones to environmental variability, entailing further study on their processes, and helping political decisions for their conservation.

In addition, the approach used herein can be used as a decision support system for the interpretation and classification of relatively large data sets and for reliably ascertaining biodiversity patterns at a high number of waterbodies.

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APPENDIX

Plant species identified in the riparian zone of 189 central Pyrenean water-bodies

Aconitum spp.	*Cryptogramma crispa*	*Luzula desvauxii*	*Rhinanthus minor*
Adenostyles alliariae	*Deschampsia cespitosa*	*Luzula luzuloides*	*Rhododendron ferrugineum*
Agrostis capillaris	*Dethawia tenuifolia*	*Luzula nutans*	*Rumex alpinus*
Alchemilla alpina	*Doronicum austriacum*	*Luzula sudetica*	*Rumex crispus*
Alchemilla vulgaris	*Draba aizoides*	*Lychnis alpina*	*Rumex scutatus*
Allium schoenoprasum	*Empetrum nigrum*	*Menyanthes trifoliata*	*Sagina procumbens*
Androsace carnea	*Epilobium alsinifolium etc*	*Merendera pyrenaica*	*Salix herbacea*
Antennaria dioica	*Equisetum variegatum*	*Meum athamanticum*	*Salix reticulata*
Anthoxanthum odoratum	*Erica sp.*	*Minuartia sedoides*	*Sanguisorba officinalis*
Anthyllis vulneraria	*Eriophorum latifolium*	*Molinia caerulea*	*Saxifraga aizoides*
Armeria alliacea	*Euphrasia sp.*	*Myosotis alpina*	*Saxifraga oppositifolia*
Armeria maritima alpina	*Festuca eskia*	*Myosotis scorpioides*	*Saxifraga stellaris*
Arnica montana	*Fontinalis antipyretica*	*Nardus stricta*	*Sedum album*
Bartsia alpina	*Galium pyrenaicum*	*Nigritella nigra*	*Selaginella selaginoides*
Bellis perennis	*Galium verum*	*Oxyria digyna*	*Sempervivum arachnoideum*
Betula pendula	*Gentiana acaulis*	*Oxytropis campestris*	*Sempervivum montanum*
Botrychium lunaria	*Gentiana lutea*	*Oxytropis pyrenaica*	*Sesamoides pygmaea*
Callitriche palustris	*Gentiana verna*	*Parnassia palustris*	*Sibbaldia procumbens*
Calluna vulgaris	*Geranium cinereum*	*Pedicularis mixta*	*Silene acaulis*
Caltha palustris	*Geranium sylvaticum*	*Phleum alpinum*	*Soldanella alpina*
Campanula rotundifolia	*Geum montanum*	*Phyteuma orbiculare*	*Sorbus aucuparia*
Cardamine raphanifolia	*Globularia repens*	*Pinguicula grandiflora*	*Sparganium angustifolium*
Carduus carlinoides	*Glyceria fluitans*	*Pinguicula vulgaris*	*Sphagnum sp.*
Carex atrata	*Gnaphalium supinum*	*Plantago alpina*	*Succisa pratensis*
Carex brachystachys	*Gnaphalium sylvaticum*	*Plantago lanceolata*	*Swertia perennis*
Carex caryophyllea	*Hieracium pilosella*	*Plantago media*	*Taraxacum sp.*
Carex curvula	*Homogyne alpina*	*Poa annua*	*Thalictrum alpinum*
Carex demissa	*Huperzia selago*	*Polygala alpina*	*Thesium alpinum*
Carex echinata	*Hutchinsia alpina*	*Polygonum viviparum*	*Thymus serpyllum*
Carex flacca	*Hypericum montanum*	*Potentilla anserina*	*Trichophorum cespitosum*
Carex flava	*Jasione montana*	*Potentilla erecta*	*Trifolium alpinum*
Carex frigida	*Juncus articulatus*	*Primula farinosa*	*Trifolium repens*
Carex hallerana	*Juncus filiformis*	*Primula integrifolia*	*Vaccinium myrtillus*
Carex macrostylon	*Juncus inflexus*	*Primula viscosa*	*Vaccinium uliginosum*
Carex nigra	*Juniperus communis ssp. nana*	*Prunella vulgaris*	*Veratrum album*
Carex pulicaris	*Kobresia myosuroides*	*Pulsatilla sp.*	*Veronica alpina*
Carex riparia	*Kobresia simpliciuscula*	*Ranunculus alpestris*	*Veronica beccabunga*
Carex rostrata	*Leontodon autumnalis*	*Ranunculus aquatilis*	*Veronica fruticans*
Carex sempervirens	*Leontopodium alpinum*	*Ranunculus pyrenaeus*	*Veronica nummularia*
Carum carvi	*Leucanthemopsis alpina*	*Ranunculus repens*	*Veronica officinalis*
Chara foetida	*Linaria alpina*	*Ranunculus reptans*	*Viola biflora*
Chenopodium bonus-henricus	*Lotus alpinus*	*Rhamnus pumilus*	*Viola palustris*
Cochlearia officinalis	*Luzula alpinopilosa*		

N(number of species)=168.

4

Ecological sensitivity of littoral organisms to local and large scale variates at high altitude lakes

Abstract

Catchment and particularly riparian surfaces are dominant input resources to altitude oligotrophic lakes; consequently the nature and properties of these surfaces, together with ecological interrelationships, may have profound effects on the littoral ecosystem. The degree of response major littoral zoobenthic taxa have to ecotope and ecological factors was assessed in a case area encompassing 114 high altitude lakes and ponds in the central Pyrenees. At each location benthic invertebrate composition was recorded together with a number of variables; i.e. geolocation (altitude, latitude and longitude), landscape (composite hydrodynamics, geo-morphology and topography), riparian vegetation structure, presence of vertebrate predators (trout and frogs), water pH and conductivity.

A twofold fuzzy set ordination (FSO) - multidimensional FSO (MFSO) applied to benthic biota composition and environmental variates revealed that longitude, altitude and latitude gradients were able to significantly affect zoobenthos composition. Littoral organisms also responded considerably to the composite variables topography (through its effects on catchment type, shore and catchment snow coverage, connectivity with other lakes) and hydrodynamics (waterbody size, type and volume of input/output). These variables may act through habitat creation, water flow/nutrient input and connectivity; and together allow the persistence of littoral groups with physiological mechanisms capable of dealing with different environments in these lakes.

Riparian vegetation composition appeared to interact with littoral invertebrate community structure, richness and morphotype diversity. This highlights the sensitivity of the littoral ecosystem of high elevation lakes to vegetation changes in their riparian zone. Neither predation, nor water pH or conductivity appeared to significantly influence the composition of major benthic organisms. Flexible clustering and indicator species analyses identified three eurytopic littoral associations, of generally ubiquitous distribution, together with the lakes for which they had significant affinity.

The results have implications for understanding the role of altitude lakes as important sentinels/sensors of environmental change in the catchment and beyond.

Keywords: macroinvertebrates, altitude lakes, ecotope, landscape factors, terrestrial vegetation, riparian zone, predation, Pyrenees

1. Introduction

Recently, research efforts have been widely intensified regarding lake littoral dynamics, and a true whole-lake perspective is re-emerging in lake ecology (ASLO, 2010). Regardless of waterbody size, its littoral zone generally harbours a rich diversity of life forms, and littoral production is critically important for lake food webs contributing substantially to the whole lake ecosystem energy budget (Vander-Zanden et al., 2006). The littoral zone is also in a tight relationship with the riparian ecotone, i.e. the interface between lakes and the terrestrial landscape, leading to important cross-ecosystem fluxes of nutrients and energy (Paetzold and Tockner, 2006). At high altitude lakes. the littoral zone together with the riparian zone are commonly the focal point of a rich diversity of biota, far exceeding that of the surrounding landscape.

Generally the topography of a catchment, its hydrography, the bedrock geology and the climate control the intensity of erosional processes and the transport of nutrients into a lake; together they influence its sediment and water chemistry as well as its biota structure (Vollenweider, 1968). In resource-poor alpine systems, the riparian zone is a major energy resource (both, autochthonous and allochthonous) for aquatic food webs as well as for emerging stages of many aquatic taxa such as most benthic insects (Gregory et al., 1991; Kopacek et al., 2000; Jonsson and Wardle, 2009). These groups are highly sensitive to environmental conditions (Bandyopadhyay et al., 1997), and are key to understanding both riparian and aquatic ecosystems. Without doubt benthic biota living in high altitude lakes have to defeat harsh conditions such as low food availability, a short growing season, and strong seasonal temperature, radiation, and water level fluctuations (Bretschko, 1995); most of them finding here their distributional boundaries. For example, a major factor shaping population dynamics of aquatic insects in alpine waterbodies is winter mortality (Oswood et al., 1991). The availability of food together with the variability in biotic sensitivity to the external factors described above can potentially result into typical fauna assemblages. These communities are expected to be relatively simple but highly adapted to the particular ecotopes they inhabit. Despite their ecological importance and sensitivity to environmental variation, the littoral zones/processes in the alpine biome remain one of the least studied areas of lake ecology.

Research shows that in alpine lakes variability in local conditions is likely to determine species abundance due to differences in proximal environment (Kernan et al., 2009). For instance, littoral invertebrates have been shown to react to food availability and duration of ice/snow cover during winter (Bretschko, 1995). They can respond to nitrate and ammonia levels, shore coverage type (Füreder et al., 2006), lake morphology and fish presence (Kernan et al., 2009). For major groups, e.g. family level, however, it is expected that geographical and landscape/catchment-scale barriers are more likely to result in a biogeographical variability of benthic ecosystem composition. Conversely, quantitative information on large-scale ecotope-biota patterns in altitude ecosystems is generally poor, being mainly a consequence of overfocus on species as units of diversity (Gaston et al., 1995). A fundamental question therefore is to what extent riparian and large-scale variates interact with major biota communities in the littoral zone. Finding such information would help complete a holistic picture of catchment-littoral communities' interaction at oligotrophic altitude environments.

A survey of a large number of altitude waterbodies (lakes, ponds and pools) in the central Pyrenees was therefore undertaken to quantify the response of major littoral zoobenthos taxa to riparian ecosystem and ecotopic gradients; and to decompose this variability into potential communities that would reflect particular ecotope requirements. The chosen case area has the advantages of extending on a simple E-W gradient with narrow N-S extent, and being at the confluence of four major biogeographical regions of Europe, i.e. Atlantic, Continental, Mediterranean, and alpine altitudinal gradient.

2. Methodology

2.1 Case area

A total number of 114 lakes were surveyed in July 2001 in the axial Pyrenees, between 42.6672° - 42.9686° N and -0.7425°-0.2553° E (Fig. 4.1). The area is within the boundaries of Pyrénées National Park. Catchment geology varies between the various valleys and it is dominated by two large geologic units: in the central area and at the extreme east, lake catchments lie on acidic bedrock (granite) while in between, granitic batholiths are surrounded by metasedimentary and sedimentary materials such as slates, limestone and sandstone (Chapter 2). However the admixture of these materials across the range makes the geology of the area rather complex.

Most of the study lakes are above the tree line (alpine domain), their water is cool, and they are largely undisturbed by human activity. Pastoralism, leisure fishing and trekking are however among the very few activities allowed in the park. Some of the waterbodies were transformed into reservoirs and are being used as freshwater reserves and for hydropower generation. The great majority of study lakes/ponds are oligotrophic. Lake close catchment area has generally low vegetation coverage (<20%), but this varies according to topography and location. Loose rocks dominate in most lake shores, though of much greater abundance on the steeply slopes of granitic catchments.

The hydrological network has a natural origin here, being a remnant of the last glaciers' retreat more than 5000 years ago. The major water input in most lakes is direct precipitation and permanent stream input; glaciers and springs were present only in few cases. Surface connectivity between lakes varies for the lakes investigated. Slope/bank snow coverage at the time of sampling was generally low, but had generally higher values

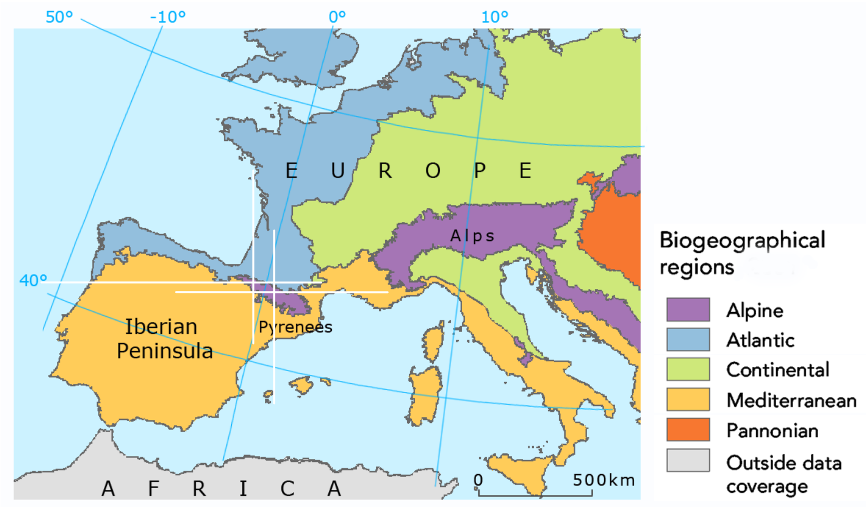


Fig. 4.1 Study area in the central Pyrenees (delimited in white) together with the biogeorgaphical regions of Europe (after EEA, 2001).

at the head of catchments. Water pH was generally neutral (mean 7.59) but varied between 5.2 - 8.8. Conductivity was also variable, ranging between 2 - 267 µS cm^{-1} (mean= 40µS cm^{-1}). Other landscape information of these lakes is provided in Chapter 2.

2.2 Sampling strategy

An exhaustive assessment was conducted for each waterbody in July 2001, in the axial region of Pyrenees National Park of France. It included littoral macrozoobenthos, water pH and conductivity, the presence of vertebrate predators, i.e. frogs and trout, ecotope properties of near catchment, riparian vegetation assemblage and geolocation.

Macroinvertebrate sampling deliberately targeted the littoral zone. This area generally supports larger and more diverse populations of benthic invertebrates than the sublittoral and profundal zones. Likewise, the littoral zone is more likely to relate to the nearby riparian factors. Semiquantitative 3 minutes kick-samples were collected in each lake using a standard pond net (Frost et al., 1971). Samples were collected at short distances while moving around the lake to cover different micro-habitats in proportion to their occurrence. All substratum types (rocks, cobbles, coarse and fine sand, epilithic moss, etc) were sampled down to 60 cm water depth. Subsequently all samples were preserved in 96% alcohol for a comprehensive laboratory sorting and analysis. Benthic organisms were identified down to the lowest possible taxonomic level (Tachet et al., 2002) and counted using a binocular and ⁄or a microscope. This taxonomic level will be regarded as morphotypes henceforth. For most statistical tests a family level resolution was used (see Appendix).

Additionally, water pH and conductivity were recorded at the surface and the bottom (±5m off the littoral) at each site with portable pH/conductivity probes. The water was collected with a standard bottom water sampler. The procedure followed a clean protocol. Presence of frogs (*Rana temporaria*) was visually inspected at each site. Trout presence data at each location was provided from the stocking records by the Pyrénés National Park.

Moreover, at each location a number of landscape factors were visually approximated according to dominant units. They were: nature of water input and output, tributary discharge, waterbody size, % vegetation covering slopes and shore, slope, geology, presence of aquatic vegetation, shore development (fractal level), presence of snow deposits on the shore and in the catchment (%), catchment type and surface connectivity with other waterbodies. Their detailed description is provided in Chapter 2.

Riparian vegetation composition was recorded down to species level in the field at each site using identification keys. A detail description of the procedure is detailed in Chapter 3. Lakes geographical positions were recorded with a portable GPS device.

2.3 Data analyses

Statistical data analyses included principal component analysis (PCA), fuzzy set ordination (FSO), multidimensional FSO (MFSO), cluster and indicator species analyses. For this, environmental factors were split into groups, i.e. geolocation, landscape/ecotope, predation, water general chemistry, and riparian vegetation. First, landscape variables were summarised as regression scores of principal components by PCA prior to being used as predictor composite factors for littoral zoobenthos response in further analysis (Table 4.1). For this an orthogonal Varimax rotation of the first two extracted PCs/axes helped maximise the variance captured by them. By default the principal components of PCA with this rotation are uncorrelated. Furthermore, because trout and frog variables were binary they were standardized by Hellinger transformation (Legendre and Gallagher, 2001) before using tem in FSO.

To analyse the relationship between littoral zoobenthos composition and environmental gradients we used fuzzy set ordination (FSO) followed by stepwise multidimensional FSO (MFSO; Roberts,

Table 4.1: Loadings of landscape variables characterising the central Pyrenees lakes on the three principal components of PCA. Highest correlation of a variable with any of the components is in bold. This allowed us to summarise PC1 as hydrodynamics, PC2 as geo-morphology and PC3 as topography formation composite factors

	Principal component		
	1	2	3
Tributary discharge	0.92		
Nature of tributary	0.90		
Nature of water output	0.87		
Lake size	0.52		
% grass covered slopes		0.72	
% grass covered shore		0.68	
Slope of lake perimeter		-0.67	
Geology		0.60	
Aquatic vegetation		0.58	
Fractal order		0.50	
Catchment snow deposits			0.86
Catchment type			0.79
Shore snow coverage			0.75
Connectivity with others			0.52
Total Eigenvalue (rotated)	3.07	2.69	2.46
% of variance explained	21.96	19.24	17.59
Cumulative %	21.96	41.20	**58.79**

Rotation method: Varimax with Kaiser normalization. Kaiser-Meyer-Olkin measure of sampling adequacy= 0.73. Bartlett's test of sphericity: approx. χ^2= 1456.9 (P<0.001).

2008). For these a distance (dissimilarity) matrix computed with Sørensen similarity index of invertebrate incidence data was first calculated. This gave a measure of similarity between sites based solely on biotic composition (Boyce, 2008). Additionally, two more variables thought to describe macrozoobenthos assemblages were considered for each lake, i.e. taxon (family) richness and sequential diversity comparison index (SCI; Mackie, 1998), where

$$SCI = \frac{no.of\ runs\ x\ no.of\ taxa}{total\, no.of\ individuals}$$

with *run* being the morphtype and *taxon*, the family

Fuzzy set ordination (FSO) concept (Roberts, 1986) is a generalised alternative to traditional ordination approaches (e.g. canonical correspondence analysis- CCA) in which cases are assigned gradual membership (fuzzy) values ranging from 0 to 1 (Roberts, 2008), instead of 0 or 1 (i.e. in or out of a given set) like in classical statistics. FSO is also expected to perform better than other approaches on more complex data sets, and it is insensitive to noise in environmental factors and rare species (Roberts, 2009).

Variables were first screened in turn in FSO and those with highest correlation with the macrozoobenthos distance matrix (at >95% efficiency) were retained for further MFSO. Technically in MFSO, first a FSO is performed on the variable that accounts for most of the variation. Then, the residuals of the analysis are used with the next most important variable, and the process is repeated until no more variables are left. Because only the fractions of variable membership that are uncorrelated are used by MFSO, each variable selected by the model can be confidently regarded as an independent axis/process. Thus, it gives a high interpretability to the model (Roberts, 2008). Visually, the effect extent of each variable can be assessed by the increment in the correlation attributable to that variable.

A number of 1000 random permutations was subsequently performed to test the significance of each variable/axis in FSO/MFSO. Where the distance matrix was disconnected (sites/groups of sites with no shared species) or the dissimilarity was too high, a step-across function was applied to improve the MFSO. This finds the shortest paths to connect groups and removes rare observations/ groups of observations (Oksanen, 2008).

Furthermore, to assess the relationship between riparian vegetation composition and major littoral invertebrate groups a Mantel test was performed on their distance matrixes. These matrixes were calculated with Baroni-Urbani & Buser similarity index. This index was preferred as it maximises the Pearson product-moment correlation coefficient between the two matrixes. A high significance of the correlation procedure was drawn after 9999 random permutations of Monte Carlo test.

Finally, the littoral macrozobenthos data (family incidence) were analysed for co-occurrence (associations) and their ecotope preferences. These communities were constructed by clustering the sites on the basis of shared species and applying indicator species analysis for each resulting cluster. First a flexible linkage Pair-Group Method using the Arithmetic Averages (PGMA; method parameter = 0.85) cluster analysis was run on a distance matrix computed from Sørensen similarity matrix. Plotting cluster solutions in discriminating space helped evaluate the reliability of cluster solution.

Secondly, indicator species analysis was run at the nodes of the major clusters to identify the invertebrate families that are likely to represent resulting lake clusters. FSO and LABDSV packages were used for FSO and MFSO (Roberts, 2007a; Roberts, 2007b); ADE4, CLUSTER and FPC packages for Mantel test, clustering (Thioulouse et al., 1997; Kaufman and Rousseeuw, 1990; Hennig, 2005), and LabDSV for indicator species analysis (Dufrene and Legendre, 1997), all for the R statistical language and environment (R Development Core Team, 2005).

3. Results and discussion

3.1 Response of littoral organisms to wide scale and catchment scale factors

Response to geoposition gradients

Species composition of different biomes can vary along large horizontal and vertical gradients such as latitude, longitude and altitude, and they can potentially change over time in response to environmental changes (Colwell et al., 2008). To understand how these geographical gradients interact with major littoral invertebrate community structure, fuzzy set ordination (FSO) and multidimensional FSO (MFSO) of family composition (distance matrix) against altitude, latitude and longitude were carried out. Figure 4.2 presents the correlations achieved by the unidimensional solutions of FSO together with their likelihood. The figure shows that independently, the three large scale gradients, i.e. altitude, latitude and longitude, were able to reliably predict the variability in gross littoral biota. The cumulative effect of these variables on invertebrate composition is best illustrated by MFSO (Fig. 4.3). It shows that collectively, longitude, altitude and latitude, in this order of variance explained, exert a significant influence on the composition of major littoral communities in altitude lakes. Altitude influence on zoobenthos communities, especially in stream systems, is well exemplified in the literature, and it is known to affect the functional ecology of these ecosystems, with shredders generally being more abundant in upstream sites while downstream they are gradually replaced by collectors (Vannote et al., 1980; Baumgartner and Waringer, 1997). The proportion of eucrenal species, typical to cold waters, is also reported to decrease downstream (Baumgartner and Waringer, 1997). Our results therefore suggest that altitude lakes are under significant gross taxa replacement along altitudinal gradient. This is likely due to biota physiological limitations and being influenced by the degree of connectivity between waterbodies.

The findings of littoral invertebrate variability along planimetric gradients (latitude and longitude) are consistent with previous studies conducted over extended regions (Johnson, 2000). However the short latitudinal gradient our study lakes span over raises the question of why this should be observed over such a narrow area. A plausible explanation is that the Pyrenees, an E-W geographical barrier that separates the Iberian Peninsula from continental Europe, marks the ecotonal transition between three major biogeographic regions, i.e. Atlantic and Continental remnants from the N, Mediterranean from the S, plus the Alpine domain. The littoral communities' structure thus appears to be sensitive enough to pick up transitional differences between these regions. This is also consistent with previous results which found a sensitive response from riparian vegetation composition to these geographic gradients in the area (Chapter 3).

Response to external landscape characteristics

A principal component analysis (PCA) helped first summarising the assessed landscape variables into a limited number of factors/composite variables (PCs), before using them as predictors of littoral zoobenthos composition in M(FSO) (Table 4.1). They were interpreted as hydrodynamics (summarising input size, input and output nature, and lake size; PC1), geo-morphology (i.e. % vegetated shores and slopes, shore slope, geology, aquatic vegetation and shore development; PC2) and topography formation (catchment type, % shore and catchment snow coverage, connectivity with other lakes; PC3). A detailed description of these ecotope factors is given in Chapter 2. The response of littoral organisms to composite catchment factors is illustrated in Fig. 4.2 and 4.3. Both univariate and multivariate solutions of FSO show that topography and hydrodynamics, in this order, are able to predict the variability of major littoral biota communities with 99% degree of significance. Topography exerts its influence mainly through its structural variables: catchment type, shore and catchment snow coverage and connectivity with other lakes. These variables may act through habitat creation and population connectivity, especially for benthic taxa which have a high degree of affinity to aquatic and riparian habitats. For instance in lakes/ponds at the head of glacial valleys, with snow presence most part of the year, the littoral zone would be able to hold taxa with special adaptation for cryal environment, low nutrient input, and short reproductive time. On the other hand, on valley floors lake littoral zones would sustain organisms with a longer emergence period, needing more nutrient and material inputs from the catchment which allow more diverse periphyton communities to develop and create more diverse microhabitats. Biota structure here would also likely be more vulnerable to larger periods of snow presence.

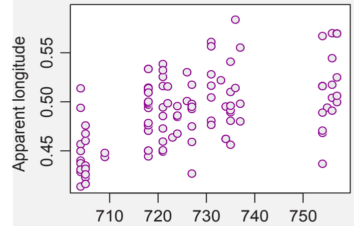
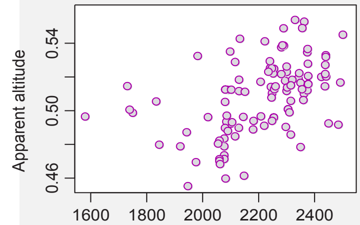
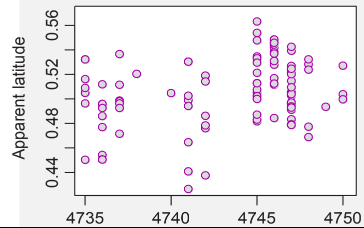
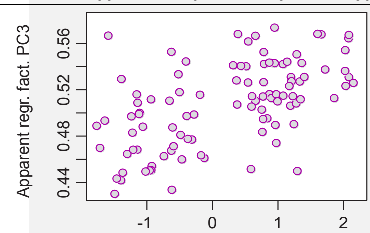
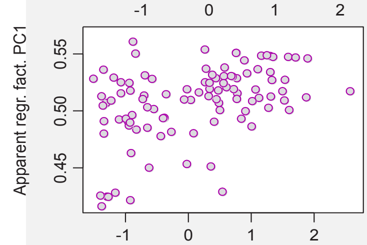
Factor	*r* (Pearson)	*P*	FSO plot (x-factor/y-apparent factor as predicted by biota)
[a]Longitude (UTM)	**0.547**	0.001	
[a]Altitude (m a.s.l.)	**0.470**	0.001	
[a]Latitude (UTM)	**0.336**	0.001	
[b]Topography formation (PCA regression factor scores)	**0.566**	0.001	
[b]Hydrodynamics (PCA regression factor scores)	**0.439**	0.001	
[b]Geo-morphology (PCA regression factor scores)	-0.061	0.627	
[c]Trout (presence/absence)	0.068	0.277	
[c]Frogs (presence/absence)	0.052	0.296	
[d]pH(bottom)	0.235	0.047	
[d]pH(surface)	0.074	0.278	
[d]Conductivity (surface)	0.003	0.419	
[d]Conductivity (bottom)	-0.009	0.457	

Fig. 4.2 One-dimensional fuzzy set ordination (FSO) showing the response of littoral invertebrate family structure to environmental variables in central Pyrenees lakes. Indices represent: (a) geolocation, (b) composite landscape (detailed in Table 4.1), (c) predators and (d) water physico-chemistry. Correlations are listed in descending order. Variables with highest influence in the ordination (correlations >0.3, in bold), also shown in plots, were retained for further MFSO analysis. *P* represents the probability. Predator variables were Hellinger transformed (Legendre & Gallagher, 2001) previously to being used as constrain variables in the analysis.

The response of littoral biota to lake hydrodynamics adds to the variability of topography formation and suggests it is a reflection of water source and lake area. For instance large stream-fed lakes, which generally maintain a continuous surface flow throughout the summer, would also maintain a generally low temperature and a heterogeneous structure of littoral habitats. Conversely, in relatively smaller waterbodies, which are dominated by catchment runoff and/or snow melt (therefore not sourced by continuous streams), the extent of littoral surface can vary seasonally and warm faster. These different ecotopes will therefore allow the persistence of littoral groups with special mechanisms adapted to deal with the particular conditions of each environment type. This is also supported by the results of recent studies conducted in altitude oligotrophic environments, which found clear differences in biotic assemblages in spring-fed streams under different flow regimes (Danehy and Bilby, 2009).

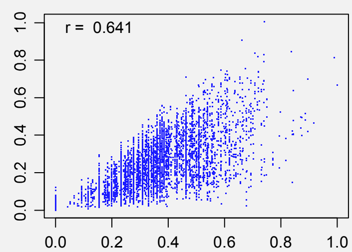
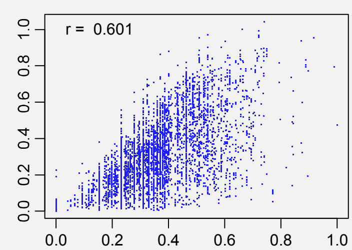
Axis (log)	Cumulative *r*	Increment *r*	*P*-value	*γ*	MFSO plot (x-matrix dissimilarity/y-ordination distance
Geoposition					
Longitude	**0.499**	0.499	0.044	1.000	
Altitude	**0.623**	0.124	0.167	0.360	
Latitude	**0.641**	0.018	0.764	0.063	
Landscape					
Topography formation	**0.491**	0.491	0.064	1.000	
Hydrodynamics	**0.601**	0.110	0.373	0.797	

Fig. 4.3 Multidimensional response of major littoral invertebrate composition to geoposition and composite landscape factors in multidimensional FSO (MFSO) with step-across improvement. Variables/axes are listed in the order of their input into the model. They are input into MFSOs as log transformed, in the order of their decreasing fuzzy correlation (Pearson) with the dissimilarity matrix. Number of permutations = 1000. *γ* (gamma) = a vector of the fraction of variance for an axis that is independent of all previous axes. Due to the high-dimensional variability of the dissimilarity matrix, the correlation probability for the one-dimensional solution sometimes has low significance but it is still valid.

Response of littoral organisms to riparian vegetation composition

The relationship between riparian vegetation and littoral organisms in altitude environments can go beyond the simple neighbourhood of these two environments. Riparian vegetation can, for instance, provide microhabitat resources for invertebrate protection from high solar radiance, be source of nutrients in the poor environment; moreover it is also a potential resource for the generally weak-flight capability emergent adults of many insects with aquatic phases (Gregory et al., 1991). We tested for the role riparian composition has on major littoral invertebrate groups by (M)FSO and Mantel tests. For this we used vegetation structure (Sorensen similarity) and invertebrates family structure, richness and morphotype diversity.

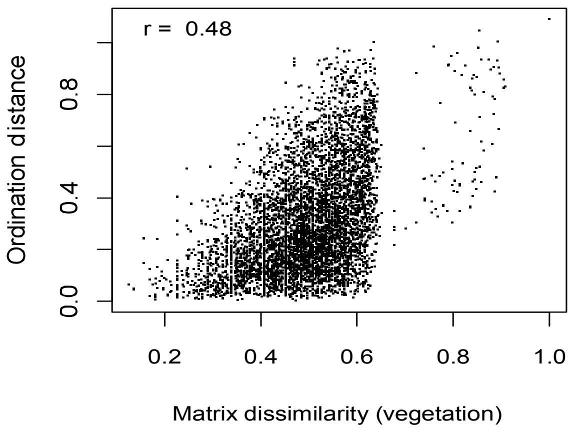


Fig. 4.4 Relationship between riparian vegetation structure and littoral invertebrate morphotype diversity and family richness in a bidimensional FSO. A step-across function improved the ordination. Number of permutations = 1000.

Though relatively weak we found a significant relationship between vegetation species structure and littoral invertebrate diversity and family richness (cumulative r=0.48, Fig. 4.4). Likewise, Mantel test revealed a relatively low but significant relationship between the structures of riparian vegetation and littoral invertebrate families (Monte Carlo r= 0.16, p<0.01). It appears therefore that riparian vegetation composition at species scale can influence the variability of major benthic invertebrate groups from altitude lakes; i.e. small differences in the occurrence of major invertebrate groups are generally seen between commonly associated plant species. Several studies have highlighted the importance of riparian vegetation to macroinvertebrate communities, especially in strong transitional gradients such as grassland-forest (e.g. vegetation coverage; Stone et al., 2005), but also vegetation type (Cummins et al., 1989; Angradi et al., 2001) perhaps due to the intricate influence of vegetation/ land cover on nutrient supply for functional feeding groups (Dudgeon, 2009). Our findings add to this view and show that in the typically sparsely vegetated altitude catchments, vegetation composition around the lakes has the potential to influence the diversity, richness and composition of major invertebrate groups dwelling in the littoral zone. This is particularly important as it shows a sensitive link between these two bordering ecosystems. Further testing, e.g. using gross vegetation composition can further help assess the degree of influence major plant groups have on benthic community.

The results, i.e. the relationship observed with large gradients and catchment characteristics illustrate the high capacity of altitude lakes to integrate a complex pool of ecotopic and biotic factors from the surrounding terrestrial system. These results can therefore help understanding the terrestrial-aquatic interactions and metabolism at high altitudes.

Response to vertebrate predation, water pH and conductivity

Presence of predators such as fish or frogs in an oligotrophic altitude waterbody can result in a top-down driven ecosystem (Eriksson et al., 1980), although this may depend on fish species and their level of influence on littoral groups. A close examination of the relationship between predator (trout and frogs) and invertebrate groups surprisingly found no clearly visible influence of the formers on gross macrozoobenthos composition (Fig. 4.2). This is evidence that vertebrate predators did not disrupt the broad composition of sampled littoral fauna. It might be possible that the food chain at these sites is regulated at lower compositional scales (species level), size selective; or predators may show their influence through the regulation of abundance levels of certain groups such as chironomids (Orthocladiinae and Chironominae) and planktonic Crustacea, as has been previously reported for trout (Kernan et al., 2009; Syväranta and Jones, 2009; Schilling et al., 2009). Our results are also in agreement with the observations of Carlisle and Hawkins (1998) who reported that physical habitat might be more important than predation in structuring benthic communities in trout-stocked mountain lakes. The lack of predation effect observed from frog data may be due to food niche segregation. This would imply frogs preying largely on the more abundant terrestrial adult stages of the insects (Vieites et al., 1997) to maximise resource sequestration during the short period the lakes remain unfrozen. Clearly these are interesting results that merit further evaluation.

pH is an important lake chemistry factor, but seems not to be involved in the variation of major macrozoobenthos groups at the study sites (Fig. 4.2). It is acknowledged that generally pH in a mountain lake can change significantly during thaw periods and this can influence biota composition (Olofsson et al., 1995). However, the low relationship observed with either surface or bottom pH from a large number of waterbodies suggests that even if pH slightly changed following spring/summer thaw, this did not necessarily affect biota composition at a high taxonomic level. Conductivity showed no relationship with littoral biota variability (Fig. 4.2).

3.2 Co-occurrence analysis of major littoral groups

Given the poor life supporting conditions present at headwater habitats, littoral biota may present discontinuous distributions, being represented by associations of similar ecotope requirements. To test for invertebrate families' associability and their littoral environment affinities, a flexible hierarchical clustering together with indicator taxa analysis were carried out. The results show an effective clustering of three large site/lake groups based on the similarity in their shared organisms (Fig. 4.5). The invertebrate groups with strong preference for these sites have a relatively simple structure, which is illustrated in Table 4.2.

First lake group, represented by littoral community type A, includes a significant number of midge taxa (Chironominae, Tanypodinae and Orthocladiinae families) and oligochaete worms (Enchitraeidae ice worms, Lumbriculidae and Naididae; Table 4.2). Likewise, the large group of Limnephilidae cadisflies (Trichoptera) larvae with crenobiotic / crenophilous representatives, together with biting midges (Ceratopogonidae), mayflies (Baetidae), Sphaeridae bivalves, and the nematode parasites associated with the same group (Table 4.2). These are relatively eurythermic taxa (i.e. tolerant of a wide temperature range) of diverse water flow regimes, altitudinal ranges and micro-habitats (e.g. epibenthic and endobenthic, rock surfaces and epiphytic). They are also of wide pH tolerance, mostly of tegumentary and gill respiration. They feed largely on detritus and microphytes; however a small number of taxa are predatory (e.g. Tanypodinae midge larvae) and parasitic

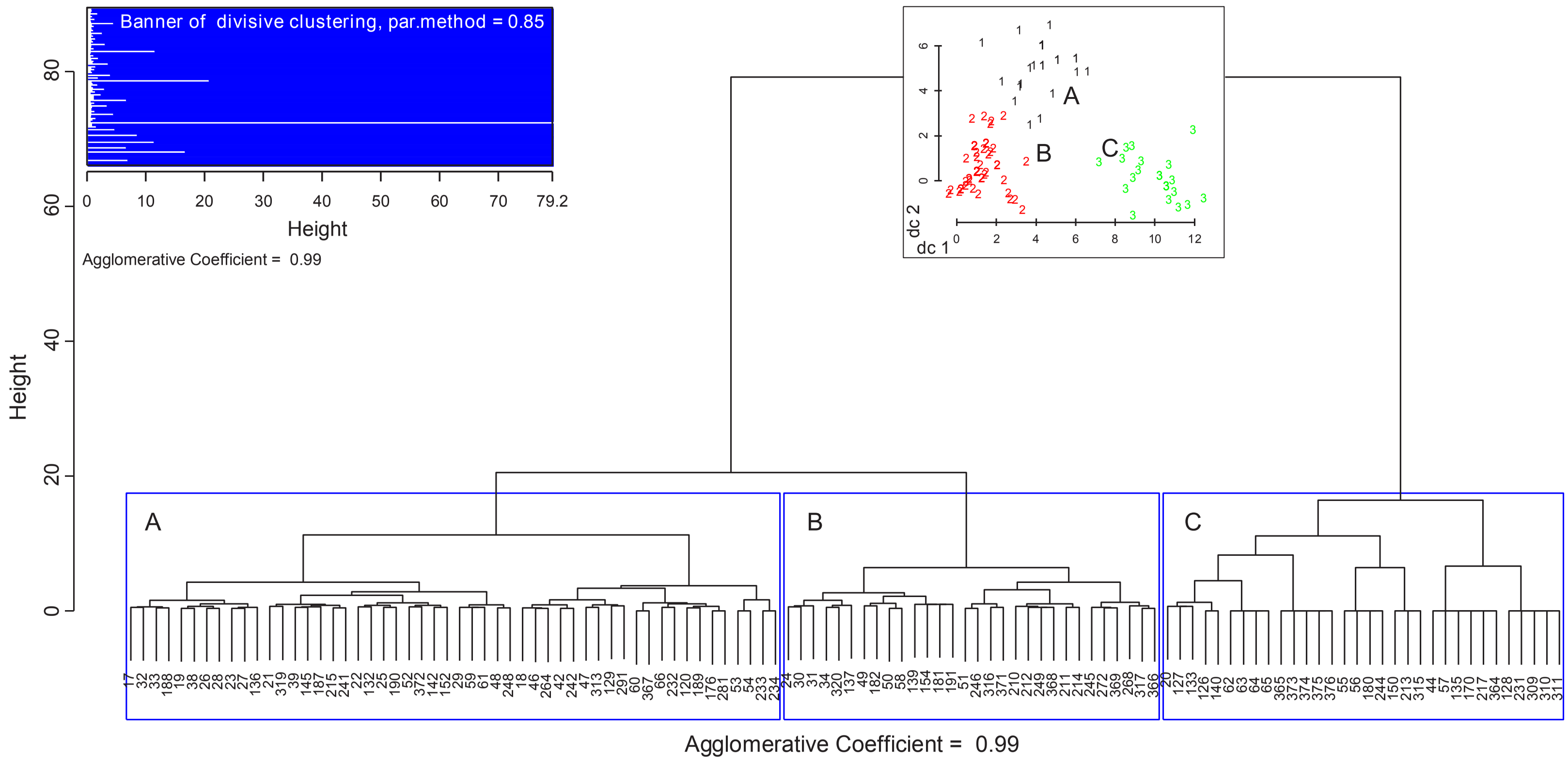


Fig. 4.5 Three major site/lake groups (A, B and C) identified by pair-group average method hierarchical cluster analysis (PGMA; flexible linkage, parameter = 0.85) based on shared littoral invertebrate families (computed with a Sørensen similarity index of species incidence data). A plot of cluster solutions in discriminating space (inset) shows an effective clustering. The results are from an analysis of 114 lakes and 46 major invertebrate groups.

(nematodes). The relatively wide ecological characteristics of this group identify it as a eurytopic group, i.e. a complex community with large niche breadth, present in a variety of habitats. The association of Sphaeridae bivalves with Oligochaeta worms has also been reported in headwater springs with fluctuating flow regimes (Danehy and Bilby, 2009). Likewise, Lumbriculidae worms' presence in the community resembles data obtained from Himalayan altitude lakes where oligochaetes have been found to dominate the bottom communities (Manca et al., 1998). The dispersion mode of this group is mostly aquatic passive, but can also be aerial passive for some taxa, which implies a high degree of connectivity between habitats (Tachet et al., 2002). The lakes where this community is most present are presented in Fig. 4.5.

Second lake group, with littoral community type B, is represented by two major taxa, i.e. omnivorous Haliplidae beetles and carnivorous Aeshnidae dragonflies; both have relatively strongly flying adults, capable of colonisation and maintaining the connectivity between populations which are not always at easy reach (Table 4.2). They are characterised by a relatively long life cycle (>1year), feed on live plants and macroinvertebrates, and are eurythermic. They have affinity to low water flow regime and heterogeneous microhabitat characteristics (Tachet et al., 2002). The waterbodies sharing this littoral group are presented in Fig. 4.5.

Third lake category is represented by littoral community type C with Limoniidae flies, Culicidae mosquitoes and Helophoridae beetles. Associated to these are also the parasitic hair worms Gordiacea. This community shares an aerial passive or active dispersion mode, aerial respiration (except gordiacea which are endoparasites in their larval stage). They are eurythermic and share a wide range of epibenthic microhabitats, with easy access to water surface. Their feeding strategy is also diverse: from shredders (Limoniidae) to microphytes (Helophoridae) and, microinvertebrates and fine suspended matter (Culicidae) (Tachet et al., 2002).

Table 4.2: Zoobenthos groups with highest fidelity to lakes clusters (resulted from cluster analysis), as given by indicator analysis. A subject was classified into a group for which the indicator value of group membership was higher and significant (i.e. strong preference). The significance is <0.05, unless stated

Taxon	Cluster	Indicator value
Chironomidae Chironominae	A	0.67
Enchytraeidae	A	0.62
Chironomidae Tanypodinae	A	0.46
Chironomidae Orthocladiinae	A	0.46
Limnephilidae	A	0.32
Sphaeriidae	A	0.23
Lumbriculidae	A	0.22
Naididae	A	0.22
Nematoda	A	0.21
Ceratopogonidae & Thaumaleidae	A	0.15
Baetidae	A	0.11
Haliplidae	B	0.16
Aeshnidae	B	0.31 (P=0.55)
Limoniidae	C	0.07
Culicidae	C	0.03
Gordiacea	C	0.03
Helophoridae	C	0.12 (P=0.16)

N(number of taxa used in the analysis) = 46 families from 114 central Pyrenean lakes, ponds and pools.

Although the studied families showed associative behaviour (i.e. they were statistically associated with one another), most of them exhibited rather ubiquitous distribution; none of the groups showed any apparent preference along the assessed landscape factors (results of boxplot distributions not shown). It suggests a continuous gradient distribution of the littoral associations, possibly being largely dependent on the local factors.

Conclusions

The results illustrate that major littoral invertebrate taxa (i.e. families) from altitude lakes of central Pyrenees are sensitive to external ecotope factors as well as to riparian vegetation structure. Catchment variables, topography and hydro-dynamics significantly influenced the major structure of littoral invertebrate groups. Topography may have acted through morphometric regulation of a lake's basin and its riparian zone (habitat control), a major driver of a lake ecosystem. The influence of hydro-dynamics (lake size, size and type of tributary/output) suggests that larger lakes hold different littoral invertebrate assemblages than do smaller ones. This could be a condition of water flow and food resources brought to the littoral zone.

It appears that although poorly developed, vegetation structure around the lakes can add an effect on littoral invertebrates' composition, richness and diversity. This is particularly important as it implies these aquatic ecosystems are sensitive to external ecosystem factors such as changes in vegetation composition, and may change drastically if vegetation changes due to changes in environmental condition, e.g. drought in the riparian zone.

Littoral invertebrates' structure also showed significant variability along the large scale geographical gradients longitude, altitude and latitude. It is likely that biogeographical variability in communities' structure across the central Pyrenees have arisen as a result of differences in the colonisation capacity of major groups following Holocenic deglaciation along the altitudinal potamon-rhitron-crenon gradient, overlapping a larger N-S transition between major European climates. The Pyrenean region should thus not be considered a homogeneous ecoregion since there are ecotopic and large scale differences which determine the settlement of particular ecological groups. This needs to be considered if hypotheses are tested in lakes from different catchments. Concurring with Johnson and Goedkoop (2000) and Kernan et al. (2009) our results suggest that the use of regional scale to characterize biota assemblages is sufficiently robust, yield a high sensitivity to landscape and large scale factors, and can be confidently used to characterise ecological processes occurring at high altitude lake environments.

Neither vertebrate predators (trout and frogs), nor water pH or conductivity appear to clearly influence the general structure of littoral fauna in the studied lakes. However, it is possible that these factors may act at different scales, e.g. species or abundances level, a subject open for further enquire.

Flexible hierarchical clustering and indicator taxa analyses provided a good classification framework of lakes and co-occurring biota. This helped unravel relatively simple but eurytopic littoral associations at high altitudes, together with the groups of lakes/ponds for which they have significant affinity. These associations however, did not show any particular clustering along the large or catchment-scale factors. This would suggest a rather ubiquitous distribution across the mountain range, possibly a result of relatively uniform colonisation during lake ecosystem evolution.

High elevation aquatic systems are generally poor in resources. The results of this study show that their littoral ecosystem is closely tied to certain ecotopic and ecological attributes from the surrounding terrestrial system. This has implications for the understanding of altitude lakes sensitivity to landscape forcing and future environmental changes.

Aknowledgements

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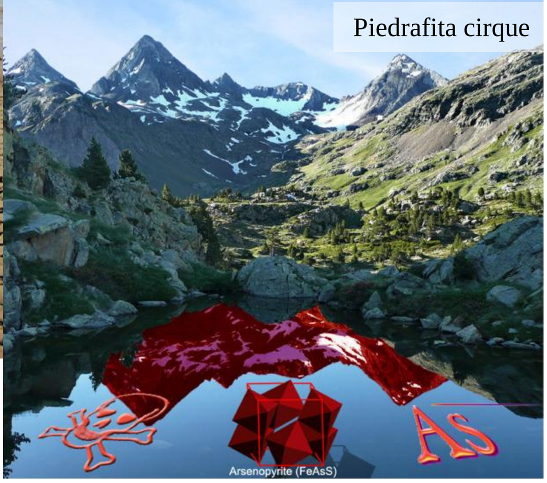
APPENDIX

List of major macrozoobenthos groups identified in 114 lakes, ponds and pools of central Pyrenees
O. Diptera, sO. Nematocera, SF. Psychodoidea, F. Psychodidae
O. Diptera, sO. Nematocera, SF. Culicoidea, F. Dixidae
O. Diptera, sO. Nematocera, SF. Culicoidea, F. Culicidae
O. Diptera, sO. Nematocera, SF. Chironomoidea, F. Ceratopogonidae & F. Thaumaleidae
O. Diptera, sO. Nematocera, SF. Chironomoidea, F. Chironomidae, sF. Tanypodinae
O. Diptera, sO. Nematocera, SF. Chironomoidea, F. Chironomidae, sF. Chironominae
O. Diptera, sO. Nematocera, SF. Chironomoidea, F. Chironomidae, sF. Orthocladiinae (lato sensu)= (stricto sensu) sF. Orthocladiinae+ sF. Diamesinae+ sF. Prodiamesinae
O. Diptera, sO. Nematocera, SF. Tipuloidea, F. Tipulidae
O. Diptera, sO. Nematocera, SF. Tipuloidea, F. Limoniidae
O. Diptera, sO. Brachycera, SF. Empidoidea
O. Trichoptera, GR. Spicipalpia, SF. Rhyacophiloidea, F. Rhyacophilidae
O. Trichoptera, GR. Spicipalpia, SF. Hydroptiloidea, F. Hydroptilidae
O. Trichoptera, GR. Integripalpia, SF. Limnephiloidea, F. Limnephilidae
O. Trichoptera, GR. Integripalpia, SF. Limnephiloidea, F. Uenoidae
O. Coleoptera, sO. Adephaga, F. Haliplidae
O. Coleoptera, sO. Adephaga, F. Dytiscidae
O. Coleoptera, sO. Polyphaga, GR. Haplogastra (=GR. Palpicornia), SF. Hydrophiloidea, F. Hydrophilidae
O. Coleoptera, sO. Polyphaga, GR. Haplogastra (=GR. Palpicornia), SF. Hydrophiloidea, F. Helophoridae
O. Coleoptera, sO. Polyphaga, GR. Heterogastra, SF. Byrrhoidea, F. Elmidae (=F. Helminthidae, =F. Elminthidae)
O. Megaloptera, F. Sialidae
O. Heteroptera, iO. Nepomorpha, F. Corixidae
O. Heteroptera, iO. Gerromorpha, F. Mesoveliidae
O. Heteroptera, iO. Gerromorpha, F. Veliidae
O. Heteroptera, iO. Gerromorpha, F. Gerridae
O. Odonata, sO. Anisoptera, F. Aeshnidae
O. Odonata, sO. Anisoptera, F. Gomphidae
O. Plecoptera, SF. Nemouroidea, F. Nemouridae
O. Plecoptera, SF. Nemouroidea, F. Capniidae
O. Plecoptera, SF. Perloidea, F. Chloroperlidae & F. Perlodidae
O. Ephemeroptera, F. Baetidae
O. Ephemeroptera, F. Siphlonuridae
O. Ephemeroptera, F.Heptageniidae
Cl. Lamellibranchia, SF. Corbiculacea, F. Sphaeriidae
Cl. Gasteropoda, sCl. Prosobranchiata, F. Valvatidae
Cl. Gasteropoda, sCl. Prosobranchiata, F. Hydrobiidae
Cl. Gasteropoda, sCl. Pulmonata, F. Ancylidae
Cl. Gasteropoda, sCl. Pulmonata, F. Lymnaeidae
Phyl. Annelida, Cl. Hirudinea, O. Rhynchobdelliformes, F. Glossiphoniidae
Phyl. Annelida, Cl. Oligochaeta, F. Naididae
Phyl. Annelida, Cl. Oligochaeta, F. Tubificidae
Phyl. Annelida, Cl. Oligochaeta, F. Lumbriculidae
Phyl. Annelida, Cl. Oligochaeta, F. Enchytraeidae
Phyl. Annelida, Cl. Oligochaeta, F. Lumbricidae & F. Sparganophilidae
Phyl. Nemathelminthes, Cl. Nematoda
Phyl. Nemathelminthes, Cl. Gordiacea
Phyl. Plathelmintes, Cl. Turbelariata, O. Triclades, F. Planariidae

Abbreviations coding: Phyl.= Phylum; Cl.= Class; O.= Order; GR.= Group and F.= Family.
Prefixes: S= super-; s=sub- and i= infra-.

PART II

Hazard risks from geogenic metal loads



5

Trace metals and their source in the catchment of the high altitude Lake Respomuso, Central Pyrenees

Abstract

Lake Respomuso is a dammed lake of glacial origin at 2200m altitude in the central Pyrenees. This study investigated the source of a number of trace elements (As, Cd, Co, Cu, Mn, Ni, Pb and Zn) in its catchment and their possible link to the local geology. Altogether 24 sediment and 29 water samples were collected from all major streams feeding the lake. The sediments were analysed for trace elements, major mineral components, minerals and organic matter whilst water samples were analysed for dissolved metal concentrations.

The trace element levels in the catchment sediment and water were relatively high compared to other similar altitude sites, with concentrations in the headwaters being generally higher than in the lower basin because of the source being concentrated in these areas. The principal component analysis revealed that the source of sediment-bound trace elements in the Lake Respomuso catchment is geogenic, and originated possibly in the sulphide minerals from slate formations.

Except at one site, none of the water samples exceeded the WHO drinking water guideline for arsenic. Arsenic in water was significantly correlated with its concentration in the sediments, possibly due to the oxidation of arsenic bearing minerals. The dissolved concentrations of all other trace elements were generally lower than the WHO drinking water guide values and they were not related to their sediment concentrations.

The As, Cd, Ni contents in sediment from several catchment streams exceeded their sediment quality thresholds. This geogenic source may pose risk to the stability of fragile local biodiversity and to the wider environment in the valley below particularly if the metals are mobilised, possibly due to environmental change.

Keywords: Trace elements, geogenic, sediment, water, principal component analysis, risk assessment, high altitude lake

1. Introduction

High altitude lakes are generally oligotrophic; they are located commonly on non-sedimentary basins and remain ice-covered during a large part of the year. The hydrochemistry (e.g. nutrients and trace elements) of these water bodies is predominantly influenced by the lithology of their catchment i.e. the geological structure, the mineralogical/chemical composition of the rocks, the proportions of rock types and the weathering resistance (Lewin and Macklin, 1987). The biogeochemical cycling of trace elements in such environments is generally governed by a weathering-limited regime

(Stallard and Edmond, 1983), with aqueous concentration often not more than 1-2 µg L^{-1} (Markert et al., 1997).

The geogenic inputs of trace elements to high altitude pristine lakes may be enhanced by change in the local environment, e.g. acid deposition and climate change (Román-Ross et al., 2002), which may enhance the weathering of metal-bearing minerals. Examples of such enhanced weathering related metal inputs are however rare in the literature (Zakharova et al., 2007).

Atmospheric deposition of air pollutants from industrialised areas, however, can also add a significant trace element burden to high altitude lakes as indicated by trace element levels in rainwater, snow (McBean and Nikleva, 1986; Schnoor and Stumm, 1986; Halstead et al., 2000) and the sediment cores (Rose and Rippey, 2002; Yang and Rose, 2005; Han et al., 2007).

The burden of trace elements may have potential implications for the ecological status of these pristine lakes as well as the

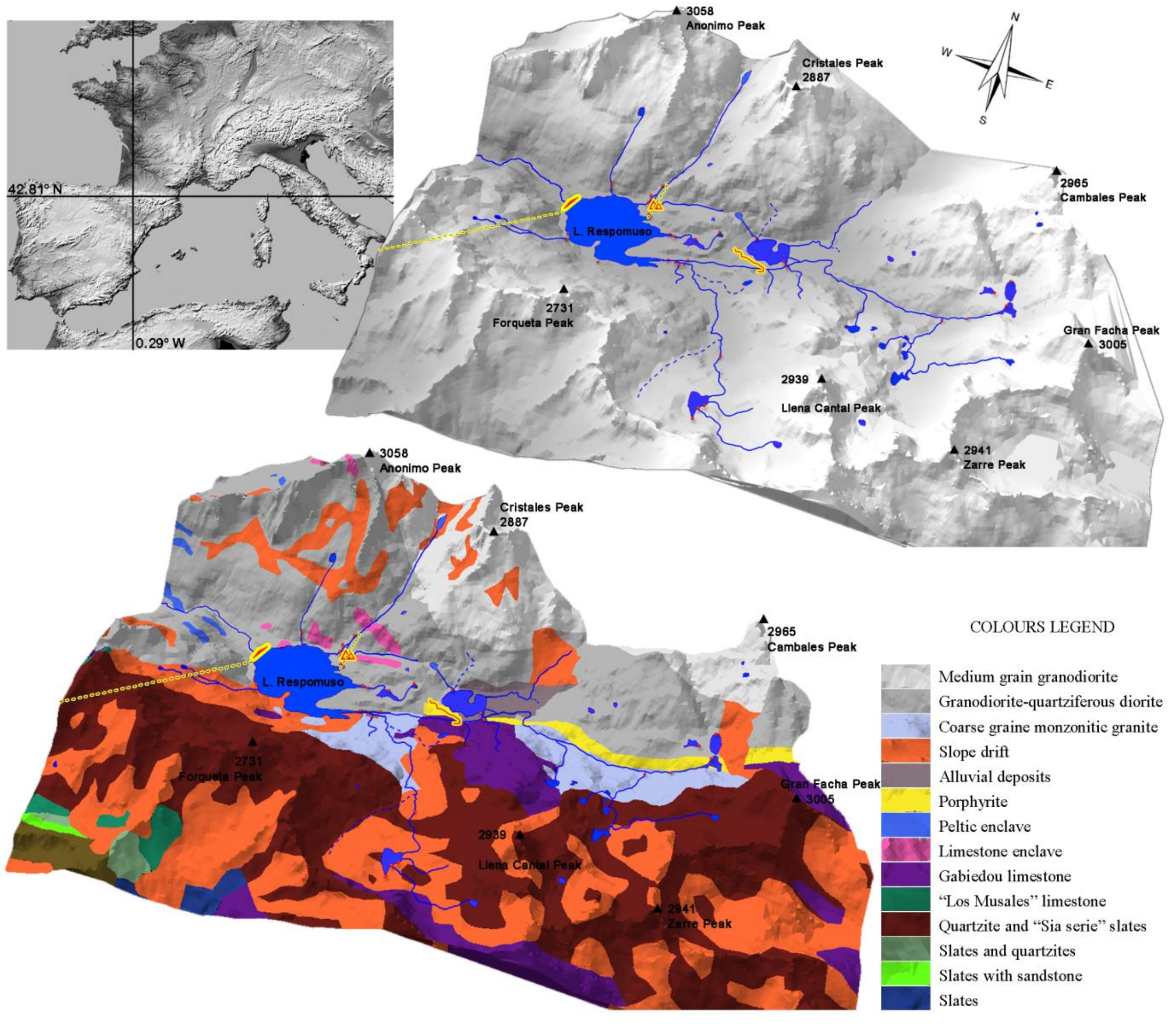


Fig. 5.1 Hydrological and geological maps of Piedrafita cirque, the Central Pyrenees.

wider remote environments because of their persistence and toxicity (Klavins et al., 2000; Yuan et al., 2004). Whilst the burden of trace elements in high altitude water bodies can arise from geogenic and atmospheric sources, the relationship between their concentrations in water and sediments or the lithology has not been entirely established.

A previous study reported the presence of metal rich minerals near Piedrafita cirque area - a remote high altitude cirque in the Central Pyrenees (Subías et al., 1993). This study was therefore designed to ascertain the extent and distribution of a number of trace elements within the Lake Respomuso catchment and the relationship they might have with the sediment mineral composition. The specific objectives of this study reported here were:

(a) To assess the level of As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn in catchment sediments;
(b) To determine the relationship between metal concentrations in the sediments and their mineral composition so as to assess the nature of the source; and
(c) To investigate if the water column metal concentrations are related to their sediment counterparts.

2. Geological and hydrological settings

Lake Respomuso is a remote high-altitude (2130m) lake of post-glacial origin, which is located in the central Pyrenees (Spain). The lake lies in the Piedrafita cirque (42.79-42.83N, 0.23-0.30W), which is surrounded by high summits, some of them >3000m a.s.l. The 24.80 km^2 catchment includes many ponds and small lakes which through a network of streams feed Lake Respomuso (Fig. 5.1). These waterbodies are typical headwater streams/ponds and their streambed is composed of boulders, cobbles and coarse sand. Riparian vegetation is poor and consists mainly of grasses and *Rhododendron* shrubs. The average annual precipitation for the catchment is 1352 mm, with the lake mean annual outflow of $75hm^3$ (MMA, 2006).

The lake drains to the west through Aguas Limpias stream and to the south-west through an underground pipe feeding Lanuza hydroelectric power plant downstream. The water from this lake is also used for drinking and irrigation purposes in the valley below.

The catchment is dominated by the granitic core of Cauterets on the north, shaped by limestone and detritic materials affected by low-grade metamorphism (Fig. 5.1). There has been reports of significant presence of F-Zn-Pb vein-type deposits near the catchment, which are developed in the limestone and detritic rocks of upper Devonian age (Subías, 1993). These deposits contain fluorite (CaF_2), sphalerite, galena (PbS), pyrite (FeS_2), chalcopyrite ($CuFeS_2$), siderite ($FeCO_3$) and green and white fluorite (Subías, 1993). Pyrite in the veins has arsenic concentrations of 250± 40 mg kg^{-1}, while the detritic hosting rock arsenic content is relatively smaller (87.5±0.5 mg kg^{-1}) and more consistent (Subías et al., 1993).

3. Material and methods

3.1 Sampling strategy and sample preparation

The sampling strategy was designed to cover all significant water courses and their bottom sediments. This included all significant tributaries, ponds and lakes which fed into Lake Respomuso (Fig. 5.2). Altogether 24 sediment and 29 water samples were collected in July 2006. The sediment samples were collected from same locations as the water samples, except in situations where sediment collection was not feasible (see Table 5.1 and Fig. 5.2). The stream/pond bottom comprised of broken rocks, coarse sands and fine material. As the rocks or coarse material were not expected to relate to metals in the water column, sampling deliberately targeted the finer fraction. The sediment samples were collected using a polythene trowel, with a maximum sample depth of 5cm. Each sediment sample included 10-12 randomly selected subsamples.

The sediment samples were dried at 40°C for 2 days and sieved through a 2mm sieve. Given the large variation in particle size within the fine fraction sampled and between the samples, they were further ground to < 1mm. Water samples were collected directly into Sterilin sample bottles. All water samples were prepared for analysis by filtering through 0.45µm cellulose nitrate membrane and then acidified to pH <2 using Aristar HNO_3. The filtered and acidified samples were stored at <5ºC until their analysis. The sediments were digested by following the procedure as outlined in US EPA Method 3050B for ICP-AES (US EPA, 1999). Organic matter content was estimated gravimetrically as percent loss on ignition (% LOI) at 550ºC for 4h (Rowell, 1994).

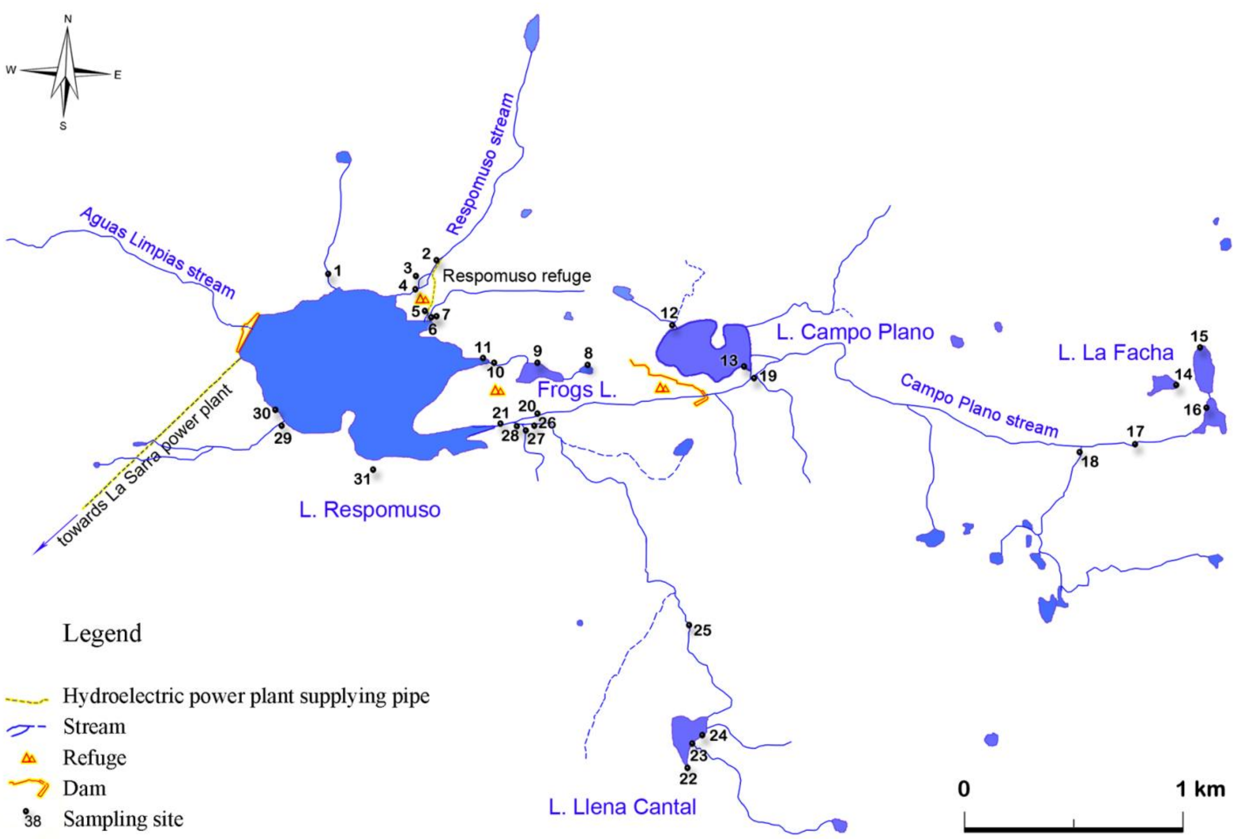


Fig. 5.2 Respomuso lake catchment and the location of sampling sites.

3.2 Trace, major elements and mineral analyses

All digested sediment samples were analysed by inductively coupled plasma atomic emission spectrometry (ICP-AES), while the water samples were analysed by inductively coupled plasma – mass spectrometry (ICP-MS). Both sediment and water samples were analysed for As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn using standard ICP-AES/MS operating conditions. The analyses followed standard procedures and QA/QC protocols.

Major elements in sediments were characterised by X-ray fluorescence spectrometry (XRF). A portion of 5–6 g of ground sediment was prepared as lithium tetraborate melt for the determination of major components (SiO_2, Al_2O_3, Fe_2O_3, TiO_2, CaO, MgO, K_2O, Na_2O and P_2O_5). Fusions were performed in Pt-Au crucibles. Calibration was carried out using certified reference materials from National Research Council of Canada, NRCC (SO-3, SO-4, HISS-1, MESS-3 and PACS-2, soils and sediments) and from South Africa Bureau of Standards, SACCRM (SARM 52, stream sediment). The recovery figures for the reference materials were within an acceptable range for all major elements (±10%).

The sediment mineralogy was characterised by X-ray powder diffraction analysis (XRD). All samples were ground to powder and the mounts were examined in a Siemens D5000 diffractometer using Cu K-α radiation operated at 40 kV, 30 mA. The samples were routinely run from 2.0 to 70.0 degrees with a step size of 0.02º and application time of 4 seconds. Mineral phases were identified by comparing diffraction patterns with the reference standards in the electronic database JCPDS-ICDD. The definition of the intensity peaks was carried out using standards in the electronic archive JCPDS (Joint Committee on Powder Diffraction Standards), compiled by the International Centre for Diffraction Data (ICDD). The XRD data was analysed in a semi-quantitative way, i.e. mainly for the purpose of identifying minerals. Quartz was the dominant mineral and showed great homogeneity among samples, therefore had to be excluded from the final Principal Component Analysis (PCA).

3.3 Quality assurance protocol

To maintain integrity of the results several quality control protocols were implemented. For sediment trace element analysis, replicated certified reference materials NIST 2704 (Buffalo River sediment) and procedural blanks were included in each digestion batch. Additionally a given sample was analysed several times during the analysis run. The analysis was highly precise with % coefficient of variability (%CV) between replicates being <5% and % relative standard deviation, RSD (1σ) between measurements of the same sample <2%.

The percent recovery of Cd, Co, Cu, Mn, Ni, Pb and Zn was generally within the limit for the test used (US EPA, 1999). For As and Cr, the recovery figures of 66% and 62%, respectively were low. This suggests that the digestion procedure was less effective in the dissolution of As and Cr bearing minerals. It is however known that the USEPA 3050B digestion method recovers significantly lower As and Cr compared to aqua-regia and HF based digestion procedures (Scancar et al., 2000; Tighe et al., 2004). Nevertheless the significantly lower recoveries of As and Cr mean these two elements may have been underestimated in the catchment sediment.

All reagents were of ultra-pure quality (Aristar grade). Stock standard solutions were

Merck Certificate AA standards. Ultra-pure (Milli-Q) water was used in all samples, standard solutions, and dilutions as appropriate.

3.4 Statistical analysis

The data from both sediment and water analyses were manipulated in SPSS 15 package and R (v. 2.5.1) for Windows for statistical analysis, including data normalization and principal component analysis (PCA). PCA was run on the correlation matrix. An orthogonal Varimax rotation was applied to factor solutions. This is used to rotate the axes so that they fit better through the variable cluster (Tabachnick and Fidell, 2007). PCA is a powerful tool for identifying latent relationships that are not readily evident from simple correlation analysis (Hooda et al., 1997). Pearson product moment correlation coefficient (r) was used to examine the relationship between trace

Table 5.1: Total content of trace elements (mg kg^{-1}) in the < 1mm sediment fraction of Lake Respomuso catchment (number of samples, n=24) together with the US EPA ERL and ERM recommended limits (SQGs, 1999)

Site no.	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
2	37.02	1.75	12.62	24.59	11.80	941.89	19.34	37.63	118.71
3	23.64	1.45	10.61	20.44	9.85	883.50	18.39	24.03	67.97
4	22.83	1.31	10.30	21.83	7.15	919.94	19.28	19.41	61.43
6	25.53	1.69	10.38	42.65	8.91	357.10	15.88	53.95	105.19
7	6.68	1.46	6.49	24.59	2.60	141.55	9.57	33.03	47.73
8	2.48	1.22	10.33	51.24	5.08	257.59	16.78	31.00	76.55
9	13.64	1.25	8.84	40.10	0.08	225.21	12.85	10.93	51.5
10	7.32	1.23	9.99	40.15	3.22	274.24	13.98	21.41	60.9
11	17.19	1.59	11.14	44.32	7.31	347.90	16.78	42.52	91.85
13	55.55	2.01	9.20	25.31	7.16	327.79	21.61	14.66	51.15
14	27.43	2.11	14.94	42.78	20.75	323.18	27.87	152.20	183.73
15	23.72	1.44	11.33	23.40	10.01	406.62	14.28	37.07	123.21
17	21.78	1.65	13.42	19.23	8.29	463.36	21.03	15.19	32.01
18	46.20	1.86	7.30	19.28	1.98	307.63	15.15	19.99	36.53
19	55.21	2.23	15.89	29.04	15.57	1134.48	28.03	17.91	67.37
20	52.53	2.22	13.76	29.94	10.32	760.67	25.41	19.64	76.04
21	95.54	3.18	20.97	33.20	30.47	1557.25	31.89	60.59	113.77
22	135.60	3.21	38.97	41.52	51.32	5622.67	53.50	68.72	133.62
24	161.24	3.25	26.24	44.51	20.53	3250.99	37.82	48.23	69.13
25	104.80	2.55	27.20	34.79	29.74	2324.55	48.68	31.26	85.77
26	59.97	2.29	13.73	28.06	12.58	1394.33	31.72	18.08	65.10
28	107.51	2.28	10.62	20.25	14.82	813.72	17.06	23.35	72.32
29	41.49	1.44	17.56	27.00	12.70	2987.41	18.02	35.79	80.34
30	47.64	1.60	15.76	28.50	12.99	2081.15	19.88	38.45	95.80
Mean	49.69	1.93	14.48	31.53	13.13	1171.03	23.12	36.46	81.99
SD	42.17	0.62	7.40	9.62	11.23	1293.62	10.98	28.92	34.53
CV (%)	84.9	32.1	51.1	30.5	85.5	110.5	47.5	79.3	42.1
ERL	**8.2**	**1.2**	**-**	**80**	**34**	**-**	**21**	**47**	**150**
ERM	**70**	**9.6**	**-**	**370**	**270**	**-**	**52**	**218**	**410**

ERL- Effects range low
ERM- Effects range median

elements content in water and sediment. The dataset for this analysis were Log transformed.

4. Results and discussion

4.1 Trace elements in sediments

The "total" content of the trace elements, measured in the sediments from the various locations of the Lake Respomuso catchment, is presented in Table 5.1. The concentrations displayed a wide range, both within and between the elements, possibly a reflection of their natural variability in the catchment rocks. Among the elements Cr and Cd showed least variability while Mn, Cu, As and Pb showed a considerable variability in their distribution within the catchment (Table 5.1). The contents of Co, Cr, Cu and Ni while they show variability in their distribution in the catchment sediments, are generally not high for such environments. Likewise, the mean Pb content (36.5 mg kg^{-1}) seems to suggest no real concern, although as high as 152.2 mg Pb kg^{-1} was measured at one of the sampling locations (Table 5.1). The sediment Zn content (32.0 – 183.7 mg kg^{-1}) is higher than that of Pb; this however may be due to its higher concentration in the local rock material or because of its greater solubility or weathering of Zn-bearing minerals compared to Pb.

With the exception of Pb, the Llena Cantal Lake site showed clearly the highest metal contents whilst the highest amount of Pb was measured at La Facha lakes. The mean concentrations of As, Cd and Ni found in this study were higher than the values reported for other pristine sites in Europe, North and South America (Rognerud et al., 2000; Birch et al., 1996).

4.2 Occurrences and sources of trace elements

Trace elements in sediments can be of geogenic origin as well as sequestered from anthropogenic inputs and/or local mobilisation. To determine the nature of metal source in the catchment sediments, the sediment metal content and its mineral composition together with the percentage organic matter were analysed by principal component analysis (PCA). PCA is an ordination method in which linear combinations of the original variables are created that characterise maximum possible variance in the data (Scott and Clarke, 2000). The variables in the first principal component (PC1) will explain most variation, and their weightings help identify what contribute most to the differences between the individual cases/sites (Dytham, 2003). The first three principal components (PC1-3) together accounted for more than 72% of the total variation in the dataset, i.e. sediment metal contents and its mineral composition (PCA output matrix not shown). The interrelationship among the elements and the minerals is displayed in the projection of components 1 and 2 and 1 and 3, respectively (Fig. 5.3A and 5.3B). As can be seen from Figure 5.3 As, Cd, Cu, Co, Ni, Pb and Zn in the sediment cluster together with Fe_2O_3 and Mn on the positive side of the first component. Likewise the lithophiles Ti and P are associated to the same cluster. This clustering of the trace elements and metal-bearing minerals, e.g. Fe_2O_3, TiO_2, P_2O_5 (Fig. 5.3), shows that the elements are of geogenic origin.

The highest loadings on the second component (PC2) were positively related with Al_2O_3, chlorite, MgO, amphibole, albite, illite, suggesting a common source of these

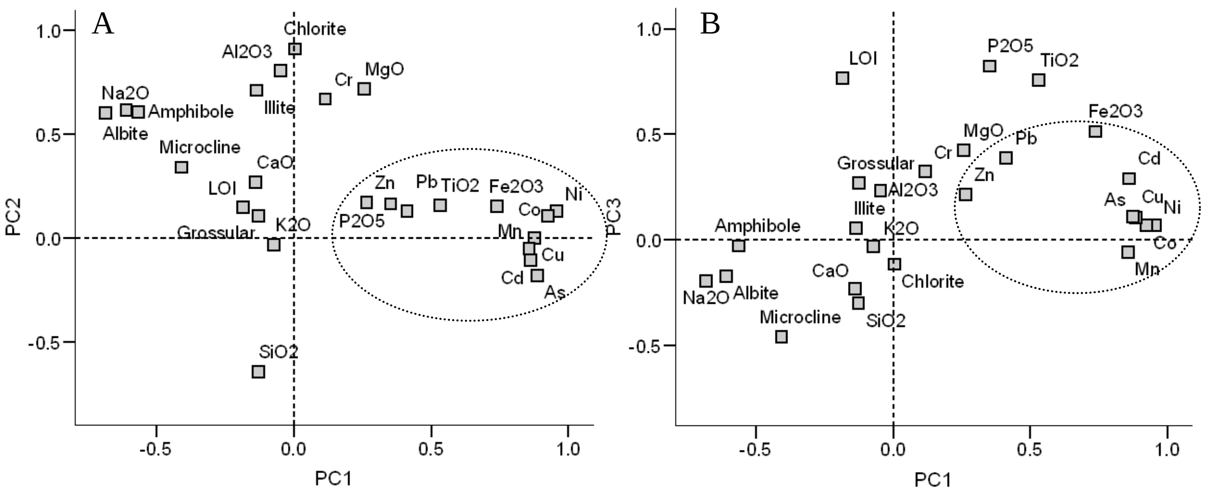


Fig. 5.3 PCA of trace metals, major components and minerals in the sediments. Correlation between the elements and principal components: (A) in the projection of components 1 and 2, and (B) in the projection of components 1 and 3. LOI indicates % organic matter.

components (Fig. 5.3). The organic matter (LOI) clusters apart, close to the positive side of the third component (PC3) but with no visible relationship to the rest of the components, including the trace elements. This means that organic matter had no

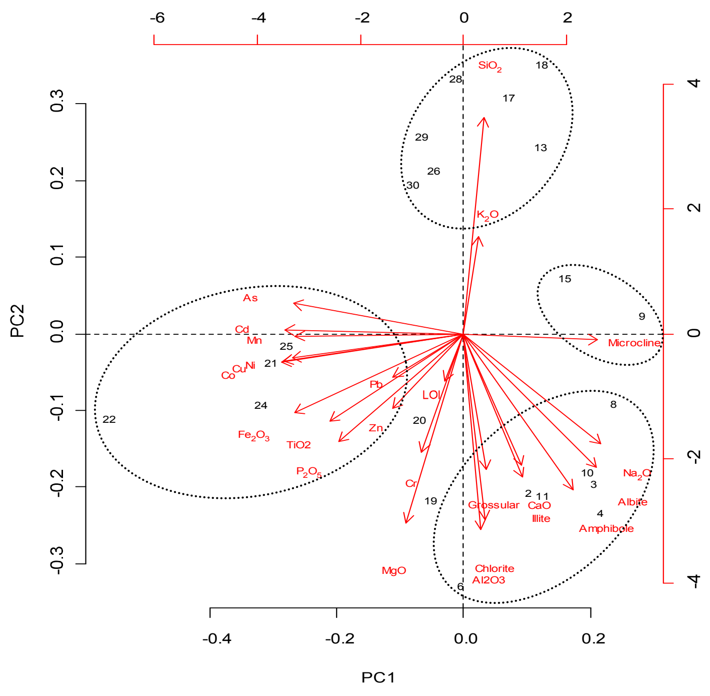


Fig. 5.4 Biplot of sites projected to principal components 1 and 2. The sites numbers correspond to Fig. 5.2 (sites 21, 22, 24 and 25- Lake Llena Cantal and the output stream).

significant contribution (either directly or indirectly through mobilization control) to the total trace elements burden into the catchment. This provides further evidence of the trace elements being of geogenic-origin. The sediment organic matter would have clustered with the elements had they sequestered them, which is expected in situations where their source is largely either anthropogenic or their significant contribution is also from the local mobilisation processes.

The positive correlation among As, Pb and Cd is hardly surprising since they exhibit similar geochemical behaviour with regard to the internal growth of the crystal lattice and the formation of rocks (Liu, 1987). In general the main sources of natural As are hydrothermal and magmatic ore deposits, in granites or metamorphic rocks where it can occur in association with other elements such as Fe, Co, Ni and Cu in sulphide minerals including arseno-pyrite or mispickel (FeAsS), realgar (AsS), and orpiment (As_2S_3) (O´Day, 2006; Wang and Mulligan, 2006; Ritter et al., 2002). Likewise, some shales, sandstones and phosphate rocks (Baur and Onishi, 1978) often contain significant amounts of arsenic. Natural weathering processes can result in significant amount of arsenic and other metals being mobilised (Camarero et al., 2004). The occurrences of these forms of minerals have been reported near the catchment ranging from monomineralic fluorite ores to polymetallic deposits with abundant fluorite containing dark-sphalerite + galena + pyrite + chalcopyrite (Subías et al., 1997).

To help locate the source sites of the trace elements in sediments the plots of the principal component scores for the locations in the planes of components 1 and 2 are displayed in Figure 5.4. Lalor and Zhang (2001) suggested that greater score distances from the vector origin in the projections are an indication of anomalously high and localised metal sources. Large scores on the first component therefore should indicate their source location in the catchment. This is the case for site 22 in a cluster of sites 21-25 (Fig. 5.4). Site 22 is located at the southernmost side of Lake Llena Cantal whereas site 24 is from the east side of this lake (Figs. 5.1 and 5.2). In the outflow stream of this lake lies site 25, about 500m downstream. This stream merges with Campo Plano stream (with its headwater in the east) and site 21 lies after their confluence before draining into Lake Respomuso (Fig. 5.2). It seems therefore that the area surrounding Lake Llena Cantal is the main source of trace metal bearing minerals (and hence their sediment content) in the catchment. The parent rock here is dominated by quartzite and “Sia serie” slates, suggesting that these formations may have a number of trace element-bearing rocks/minerals possibly associated with sulphides in the slate deposits.

4.3 Trace elements in water and their relationship with the sediment composition

Although the content of trace metals in the sediments is relatively high, its concentration in the aquatic phase is relatively low. Table 5.2 presents the concentrations of the trace elements in water for the sampling sites. Concentrations of dissolved Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn were low at most sites; however, arsenic as high as 14.22 μg L^{-1} was measured, which can be a cause for concern as it exceeds the WHO guide value for drinking water (10μg As L^{-1}). The mean As concentration, however, was well within the US and EU regulatory As limit for drinking water (Table 5.2).

Table 5.2: Concentration of trace elements (µg L-1) in water samples collected from the Respomuso lake catchment. Bold letters stand for concentrations above the sediment quality guide values

Site no.	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
1	0.06	0.08	0.04	0.76	2.43	6.68	1.56	0.44	10.26
2	1.89	0.23	0.11	0.54	33.48	5.88	4.30	2.50	22.19
4	2.21	0.27	0.18	0.87	46.80	6.24	12.51	1.62	30.11
5	1.88	0.16	0.07	0.61	26.30	2.68	1.82	1.57	7.90
6	1.31	0.05	0.08	0.34	26.38	3.49	2.35	0.48	5.17
8	0.29	0.06	0.03	0.48	3.83	1.38	1.59	0.13	5.77
9	2.74	0.04	0.08	0.79	28.25	3.15	3.16	3.39	3.90
10	2.45	0.05	0.12	0.65	22.23	2.85	2.48	0.56	3.35
12	4.15	0.06	0.11	0.37	6.46	0.96	2.77	0.20	3.81
13	5.54	0.12	0.06	0.28	6.95	1.53	1.99	0.28	10.48
14	0.35	0.03	0.02	0.14	0.98	1.66	0.87	0.07	3.14
15	0.25	0.06	0.05	0.22	2.21	1.47	2.34	0.23	5.47
16	0.84	0.08	0.17	0.79	3.08	8.63	19.96	1.15	16.72
17	0.96	0.03	0.01	0.13	1.37	0.42	0.94	0.04	2.43
18	**14.22**	0.04	0.02	0.18	0.93	0.49	0.88	0.18	2.86
19	**9.65**	0.13	0.03	0.28	2.63	2.74	0.86	0.15	4.16
20	5.77	0.07	0.04	0.26	1.85	1.07	1.91	0.67	4.61
21	4.13	0.06	0.07	0.21	3.68	2.52	3.58	0.10	3.80
22	3.80	0.05	0.10	0.21	2.21	1.84	1.97	0.15	4.64
23	3.94	0.08	0.04	0.20	1.09	1.58	0.98	0.09	2.94
24	3.04	0.99	0.26	1.03	35.38	10.55	38.61	2.01	545.74
25	5.48	0.58	0.27	0.42	21.49	8.21	29.26	2.24	57.96
26	4.33	0.06	0.03	0.25	2.51	0.80	1.08	0.11	3.65
27	4.13	0.03	0.03	0.20	3.18	0.59	0.54	0.09	2.14
28	3.51	0.04	0.12	0.27	2.34	5.14	3.34	0.27	5.37
29	2.39	0.03	0.09	0.18	2.64	1.93	2.42	0.05	2.13
30	2.52	0.04	0.02	0.14	1.08	1.24	1.04	0.06	2.36
Mean (n =27)	3.40	0.13	0.08	0.40	10.81	3.17	5.37	0.70	28.63
Standard Deviation	3.04	0.21	0.07	0.26	13.50	2.78	9.26	0.91	104.02
CV (%)	89.4	161.5	87.5	65.0	124.9	87.7	172.4	130.0	363.3

The As, Cd, Cu, Ni, Pb and Zn concentrations in the Respomuso catchment water were higher than the freshwater world average (Margalef, 1983; Kabata-Pendias and Mukherjee, 2007) and other remote pristine water bodies (Salbu and Steinnes, 1995; Markert et al., 1997; Tarvainen et al., 1997). The As concentrations in the Respomuso catchment water, however, are far higher than those reported for other pristine and not contaminated sites (Moiseenko and Gashkina, 2007; Vazquez et al., 2004). This may present a risk to arsenic sensitive biota in the catchment.

The correlation analysis between trace elements in the sediments and their counterparts in the water samples showed that with the exception of As, which showed a positive correlation between its content in water and sediment ($r = 0.59$, $p < 0.001$), the other elements had no correlation between the two compartments. This suggests that elements other than As are not readily mobilised/solubilised from their mineral phases in the sediments. Given the local geochemical conditions (e.g. shallow, oxic, oligotrophic running water) reductive (chemical or microbial) release of As is least

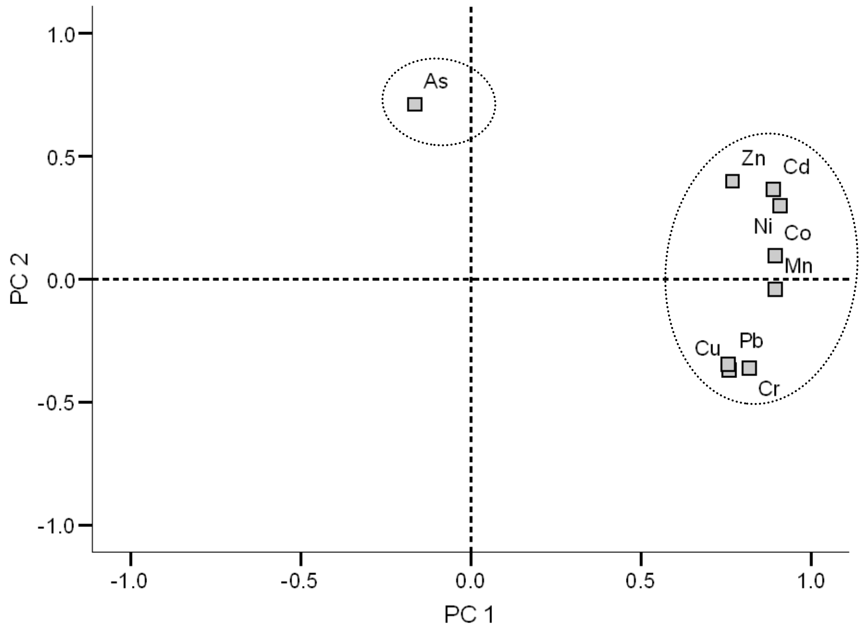


Fig. 5.5 Principal component analysis of trace metals in water of Respomuso catchment, with correlation between the elements in the projection of principal components 1 and 2.

likely a mechanism of its mobilisation from arsenic-bearing sediment minerals. This then raises a question as to why arsenic in water should relate to its content in the sediment, particularly when no such relationship was found for the other trace elements. The oxidation of arsenic-rich pyrite however has been suggested as a possible mechanism of As release from sediments (Das et al., 1996; Chowdhury et al., 1999). Clearly arsenic in the Respomuso catchment presents a contrasting geochemical behaviour compared to Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn. This was supported by an analysis of correlation between trace elements determined in the catchment water, where except arsenic all the other elements were highly correlated with each other (data not shown). The PCA plot of the water metal concentration data clearly shows this disparity between arsenic and other trace element, as they cluster apart on the projected components (Fig. 5.5).

4.4 Sediment quality assessment

Significant elevation of trace metals/metalloids in sediments may pose a risk to the benthic biota and could become source of metal/metalloids release into the overlying water column. Although the direct effects of sediment metal concentrations on the biota were not targeted in this study, the potential ecological effects were evaluated by following a widely used US EPA procedure for sediment quality assessment. This procedure entails sediment quality guidelines (SQGs) - ERL (Effects Range Low) and ERM (Effects Range – Median). ERL is the 10th percentile of the effects database, below which harmful effects on aquatic biota are rarely observed. Whereas ERM represents the 50th percentile values in the effects data, indicative of concentrations above which harmful effects are often observed (SQGs, 1999). The ERL and ERM sediment quality guidelines are not toxicity thresholds, instead they estimate safe concentrations, below which toxicity is least likely (SQGs, 1999).

Table 5.3: The sediment quality guidelines (SQGs) and their percent incidence of effects

Element	SQL, mg kg^{-1}		% incidence of effects*	
	ERL	ERM	ERL-ERM	>ERM
As	8.2	70	11.1 (67) ¥	63.0 (21)
Cd	1.2	9.6	36.6 (100)	65.7 (0)
Ni	20.9	51.6	16.7 (38)	16.9 (4)

* represents values as suggested by Long et al., 1995 from the observed biological effects database

¥Figures in bracket indicate % sampled sites which exceed SQG limits

Arsenic exceeded the ERL threshold (but not ERM) at 67% of the sites investigated. This increases the possible incidence of adverse biological effects by 11.1% (SQGs, 1999). In 21% of the sites, As exceeded the ERM limit; this increases the possible incidence of effects by 63% (Table 5.3). All high As concentrations were found on the south side of Lake Respomuso, within the small basin of Lake Llena Cantal. This suggests that the highest potential for As in the sediments to cause some ecological damage is within this area. Since the digestion procedure used did not fully recover arsenic from the reference sediment, it is possible that its concentration in the catchment sediment may have been underestimated. It is therefore entirely plausible that the above-mentioned potential ecological implications may have been underestimated. This is important as arsenic is classified as a priority pollutant by the US EPA with carcinogenic classification (USEPA, 1999), and is also a List II substance under the EU Dangerous Substances Directive (2006/11/EC).

Cadmium exceeded the ERL limit in all study sites. (Table 5.3). This means the incidence of effects increased to 36.6% (SQGs, 1999). Highest cadmium was found in two regions: 2.28-3.25 mg kg^{-1} at Lake Campo Plano (Fig. 5.2) and its outflow stream, and 2.01-2.23 mg kg^{-1} at La Facha lakes and their common outflow stream (Fig. 5.2). None of the investigated sites, however, exceeded the ERM criterion for Cd.

Nickel exceeded the ERL threshold at 38% of the sites, with an increase of the possible incidence of effects to 16.7%. At 4% of the sampling sites Ni exceeded the ERM limit, with similar % incidence as for ERL (Table 5.3). Overall, Ni exceeding SQGs showed two trends: a 21.61-28.03 mg kg^{-1} range in the La Facha lakes basin and about twice this concentration, reaching the ERM limit for Llena Cantal lakes basin (Fig. 5.2). It should be noted that the ERM criterion for Ni is less reliable compared to Cd and As in predicting the probability of its potential adverse effects (SQGs, 1999). The concentrations of Cr, Cu, Pb and Zn in the sediments did not exceed the SQG limits for sediments, and these limits have not been proposed for elements like Co and Mn.

Conclusions

The findings show that the trace element levels in the Respomuso catchment are relatively high compared to other similar high altitude catchments. The sediments-bound trace elements constitute a considerable metal burden in the high altitude Respomuso catchment. This is particularly important for As, Cd and Ni as their levels exceed the sediment quality guidelines. The relatively large sediment-metal store can pose an ecological risk, particularly if sediment-bound metals are mobilised, e.g. due to local environmental change.

The metal concentrations were usually higher in the headwater sediments than in the lower basin streams and lakes, with the sources found concentrated in the area surrounding Lake Llena Cantal on the southern slopes of the basin. This area is dominated by quartzite and ‘Sia Serie’ slates bedrock, both known to be rich in metal-bearing minerals. The distribution of trace elements (As, Cd, Ni, Cu, Cr, Co, Mn, Pb and Zn) and their relationships with the major elements and mineral components evaluated by PCA showed that the metals are of geogenic origin.

The relatively high contents of trace elements in the sediments were not entirely reflected in their water concentrations. In fact, with the exception of arsenic, sediment-bound trace elements had no relationship with their counterparts in water samples collected from the same locations. As for the presence of relatively high arsenic concentrations in water, it may have resulted from its higher mobility from the sediments or surrounding metal rich geology under the oxic condition of the streams.

Acknowledgements

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6

On the arsenic-source mobilisation and its natural enrichment in a high mountain cirque in the Pyrenees

Abstract

Recently arsenic contamination and its environmental and human health problems have been raising concerns worldwide. The occurrence of natural high levels of arsenic contamination has generally been reported for low altitude environments. Here we report a study conducted to assess the extent of arsenic mobilisation/transport from previously identified arsenic source areas in a high altitude cirque of the Pyrenees as well as the potential contribution of As by snow.

The concentration of arsenic in sediments of several tributaries was enriched up to about ten-fold due to mobilisation of arsenic from the source areas within the catchment. The highest arsenic enrichments were found in an area dominated by quartzite and slate formation in the southern side of the basin, and it generally diminished towards the major lake downstream, possibly due to mixture with sediments from non-source areas. At these sites arsenic exceeded the Hazard Quotient (HQ) limits for the protection of aquatic life. The potential hazard of the As-enriched sediments may be further enhanced outside the catchment as samples collected downstream from the cirque have also shown arsenic concentration exceeding HQ unity.

The arsenic concentrations in the water collected at a number of sites exceeded its guide value for the protection of aquatic life. The potential As contribution by snow in the area was low and was largely of lithospheric origin.

The PCA analysis showed strong association of arsenic in sediments with the sediment mineral composition (Fe_2O_3, TiO_2 and Mn). Arsenic in water was positively correlated with its concentration in the sediments and could potentially increase if the environmental/climate conditions change.

Keywords: arsenic, natural enrichment, sources, sediment, water, snow, altitude cirque, principal component analysis, ICP-AES, ICP-MS, XRF

1. Introduction

Among the trace elements arsenic (As) has received much attention since its recognition in the 1990s as a naturally occurring contaminant in many parts of the world (Bissen and Frimmel, 2003). Arsenic in water is potentially toxic to biota and is a hazard to human health due to its carcinogenic nature (Smith et al., 1992). For example, As in groundwater in Bangladesh, West Bengal in India and other parts of Southeast Asia (Charlet and Polya, 2006) as well as in regions of Europe, North and South America (Smedley and Kinniburgh, 2002; Marshall et al., 2007) has become a major hazard to the health of people using these waters. The source of arsenic contamination in these regions is however the presence of arsenic-rich bedrock.

Slates and phyllite rocks generally contain significant amounts of arsenic, associated with sulphide and sulfosalt minerals (Rose et al., 1979; Smedley and Kinniburgh, 2002). Pyrite is a common sulphide mineral known to host arsenic in most rocks (Kolker and Nordstrom, 2001). Weathering of arsenic bearing bedrock is considered to be the dominant source of As in lake sediments (Tamaki and Frankenberger, 1992). Local environmental conditions can release sediment-bound arsenic *via* both acidity and redox-driven dissolution processes (Deuel and Swoboda, 1972; Chowdhury et al., 1999).

While arsenic in groundwater and associated environmental and human health problems have received considerable scientific attention (e.g. Smith et al., 1992; Charlet and Polya, 2006; Smedley and Kinniburgh, 2002), studies of its occurrence or geochemical behaviour in high altitude environments are rare (Romo-Kröger and Llona, 1993). Relatively high As concentrations (13–26μg As L^{-1}) have however been measured in spring waters from the Panticosa resort area (1700m a.s.l.) in the central Pyrenees (Garrido et al., 2001). Likewise lake bottom sediments concentrations as high as 339 mg As kg^{-1} were reported for Lake Respomuso at an altitude of 2130m (Lavilla et al., 2006). This is a very high level of As which exceeds most sediment quality criteria for the protection of aquatic life and can have potentially deleterious effects on the aquatic resources as well as the wider environment (Smith et al., 1992).

The burden of As in remote high altitude water bodies may arise from geogenic and atmospheric sources (e.g. long range transport from burning of fossil fuels; Bissen and Frimmel, 2003); however the relationship between its concentrations in water and sediments or the lithology in such environments has not entirely been established. The study reported herein makes use of data from a broader survey of trace elements occurrence in Lake Respomuso area, the central Pyrenees (Zaharescu et al., 2009). The work showed distribution and a general source of a number of trace elements in the catchment. However questions with regard to mobilisation/transportation and atmospheric deposition of arsenic still remain open. The main focus of this paper is to further ascertain the source of arsenic in the catchment and to establish the link between the arsenic source and its distribution. For this we assess the enrichment of arsenic in the catchment sediments as well as the bottom sediments of the main lake. The degree of sediment-arsenic enrichment around the source and non-source areas as well its relationship with lake-bottom sediments should help establish the source of arsenic and its transportation within the catchment. Also, some snow-arsenic data are presented to determine the contribution, if any, of atmospheric arsenic deposition.

1.1 Study site

Piedrafita Cirque is a postglacial high-altitude cirque (2200m) in the central Pyrenees, Spain (42.79-42.83N, 0.23-0.30W; NASA World Wind v1.4) (Fig. 6.1). The cirque is snow covered during a large part of the year, with snow deposits generally lasting until the mid-summer. The sediments of cirque's waterbodies are dominated by relatively coarse materials, comprising fragmented rocks, small stones, coarse and fine material. A detailed description of the area is presented elsewhere (Zaharescu et al., 2009).

The area is dominated by a granitic core (Cauterets-Panticosa) in its northern side, which is surrounded by a low grade metamorphic aureole affecting mainly the limestone and detritic materials (Fig. 6.1). It has significant presence of W-Au skarn deposits (Subías et al., 2007), and pyrite in vein-type mineralization located near the southernmost part of the catchment (Subías, 1993), with arsenic concentrations in pyrite of 250± 40 mg kg^{-1}(Subías et al., 1993). This represents a relatively significant source of As in the catchment geology. No significant industrial or extensive agricultural activities exist in the surrounding area. The water from the catchment area is used for hydroelectricity generation, potable and irrigation purposes in the valley below.

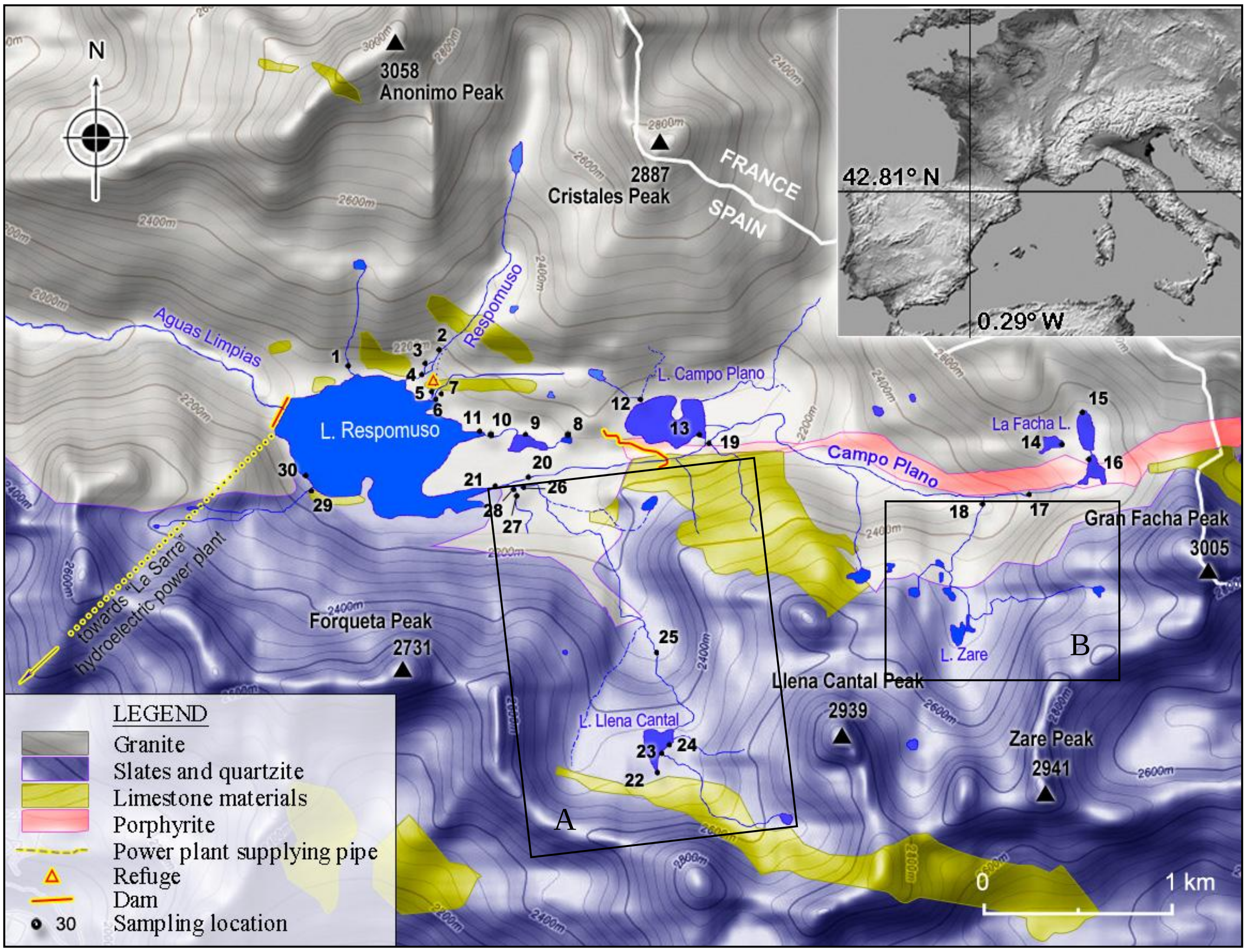

Fig. 6.1 Digital elevation model of Piedrafita cirque (Central Pyrenees) with hydrological and geological features and the location of sediment and water sampling sites. The areas with high sediment (A) and water (B and A) arsenic contents are enclosed in squares. Radar map of SW Europe is from JPL. Geology of the area is after Aragües et al. (1987).

2. Methodology

Water and sediment samples were collected during a sampling campaign in July 2006. The sampling was intended to cover all significant streams, ponds and lakes in the cirque which feed into Lake Respomuso (Fig. 6.1). The sediments were collected from lake sides and tributaries with a clean polythene trowel at a maximum sample depth of 5cm. At a number of locations, particularly in small streams the limited sediment deposition meant the sample depth was <5cm. At each sampling location 10-12 randomly selected sediment subsamples were collected to make a composite sample. The water samples were collected from the same locations as the sediment samples. All samples (sediment and water) were stored at <5°C before being prepared for analysis.

Additionally 19 surface (0-2cm) and subsurface (5-7cm) samples were collected from different snow profiles on the inside and exterior slopes of the cirque (altitudes ranging 1700-2200 a.s.l.; sites not included on map), in July 2006 and March 2008, respectively. Each profile was constituted of depositional layers, which is expected to reconstitute the aerial deposition of As during different snow events and inter-periods, after the seasonal snow starts to accumulate on the slopes. The snow sampled in July 2006 was from a remaining snow patch at the south side of Lake Respomuso. The snow sampling followed clean procedure to avoid contamination. The samples were kept until melting in sampling plastic bags, then transferred to Sterilin sample tubes and kept at < 4ºC until their laboratory analysis.

2.1 Sample preparation and digestion

The sediment samples were dried at 40°C for 48 h and sieved through a 2mm nylon sieve. As the resulting fraction had a large variation both between and within samples, it was ground with a ceramic pestle and mortar to pass through a 1mm sieve. This was considered necessary to minimise sub-sample errors which may arise from the large variation seen in the >2 mm fraction. All water and snow-melt samples were filtered through 0.45μm cellulose nitrate filter membranes and then acidified to pH <2 using Aristar grade HNO_3.

The sediment samples (<1mm), in duplicate, were digested by following USEPA Method 3050B (USEPA, 1999). Organic matter was estimated as percent loss on ignition (LOI) from 3g sediment at 550ºC for 4 hours.

2.2 Trace elements analysis

The sediment digestates were analysed by ICP-AES, while the water and snow-melt samples were analysed using an ICP-MS. Both sediment and water samples were analysed for As and Mn, using standard ICP-AES/MS operating conditions and QA/QC protocols. Manganese was included due to its general association with geogenic occurrence of arsenic (Oscarson et al., 1981). To determine the validity of the extraction and analysis procedures three replicates of certified reference material (CRM) SRM-2704 and three replicates of procedural (laboratory) blank were included in each digestion batch. The results were reliable, with % variability between replicates being <5%, and the relative standard deviation (% RSD; 1σ) being <2%. The percentage recovery of Mn was generally within the acceptable range for the test used. For As, the recovery figure of 66% (range, 64.2%-66.2%) was low but consistent. This suggests that the digestion procedure was less effective in the dissolution of As from its bearing minerals. The ICP-AES was highly sensitive for the two elements in terms of its detection limits and reproducibility.

For water analysis by ICP-MS, % RSD for both As and Mn was <5%, and both elements were well above their detection limits, based upon their background measurements in 2% Aristar HNO_3.

2.3 Major components analysis

Major components in the sediments were determined by X-ray fluorescence spectrometry (XRF). A portion of 5-6g of ground sediment sample was prepared as lithium tetraborate melt and analysed for SiO_2, Al_2O_3, Fe_2O_3, TiO_2, CaO, MgO, K_2O, Na_2O and P_2O_5. Fusions were performed in Pt-Au crucibles. Calibration was carried out using certified reference materials from South Africa Bureau of Standards, SACCRM (SARM 52) and from National Research Council of Canada, NRCC (SO-3, SO-4, HISS-1, MESS-3 and PACS-2). The analytical uncertainties for all major components lay within ±10% of the certified values.

2.4 Data processing

The statistical analysis of the data from both sediment and water analyses included data standardisation (mean, μ =0 and standard deviation, σ =1) and principal component analysis (PCA). The Varimax rotation was applied to factor solutions in the PCA in order to maximise the variance captured by the loading components (Abdi, 2003). To examine the correlation between the arsenic content in water against sediment, nonparametric Spearman rank correlation (ρ) and nonparametric regression with distance weighted least squares fit line were applied. Because the data in this case showed a log-normal distribution, it required log10 transformation before the analysis. The statistical processing was performed in STATISTICA and SPSS packages for Windows.

3. Results and discussion

3.1 Arsenic in sediments

The pseudo-total As and Mn, and the total content of the major components measured in the sediments are displayed in Table 6.1. Both As and Mn showed a wide range, possibly a reflection of their natural variability in the catchment rocks and/or the different rock weathering rates. Among the major components, oxides of Ca and Na showed largest variation while Si and Al were uniformly distributed in the catchment (Table 6.1), reflecting the basin geology (Fig. 6.1). The weathering indicator oxides such as Al_2O_3, K_2O and MgO[24] were also uniformly distributed (Table 6.1), suggesting a similar weathering pattern in the basin (Nesbitt and Wilson, 1992).

Arsenic in the sediments ranged from 2.5 to 161.2 mg kg^{-1}, with a mean value of 49.69 mg kg^{-1} (Table 6.1). The Mn content ranged from 141.5 to 5622.6 mg kg^{-1}, with a relatively high mean value (1171.0 mg kg^{-1}). The highest values for both elements were found on the south slopes of the basin, in the area surrounding Llena Cantal Lake (Fig. 6.1). The mean content of arsenic in the sediments (~50 mg As kg^{-1}) is much higher than its world average in river sediments (~5 mg kg^{-1}) and its crustal (~1.5 mg kg^{-1}) or slate (~18 mg kg^{-1}) abundances (Vaughan, 2006). Also, compared to other reference water-bodies, the level of As in the sediments is higher than that reported for other pristine sites in Europe, North and South America (Table 6.2). However, the mean As concentration in the lake catchment sediments was lower than that at some sites with significant human impacts (e.g. landfill and mine tailings) (Table 6.2).

Table 6.1: Descriptive statistics of arsenic, manganese (mg kg^{-1}) and major elements (% mass/mass) in surface sediments (< 1mm) of Piedrafita cirque

	As	Mn	Fe_2O_3	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2
Min	2.48	141.6	3.25	0.14	1.12	10.81	52.23	0.06	1.65	0.31	0.42
Max	161.2	5622.7	8.57	2.38	2.95	17.01	73.11	0.30	3.66	16.55	1.01
Mean	49.7	1171.0	5.35	1.00	1.97	14.34	63.12	0.15	2.63	3.50	0.70
Std Dev	42.2	1293.6	1.56	0.71	0.58	1.81	6.40	0.07	0.55	4.30	0.20
% CV	84.9	110.5	29.1	70.1	29.3	12.6	10.1	45.5	21.1	122.7	28.7

N (number of samples) = 24.

Clearly, the catchment sediments contain significant levels of arsenic which could potentially become bioavailable. These levels may be further enhanced, as changes in the local climate could increase the erosion of catchment slopes, as has been reported for other parts of the Pyrenees (Camarero et al., 2004).

Arsenic source

For the purpose of identifying mineral sources of arsenic, multivariate analysis of the whole dataset (As, Mn, major element oxides and organic matter) was carried out using the principal component analysis (PCA). The first three principal components together accounted for more than 75% of the total variation. Arsenic in water plotted in the same cluster with As, Mn, Fe_2O_3 and minerogenic Ti in the sediments, displaying a clear positive loading on PC1 in the projection of PC1/PC2 and PC1/ PC3 (Fig. 6.2). This lead us to interpret the first PC as the component that overall influences the arsenic source. The high positive correlation of arsenic and associated elements (Fe, Mn, and Ti) with the first principal component (Fig. 6.2) provides a strong evidence of its geogenic origin in the catchment. This is not surprising as redox sensitive Fe-Mn and lithophile (Ti) oxy/hydroxides are known arsenic-rich mineral components, and hence they play a

Table 6.2: Comparison of mean and range of As concentrations (mg kg^{-1}) in sediments from the Respomuso catchment with sediments from other contaminated and naturally uncontaminated sites

Location	As, mg kg^{-1}	Reference
This study*	49.69 (2.48 - 161.24)	-
Lake Respomuso, Spain*	87.30 (15.30 - 339.50)	Lavilla et al., 2006
33 lakes in S Norway (preindustrial values)*	2.56	Rognerud et al., 2000
Nahuel Huapi Lake, Argentina*	4.82	Ribeiro-Guevara et al., 2002
Canadian sediments*	68 (6-100)	Ollson, 1999
Lake in Maine^{+}	201.50	Nikolaidis et al., 2004
Rat Lake, Canada^{++}	820	Ollson, 1999

The symbol * Indicates natural, uncontaminated sites.
Sites with anthropogenic contamination: $^{+}$landfill and $^{++}$mine tailings.

major role in arsenic distribution in sediments (Zhang et al., 2007).

On the other hand, the loading of Na_2O at the negative side of the first group /component means that areas within the catchment dominated by Na_2O-type mineralogy are least likely to have any significant arsenic source. Also, the organic matter (measured as LOI) plots independently (Fig. 6.2). This clearly shows that organic matter has no significant control over the arsenic distribution (either directly or indirectly) in the catchment. Since organic matter is known to sequester anthropogenic inputs of trace elements as well as those locally mobilised, the lack of any relationship with arsenic (Fig. 6.2) further supports the hypothesis of arsenic being of geogenic-origin.

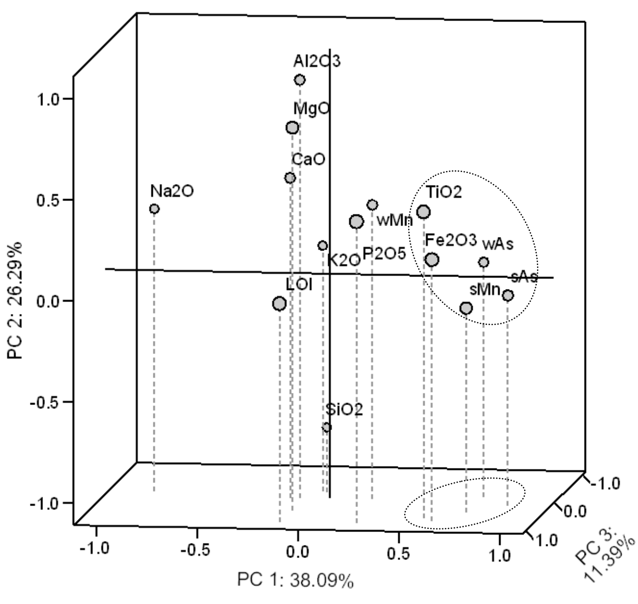

Fig. 6.2 Principal Component Analysis plot of arsenic, manganese, % organic matter (LOI) and major sediment mineral components. The plot shows correlation between the elements and principal components in the projection of principal components 1, 2 and 1, 3. PC1 represents the component explaining arsenic origin. Elements with prefix *s* or *w* represent sediment and water, respectively.

Arsenic transportation from the source and its potential hazard in surface sediments

In order to determine the degree of sediment contamination with a given metal/metalloid, and hence to confidently discriminate its sources, a common practice is to calculate enrichment factors, which can be defined as the ratio between the sample concentration of a metal/metalloid and its natural background concentration (Sutherland, 2000). In general authors refer to world average values of elements in shales and/or crustal composition for the determination of anthropogenic enrichments. Yet the nature of our data which are representative of local geology (natural background levels) could mislead this interpretation. To overcome this difficulty we reported arsenic concentrations with reference to aluminium, which is a commonly used background normalizer (Schropp, and Windom, 1988). The relatively constant distribution of aluminium oxide in the sediments from our dataset (Al %SD=12.6) meant it is a better suited estimator of natural metal enrichment than using literature reference values. The level by which surface sediments were enriched in arsenic was therefore estimated as the ratio of its measured concentration to that of aluminium oxide level at each location.

On average, the enrichment of the sediments with arsenic in Piedrafita cirque was about 3.8 (±3 SD)-fold comparing with the lowest (baseline) level as predicted by aluminium. The plots of arsenic enrichment at each site (Fig. 6.3) show three significantly different levels of enrichment (ANOVA $F= 86.5$, $p<0.01$) in Piedrafita cirque. A relatively low enrichment level was recorded on sites generally from the northern slopes of the cirque, which are dominated by the “Panticosa-Cauterets” granitic bedrock (Fig. 6.1). Whilst this arsenic enrichment was

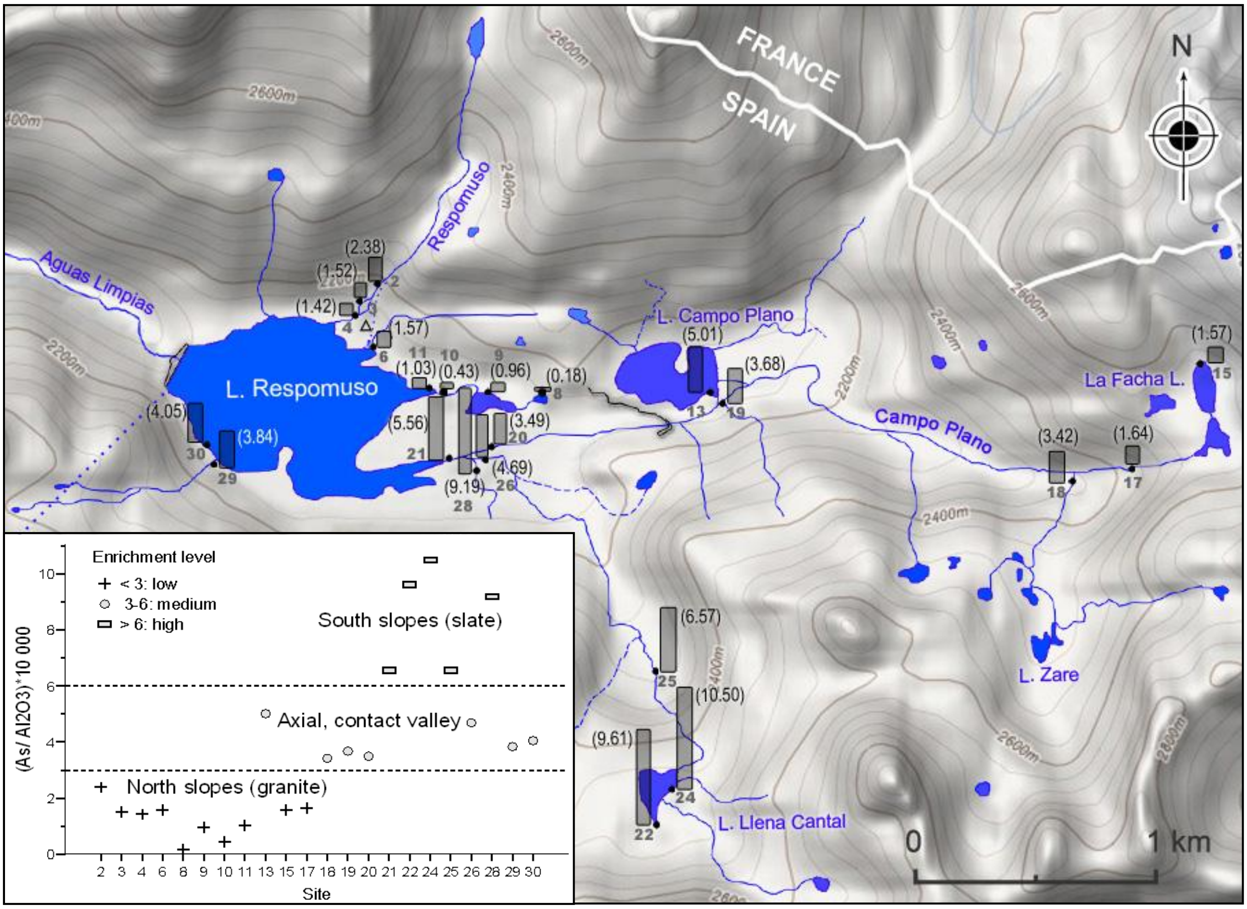

Fig. 6.3 Variation in enrichment with natural arsenic (As normalised to Al_2O_3, mg kg^{-1}) of sediments along the different stream courses/ lakes of Piedrafita cirque. Numbers represent sampling locations and enrichment values (in brackets). The embedded graph shows the association of As enrichment levels to areas with different geology of the cirque.

significantly less than that found in the rest of the areas, its concentrations were still significantly above the average arsenic concentration in granite of 1.3 mg kg^{-1} at most locations (Vaughan, 2006). This suggests a relatively high background arsenic content in granite at these sites. A markedly higher enrichment level, of up to about six to ten-fold, was recorded on the locations receiving sediments from the southernmost slopes of the cirque (Fig. 6.3). This area has high presence of "Sia serie" slates, quartzite and limestone materials (Fig. 6.1). Arsenic is commonly known to be a guide element of slate/shale rocks or their sulphide minerals such as pyrite, realgar and orpiment (Yang and Blum, 1999; Vaughan, 2006). Weathering of these rock types could therefore be the primary source for relatively high arsenic enrichment of the sediments at these locations. Finally, an intermediary level of arsenic enrichment, of about 3-6 -fold was recorded on sites in the axial contact valley collecting sediments from both, the northern plutonic granite and the southern, metamorphic side of Piedrafita cirque (i.e. low and high arsenic areas, respectively; Fig. 6.3 and Fig. 6.1).

It is also important to mention that most high enrichment levels in sediments are from upstream locations of the cirque, and their values generally decreased downstream (Fig. 6.3). A clear example is Llena Cantal lake and its output stream from the south side of the cirque (i.e. locations # 22, 24, 25 and 26; Fig. 6.3). This group of sites is characterized by relatively high sediment As enrichment. The mineral components with a strong presence here are Fe_2O_3, TiO_2 and possibly MnO_2 as indicated by the association of Mn in the PCA plot (Fig. 6.2). This clearly shows a spatial distribution of sediment arsenic enrichment with the source being concentrated in the headwaters, especially from the southernmost slopes of Piedrafita cirque (Fig. 6.1). The general decrease of arsenic enrichment along the stream courses implies that arsenic-rich sediments are mobilised/ transported from localised sources in the cirque and follow a progressive dilution by mixing with sediments from adjacent areas downstream. This assumption is also supported by relatively lower enrichment levels calculated for the lake Respomuso bed sediments (locations # 11 and 30; Fig. 6.3) as well as the enrichment level of 1.84 calculated for the upper sediments (<5cm) of a core collected from the central part of the same lake in 2002 (not shown on map). This also suggests that arsenic association with fine grain sediments and its transportation through sediment sorting downstream may be relatively limited in the studied area and may be governed by the shallow and rapid nature of the streams in this relatively small catchment.

Aluminium has been largely used as a normaliser element for the prediction of background values of trace elements from which anthropogenic enrichments are calculated (Schropp and Windom, 1988;

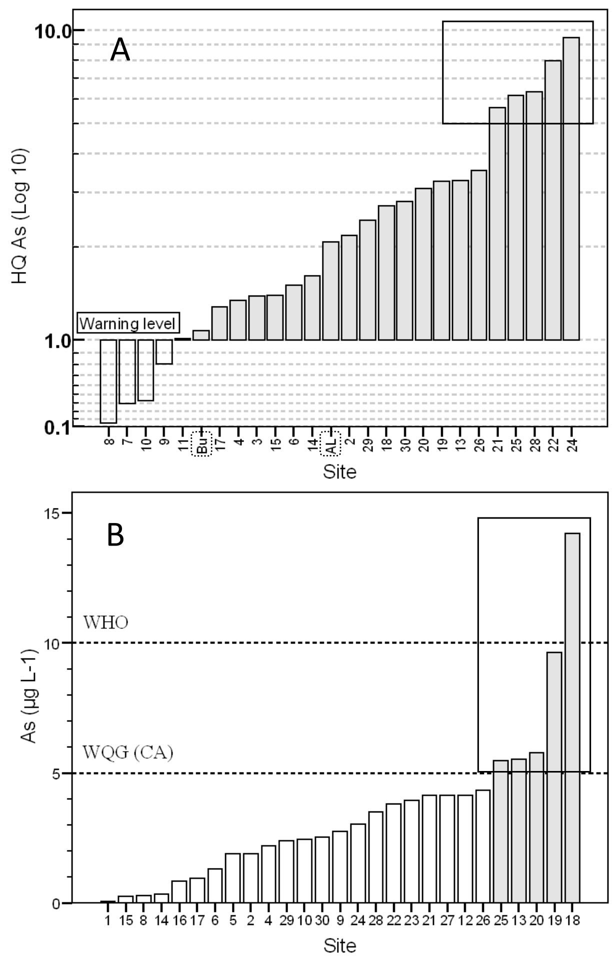

Fig. 6.4
a) Classification of sediment sampling locations according to the hazard quotient (HQ). HQ is expressed as the ratio between sediment arsenic concentrations and the probable effects level (PEL) value, as given by Smith et al. (1996). The locations are as in Fig. 6.1. Bu and AL represent Bubal Lake and Aguas Limpias stream, respectively, both downstream from Respomuso reservoir. Sites with HQ>5 from the south side of the basin are enclosed.
b) Arsenic concentrations in water at sampled locations. The lines across the plot represents the current WHO guide value for arsenic in drinking water and the Canadian guide value for the protection of aquatic life. Locations from the south slopes which exceed these guide values are enclosed.

Daskalakis and O´Connor, 1995). The lack of metal-Al relationship shown by our results suggests, however, that alternative elements, such as titanium (Fig. 6.2), may be a better estimator of anthropogenic enrichment in areas of complex geology.

Hazard quotient assessment. High background levels of potentially toxic trace elements (e.g. As, Cd) in sediment may pose risk to the aquatic ecosystem and its biota and they could be released into the overlying water column. Although little is known about the degree of risk of major contaminants such as arsenic at high altitudes, a preliminary insight of its relative risk is attempted in this section. Relative risk to benthic fauna due to sediment condition was evaluated by using the widely used hazard quotient (HQ) approach. Hazard quotient represents the ratio of the concentration of a chemical over the concentration at which no adverse effects of any kind are expected (Parametrix, 2001). For the computation of HQs, the arsenic concentration at each site was divided by the value of probable effect level (PEL) as suggested by Smith et al. (1996). The reliability of this guideline has been outlined by Hübner et al. (2009). When HQs are less than one, negligible risks are expected, while an HQ value exceeding unity (i.e., 1) suggests a receptor may be at unacceptable risk. The higher the hazard quotient is, the more likely that an adverse effect will occur as a result of exposure to the chemical. HQs greater than 10 suggest a major potential risk (Parametrix, 2001). This approach is useful in identifying areas of high or low risk (USEPA, 1998).

The locations with arsenic HQs greater than 1.0 based on PEL in surface sediments of Piedrafita cirque are displayed in figure 6.4a. The sites # 7, 8, 9 and 10, all located on the granitic half of the cirque (Fig. 6.1), had HQs less than unity, which classifies them as ”Lowest Priority Sites”. Except these sites, all other sampled locations exceeded sediment HQ of 1. Lake Respomuso sediments (i.e. locations #11 and 30) also exceeded the unity although the northern side of the lake, receiving sediments from granite bedrock (#11 in Fig. 6.1) to much lesser extent (Fig. 6.4a). Furthermore, a sediment core extracted in 2002 from Respomuso lake bed had HQ=1.9 in the < 5 cm sediment depth (see also Lavilla et al., 2006). This might indicate a relatively substantial background risk to benthic biota from arsenic. In a hotspot area represented by Llena Cantal lake sub-catchment, at an altitude of ~2450m a.s.l (Fig. 6.1), the HQ for arsenic varied between 5 to about 10 (Fig. 6.4a), being close to the As source area. In theory this area would be classified as a “High Priority Site” with the greatest potential to cause ecological damage. As the sampled sediments are from well aerated stream/lake environments, arsenic bioavailability and its potential to cause biological effects may be further enhanced (Zhuang et al., 1994). This is largely because in highly oxidised sediments, as the metal-binding sites of particles become saturated the sediment toxicity is likely to increase (Zhuang et al., 1994).

The fairly elevated sediment arsenic in Piedrafita cirque then raises a question whether this contamination may extend further downstream. Sediment samples collected in summer 2005 in Aguas Limpias stream (~9km downstream from Lake Respomuso) before flowing through the first populated area (Sallent de Gállego) as well as from Bubal, a reservoir lake ~18 km downstream (not included on map), showed arsenic HQ of about two, and one, respectively, which is within the HQ range values recorded inside the cirque (Fig. 6.4a). This clearly indicates that the extent to which arsenic enriched sediment transportation from the source areas and hence the potential biological effects are likely to range beyond

Table 6.3: Comparison of mean arsenic content (µg L^{-1}) in the snow samples collected in the Pyrenees with snow from areas of North America, Europe and Asia

Location	As, µg L^{-1}	Reference
This study (July 2006)	0.06	-
This study (March 2008)	0.02	-
Filtered snow near Ni factory, N Europe	0.02-3.3	Reimann et al., 1996
Mt. Everest, surface snow	0.18	Kang et al., 2007
Mt. Everest, firn core	0.03	Kang et al., 2007
Arctic Atqasuk, surface snow	0.11	Douglas and Sturm, 2004

the geographical limits of the cirque. The major caution in this interpretation resides yet in the potential development of natural tolerance by the benthic biota to the relatively high background levels (Chaffin, 2003). Certainly further study would be required to understand the pathways and the effects of arsenic bioaccumulation at these altitudes.

3.2 Potential contribution of arsenic by snow

While the analysis of arsenic enrichment showed localised arsenic sources, it also suggests that atmospheric input of arsenic is not likely to be significant in the cirque. The three snow samples collected from the remaining snow patches during July 2006 sampling campaign averaged 0.06 µg As L^{-1}. Furthermore, the 16 fresh surface and subsurface samples collected during late March 2008 had low levels of As (<0.005 – 0.079 µg As L^{-1}; mean As = 0.02 µg L^{-1}). All subsurface snow arsenic contents are similar to values reported for other unpolluted sites such as Mt. Everest firn core (Table 6.3), which implies that long range transport of arsenic contributed by snow in the area must be very limited. Besides, a positive linear relationship of arsenic with the manganese in the snow (r^2 =0.67; $p<0.05$) suggests arsenic being largely of crustal origin (Weiss et al., 1978). While these preliminary data may be limited to make a general conclusion, it seems that aerial arsenic contribution, while low, rests largely on the natural deposition of weathered lithospheric dust especially during warmer periods between snow events.

3.3 Relationship between arsenic in sediment and water

Arsenic concentrations in the aquatic phase were generally low, ranging from 0.06 to 14.22 µg L^{-1} (Fig. 6.4b). The Spanish regulatory limit as well as the WHO guide value for As in drinking water is 10 µg L^{-1}, while the Canadian guide value for the protection of aquatic life is set at 5 µg L^{-1}. The mean As concentration in the catchment streams and small lakes (Table 6.4), as well as in the main waterbody, lake Respomuso (locations #11 and #30 in Fig. 6.1) is well within its limit for drinking water as well as for its guide value for the protection of aquatic life; however WHO limit was exceeded at site #18 (14.22 µg L^{-1}), and As concentration at site #19 was close to the limit (Fig. 6.4b). Additionally, sites # 13, 20 and 25 were also excessive if the Canadian guide value for the protection of aquatic life is to be considered. Majority of these sites (i.e. # 18, 19, 20 and 25) receive runoff from a sub-catchment on slates- quartzite bedrock from the SE and S slopes of the cirque, surrounded by the peaks of Gran Facha, Zare and Forqueta (Fig. 6.1). This may explain the relatively high As concentration found in the water, as these

Table 6.4: Mean and range As water concentrations in the Respomuso catchment and other pristine sites across the world (all values are in µg L^{-1}).

Location	As	Reference
This study*	3.40 (0.06- 14.22)	
South Patagonia lakes, Argentina*	n.d.- <1.20	Markert et al., 1997
Lake Ransaren, Sweden*	0.18	Salbu and Steinnes, 1995
152 headwater lakes in Finland*	0.08- 5.20	Tarvainen et al., 1997
European tundra lakes*	<0.10- 0.30	Moiseenko and Gashkina, 2007
River water (baseline)	0.83	Vaughan, 2006

*Reference natural concentrations (high altitudes or latitudes)

rocks are known to host trace element-bearing minerals such as pyrite and other sulphides (Yang and Blum, 1999). It is plausible that the presence of skarn deposits (i.e. deposits occurring at the contact of granites with limestone), rich in As-bearing minerals, reported in the metamorphic aureole in the area (Subías, 1993) may also account for the relatively high arsenic concentration in the water.

Arsenic in the Respomuso catchment water is generally higher than the riverine water baseline and its concentrations published for other pristine sites in Europe, North and South America (Table 6.4). This may present risk to local biota. While atmospheric input of arsenic in the catchment through snow is fairly low, the PCA provided a strong evidence for arsenic being largely of geogenic origin, arising mainly from natural weathering of parental rock and the mobilisation of sediment-As *via* mineralization processes. Arsenic in water also plotted in the geogenic group of elements

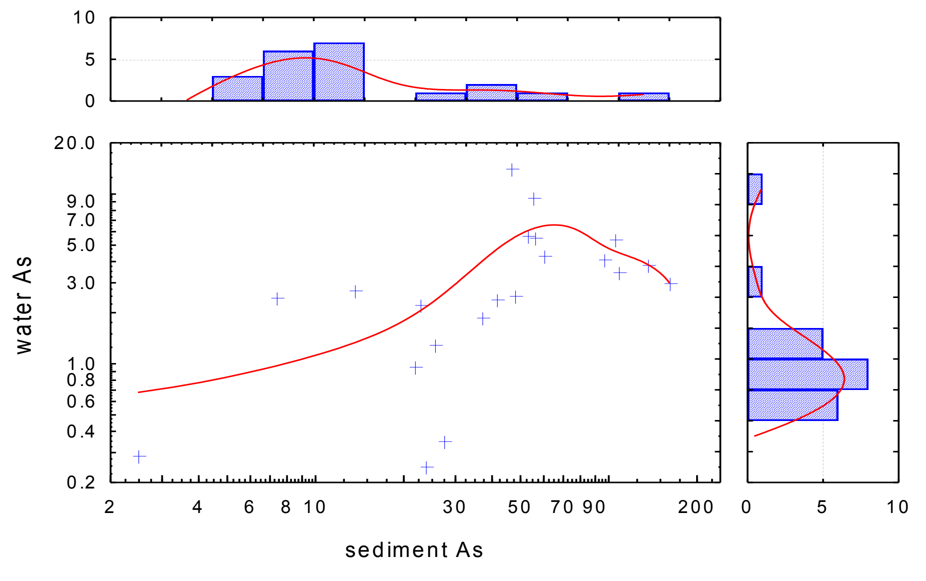

Fig. 6.5 Nonparametric regression (distance weighted least squares) fit line on scatterplot and frequency plots for arsenic in water against sediment. Spearman $\rho = 0.661$, $p < 0.01$.

(Fig. 6.2) indicating its close association with arsenic in sediments. A nonparametric Spearman correlation coefficient (ρ) showed a positive relationship between As in the two compartments (ρ = 0.66, $p< 0.01$; Fig. 6.5) strengthening our hypothesis of arsenic in water being of geogenic origin. However, the absence of a well defined regression fit line is consistent with our findings of localised As sources along the stream courses. It is entirely plausible that the geochemical oxidation of exposed arsenic-bearing sulphides under the oxic condition of the shallow and highly dynamic streams may be responsible for the release of arsenic from the sediments/rocks (Armienta et al., 1993; Prior and Williams, 1996). Further research is however required to assess the extent and nature of arsenic mobilisation processes which control its release from the localised sources identified in this study.

Conclusions

Clearly, this study has established a baseline dataset of natural arsenic levels and its distribution in a high altitude environment. The findings show that the arsenic levels in the Piedrafita cirque are relatively high compared to other similar high altitude/high latitude sites.

The As enrichment levels were usually higher in the headwater sediments than in the lower basin streams and lakes, largely because the source was found concentrated in the headwater areas, characterised by quartzite and slate bedrock which are known to host consistent amounts of metal-bearing minerals. The levels of arsenic enrichment in sediments from the southern side of Piedrafita cirque were significantly higher than those found in the rest of the area and indicative of consistent natural contamination.

Arsenic in the sediments constitutes a considerable burden in the cirque, as its level exceeds the hazard quotient unity for the protection of aquatic life at most sites. HQ exceeding unity has also been found in two locations downstream of the cirque catchment pointing out to a potential extension of the risk beyond its borders. The relatively large sediment-As store poses a possible ecological risk, as it could be mobilised due to changes (e.g. acidity, redox) in the local environment. Further study is required to assess to what extent the levels of arsenic from Piedrafita cirque can affect the local biota as well as the downstream human populations using its water.

The distribution of arsenic and its relationship with other major elements/components (Mn, TiO_2 and Fe_2O_3) and the absence of any relationship with the organic matter indicate that the source of arsenic in the catchment is geogenic. As for the presence of some high arsenic concentrations in the water, the results indicate that it most likely resulted from natural weathering from the surrounding metal-rich geology as well as its mobilisation from arsenic-bearing minerals in the sediments. The analysis of snow shows that long range transport/deposition of arsenic is relatively limited in the area and likely originated in the weathered dust from within or outside the catchment.

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7

Natural metal source mobilisation by climate change threatens altitude environments

Abstract

Recently concerns have been growing regarding the sensitivity of mountain regions to climate change. Here we report on the effects of key climatic factors on trace metals (As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn) accumulation in a lakebed sediment core extracted from a mountain lake in the central Pyrenees. The sediment metal contents showed a general increasing accumulation trend over time, which coincides with recent climate change. Multivariate analysis showed strong associations between trace metal accumulation and a number of relevant climatic factors. The findings further revealed that recent changes in climate patterns such as the elevation of freezing level, a general increase in the frequency of drier periods and reducing snow cover since the early 1980s are likely to be responsible for the increased accumulation of trace metals observed. Arsenic and nickel in surface sediments exceeded their safe concentrations for the protection of aquatic life, pointing out to a significant hazard for the exposed ecosystem.

As most climate models predict further climate change over the next decades, it is likely that mountain catchments on metamorphic basins may become significant sources of trace metals, with potentially harmful consequences for the wider environment.

Keywords: climate change, trace elements, mountain lake

1. Introduction

Crossing certain boundaries of climate thresholds could have disastrous consequences for mankind, including major changes in other global systems, such as the water and geochemical cycles (Rockström et al., 2009). Similar to Polar Regions, high altitude environments are generally more sensitive to climatic change and hence are likely to experience the consequential effects first. This sensitivity comes from the closer interaction between the general circulation of the atmosphere and the orography, resulting in greater changes in the local environment, e.g. cloud formation and precipitations, snow/ice level, surface moisture regime, heat transfer on the vertical and foehn winds (Geiger, 1965; Beniston et al., 1997). This is supported by the rise in temperature observed in mountain regions in the last three decades, which in some places is about five-fold greater than the global warming average (Diaz and Bradley, 1997; Beniston et al., 1997).

Shifts in weather patterns, particularly temperature and precipitations were shown to strongly impact the mountain catchments through changes in hydrology, snow cover, weathering regime, soil erosion, all these directly influencing the biogeochemical cycles (White and Blum, 1995; Sommaruga-Wögrath et al., 1997; Camarero et al., 2004).

In alpine and subalpine catchments the biogeochemical cycling of trace elements (TEs) is generally governed by a weathering-limited regime (Stallard and Edmond, 1983). The geogenic inputs of TEs to mountain lakes may however be enhanced by climate change (Román-Ross et al., 2002) driven weathering of metal-bearing minerals. Increased mobilization of TEs (due to enhanced weathering of metal-bearing minerals) can have adverse impacts on the wider environment, including water quality (Savage et al., 2000) and human health (Charlet and Polya, 2004).

Despite various attempts to understand the influences of climate/environment change on mountain geochemical processes (Psenner and Schmidt, 1992; Sommaruga-Wögrath et al., 1997), the potential impact of climate change on TEs release in mountain catchments remains a major question, partly due to the complex nature of the processes involved. Secondly, any direct approach is not likely to provide reliable information on how weathering/mineralisation may have changed through time and on its coupling with climate change.

Lake sediments are one of the endpoints for trace elements emitted from both natural and anthropogenic sources; they can provide an accurate archive of changes in the surrounding landscapes (Yang et al., 2003), including geochemical cycling of TEs. Here we examine the potential effects of a number of climatic factors on trace element accumulation in a Pyrenean lakebed sediment core, covering > 3 decades of historical record.

2. Hydrological and geological settings

2.1 Hydrology and climate

Reservoir lakes are generally good sentinels of climate change as they can reflect changes in the catchment environment over given periods of time since their construction, usually by erecting dams (Williamson et al., 2009). The study was conducted in the headwaters of Gallego river (Bubal lake catchment), a postglacial valley in the Central Pyrenees (42.68-42.85N, 0.18-0.42W, Spain; fig. 7.1). This catchment, of about 305.5 km^2, follows a north-south orientation and is characterised by a series of interconnected lakes and typical altitude streams that drain water from the surrounding mountain slopes. Some of the lakes were transformed into reservoirs in the 1950s-60s and have been used since then for both hydroelectricity and supplying water for agriculture and potable purposes in the valley and the region further downstream. Gallego is the main river in the valley to which all the tributaries and lakes discharge (fig. 7.1). The average annual precipitation in the catchment is 1077mm (averaged 1972-2005), with the mean annual outflow of the largest lake Bubal of 382 hm^3 (MMA, 2006). The sediment input to lakes is primarily supplied during spring melts and precipitation events and to a lesser extent by the permanent tributaries during dryer inter-periods. The reservoir’s basin follows the relatively steep slopes of the valley with the sedimentation taking place mainly in its deepest parts.

Snow-thaw and rainwater comprise the major water input and no significant industrial or extensive agricultural activities exist/existed in the region. Therefore, the potential source of trace elements (TEs) is mainly from the surrounding geology.

The dominant air mass direction in the area is

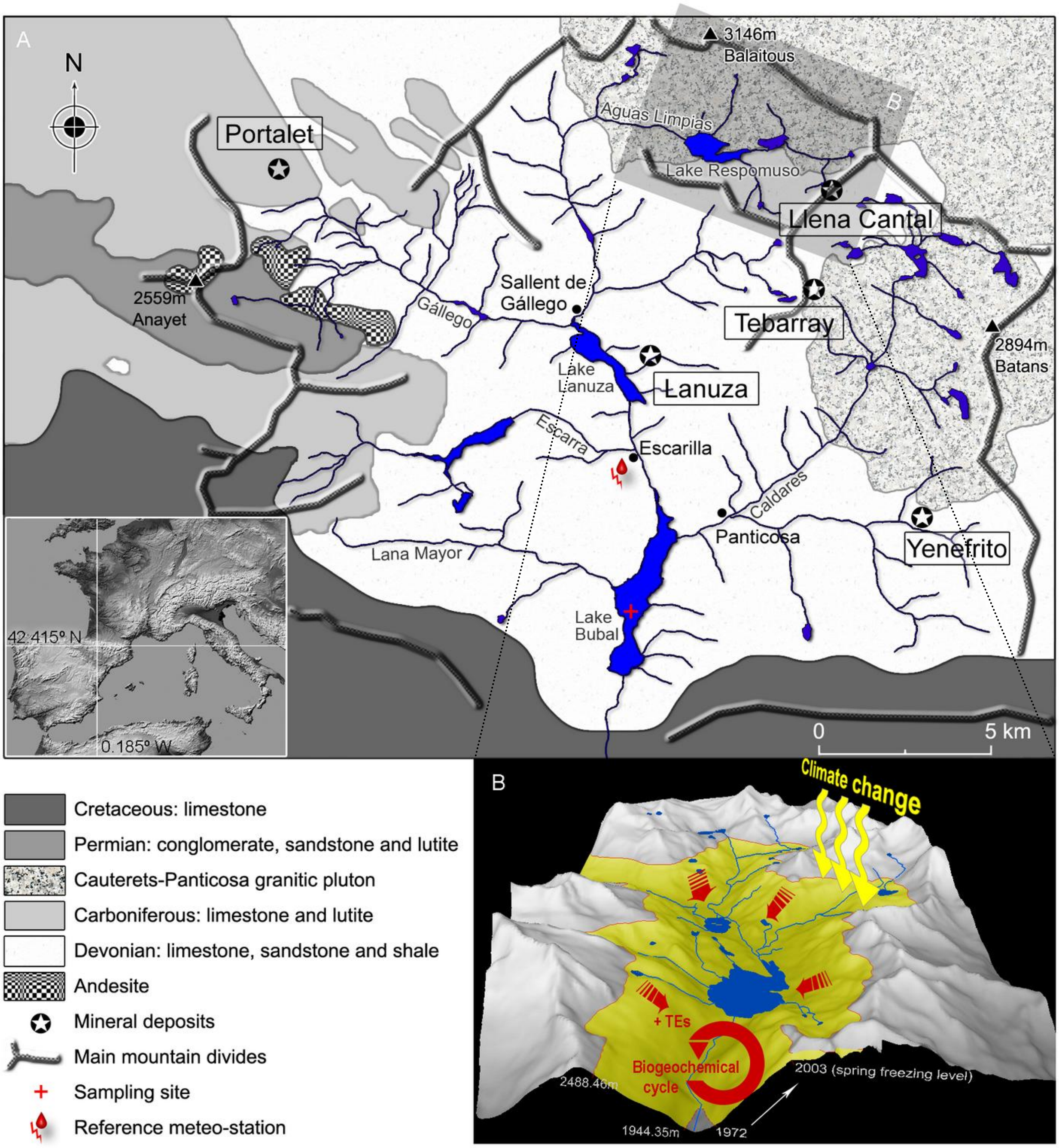


Fig. 7.1 Hydro-geological context of the Gallego river headwater catchment in the Central Pyrenees (A) with the representation of mineralization areas and the sampling sites. Inset (B) is a conceptualised example illustrating the increased TEs release in the catchment following the sharp elevation of spring freezing level (increasingly unfrozen surface, in yellow) and changes in climate patterns in the past three decades. The estimates show that a great part of the catchment (or above 1944 m above sea level) was snow covered before 1972 but that coverage dramatically decreased in recent years (yellow area). For this representation a digital elevation model of Respomuso subcatchment was used.

from W-NW bringing precipitations mainly from the Atlantic (Dessens and Bücher, 1997). Hence, the long-distance aerial transport of contaminants must be limited in this region. The bulk precipitation in the Central Pyrenees is more alkaline than in other Central European sites (e.g. Alps) mainly due to lower acidic pollutant levels (SOx and NOx) (Camarero and Catalan, 1993). There is also a reported decrease in acid depositions in the high Pyrenees during the last decades following the overall reductions in industrial emissions (Mosello et al., 2002).

2.2 Geology

The area is dominated by Devonian deposits (limestone, sandstone and lutite) surrounded by Permian and Carboniferous materials west and Cretaceous limestone south (Fig. 7.1). This geology is marked by the extrusion of Cauterets-Panticosa granitic batholith on the NE which generated a low-grade contact metamorphism aureole (Subías and Fernandez-Nieto, 1995). This has significant presence of W-Au skarn and F-Zn-Pb vein mineralisations formed in the Devonian limestones that contain fluorite (CaF_2), sphalerite, galena (PbS), pyrite (FeS_2), chalcopyrite ($CuFeS_2$), siderite ($FeCO_3$) and green and white fluorite (Subías, 1993). These deposits, known since the mid-seventeenth century, were mined for lead, silver and fluorite (Subías and Fernandez-Nieto, 1995). Pyrite in mineral deposits has As concentrations reaching 250± 40 mg kg-1 (Subías, 1993), while the hosting rock As content is relatively smaller and more consistent (87.5±0.5 mg kg-1) (Subías, 1993). This suggests that pyrite in the veins is a potential geological source of As. Geogenic input of As and other metals has been reported in the waters and sediments of this zone, particularly in the eastern side (Garrido, 2002; Zaharescu et al., 2009) (Fig. 7.1).

The economy in the valley is mostly tourism dependent. Vegetation cover and land use have not changed markedly over the last decades.

3. Methodology

3.1 Sample collection and profile characteristics

The sampling strategy was designed to cover the sedimentary record from the major catchment depository: Lake Bubal, 1085 m a.s.l. (Fig. 7.1). A sediment core was extracted from the lake in bathymetric depression toward the edges of the reservoir’s former river and where the interferences from sediment slumping or turbidity were minimal. The sampling was conducted in the summer of 2005 when the lake level was low due to an extreme drought. The cobles and forest soil at the bottom of the core clearly indicated the depth above which the new deposits were formed. The core was therefore expected to comprise a record starting from 1972, the year when the river was transformed into a reservoir.

The core was mostly brownish, indicative of oxic environment. Sediment organic content (determined as % loss-on-ignition, LOI) was low (3.39±1.5%). The profile, visually composed of fine alluvial sediments (silts - fine sands) showed a continuous record of sedimentation and no important textural evidence of erosion. It is known that, in the absence of significant changes in core texture, the variation in trace element contents along the sediment profile can reflect the historical variation in metal input (Santschi et al., 1984; Mecray et al., 2001). Likewise, we assumed the effect of bioturbation in central lake sediments to be relatively small.

The core was sectioned in the field using a stainless steel slicer at 1.5 cm intervals. This is consistent with the averaged deposition of 1.5 cm year $^{-1}$ for the core extracted from upper Lake Respomuso (Lavilla et al., 2006; Fig. 7.1) and also the relatively low depositional rates reported for other Pyrenean reservoirs (Valero-Garcés et al., 1999). It also roughly corresponded to the sedimentation laminae (probably produced during spring thaw) along the profile, which implies sediments were not disturbed by mixing. Climate data were provided by the Spanish National Institute of Meteorology, Madrid (INM) and covered the period 1972-2005.

3.2 Sample preparation and digestion

The samples were oven dried at 40ºC for 2 days, gently ground using ceramic pestle and mortar. The ground sediment was sieved through a 0.25mm sieve, homogenised and stored in plastic bags until analysis. The < 0.25mm sediment fraction was then subjected to digestion following USEPA Method 3050B for ICP-MS (US EPA, 1999). This method is able to extract the trace elements (TEs) that could become environmentally available (US EPA, 1999). It will therefore represent an estimation of pseudo-total metal content in the sediments.

3.3 Trace, major elements and organic matter analysis

As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn were determined by inductively coupled plasma mass spectroscopy (ICP-MS), using standard operating conditions and following standard QA/QC protocols. The ICP-MS was highly sensitive for the elements in terms of detection limit and reproducibility.

The analysis was subjected to quality protocols to avoid random errors. Replicated certified reference materials (standard reference sediments SRM 2704, GSD-1 and GSD-4), and reagent blanks were used to estimate the accuracy of the analytical method. Additionally, sample duplicates were analysed at the same time for the analytical quality control procedure.

Overall the analysis was highly reliable with variability, %CV between replicates and between measurements of the same sample being < 5%. The coefficient of variance for Cd, which was about 25%, was not satisfactory enough. However, when concentrations are close to the detection limit, %CVs may be high but they are still acceptable.

The percent recoveries of the analysed elements were generally consistent with the test used.

Major minerogenic elements Al and Li were characterised following USEPA Method 3051A for ICP-OES (US EPA, 2007). A portion of 0.1g dried sediment was ashed at 550ºC for 10 hours to remove organic matter before being digested using 1.0 ml H_2O, 0.5 ml HCl, 1ml HNO_3 and 0.1 ml perchloric acid ($HClO_4$). The samples were subjected to ultrasound assisted digestion at 60ºC for 15 min, then kept on 125ºC sand bed until nearly complete evaporation. A certified reference material from the National Water Research Institute of Canada (CRM WQB3), procedural blank and three samples were analysed in triplicate to optimize the accuracy, reproducibility and recovery rate of the extraction procedure. After digestion, samples were filtered through Whatman filter 541 and made up to 50 ml with MiliQ ultrapure water.

PTF Teflon beakers were used throughout the analyses. All reagents were ultra-pure Aristar grade. Stock standard solutions were Merck Certificate AA standards. Milli-Q water was used in all samples, dilutions and standard solutions, as appropriate.

Organic matter content was estimated gravimetrically as loss on ignition (% LOI) of 3g dried sediment sample at 550ºC for 4h (Rowell, 1994). This method excludes the inorganic carbon bound in carbonates.

3.4 Statistical analysis

Data representing average monthly temperature and precipitation at Bubal included: maximum and mean temperature, total precipitation (mm), and the frequency of days with rain, snow, hail and storm. The climate was reconstructed from the monthly means of variables at Escarilla reference station (1170m a.s.l.; Fig. 7.1) (Agustí-Panareda et al., 2000). The freezing level was estimated from the mean monthly air temperature at a standard adiabatic lapse rate of 0.65ºC/100m (Thies et al., 2007).

Where temperature values were missing in the reference (Escarilla) dataset, the gaps were completed with data from the nearest neighbouring station after previously making corrections for the monthly mean differences between the nearest (previous and subsequent) common years (Rosenblüth et al., 1997; Peterson et al., 1998). Except for 6 cases (months) for which the average temperature needed to be transferred from a lower station (60km south), the stations used for correction were all in the valley within 7 km radius of the main station. The accuracy of the method was tested using various methods. First, a Pearson product moment correlation of the instrumental data between stations showed coefficients > 0.8 at above 99.9% significance level. Subsequently, a cross-validation test (Michaelson, 1987) found reasonably low errors, considering the mountain topography, of < 0.63ºC/month between the obtained values and the instrumental records. Furthermore, the interpolated and the measured values were highly related (r^2> 0.97). This indicated that the method used was reliable. Precipitation (amount and frequency) variables did not require transformation as the station used for correction was within 1km distance from the reference station.

To filter out the interannual variability/noise, and therefore increase the interpretability of the long term behaviour of climatic factors, the variables were smoothed along time using locally weighted scatterplot smoothing (LOESS). A 0.5 parameter (α) was used to infer major modifications in temperature and precipitation patterns between the beginning and the end of the record period.

The multivariate association between sediment components (i.e. trace and major elements) and the predictor climatic variables were tested by principal component analysis (PCA). For this analysis LOESS filtered climate variables at a span α =0.1 were used, allowing substantial variation to be captured in the model. Likewise the TEs (i.e. As, Co, Cr, Cu, Mn, Ni, Pb and Zn) were summarised as regression factor scores of PCA before useing them as response variables. The data were manipulated in SPSS, Statistica and Statistix packages for Windows. Moreover, an exemplification of the increase of spring freezing level along the record period was represented on a digital elevation model in ArcInfo package.

4. Results and discussions

4.1 Geochemical sources of trace elements

The principal component analysis (PCA) identified two factors (PC1and PC2)
that accounted for most of the variability (76%) in trace and major element

accumulation in the sediment core (Fig. 7.2B). The factors related As, Zn, Cu, Ni, Pb, Mn and Cr with both major mineral constituents, Al and Li. This association supports the geogenic origin of these TEs. Trace element distribution profiles in the sediment core over time show a similar pattern (Fig. 7.2A). This pattern could be caused by (a) redox-driven remobilisation within the sediment column, and (b) increased mobilisation from the catchment. The common distribution pattern of profiles (Fig. 7.2A) together with clustering of the elements (Fig. 7.2B) clearly demonstrates that the observed changes are not due to any remobilisation as this would have separated the elements into two distinct groups, i.e. redox sensitive (As, Co, Cr, Mn, and Ni) and non-sensitive (Cd, Cu, Pb, Zn, Al and Li) elements. The clustering of all these elements together points out clearly to a common origin as well as mechanism of their mobilisation e.g. via erosion and burial. This is further supported by the major elements Mn, Al and Li, which are components of well known trace metal bearing minerals such as aluminosilicates and metal (hydro)oxides. Given the regular inflow-outflow of water in/from the reservoir, largely ice-free winter and a low sediment organic content (3.39±1.5%), it is not surprising that no evidence of redox-driven change in TEs mobilisation was found, the geochemistry of the core being generally intact.

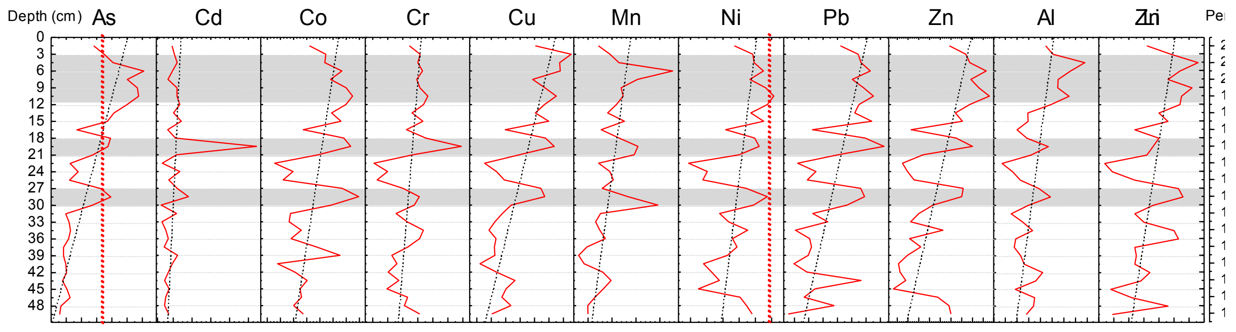
Surprisingly Cd plots apart, indicating no association with the TEs cluster. This, however, could possibly be due to an unusually large peak (Fig. 7.2A) in its sediment profile, offsetting the expected correlation.

4.2 Changes in metal concentrations along the sediment profile

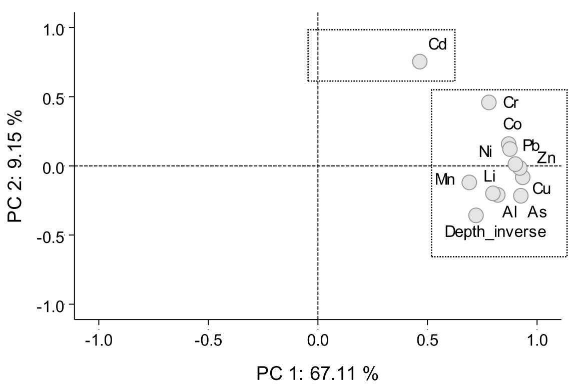
The sediment column trace element contents show a relatively low variability, with CV% of 8.7-27.9% (Table 7.1), reflecting the extent of the variation in their input from the catchment. Except Cd and Cr, all other TEs show increasing trends along their profiles, from lower values in the 1970s and the 1980s to higher concentrations in recent years (Fig. 7.2A). This trend was also supported by a significant association of TEs with depth (Fig. 7.2B). Three clearly visible trace element peaks in the depth profiles were observed at 27-30cm, 18-21cm and a relatively broader increase between 3 and 12cm depth (Fig. 7.2A). This points out to three major metal input events, corresponding

Table 7.1: Descriptive statistics of trace element content (mg kg^{-1} dry weight) in the < 0.25mm sediment fraction of Bubal lake core

	Al	Li	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
Minimum.	13439.0	62.0	11.1	0.24	16.6	16.2	12.4	460.6	25.8	19.1	83.2
Maximum.	27574.0	93.0	22.2	0.74	23.0	27.8	25.1	853.4	36.3	32.5	127.9
Mean	19050.5	78.1	15.1	0.31	19.8	20.9	18.0	596.8	32.0	25.7	104.5
SD	3280.8	8.2	3.5	0.09	1.9	2.3	3.7	86.3	2.8	4.0	13.6
CV(%)	17.2	10.5	22.9	27.9	9.4	10.9	20.3	14.5	8.7	15.5	13.1



A



B

Fig. 7.2 Depth profiles of (A) trace and major elements (mg kg^{-1}) in bottom sediments of Lake Bubal (Central Pyrenees), with major trends represented by dashed black lines. The elements exhibit clearly visible peaks in concentrations at 27-30, 18-21 and 3-12 cm depths. Vertical (dashed) lines in red represent sediment guide values for the protection of aquatic life (CCME, 1999). (B) A principal component analysis plot showing the relationship between trace and major element contents in the lakebed sediments and their variability with depth.

to the estimated periods 1985-1987, 1991-1993 and 1987-2003, respectively. One possible reason for the general increasing TEs deposition in the sediments could be due to an increased air-borne proton input mobilising metal-bearing minerals in the catchment. It is also possible that this could be an outcome of increased weathering of bedrock mineralogy driven by change in the climate.

Rain acidity and airborne pollution inputs are relatively low in the Pyrenees compared to other European mountain ranges, and they have significantly decreased with the implementation of industrial emission control technologies since the early 1970s (Mosello et al., 2002). This means acidity input is not likely to have increased the mineralisation/ dissolution rates. Catchment vegetation is also not likely to be responsible for TEs mobilisation, as the land cover has not undergone any major changes during the record period. Inevitably this leaves climate change as the most probable driver of TEs mobilisation through enhanced weathering. For this here we evaluate the impact of climate change on the sediment metal accumulation record for the sedimentation period, 1972-2004.

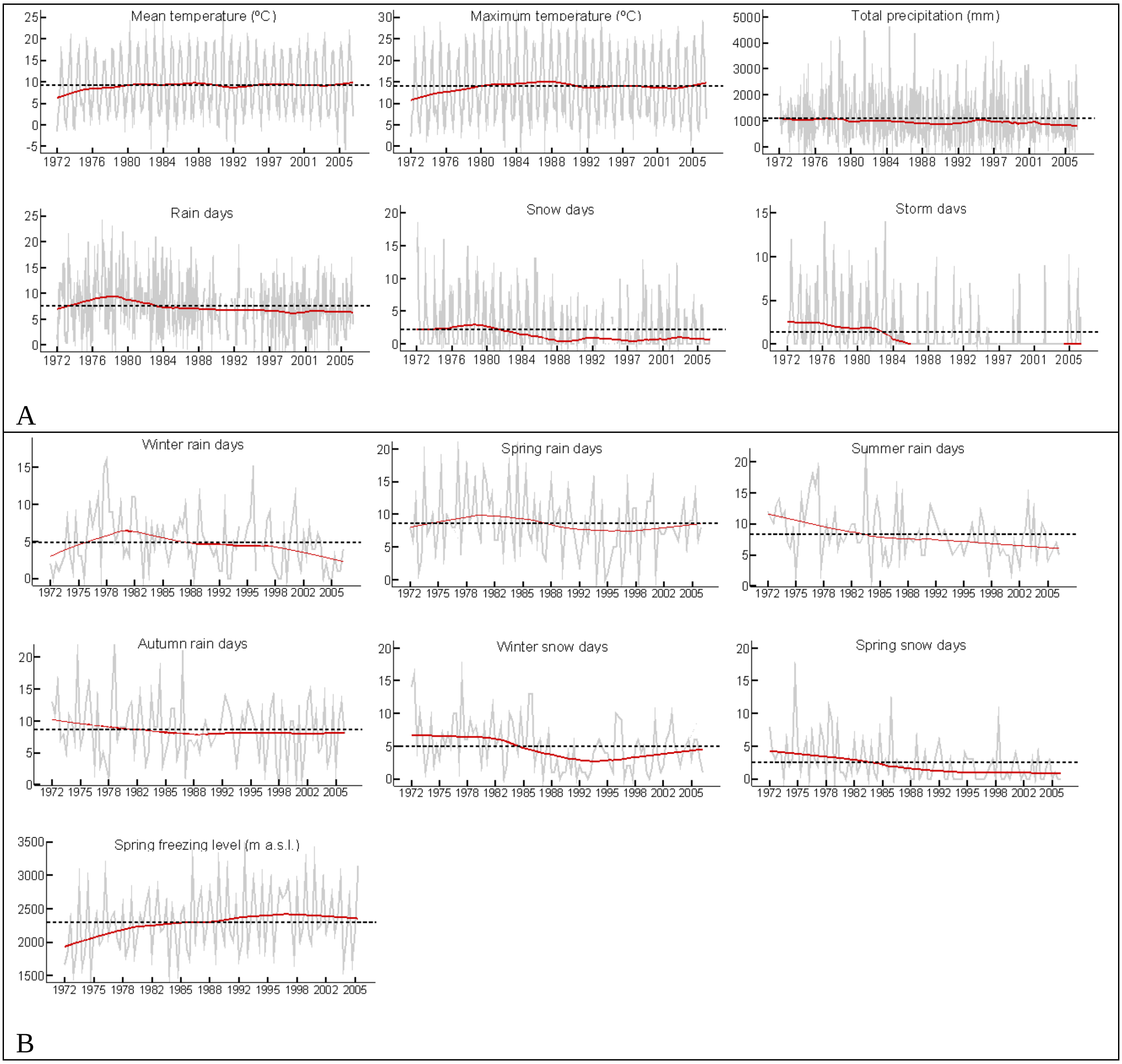


Fig. 7.3 (A) Trends in monthly precipitation and temperature variables in Bubal lake catchment during the 33 years period (1972-2005). Long term trends are indicated by LOESS fit line at 0.2 (α) span. Dashed horizontal lines are set at mean values. (B) Seasonal behaviour of frequencies of rain and snow days, and freezing line in the catchment. A 0.5 (α) span LOESS fit line (red) outlines the major trends. Dashed horizontal line represents mean value of the period.

4.3 Relationship between climate and trace element records

The annual temperatures in Bubal lake catchment showed decadal fluctuations with overall increases between the late 1970s and the early 2000s of about 1.34ºC and 1.38ºC for the mean and maximum temperatures respectively (Fig. 7.3A). This is similar to the global temperature rise in mountain regions, and is more than twice that for the northern hemisphere average (Carrasco et al., 2005; Sommaruga-Wögrath et al., 1997). The precipitation amount slightly decreased (4.06%) over the period; however the frequency of rain and snow days decreased by 19.35 and 41.84%, respectively. This indicates that precipitations became less frequent but more intense. This obviously indicates substantial reduction in permanent streamflow but increase in temporary runoff and drier soil surfaces.

The seasonal changes in the climatic parameters broadly followed the annual trends, with lower frequency of winter and spring snow and rain events, particularly since the late 1980s (Fig. 7.3B). This reveals a shift in the climate scenario since the late 1980s/early 1990s to mildly warmer seasons with drier winters, and less snow accumulation. The rise in temperature also meant an elevation of the freezing line by about 544m altitude (from 1944m in 1972 to 2488m in 2003), with consequential increase in the catchment surface area remaining below 0ºC isotherm (i.e. uncovered, Fig. 7.3B and Fig. 7.1B).

The aforementioned changes in temperature, precipitation and freezing line could alter weathering processes, snow-cover period, water bodies' heat balance and metabolism (White and Blum, 1995). All these could result in greater mobilisation and transport of TEs in the catchment. To test if climate change coincided with the increased trace element accumulation in the lakebed sediment, we evaluated the dataset by principal component analysis.

Spring freezing line, record period, sediment content of trace and major mineral constituents, were inversely associated with the precipitation variables and projected together on the first component (Fig. 7.4).

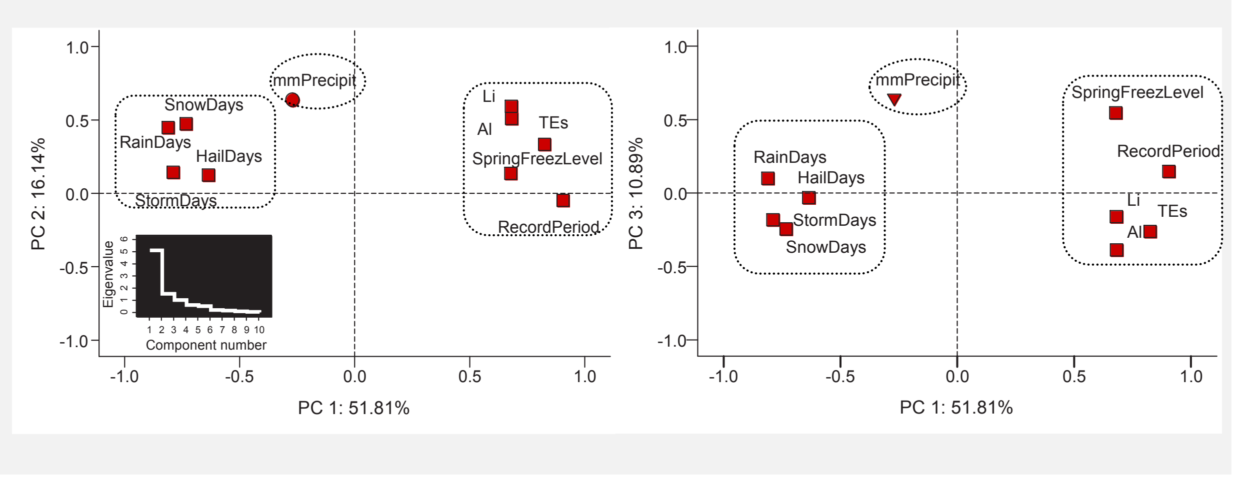


Fig. 7.4 Relationship between climate variables (as LOESS predicted values at 0.1 span), trace elements (As, Co, Cr, Cu, Mn, Ni, Pb and Zn, summarised as PCA regression factor scores), major elements aluminium and lithium, and record period shown in the projection of PC1- PC2 and PC1- PC3 of principal component analysis. Figures highlight a tight relationship between sediments trace elements input, precipitation frequency and spring freezing level, thus supporting the hypothesis of an increased metal mobilisation with climate change. Symbol key: ■- elements correlating to PC1; ●- element correlating to PC2 and ▼- element correlating to PC3. "mmPrecipit" stands for precipitation amount.

This means an increase in drier periods (as defined by the frequency of precipitation events) could have increased weathering of the catchment slopes/geology, possibly enhancing the amount of trace elements release/burial into the lakebed sediments. This is consistent with chemical weathering of metal sulphides, e.g. pyrites, which during the dry span within the wet-dry cycles oxidise to metal sulphates and oxides. During subsequent wet cycles these metal-rich weathering byproducts can easily be lixiviated/flushed (Van Griethuysen et al., 2005) into the catchment waterbodies, being aided by relatively poorly developed soils on the mountain slopes. The climate change mediated increased weathering is further supported by the plotting together of catchment major weathering indicators (Al and Li) with TEs in the sediment.

The reduction in snow-cover, together with the elevation of spring freezing line (increasingly unfrozen surfaces) also seems to have contributed significantly to enhanced release of TEs by exposing additional rock/soil surfaces to weathering processes (Rogora et al., 2003). It has been shown that weathering rates in granitic catchments may increase about one order of magnitude when uncovered mineral surface experiences substantial warming while precipitation volume is constant (White and Blum, 1995). Such increases in mineral surface temperatures are possible during spring/summer on the south facing slopes of catchments that remain increasingly snow-uncovered especially when precipitation is also scarce. In Bubal lake catchment, the drainage of mineral deposits from the Panticosa-Cauterets metamorphic belt is the major potential source of TEs (Fig. 7.1). These ores have significant presence of TEs in vein-type mineralization with As contents as high as 250 ± 40 mg As kg^{-1} (Subías et al., 1993). These As/TEs containing sulphides can oxidise relatively rapidly under neutral pH and therefore naturally release As and other elements in the environment at high rates (Davis et al., 2006), being aided by a relatively high diffusion factor of oxygen in drier surfaces. Total precipitation, which is usually ascribed to intensify weathering, showed however, no particular influence. This would suggest that the pattern of precipitation in this case was more important than the total amount of precipitation in TEs mobilization mechanisms.

4.4 Potential hazard to the wider environment

The incremental metal release with changing climatic conditions raises then the question on potential risks to the environment. Arsenic in surface sediments (<15cm) exceeded its safe guide concentration of 17 mg kg^{-1} for the protection of aquatic life (Smith et al., 1996, CCME, 1999; Fig. 7.2A). This is significantly important since arsenic is a priority carcinogenic pollutant ranking first in international hazard substances lists. Nickel also crossed its safe value of 36 mg kg^{-1} (CCME, 1999) in surface sediments (Fig. 7.2A). Sediments with one or more TEs exceeding safe limits are considered to represent serious hazard to the exposed ecosystems (CCME, 1999) and can pose significant threat to the wider environment and human populations especially when they occur at elevated natural background concentrations (CCME, 1999; Dani, 2010). Such high background As and Ni exceeding safe levels have been reported for surface sediments and water at the north of this catchment (Zaharescu et al., 2009) increasing therefore the hazard risk from these elements. Commonly, mountain reservoirs are at least partly located on fluvio-glacial gravel and the corresponding aquifers are used for drinking water. Mobilization of sediment-borne contaminants into the water column may occur in these lakes as a result of water management or pH/redox changes due to regional climate change (Van Griethuysen et al., 2005). These changes may trigger an inevitable environmental risk of the contaminant load.

Conclusions

We acknowledge that the relationship between climate change and TEs mineralisation/ mobilisation and their accumulation is complex. Here we provided evidence of changes in key climate variables and TEs accumulation in lakebed sediments. The data analysis demonstrated a reasonable link between the key climate drivers and the increasing trend of TEs accumulation in the sediment. Arsenic and Ni, two hazardous elements, crossed their safe concentrations for the protection of aquatic life in surface sediments. This points out to potential threat to the wider environment, especially as these TEs come associated to high background levels in the catchment. Given that most climate models predict serious modifications in climate patterns over the coming decades, it is likely that mountain catchments on metamorphic basins may become increasingly impacted by elevated TEs levels, with potentially adverse consequences for the ecosystems and beyond. To determine whether the increased mobilisation of natural metal sources is an extended and ongoing process there is an urgent need of large scale surveys in such sensitive regions.

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8

SUMMARY and PERSPECTIVES

Keywords:
High altitude lakes, landscape processes
Ecosystem formation: hydrodynamics, geo-morphology, topography formation
Ecosystem functioning: riparian vegetation structure, littoral zoobenthos structure, biota sensitivity to the environment
Hazard risks: trace metals, distribution, levels, source, mobilisation, link with climate change

8.1 SUMMARY OF FINDINGS

High elevation lakes are generally pristine waterbodies with a key location at the top of the landmasses. This allows a close interaction with the general circulation of the atmosphere which gives them a high sensitivity to changes in the surrounding environment. Moreover, there is a growing need in environmental sciences to understand how processes within a sensitive ecosystem interact with external factors, and how these can affect current and future ecosystem dynamics. This work was motivated by our interest in landscape processes on elevated topography and the goal to achieve a synergistic understanding of how altitude environment including climate, geochemistry and landscape shape the structure and functioning of these waterbodies with particular emphasis on their ecological and geochemical characteristics. One of the main challenges in addressing such fundamental problems resides nonetheless in that the ecological and geochemical processes on alpine surfaces are generally difficult to test due to a number of limitations including the difficulty of accessing/sampling large and rough terrain, the many direct and indirect linkages between landscape features and processes involved, and the short period of time landscape features are visible. To overcome these difficulties I chose a sampling area which encompasses a relatively high density and diversity of altitude waterbodies in the central Pyrenees, roughly 80 km across. Moreover, I worked in often large teams to conduct intense sampling of large surfaces over relatively short periods of time, which allowed a comprehensive assessment of the waterbodies. Finally I employed approaches spanning various disciplines for sampling, sample processing, data analysis and interpretation.

The aim of my work was to identify key aspects of ecotopic and ecosystem structure and functioning at high altitude lakes, as well as potential hazard risks from geogenic metal loads. It is expected that a deep insight into the processes occurring at these sites can bring out desirable attributes with potential application for the wider environment. I achieved significant understanding of lake's ecotope and ecosystem formation and functioning, together with the depiction of a number of potential hazards arising from the local geology. Knowledge of these aspects advances the understanding of landscape ecological and geochemical processes at high elevation lakes and will strengthen their use as sensors of global environmental change, a core in the global monitoring of the mountain biome.

The specific objectives were:

1. Evaluating the role of landscape factors in ecotope structuring at altitude lakes, ponds and pools;
2. Assessing the influence of external (geoposition and catchment) and lake (sediment and water physico-chemistry) variates on riparian vegetation structure;
3. Measuring the degree of response of littoral biota to terrestrial and aquatic factors;
4. Ascertaining the extent of contribution and the distribution of a number of trace metals in sediments and water from a whole catchment perspective, together with the relationship they might have with local mineralogy. Likewise to predict the potential effects on the local biota;
5. Examining the arsenic source mobilisation from source areas of an altitude catchment, and
6. Determining the potential relationship between changes in climate parameters and trace metal release and accumulation in lakebed sediments covering more than three decades of historical record.

The results were developed in six papers organised in two sections:

Part I: Ecosystem structure of high altitude lakes

The architecture for ecotope formation at high altitude lakes

Generally, lake ecosystems are governed by a physical template, i.e. ecotope, which includes geomorphology, climate and surrounding land cover. This paper attempted to elucidate the role of catchment features in lake ecotopes at high altitudes. For this a wide range of landscape variables were sampled from practically the full spectrum of waterbodies, i.e. from large lakes to small ponds (n=354), in a region of high lake density the central Pyrenees.

Three major composite factors can explain the lake ecotope characteristics. They were: (i) hydrodynamics, (ii) bedrock geo/morphology, and (iii) topography. Of these, bedrock geo/morphology and topography formation also showed significant coupling with altitudinal and latitudinal gradients in terms of their influence on ecotope formation. An analysis of related categories forming each factor allowed a typification of water-bodies into a number of ecotope units, which were characterised by particular landscape parameters. These units represent distinctive abiotic settings for flora and fauna communities at these altitudes.

The results indicated that the structure of different high altitude lake ecotopes is determined by hydrological, geo-morphological and topographical drivers, and follows large geographical gradients. This was interpreted as a major evidence of the Holocenic landscape evolution, following the glaciers' retreat circa 11 000 years ago, which created particular physical niches for biota settings. Here I also proposed a conceptual model of lake ecotopes at high altitudes, which integrate physical, geological and climatic processes that shape their formation. Our conceptualised model can be further used in both scientific hypothesis testing and improving policies on altitude lake management and conservation. This is important as ecological studies often require diverse and well defined habitat units where processes are to be studied.

An ecotope perspective of riparian vegetation at high altitude lakes

Riparian zones are the delicate interfaces between aquatic and terrestrial ecosystems. Limitations from ecotope characteristics in altitude lakes, together with tight interactions among its components and the wider environment can determine the settlement and functioning of unique vegetal communities near these waterbodies. This then raises a fundamental question on how riparian communities interact with the surfaces they inhabit at these sites, a process generally poorly understood. To disentangle this process the riparian vegetation species structure was analysed in correlation with a number of composite landscape, geochemistry and geolocation factors from an area encompassing a total of 189 highly protected lakes and ponds in the central Pyrenees. Secondly I tested for species co-occurrence patterns and their ecotope preferences.

Complex interactions between hydrodynamics, topography and geo-morphology it was found to explain the riparian vegetation structure around the Pyrenean lakes. This catchment scale variability in vegetation composition was considerably related to latitudinal and altitudinal gradients, possibly a signal of larger climatic transitions between the paneuropean zones Continental, Atlantic, Mediterranean and Alpine affecting this region. At the local scale, sediment Mg and Pb, and water Mn and Fe contents influenced the vegetation structure. This is likely a reflection of bedrock geology and hydrological fluctuations in the riparian zone.

By analysing species co-occurrence behaviour I identified 4 riparian phyto-communities of relatively large niche breadth, which characterise different lake riparian environments. These communities showed strong preferences for (i) damp ecotones, (ii) snow bed-Si bedrock, (iii) wet heath, and (iv) one group possibly indicative of calcareous substratum. The findings have implications for the understanding of the mechanisms behind riparian vegetation establishment and distribution at high altitude waterbodies and their potential response to environmental variations.

Ecological sensitivity of littoral organisms to local and large scale variates at high altitude lakes

At alpine waterbodies, littoral zones together with riparian surfaces generally harbour a rich diversity of life forms, far exceeding that of the surrounding landscape. Likewise, in these oligotrophic systems catchment and riparian production is critically important for the littoral food webs; hence they can potentially have profound effects on ecosystems. An imperative problem is therefore to understand the sensitivity of littoral ecosystems to the challenging catchment and waterbody characteristics (e.g. ecotopic and ecological). A survey of 114 altitude waterbodies in the central Pyrenees was undertaken to quantify the degree of response of major littoral macro-zoobenthos taxa to a complex pool of environmental factors. At each location benthic invertebrates' family composition was recorded together with geolocation (altitude, latitude and longitude), landscape (composite hydrodynamics, geo-morphology and topography), riparian vegetation structure, presence of vertebrate predators (trout and frogs), water pH and conductivity.

Overall, the littoral ecosystem was highly sensitive to external ecotopic factors as well as to riparian vegetation structure. The zoobenthos responded considerably to the composite factors topography formation (through its effects on catchment type, shore and catchment snow coverage and connectivity with other lakes) and hydrodynamics (waterbody size, type and volume of input/output). These factors presumably act through habitat creation, water flow/nutrient input and connectivity, and together allow the persistence of littoral groups with physiological mechanisms capable of coping with different environments at these lakes.

Although poorly developed, riparian vegetation structure appeared to interact with littoral invertebrate community structure, richness and diversity. This is particularly important as it unveils the sensitivity of the littoral ecosystems of high altitude lakes to vegetation changes in their riparian zones. Large scale variability in zoobenthos composition was also observed along altitudinal, longitudinal, and latitudinal gradients. It implies that central Pyrenees should not be considered an ecologically homogenous region. Therefore a regional scale should be considered sufficiently robust to test ecological processes in these environments.

Neither predation, nor water pH or conductivity appeared to significantly influence the composition of major benthic biota. The analysis of families' co-occurrence pattern identified three eurytopic associations. They generally had an ubiquitous distribution across the mountain range, possibly a result of relatively uniform colonisation during lake ecosystem evolution.

Altitude waterbodies are generally poor in resources. Our results illustrate that they have a high capacity to reflect in their littoral ecosystem a complex set of geographical and catchment attributes from the surrounding terrestrial system. This is important for our mechanistic understanding of terrestrial-aquatic linkages at altitude lakes, their vulnerability to landscape forcing and promotes them as sensitive sentinels and integrators of environmental changes.

Part II: Hazard risks from geogenic metal loads

Trace metals and their source in the catchment of the high altitude Lake Respomuso, Central Pyrenees

Remote altitude lakes are nutrient-poor systems. Their chemistry (e.g. nutrients, major and trace element contents) is usually governed by a weathering-limited regime. The inputs of elements such as trace metals into these environments is largely controlled by their bedrock geology, but may potentially be enhanced by changes in the environment, e.g. acid deposition, long range atmospheric transport and deposition of pollutants from industrialised areas and climate change. All these have potentially adverse implications for the ecological status of these environments.

At 2200m altitude in the Central Pyrenees Lake Respomuso catchment is underlain by two major geological units: granitic bedrock north, which is bordered by metamorphosed sedimentary materials south. These materials are known to contain significant metal mineralisations. The level of contribution and the source of a number of trace metals (As, Cd, Co, Cu, Mn, Ni, Pb and Zn) was ascertained in the catchment waterbodies (lakes, ponds and streams), together with their potential environmental implications. To this end a comprehensive sampling of sediments and water was conducted in nearly all tributaries in the catchment.

We found relatively high levels of trace metals in the sediment and water of Respomuso lake catchment compared to other similar altitude sites. Metal concentrations were generally higher in the headwaters than in the lower basin because of the source being concentrated in these areas. The distribution of trace metals and their relationships with major elements and mineral components revealed that the source of sediment-bound trace metals in the catchment is the local geology. The sediment-bound trace metals represent a considerable metal burden in the catchment, with the levels of As, Cd and Ni exceeding the sediment quality guidelines for the protection of aquatic biota.

The water metal contents were generally below the World Health Organisation (WHO) guidelines for drinking water. However arsenic in water at one site crossed its WHO threshold and it was also correlated with its concentration in the sediment samples. This may have resulted from its higher mobility from the sediments or surrounding metal rich geology under the oxic condition of the streams. The dissolved concentrations of all other trace metals were not related to their sediment concentrations possibly due to a low solubility in these environments.

This geogenic source may represent a significant risk for the fragile local biodiversity and for the wider environment in the valley below, particularly if highly toxic metals such as arsenic are mobilised, e.g. due to environmental change.

On the arsenic-source mobilization and its natural enrichment in a high mountain cirque in the Pyrenees

Due to its high persistence and carcinogenetic nature arsenic has recently received major attention worldwide, being recognised as a naturally occurring hazard in many parts of the world. By and large contamination with arsenic has been reported for groundwater environments at low altitudes, with sources being the presence of arsenic-rich sedimentary bedrock. In this context questions with regard to arsenic mobilisation/transport from remote altitude environments such as Respomuso lake catchment, and potential atmospheric arsenic transport and deposition in such regions still remain open. Our goal here was to determine the extent of arsenic mobilisation/ transport from arsenic source areas previously identified in a high elevation cirque of the Pyrenees. Additionally, snow-arsenic data is presented to determine the contribution, if any, of atmospheric arsenic deposition.

Overall, we established a baseline dataset of high natural arsenic levels and its distribution in a high altitude environment. The concentration of arsenic in the sediments of several tributaries was enriched up to about ten-fold due to mobilisation from the source areas within the catchment. The highest arsenic enrichments were from an area dominated by quartzite and slate formation in the southern side of the basin, and it generally diminished towards the major lake downstream, possible due to mixture with sediments from non-source areas. At these sites arsenic exceeded its hazard quotient limit for the protection of aquatic life. Warning values have also been detected in two locations downstream of the cirque catchment pointing out to an extension of the hazard beyond its borders. The relatively large sediment-As load poses a possible ecological risk and can affect the human populations downstream, as it may be mobilised due to changes (e.g. acidity, redox) in the local environment.

The arsenic concentrations in the water collected at a number of sites also exceeded the guide value for the protection of aquatic life. The results indicated that the arsenic most likely resulted from natural weathering of the surrounding metal-rich geology as well as its mobilisation from arsenic-bearing minerals in the sediments. This is a significant result as it could potentially increase if the environmental/climate conditions change. The analysis of snow suggests that long range transport/deposition of arsenic is relatively limited in the area and originated in the weathered dust from within or outside the cirque.

Natural metal source mobilization by climate change threatens altitude environments

Recently the science of climate change and its environmental implications has been attaining increasing complexity. One of the major concerns is that crossing certain boundaries of climate thresholds could have major consequences for other planetary systems, such as the water and geochemical cycles. Among the first to respond to these changes are sensitive regions such as the alpine biome. In these regions alterations of weather patterns, particularly temperature and precipitations can cause serious changes in hydrology, snow cover, weathering regime and soil erosion; all these potentially influence the biogeochemical cycles of hazardous elements such as trace metals. A fundamental question was therefore to test to which extent change in key climate patterns can influence the mobilisation of trace metals in areas of exposed geology. To address this question I examined the potential relationships between key climatic factors and trace metal (As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn) accumulation in a lakebed sediment core extracted from a mountain lake in the central Pyrenees. The core covered more than three decades of depositionary record.

The sediment metal contents showed an increasing accumulation trend over time, which coincides with recent climate change. The findings further revealed that recent changes in climate patterns, particularly the elevation of freezing level, a general increase in the frequency of drier periods and reducing snow cover since the early 1980s, are the most likely to be responsible for the increased accumulation of trace metals observed.

Among the metals, arsenic and nickel, two hazardous elements, crossed their safe concentrations for the protection of aquatic life in surface sediments. This points out to a potential threat to the wider environment, especially as these metals are associated to high background levels in the catchment. Given that most climate models predict further climate change over the next decades, it is likely that mountain catchments on metamorphic basins may become significant sources of trace metals, with potentially adverse consequences for the ecosystems and beyond. While the finding may raise as many questions as it answers, I believe it has the potential to open new research direction in this challenging field.

8.2 WHAT SHOULD HAPPEN NEXT ?

It is generally accepted that landscape evolution sets up the physical niches for ecosystem development. Nonetheless very little empirical data has so far been provided that quantifies the influence of various factors on ecotope development and its relationship on biota setting, particularly in high altitude environments. Likewise, the effects of recent climate change on metal source mobilisation from areas of exposed geology were practically unknown.

One of the most important directions the present research entitles is setting up hypotheses in the conceptual framework of lake ecotope models presented. Beside conservational implications, this may include testing riparian and aquatic biota's response to habitat advance/retreat (e.g. tolerance limit shifts) due to climate change, assessing the role of scale in aquatic-terrestrial interrelationships and, ascertaining species dispersion/colonisation in the new mountain ecotopes opened up the deglaciation episode we are experiencing.

Another route to be pursued by the research in the field is to finely tune the most appropriate taxonomical/ecological scale at which riparian-littoral-aquatic biota interactions are strongest, so as to allow accurate predictions of their response to changes in the surrounding environment. Further research is also needed to fully explain the observed interaction between elements such as Mg, Pb, Mn and Fe, and riparian vegetation at high altitude waterbodies.

Regarding the finding of relatively high geogenic metal stores at these pristine sites, one of the future directions is to elucidate the geochemical mechanisms of their mobilisation from the exposed mountain geology, and whether this is extended to other regions with significant metal mineralisation. Likewise, it is imperative to determine to what extent such metal stores are bioavailable and uptaken by local biota and human populations inhabiting these regions. This can be achieved by using field data or lab bioassays on various organisms along the food chain.

Climate change science is a challenging but rapidly growing field which is becoming increasingly complex. As more bits are added from different disciplines to form a complete picture of its environmental implications, it is clear that its importance for the entire society also increases. While our research has unveiled the potential of climate change to increase metal mobilisation and deposition in mountain environments, many other questions are emerging. The next challenge of future research will be to determine whether the increased mobilisation of natural metal sources by climate change is an extended and ongoing process with major implications for the wider environment. There is therefore an urgent need of large scale surveys in such sensitive regions.

RESUMEN Y DIRECCIONES FUTURAS

Palabras clave:

Lagos de altitud, procesos del paisaje

Formación del ecotopo: hidrodinámica, geo-morfología, forma topográfica

Funcionamiento del ecosistema: estructuración de la vegetación riparia, estructuración del zoobenthos litoral, sensibilidad de la biota al ambiente

Riesgos asociados: metales traza, distribución, niveles, origen, movilización, relación con cambio climático

1. RESUMEN DE LOS RESULTADOS

Debido a una localización clave en las partes más altas de la topografía (permitiendo una estrecha interacción con la atmósfera) y a la condición prístina que los está caracterizando, los lagos de altitud son altamente sensible a cambios en el ambiente circundante. Por otra parte, hay una necesidad reciente en las ciencias ambientales de comprender las respuestas de un ecosistema sensible a las interacciones con los factores externos, y cómo éstos pueden afectar la dinámica actual y futura del ecosistema. El presente trabajo ha sido motivado por nuestro interés en los procesos paisajísticos de la topografía alpina y nuestro objetivo de alcanzar una visión sinérgica de cómo el ambiente de alta montaña, incluyendo clima, geoquímica y la estructura del paisaje, determinan la organización y el funcionamiento de los sistemas lacustres alpinos, con particular énfasis en sus características ecológicas y geoquímicas.

Uno de los desafíos principales al abordar estos problemas fundamentales reside en que los procesos ecológicos y geoquímicos en las superficies alpinas son generalmente difíciles de examinar debido a un número de limitaciones incluyendo la dificultad de acceso /muestreo de grandes superficies, a la topografía accidentada, a las diversas relaciones directas e indirectas entre las características del paisaje y los procesos implicados y al corto período de tiempo en que estos rasgos del paisaje son visibles.

Para superar estas dificultades elegimos un área de estudio en los Pirineos centrales que abarca una densidad y diversidad de cuerpos lacustres relativamente alta, extendiéndose a lo largo de aproximadamente 80 kilómetros. Por otra parte se trabajo a menudo con equipos grandes llevando a cabo muestreos intensos que cubrieron superficies extensas en períodos de tiempo relativamente cortos, lo que permitió una evaluación exhaustiva de los sistemas lacustres de esta zona. Finalmente se emplearon diversos métodos de varias disciplinas para muestreo, procesamiento de muestras, análisis de datos e interpretación.

El propósito del presente trabajo ha sido identificar aspectos clave en la estructura y funcionamiento de los ecotopos y ecosistemas lacustres de alta montaña, así como indagar sobre riesgos ambientales potenciales que puedan surgir en estos medios. Se espera que un conocimiento más profundo de los procesos presentes en estos medios pueda aportar características importantes, de gran aplicación en el estudio del medio ambiente. Hemos logrado una amplia comprensión sobre la formación y el funcionamiento de los ecotopos y los ecosistemas lacustres de alta montaña, así como una identificación e interpretación de un número de riesgos potenciales derivados de la geología local. Entender estos aspectos constituye un importante avance en el conocimiento de los procesos ecológicos y geoquímicos del paisaje lacustre alpino, lo que consolidará su uso como sensores e integradores del cambio ambiental, base en el monitoreo global del bioma de montaña.

Los objetivos específicos han sido:

1. Examinar el papel de los factores paisajísticos en la formación de ecotopos lacustres de alta montaña;
2. Determinar la influencia de variables externas (posición geográfica y características de la cuenca) y lacustres (fisicoquímica del sedimento y el agua) en la estructuración de la vegetación riparia;
3. Medir la variación en la respuesta de la macrofauna bentónica litoral a los factores acuáticos y terrestres circundantes;
4. Analizar el rango de contribución y la distribución de un número de metales pesados en sedimentos y agua desde una perspectiva completa de la cuenca; asimismo, determinar la relación que estos puedan tener con la mineralogía local y el efecto potencial sobre la biota;

5. Examinar la movilización del arsénico desde las áreas donde origina a dentro y fuera de un circo de alta montaña, y

6. Evaluar la relación potencial entre cambios en parámetros climáticos y la acumulación de metales traza en sedimentos lacustres de montaña cubriendo más de tres décadas de registro histórico.

Los resultados han sido desarrollados en seis artículos organizados en dos secciones:

Parte I: Organización de los ecotopos y ecosistemas en lagos de alta montaña

La arquitectura para la formación de ecotopos en lagos de altitud

Generalmente, los ecosistemas lacustres están sostenidos por una infraestructura física (ecotopo), que incluye geomorfología, clima y cobertura del suelo circundante. En este artículo hemos intentado elucidar el papel que las características de cuenca juegan en la formación de ecotopos lacustres en la alta topografía. Para esto, se ha muestreado una amplia gama de variables paisajísticas de un rango prácticamente completo de cuerpos de agua, es decir desde lagos grandes a pequeños estanques (n=354), en una región de alta densidad lacustre del Pirineo central.

Hemos encontrado tres importantes factores compuestos que pueden explicar las características de los ecotopos lacustres: (i) hidrodinámica, (ii) geo-morfología de la roca madre y, (iii) forma topográfica. Entre ellos, la geo-morfología y la topografía mostraron correlación significativa con los gradientes altitudinal y latitudinal con respeto a su influencia en la formación de ecotopos. El análisis de intercorrelación entre las categorías que componen cada factor permitió clasificar los cuerpos de agua en un número de unidades ecotopicas, con características paisajísticas únicas. Estas unidades crean escenarios físicos distintos para la colonización de comunidades vegetales y animales a estas altitudes.

Los resultados indicaron que la formación de diversos ecotopos en lagos de alta montaña está controlada por reguladores hidrológicos, geomorfológicos y topográficos, y sigue grandes gradientes geográficos. Hemos interpretado esto como una importante evidencia de la evolución del paisaje Holocenico, que siguió tras la retirada de los glaciares Pirenaicos hace circa 11 000 años, y que crearon nichos físicos particulares para el establecimiento de las comunidades bióticas. Asimismo hemos propuesto un modelo conceptual para los ecotopos lacustres de alta topografía, que integran los procesos físicos, geológicos y climáticos que determinan su formación. Nuestro modelo conceptual puede ser utilizado tanto para probar hipótesis científicas, como en la mejora de políticas de gestión y conservación de los lagos de altitud. Esto es muy importante ya que los estudios ecológicos a menudo requieren unidades de hábitat diversas y bien definidas donde los procesos ambientales puedan ser estudiados.

Una perspectiva ecotopica de la vegetación riparia en los lagos de alta montaña

Las zonas riparias son las delicadas interfaces entre los ecosistemas acuáticos y terrestres. Limitaciones por las características ecotopicas en los lagos de altitud, junto con estrechas interacciones entre sus componentes y el medio colindante pueden determinar el establecimiento y el funcionamiento de comunidades vegetales únicas alrededor de estos cuerpos de agua. Esto plantea una cuestión fundamental sobre cómo las comunidades riparias en estas zonas interactúan con las superficies que habitan, un proceso que es generalmente poco conocido. Para dilucidar este proceso hemos analizado la estructura de la vegetación riparia a nivel de especie en correlación con un número de factores compuestos del paisaje, factores geoquímicos y posición geográfica de un área que abarca un total de 189 lagos altamente protegidos del Pirineo central. En segundo lugar hemos examinado los patrones de coincidencia (co-presencia) de las especies y sus preferencias de ecotopo.

Hemos hallado que interacciones complejas entre la hidrodinámica, la forma topográfica y la geo-morfología pueden explicar la estructura de la vegetación riparia en los lagos pirenaicos. Esta variabilidad en la composición de la vegetación a escala de cuenca ha sido relacionada considerablemente con los gradientes latitudinal y altitudinal, posiblemente una indicación de grandes transiciones climáticas entre las zonas pan-europeas continental, atlántica, mediterránea y alpina que influyen en esta parte de la cadena montañosa. A la escala local, el magnesio y el plomo del sedimento, y los contenidos de manganeso e hierro del agua influyeron la estructura de la vegetación. Esto es probablemente un reflejo de la geología de la roca base y de las frecuentes fluctuaciones hidrológicas en la zona riparia.

Analizando el comportamiento de co-incidencia de las especies identificamos 4 fito-comunidades riparias de amplitud de nicho relativamente grande, que caracterizan diversos ambientes riparios de los lagos. Estas comunidades mostraron fuertes preferencias para (i) ecotono muy húmedo, (ii) manto de nieve sobre roca base siliciosa, (iii) brezal húmedo y (iv) grupo posiblemente indicativo de substrato calcáreo. Los resultados tienen implicaciones en la comprensión de los mecanismos responsables del establecimiento y de la distribución de la vegetación riparia que habita los cuerpos de agua de altitud y de su potencial respuesta a las variaciones ambientales.

La sensibilidad ecológica de los organismos litorales a características locales y a gran escala en lagos de altitud

En los lagos alpinos la zona litoral junto con las superficies riparias generalmente albergan una alta biodiversidad, a menudo mucho mayor que la del paisaje circundante. Asimismo, en estos sistemas oligotróficos la producción de la cuenca junto con la de la zona riparia son críticamente importantes para las cadenas tróficas del litoral; en consecuencia pueden tener efectos profundos sobre estos ecosistemas. Un problema imperativo es por lo tanto entender la sensibilidad del ecosistema litoral a las ásperas características de la cuenca y del medio lacustres alpino (e.g. condiciones de ecotopo y ecológicas). Un análisis exhaustivo de 114 cuerpos de agua de altitud en el Pirineo central ha sido llevado a cabo con el propósito de cuantificar el grado de respuesta de los mayores grupos de fauna macro-zoobéntica litoral a un conjunto complejo de factores ambientales. En cada punto de muestreo hemos inspeccionado la composición de grandes grupos de invertebrados bénticos (nivel de familia) junto con la posición geográfica (altitud, latitud y longitud), factores compuestos paisajísticos (hidrodinámica, geo-morfología y forma topográfica), la estructura de la vegetación riparia, la presencia de depredadores vertebrados (truchas y ranas), el pH y la conductividad del agua.

En general, el ecosistema litoral de los lagos mostro una alta sensibilidad a los factores físicos externos (ecotopo) así como a la estructura de la vegetación riparia. El zoobenthos respondió considerablemente a la forma topográfica (a través de sus efectos sobre el tipo de cuenca de drenaje, la cobertura de nieve en la orilla y la cuenca y la conectividad con otro lago) y la hidrodinámica (tamaño y tipo del lago, y volumen del entrante/saliente). Estos factores actuarían a través de la creación de hábitat, la aportación de nutrientes y la conectividad; juntos permiten la persistencia de grupos litorales adaptados fisiológicamente para hacer frente a las condiciones ambientales específicos a estos lagos.

Aunque relativamente poco desarrollada la vegetación riparia aparentemente está interactuando con la estructura, la riqueza y la diversidad de las comunidades litorales de invertebrados. Esto es particularmente importante ya que muestra la sensibilidad del ecosistema litoral en los lagos de altitud a cambios en la vegetación en sus zonas riparias. Asimismo, se observo una variabilidad en la composición del zoobenthos a gran escala, a lo largo de los gradientes altitudinal, longitudinal, y latitudinal. Esto implicaría que el Pirineo central no debe considerarse como una región ecológicamente homogénea. Por lo tanto estudios a escala regional pueden aportar datos robustos para las hipótesis ecológicas en los ambientes de alta montaña.

La presencia de depredadores vertebrados, el pH del agua o la conductividad no aparecen afectar visiblemente la composición de los grandes grupos de taxones bénticos. El análisis del patrón de co-incidencia de estos grupos, a nivel de familia, identificó tres asociaciones euritopicas, es decir que ocupan una amplia variedad de hábitats. Estas asociaciones tienen generalmente una distribución ubicua a lo largo del transecto de montaña estudiado, posiblemente resultado de una colonización relativamente uniforme durante la evolución del ecosistema lacustre Pirenaico.

Los cuerpos lacustres de alta montana son generalmente pobres en recursos. No obstante nuestros resultados revelan que tienen una alta capacidad de reflejar en sus ecosistemas litorales un conjunto complejo de atributos geográficos y paisajísticos del sistema terrestre circundante. De esta manera se pueden comprender mejor los mecanismos de interacción entre el medio terrestre y acuático en los lagos de altitud, su vulnerabilidad a las fuerzas del paisaje y promoverlos como sensibles centinelas de cambios ambientales.

Parte II: Factores de riesgo asociados a los contenidos de metales pesados

Distribución de metales pesados y su fuente en la cuenca del lago de alta montaña Respomuso, Pirineo central

Los lagos remotos de gran altitud son sistemas pobres en nutrientes. Su química (e.g. contenido en nutrientes, elementos mayoritarios y traza) está generalmente gobernada por un régimen erosionario limitado. La aportación de oligoelementos tales como metales pesados en estos ambientes está en gran parte controlada por la geología local; no obstante estas concentraciones puede incrementar por cambios en el medio ambiente, e.g. deposición ácida, transporte a larga distancia y deposición atmosférica de agentes contaminantes desde áreas industrializadas, y cambios climáticos. Todos esto tiene alcance potencialmente adverso para el estado ecológico de los ecosistemas lacustres.

A unos 2200m altitud en el Pirineo central, la cuenca del lago Respomuso está dominada por dos unidades geológicas importantes: una base granítica en el norte, que está bordeada por materiales sedimentarios metamorfoseados al sur. Estos materiales contienen mineralizaciones metálicas significativas. Hemos estudiado el nivel de aportación y el origen de un número de metales pesados (As, Cd, Co, Cu, Mn, Ni, Pb y Zn) en los cuerpos de agua (lagos, charcas y corrientes) de la cuenca junto con sus potenciales implicaciones ambientales. Para este fin hemos llevado a cabo un muestreo exhaustivo de sedimentos y agua de casi todos los tributarios de la cuenca.

Hemos encontrado niveles relativamente altos de metales pesados en el sedimento y el agua de la captación del lago Respomuso, comparando con otros lagos de altitud similares. Las concentraciones de metales han sido generalmente más altas en las cabeceras de las valles que en el fondo de la cuenca, debido a sus fuentes que están distribuidas en estas áreas. La distribución de los metales y sus relaciones con los elementos mayoritarios y los componentes minerales revelaron que el origen de metales pesados en el sedimento de la cuenca está en la geología local. La carga de metales en el sedimento representa un riesgo considerable para la cuenca, con los niveles de arsénico, cadmio y niquelo excediendo los límites de calidad del sedimento para la protección de la vida acuática.

El contenido de metales en el agua estuvo generalmente por debajo de los niveles estipulados en las directivas de la Organización Mundial de la Salud (OMS) para el agua potable. Sin embargo, en un sitio de muestreo el arsénico del agua alcanzo un nivel muy alto, excediendo los valores recomendados por OMS y se correlacionó con su concentración en las muestras de sedimento. Una disolución más alta del sedimento o de la geología circundante rica en metales, bajo las condiciones óxicas en los arroyos de alta montaña pudo haber causado el incremento observado del nivel de arsénico. Las concentraciones disueltas de los demás metales pesados no mostraron relación ninguna con sus concentraciones en el sedimento, posiblemente debido a una solubilidad baja en estos ambientes.

Esta fuente geogénica puede representar un riesgo significante para la frágil biodiversidad local y para el medio ambiente en el valle rio-abajo, particularmente si metales altamente tóxicos tales como el arsénico resultan movilizados, e.g. debido a cambios ambientales.

Mmovilización de las fuentes de arsénico y su enriquecimiento natural en un circo de alta montaña de los Pirineos

Debido a su alta persistencia en el ambiente y su naturaleza carcinogenética el arsénico ha recibido recientemente una atención importante a nivel mundial, siendo reconocido como riesgo natural en muchas partes del mundo. Generalmente la contaminación con arsénico ha sido reportada para ambientes acuáticos subterráneos a bajas altitudes, con el origen en la roca base sedimentaria, rica en arsénico. En este contexto preguntas con respecto a la movilización/transporte de arsénicos en ambientes remotos de grandes altitud, tales como la cuenca del lago de origen glaciar Respomuso, y el potencial transporte y deposición atmosférica de arsénico en estas regiones, todavía siguen abiertas. Nuestro siguiente objetivo ha sido determinar el grado de movilización/transporte de arsénico desde las áreas fuente previamente identificadas en un circo elevado del Pirineo. Asimismo, presentamos sobre las concentraciones de arsénico en la nieve para determinar la posible deposición atmosférica de este elemento.

En general, hemos aportado un set de datos de referencia sobre niveles naturales relativamente altos de arsénico y de su distribución en un ambiente de alta montaña. La concentración de arsénico en los sedimentos de varios tributarios en el circo está enriquecida hasta diez veces debido a su movilización desde áreas fuente. Los valores más altos de enriquecimiento se encontraron en un área dominada por cuarcita y depósitos de flysch en el lado meridional de la cuenca, y generalmente disminuyeron hacia el lago principal rio abajo, posiblemente debido a las mezclas con sedimentos de áreas colaterales con bajos contenidos. En estos sitios el arsénico excedió su límite de riesgo para la protección de la vida acuática. Niveles alertadores también han sido detectados en dos localizaciones rio abajo del circo, indicando una extensión del peligro más allá de sus fronteras. La relativamente alta carga de arsénico en los sedimentos plantea un posible riesgo ecológico elevado que puede alcanzar las poblaciones humanas rio abajo, ya que podría movilizarse debido a cambios en el ambiente local (e.g. acidez, condición redox).

Las concentraciones de arsénico en el agua de un número de sitios de muestreo también excedieron el límite para la protección de la vida acuática. Los resultados apuntaron a que esto es debido a la meteorización natural en la geología circundante rica en metales, así como la movilización de los minerales asociados con arsénico del sedimento. Este resultado es significativo ya que el contenido de arsénico en el agua podría aumentar si las condiciones ambientales/climáticas cambian. El análisis de la nieve sugiere que el transporte/deposición de arsénico a larga distancia ha sido relativamente limitado en el área y podría originarse por la meteorización en las partes interior y exterior del circo.

La movilización natural de las fuentes de metales pesados por cambios en el clima afecta los ambientes de montaña

Recientemente la ciencia del cambio climático y sus implicaciones ambientales ha estado adquiriendo una complejidad cada vez mayor y un incremento en el interés científico. Una de las preocupaciones principales es sobrepasar ciertos límites en los umbrales del clima que podrían tener consecuencias mayores en otros sistemas del planeta, tales como los ciclos del agua y los geoquímicos. Entre los primeros a responder ante estos cambios están las regiones sensibles como el bioma alpino. En estas regiones alteraciones en los patrones climáticos, particularmente temperaturas y precipitaciones pueden causar cambios serios en la hidrología, la cubierta de nieve, los regímenes de meteorización y erosión del suelo; todos ellos potencialmente influencian los ciclos biogeoquímicos de contaminantes como los metales pesados. Una pregunta fundamental ha sido por lo tanto examinar hasta qué punto cambios en patrones claves del clima puede influir en la movilización de metales pesados en áreas de geología expuesta. Para intentar resolver esta incógnita hemos examinado las potenciales relaciones entre factores climáticos y la acumulación de metales pesados (As, Cd, Co, Cr, Cu, Mn, Ni, Pb y Zn) en un corer sedimentario extraído de un lago de la montaña del Pirineo central (Bubal, 1085m altitud). El corer cubre más de tres décadas de registro de deposición.

El contenido de metales en el sedimento mostró una tendencia de aumento con el tiempo en la acumulación, lo que coincide con cambios recientes en el clima. Adicionalmente, los resultados revelaron que cambios recientes en patrones climáticos, particularmente la elevación de la línea de helada, un aumento general en la frecuencia de períodos secos y la reducción de la cubierta de nieve desde el principio de los 1980, son los más probables responsables del incremento observado.

Entre los metales, el arsénico y el níquel, dos elementos altamente peligrosos, sobrepasaron sus niveles de seguridad para la protección de la vida acuática en los sedimentos superficiales. Esto representa una potencial amenaza para el medio ambiente, especialmente ya que estos metales vienen asociados a altos niveles en la geología local. Dado que la mayoría de los modelos climáticos predicen cambios adicionales durante las próximas décadas, es posible que las cuencas de montaña sobre rocas metamórficas puedan convertirse en fuentes significativas de metales pesados, con consecuencias adversas para los ecosistemas y el extenso medio ambiente. Aunque nuestros resultados pueden levantar tantas preguntas como las que contestan, creemos que tienen el potencial de abrir nuevas vías de investigación en este provocativo campo.

2. PERSPECTIVAS

Está generalmente aceptado que la evolución del paisaje fijó los nichos físicos para el desarrollo de los ecosistemas. No obstante hay muy pocos datos empíricos hasta ahora que cuantifiquen la formación de ecotopos y su influencia en la colonización de la biota, particularmente en ambientes de gran altitud. Asimismo, los efectos de los cambio recientes del clima sobre la movilización de las fuentes de elementos pesados en áreas con geología expuesta han sido prácticamente desconocidos.

Una de las vías de investigación más importantes a la que nuestra investigación invita es comprobar hipótesis en el marco conceptual de los modelos de ecotopo lacustre que hemos desarrollado. Además de implicaciones para la conservación, esto puede incluir determinar las respuestas de la biota acuática y riparia al avance/retroceso de hábitat (e.g. cambios en los límites de tolerancia) debido a cambios climáticos. Otras aplicaciones serían establecer el papel de la escala en las relaciones medio acuático-terrestre y examinar la dispersión/colonización de especie en distintos ecotopos lacustres del bioma de alta montaña.

Otra línea de investigación a seguir en este campo es identificar la escala taxonómica/ecológica más apropiada a la que las interacciones bióticas riparia-litoral-acuática son las más estrechas. Esto permitirá hacer predicciones adecuadas de las respuestas bióticas a los cambios en el ambiente circundante. Investigación adicional también se necesita para explicar debidamente la interacción interesante observada entre la vegetación riparia y elementos como magnesio, plomo, manganeso y hierro de los cuerpos lacustres de altitud.

Con respecto a las acumulaciones relativamente altas de metales de origen geogénico en estas zonas prístinas, una de las potenciales direcciones futuras es esclarecer los mecanismos geoquímicos responsables de sus movilizaciones de la geología expuesta de alta montaña, y si este proceso está extendido a otras regiones de elevadas mineralizaciones. Asimismo, es imprescindible determinar hasta qué punto los depósitos de metales traza están biodisponibles y captados por la biota local y las poblaciones humanas que habitan estas regiones. Este objetivo puede alcanzarse usando datos de campo o ensayos biológicos de laboratorio en varios organismos a lo largo de la cadena trófica.

La ciencia del cambio climático es un campo provocativo con rápida expansión que está siguiendo vías cada vez más complejas. A medida que más piezas van agregándose desde varias disciplinas para formar un escenario completo sobre sus implicaciones ambientales, está claro que su importancia para la sociedad está también aumentando. Mientras que nuestra investigación ha revelado el potencial del cambio climático de incrementar la movilización y deposición de metales pesados en el ambiente de montaña, muchas otras preguntas van surgiendo. El desafío siguiente de la investigación será determinar si el aumento en la movilización de las fuentes naturales de metales pesados por cambios en el clima es un proceso extendido y en curso, con alcances importantes para el medio ambiente. Existe por lo tanto una necesidad urgente de estudios a gran escala en estas regiones sensibles.

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