Universitat de Girona

TRACE ELEMENTS BIOGEOCHEMISTRY IN HIGH MOUNTAIN LAKE CATCHMENTS: IDENTIFYING ANTHROPOGENIC VERSUS NATURAL COMPONENTS FROM THE ATMOSPHERIC CONTAMINATION LEGACY IN REMOTE NATURAL AREAS

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Dipòsit legal: GI-1024-2011
http://hdl.handle.net/10803/32149

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Universitat de Girona

CSIC

Doctoral Thesis

Trace element biogeochemistry in high mountain lake catchments: identifying anthropogenic versus natural components from the atmospheric contamination legacy in remote natural areas

Montserrat Bacardit Peñarroya
2011

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Trace element biogeochemistry in high mountain lake catchments: identifying anthropogenic versus natural components from the atmospheric contamination legacy in remote natural areas

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2011

Fundamental and Applied Ecology

Directed by: Dr. Lluís Camarero, Department of Continental Ecology, Centre for Advanced Studies of Blanes, CSIC
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A thesis submitted for the degree of Doctor of Philosophy in the University of Girona

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CERTIFIES:

that the book entitled “Trace element biogeochemistry in high mountain lake catchments: identifying anthropogenic versus natural components from the atmospheric contamination legacy in remote natural areas”, submitted by Montserrat Bacardit Peñarroya for the degree of Doctor of Philosophy, has been prepared under my supervision and fulfills the requirements for the European Doctorate Mention.

Signature

Blanes, 08/03/2011

This thesis is based on the following papers, which will be referred to in the text by their Roman numerals:

Paper I. Bacardit, M.; Camarero, L. 2009, Fluxes of Al, Fe, Ti, Mn, Pb, Cd, Zn, Ni, Cu, and As in monthly bulk deposition over the Pyrenees (SW Europe): The influence of meteorology on the atmospheric component of trace element cycles and its implications for high mountain lakes, Journal of Geophysical Research-Biogeosciences 114, G00D02, doi:10.1029/2008JG000732.

Impact Factor 3.147 in the 2008 Journal Citation Reports.

Paper II. Bacardit, M.; Camarero, L. 2010, Atmospherically deposited major and trace elements in the winter snowpack along a gradient of altitude in the Central Pyrenees: the seasonal record of long-range fluxes over SW Europe, Atmospheric Environment, 44, doi: 10.1016/j.atmosenv.2009.06.022.

Impact Factor 2.890 in the 2009 Journal Citation Reports. 40 Issues per year.

Paper III. Bacardit, M.; Camarero, L.; Camusso, M.; Guzzella, L.; Hardekopf, D.W.; Nickus, U.; Rose, N.L.; Stuchlik, E. Atmospheric trace element contamination in European mountain catchments, as determined from direct bulk deposition records, submitted to Atmospheric Chemistry and Physics.

Impact Factor 4.881 in the 2009 Journal Citation Reports. 24 Issues per year. Open Access Journal.

Paper IV. Bacardit, M.; Camarero, L. 2010, Major and trace elements in soils in the Central Pyrenees: high altitude soils as a cumulative record of background atmospheric contamination over SW Europe, Environmental Science and Pollution Research, 17, doi: 10.1007/s11356-010-0349-4.

Impact Factor 2.411 in the 2009 Journal Citation Reports. 7 Issues per year.

Paper V. Bacardit, M.; Krachler, M.; Camarero, L. Whole-catchment inventories of trace metals in soils and sediments in mountain lake catchments in the Central Pyrenees: apportioning anthropogenic and natural contributions, accepted to Geochimica et Cosmochimica Acta.

Impact Factor 4.385 in the 2009 Journal Citation Reports. 24 Issues per year.

Paper VI. Bacardit, M.; Camarero, L. 2010, Modelling Pb, Zn and As transfer from terrestrial to aquatic ecosystems during the ice-free season in three Pyrenean catchments, Science of the Total Environment, 408, doi: 10.1016/j.scitotenv.2010.07.088.

Impact Factor 2.905 in the 2009 Journal Citation Reports. 24 Issues per year.

Front cover picture: Estanh Redon by Juli Soler i Santaló in Soler i Santaló, J. 1998, La Vall d'Aran: 1906, Tremp, Garsineu Ed., 370 pp

This photograph is probably the first taken of Lake Redon, a high mountain lake located on the southern slope of the Aran valley, Central Pyrenees, by the photographer and mountaineer Soler i Santaló. At the beginning of the twentieth century, mountaineering as a sport and tourist activity was introduced in the Pyrenees by enthusiastic mountaineers such as Soler i Santaló. During the same period, mines opened in the nearby northern areas of Bossòst and Liat and the southern area of Cierco (Johnson et al., 1996; Cardellach et al., 1996), which operated until the beginning of the 1980s (Camarero et al., 1998). Mining activities from the start of this twentieth century thus caused a yearly increase in the percentage of lead in contemporary Pyrenean lake sediments. This is unequivocally demonstrated by a dated lake sediment core retrieved from Lake Redon (Camarero et al., 1998).

Contents

Foreword

This book is the dissertation I am presenting to obtain a PhD in Ecology at the University of Girona. Each main chapter was written as an independent scientific article that reports original work on a particular topic and contains its own introduction and conclusions. All the articles in the thesis have been published, accepted or submitted to peer-reviewed journals. Nevertheless, this thesis is more than a compendium of research articles. The articles were designed for this book, and are organised around the idea that high mountain lake catchments are sentinels of long-range contamination. The articles also discuss many other aspects of global environmental change.

This thesis focuses in particular on the biogeochemistry of trace elements in high mountain lake/catchment systems, with special emphasis on separating “natural” from “anthropogenic” components. The results are presented in two main parts, which cover the contemporary atmospheric trace element fluxes in high mountain areas (Part I), and the long-term atmospheric deposition, storage, transport and fate of trace elements in high mountain lake catchments (Part II). Most of the studies in this thesis were conducted at a few high mountain sites in the Central Pyrenees, whereas a set of other high mountain sites in Europe was considered in the study related to Paper III, to introduce a geographical perspective of the current atmospheric trace element fluxes at European scale. The results are mainly discussed on the basis of geophysical and geochemical processes, but some biological and ecological aspects are also included, since trace elements are globally cycled within both abiotic and biotic compartments and fluxes.

The Abstract is presented in three languages: English, Catalan and Aranese. I chose Catalan and Aranese because both languages have coexisted in the Pyrenees for centuries. Catalan is my native language, whereas Aranese is a dialectical variant of the Occitan language that is officially recognised by the Catalan government only in a small Pyrenean county named “Val d’Aran”.

The Introduction presents the state-of-the-art of the main subject of this thesis and ends with a description of the objectives and the experimental design, a summary of the results and a discussion that brings together the new findings and concepts from the different papers. In the Conclusions and Further Remarks section, concluding statements highlight the answers provided by this thesis, but also propose some new areas for further work. I have tried to keep this book as short as possible by avoiding unnecessary repetition of the description of materials and methods, the study sites and the literature, whilst still providing the complete story.

Teamwork is very important in science. Therefore, I recognize the contribution of a number of researchers and technicians who were involved in the research for this thesis, and appear either as co-authors or in the acknowledgements section of each article. Financial and logistic support is another essential component of science. Hence, I acknowledge all public institutions and facilities that supported the research projects and the work undertaken for each corresponding article.

I want to express my gratitude to my advisor Dr. L. Camarero for involving me and guiding me in this project in the Central Pyrenees, far from Barcelona, which took place some years ago. I am thankful for his active participation in the field and in the discussions, for his good advice and timely encouragement, for introducing me to ski mountaineering and alpinism, and specially, for his absolute confidence and friendship. I am also extremely grateful to Prof. P. Appleby and Prof. W. Shotyk, who hosted and advised me during two fruitful short stays in Liverpool and Heidelberg, respectively.

Naturally, I am also indebted to a large number of people who are close to me and without whom this thesis could not have been completed. They include: Prof. J. Catalan and all my colleagues from the Limnology Group; Prof. E. Ballesteros for both scientific and personal support; Maddi, Mireia, Dani, Lourdes, Roberto and many other PhD fellows from CEAB, UB, IQAB and UdG for their great company during doctoral courses, project meetings and conferences as well as in the field, often carrying huge backpacks, and in the lab at the High Mountain Research Centre; a special mention to Sonja and Christian from Heidelberg; and to all my friends in the Pyrenees for their absolute support. Thanks a million to all of you!

My thanks to Merce and Xavi, who helped with the revision of the Catalan and Aranese abstracts, respectively.

Finally, I would like to dedicate this thesis to my closest and loved people: my parents, Jaume and Montserrat, to my brothers and sisters, Maria, Jaume, Jordi and Mercè, and especially to my best supporter Carles. *Sense vosaltres, aquesta tesi no hauria vist la llum. Moltes gràcies!*

Abstract

Human activities have been interfering with the natural biogeochemical cycles of trace elements since the ancient civilizations. Although they are inaccessible and remote, high mountain lake catchments are irrefutably trace-element contaminated by anthropogenic emissions, which can travel by long-range atmospheric transport before they are deposited. This has been revealed by several natural archives.

High mountain lake catchments are thus excellent sentinels of long-range contamination. Continuous accumulation can lead to a build up of potentially toxic trace elements in these remote, or relatively remote, ecosystems.

The thesis focuses on the biogeochemistry of a suite of trace elements of environmental concern (Ni, Cu, Zn, As, Se, Cd and Pb) in Pyrenean lake catchments, with special emphasis on discerning the “natural” components from the “anthropogenic” contributions. Five other metallic elements (Al, Fe, Ti, Mn and Zr) have also been studied to trace natural fluxes and biogeochemical processes within the lake catchment systems.

Current atmospheric major and trace element fluxes over the Pyrenees were directly measured from monthly bulk deposition records. In this study, prevailing meteorological factors were related (quantitatively and qualitatively) to element deposition fluxes. In a different study, seasonal atmospheric major and trace element fluxes were estimated from the winter snowpack sampled along a gradient of altitude. On the basis of these two studies, we conclude that concentrations of airborne trace elements in the Central Pyrenees can be considered representative of the background contamination levels of remote areas in Europe. However, only the trace element composition collected above ~2100-2300 m a.s.l. in the Central Pyrenees can reliably be used as a signature of background long-range fluxes in SW Europe, as at a lower altitude the local effects are perceptible.

In addition, bulk atmospheric deposition measurements of major and trace elements were obtained from five other European high mountain sites for comparison. Remarkably, Al, Ti, Fe, Mn and As were found in higher concentrations in the Central Pyrenees. These elements were identified as part of the dust carried from the Iberian Peninsula and North Africa. During episodic events, this dust reaches the Pyrenean range in considerably higher amounts than in other more northern European high mountain sites. By contrast, Pb, Zn, Ni, Cu, As and Cd were found in higher concentrations in the Tatra Mountains, Ticino and Piemonte. Lower concentrations occurred in the Tyrol and intermediate concentrations appeared in the Pyrenees and the Grampian Mountains.

Long-term, historical trace element deposition over the Pyrenees was examined using soil records and lake sediment cores, which take into account post-depositional processes that occur in the terrestrial catchment and additional inputs from the catchment to the lake, respectively. Trace element concentrations in Pyrenean soils were consistent with those recorded in soils from other mountainous areas in Europe and were, in many cases, above the thresholds recommended for ecosystem protection. In conclusion, Pyrenean high mountain soils had a ~2- to 5-fold increase in Pb, Ni and Cu as a result of long-range contamination, whereas enrichment of As was most probably caused by localised As-bearing veins in the area.

Cumulative whole-catchment inventories of Pb, Zn, Cu, Ni and Cd were calculated for three Pyrenean lake catchments. In this study, Pb isotopes were successfully used to reliably estimate the natural and anthropogenic contributions of Pb both in catchment soils and lake sediments, and then calibrate the relative apportioning for the other trace metals. Lead and Zn anthropogenic inventories were in good agreement with those in other mountainous and rural areas in northern and eastern Europe, whereas Ni, Cu and Cd anthropogenic inventories were lower in the Pyrenees. Interestingly, the estimated trace metal inventories were three orders of magnitude higher than the current annual atmospheric deposition to the Central Pyrenees. This result highlights the potential of sediments and soils as sources of delayed, long-lasting contamination if possible environmental changes favour the remobilisation of anthropogenic trace metals accumulated over the course of time.

Finally, a simple transport model of atmospheric trace elements through the catchment/lake system during the snow and ice-free season was applied for the three Pyrenean catchments. Results showed a net export of Pb and As from the catchments whereas Zn was largely retained. We propose that Pb originates from the delayed release of previously accumulated anthropogenic Pb contamination and the weathering of As-rich rocks is the most likely source of As. By contrast, possible saturation of Zn in the catchments can also make them a source of Zn contamination.

Ultimately, several aspects of concern in this thesis indicate that further long-term atmospheric deposition monitoring is required at a greater number of mountain sites. Likewise, we should also carry out integrated long-term monitoring of atmospheric deposition, stream and lake water transport, sediment fluxes and vegetation uptake in mountain catchments.

Keywords: trace element, high mountain lake catchment, long-range contamination, atmospheric deposition, enrichment, Pb isotope, transport model, Central Pyrenees

Resum

Les activitats humanes han interferit en els cicles biogeoquímics naturals dels elements traça des de les antigues civilitzacions. Malgrat ser inaccessibles i remotes, les conques lacustres de muntanya es troben clarament contaminades pels elements traça procedents d’emissions antropogèniques, que s’hi han desplaçat per mitjà del transport atmosfèric de llarg abast i la subseqüent deposició, tal com revelen diversos arxius naturals.

Per tant, les conques lacustres de muntanya són indicadores excel·lents d’aquesta contaminació de llarg abast. La seva contínua acumulació ha deixat una quantitat important d’elements traça potencialment tòxics en aquests ecosistemes remots o relativament remots.

La tesi se centra en la biogeoquímica d’un conjunt d’elements traça de rellevància ambiental (Ni, Cu, Zn, As, Se, Cd i Pb) en conques lacustres pirinenques, amb especial èmfasi en distingir els components “naturals” de les contribucions “antropogèniques”. A més a més, s’han estudiat cinc metalls més (Al, Fe, Ti, Mn, Zr) per traçar fluxos i processos biogeoquímics naturals en els sistemes lacustres.

S’han fet mesures directes dels actuals fluxos atmosfèrics d’elements majoritaris i traça a partir de registres de deposició total mensual. En aquest estudi, s’han relacionat (quantitativament i qualitativament) factors meteorològics predominants amb els fluxos de deposició elementals. En un estudi diferent, s’han estimat els fluxos estacionals atmosfèrics d’elements majoritaris i traça a partir del paquet de neu hivernal mostrejat al llarg d’un gradient altitudinal. En base a aquests dos estudis, concloem que les concentracions d’elements traça aerotransportats en el Pirineu Central poden ser considerades representatives dels nivells de contaminació de fons d’àrees remotes d’Europa. Tanmateix, només la composició d’elements traça recollida per sobre ~2100-2300 m s.n.m. en el Pirineu Central pot ser utilitzada amb certesa com una senyal de fons dels fluxos de llarg abast del sud-oest d’Europa, ja que a més baixa altitud els efectes locals són perceptibles.

A més a més, s’han obtingut mesures de la deposició atmosfèrica total d’elements majoritaris i traça de cinc altres indrets d’alta muntanya europeus per comparar-les. Cal remarcar que Al, Ti, Fe, Mn i As s’han trobat amb concentracions més elevades al Pirineu Central. Aquests elements formen part de la pols transportada des de la península Ibèrica i el nord d’Àfrica que episòdicament arriba en quantitats importants al Pirineu respecte altres indrets d’alta muntanya europeus localitzats més al nord. Per contra, s’han trobat concentracions elevades de Pb, Zn, Ni, Cu, As i Cd a les muntanyes dels Tatra, al Ticino i al Piemont, concentracions baixes al Tirol i intermèdies al Pirineu i a les Grampian.

S’ha examinat la deposició històrica a llarg termini dels Pirineus a partir de registres en sòls i testimonis de sediments lacustres, els quals incorporen processos postdeposicionals a la part terrestre de la conca i entrades addicionals de la conca a l’estany, respectivament. Les concentracions d’elements traça als sòls pirinencs són comparables als registres en sòls d’altres zones de muntanya europees i són, en molts casos, superiors als límits recomanats per la protecció dels ecosistemes. En conclusió,

els sòls d’alta muntanya del Pirineu revelen un increment de ~2 a 5 vegades de Pb, Ni i Cu resultat de la contaminació de llarg abast, mentre que l’enriquiment d’As és probablement degut a venes locals riques en As.

En un estudi diferent, s’han calculat els inventaris cumulatius a nivell de tota la conca de Pb, Zn, Cu, Ni i Cd per tres conques lacustres pirinenques. En aquest estudi, s’han utilitzat amb èxit isòtops de Pb per estimar amb confiança les contribucions naturals i antropogèniques de Pb en els sòls de les conques i els sediments lacustres, i aleshores s’han calibrat les aportacions relatives pels altres metalls traça. Els inventaris antropogènics de Pb i Zn concorden amb els d’altres zones de muntanya i rurals de localitats septentrionals i orientals d’Europa, mentre que els inventaris antropogènics de Ni, Cu i Cd del Pirineu són més baixos. És d’interès que els inventaris antropogènics d’elements traça estimats són tres ordres de magnitud més grans que els actuals fluxos atmosfèrics anuals al Pirineu Central. Aquest resultat fa ressaltar el potencial dels sediments i els sòls com a fonts de contaminació retardada a llarg termini si els possibles canvis ambientals afavoreixen la remobilització dels metalls traça antropogènics acumulats al llarg del temps.

Finalment, s’ha aplicat un model simple de transport d’elements traça d’origen atmosfèric a través del sistema conca/estany durant l’època sense neu i gel per les tres conques pirinenques. Els resultats mostren una exportació neta de Pb i As a les tres conques mentre que el Zn és retingut en gran part. Proposem que el Pb s’origina d’un alliberament retardat de la contaminació de Pb antropogènic acumulada prèviament i que la meteorització de roques riques en As és la font més probable d’As. Per contra, la possible saturació de Zn a les conques també pot convertir-les en fonts de contaminació de Zn.

Al cap i a la fi, diversos aspectes assenyalats a la tesi justifiquen la necessitat de continuar a llarg termini les observacions de deposició atmosfèrica en un nombre més ampli d’indrets de muntanya. Igualment, també caldria dur a terme l’observació integrada a llarg termini de la deposició atmosfèrica, el transport fluvial i lacustre, el flux als sediments i la incorporació d’elements traça per part de la vegetació en conques de muntanya.

Paraules clau: element traça, conca lacustre d’alta muntanya, contaminació de llarg abast, deposició atmosfèrica, enriquiment, isòtop de Pb, model de transport, Pirineu Central

Resumit

Es activitats umanes an interferit es cicles biogeoquimics naturaus des elements traça des antigues civilizacions. Maugrat èster inaccessibles e remòtes, es conques lacustres de nauta montanha se tròben claraments contaminades per elements traça provenents d’aguestes emissions antropogeniques, que se i an desplaçat per mejan de transpòrt atmosferic de longa distància e subseqüenta deposicion, com ac revèlen diuèrsi archius naturaus.

Es conques lacustres de montanha, donc, son indicadores excellentes d’aguesta pollucion de longa distància. Era sua acumulacion contunhada a deishat quantitats importantes d’elements traça potenciauments toxics en aguesti ecosistèmes remòts o relativament remòts.

Era tèsi se centre ena biogeoquimica d’un conjunt d’elements traça d’importància ambientau (Ni, Cu, Zn, As, Se, Cd e Pb) en conques lacustres pirenenques, damb especiau interès en distinguir es elements “naturaus” des contribucions “antropogeniques”. Tanben s’an estudiat cinc metaus mès (Al, Fe, Ti, Mn, Zr) entà traçar fluxes e procèssi biogeoquimics naturaus enes sistèmes lacustres.

S’an hèt mesures dirèctes des actuaus fluxes atmosferics d’elements majoritaris e traça, a compdar de registres de deposicion totau mensuau. En aguest estudi, s’an relacionat (qualitativament e quantitativament) factors meteorologics predominants damb es fluxes de deposicion elementaus. En un estudi diferent, s’an estimat es fluxes sasoèrs atmosferics d’elements majoritaris e traça a compdar deth celh de nhèu iuernau escandilhat ath long d’un gradient de nautada. A compdar d’aguesti dus estudis, afirmam qu’es concentracions d’elements traça aerotransportats en Pirenèu Centrau pòden èster considerades representatives des nivèus de contaminacion de hons de territòris remòts d’Euròpa. Mès, sonque era composicion d’elements traça arremassada per dessús de ~2100-2300 m d.n.m. en Pirenèu Centrau pòt èster utilizada damb certesa coma un senhau de hons des fluxes de longa distància deth sud-oèst d’Euròpa, pr’amor qu’a mès baisha altitud es efèctes locaus son mès perceptibles.

Tanben s’an obtengut donades dera deposicion atmosferica totau d’elements majoritaris e traça en cinc d’auti lòcs de nauta montanha europèus entà comparar-les. Cau remercar que Al, Ti, Fe, Mn e As s’an trobat damb concentracions mès nautes en Pirenèu Centrau. Aguesti elements formen part deth povàs transportat dera Peninsula Iberica e deth nòrd d’Africa qu’arribe episodicaments damb quantitats importantes en Pirenèu respecte d’auti lòcs de nauta montanha europèus localisats mès tath nòrd. Per contra, s’an trobat concentracions nautes de Pb, Zn, Ni, Cu, As e Cd enes montanhes des Tatra, Ticino e Piemont, concentracions baishes en Tiròl, e intermieges en Pirenèu e enes Grampian.

S’a examinat era deposicion istorica a long tèrme deth Pirenèu a compdar de registres en sòus e testimònis de sediments lacustres, enes quaus s’incorpòren es procèssi postdeposicionaus ena part terrèstra dera conca e entrades addicionaus dera conca ar estanh, respectivaments. Es concentracions d’elements traça enes sòus pirenencs són comparables as registres en sòus de d'auti parçans de montanha europèus e son, fòrça viatges, superiors as limits recomanats pera proteccion des ecosistèmes. En conclusion, es sòus de nauta montanha deth Pirenèu revèlen un increment de ~2 a 5 viatges de Pb, Ni e Cu resultat dera contaminacion de longa distància, mentre qu'er enriquiment d'As ei degut probablaments a vetes locaus riques en As.

En un estudi diferent, s'an calculat es inventaris cumulatius a nivèu de tota era conca de Pb, Zn, Cu, Ni e Cd per tres conques lacustres pirenenques. En aguest estudi s'an utilizat damb boni resultats isotòps de Pb entà estimar damb confiança es contribucions naturaus e antropogeniques de Pb enes sòus des conques e enes sediments lacustres, e s'an calibrat es aportacions relatives as auti metaus traça. Es inventaris antropogenics de Pb e Zn concòrden damb es d'auti parçans de montanha e ruraus de localitats septentrionaus e orientaus d'Euròpa, mentre qu'es inventaris antropogenics de Ni, Cu e Cd deth Pirenèu son mès baishi. Ei interessant qu'es inventaris antropogenics des elements traça estimats son tres ordes de magnitud mès grani qu'es actuaus fluxes atmosferics annaus en Pirenèu Centrau. Aguest resultat remèrque eth potenciau des sediments e des sòus coma hònts de contaminacion retardada a long tèrme s'es possibles cambis ambientaus afavorissen era remobilizacion des metaus traça antropogenics acumulats ath long deth temps.

Fin finau, s'a aplicat un modèl simple de transpòrt d'elements traça d'origina atmosferica a trauès deth sistèma conca/estanh pendent era sason sense nhèu ne gèu entàs tres conques pirenenques. Es resultats mòstren ua exportacion neta de Pb e As enes tres conques, mentre qu'eth Zn ei retengut ena màger part. Prepausam qu'eth Pb s'origine a conseqüéncia d'ua liberacion retardada dera contaminacion de Pb antropogenic acumulada preliminarament e qu'era meteorizacion des ròques riques en As ei era hònt mès probabla d'As. Per contra, era possibla saturacion de Zn enes conques tanben pòt convertir-les en hònts de contaminacion de Zn.

Ara fin, diuèrsi aspèctes nomentats ena tèsi justifiquen eth besonh de contunhar a long tèrme es observacions de deposicion atmosferica en un nombre mès gran de lòcs de montanha. Tanben ei de besonh era observacion integrada a long tèrme dera deposicion atmosferica, eth transpòrt fluviau e lacustre, eth flux entàs sediments e era incorporacion d'elements traça per part dera vegetacion enes conques lacustres de montanha.

Paraules clau: element traça, conca lacustra de nauta montanha, contaminacion de longa distància, deposicion atmosferica, enriquiment, isotòp de Pb, modèu de transpòrt, Pirenèu Centrau

Introduction

Figure 1. View of the Earth from Apollo 17 in 1972 (from http://eol.jsc.nasa.gov/)

Definition of trace elements

There is no universal definition of “trace element”. Instead, the literature includes a range of explanations, depending on the scientific approach. In analytical chemistry, a trace element is an element in a sample that has an average concentration of less than 100 parts per million measured in atomic count, or less than 100 micrograms per gram. In geochemistry, a trace element is a chemical element whose concentration is less than 1000 ppm or 0.1% of a rock's composition, whereas in biochemistry, a trace element is an element that occurs in the body in mg kg^{-1} of body weight or less. Some trace elements (e.g., copper, selenium and zinc) are nutritionally essential elements (i.e. micronutrients) for biota at low levels, but toxic at higher levels. Other trace elements (e.g., lead, arsenic and mercury) have no known biological functions (i.e. they are nonessential) and are highly toxic. All the trace elements are thus toxic when intake is excessive.

Currently, the term “trace element” is increasingly preferred in environmental literature to the meaningless term “heavy metal”, which was widely used in the recent past (and is still used) to denominate a group name for metals and semimetals (i.e. metalloids) that have been associated with contamination and potential toxicity or ecotoxicity (see Duffus, 2002 and Hodson, 2004 for a review of this topic). I will mainly use the term “trace element” throughout this thesis. The term “trace metal” will also be used to refer to a closed group of “true” metals in a strictly chemical sense.

Trace elements in the environment

Trace elements are naturally occurring constituents on the Earth and vary in concentration in air, rock, soil, sediments and biota across geographic regions (Bowen, 1979). As part of the natural biogeochemical cycle, trace elements are released from rocks by weathering processes. They are then distributed through various environmental compartments by biotic and abiotic processes, and ultimately enter oceans as sediments. With sufficient geological time, they become “rocks” again, tectonic processes form new land, and the cycle continues (Garrett, 2000). However, since the advent of man, anthropogenic inputs have overwhelmed the natural trace element cycling and have led to increased concentrations and an accumulation of trace elements in the environment as well as strong interference in the transport fluxes and rates between biogeochemical compartments in both terrestrial and aquatic ecosystems (Nriagu, 1988). As a consequence of such vast anthropogenic activity, Earth’s element cycles are currently referred to as “anthrobiogeochemical” cycles (Rauch and Pacyna, 2009).

Therefore, trace element contamination (i.e. the presence of a trace element where it should not be or at concentrations above the natural background) is unquestionably present everywhere on the Earth. In addition, such contamination can result in pollution when the contamination has adverse biological effects on the natural environment (Chapman, 2007). In this context, trace elements are recognised as potential pollutants in the environment on the basis of the following worrying properties: bioaccumulation, toxicity and persistence (Kabata-Pendias and Pendias, 2001). Due to their natural occurrence, trace elements, unlike organic chemicals, are neither created nor destroyed by biological or chemical processes. However, such processes can transform trace elements from one species to another and can convert them from inorganic to organic forms, as well as soluble to insoluble forms and vice versa. The pH, redox potential and organic content are key parameters in the phase partitioning, and thus, in the mobility of trace elements in the environment. Trace elements are frequently associated with particular mixtures of various elements, due to similar physicochemical properties. Such mixtures can be used to identify sources of trace elements. The availability, absorption, distribution, transformation, and excretion of a trace element within an organism depends on the trace element itself, its form or its compound in the media, and the organism's ability to uptake, regulate and/or store it.

The atmospheric component plays a key (and major) role in the widespread trace element contamination beyond other Earth compartments (i.e. the lithosphere, hydrosphere and biosphere). In the atmosphere, trace elements mostly occur as, or are adsorbed to, particles, which can be long-range transported from their sources before being redeposited in ecosystems (Patterson and Settle, 1987). Historically, the rate of emissions was low, because of the low volatility of most trace elements. However, increased emissions due to high temperature processes driven by mankind (particularly, smelting and fossil fuel combustion) have led to increased trace element concentrations in the atmosphere and a rise in atmospheric deposition (Galloway, 1982). Yet, elevated concentrations or fluxes in deposition are not always the result of human activities. For instance, atmospheric aerosols, such as mineral dust and biogenic aerosols, entrained massively into the atmosphere can have broad environmental impacts, such as removing and transporting atmospheric contaminants (Carmichael et al., 1996; Dentener et al., 1996), and affecting the chemical composition of surface waters (Camarero et al., 1995; Hsu et al., 2010; Mannio et al., 1995; Prospero and Arimoto, 2009). Consequently, natural processes can enhance the spread of atmospheric trace elements of anthropogenic origin. Moreover, human activities are responsible for the increase not only of atmospheric aerosols of anthropogenic origin, but also of aerosols from natural sources and the reemission of previously deposited particles enriched in trace elements. Currently, there is intense interest in the role of aerosols in climate change and atmospheric chemistry, and the interactions between both (Andreae and Crutzen, 1997; Griffin, 2001; Isaksen et al., 2009; Psenner, 1999). Overall, despite the complexity of the issue, we need to know the sources and transport mechanisms of atmospheric trace elements that have given rise to ubiquitous, global, background atmospheric trace element contamination in natural ecosystems. This has become a cause of great concern over past and present decades.

Trace element contamination from temporal and geographic perspectives

The mining and metallurgy of trace elements has possibly had the oldest, atmospheric, human-driven impact on Earth. With the discovery of mining and metallurgy techniques, the close link between trace elements, trace element contamination and human history was formed (Nriagu, 1996). Of the historically mined metals, lead (Pb) has been a focus of concern and thus of research in many aspects (Shotyk and Le Roux, 2005). Settle and Patterson (1980) first established the history of world Pb production over the last five millennia, mainly from archaeological data (Figure 1, adapted from Settle and Patterson, 1980). After the start of cupellation 5000 years ago, Pb production (and that of several trace elements related to Pb ores that followed this trend) increased dramatically with the introduction of the coinage 2600 years ago, and persisted during

Greek/Phoenician and Roman periods. Remarkably, most of the Roman production was located in the Iberian Peninsula, particularly in the Rio Tinto mines, SW Spain. At the beginning of the Medieval Age, production of Pb was restarted in Germany and Great Britain, and by Spanish colonizers in the Americas. With the Second Industrial Revolution in 1850, the production of metal and other trace elements was considerably developed. In modern times, the main anthropogenic sources of trace elements to air are various industrial processes, mining, foundries, smelters, the combustion of fossil fuels including petrol, and waste incinerators (Pacyna, 1984).

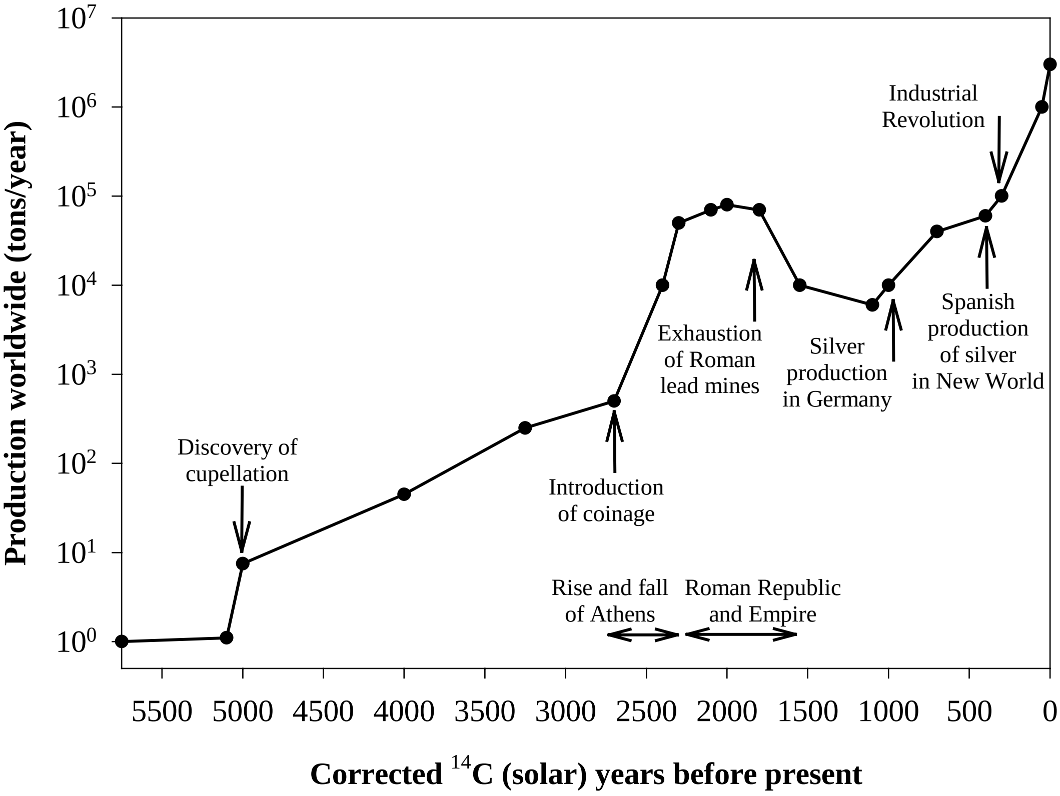

Figure 2. World lead production over the past 5500 years, including certain historical events that have influenced it (redrawn from Settle and Patterson, 1980).

The irrefutably widespread, long-term trace element contamination related to humankind has been recorded and investigated using several different natural archives such as snow/firn and ice (Hong et al., 1994; Krachler et al., 2009; Zheng et al., 2007), peat (Martínez-Cortizas et al., 1997; Shotyk et al., 1998), soils (Klaminder et al., 2008), marine (Alfonso et al., 2001) and lake sediments (Renberg et al., 1994, Yang and Rose, 2005), coral (David, 2003) and tree-rings (Bindler et al., 2004). The literature on this topic is extensive and detailed. However, it mostly covers the Northern Hemisphere and Antarctica.

Monitoring to directly study the trends in atmospheric deposition of trace elements is a relatively new activity due to the inability, until recently, to analyse quantitatively constituents in water at the mg L^{-1} level or less and to ignorance of the potential significance of this deposition (Galloway, 1982). The first measurements were made in the late 1960s (Lazrus et al., 1970). Since then, direct measurements on dry, wet, cloud or bulk deposition have been carried out in urban, rural and remote environments. Measurements conducted close to the point sources reflect the degree of local contamination, whereas measurements from rural and remote sites are representative of atmospheric trace element contamination at regional and global scales, respectively. Alternatively, the examination of trace elements in mosses and lichens is commonly conducted as an effective surrogate of the current atmospheric trace element contamination at any site (Doucet and Carignan, 2001; Fernandez et al., 2002; Harmens et al., 2008; Poikolainen et al., 2004).

During the last three decades considerable attention has been paid to the potential risks of increasing trace element concentrations in atmospheric deposition and whether these concentrations threaten human, organism or ecosystem health. Consequently, the control of trace element emissions has become of key importance. Between the early 1980s and the mid-1990s, European and North American anthropogenic emissions into the atmosphere were halved for several trace elements, due to improvements in the efficiency of the technological measures introduced at power plants and waste combustion facilities. The increased use of oil and natural gas for electricity generation instead of coal also reduced trace element emissions in Europe. However, demand for coal-based energy in Asian countries increased significantly between the beginning of the 1980s and mid-1990s. Therefore, the emissions of metals including Cd and Pb from stationary fossil fuel combustion did not change significantly on a global basis until the mid-1990s. Then, regulatory actions under new legislation resulted in significant, measurable reductions in trace element inputs to air. For instance, the Executive Body of the Convention on Long-range Transboundary Air Pollution adopted the Protocol on Heavy Metals on 24 June 1998 in Aarhus (Denmark). It targeted three particularly harmful metals: Cd, Pb and Hg. Parties had to reduce their total annual emissions for these three metals below their 1990 levels (or an alternative year between 1985 and 1995). The Protocol aimed to cut emissions from industrial sources, combustion processes and waste incineration. It lowered limit values for emissions from stationary sources and suggested best available techniques for these sources. The Protocol also required the parties to phase out leaded petrol.

In Table 1, the worldwide atmospheric emissions of several trace elements from natural sources (Nriagu, 1989) are compared to anthropogenic emissions to air estimated in the mid-1990s (Pacyna and Pacyna, 2001). Natural emissions of As, Cr, Cu, Hg, Mn, Mo, Sb and Se prevailed over anthropogenic emissions, whereas atmospheric emissions of Cd, Ni, Pb, V and Zn due to human activity were dominant. By contrast, a subsequent study carried out at the Geological Survey of Canada (Richardson, 2001) presented estimates of Cd, Cu, Hg, Ni, Pb and Zn global emissions from natural sources (with 90% confidence limits) between one and two orders of magnitude greater than those of Nriagu (1989). These estimates, whether true or not, have major implications on the anthropogenic-to-natural emission ratios. Nevertheless, a recent review of the Earth’s global cycles of a suite of metals proposes that anthropogenic emissions of Cr, Cu, Ni and Zn are between a third and a half of natural emissions, whereas anthropogenic Pb emissions are comparable to the natural fluxes (Rauch and Pacyna, 2009).

Despite international efforts to reduce emissions during recent decades, a large number of the Earth’s ecosystems are still considered to be at risk because of an excess of

Table 1. Global atmospheric emissions of trace elements from natural sources compared to emissions from anthropogenic sources in the mid-1990s.

Natural emissions[a] (x10^6 kg yr^{-1})	**As**	**Cd**	**Cr**	**Cu**	**Hg**	**Mn**	**Mo**	**Ni**	**Pb**	**Sb**	**Se**	**V**	**Zn**
Wind-borne soil particles	2.6	0.21	27	8.0	0.05	221	1.3	11	3.9	0.78	0.18	16	19
Sea salt sprays	1.7	0.06	0.07	3.6	0.02	0.86	0.22	1.3	1.4	0.56	0.55	3.1	0.44
Volcanoes	3.8	0.82	15	9.4	1.0	42	0.4	14	3.3	0.71	0.95	5.6	9.6
Wild forest fires	0.19	0.11	0.09	3.8	0.02	23	0.57	2.3	1.9	0.22	0.26	1.8	7.5
Biogenic													
Continental particulates	0.26	0.15	1.0	2.6	0.02	27	0.40	0.51	1.3	0.2	1.12	0.92	2.6
Continental volatiles	1.3	0.04	0.05	0.32	0.61	1.3	0.06	0.10	0.20	0.04	2.6	0.13	2.5
Marine	2.3	0.05	0.06	0.39	0.77	1.5	0.08	0.12	0.24	0.05	4.7	0.16	3.0
Total[a]	12	1.3	44	28	2.5	317	3.0	30	12	2.4	9.3	28	45
Total[b]		41		2,000	58			1,800	1,800				5,900
Total[c]			173	109				69	126				301
Anthropogenic emissions in 1995[d] (x10^6 kg yr^{-1})	**As**	**Cd**	**Cr**	**Cu**	**Hg**	**Mn**	**Mo**	**Ni**	**Pb**	**Sb**	**Se**	**V**	**Zn**
Stationary fossil fuel combustion	0.81	0.69	10.15	7.08	1.48	9.42	2.64	86.11	11.69	0.73	4.10	240.08	9.42
Vehicular traffic									88.74				
Non-ferrous metal production	3.46	2.17	-	18.07	0.16	0.06	-	8.88	14.82	0.55	0.47	0.01	40.87
Iron and steel production	0.35	0.06	2.83	0.14	0.03	1.06	-	0.04	2.93	0.01	0.01	0.07	2.12
Cement production	0.27	0.02	1.34	-	0.13	-	-	0.13	0.27	-	0.003	-	2.67
Waste disposal	0.12	0.04	0.43	0.62	0.11	0.51	-	0.13	0.82	0.27	0.02	0.02	1.93
Other					0.33								
Total[d]	5.01	2.98	14.73	25.92	2.24	11.05	2.64	95.29	119.26	1.56	4.60	240.26	57.01
Total in 1983[e]	18.82	7.57	30.48	35.37	3.56	38.27	3.27	55.65	332.35	3.51	3.51	86.00	131.88
Total in 2000[c]			79.13	48.28				33.01	119.10				99.80
Anthropogenic[d]/Natural[a] emission ratios (in 1995)	**0.42**	**2.3**	**0.33**	**0.93**	**0.88**	**0.03**	**0.87**	**3.2**	**9.9**	**0.67**	**0.49**	**8.6**	**1.3**
Anthropogenic[c]/Natural[c] emission ratios (in 2000)			**0.46**	**0.44**				**0.48**	**0.94**				**0.33**

[a] Nriagu, 1989; [b] Richardson, 2001; [c] Rauch and Pacyna, 2009; [d] Pacyna and Pacyna, 2001; [e] Nriagu and Pacyna, 1988. [a, b, c] Totals are computed from three different reviews on global natural atmospheric emissions. The later estimations integrate, update and expand upon previous natural emission inventories. [c, d, e] Totals are quantified from three different assessments of global anthropogenic emissions to the atmosphere for the years 2000, 1995 and 1983 respectively. Differences show both increasing and decreasing emission tendencies amongst the trace elements over the last two decades.

certain trace elements in the atmospheric deposition, which may cause adverse effects on wild life and human health (van het Bolcher et al., 2006). Moreover, continued cycling in the environment of accumulated pools of persistent contaminants such as trace elements can result in continued exposure long after controls have been enforced (Klaminder et al., 2006a; Rothwell et al., 2008; Yang et al., 2007). In this context, concern is currently growing that cold areas of the Earth are sensitive zones for the accumulation of long-range transported contaminants. These areas include the poles and high mountains, which are considered “cold fingers” that act as a trap and in which contaminants have been accumulating in permanent ice- and snow-fields. Furthermore, in a situation of global warming, contaminants are more likely than ever to be released owing to the melting of ice and snow or the respiration of organic-enriched soils and peats (Bargagli, 2008; Klaminder et al., 2010; Noyes et al., 2009).

Apportioning between natural and anthropogenic sources

Contamination studies of trace elements are conducted from either chronological records or direct measurements, and implicitly need to separate the contaminant (i.e. anthropogenic) from the natural (i.e. lithologic) components. Several methods have been used to assess the anthropogenic contribution in a range of environmental samples. For instance, a direct comparison of the concentrations of samples from high atmospheric contamination loads and those of samples from pre-contamination events may give an estimate of the increment due to such events. This classical approach was used in a lake sediment study in Sweden by Renberg and collaborators (1994). Complementarily, the study of correlations between pairs of trace elements may reflect different origins in pre-industrial and modern sediments (Camarero, 2003; Camarero et al., 2009) or atmospheric deposition samples (Maneux et al., 1999).

However, since variations in trace elements may not only be due to contamination inputs, a more appropriate way to elucidate the contamination component is to correct the trace element concentrations using a reference element of major lithologic origin to obtain the “natural ratios” or the “elemental signatures”. Hence, the extent of the contamination within the record can be calculated on the basis of enrichment factors (EF), which are defined as the quotient between the ratio in a certain sample, with respect to the natural background ratio. Furthermore, the anthropogenic trace element concentration profile can be reconstructed from the natural concentration profile, which in turn is determined from the natural ratios. This method has frequently been used in ice (Krachler et al., 2009), peat bogs (Shotyk et al., 2002) and lake sediments (Blais and Kalff, 1993). EF can similarly be calculated in other records such as soils, aerosols, deposition samples or surrogates (e.g. bioindicators). In these cases, the average composition of the upper continental crust (UCC) is used as the natural background ratio (Li et al., 2009; Veysseyre et al., 2001). However, caution must be exercised in the interpretation of the EF relative to an average crustal reference in environmental geochemistry (Reimann and de Caritat, 2005) for several reasons. The composition of the Earth’s crust in different areas is spatially variable in relation to the global average continental crust, and natural fractionation of elements may occur during near-surface processes. Consequently, anomalously high enrichment factors may be due to natural rather than anthropogenic sources, as suggested by Duce and collaborators (1975) when the EF concept emerged. To take into account these considerations, EF can be computed by choosing a regional or local source material such as the bedrock or the lower soil horizon (Bergamaschi et al., 2002; Blaser et al., 2000), or a natural point-source of trace elements that specifically affect the study area, such as aerosols from the Sahara desert or the sea water (Atteia, 1994).

Amongst the range of trace element contaminants of historical concern, Pb has the unique property of being present in the environment as a mixture of four isotopes (204Pb, 206Pb, 207Pb and 208Pb) that vary in different regions of the Earth for geological reasons. In addition, the isotopic composition of Pb ores is usually different from that of bedrock (Faure, 1986), which means that the provenance of Pb contamination in the environment can be inferred from the Pb isotopic composition (Renberg et al., 2002). Analyses of stable Pb isotopes, in which the $^{206/}$Pb/^{207}Pb ratio as the most frequently used isotope signature, combined with the Pb concentration data has become a useful method for tracing Pb from different sources in environmental studies. Recent examples include the study of aerosols (Deboudt et al., 1999), precipitation (Des Jardins et al., 2004), ice and snow (Rosman et al., 1997), peat bogs (Weiss et al., 1999), sediments (Brannvall et al., 1999), soils (Bindler et al., 1999) and water fluxes within a catchment (Graham et al., 2006). Hence, the amount of anthropogenic Pb contained in a sample can be calculated by applying a simple mixing model:

$$[Pb]_{anthropogenic} = \frac{(^{206}Pb/^{207}Pb)_{sample} - (^{206}Pb/^{207}Pb)_{background}}{(^{206}Pb/^{207}Pb)_{anthropogenic} - (^{206}Pb/^{207}Pb)_{background}} \times [Pb]_{total\_sample} \quad (1)$$

where ^{206}Pb/^{207}Pb$_{\text{sample}}$ is the isotope ratio of a given sample, ^{206}Pb/^{207}Pb$_{\text{background}}$ is the isotope ratio of reference, ^{206}Pb/^{207}Pb$_{\text{anthropogenic}}$ is the isotope ratio of anthropogenic Pb, and [Pb]$_{\text{total\_sample}}$ is the Pb concentration of a given sample. Thus, it is necessary to have previously defined both the background and anthropogenic Pb isotope signatures.

The solubility of atmospherically derived trace elements is controlled, amongst other factors, by their nature, and hence by the source of the particulates contained in the sample. It has been established that anthropogenic and marine sources are associated with a higher percentage of soluble phases than crustal sources (Giusti et al., 1993). Consequently, several studies have addressed the partitioning of trace elements between soluble and insoluble fractions as a factor that can help to estimate the anthropogenic influence. Examples include the study of dry and wet deposition (Chester et al., 1999), fog water (Millet et al., 1995) and snow (Landsberger et al., 1989). Additionally, the solubility of atmospherically derived trace elements has implications on their fate in receiving terrestrial and aquatic ecosystems. For instance, soluble forms may be favoured over the retention and accumulation of elements tightly bound to particles in soils (Chopin and Alloway, 2007). In addition, soluble forms are known to be more bioavailable to organisms (Borgman, 2000; Cizmecioglu and Muezzinoglu, 2008).

High mountain lake catchments: the Pyrenees

Mountain lake catchments are viewed as excellent sensors of background diffuse contamination. Given their relative remoteness, mountain lake catchments are very sensitive to atmospheric contamination that is transported at a long-range distance (Battarbee et al., 2002; Camarero et al., 2009). Moreover, as the catchment surface is commonly smaller than lowland lakes, both atmospheric deposition and catchment weathering become important in the determination of lake water chemistry (Catalan et al., 1993; Camarero et al., 1995). In addition, as mountain lakes have quite extreme climatic regimes, they are very sensitive to climatic variations (Catalan et al., 2002; Lami et al., 2000). All these features make mountain lake catchments excellent “sentinels” and recorders that provide signals of past and present global environmental changes (Catalan et al., 2006; Williamson et al., 2009). In other words, a high mountain lake catchment is seen as a valuable “sentinel ecosystem”, because it is a well understood system that have substantial datasets and is monitored in a long-term manner forming an early warning and core system for broader regional and global change (Christian and Mazzilli, 2007).

Studies of atmospheric trace element biogeochemistry (including atmospheric inputs, accumulation, transport, distribution and fate) in remote (or relatively remote) lake catchment systems have revealed the following aspects of interest, amongst others: the atmospheric deposition at these sites is representative of the current background atmospheric contamination levels at a broad (regional or global) scale; once the contaminants have been deposited in these systems, they can be differentially stored and redistributed through their biogeochemical compartments (soil, lake water, sediments, and terrestrial and aquatic biota); historical reconstructions of atmospheric contamination can be made from lake sediments, which act as natural archives of the deposition of contaminants; all these transfer processes (deposition, storage, redistribution, etc.) of contaminants can be spatially different, as they may follow the latitudinal or altitudinal gradient at these sites.

Furthermore, it may be useful to measure the inputs and outputs of trace elements and their distribution within the various ecosystem compartments, and then to use mass transport models. This method could help to specifically study the contaminant dynamics through the whole catchment/lake system. In particular, this modelling approach may provide evidence for the retention or the transfer of previously deposited atmospheric contaminants from catchments to lakes. If transport from catchment occurs, then great care must be taken when using lake sediments to describe trends in atmospheric deposition. Moreover, the restoration of the natural catchment/lake system is then compromised by the long-lasting effects of the historical atmospheric contamination, despite the recent control of contaminant emissions.

Overall, since the historical deposition of trace elements is highly relevant for biogeochemical cycling today, there is a clear connection between the record of atmospheric trace element contamination preserved in the lake sediments, soil or peat and the present-day biogeochemical cycling of potentially contaminating trace elements in natural areas (Bindler et al., 2008). For example, a comprehensive view of integrated historical and contemporary perspectives was drawn up for Pb and Hg in a Scottish mountain lake catchment (Yang et al., 2002a) and for Pb both in an upland Scottish catchment (Bacon and Hewitt, 2005; Graham et al., 2006) and in the Swedish boreal forest (Bindler et al., 2008).

In the Pyrenees, trace element contamination studies began with the reconstruction of atmospheric Pb fluxes from a dated lake sediment core (Camarero et al., 1998). This study revealed that atmospheric Pb contamination has occurred in the Pyrenees since Antiquity and is largely related to human activities. Ancient trace element contamination is mostly attributed to the mining of metal ore deposits in the surrounding area. Contemporary trace element enrichment is due to modern mining and smelting activities (Figure 2, from Camarero et al., 1998), but may also be related to fossil fuel combustion and, since around 1950, leaded gasoline consumption (Dörr et al., 1990). Subsequently, regional atmospheric contamination of Pb and other trace elements with respect to a pre-Industrial background was evidenced on the basis of an extended lake sediment survey in the Pyrenees (Camarero, 2003). In addition, a study of atmospheric trace element and radionuclide contamination through the lake catchment system, which started with measurements of atmospheric inputs and ended with the sedimentary record, was carried out in a set of European high mountain lakes, including one site in the Pyrenees (Plöger, 2004). The data were then used to establish the mass balances of contaminant substances, to estimate catchment inputs to the lake and losses from the outflow, and to assess whether a transport model for catchment/lake systems that was originally designed for fallout radionuclides was valid for trace elements.

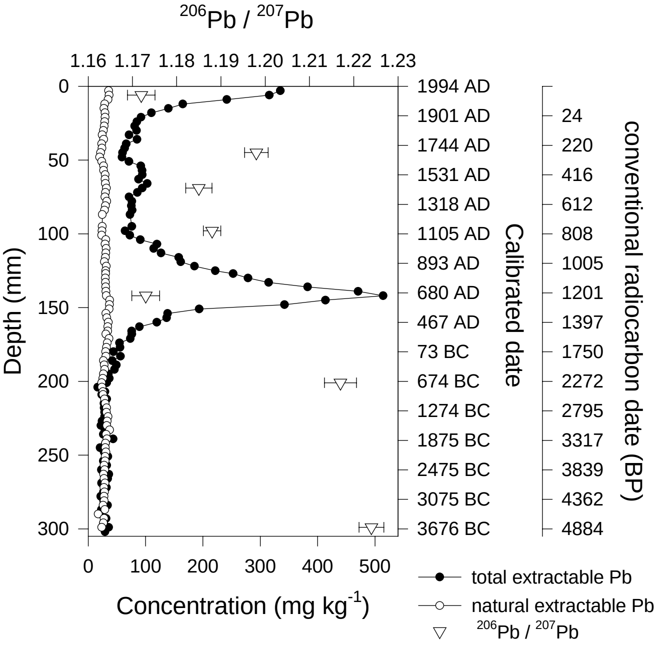

Figure 3. Lead (Pb) concentration profiles from a dated lake sediment core in the Pyrenees (from Camarero et al., 1998). Both peaks showed coincident isotopic signatures that revealed the same origin of Pb. Thus, mining and smelting at a relative large scale must have taken place in the surrounding area during post-Roman times.

With regard to the study of direct contemporary atmospheric trace element inputs, a closer analysis of several biogeochemical features of atmospherically derived trace elements could help to determine sources, controlling factors, and the potential impact of deposited trace elements on ecosystems. In addition, the examination of meteorological factors that influence trace element depositional fluxes would provide insight into spatial and temporal variability. Until then, we cannot effectively apportion between anthropogenic and natural trace element fractions in inventory calculations, especially in soil cores. This problem could be solved by measuring Pb isotopes in soil and sediment profiles. Trace element analysis of collected sediment trap material could provide further information on the transport of trace elements through the water column. The terrestrial and/or aquatic vegetation in the catchment/lake system may also play a role as sources or sinks of trace elements. Thus, these biotic compartments could also be considered in the catchment/lake transport model. Moreover, the study of the input and transmission of trace elements through the catchment/lake system could be extended to other sites with an altitudinal gradient covering a range of environmental properties.

In conclusion, although a link has already been made between the data recorded in the natural archives and the contemporary trace element biogeochemistry in Pyrenean high mountain lake catchments, several issues raised in previous studies require further investigation to achieve a whole-catchment, comprehensive understanding of trace element cycling and the fate of trace elements in such relatively remote ecosystems.

Objectives of the present study

The aim of this thesis was to test the Pyrenean high mountain lake catchments as sentinel ecosystems by providing signals of both historical and contemporary trace element contamination.

The evaluation of this status was attempted by the following specific objectives. A first objective was to examine historically accumulated burdens and present-day fluxes of a suite of trace elements in Pyrenean high mountain lake catchments. A second objective was to evaluate trace element deposition, transport and distribution through the biogeochemical compartments, and ultimately, to determine their fate in such relatively remote ecosystems. A further objective was to separate “natural” components from those that can be termed “anthropogenic” in these past and modern pools of trace elements.

Experimental design

In the present study, the concentrations of several major (Al, Ti, Mn and Fe) and trace (Ni, Cu, Zn, As, Se, Zr, Cd and Pb) elements were evaluated in a variety of samples: snow, rainwater, lake water, soils, sediments and biological samples. Amongst the major and trace elements, “lithologic” sources of Al, Ti, Mn, Fe and Zr are generally considered to be much more relevant than “anthropogenic” ones in the environment. For instance, although Al and Fe represent >95% by mass of all metals mined in the world, global natural cycles of Al and Fe still exceed by one order of magnitude or more the global anthropogenic flows of these two elements (Rauch and Pacyna, 2009). Therefore, these five metallic elements were selected a priori to trace various natural fluxes and biogeochemical processes within the studied catchment/lake systems. By contrast, total (i.e. to air, water, and land) natural and anthropogenic fluxes of Ni, Zn, Cd and Pb have approximately the same order of magnitude, and total anthropogenic fluxes of Cu even exceed natural fluxes by one order of magnitude or more (Rauch and Pacyna, 2009). Anthropogenic fluxes of As and Se also play a major role in perturbing the natural distribution of these elements over the Earth (Plant et al., 2003; Matschullat, 2000). In addition, As is an element of special concern in the Pyrenees, since Pyrenean plutonic rocks are naturally enriched in As with respect to other mountainous massifs (Arranz, 1997). Hence, Ni, Cu, Zn, As, Se, Cd and Pb were chosen as trace elements of environmental concern in the several studies conducted in this thesis.

The surveys attempted to address two major topics: contemporary atmospheric fluxes of trace elements in high mountain areas and the long-term atmospheric deposition, storage, transport and fate of trace elements in high mountain lake catchments. The resultant research articles are presented here within these two themes as Part I and Part II, respectively.

In **Part I**, current atmospheric trace element fluxes to high mountain lake catchments were measured from bulk deposition and snow samples. Here, special attention was paid to the study of meteorological factors that influence atmospheric trace element fluxes in the Central Pyrenees (**Paper I**). Seasonal atmospheric trace element fluxes in the Central Pyrenees were estimated from the winter snowpack sampled along a gradient of altitude (**Paper II**). The atmospheric trace element fluxes were assessed from bulk deposition samples at six remote high mountain sites in Europe over a period of two years (**Paper III**).

In **Part II**, long-term, historical deposition was examined from soil records and lake sediment cores. Soil records provided the cumulative atmospheric trace element deposition on a long-term scale, taking into account post-depositional processes in soil that influence the atmospherically derived trace element record. Lake sediments provided a chronological, dated record of cumulative atmospheric trace element deposition, which in turn can be subject to additional inputs transported from the catchment. The long-term record of atmospheric trace element fluxes in the Central Pyrenees was examined in detail from a soil transect along a high elevation gradient (**Paper IV**).

In addition to the trace element concentration analyses, Pb isotope ratios were determined to apportion different Pb sources in soil and sediment records retrieved from three Pyrenean lake catchment systems located along a gradient of altitude, and to validate estimates of other trace metals with no available isotopes (**Paper V**). In this study, there was a special emphasis on methodological aspects, to reliably estimate natural and anthropogenic contributions to the whole-catchment trace element inventories.

Finally, a mass transport model was used for the three catchments to estimate the present-day transport of trace elements from terrestrial to aquatic ecosystems, and ultimately their fate, in high mountains during the snow- and ice-free period. In this study, trace element measurements were carried out on bulk deposition, lake water, sediment traps and plant samples (**Paper VI**).

Further important aspects of the trace element biogeochemistry within remote (or relatively remote) mountain lake/catchment ecosystems are considered in the different chapters. For instance, the partitioning between soluble and insoluble phases of trace elements was assessed in aqueous samples (**Papers I**, **II**, **III** and **VI**). Speciation studies provide information on the origin of trace elements and on their availability for biota, and serve as a basis to gain insight into their potential fate in the environment. In addition, spatial gradients were assessed to evaluate atmospheric trace element deposition patterns across geographic regions (**Paper III**), and along altitudinal gradients (**Papers II**, **IV**, **V** and **VI**). Variable trace element fluxes in different European mountain areas may be related to varying levels of regional atmospheric contamination. With regard to altitudinal gradients, increasing trace element deposition could be related to increasing precipitation at higher altitudes. A high altitude gradient in remote (or relatively remote) sites can also be useful for discarding local from long-range atmospheric fluxes. Altitudes above the local influences are thus valuable to assess the extent of global/regional contamination and to define background contamination levels. Additionally, retention (or remobilization) of trace elements from terrestrial to aquatic ecosystems can be related to a number of environmental factors that are directly associated with climatic parameters, which in turn are determined by altitude (**Papers IV** and **VI**).

Results

Part I. Contemporary atmospheric fluxes of trace elements in high mountain areas

Paper I. Fluxes of Al, Fe, Ti, Mn, Pb, Cd, Zn, Ni, Cu and As in monthly bulk deposition over the Pyrenees (SW Europe): the influence of meteorology on the atmospheric component of trace element cycles and its implications for high mountain lakes

M. Bacardit and L. Camarero, 2009. Journal of Geophysical Research-Biogeosciences, 114, G00D02, doi:10.1029/2008JG000732

Figure 4. Atmospheric bulk deposition sampler, automatic weather station and field laboratory at Lake Redon, Central Pyrenees (by M. Bacardit).

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 114, G00D02, doi:10.1029/2008JG000732, 2009

Fluxes of Al, Fe, Ti, Mn, Pb, Cd, Zn, Ni, Cu, and As in monthly bulk deposition over the Pyrenees (SW Europe): The influence of meteorology on the atmospheric component of trace element cycles and its implications for high mountain lakes

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Received 20 March 2008; revised 22 August 2008; accepted 19 December 2008; published 27 March 2009.

[1] The atmospheric bulk (wet plus dry) deposition of trace elements was measured monthly at Lake Redon (2240 m above sea level, Central Pyrenees, Spain) in 2004–2006. Aluminum, Ti, Fe, Mn, and As were part of the dust carried from the Iberian Peninsula and North Africa: these elements presented low enrichment factors and occurred (except Mn) as particles. Lead, Zn, Cd, and Cu showed a polluting character: their enrichment factors were clearly above those that can be caused by natural fractionation processes; and they were found in a variable, though always large proportion as soluble forms. Nickel had intermediate properties suggesting a balance of both natural and polluting sources. Temporal variations of trace element deposition were related to the prevailing meteorological conditions. Deposition of dust, Pb, Ni, and Cd was higher during the year in which a larger proportion of precipitation came from the Iberian Peninsula–North Africa and followed low-altitude trajectories. On a seasonal scale, deposition of dust and Pb was similarly related to southern air masses occurring during June–November. Possible changes in the general atmospheric circulation patterns as a result of climate change may cause a shift in the proportion of air masses coming from different locations and hence in the fluxes of the elements received by the catchments. Such atmospheric fluxes have caused high concentrations of several trace elements in Pyrenean lake sediments at a level which may be of ecotoxicological relevance.

Citation: Bacardit, M., and L. Camarero (2009), Fluxes of Al, Fe, Ti, Mn, Pb, Cd, Zn, Ni, Cu, and As in monthly bulk deposition over the Pyrenees (SW Europe): The influence of meteorology on the atmospheric component of trace element cycles and its implications for high mountain lakes, *J. Geophys. Res.*, *114*, G00D02, doi:10.1029/2008JG000732.

1. Introduction

[2] Atmospheric fluxes are an important component of the global cycle of a number of elements. In many cases these fluxes are caused by the long-range transport of elements from distant source areas to terrestrial and aquatic ecosystems, where they may acquire biogeochemical relevance [*Schlesinger et al.*, 1982; *Okin et al.*, 2004; *Morales-Baquero et al.*, 2006; *Pulido-Villena et al.*, 2006]. Airborne trace elements may play different roles in ecosystems: they may be important as micronutrients, but also have negative toxic effects [*Nriagu and Pacyna*, 1988]. Trace elements in the atmosphere can originate from diverse sources [*Pacyna and Pacyna*, 2001], either natural (soil and rock dust, sea spray, volcanic activity, natural forest fires) or artificial (burning of urban residues, smelting and other industrial processes, fossil fuel combustion). The atmospheric flux of trace elements has changed over time on a global scale, as proved by chronological sequences retrieved from the remotest sites on Earth, such as glacier ice from the Arctic [*Hong et al.*, 1994] and high mountains [*Van de Velde et al.*, 2000]. These changes have caused variations in the biogeochemistry of trace elements in ecosystems, as revealed for instance by natural records from sources as diverse as peat bog sequences [*Brännvall et al.*, 1997; *Shotyk et al.*, 1998; *Martinez-Cortizas et al.*, 2002], lake sediments [*Renberg et al.*, 1994; *Camarero et al.*, 1998], tree rings [*Baes and McLaughlin*, 1984], and coral formations [*David*, 2003].

[3] Undoubtedly, by increasing their emission to the atmosphere, human activities have altered the global cycles of several trace elements since ancient Greek and Roman times [*Nriagu*, 1990]. Despite current international efforts to reduce emissions, a large number of the Earth's ecosystems are still considered to be at risk because of an excess of certain trace elements in the atmospheric deposition, which may cause adverse effects on wildlife and human health [*van het Bolcher et al.*, 2006]. However, it is not only anthropogenic sources that must be considered. In particular, Saharan dust outbreaks are recognized to cause significant natural input of a wide range of elements to areas as extensive as the whole European continent, from the Iberian Peninsula [*Escudero et al.*, 2005] to alpine and sub-Arctic zones [*Prodi*

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and Fea, 1978; *Franzén et al.*, 1994; *Ansmann et al.*, 2003], and as far as the Caribbean Sea [*Li et al.*, 1996] and the southeast United States [*Prospero*, 1999]. Furthermore, dust may act as a carrier of an enriched cocktail of diverse trace metals and metalloids [*Moreno et al.*, 2006]: although significant amounts of volatile metal and metalloid species can be released in a gas phase from both natural [*Ito and Shooter*, 2004] and anthropogenic emissions [*Hirner et al.*, 1993], atmospheric metals and metalloids are mostly adsorbed onto particles [*Morselli et al.*, 2003], whose size ranges from 0.001 μm to more than 10 μm [*Shrivastav*, 2001]. Changes in the large-scale atmospheric fluxes of trace elements and their effects on ecosystems are therefore not only due to variations in emission rates, but also to changes in the transport and deposition pathways of the carrier particles controlled by climatic conditions [*Prospero and Lamb*, 2003; *Rogora et al.*, 2004; *Jickells et al.*, 2005].

[4] High mountain emplacements are suitable for detecting global environmental signals [*Battarbee et al.*, 2002] because of the absence of direct local impacts that could mask such large-scale signals. Thus, the current content of several trace elements measured in soils and snow above approximately 2000 m above sea level (asl) in the Pyrenees has been viewed as a signature of long-range atmospheric fluxes, unlike at lower altitudes where local influence can still be detected (M. Bacardit and L. Camarero, Atmospherically deposited trace elements in the winter snowpack along a gradient of altitude in the Central Pyrenees: The seasonal record of long-range fluxes over SW Europe, submitted to *Atmospheric Environment*, 2008a; M. Bacardit and L. Camarero, Polluting and natural metals in soils along a gradient of altitude in the Central Pyrenees: A long-term record of background atmospheric pollution over SW Europe, submitted to *Environmental Pollution*, 2008b). The Pyrenees lie on the transition zone between the Mediterranean and Atlantic climatic regimes. This borderline position, combined with the particular climatic features of mountains [*Beniston*, 2005], makes the Pyrenees especially sensitive to global climate effects in SW Europe, one of the areas in Europe where the largest rates of climatic change are expected [*Intergovernmental Panel on Climate Change*, 2007]. Climate has an influence on the airborne element fluxes over this region through the atmospheric circulation patterns associated with different climatic situations. Wet air masses and storm episodes over the Pyrenees come mainly from two directions: those coming from N and NW directly from the northern Atlantic, and those coming from S and E originating from either the central Atlantic or the Mediterranean Sea and crossing land areas in northern Africa and the Iberian Peninsula. Their occurrence varies over time, and because of their different provenance they have a distinct composition of major chemical compounds: precipitation coming from the northern side of the Pyrenees is generally dilute and slightly acidic, in contrast with the alkaline, solute-enriched precipitation coming from the southern side [*Camarero and Catalan*, 1996]. This suggested the working hypothesis that the composition of trace elements may also be different.

[5] Lake sediments are the ultimate fate of elements atmospherically deposited in a catchment. The transfer of elements to sediments may be particularly important in high mountain catchments. Here, retention in the terrestrial part may be comparatively low with respect to lowland catchments, because a large proportion of the catchment's area is covered by bare rock, soils are thin, and vegetation is scarce. This has lead for instance to the buildup of high concentrations of several trace elements in Pyrenean lake sediments [*Camarero et al.*, 1998; *Camarero*, 2003], at a level which may be of ecotoxicological relevance.

[6] In this study, we aimed to characterize both quantitatively and qualitatively the atmospheric fluxes of trace elements over the Pyrenees, which can be considered as one measure of the regional fluxes in SW Europe. We also aimed to gain insight into the geophysical influences on such fluxes; that is, how the prevailing meteorological conditions determine the transport of trace elements over the region. To accomplish these objectives, the atmospheric bulk deposition of a group of trace elements was measured monthly over 2 years at a site more than 2000 m asl in the Central Pyrenees. Our results allowed us to (1) establish the current deposition levels of trace elements in the Central Pyrenees, which can be considered as the background level for the region; (2) determine several biogeochemical characteristics of atmospheric deposition that helped to identify sources, controlling factors, and potential postdepositional behavior of deposited trace elements; (3) show the influence of broad regional atmospheric transport pathways on trace element concentrations and fluxes at both the seasonal and interannual timescales; and (4) discuss the implications of the trace element deposition for mountain lakes and their sediments in particular.

2. Materials and Methods

2.1. Sampling

[7] Atmospheric bulk deposition was collected at the Lake Redon (formerly Lake Redó) field station (42° 38′ 36″N, 0° 46′ 48″E, 2240 m asl), in the Central Pyrenees (Figure 1). A detailed description of the station, the lake and its catchment can be found in the paper by *Ventura et al.* [2000]. An automatic weather station (AWS) records air temperature, humidity, wind speed, wind direction, sun radiation and precipitation every thirty minutes. A field laboratory facilitates on-site work all year round. Bulk precipitation samples were collected every fourth week from 29 April 2004 to 14 December 2006. In summer, precipitation was sampled with a 22 cm diameter polyethylene funnel connected to an 8 l polyethylene reservoir by a tube, in which a 250 μm nylon mesh was placed to prevent large particles, such as insects or leaves, from entering the water tank. In winter, when precipitation occurs as snow, a 15 cm diameter, 30 cm long polystyrene tube assembled on top of a 30 l polyethylene tank was used for sampling. A wind screen was placed around the collector's mouth to prevent biased snow collection due to wind disturbance. This kind of passive collectors were preferred to wet- and dry-only samplers (WADOS) because the harsh environmental conditions make the functioning of WADOS unreliable when they have to be left unattended in high mountain emplacements, which require constant power supply and have mobile mechanical parts with electronic controls. Both samplers were placed 1.5 m above ground level, close to the AWS precipitation gauge. The amount of precipitation was estimated as the average of the volume collected in the sampler and two more collectors deployed for other purposes.

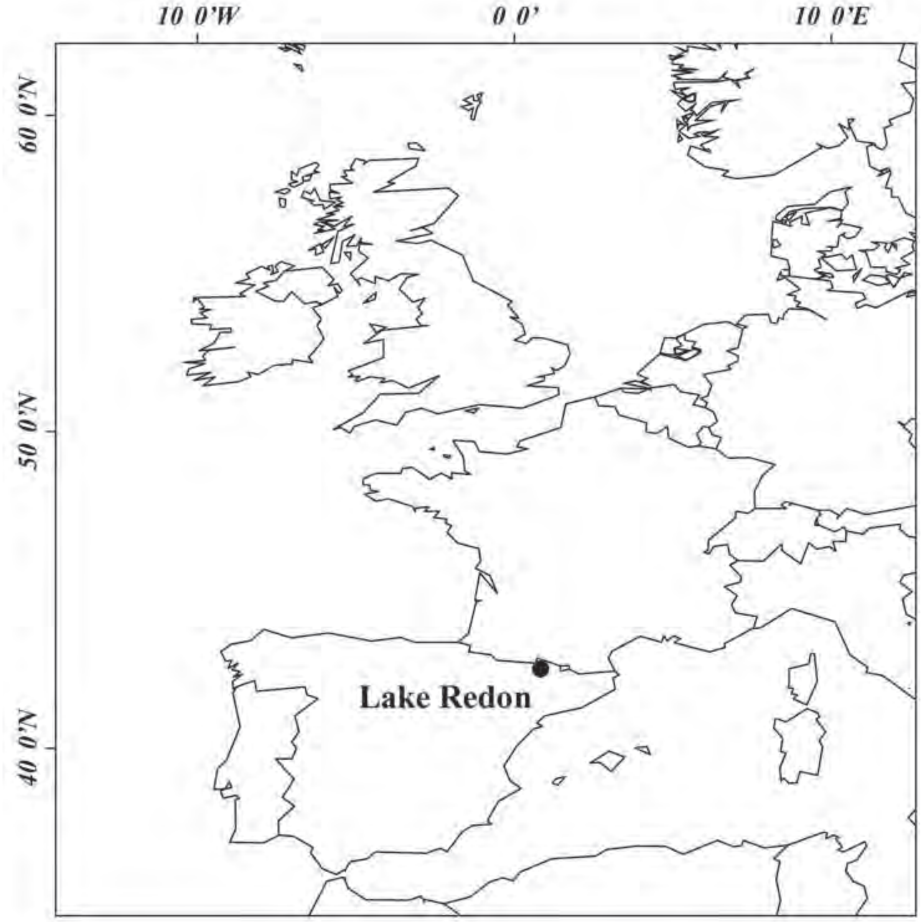

Figure 1. Study site location.

These estimates were checked against the measures provided by the AWS, which was equipped with a Geonor T-200B precipitation gauge with a wind screen aerodynamically designed to minimize wind effects (http://www.geonor.com/precipitation_gauge.html). The measures were generally comparable, suggesting that a strong bias in collection due to wind cannot be suspected for rain and snow, and possibly also for dry-deposited particles, in the bulk collectors. During the period from mid-October to mid-December 2004 snowstorms occurred earlier than usual, and funnel-type rain collectors had not been still substituted by snow collectors, causing the precipitation to be underestimated. The AWS precipitation gauge was not working either, and the volumes for the two corresponding sampling intervals were obtained from the nearest meteorological station in Vielha, a town sited at 980 m asl and 7 km north of the Lake Redon station. Immediately after collection, samples were filtered on site using Whatman cellulose nitrate filters (47 mm diameter and 0.45 μm pore size) at the Redon field station. Snow samples were first melted with a gentle steam bath. Filters used to collect the particulate fraction were kept inside polypropylene vials, and 100 mL of filtered water (dissolved fraction) was acidified with 1% Merck Suprapure nitric acid in polypropylene bottles. Both particulate and dissolved fraction samples were kept frozen until analysis. A precipitation subsample was taken for measuring pH within 2–3 h after collection.

2.2. Analysis

[8] Acidified samples for the dissolved fraction were not treated further before analysis. Filters with the particulate fraction were digested using 2 mL Merck Suprapure nitric acid and 1 mL Merck Suprapure hydrogen peroxide in closed Teflon beakers at 95°C for 16 h. After this step, beakers were rinsed three times with 10 mL of deionized water, making a total extract volume of 33 mL. This is not a total digestion, but an extraction process similar to U.S. EPA Method 3050b, generally used in environmental exposure assessment. Four different reference materials (CRM141r calcareous loam soil certified by the Community Bureau of Reference; GSS4 soil, GSR6 limestone and GSD5 stream sediment all certified by the Institute of Geophysical and Geochemical Prospection) were processed to assess the fraction of elements extracted with this method with respect to the certified total content (see section 4.1). Trace element analyses were performed by Inductively Coupled Plasma (ICP). Iron was quantified by Optical Emission Spectrometry (ICP-OES) with a Perkin Elmer OPTIMA 3200 RL instrument. Aluminum, Ti, Mn, Ni, Cu, Zn, As, Cd and Pb were measured by Mass Spectrometry (ICP-MS) with a Perkin

Table 1. Analytical Quantification Limits and Concentration of Blanks[a]

	Al	Fe	Ti	Mn	Zn	Ni	Cu	As	Se	Cd	Pb
Quantification limits	5.00	10.00	0.50	0.10	0.20	0.20	0.05	0.10	1.00	0.05	0.05
					Dissolved (n = 48)						
Mean	1.32	0.27	n.d.	0.01	0.23	0.06	0.01	n.d.	n.d.	n.d.	n.d.
SD	4.18	1.47	-	0.05	0.48	0.05	0.03	-	-	-	-
					Particulate (n = 20)						
Mean	11.00	9.16	0.37	0.17	1.23	0.61	0.19	n.d.	0.07	0.23	0.08
SD	6.82	3.98	0.25	0.05	0.50	0.13	0.19	-	0.10	0.42	0.04

[a] Reported values for the particulate fraction correspond to the measures in the extracts, which should be divided by a factor of ~6 to make them comparable with concentrations in the precipitation. Here n.d. indicates nondetectable. With the exception of Zn, all blanks for the dissolved fraction were below the quantification limit (QL). In the case of the particulate fraction some blanks were higher than the QL. However, blanks were well below the concentration ranges measured in precipitation samples in this study. Values are in μg l^{-1}.

Elmer ELAN 6000 instrument. For instrument calibration, in every analytical run six standard dilutions were prepared from commercial, NIST traceable concentrated standard solutions, and an Rh internal solution was used as a tracer. A standard solution was injected every 20 samples to monitor instrumental drift, and the instrument recalibrated when necessary.

2.3. Analytical Quality Control

[9] During all manipulations, clean procedures were used to avoid contamination. Latex gloves were used both in the fieldwork and laboratory tasks. All sampling and laboratory materials were rigorously cleaned in a 5% nitric acid bath overnight, rinsed thoroughly several times with ultrapure deionized water (MilliQ, Millipore) and air-dried at room temperature in an isolated zone of the laboratory prior to use. Samples were not processed in a fully classified clean bench or room. Filtration was done on site in a small field laboratory on the lake shore, and extractions were performed in the laboratory of our main field station; in both cases the levels of suspended particles containing trace elements are expected to be lower than in ordinary air in urban labs. In order to accurately check for possible contamination during manipulations, a number of blank tests were performed both in the field and laboratory at several stages of the procedure. Collector's blanks were performed by pouring 10 l deionized water into the system and storing it for four weeks before analysis. No contamination was detected for any of the elements analyzed. One filtering blank was produced every sampling day using deionized water and obtaining both dissolved and particulate fractions, which were processed later on as regular samples. Two reagent blanks and two filter blanks were processed with every batch of thirty filter extractions. Several blanks of acidified deionized water were also analyzed. Analytical quantification limits (QL) and measured concentrations in blanks are shown in Table 1. With the exception of Zn, element concentrations in blanks for the dissolved fraction were well below the QL, whereas in the case of the particulate fraction some blanks were higher than the QL. However, blanks were well below the concentration ranges measured in precipitation samples in this study.

[10] In addition to the internal controls, our laboratory regularly participates in periodical analytical quality intercomparison exercises within the International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes (ICP Waters). As a part of each exercise, dissolved metal concentrations (Fe, Mn, Zn, Ni, Cu, Cd and Pb) in paired natural water samples are determined, and the acceptability of the results is checked using the Youden method [*Hovind*, 2005, 2006]. With a few exceptions that were not attributable to systematic errors, our measurements in the 2005 and 2006 exercises fell within the established acceptance limits.

2.4. Enrichment Factors

[11] Enrichment factors (EF) were computed to investigate the relative contribution of anthropogenic sources with respect to those of a natural origin. EF is defined as the ratio of concentrations in the precipitation sample of an element X divided by the concentration of a reference element, for which sources other than natural can be assumed to be negligible (e.g., Al), normalized by the same concentration ratio in the upper continental crust (UCC) given by *Wedepohl* [1995]: $\mathrm{EF_{UCC}} = ([X]_\mathrm{S}/[\mathrm{Al}]_\mathrm{S})/([X]_\mathrm{UCC}/[\mathrm{Al}]_\mathrm{UCC})$, where X is the element of interest and the subscript $_\mathrm{S}$ denotes concentrations in the sample. Because of natural variation in the composition of rocks and soils, an EF of up to 10 times the average crustal composition is not considered to indicate natural or pollution contributions other than crustal sources, an EF between 10 to 500 is considered moderately enriched, whereas an EF higher than 500 is considered highly enriched, indicating a strong anthropogenic contribution [*Muhlbaier Dasch and Wolff*, 1989]. EF were also computed using other possible natural sources of trace elements as a reference: $\mathrm{EF_{MDT}}$ were calculated using the composition of the Maladeta granite [*Arranz*, 1997], which forms the Lake Redon catchment bedrock, and $\mathrm{EF_{WS}}$ using the composition of Western Sahara soils [*Moreno et al.*, 2006], expected to be an important aeolian contribution to dust deposited over the area.

2.5. Meteorology

[12] For every precipitation event recorded by the AWS, the 72 h backward trajectory of the air mass originating the precipitation at 3000 m asl was computed, starting from when the precipitation intensity was maximal within the event. The altitude of 3000 m asl was chosen as to be approximately the base of the clouds causing precipitation in the area. Simultaneous back trajectories at different altitudes between 2500 and 4000 m asl were computed for several events. They generally matched, confirming the choice of 3000 m asl to be representative of the air mass above the sampling point. Back trajectories were computed using the HYSPLIT Model [*Draxler and Hess*, 1998]

Table 2. Concentrations of Trace Elements in Precipitation at Lake Redon in 2004–2006[a]

Fraction	Al ($\mu g\ l^{-1}$)	Fe ($\mu g\ l^{-1}$)	Ti ($\mu g\ l^{-1}$)	Mn ($\mu g\ l^{-1}$)	Zn ($\mu g\ l^{-1}$)
			Water Year 2004–2005 (n = 13)		
Dissolved	10 (b.q.l.–40)	1 (b.q.l.–15)	b.q.l.	3.35 (0.57–10.56)	14.48 (2.00–81.92)
Particulate	209 (24–1050)	182 (24–751)	3.51 (0.98–13.53)	1.76 (0.23–6.66)	2.57 (0.31–8.11)
			Water Year 2005–2006 (n = 13)		
Dissolved	13 (b.q.l.–46)	1 (b.q.l.–17)	b.q.l.	2.41 (0.17–9.40)	3.95 (0.00–17.81)
Particulate	353 (23–2584)	277 (29–1935)	5.19 (0.68–30.15)	3.69 (0.21–37.95)	1.05 (0.10–7.37)
			Whole Sampling Period (n = 31)		
Dissolved	11 (b.q.l.–59)	1 (b.q.l.–20)	b.q.l.	2.90 (0.17 –15.42)	7.11 (b.q.l.–81.92)
Particulate	278 (5–2584)	228 (5–1935)	4.35 (0.18–30.15)	2.76 (0.08–37.95)	1.81 (0.10–8.11)
Fraction	Ni ($\mu g\ l^{-1}$)	Cu ($\mu g\ l^{-1}$)	As ($\mu g\ l^{-1}$)	Cd ($\mu g\ l^{-1}$)	Pb ($\mu g\ l^{-1}$)
			Water Year 2004–2005 (n = 13)		
Dissolved	0.22 (0.00–0.61)	0.63 (0.10–1.93)	b.q.l. (b.q.l.–0.05)	b.q.l. (b.q.l.–0.02)	0.28 (0.03–1.08)
Particulate	0.20 (0.00–0.74)	0.34 (0.07–1.48)	0.05 (b.q.l.–0.15)	0.02 (b.q.l.–0.37)	0.68 (0.03–2.57)
			Water Year 2005–2006 (n = 13)		
Dissolved	0.19 (0.00–0.51)	0.26 (0.04–0.94)	0.01 (b.q.l.–0.11)	b.q.l. (b.q.l.–0.11)	0.45 (b.q.l.–1.58)
Particulate	0.33 (0.06–2.10)	0.37 (0.06–2.06)	0.04 (b.q.l.–0.33)	0.06 (b.q.l.–0.49)	0.74 (0.18–2.71)
			Whole Sampling Period (n = 31)		
Dissolved	0.22 (b.q.l.–0.61)	0.44 (0.04–1.93)	0.01 (b.q.l.–0.11)	b.q.l. (b.q.l.–0.11)	0.34 (b.q.l.–1.58)
Particulate	0.27 (b.q.l.–2.10)	0.36 (0.02–2.06)	0.05 (b.q.l.–0.33)	0.04 (b.q.l.–0.49)	0.69 (0.03–2.71)

[a]Values are volume-weighted averages for each period, with maximum and minimum between brackets. Here b.q.l. indicates below quantification limit.

(HYSPLIT data available at http://www.arl.noaa.gov/ready/hysplit4.html) provided at the READY website (http://www.arl.noaa.gov/ready.html). The 6 hourly FNL (GDAS) global archive from the National Centre for Environmental Prediction (NECP) was the meteorological data set used to feed the model. A total of 177 backward trajectories were obtained. Every backward trajectory consisted of 12 end-points corresponding to the air mass location at 6 h intervals and characterized by their geographic coordinates (longitude X, latitude Y, and altitude Z). All backward trajectories were then classified using two criteria. First, horizontal trajectories were grouped by means of an agglomerative hierarchical clustering (AHC) method using S-PLUS 6.0 Professional software package. Second, altitude trajectories were classified according to their mean elevation into high-altitude trajectories (more than 50% of time above 1000 m asl) and low-altitude trajectories (more than 50% of time below 1000 m asl). AHC was applied following the general recommendations by *Cape et al.* [2000]: A hierarchical rather than partitioning method was preferred as a number of clusters cannot be defined a priori. Grouping into clusters is done in an agglomerative way, which provides the lowest within-cluster variance and the highest between-cluster variance. The dissimilarity measure used was the squared Euclidean dissimilarity measure computed on each corresponding XY coordinate pair, which is appropriate for geographic distances. Ward's linkage was chosen for clustering because it is generally considered an efficient, easily interpretable method for Euclidean distances.

[13] An archive of both predictions and actual African dust intrusions over the Iberian Peninsula is available on the Calima project website (http://www.calima.ws). Thermal inversion episodes occurring in the lower troposphere in the Pyrenees and surroundings were identified from the monthly climatic reports published by the Meteorological Service of Catalonia (http://www.meteocat.com). Atmospheric sounding plots were captured from the Wyoming Weather Web (Department of Atmospheric Science, Univ. of Wyoming) at http://weather.uwyo.edu/upperair/sounding.html.

3. Results

3.1. Trace Elements in the Atmospheric Deposition

[14] A total of 31 samples were obtained during the study period. Two samples were lost: that from 10 March to 7 April 2006 when the collector was blown away by extremely strong winds, and the sample corresponding to 23 October to 15 November 2006 that was not filtered for particulate and dissolved fractions. Table 2 shows the volume-weighted mean concentrations and ranges of trace elements in both dissolved and particulate fractions. Concentrations are averaged for the whole study period and for the 2004–2005 and 2005–2006 water years (from October to September) separately. The elements occurred in the following order of abundance: Al, Fe > > Zn > Mn > Ti > > Pb, Cu > Ni > As > Cd. Selenium concentrations were in almost all cases below the QL, and are not further considered in this work. The codistribution of trace elements was assessed by estimating the correlation coefficients between total (dissolved plus particulate) concentrations during the whole sampling period (Table 3). Highly significant correlations were found between Al, Fe, Ti, Mn, Ni and As. Copper and Pb were well correlated with the first group of elements but not between themselves. Zinc and Cd were independent with respect to all other elements.

[15] EF values are shown in Figure 2. For Ti, Fe, and Mn they were generally below 10, indicating no significant enrichment. Nickel, Cu and Pb were moderately enriched with a number of cases with EF between 10 and 100, whereas Zn and Cd showed moderate to high EF. In general, EF were lower when using MDT and WS than when UCC was used as a reference. This was particularly remarkable in

Table 3. Linear Correlations Between Trace Elements

	Al	Fe	Ti	Mn	Zn	Ni	Cu	As	Cd	Pb
Al	1.00	0.99[a]	0.99[a]	0.97[a]	0.07	0.93[a]	0.63[a]	0.87[a]	−0.21	0.51[a]
Fe		1.00	0.99[a]	0.97[a]	0.08	0.93[a]	0.61[a]	0.88[a]	−0.22	0.53[a]
Ti			1.00	0.97[a]	0.08	0.94[a]	0.63[a]	0.89[a]	−0.24	0.52[a]
Mn				1.00	0.17	0.93[a]	0.65[a]	0.89[a]	−0.22	0.56[a]
Zn					1.00	0.13	0.13	0.15	−0.11	−0.01
Ni						1.00	0.73[a]	0.89[a]	−0.26	0.57[a]
Cu							1.00	0.64[a]	−0.27	0.33
As								1.00	−0.29	0.53[a]
Cd									1.00	−0.11
Pb										1.00

[a]Significant at $p < 0.01$. N = 31.

the case of As, which had a median EF_{UCC} around 10 but both EF_{MDT} and EF_{WS} very close to 1.

[16] The solubility of the studied elements was assessed by determining the partition coefficient (C_P), which is defined as the ratio of the particulate fraction to the total concentration: $C_P = [Y]_{part}/([Y]_{part} + [Y]_{diss})$, where $[Y]_{part}$ and $[Y]_{diss}$ are the particulate and dissolved fractions of the element Y respectively. Partition coefficients were calculated for all samples and the average weighted by the precipitation volume (Table 4). Aluminum, Fe, Ti and As were mostly found associated with particles ($C_P > 0.90$). Nickel, Cu, Cd and Pb showed intermediate partition coefficients ($0.90 > C_P > 0.40$). Manganese and Zn were mostly found as soluble forms ($C_P < 0.25$). However, except for Ti, Fe and Al, the C_P was highly variable among samples. The acidity of the precipitation was tested as a factor that may explain the variability in the phase distribution of trace elements between dissolved and particulate matter by obtaining linear regressions between pH and C_P. Results for this test are shown in Table 4. The pH range was 4.69–7.31. The C_P of Mn, Zn, Cu and Pb showed a positive significant dependence on precipitation pH (p-value < 0.01, Figure 3) whereas there was no significant dependence for the other elements.

[17] The relative importance of in-cloud versus below-cloud processes in determining the concentration of trace elements in atmospheric deposition was evaluated by using a simple model [*Mészáros*, 1981]. The final concentration of an element in precipitation (C_f) is the sum of the in-cloud concentration (C_i) plus the below-cloud concentration, (C_b),

$$C_f = C_i + C_b \tag{1}$$

C_b can be computed as a scavenged or dry deposited quantity Q of the element dissolved in a precipitation volume V,

$$C_b = Q/V = Q \times 1/V \tag{2}$$

Substituting in equation (1), the mathematical expression of the model is

$$C_f = C_i + (Q \times 1/V) \tag{3}$$

C_i and Q can be estimated respectively as the independent term and the slope of the linear regression fitting of the measured concentrations (C_f) and the inverse of the precipitation volume ($1/V$). In this model, C_i has no relation with V, whereas C_b has a functional dependence on Q and V. Such a dependence results in a correlation between C_b and the inverse of V, even for randomly distributed Q and V. Therefore, the correlation level between C_f and $1/V$ can be interpreted as an indication of the relative weight of in-cloud and below-cloud components: a good correlation would indicate that C_b was important in determining the final concentration; otherwise C_i was more important. The results of this regression analysis are shown in Table 5. Dissolved Al, Fe, Mn, Ni and Cu and total Cu were significantly dependent on the amount of precipitation, but only at a p-level < 0.05 and the regressions only explained 13–20% of the variance (Figure 4). None of their particulate concentrations nor any other metal concentrations were significantly influenced by precipitation volume, suggesting that dry deposition had a minor weight in total deposition.

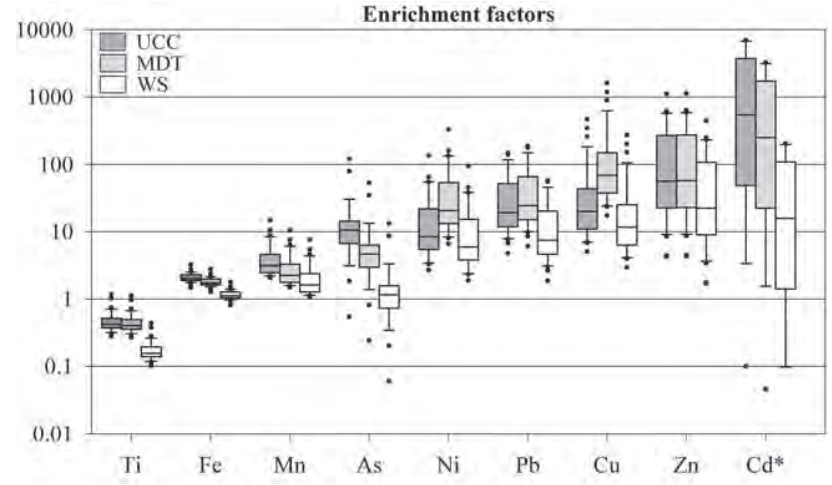

Figure 2. Enrichment factors of elements in atmospheric deposition samples from Lake Redon relative to the average element composition in the upper continental crust (UCC), the granite bedrock of Maladeta (MDT), and Western Sahara soils (WS). Asterisk indicates that only 16 samples were used to compute EF for Cd.

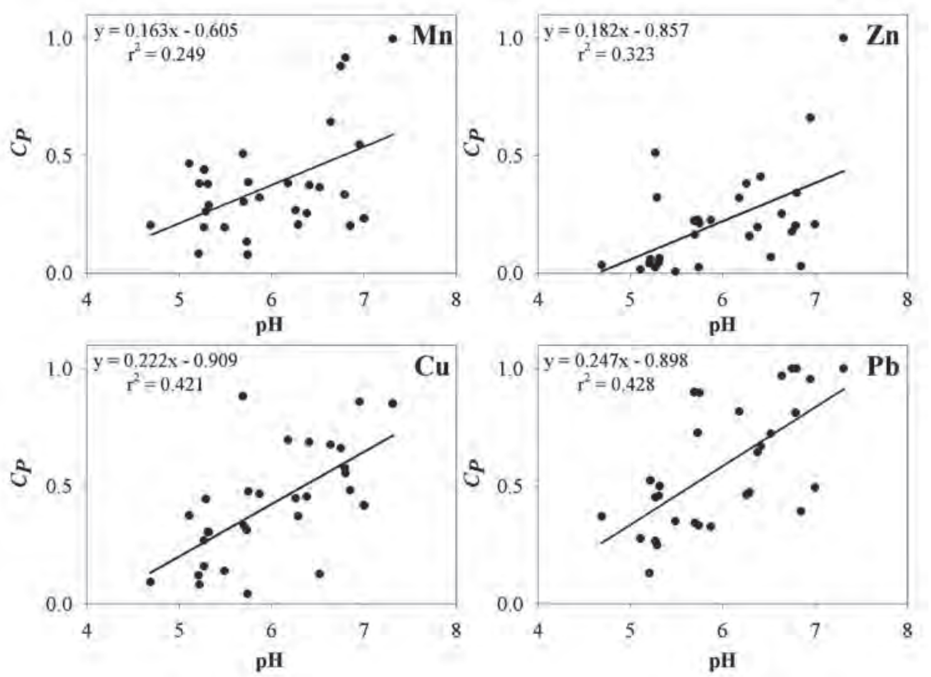

Figure 3. Regression plots between pH and the partition coefficient between dissolved and particulate forms (C_p) of Mn, Zn, Cu, and Pb in atmospheric precipitation.

[18] This is consistent with previous measurements of major solutes deposition in the area, which also showed that the dry deposited fraction was minor. Atmospheric deposition was sampled starting 5 July 1997 until 11 January 1998 in the vicinities of Lake Redon, at the High Mountain Research Centre station at 1600 m asl. Precipitation was collected using a bulk collector similar to that used in the present study. Samples from the collector were taken daily. The days without wet deposition, the funnel and sampling tank were carefully washed with a known amount of deionized water, and a sample of this washing water was taken for chemical analysis. Major cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+) and anions (Cl^-, SO_4^{2-}, NO_3^-) were determined by capillary electrophoresis (Quanta 4000, Waters). Precipitation over this period was 966 mm, and occurred in 137 days versus 83 dry days. The percentage of solutes deposited as wet deposition with respect to total deposition varied between elements, but was always the largest fraction (Table 6): ~95% in the case of NO_3^- and SO_4^{2-}, 81–89% NH_4^+, Ca^{2+}, Mg^{2+}, Cl^- and Na^+, and 65% for K^+.

[19] Annual deposition fluxes of the studied trace elements are presented in Table 7. Fluxes of all elements except Zn, Cu and As increased in the 2005–2006 water year with respect to 2004–2005. The four weekly deposition fluxes during the whole study period are displayed in Figure 5. Fluctuations were observed for most elements. In general, fluxes tended to be higher in warm months (June–November) than in cold months (December–May). Fluxes peaked during summer whereas the lowest fluxes were measured in winter. The data set was too short (less than three complete cycles) for a proper application of time series analysis techniques to test for seasonality [*Legendre and Legendre*, 1998]. As an alternative, the differences between the mean deposition fluxes of elements in warm and cold periods were tested for significance with a two-sample T-test (see Table 8). Aluminum, Fe, Ti, Mn, As and Pb fluxes were significantly higher (p-level < 0.05) during the June–November periods.

3.2. Circulation of Air Masses

[20] The calculated back trajectories were grouped into ten clusters after applying the AHC analysis (Figure 6). On

Table 4. Volume-Weighted Means and Standard Deviations of Element Partition Coefficients in Atmospheric Deposition Samples and Resulting Parameters (r^2, p-value) Obtained From Linear Regressions Between pH and C_P

	Al	Fe	Ti	Mn	Zn	Ni	Cu	As	Cd	Pb
Volume-weighted means	0.91	0.99	1.00	0.38[a]	0.26[a]	0.57	0.46[a]	0.95	0.69	0.61[a]
SD	0.10	0.03	0.00	0.23	0.26	0.30	0.25	0.31	0.34	0.27
r^2	0.086	0.002	0.032	0.249[a]	0.323[a]	0.107	0.421[a]	0.026	0.009	0.428[a]
p-Value	0.113	0.796	0.345	0.005[a]	0.001[a]	0.084	<0.001[a]	0.475	0.744	<0.001[a]

[a] Significant at p-level < 0.01. C_P = [particulate]/[particulate + dissolved].

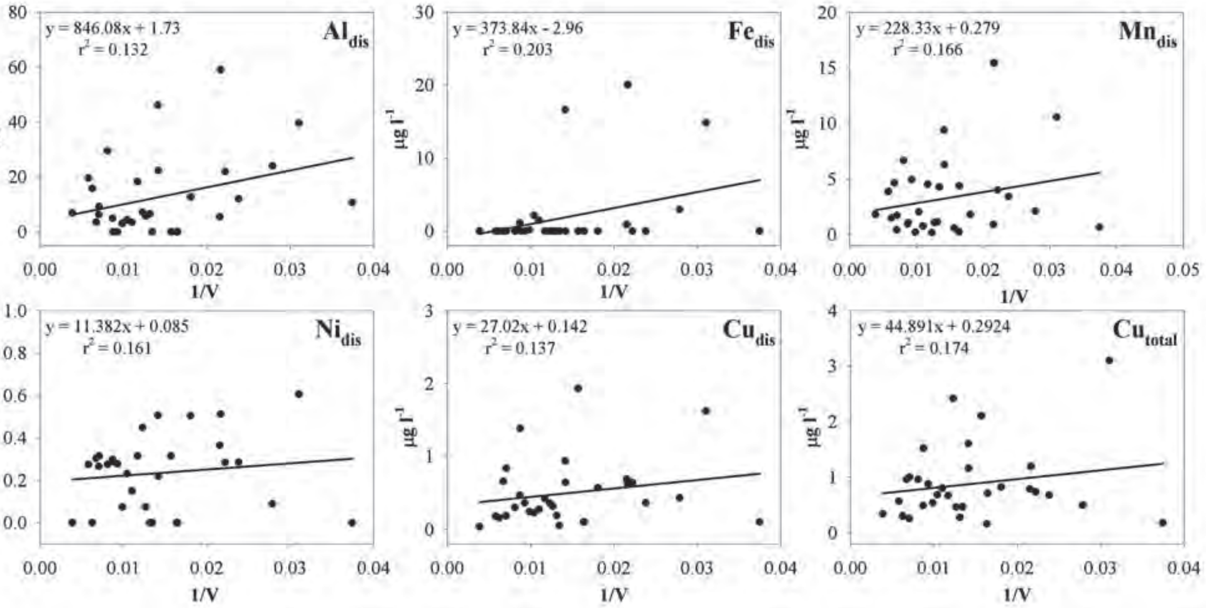

Figure 4. Regression plots between the inverse of precipitation volume (1/V) and the concentration of dissolved Al, Fe, Mn, Ni, and Cu and total Cu.

the basis of the geographic area crossed along by the trajectories, these ten clusters were grouped into three trajectory types: Group A (including clusters 1–4) corresponded to Atlantic trajectories, which accounted for 41% of the precipitation during the whole study period. Group B (clusters 5–9) included trajectories crossing North Africa and/or the Iberian Peninsula, which contributed 57% of the total precipitation. Group C (cluster 10) included a few Central European trajectories which only corresponded to 2% of the precipitation. As for the altitude of the airflow, 72% of the total precipitation corresponded to air masses flowing at high elevations (>1000 m asl) whereas only 28% of the precipitation originated from air masses circulating at low altitude (<1000 m asl).

[21] Table 9 shows the relative contribution of each cluster to the precipitation corresponding to different annual and seasonal periods. In terms of annual budgets, Atlantic trajectories contributed 51% of the precipitation whereas Iberian–North African trajectories represented 43% of the precipitation during the 2004–2005 water year. In the 2005–2006 water year, Atlantic trajectories decreased to 35% of the precipitation whereas Iberian–North African trajectories contributed 65%. High-altitude trajectories dominated during the whole study period. However, precipitation associated with low-altitude trajectories increased from 24% in the 2004–2005 water year to 35% in 2005–2006. On a seasonal timescale, trajectories with an Iberian–North African component were predominant during the warm months (from June to November): 72% in 2004, 83% in 2005, and 87% in 2006. Conversely, Atlantic trajectories predominated during December–May: 83% in 2004–2005 and 51% in 2005–2006. As for the altitude of trajectories, high trajectories were the majority in all cases, and the differences in proportions of low trajectories between warm and cold months were not clear: in June–November low trajectories were between 27 and 42%; in December–May

Table 5. Parameters From Linear Regressions Between Dissolved, Particulate, and Total Concentrations of Trace Elements and the Inverse of the Precipitation

Parameter	Al	Fe	Ti	Mn	Zn	Ni	Cu	As	Cd	Pb
					Dissolved					
r^2	0.13[a]	0.20[a]	0.06	0.17[a]	0.02	0.16[a]	0.14[a]	0.11	0.09	0.07
p-Value	0.04[a]	0.01[a]	0.17	0.02[a]	0.48	0.03[a]	0.04[a]	0.07	0.11	0.14
					Particulate					
r^2	0.02	0.02	0.02	0.00	0.00	0.02	0.07	0.02	0.04	0.02
p-Value	0.41	0.42	0.41	0.79	0.83	0.47	0.16	0.44	0.28	0.40
					Total					
r^2	0.03	0.02	0.02	0.05	0.02	0.06	0.17[a]	0.06	0.05	0.07
p-Value	0.38	0.41	0.40	0.21	0.47	0.17	0.02[a]	0.17	0.21	0.14

[a] Significant at p-level < 0.05.

Table 6. Comparison of Wet and Dry Deposition of Major Solutes Collected at the Nearby High Mountain Research Centre Station From 5 July 1997 Until 11 January 1998

	Precipitation Height (mm)	Occurrence (days)	Unit	Cl^-	SO_4^{2-}	NO_3^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}
Wet	966	137	kg ha^{-1}	2.9	3.7	1.4	2.4	2.1	0.6	4.2	0.3
			eq ha^{-1}	85	77	102	170	90	16	212	27
Dry		83	kg ha^{-1}	0.7	0.2	0.1	0.3	0.4	0.3	0.5	0.05
			eq ha^{-1}	20	4	6	23	18	9	27	4
Wet (% of bulk)				81.3	95.3	94.4	88.2	83.5	65.3	88.6	86.1

they were 12% in 2004–2005, but comparable to the warm months (31%) in 2005–2006.

4. Discussion

4.1. Composition of Atmospheric Deposition: Clues on the Sources and Fate of Trace Elements

[22] The concentrations of trace elements in the atmospheric deposition measured in the present study are compared with previous studies in Table 10. Although other studies on direct deposition or recently deposited snow exist [e.g., *Gabrielli et al.*, 2006; *Halstead et al.*, 2000; *Takeda et al.*, 2000; *Veysseyre et al.*, 2000], we have restricted our comparison to relatively remote sites (mainly mountains) from where at least 1 complete year of multielement deposition data are available. Concentrations of Fe, Al and Ti were remarkably higher in the present study than in any other, including the previous data from Lake Redon. This could be due to the different pretreatment of samples: a strong extraction procedure at high temperature was used in this study to measure concentrations in the particulate fraction on filters in addition to the dissolved fraction, whereas a weaker acid extraction on unfiltered samples was used in most of the previous studies; in one case (Eastern Channel) only dissolved forms were analyzed. Iron, Al and Ti probably came from mineral particles of geologic origin, which could have been more efficiently extracted with the method used here than with the weaker extraction used in previous studies. This interpretation is consistent with the low solubility ($C_P > 0.9$) and the low or null enrichment (EF ~ 1) estimated for Fe, Al and Ti. In contrast, the concentrations of the other trace elements were within the same ranges at all sites despite the different extractions used. The higher solubility, as indicated by their low C_P, would mean that they were present in relatively labile forms more easily extractable with any of the methods used. The similar composition at all sites supports the possibility of using them to measure general background levels of pollution in atmospheric precipitation, at least in the European context. Concentrations were somewhat higher at Lake Redon in 2000–2001 than in 2004–2006. This observation could be simply due to interannual variations (see below), but it was also consistent with the current global decreasing trend in atmospheric pollution levels reported by *Reuer and Weiss* [2002] and EU emission inventories [*Ilyin et al.*, 2007] (European Pollutant Emission Register data available at http://www.eper.ec.europa.eu).

[23] The degree of correlation between elements was related to their enrichment: Al, Fe, Ti, Mn and As constituted a group of strongly correlated elements and exhibited the lowest EF, indicating that they had a common natural (most

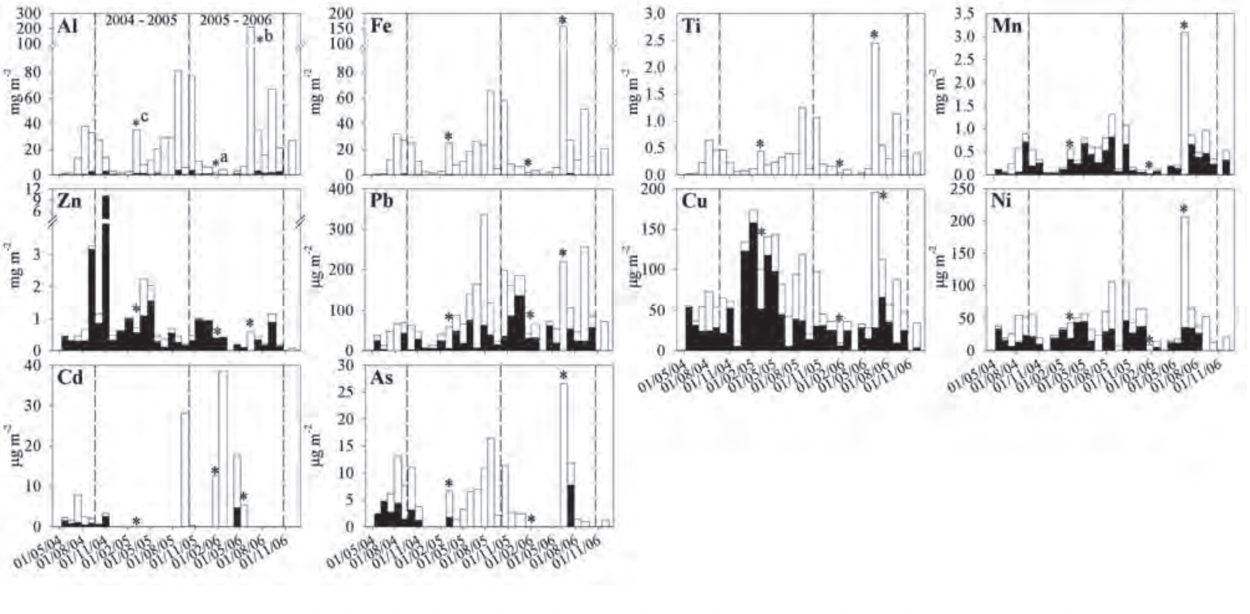

Figure 5. Four weekly dissolved (black) and particulate (white) atmospheric fluxes of trace elements at Lake Redon. Dashed lines indicate water years, and asterisk denotes the three periods discussed in further detail in the text and in Figure 7.

Table 7. Annual and Seasonal Fluxes of Trace Elements, With Indication of the Percentage Increment Between 2004 and 2005 and 2005 and 2006[a]

Period	Al	Fe	Ti	Mn	Zn	Ni	Cu	As	Cd	Pb
Oct 2004 to Sep 2005	267	222	4.27	6.22	20.74	0.52	1.19	0.07	0.03	1.17
Oct 2005 to Sep 2006	457	347	6.48	7.62	6.26	0.65	0.79	0.06	0.07	1.50
Δ%	71	56	52	23	−70	25	−34	−17	132	28
Jun to Nov 2004	126	107	2.05	2.66	16.07	0.23	0.35	0.05	0.02	0.31
Dec 2004 to May 2005	61	49	1.12	1.91	7.19	0.21	0.70	0.01	0.00	0.27
Jun to Nov 2005	252	204	3.73	4.66	3.74	0.38	0.50	0.06	0.03	1.15
Dec 2005 to May 06	22	20	0.46	0.64	2.13	0.12	0.14	0.00	0.07	0.42
Jun to Nov 2006	349	261	4.76	5.74	2.60	0.38	0.50	0.04	0.00	0.72

[a] Values are in mg m^{-2} a^{-1}.

likely lithologic) origin. As long as the enrichment of other elements increased, their correlation with this group of crustal elements was weaker. The correlation between Ni and the group of crustal elements was still good even though the deposition was moderately enriched in Ni. Copper and Pb lay in an intermediate position regarding both correlation and EF. Zinc and Cd presented the highest EF and were not correlated with any other element. Assuming that the high EF measured are unlikely to be caused by natural processes alone and are rather due to atmospheric pollution, both indicators reflected the proportion of each element derived from lithologic and anthropogenic sources. The ranking of elements in this geological-anthropogenic origin gradient was thus Al, Fe, Ti, Mn, As > Ni > Cu, Pb > Zn, Cd. It is remarkable that there was no correlation between the elements with a more marked polluting character (Cu, Pb, Zn and Cd), and that there were strong differences in solubility (C_P ranged from 0.27 for Zn to 0.72 for Cd). These two features indicate a decoupling in the timing of deposition that may be due to differences in the sources, transport pathways and deposition mechanisms.

[24] To avoid disregarding the importance of biogeochemical processes in influencing elemental cycles, caution must be used in the interpretation of the EF_{UCC} in environmental geochemistry [*Reimann and de Caritat*, 2000] for several reasons. The composition of the Earth's crust in different areas is spatially variable in relation to the global average UCC, and natural fractionation of elements may occur during near-surface processes. In the present case, this variability was indeed manifested as differences in EF calculated using the three references (UCC, MDT, and WS). For the terrigenous elements, EF_{MDT} and EF_{WS} were closer to the expected value of 1 than EF_{UCC}, suggesting that MDT and WS may be more appropriate references for the Pyrenean area than UCC, and that the enrichment in pollutant trace elements may therefore be overestimated by using EF_{UCC}. Contamination of samples by redeposited local soil particles may also be of concern. However, in our particular case EF measured in soils in the area are in the range of 2–5 for all the metals analyzed (M. Bacardit and L. Camarero, submitted manuscript, 2008b). Therefore, a possible contamination by resuspended soil particles cannot account for EF in bulk precipitation that are in most cases between 10 and 100. Analytical problems have to be taken into account as well. For instance, the commonly used weak acid digestions can produce an incomplete and/or differential dissolution of minerals. In contrast with previous studies, effort has been made here to accurately characterize the trace element chemistry of the particulate fraction of the deposition. The tests using certified reference materials showed that more than 70% of Al and As and more than 85% of the other elements were extracted from the mineral samples (M. Bacardit and L. Camarero, submitted manuscript, 2008b). The only element that was poorly extracted was Ti, at less than 20%, which may explain why the estimated EF for Ti is lower than 1.

[25] The measured partition coefficients (C_p) reported here do not necessarily correspond to the fraction in which the trace elements are in the atmosphere or are deposited. It is possible, and even likely, that redistribution between particulate and dissolved forms takes place because of adsorption/desorption within the collection vessel during the lag time between deposition and retrieval of the sample. This may be especially true in the case of elements present as dissolved species. In this sense, our C_p are an indicator of the affinity of the deposited elements for particles rather than a true measure of the forms in which the elements are deposited. Such affinity may influence the fate of deposited trace metals: transport of soluble elements with runoff may be favored versus the retention and accumulation of elements tightly bound to particles in soils [*Chopin and Alloway*, 2007]. The affinity for particles also influences the bioavailability of trace elements, as soluble forms are more easily taken up by organisms [*Borgmann*, 2000; *Navas and Lindhorfer*, 2005] than particulate forms. This has particular relevance in the case of polluting trace elements because of their potential toxicity. In this sense, a ranking based on the potential mobility and bioavailability of metals, as indicated by their C_p, would be: Zn > Cu > Ni > Pb > Cd. The acidity of the precipitation has frequently

Table 8. T-Test for Independent Samples of Atmospheric Element Fluxes (mg m^{-2}) in Colder Months (Group 1, December–May) Against Warmer Months (Group 2, June–November)

	Mean 1	Mean 2	t-Value	Degrees of Freedom	p-Level
Al[a]	7003	39,674	−2.36596	29	0.025
Fe[a]	5788	31,224	−2.47181	29	0.020
Ti[a]	133	576	−2.66934	29	0.012
Mn[a]	222	715	−2.45357	29	0.020
Zn	815	1184	−0.54059	29	0.593
Ni	31	53	−1.55282	29	0.131
Cu	75	73	0.13298	29	0.895
As[a]	1.3	7.6	−3.19331	29	0.003
Cd	6.4	2.5	1.20301	29	0.239
Pb[a]	61	118	−2.09868	29	0.045

[a] Significant differences between means.

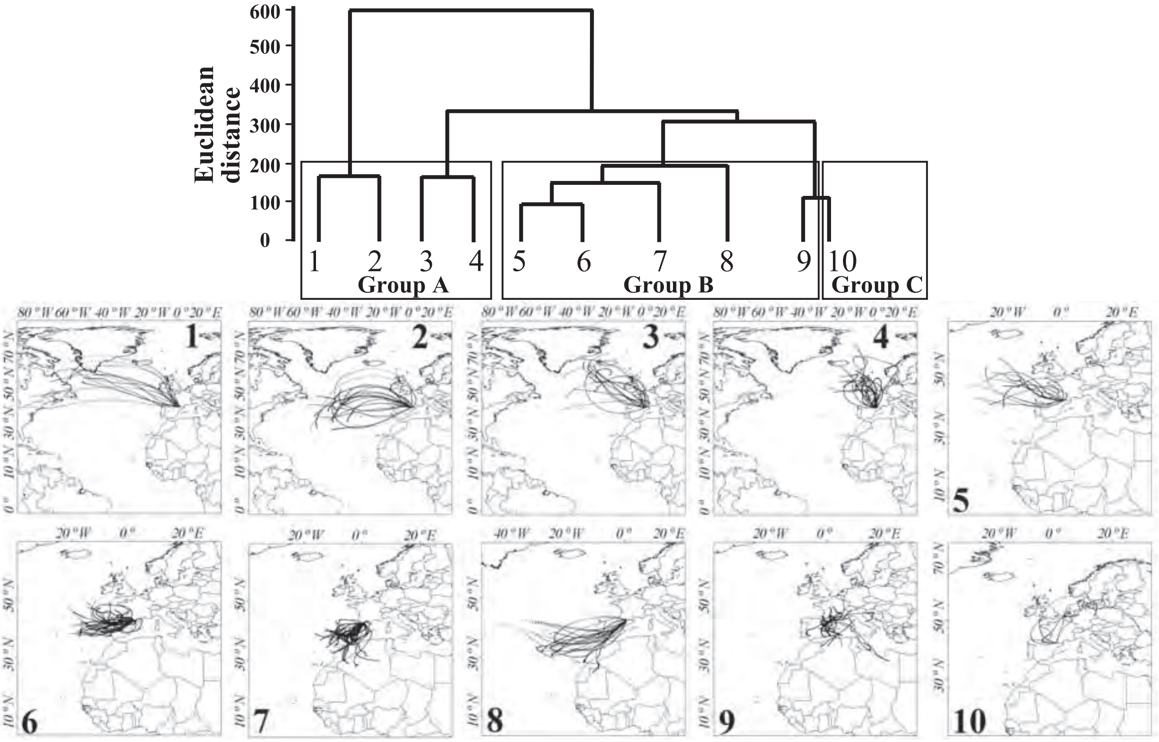

Figure 6. Classification of the back trajectories of the air masses that caused the precipitation events recorded during the study: clustering tree obtained by Agglomerative Hierarchical Clustering, showing the grouping into type A (Atlantic), type B (Iberian and North African), and type C (central European) trajectories and the trajectories of each resulting cluster.

been reported as a key factor in determining the solubility of different trace elements in aqueous media [e.g., *Chester et al.*, 1993; *Kaya and Tuncel*, 1997]. In this study, a positive significant dependence between the C_P and the precipitation pH was found for the elements with an average C_p less than ~ 0.6 (Pb, Cu, Zn and Mn), whereas no relationship was found for elements above this limit (Al, Fe, Ti, As, and Cd). Nickel was an exception to this, showing an average C_P close to the limit ($C_P = 0.57$) but having no relationship between C_P and pH.

4.2. Interannual and Seasonal Variations and Their Relationship With Meteorology and Climate

[26] Although some trace elements have gaseous forms (e.g., methylated compounds) that may play an important role in their atmospheric cycling [*Lahoutifard et al.*, 2005], for most of them the transport is more greatly linked to the flux of particles in the atmosphere. The size of the particles determines the pathways and mechanisms of transport to which they are submitted. In general, finer particles are transported high into the troposphere and incorporated into raindrops, contributing to the in-cloud component of wet deposition; on the contrary, larger particles usually do not reach altitudes where rain forms, and therefore they are deposited as dry deposition or scavenged during rainfall episodes, constituting the below-cloud contribution [*Galloway*, 1982]. Dust particles can be in the submicrometer range, be long-range transported and act as condensation nuclei in clouds, and therefore contribute to the in-cloud chemistry.

Table 9. Total, Annual, and Seasonal Percentages of Precipitation Originated by Air Masses Corresponding to the Three Main Horizontal Trajectories Identified in the Cluster Analysis and Two Altitude Trajectories[a]

		Horizontal Trajectory (%)			Altitude Trajectory (%)	
Period	Precipitation Height (mm)	Group A (Atlantic)	Group B (Iberian–North African)	Group C (Central Europe)	High	Low
Apr 2004 to Dec 2006	3072	41	57	2	72	28
Oct 2004 to Sep 2005	1217	51	43	6	76	24
Oct 2005 to Sep 2006	1354	35	65	0	65	35
Jun to Nov 2004	504	23	72	5	73	27
Dec 2004 to May 2005	559	83	10	7	88	12
Jun to Nov 2005	665	16	83	1	58	42
Dec 2005 to May 2006	473	51	49	0	69	31
Jun to Nov 2006	682	13	87	0	72	28

[a] Cluster analysis was performed for Atlantic, Iberian–North African, and Central European, and two altitude trajectories (most of the time above or below 1000 m asl).

Table 10. Comparison of Average Trace Element Concentrations in Lake Redon Atmospheric Deposition With Other Sites in Previous Studies[a]

Site	Area	Sample Type	Period	Al	Fe	Ti	Mn	Zn	Ni	Cu	As	Cd	Pb	Reference
Redon, Central Pyrenees, Spain	mountain	dissolved plus particulate	2004–2006	1.7	236	4.5	5.8	8.9	0.5		0.06	0.05	1.1	this study
Redon, Central Pyrenees, Spain	mountain	acid-soluble fraction	2001–2002	83	64	1.0	5.5	28.9	1.7		0.09	0.07	1.6	*Plöger* [2004]
Aspe Valley, Atlantic Pyrenees, France	mountain	acid-soluble fraction	2003–2004	25			5.2	13.5		1.3		0.03	0.5	*Veschambre* [2006]
Holme Moss, West Yorkshire, United Kingdom	mountain	acid-soluble fraction	2004–2005	16	21	0.4	2.4	12.1	0.3	1.5	0.46	0.04	2.3	*Fowler et al.* [2006]
Bowbeat, Scottish borders, United Kingdom	mountain	acid-soluble fraction	2004–2005	10	15	0.4	1.9	10.2	0.3	1.0	0.12	0.07	1.7	*Fowler et al.* [2006]
Lochnagar, Highlands, Scotland, United Kingdom	mountain	acid-soluble fraction	1997–1998					21.5	0.8	2.5		0.18	1.1	*Yang et al.* [2002]
Robiei, Central Alps, Switzerland	mountain	acid-soluble fraction	2000–2002	103	81	4.1	5.7	14.0	0.4	1.4	0.13	0.04	1.4	*Plöger* [2004]
L'adové, Tatras, Slovakia	mountain	acid-soluble fraction	2000–2001	30	15	0.5	2.4	7.6	0.2	0.8	0.17	0.10	2.3	*Plöger* [2004]
Eastern Channel, Northern France	coastal	dissolved fraction	1995–1996					15.5		0.7		0.10	2.0	*Deboudt et al.* [2004]
Karvatn, Norway	high latitude	acid-soluble fraction	1996–1997				1.2	2.2	0.2	0.3	0.11	0.02	0.8	T. Berg (personal communication, 2004)
North American Great Lakes, United States	lowland	acid-soluble fraction	1993–1994				2.7	5.4	0.3	0.9	0.10	0.10	0.9	*Sweet et al.* [1998]

[a]Values are in μg L^{-1}.

However, the bulk (70–80% of mass) of the dust aerosol produced in the emission points consists in particles larger than ~10 μm [*Castillo et al.*, 2008]. These very large particles tend to be progressively removed from the aerosol by dry deposition (and below cloud processes in general) during the first few days after emission [*Noll and Aluko*, 2006]. In contrast, aerosols in the free troposphere (i.e., those contributing to in-cloud composition) tend to have a higher proportion of submicrometer particles. Mineral dust can be a fraction of this, but the proportion of other kind of particles (many of them of anthropic origin) is large. Distinguishing between the in-cloud and below-cloud components of deposition is therefore important because they may have independent origins and different compositions, and may have a different weight in bulk precipitation samples integrating a certain period of time (four weeks in this study). Results of the regression analysis between the concentration and the precipitation volume (Table 4) suggest that the below-cloud contribution had a minor effect on the final concentration of trace elements in the precipitation samples collected. The same has been seen for major solutes in previous studies [*Camarero and Catalan*, 1993, 1996]. The direct measurements of dry and wet deposition reported here indicated that dry deposition of major solutes was between 5 and 20% of bulk deposition, depending on the solute. These results imply that, since a large percentage of major and trace elements deposited come with the wet air masses causing precipitation, their origin can be confidently determined by tracking the trajectories of these wet air masses and ignoring possible dry inputs from other air masses.

[27] Interannual changes in trace element deposition and the provenance of storms during the 2 years sampled may therefore be related. Type B trajectories (Iberian and North African) increased from 43% in the water year 2004–2005 to 65% in 2005–2006, and deposition of terrigenous elements (Al, Fe, Ti, Mn) increased in 2005–2006 by 23–71% with respect to the previous year. Nickel, Cd and Pb also increased in 2005–2006, whereas Zn and Cu decreased. The decrease in As was, in absolute values, negligible. These results suggest that type B trajectories tended to bring more terrigenous elements (dust) and those elements with more affinity for particles ($C_p > 0.5$), while type A trajectories (N Atlantic) favored the deposition of more soluble elements ($C_p < 0.5$). But it is not only the horizontal displacement of the air masses that is important, the altitude at which the air masses flow also has an effect. Low-altitude trajectories, closer to the emission areas and crossing the mixed boundary layer in the lower atmosphere, may result in a higher load of trace elements. The results obtained here point to this: the percentage of low-altitude trajectories increased in 2005–2006 with respect to 2004–2005, along with the deposition of trace elements preferentially bound to particles.

[28] The same arguments explain the seasonal differences in trace element deposition: there was a predominance of type B and low-altitude trajectories during the warm months (June–November), and the deposition of the terrigenous elements (Al, Fe, Ti, Mn) and Pb was higher during this period than during the rest of the year. This is consistent with previous studies reporting that the maximum dust transport from North Africa to Europe and the Middle East usually occurs in summer [*Moulin et al.*, 1998]. On the other hand, the changing vertical structure of the boundary

air layer can also act as a controlling factor of the regional atmosphere [*O'Dowd and Smith*, 1993; *Kukkonen et al.*, 2000; *André et al.*, 2007], and thus the seasonal variability of deposition fluxes. During cold months, a high-pressure anticyclone is frequently located over central and southern Europe for several days or weeks. This synoptic condition produces a thermal inversion of subsidence in an atmospheric layer of a few hundred meters at approximately 1000–1500 m asl, which often spans over the whole area under the anticyclone. In mountainous ranges, the thermal inversion has a capping effect, thereby limiting the transport of atmospheric substances from the lowlands to the higher-altitude areas. In contrast, during warm months a thicker and well-mixed boundary layer allows continuous upward transport [*Anquetin et al.*, 1999]. Thus, for instance, seasonal variations of trace metals in ice in the Alps have been attributed to variations in the vertical extension of the atmospheric boundary layer [*Van de Velde et al.*, 1998].

[29] Closer examination of the particular meteorological conditions that occurred during the periods with high and low depositional fluxes of trace elements illustrates the ways in which meteorology influences, as discussed above, these fluxes:

[30] The element fluxes measured in the sample corresponding to 11 January 2006 to 6 February 2006 were among the lowest (Figure 5). This sample was a collection of four precipitation events (Figure 7a): the first three, occurring on 12–14 (4.1 mm), 18–20 (23.3 mm) and 24–25 January 2006 (3.9 mm), were produced by northern Atlantic air masses (type A) with high-altitude trajectories. The fourth event, on 29–31 January 2006 (31.2 mm), originated from a North African air mass (type B), but was not accompanied by suspended dust. Thermal inversion episodes occurred on both sides of the mountain range in the region around the Pyrenees during 11–12 and 19–25 January 2006, which limited the dispersion of atmospheric pollutants from the lowland source areas to mountain receptor areas for several days. The combination of these two phenomena, 'clean' northern precipitation events and thermal inversion, led to a remarkable decrease in atmospheric trace element deposition.

[31] The highest fluxes were measured in the sample corresponding to 1–29 June 2006 (Figure 5). During this period, long episodes of African dust intrusions affected the whole Iberian peninsula (7–9 and 15–30 June 2006). The dust outbreaks were accompanied by two precipitation events coming from North Africa (type B), which occurred on 9 June 2006 (12 mm) and 16–18 June 2006 (38 mm) (Figure 7b). The particles transported by wet air masses plus the scavenging of suspended particles by rain caused the highest deposition rates observed.

[32] Although dry deposition had a minor role in general terms, it was important in particular episodes. An example of this is the period 23 February 2005 to 22 March 2005 (Figure 5), in which deposition of trace elements was in the medium-high range. Three precipitation events occurred within this period (Figure 7c): the first (26 February 2005, 3.0 mm) had a Central European origin (type C), whereas the other two, which occurred on 3 and 5 March 2005 (0.4 and 13.0 mm), had an Atlantic provenance (type A). Because of their origin, it can be assumed that these precipitation events did not bring large amounts of trace elements. However, an African dust intrusion, not accompanied by rain or snowfall, was registered in the northeastern Iberian peninsula during 16–24 March 2005, which presumably contributed to the bulk atmospheric deposition sample as dry deposition.

4.3. Some Considerations on the Effects of Atmospheric Trace Element Deposition on the Pyrenean Lakes

[33] Among the airborne trace elements with potential toxic effects, Pb is the one that may have caused a greater impact in the Pyrenean lake ecosystems. In the particular case of Lake Redon, its palaeorecord shows an increase in the concentration of acid extractable Pb in sediments from a background value of ~20 mg kg^{-1} in deep sediments up to ~350 mg kg^{-1} in the most recent sediments [*Camarero et al.*, 1998], with an enrichment factor of more than 15. This high enrichment was likely due in a large part to local sources, i.e., mining in the vicinities of Lake Redon catchment, starting as early as the 5th century and peaking around the 7th century and the 1900–1950s. At a regional scale, the average Pb enrichment in modern sediments with respect to preindustrial sediments is 2.1 [*Camarero*, 2003], a more moderate figure that can be considered as an estimation of the increase in the background Pb supply caused by broad regional pollution. The regional enrichment in other metals like Zn, Cd, and Cu is lower, ~1.2–1.3 in average. In terms of concentration, Pb also has potentially higher ecotoxicological relevance. Thus, the average Pb concentration in modern sediments is 95 mg kg^{-1}, which is above the reported ~30–70 mg kg^{-1} minimal or lowest effects level (MEL, LEL), i.e., the level below which no adverse effects have been found in bioassays with diverse organisms [*Ontario Ministry of the Environment*, 1992; *Del Valls and Chapman*, 1998]. The average concentrations of Zn (116 mg kg^{-1}) and Cu (27 mg kg^{-1}) are within the reported LEL ranges, but a certain number of Pyrenean lakes are still above those levels.

[34] The predominance of Pb as a polluting element in the lake sediments contrasts with our present-day deposition data. According to our measurements, Zn deposition is at present almost one order of magnitude higher than Pb deposition, and Cu and Ni deposition is just slightly lower than Pb deposition. Lead shows only a moderate enrichment in atmospheric deposition, while Zn and Cd exhibit high enrichments. This is consistent with a decrease in Pb deposition owing to the reduction in Pb emissions, both at the local (closing of near-by mines in the 1950s) and regional (banning of leaded gasoline) scales, although a different biogeochemical behavior may also partly explain a greater accumulation of Pb in sediments. The present-day composition of precipitation also suggests that other metals, especially Zn, may become more important from an ecotoxicological point of view. However, the potential importance of historically stored Pb, not only in sediments but also in soils [*Camarero et al.*, 1998], as a future source to the lake ecosystems must not be neglected.

[35] The very low concentration of As we have found in atmospheric deposition in this study, especially when compared to the high content in sediments, confirms the interpretation that rocks are the major source of As in the Pyrenean lake sediments [*Camarero*, 2003].

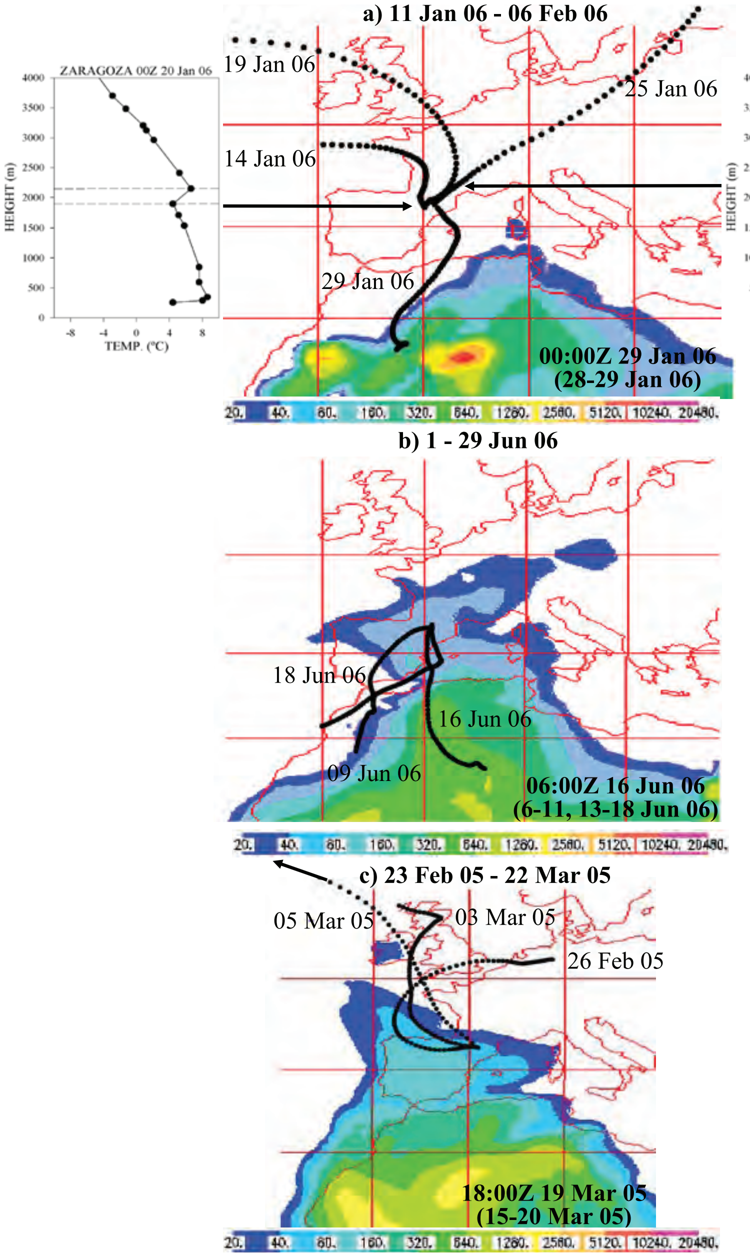

Figure 7. Graphs synthesizing the African dust intrusions and precipitation events that occurred during the periods with the (a) lowest and (b) highest trace element deposition and (c) a period with significant dry deposition. Surface concentrations of dust (in mg m^{-3}) shown by the isolines plot correspond to the moments of maximum penetration of dust during each event. Duration of the complete dust intrusion events is indicated in brackets. In Figure 7a, the plots of temperature soundings on both sides of the Pyrenean chain, Zaragoza (Spain), and Nîmes (France) show thermal inversion of the atmosphere over the region.

[36] Despite in this study Cu, Pb, Zn and Cd in atmospheric deposition showed no correlation on a monthly basis, the overall long-term trend in the Pyrenean region has been an increased codistribution of atmospherically deposited metals, as indicated by the composition of contemporary polluted sediments with respect to preindustrial sediments [*Camarero*, 2003]. The interpretation is that the timing in transport and deposition may differ between elements, but the main sources and pathways of the generalized pollution over the region are the same. In relation to this, a higher enrichment by Pb and Hg was found in contemporary sediments from lakes in the eastern Pyrenees with respect to those in the western part of the range [*Camarero*, 2003]. It can be hypothesized that such a geographic pattern may be caused by a differential transport: southern precipitation, which occurs in a higher proportion in

eastern Pyrenees locations [*Camarero and Catalan*, 1993], brings larger amounts of Pb, according to our results.

5. Conclusions

[37] The atmospherically deposited trace elements analyzed in this study can be split into two groups. The first group includes Al, Ti, Fe, Mn, and As; elements that are associated with dust coming from the Iberian Peninsula and North Africa. They all occurred (with the exception of Mn) as part of (or tightly bound to) particles and their concentrations were well correlated, indicating a common origin. They also presented low enrichment factors with respect to the most probable distant (Western Sahara) and local (Maladeta massif) lithologic sources of aeolian particles, indicating a natural origin. The second group includes Pb, Zn, Cd, and Cu, elements that have a marked polluting character: they presented intermediate to high enrichment factors; they were not correlated with each other, indicating different sources (although Pb and Cu had some correlation with the elements in the first group); and they were present in a variable but significant proportion as soluble forms. Nickel was somewhere in between the two groups, with an intermediate enrichment factor and solubility, and a very good correlation with all terrigenous elements, suggesting a similar importance of both natural and pollution sources of Ni.

[38] Temporal variations in trace element deposition can be related to the prevailing meteorological conditions. In the water year 2005–2006 there was a larger proportion of precipitation originated by air masses coming from the Iberian peninsula and North Africa and following lower-altitude trajectories than in 2004–2005. Correspondingly, deposition of the elements that make up dust (Fe, Al, Ti, Mn, As) and of those showing a greater affinity for it (Pb, Cd, Ni) was higher during 2005–2006. The opposite was true for Zn and Cu deposition. Seasonal differences can be explained in a similar way. During June–November, when southern air masses provided proportionally more precipitation, deposition of dust and Pb was higher than in December–May. These results imply that possible changes in the general atmospheric circulation patterns as a result of climate change may have an influence on the airborne fluxes of trace elements, in particular those associated with particles. For instance, an increase in the proportion of air masses coming from south may enhance the deposition of the elements that form part of the mineral composition of dust and those for which dust acts as a carrier.

[39] Previous studies have shown that past deposition has resulted in generalized enrichment in certain trace elements of surface lake sediments with respect to preindustrial levels, with concentrations that may have ecotoxicological effects. In contrast with sediments, where Pb presents signs of a strong pollution, Pb in present-day deposition is much lower than Zn, and comparable to Ni and Cu. This suggests a contemporary decrease in atmospheric Pb deposition. The larger input of Pb caused by southern precipitation might explain the higher Pb enrichment in the sediments of lakes observed in a previous study in the eastern Pyrenees, where the proportion of southern precipitation tends to be higher.

[40] **Acknowledgments.** This study was supported by the EU-funded project Euro-Limpacs (GOCE-CT-2003-505540) and by the Spanish Council for Scientific Research (CSIC) through an I3P predoctoral grant to M. Bacardit. The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT model. Data on African dust intrusions were provided by the Calima project to study and evaluate pollution by suspended particulate matter in Spain, carried out in collaboration by the General Directorate of Quality and Environmental Evaluation of the Spanish Ministry of Environment, the Spanish Council for Scientific Research (CSIC), and the National Institute of Meteorology (INM). We also acknowledge the Meteorological Service of Catalonia for providing the meteorological data from the AWS and the information on thermal inversions, and the Department of Atmospheric Science, University of Wyoming for providing sounding plots. This study is a result of the activities of the Limnological Observatory of the Pyrenees (LOOP), a joint initiative of the Center for Advanced Studies-CSIC and the Center for High Mountain Research, University of Barcelona.

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Paper II. Atmospherically deposited major and trace elements in the winter snowpack along a gradient of altitude in the Central Pyrenees: the seasonal record of long-range fluxes over SW Europe

M. Bacardit and L. Camarero, 2010. Atmospheric Environment, 44, doi: 10.1016/j.atmosenv.2009.06.022

Figure 5. Snowpack sampling in the Maladeta valley, Central Pyrenees. The sampling site in the picture is the highest point within the altitudinal gradient at 3200 m a.s.l., at the head of the retreating glacier (by L. Camarero).

M. Bacardit and Ll. Camarero. “Atmospherically deposited major and trace elements in the winter snowpack along a gradient of altitude in the Central Pyrenees: The seasonal record of long-range fluxes over SW Europe”. *Atmospheric environament*. Vol. 44, issue 4 (february 2010) : p. 582-595

http://www.sciencedirect.com/science/article/pii/S1352231009005251

http://dx.doi.org/10.1016/j.atmosenv.2009.06.022

Received 2 December 2008; revised 11 June 2009; accepted 15 June 2009.
Available online 23 June 2009.

Abstract

The chemistry of high mountain snowpacks is a result of the long-range atmospheric transport and deposition of elements. Pyrenean snowpacks contain information about the fluxes of elements over SW Europe in winter. Here we analysed Al, Ti, Mn, Fe, Ni, Cu, Zn, As, Se, Cd and Pb in the 2004–05 winter snowpack in the Central Pyrenees, at an altitude range of 1820–3200 m a.s.l. Ni, As, Se and Cd were not detected in most cases. The concentrations of the remaining elements were comparable to those found in other high mountain areas in Europe and North America considered representative of regional background of atmospheric deposition in populated areas. In contrast, our measurements were higher than those of polar areas, which represent the global background. Single measurements of concentrations and snow accumulation were subject to considerable spatial variability, which may be attributable to strong wind drift and other post-depositional processes. The major ions chemistry of the snow indicated three possible origins for the solutes: terrigenous dust, sea salt spray and polluting S and N aerosols. We found no association between Cu, Zn and Pb and any of these possible sources. This observation therefore indicates that these elements were not preferentially bound to any particular kind of aerosol. Snow collected at altitudes of up to 2050 m a.s.l. presented higher concentrations of several elements than snow above this altitude, thereby indicating a local influence. Snow collected above 2300 m a.s.l. was therefore more representative of broad regional inputs. At these higher altitudes, snow was not enriched in Al, Ti, Mn, Fe or As compared with the composition of the upper continental crust and the local lithology, and these elements (except Mn) appeared almost exclusively in the particulate fraction. This observation indicates that Al, Ti, Mn, Fe and As were present mainly as part of dust particles of terrigenous origin. In contrast, Cu, Zn, and Pb presented medium to high enrichment factors and showed a higher proportion of soluble forms, thereby indicating their polluting character.

Keywords: Major and trace elements; Long-range pollution; Snowpack; High mountain; Pyrenees

Paper III. Atmospheric trace element contamination in European mountain catchments, as determined from direct bulk deposition records

M. Bacardit, L. Camarero, L. Camusso, M.; Guzzella; D.W. Hardekopf, U. Nickus, N.L. Rose, and E. Stuchlik, 2010. Atmospheric Chemistry and Physics, under review

Figure 6. Atmospheric trace element deposition sampling at Lake Lochnagar, Grampian Mountains, Scotland (by M. Bacardit).

Atmospheric trace element contamination in European mountain catchments as determined from direct bulk deposition records

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Abstract

Atmospheric bulk deposition samples were collected periodically over a two-year period (May 2004 – May 2006) in a range of remote mountain sites in Europe. They were analysed for acid-extractable major metals (Al, Fe, Ti and Mn) and trace elements (Zn, Ni, Cu, As, Se, Cd and Pb), both in bulk samples and in particulate and dissolved fractions separately. Aluminium, Fe, Ti and Mn were found in higher concentrations in the Central Pyrenees. These major metals were of a lithologic origin and were associated with dust events affecting this mountain range in particular. Lead, Zn, Ni, Cu, As and Cd were found in higher concentrations in the Tatra Mountains, Ticino and Piemonte, with lower concentrations in the Tyrol, and intermediate concentrations in the Pyrenees and Grampian Mountains. This group of trace elements showed a variable component of both natural and anthropogenic sources. Furthermore, Mn, Zn, Ni, Cu, As, Cd, and Pb were found in high, but variable, proportions as soluble forms, indicating their potentially high bioavailability in receiving ecosystems. The trace element fluxes showed seasonal and inter-annual patterns, likely related to the variability of meteorological conditions affecting each mountain range. A comparison with previous measurements of trace element concentrations in atmospheric deposition showed a general decreasing trend over European mountain ranges during the last decade. The annual trace element fluxes exceeded (or were close to) the predicted critical loads (CL) in some cases, while the annual Pb and Cd inputs showed some discrepancies with EMEP modelled deposition maps for Europe.

1 Introduction

Mountain ranges, together with high latitude regions, are viewed as relatively pristine, undisturbed areas, in which atmospheric transport and subsequent deposition from remote emission sources is the major mechanism of contaminant supply. Furthermore, these cold areas on the globe may be particularly sensitive to long-range transported contamination since they are recognized as regional convergence zones for selected persistent organic pollutants and trace metals accumulated in seasonal or permanent snow- and ice- fields (Yang et al., 2007). The enhanced deposition of atmospheric contaminants transported in the gas phase or bound to aerosol particles may occur due to cold condensation (Blais et al., 1998; Wania and Mackay, 1996), effective snow fall scavenging (Franz and Eisenreich, 1998) and orographic precipitation (Loewen et al., 2005).

Most trace elements enter the atmosphere as natural and anthropogenic aerosols. Natural emissions include eroded windblown rock and soil dust, volcanism and natural forest fires, release from biological activity (Hg, As, Se), and sea surface fractionation during production of atmospheric sea salt particles (Nriagu, 1989). Anthropogenic emissions are mainly due to burning of fossil fuels, mining and smelting of metal ores, and incineration of urban wastes (Nriagu, 1996; Rauch and Pacyna, 2009).

Many of the diverse aspects of climate change (e.g. temperature increase, variations in rainfall, wind patterns and dust deposition) (IPCC, 2007) may affect the distribution and mobility of potentially toxic substances, such as trace metals and metalloids (i.e. trace elements), in freshwater systems. For instance, global warming is likely to release such contaminants from melting snow and ice (Noyes et al., 2009). An increased rate of carbon mineralization in mountain soils (Drewnik, 2006) and an elevated rate of erosion of upland organic soils (Rose et al., under review) are also expected in response to the predicted climatic changes. These soils may have accumulated significant amounts of anthropogenic trace elements (Bacardit and Camarero, 2010; Camarero et al., 1998; Soltes, 1992; Yang et al., 2002a; Zechmaister, 1995). As a consequence, these contaminating trace elements may be transported downstream from headwaters in mountainous regions and have an impact in receiving terrestrial and aquatic environments, including modified biogeochemical cycles (Andreae and Crutzen 1997; Schlesinger et al., 1982) and an accumulation of such toxic contaminants in the human food chain (Nriagu, 1988).

Precipitation and snowmelt in European high mountain ranges are the major source water for some of the largest rivers on the continent. In order to foresee future impacts of atmospheric trace element contamination on these headwater systems as a consequence of climate change, the influence of atmospheric variability on the deposition of long-range transported trace elements to remote areas needs to be assessed. By determining the role of factors such as wind patterns, synoptic weather conditions, seasonality and dust load on trace element transport and deposition, predicted climate scenarios can be interpreted with respect to the transfer of contaminants from the atmosphere to the hydrosphere. Moreover, by determining dissolved and particulate phase distribution, the bioavailability and potential toxicity of atmospherically derived trace elements can be assessed.

Here, we discuss the composition of a suite of major metals and trace elements in bulk deposition samples collected periodically over two consecutive years at six European mountain sites. Spatial and temporal patterns of airborne fluxes of Al, Fe, Ti, Mn, Zn, Ni, Cu, As, Cd and Pb were monitored.

The partitioning into dissolved and particulate fractions and their enrichment factors were examined in order to define their sources, transport and deposition mechanisms. Our aims were: (1) to determine the current extent of atmospherically deposited trace elements in European mountainous catchments; (2) to estimate the relative contributions from natural and anthropogenic sources and potential bioavailability and ecotoxicity; (3) to assess the spatial and temporal depositional patterns related to anthropogenic emission reductions in Europe and regional meteorological and climatic regimes over European mountainous catchments; and (4) to consider the possible impacts of trace element fluxes on ecosystem functioning and human health and the validity of modelled deposition maps for Europe at our study sites.

2 Materials and methods

2.1 Study sites

Atmospheric deposition samples were collected at six sites located in several mountain areas in Europe: the Pyrenees (Lake Redon, formerly Lake Redó), the Alps (Gossenköllesee in the Tyrol, Alpe Devero in the Piemonte, Robiei in the Canton Ticino), the Tatra Mountains (Skalnate pleso) and the Grampian Mountains (Lochnagar). Location and physical characteristics of these sites are shown in Fig. 1 and Table 1. These sites, or others close to them in the same mountain ranges, have been the object of several studies for more than 15 years to characterise the major chemistry of regional atmospheric deposition (Curtis et al.,; 2005; MOLAR, 1999; Rose et al., 2001; Thies et al., 1999; Wathne et al., 1995).

2.2 Sampling

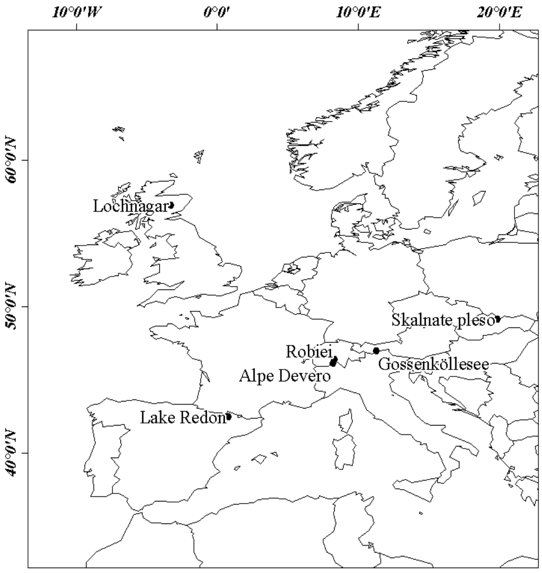

Figure 1. Location of the study sites.

Bulk collectors (which integrate ‘wet and ‘dry’ inputs) were used to collect deposition samples at intervals ranging from between two weeks and one month depending on the location (Table 1) from May 2004 to April 2006, with the exception of Gossenköllesee where sampling was delayed by one month. Samplers consisted of polyethylene devices placed 1.5 m above ground level. In summer, precipitation was collected with a funnel connected to a reservoir by a tube, whereas in winter, when precipitation occurs as snow, either a wider tube assembled on the top of a tank or cylindrical collectors were used for sampling. In sites where frequent snow melt through the winter prevented snow accumulation in the funnel or loss from it over the sampling period (i.e. Lochnagar), the funnel-type collectors were used all year round. A wind screen was placed around the mouth of the collector to prevent biased snow collection due to wind disturbance. Total precipitation volumes collected were checked against adjacent automatic weather stations (AWS). Final precipitation amounts were determined by averaging the records from both collectors and AWS, and were usually very similar.

2.3 Analyses

Element concentrations were determined from the acid-soluble fraction. Samples were acidified with 1% ultra-pure nitric acid in polypropylene bottles, and stored 1-7 days at 4ºC. Afterwards, they were frozen until analysis. For a subset of sites (Lake Redon, Gossenköllesee, Skalnate pleso), concentrations were measured in order to distinguish dissolved and particulate fractions. These samples were filtered through Whatman nitrate cellulose filters (47 mm diameter; 0.45 m pore size) and the filters (particulate fraction) were then extracted with 2 mL ultra-pure nitric acid and 1 mL ultra-pure hydrogen peroxide in Teflon closed beakers at 95 ºC for 16h. 100 mL of the filtrate (‘dissolved’ fraction) was acidified with 1% ultra-pure nitric acid in polypropylene bottles and stored frozen. Extracts were diluted three times with 10 mL ultra-pure (grade 3) water up to a total volume of 33 mL and stored at 4 ºC until analyses. In order to assess the comparability of the extraction performance between the different methods used here, six bulk deposition samples from Lake Redon were treated using both methods. Measured concentrations from the acid-soluble fraction were comparable to the sum of concentrations determined from the dissolved and particulate fractions.

Analyses were performed at three different laboratories: Serveis Científico-Tècnics, University of Barcelona (SCT-UB), Barcelona (Spain); Kingston University, London (UK); and Institute for Ecosystem Studies, Hydrobiology and Ecology of Inland Waters Section (ISE), Pallanza (Italy). Analysis was by Inductively Coupled Plasma (ICP): Fe was determined by ICP-OES whereas Al, Ti, Mn, Ni, Cu, Zn, As, Cd and Pb were measured by ICP-MS. In samples from Alpe Devero and Robiei, Ti and Cu were not measured. In samples from Lochnagar, Fe, Al, Ti and Mn were not determined. In every analytical run, several standard solutions were prepared for calibration and an Rh internal solution was used as a tracer. Typical quantification limits were (in µg L^{-1}) 10 for Fe, 5 for Al, 0.50 for Ti, 0.10 for Mn, 0.034-0.20 for Zn, 0.016-0.20 for Ni, 0.022-0.05 for Cu, 0.012-0.10 for As, 0.003-0.05 for Cd and 0.005-0.05 for Pb. Ranges indicate different quantification limits at different laboratories. Diverse procedural blanks were analysed with each sample batch and subtracted from the sample results when appropriate (Bacardit and Camarero, 2009).

The SCT-UB and ISE labs participated in periodic analytical quality control exercises including the International

Table 1. Study site list.

Site	Range	Country	Latitude	Longitude	Altitude (m a.s.l.)	Rainfall* (mm y^{-1})	Sampling dates	Frequency
Redon	Pyrenees	Spain	42º 39' N	0º 47' E	2240	1300	29/04/04 - 04/05/06	4-weekly
Alpe Devero	Alps – Piemonte	Italy	46° 19' N	8° 15' E	1640	1770	03/05/04 - 01/05/06	monthly
Robiei	Alps – Ticino	Switzerland	46º 27' N	8º 31' E	1890	2120	05/05/04 - 30/04/06	monthly
Gossenköllesee	Alps – Tyrol	Austria	47º 14' N	11º 1' E	2417	1200	09/06/04 - 30/06/06	monthly
Skalnate pleso	Tatra Mts.	Slovakia	49° 11' N	20° 14' E	1778	1340	01/05/04 - 02/05/06	monthly
Lochnagar	Grampian Mts.	UK	56º 57' N	3º 13' W	785	1536	05/05/04 - 04/05/06	every 15 days

*Long-term (30 years) average.

Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes (ICP Waters). As part of each exercise, concentrations of dissolved Fe, Mn, Zn, Ni, Cu, Cd and Pb in paired natural reference water samples are measured, and the acceptance of the results checked using the Youden method (Hovind 2005 and 2006). With some few exceptions not attributable to systematic errors, measurements in the 2005 and 2006 exercises fell within the established acceptance limits. The Kingston University laboratory has a quality assurance system based on ISO/IEC 17025:2005 and is working towards UKAS accreditation. Standard reference samples, e.g. Standard Reference Material® 1640, were typically analysed every fifth sample.

2.4 Numerical methods

The relative importance of in-cloud versus below-cloud processes in determining the concentration of trace elements in atmospheric deposition was evaluated by using a simple model (Mészáros, 1981). The final concentration of an element in precipitation (C_f) is the sum of the in-cloud concentration (C_i) plus the below-cloud concentration (C_b):

$$C_f = C_i + C_b \quad (1)$$

C_b can be computed as a scavenged or dry deposited quantity Q of the element dissolved in a precipitation volume V:

$$C_b = Q/V = Q \times 1/V \quad (2)$$

Substituting in Eq. (1), the mathematical expression of the model is:

$$C_f = C_i + (Q \times 1/V) \quad (3)$$

C_i and Q can be estimated as the independent term and the slope of the linear regression fitting the measured concentrations (C_f) and the inverse of the precipitation volume (1/V) respectively. In this model, C_i has no relationship with V, whereas C_b has a functional dependence on Q and V. Such a dependence results in a correlation between C_b and 1/V, even for randomly distributed Q and V. Therefore, the correlation level between C_f and 1/V can be interpreted as an indication of the relative weight of in-cloud and below-cloud components. A good correlation would indicate that C_b is important in determining the final concentration; otherwise C_i is more important.

The co-distribution of selected elements at each study site was assessed by obtaining the correlation matrix from concentration data, whose elements are the coefficients of linear correlation (Pearson *r*).

The enrichment factor (EF) approach was used to estimate the contributions of elements in atmospheric deposition from natural or anthropogenic sources other than the Earth's crust. The EF is defined as the ratio of a given element concentration to that of Al for which sources other than natural can be assumed to be negligible. Due to its high oxide boiling point, Al has no volatility in the atmosphere and thus in precipitation is mostly found in particulate form associated with the wash-out of windblown rock and soil dust or aerosols. This ratio is then normalised to the same reference ratio characteristic of the upper continental crust (UCC) given by Wedepohl (1995). Thus, the EF were calculated as follows:

$$EF = ([Y]_S/[Al]_S)/([Y]_{UCC}/[Al]_{UCC}) \quad (4)$$

where Y is the element of interest and the subscripts '$_S$' and '$_{UCC}$' denote concentrations in the sample and the average Earth's crust respectively. Due to the large variations in the composition of rock and soil in the Earth's crust, and the natural fractionation of elements relative to Al, enrichment factors ±10 times the mean upper crustal composition may not indicate sources other than natural crustal sources. Enrichment factors larger than 10 may suggest enrichment from other sources, values from 10 to 500 are considered moderately enriched, and values higher than 500 are highly enriched and indicate a strong anthropogenic contribution (Dasch and Wolff, 1989).

The dissolved and particulate phase distribution of elements in bulk deposition samples was assessed by calculating the partition coefficient (C_P), which has no dimension and is defined as the ratio of the particulate fraction to the total concentration:

$C_P=[Y]_{part}/([Y]_{part}+[Y]_{diss})$ (5)

where $[Y]_{part}$ and $[Y]_{diss}$ are the particulate and dissolved fractions of the element Y respectively.

The role of the acidity of precipitation and the nature of element sources on the dissolved and particulate phase distribution of selected elements was evaluated by performing a linear regression between C_P, as response variable, and both the precipitation pH and the EF as independent variables.

3 Results

3.1 Comparison of extraction performance

Table 2 shows the linear relationships between concentrations measured as the total acid-soluble fraction and the sum of dissolved and particulate fractions extracted separately in Lake Redon samples. The slopes for Al, Fe and Ti were low, showing that these elements were poorly extracted in the acid-soluble fraction in comparison to the concentrated nitric acid extraction applied to the particulate fraction after filtering the sample. This indicates that Al, Fe and Ti are strongly bound to particles. The slope for Ni is intermediate, indicating that it was moderately extracted in the acid-soluble fraction. By contrast, Zn, Cu, Pb and Mn showed slopes close to unity, as these elements were similarly extracted using both methods. Linear relationships for As and Cd were not established as concentrations measured from the acid-soluble fraction were in most cases below the analytical detection limit.

Table 2. Linear relationships between concentrations measured from the acid-soluble fraction and the sum of dissolved and particulate fractions in samples from Lake Redon.

	Equation	**R^2**
Al	y = 0.3022x - 10.39	0.889
Fe	y = 0.1255x + 9.1291	0.905
Ti	y = 0.2604x - 0.2925	0.764
Mn	y = 1.1851x - 0.9251	0.552
Zn	y = 0.8084x + 1.2637	0.594
Ni	y = 0.5729x + 0.0561	0.600
Cu	y = 0.8634x + 0.0395	0.903
Pb	y = 0.9837x + 0.0871	0.758

3.2 Composition of atmospheric deposition and the relationships between concentrations and precipitation volume

Table 3 summarises the elemental composition of the atmospheric deposition samples over the two-year period at the different sampling sites. The elements can be ordered by abundance as follows: Al, Fe > Zn > Mn, Ti > Pb, Cu > Ni > Cd, As. Concentrations of Se were mostly below the analytical detection limit at all sites and so Se is not included in further discussion. The highest Al, Fe and Ti concentrations occurred at Lake Redon, with values three to six-fold higher than at the other sites. Manganese concentrations were similar at all sites except at Gossenköllesee, where concentration was on average half of that in other sites. The highest Zn concentration occurred at Robiei, with values four- to ten-fold higher than at the other sites. The highest Pb concentrations occurred at Skalnate, followed by Lake Redon, Lochnagar, Robiei, Alpe Devero and Gossenköllesee respectively, the volume-weighted mean concentration at Skalnate being five times higher than that at Gossenköllesee. The range of Cu concentrations was similar at all sites except Lochnagar where concentrations were lower. The ranges of Ni, Cd and As concentration were similar at all sites, except at Gossenköllesee, where concentrations were lower, and some unusually high Ni values were observed in a few samples from Lochnagar. The reason for these high Ni values is currently unknown.

Table 4 shows the results of the regression analysis between elemental concentrations and the inverse of the precipitation volume. At Lake Redon, with the exception of Cu (17% of the variance explained), no significant dependence on the amount of precipitation was found suggesting in-cloud concentrations are most important for this site. At Alpe Devero, only Ni (24%) and Cd (41%) showed a significant dependence on the amount of precipitation whereas there was no relationship with other elements. At Gossenköllesee, significant correlations were found for Al (20%), Fe (33%) and Ti (37%). At Skalnate pleso, significant dependence was found for several elements. High correlations were obtained for Zn (58%), Ni (59%) and Cu (68%) while moderate correlations were found for Mn (26%), As (33%) and Pb (41%). No significant dependence on the precipitation volume was found for either Robiei or Lochnagar.

3.3 Co-distribution of elements and enrichment factors

The results of the correlation matrix from concentration data are represented as correlation diagrams in Fig. 2. At Redon, high correlations were found between Al, Fe, Ti, Mn, Ni and As. Copper and Pb were less well correlated with this first group of elements, but were not themselves correlated. Zinc and Cd were independent with respect to all other elements. By contrast, at Gossenköllesee and Skalnate pleso elements were co-distributed in two distinct groups with high/intermediate correlation coefficients: Al, Fe, Ti and Mn formed one group, whereas Zn, Ni, Cu, As, Cd and Pb comprised the other. Correlations between the two groups were lower. Finally, at Alpe Devero, Robiei and Lochnagar, co-distribution of trace elements was in general less marked. High correlation coefficients were only found between Al and Fe at Alpe Devero and Robiei.

The EF results are shown in Fig. 3. Aluminium was not measured in deposition at Lochnagar and so EF could not be calculated for this site. The enrichment of elements was similar between study sites. A ranking of elements according to their level of enrichment is: Ti < Fe < Mn < As < Ni < Pb < Cu < Zn < Cd. Titanium, Fe and Mn showed, in general, low EF at all sites except Mn at Alpe Devero and Robiei. Arsenic, Ni, Pb and Cu showed, in

Table 3. Statistical descriptors of major metals and trace elements in atmospheric deposition samples from European mountain sites collected during two annual periods. vwm: volume weighted mean. b.q.l.: below quantification limit; n.d.: no data.

Site		**Al** µg L^{-1}	**Fe** µg L^{-1}	**Ti** µg L^{-1}	**Mn** µg L^{-1}	**Zn** µg L^{-1}	**Ni** µg L^{-1}	**Cu** µg L^{-1}	**As** µg L^{-1}	**Cd** µg L^{-1}	**Pb** µg L^{-1}
Redon N = 24	vwm	216	179	3.5	4.6	13.8	0.46	0.82	0.06	0.06	1.00
	median	93	79	1.7	2.8	6.9	0.40	0.76	0.04	b.q.l.	0.73
	min	10	6	0.2	0.5	2.9	b.q.l.	0.16	b.q.l.	b.q.l.	0.12
	max	1090	766	13.5	19.3	82.4	1.35	3.10	0.21	0.49	3.13
Alpe Devero N = 24	vwm	30	21	n.d.	3.0	11.2	0.46	n.d.	0.11	0.03	0.48
	median	13	17	n.d.	2.5	11.9	0.43	n.d.	0.12	0.03	0.37
	min	3	6	n.d.	1.1	1.7	0.01	n.d.	0.01	0.01	0.05
	max	143	184	n.d.	8.7	27.8	2.82	n.d.	0.32	0.08	2.68
Robiei N = 21	vwm	49	23	n.d.	3.4	45.8	0.29	n.d.	0.06	0.08	0.61
	median	51	15	n.d.	3.4	46.5	0.29	n.d.	0.05	0.08	0.56
	min	9	1	n.d.	0.8	25.5	0.01	n.d.	0.01	0.02	0.02
	max	188	101	n.d.	6.5	71.6	0.91	n.d.	0.28	0.19	1.74
Gossenköllesee N = 20	vwm	43	41	1.6	1.6	9.2	0.16	0.74	0.01	0.04	0.36
	median	27	24	1.3	1.0	5.2	0.06	0.43	b.q.l.	b.q.l.	0.31
	min	1	1	0.1	0.2	0.4	b.q.l.	0.06	b.q.l.	b.q.l.	0.04
	max	145	204	9.7	5.1	34.0	0.56	1.95	0.10	0.35	1.19
Skalnate pleso N = 24	vwm	71	64	1.4	3.2	10.0	0.26	0.88	0.08	0.07	1.52
	median	56	62	1.2	3.5	11.2	0.29	0.90	0.09	0.06	1.65
	min	9	4	0.2	0.7	5.0	b.q.l.	0.28	b.q.l.	b.q.l.	0.53
	max	561	417	8.5	18.0	107.8	1.76	8.71	0.63	0.35	11.98
Lochnagar N = 48	mean	n.d.	n.d.	n.d.	n.d.	3.7	3.25	0.48	0.08	0.05	0.87
	median	n.d.	n.d.	n.d.	n.d.	2.8	0.16	0.30	0.06	0.02	0.59
	min	n.d.	n.d.	n.d.	n.d.	0.2	0.03	0.07	0.02	b.q.l.	0.07
	max	n.d.	n.d.	n.d.	n.d.	23.8	164.00	2.77	0.20	0.12	3.32

general, moderate EF at all sites but high EF were found for As at Alpe Devero, for Pb at Alpe Devero and Skalnate pleso and for Cu at Alpe Devero, Robiei and Skalnate pleso. Zinc and Cd showed high EF at all sites except Lake Redon where EF for Zn was moderate.

3.4 Distribution between dissolved and particulate phases

Table 5 shows the partition coefficients (C_P) calculated for those sites in which dissolved and particulate fractions were determined separately. Aluminium, Fe and Ti showed the highest partition coefficients ($C_P > 0.71$), revealing a strong association with particles. Conversely, Mn, Zn, Ni, Cu, As, Cd and Pb exhibited lower C_P values, indicating high, but variable, proportions of these elements in dissolved forms. The lowest C_P for all elements were determined at Skalnate pleso.

Table 6 shows the results of the linear regressions between the C_P and both the precipitation pH and EF for selected elements expressed by the r-statistic. Aluminium, Fe and Ti were excluded from these analyses because they are found almost totally in the particulate form and showed low EF. Significant positive relationships with pH were generally found for elements with the lowest C_P values. At Lake Redon, highly significant correlations were found for Pb, Cu, Mn and Zn. At Skalnate pleso significant correlations were found for Zn, Cu and Pb, whereas at Gossenköllesee no significant relationship was observed. Several significant relationships were found between the EF values and the distribution into dissolved and particulate

Table 4. Proportion of the variance (r^2) explained by the linear regression between element concentrations and the inverse of precipitation. * and ** denote significance at p-level <0.05 and <0.01 respectively. n.a.: not available.

Site	Al	Fe	Ti	Mn	Zn	Ni	Cu	As	Cd	Pb
Redon	0.03	0.02	0.02	0.05	0.02	0.06	0.17*	0.06	0.05	0.07
Alpe Devero	<0.01	<0.01	n.a.	0.14	<0.01	0.24*	n.a.	0.03	0.41**	0.11
Robiei	0.07	0.15	n.a.	0.13	0.09	0.06	n.a.	0.02	0.06	0.05
Gossenköllesee	0.20*	0.33**	0.37**	<0.01	0.05	0.17	0.03	<0.01	0.01	<0.01
Skalnate	0.06	0.15	0.05	0.26*	0.58**	0.59**	0.68**	0.33**	0.41**	0.33**
Lochnagar	n.a.	n.a.	n.a.	n.a.	0.01	0.03	<0.01	<0.01	<0.01	<0.01

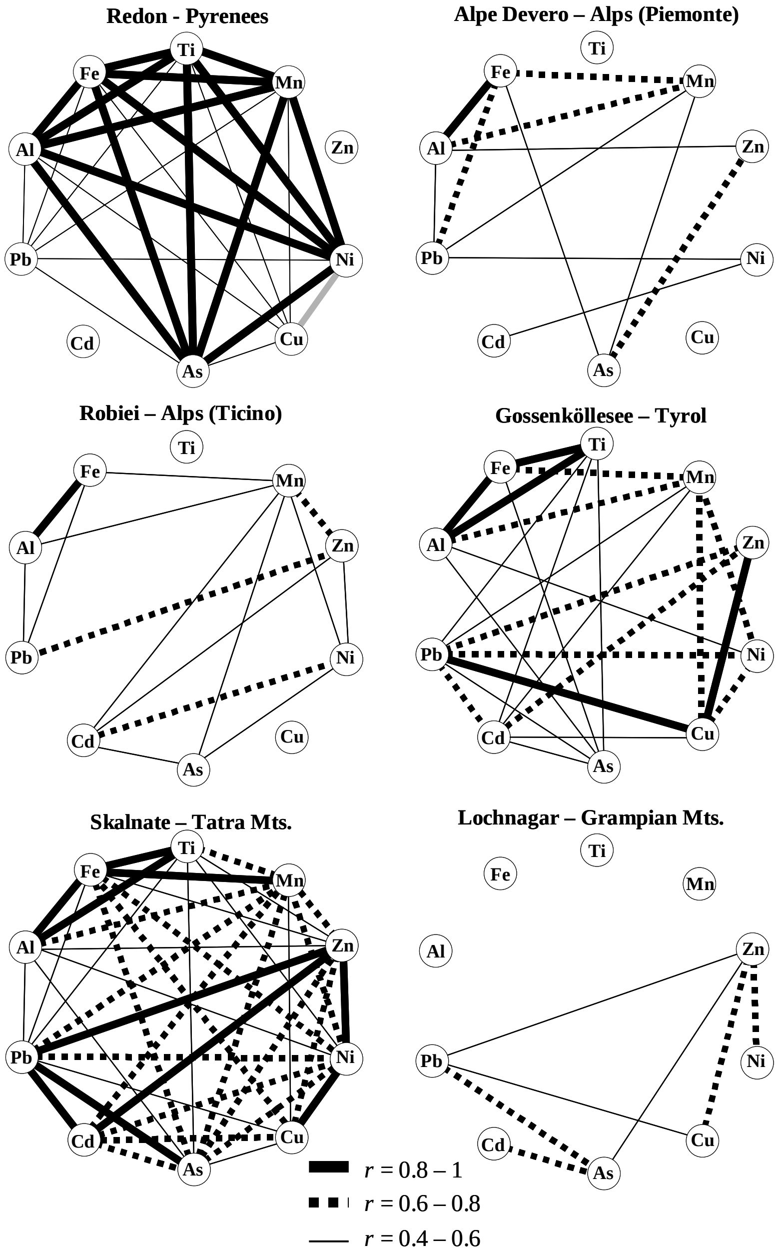

Figure 2. Linear correlation coefficients (Pearson *r*) between the different element concentrations.

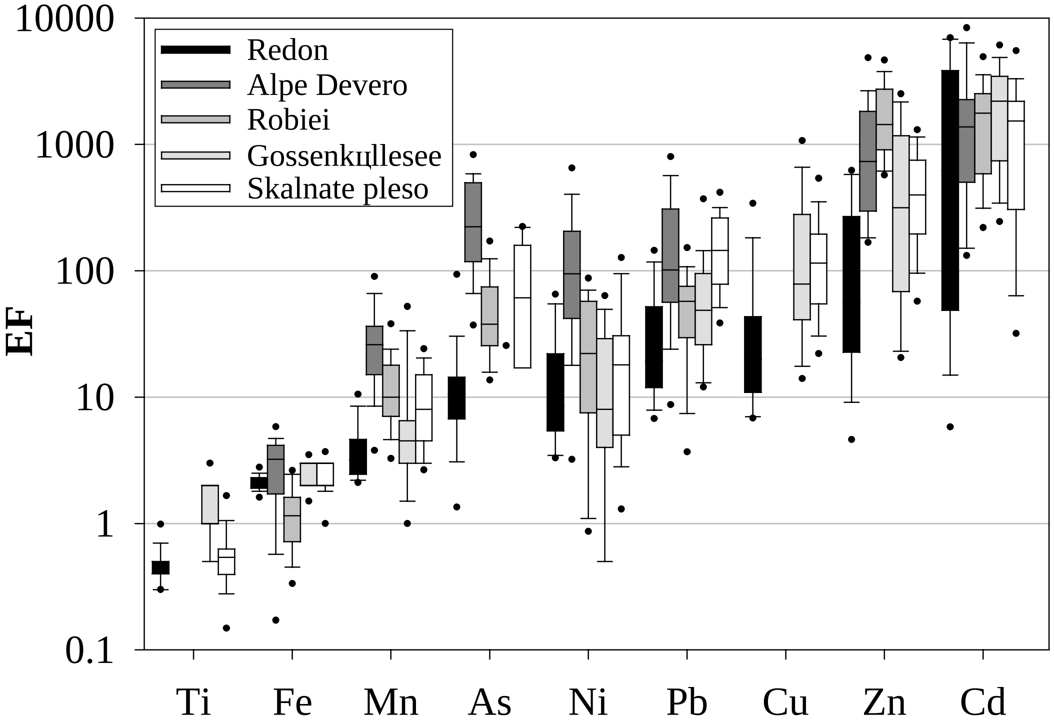

Figure 3. Enrichment factors (EF) in atmospheric deposition samples relative to the average upper continental crust composition.

forms. At Lake Redon, significant negative correlations were found for Mn, Zn, Ni, Cu, As and Pb. At Gossenköllesee, significant negative correlations were observed for Mn, Ni and Pb, whereas at Skalnate pleso, significant negative relationships were found for Mn, Ni, Cu and Pb and a significant positive dependence was observed for Cd.

3.5 Seasonal and annual depositional fluxes

In addition to concentration, the precipitation volume determines the total flux of an element deposited. The atmospheric fluxes of elements and the precipitation volumes over the sampling period are shown in Fig. 4 and 5. Certain seasonal patterns of depositional fluxes were observed at all sites, which consisted of higher fluxes during warm months of each year (June – November) compared to cold months (December – May). A Kruskal-Wallis rank test was conducted to assess statistical significance of the observed differences in atmospheric fluxes between seasons (winter, spring, summer and autumn). The test indicates whether differences are significant in the samples corresponding to at least one pair of seasons with a p-value < 0.05. The results of this test are shown in Table 7. At Skalnate pleso, differences in seasonal fluxes were statistically significant for all elements and all seasons. At Lake Redon, Al, Fe, Ti, Mn and As fluxes presented

Table 5. Volume weighted mean partition coefficient (C_P) values for major metals and trace elements.

Site	Al	Fe	Ti	Mn	Zn	Ni	Cu	As	Cd	Pb
Redon	0.90	0.99	1.00	0.36	0.22	0.47	0.39	0.82	0.59	0.58
Gossenköllesee	0.91	0.99	0.84	0.34	0.38	0.72	0.25	1.00	0.81	0.52
Skalnate pleso	0.71	0.79	0.81	0.16	0.07	0.53	0.17	0.09	0.08	0.21

significant seasonal differences, in particular between summer with respect to the other seasons. At Alpe Devero, seasonal fluxes of Zn, Ni and Cd were significantly different, in particular between winter with respect to spring and summer. At Gossenköllesee, seasonal fluxes of Mn, Cu and Pb were significantly different, in particular between winter and summer. Conversely, differences between seasonal fluxes observed at Robiei and Lochnagar were not statistically significant.

The amount of precipitation and annual inputs during May 2004 – April2005 and May 2005 – April 2006 (at Gossenköllesee, during June 2004 – May 2005 and June 2005 – May 2006) are shown in Table 8. Annual precipitation amounts recorded in this study were lower than the long-term average precipitation at each site, and were different between the two periods. At Lake Redon and Gossenköllesee, annual precipitation increased 26% and 23% respectively in May 2005 – April 2006 with respect to the 12 months, while at Skalnate pleso, Robiei and Alpe Devero decreased 40%, 28% and 23% respectively.

The atmospheric fluxes of Al, Fe, Ti, and Mn were, as with the concentration data, much higher in the Pyrenees than in the other locations, with the exception of Mn which was also of the same order in the Southern Alps. Copper deposition was similar in all sites where it was measured. In general, annual inputs of Zn and Ni were higher at southern locations (Lake Redon, Alpe Devero and Robiei) with respect to the northern sites. Annual inputs of As, Cd and Pb differed by as much as one order of magnitude between locations. Thus, a ranking of the sites can be established according to the load of Zn, Ni, As, Cd and Pb. The highest loads were measured at Robiei (with very high Zn deposition, high As, Cd and Pb, and intermediate Ni) and Lochnagar (very high Ni, high As and Pb, and intermediate Cd). The lowest loads occurred at Gossenköllesee (only Cd was intermediate) and Skalnate pleso (with intermediate levels of As and Pb). Between these high and low sites were the Pyrenees (with intermediate levels of all elements) and Alpe Devero (with high As deposition and intermediate levels of Zn and Ni).

3.6 Decadal concentration trends in precipitation over European mountain ranges

Trace element concentration in precipitation data for the last 10 years were compiled from the existing literature (Plöger, 2004; Veschambre, 2006; Yang et al., 2002a and 2002b) and annual averages for selected trace elements were plotted against time. A linear regression curve was fitted for each data series corresponding to a different mountain

Table 6. Correlation coefficients (r) obtained by the linear regression model between C_P and both precipitation pH and EF. * and ** indicate significance at p-value < 0.05 and p-value < 0.01 respectively. n.c.: not computed because too few samples were above the quantification limit.

Model	**Site**	**Mn**	**Zn**	**Ni**	**Cu**	**As**	**Cd**	**Pb**
$C_P \sim$ pH	Redon	0.518**	0.518**	0.422*	0.727**	-0.141	-0.265	0.730**
	Gossenköllesee	-0.012	-0.334	-0.389	-0.127	n.c.	0.209	-0.103
	Skalnate pleso[1]	0.235	0.725**	0.401	0.459*	< -0.001	n.c.	0.565*
$C_P \sim$ EF	Redon	-0.585**	-0.487*	-0.605**	-0.629**	-0.871**	0.545	-0.579**
	Gossenköllesee	-0.580**	0.222	-0.550*	-0.434	n.c.	0.177	-0.480*
	Skalnate pleso	-0.692**	-0.347	-0.674**	-0.537*	-0.293	n.c.	-0.596**

[1] Regression performed with 20 samples because pH of four samples was not available.

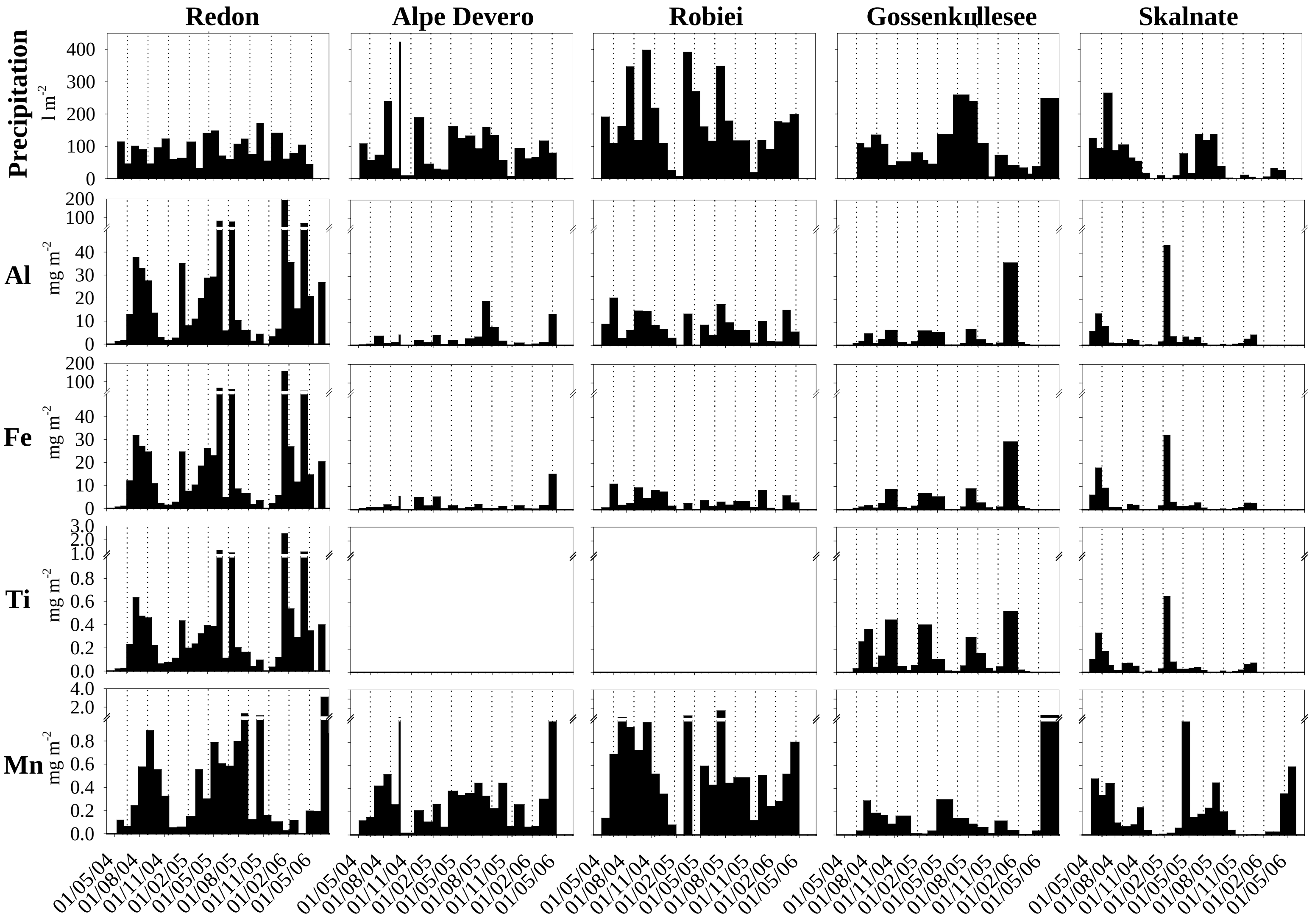

Figure 4. Precipitation and atmospheric fluxes of Al, Fe, Ti and Mn in the study sites over 2004-06.

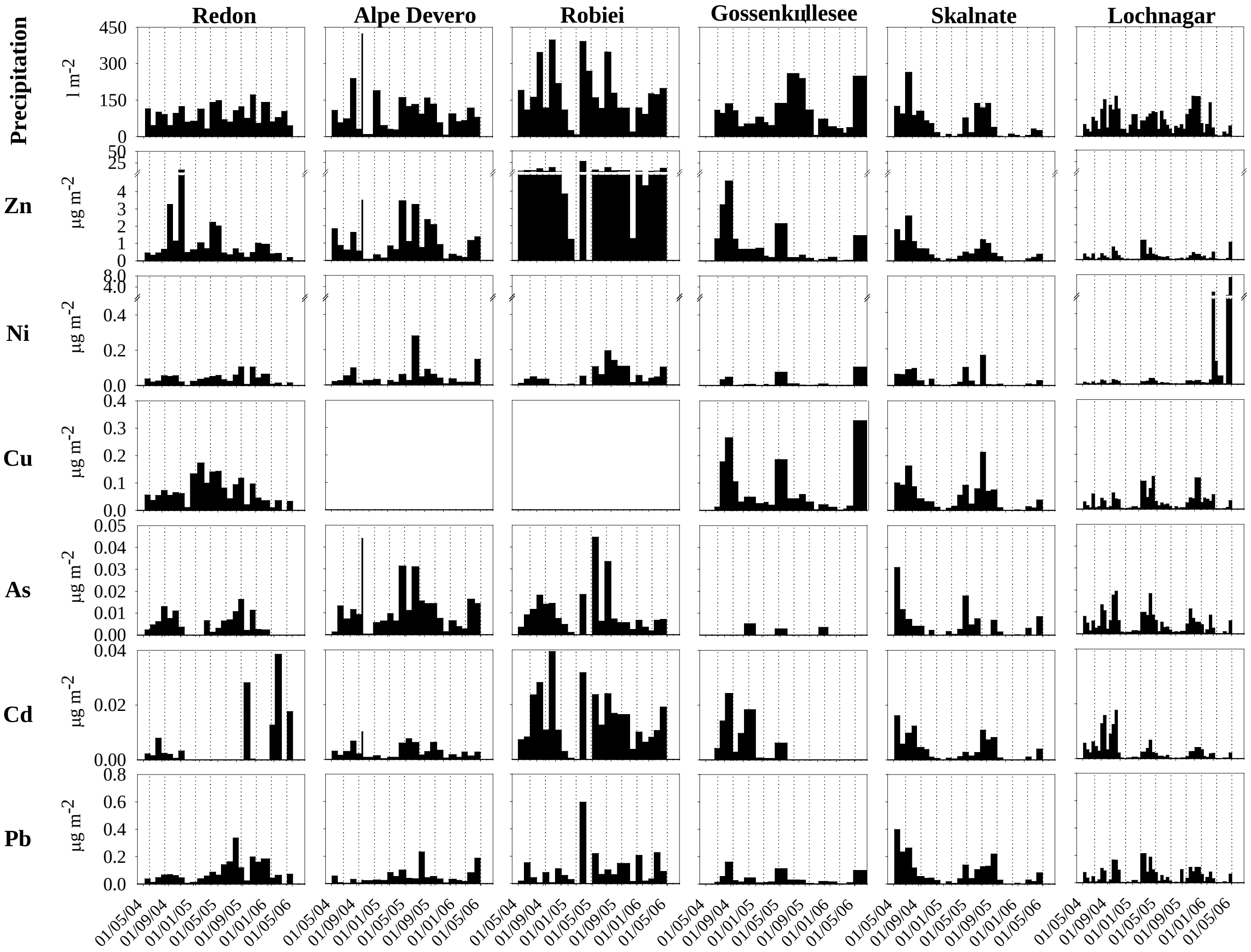

Figure 5. Precipitation and atmospheric fluxes of Zn, Ni, Cu, As, Cd and Pb in the study sites over 2004-06.

Table 7. Kruskal-Wallis rank test results expressed as p-values. * and ** denotes significant seasonal differences of element fluxes at p-value <0.05 and p-value <0.01 respectively. n.a.: not available. n.c.: not computed because too few samples were above the quantification limit.

Site	**Al**	**Fe**	**Ti**	**Mn**	**Zn**	**Ni**	**Cu**	**As**	**Cd**	**Pb**
Redon	0.010*	0.009**	0.015*	0.010	0.887	0.169	0.413	0.048*	0.916	0.271
Alpe Devero	0.232	0.973	n.c.	0.111	0.048*	0.036*	n.a.	0.184	0.028*	0.326
Robiei	0.755	0.256	n.c.	0.200	0.328	0.252	n.a.	0.121	0.234	0.771
Gossenköllese	0.350	0.217	0.276	0.012*	0.227	0.066	0.033*	n.c.	0.882	0.077
Skalnate pleso	0.003**	0.004**	0.007**	0.003**	0.002**	0.036*	0.002**	0.004**	0.001**	0.002**
Lochnagar	n.a.	n.a.	n.a.	n.a.	0.244	0.165	0.268	0.633	0.825	0.454

range (Fig. 6). Resulting regression coefficients (slopes, *b*, and coefficients of correlation, r^2) were examined as estimates of the rate of change and the variance explained by the regression model respectively. Trace element concentration shows a general decreasing trend over European mountain ranges over the last decade. The concentrations of Pb decreased most in the Pyrenees, the Canton Ticino, the Piemonte, the Tyrol and the Tatra Mountains, with slopes ranging from -0.1 to -0.2 $\mu g\ L^{-1}\ y^{-1}$ and r^2 values of 0.19 - 0.99. By contrast, in the Grampian Mountains, it showed no change. Concentrations of Zn decreased most in the Pyrenees and the Grampian Mountains, with slopes of -4.6 and -1.7 $\mu g\ L^{-1}\ y^{-1}$ and r^2 values of 0.82 and 0.37 respectively. By contrast, in the Tatra Mountains, the Ticino and the Piemonte, there was a positive Zn trend, with slopes of 1.1 and 8.0 $\mu g\ L^{-1}\ y^{-1}$ and r^2 values of 0.81 and 0.14 respectively. In the Tyrol, there was no significant trend for Zn deposition over the last decade. Concentrations of Ni decreased very little in the Tyrol (b=-0.03 $\mu g\ L^{-1}\ y^{-1}$, r^2=0.98), and increased slightly in the Ticino, the Piemonte and the Tatra Mountains (b<0.1 $\mu g\ L^{-1}\ y^{-1}$ and r^2 = 0.25 and 0.72 respectively). In the Grampian Mountains a few high values in 2006 resulted in a greater increase (b=0.5 $\mu g\ L^{-1}\ y^{-1}$, r^2=0.31). In the Pyrenees, there was no significant trend in Ni concentration. Concentration of Cu exhibited a decreasing trend in the Grampian Mountains, the Pyrenees, the Tyrol and the Tatra Mountains, with slopes of -0.19, -0.05, -0.03 and -0.01 $\mu g\ L^{-1}\ y^{-1}$ and r^2 values ranging between 0.24-0.34.

4 Discussion

4.1 Current spatial distribution and origin of atmospheric major metals and trace elements over European mountain ranges

The co-distribution of elements, the composition of aerosols and the partitioning between dissolved and particulate forms, as indicated respectively by elemental correlations, EF and C_p values, depend on the origin of the elements (Chester et al., 1993). Elements with a natural origin show low EF and are largely found in particulate forms, whereas elements with an anthropogenic origin generally have higher EF and are more abundant in dissolved forms. Co-distribution of a group of elements indicates the same source. These features are used in the following discussion to gain insight into the relative contribution of natural and anthropogenic sources to the atmospherically deposited major metals and trace elements and to assess the current extent of atmospheric contamination over European mountain ranges.

Atmospheric dust was substantially more

Table 8. Annual precipitation and depositional fluxes during 2004-05 and 2005-06. Comparison with estimated 5th percentile critical loads (CL) n.a.: not available. n.c.: not computed because too few samples were the above quantification limit.

Site	**Period**	**Precip.**	**Al**	**Fe**	**Ti**	**Mn**	**Zn^{3}**	**Ni^{1,3}**	**Cu^{1,3}**	**As^{1,3}**	**Cd$^{1\text{ to }4}$**	**Pb$^{1\text{ to }4}$**
		mm y^{-1}					**mg m^{-2} y^{-1}**					
Redon	2004-05	1030	178	147	3.0	3.9	21.7	0.42	0.96	0.06	0.02	0.55
	2005-06	1303	278	229	4.3	5.9	8.0	0.54	0.76	0.06	0.10	1.58
	CL						10 – 20	6 – 8	3 – 4	2 – 3	0.3 – 0.5	1 – 2
Alpe Devero	2004-05	1398	22	27	n.a.	3.6	14.5	0.38	n.a.	0.15	0.04	0.44
	2005-06	1130	53	27	n.a.	4.0	13.9	0.78	n.a.	0.14	0.04	0.78
	CL						40 – 50	≥ 12	4 – 5	6 – 8	> 0.5	2 – 3
Robiei	2004-05	2351	102	52	n.a.	6.7	92.6	0.22	n.a.	0.10	0.16	1.11
	2005-06	1704	83	34	n.a.	6.2	80.4	0.88	n.a.	0.12	0.15	1.20
	CL						40 – 50	≥ 12	5 – 6	6 – 8	> 0.5	< 0.5
Gossenköllese	2004-05	864	28	27	1.9	1.3	15.2	0.18	0.90	0.01	0.08	0.47
	2005-06	1066	55	52	1.3	1.8	2.6	0.14	0.52	n.c.	n.c.	0.22
	CL						20 – 30	6 – 8	3 – 4	2 – 3	> 0.5	1 – 2
Skalnate pleso	2004-05	914	81	75	1.6	2.9	9.6	0.25	0.73	0.08	0.06	1.39
	2005-06	551	17	17	0.4	1.7	4.8	0.13	0.53	0.03	0.04	0.80
	CL						< 10	≥12	1 – 2	< 1	> 0.5	0.5 – 1
Lochnagar	2004-05	1754	n.a.	n.a.	n.a.	n.a.	6.2	0.30	0.73	0.16	0.12	1.53
	2005-06	1344	n.a.	n.a.	n.a.	n.a.	4.1	9.70	0.55	0.07	0.03	0.89
	CL						30 – 40	8 – 10	3 – 4	6 – 8	> 0.5	2 – 3

The superscripts in the element symbols indicate the receptor ecosystem and endpoints of protection considered for determination of the respective CL: 1= human health effect (drinking water) via aquatic ecosystems; 2= human health effect (food quality) via terrestrial ecosystems; 3= ecotoxicological effect on terrestrial ecosystems; 4= ecotoxicological effect on aquatic ecosystems.

important in the Pyrenees than in the northern mountain ranges. This was indicated by higher concentrations of Al, Fe and Ti, which showed high correlation coefficients, low EF, and were largely found as insoluble forms. In SW Europe, Al, Fe and Ti have been identified as crustal elements forming terrigenous particles transported from the Iberian peninsula and North Africa (Bacardit and Camarero, 2009). Manganese, Ni and As were also related to dust in the Pyrenees showing high correlations with Al, Fe and Ti and low EF. By contrast, in more northern mountain areas, Mn, Ni and As had a larger anthropogenic component as they appeared well correlated with other trace elements with a clear contaminant character and were moderately enriched. Intermediate correlations of Pb and Cu with crustal Al, Fe and Ti provided evidence that Pb and Cu were partly associated with natural, terrigenous dust. However, their high correlation with other contaminating trace elements clearly suggested that these elements partly originated from sources other than rock and soil dust. The highest Pb and Cu concentrations were observed in the Tatra Mountains. Zinc was a major contaminant in all surveyed areas, as demonstrated by moderate to high EF values. In the Pyrenees, Zn likely originated from an emission source independent of the other trace elements, whereas in all other mountain ranges it was related to them (e.g. Cu, Pb, Ni and Cd). Cadmium showed the highest EF values, indicating a considerable contamination component in the regional atmospheres. In the Pyrenees, Cd was independently distributed, whereas in the other mountain regions it was related to other contaminant trace elements. This supports the view that the current enrichment of this element in the atmosphere is due to anthropogenic sources. The highest Zn and Cd concentrations occurred in the

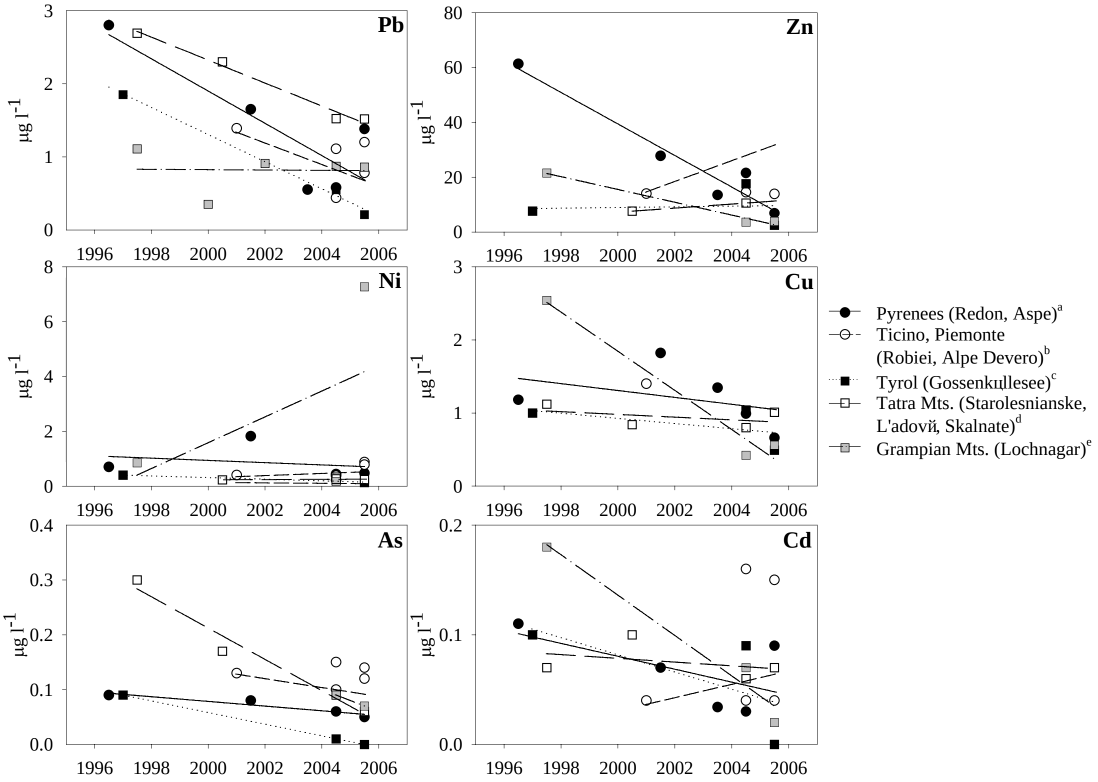

Figure 6. Depositional trends expressed as trace element concentrations in European mountain ranges from 1995 to 2006. The linear regression fittings are displayed for each data set. Data sources: [a]Pyrenees (Plöger, 2004; Veschambre, 2006; this study); [b]Ticino, Piemonte (Plöger, 2004; this study); [c]Tyrol (Plöger, 2004; this study); [d]Tatra Mts. (Plöger, 2004; this study); [e]Grampian Mts. (Yang et al., 2002a, Yang et al., 2002b, this study).

Canton Ticino. The Tyrol exhibited the lowest trace element concentrations.

4.2 Bioavailability of atmos-pherically deposited trace elements in European mountain catchments

Bioavailability is a key property determining the potential toxicity of atmospherically deposited trace elements in European mountain lake ecosystems. Trace elements present in soluble forms are more bioavailable than when bound to particulates (Giusti et al., 1993), and C_p can therefore be used thus as an indicator of their potential bioavailability. Results of this study (Table 5) show that Al, Fe and Ti, identified here as major lithogenic elements, clearly formed part of insoluble particles. By contrast, Mn, Zn, Ni, Cu, As, Cd and Pb, which originate from a wide range of sources having lithogenic and anthropogenic components, appeared in variable proportions as dissolved forms. Hence, these elements are more bioavailable and may represent a greater potential toxicity to receiving ecosystems. This is of special concern in the Tatra Mountains, where atmospherically deposited trace elements are significantly more soluble than in the other mountain ranges, in proportions ranging between 26 - 91% depending on the element.

Among other factors, pH may be of importance in determining the solubility of elements in atmospheric deposition. The effect of pH is highest on moderately soluble elements, most of them having anthropogenic sources (Cizmecioglu and

Muezzinoglu, 2008). The results of the linear regression analysis between C_p and pH revealed the influence of the acidity of precipitation on the solubility of several elements (Table 6). In this study, the effect of pH was significant in the Pyrenees (for Mn, Zn, Ni, Cu and Pb) and in the Tatra Mountains (for Zn, Cu and Pb) but not in the Tyrol. The reason for this was that pH values at Gossenköllesee were in a narrower range (5.40 ± 0.31) than in Lake Redon and Skalnate pleso (5.89-0.69 and 5.18-0.57 respectively), thus preventing a robust testing of the effect of pH by linear regression.

Particulate forms of elements originating from crustal sources are less soluble than anthropogenic components, and for this reason elements are found to be more soluble in urban than in rural aerosols which contain a higher proportion of crustal material (Collin et al., 1990). In the present study (Table 6), this was in agreement with the significant negative correlation between EF and C_p in the Pyrenees (for Mn, Zn, Ni, Cu, As and Pb), in the Tyrol (for Mn, Ni and Pb) and in the Tatra Mountains (for Mn, Ni, Cu and Pb).

4.3 Comparison with estimates of critical loads and modelled atmospheric deposition for Europe

In order to assess the potential ecotoxicological risk of atmospheric trace element fluxes over European mountain catchments, annual trace element inputs measured here were compared with estimated critical loads in Table 8. The critical load (CL) is the rate of deposition at which, at steady state, the soil or water concentration reaches a critical limit above which adverse environmental or health effects may give rise to negative effects on ecosystem functioning and / or human health. Critical limits are established for human health effects of drinking water via aquatic ecosystems (effect 1) and of food via terrestrial ecosystems (effect 2), and for eco-toxicological effects in terrestrial ecosystems (effect 3) and in aquatic ecosystems (effect 4). Critical load maps are provided by EMEP (Cooperative Programme for Monitoring and Evaluation of Long-range Transmission of Air Pollutants in Europe, see website http://www.emep.int/) in which, for each ecosystem in a 50 x 50 km grid cell, the 5th percentile of the distribution of minimum CLs is calculated, implying a CL at which 95% of the ecosystems in that grid cell are protected against any of the four effects (Hettelingh and Sliggers, 2006, Reinds et al., 2006). Certain elements measured in this study showed depositional fluxes very close to or above the established CL in some areas. For Zn, the annual flux in the Ticino was twice the CL reported for the corresponding grid-cell, and in the Pyrenees and the Tatra Mountains it was similar to the CL values. For Pb, annual fluxes in the Pyrenees, the Ticino and the Tatra Mountains were 1.5 to 2-fold the CL. For Ni, the annual flux in the Grampian Mountains was similar to the CL value. These data indicate an important, ubiquitous background atmospheric contamination of trace elements in Europe. Moreover, measurements in remote European mountain ranges can help to identify, on a regional scale, the sources that should be targeted to reduce contaminant impacts in natural areas and lower CL exceedences.

Lead and Cd are considered high priority elements by EMEP. Our measurements were compared with estimated annual inputs (Table 9) obtained from modelled deposition maps for 2005 (Ilyin et al., 2007) in order to assess the validity of the model estimates at our study sites. Figure

7 shows modelled atmospheric deposition maps for Pb and Cd for the sampling year 2005 (adapted from Ilyin et al., 2007). In the Piemonte and the Tyrol, the model predicts up to two-fold higher annual fluxes of Pb with respect to our measurements, and in the Tatra Mountains up to three-fold higher annual Pb inputs. The model underestimates the annual Pb fluxes in the Pyrenees and the Grampian Mountains, whereas it matches the annual Pb flux in the Canton Ticino. By contrast, in the Piemonte, the Tyrol and the Tatra Mountains modelled annual fluxes of Cd are two- to three- times higher with respect to observations, whereas in the Pyrenees modelled annual Cd flux matches measurements, and in the Ticino and the Grampian Mountains the model predicts lower annual Cd fluxes than measurements. Furthermore, the model tends to underestimate measurements at a number of EMEP monitoring sites, particularly, in Central Europe and Scandinavia (Ilyin et al., 2007). According to the authors, possible reasons for this include unidentified local emission sources, underestimation of wind re-suspended contributions, or peculiarities of air-mass trajectories and associated precipitation in the mountain range unsuccessfully simulated by the model.

Reliable direct deposition measurements are essential for validating and improving model predictions (i.e. critical loads, deposition maps). The discrepancies found in this study between modelled and empirical deposition levels highlight the need for further long term monitoring and improved modelling in relatively remote mountain areas, considered both wilderness reserves and sources of water to the highly populated low-land areas.

4.4 Seasonal and inter-annual patterns of atmospheric fluxes: possible implications of climate change on the deposition of trace elements

Deposition trends vary according to the rate of regional emission changes and the variability of meteorological parameters (precipitation amount, wind field and atmospheric stability) that influence atmospheric transport and deposition patterns. The change in the rate of anthropogenic emissions to the atmosphere is mainly a consequence of environmental policy constraints to corresponding industrial and urban sectors.

There has been a continuous reduction of trace element emissions in Europe over the last 40 years (Pacyna et al., 2007). This is reflected by the decreasing concentration patterns found for Pb in the Pyrenees, the Ticino, the Piemonte, the Tyrol and the Tatra Mountains, for Zn in the Pyrenees and the Grampian Mountains, and for Cu in the Pyrenees, the Tyrol, the Tatra Mountains and the Grampian Mountains. Moreover, this is in

Table 9. Comparison between observed fluxes for Pb and Cd and estimated fluxes from modelled deposition maps in year 2005. Units: mg m^{-2} y^{-1}.

Site	**Pb**		**Cd**	
	observed	**modelled**	**observed**	**modelled**
Redon	1.60	0.8 – 1.2	0.03	0.02 – 0.03
Alpe Devero	0.73	1.2 – 1.7	0.04	0.05 – 0.10
Robiei	1.45	1.2 – 1.7	0.14	0.05 – 0.10
Gossenköllesee	0.24	0.5 – 0.8	0.01	0.02 – 0.03
Skalnate pleso	0.87	> 2.5	0.04	> 0.15
Lochnagar	1.37	0.8 – 1.2	0.04	0.02 – 0.03

good agreement with a decline in trace element concentrations in the surface lake sediments from some sites across the UK (Yang and Rose, 2005).

However, changes in meteorological parameters directly affecting the transport and deposition of trace elements are certainly determined by many of the diverse aspects of climate change. For instance, in the case of the Central Pyrenees, temporal variations in trace element deposition were related to prevailing meteorological conditions. Deposition of dust, Pb, Ni and Cd was higher during the year in which a larger proportion of precipitation came from the Iberian Peninsula – N Africa and followed low altitude trajectories (Bacardit and Camarero, 2009). On a seasonal scale, deposition of dust and Pb in the Pyrenees was similarly related to southern air masses occurring during June – November (Bacardit and Camarero, 2009). In the other study locations, similar seasonal patterns were found due to uneven precipitation distributions through the year. These results imply that possible changes in general atmospheric circulation patterns and precipitation as a result of climate change may have an influence on the atmospheric fluxes of trace elements. For instance, an increase in the proportion of air masses coming from southern areas or increased precipitation may enhance the deposition of some elements.

The existence of temporal variability also means that spatial differences need to be assessed with respect to inter-annual and seasonal variability, in order to identify the true significance of different depositional fluxes between sites. Although our results point to such spatial differences, variability in deposition between sites exceeds the inter-annual variability for certain elements, and so data series longer than two years are needed before a robust statistical testing of their significance can be undertaken. Therefore, long-term monitoring is required.

5. Conclusions

Over a two-year period (May 2004 – April 2006) we measured the concentrations and fluxes of major metals and trace elements in bulk deposition in six European mountain ranges. The composition of atmospheric deposition in the Pyrenees was characterised by high concentrations of crustal major elements (Al, Fe, Ti and Mn) forming a component of dust particles transported from the Iberian peninsula and North Africa. The composition in more northern mountain areas was characterised by lower concentrations of crustal elements and a higher proportion of trace elements (Pb, Zn, Ni, Cu, As and Cd) of anthropogenic origin. The Tatra Mountains and the southern Alps (Ticino, Piemonte) received the highest trace element concentrations, being more influenced by regional industrial and urban areas in Central and Southern Europe. By contrast, the Tyrol showed the lowest trace element concentrations, reflecting a minor influence from regional atmospheric contamination sources, likely due to its location surrounded by extensive mountainous areas. Finally, the Pyrenees and the Grampian Mountains received intermediate atmospheric trace element concentrations.

A comparison with previous measurements demonstrated that trace element concentrations have shown a general decreasing trend over European mountain ranges over the last decade.

In terms of trace element fluxes, the highest deposition loads were measured at

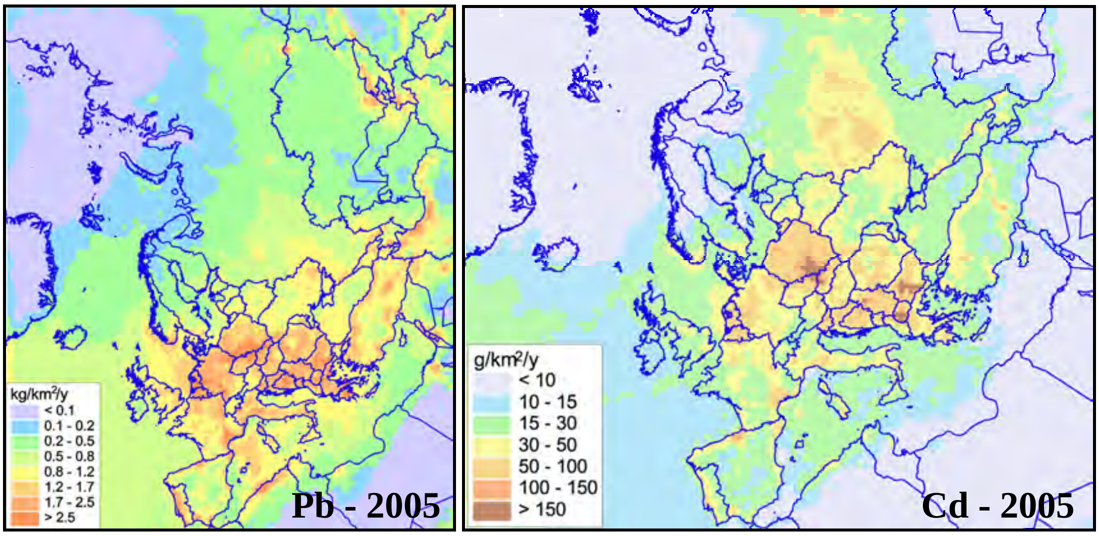

Figure 7. Modelled annual deposition of lead and cadmium in Europe and Central Asia in 2005 (adapted from Ilyin et al., 2007).

the Canton Ticino and the Grampian sites, while the lowest loads occurred in the Tyrol and the Tatra Mountains. The Pyrenees and the Piemonte were in an intermediate position. Annual trace element fluxes measured in European mountain ranges exceeded (or were close to) the estimated critical loads in some cases and showed some discrepancies with EMEP annual modelled atmospheric deposition maps of Pb and Cd in Europe for 2005. Seasonal and inter-annual trace element deposition patterns were related to air circulation patterns and precipitation regimes. Therefore, possible changes in the regional meteorological conditions as a result of climate change may have an influence on the atmospheric fluxes of trace elements.

The exceedences of atmospheric trace element fluxes with respect to their critical loads; the discrepancy between some direct measurements and the modelled deposition; the relationships between seasonal and inter-annual fluxes and the regional meteorology; and the significance of inter-annual variability with respect to spatial differences are issues that need to be further assessed by long-term monitoring.

Acknowledgements. This study was supported by the EU funded project Euro-Limpacs (GOCE-CT-2003-505540) and the Spanish MEC project GRACCIE (CSD2007-00067). M. Bacardit gratefully acknowledges the Spanish Council for Scientific Research (CSIC) for an I3P pre-doctoral grant. This study is a result of the activities of the Limnological Observatory of the Pyrenees (LOOP), a joint initiative of the Center for Advanced Studies-CSIC and the Center for High Mountain Research - Univ. of Barcelona. Thanks to Toni Padró (Serveis Científico-Tècnics – University of Barcelona) for Spain, Austria and Slovakia trace metal analysis. Thanks to Prof. Kym Jarvis (formerly of Kingston University) for UK trace metal analysis.

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Results

Part II. Long-term atmospheric deposition, storage, transport and fate of trace elements in high mountain lake catchments

Paper IV. Major and trace elements in soils in the Central Pyrenees: high altitude soils as a cumulative record of background atmospheric contamination over SW Europe

M. Bacardit and L. Camarero, 2010. Environmental Science and Polllution Research, 17, doi: 10.1007/s11356-010-0349-4

Figure 7. Soil sampling in Cregüeña valley, Central Pyrenees (by L. Camarero): sampling devices for persistent organic pollutants and major and trace elements, respectively (left-hand side) and sampling site below the timberline (right-hand side).

M. Bacartit and Ll. Camarero. “Major and trace elements in soils in the Central Pyrenees: high altitude soils as a cumulative record of background atmospheric contamination over SW Europe”. *Environmental science and pollution research*. Vol. 17, num. 9 : p. 1606-1621

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http://dx.doi.org/10.1007/s11356-010-0349-4

Abstract

Background, aim, and scope

High mountain soils constitute a long-term cumulative record of atmospherically deposited trace elements from both natural and anthropogenic sources. The main aims of this study were to determine the level of major and trace metals (Al, Ti, Mn, Fe, and Zr) of lithologic origin and airborne contaminating trace elements (Ni, Cu, Zn, As, Cd, and Pb) in soils in the Central Pyrenees as an indication of background contamination over SW Europe, to establish whether there is a spatial pattern of accumulation of trace elements in soils as a function of altitude, and to examine whether altitude-related physicochemical properties of soils affect the accumulation of major metals and trace elements.

Methods

Major metals and trace elements were measured in “top” (i.e., first 10 cm) and “bottom” (i.e., below 10 cm) soil samples along an altitudinal transect (1,520-2,880 m a.s.l.) in the Central Pyrenees. Total concentrations were determined by X-ray fluorescense spectrometry. Total major metal concentrations were analysed by conventional X-ray fluorescence spectrometry (XRF) with a Siemens SRS 303 instrument. Total trace element concentrations were determined with an energy-dispersive multielement miniprobe XRF analyser. Acid-extractable concentrations were measured by inductively coupled plasma after previous extraction with nitric acid and hydrogen peroxide in closed beakers. Acid-extractable major metal concentrations were measured by inductively coupled plasma (ICP)-Optic Emission Spectrometry with a Perkin Elmer 3200 RL Instrument. Acid-extractable trace element concentrations were determined by ICP-Mass Spectrometry with a Perkin Elmer ELAN 6000.

Results

Trace element concentration ranges were (in mg kg^{-1}, inventories in g m^{-2} between parenthesis) <2-58 (0.5-6.6) for Ni, 6-30 (0.2-3.4) for Cu, 38-236 (1.6-32.4) for Zn, 6-209 (0.2-12.8) for As, 0.02-0.64 (<0.04) for Cd, and 28-94 (0.6-13.0) for Pb. These concentrations were, in general, comparable to those recorded in soils from other European mountainous areas and were in many cases above the threshold recommended for ecosystem protection by regional and European environmental authorities. The highest concentrations were found at lower altitudes, indicating an effect of local contamination up to ~2,300 m a.s.l. Only above this altitude can trace elements in soils be considered representative of a background, long-range atmospheric contamination.

Conclusions

None of the storage capacity properties of soils examined were determinant of the differences in elemental concentrations along the altitudinal transect. At the upper altitude range, Ni, Cu, and Pb showed a approximately two- to fivefold increase over the average concentration of the local dominant lithology, reflecting the regional and global background of atmospheric contamination in the area.

Keywords Soil contamination - Inorganic contaminants - Soil properties - Enrichment factors - High mountains - Long-range contamination

Paper V. Whole-catchment inventories of trace metals in soils and sediments in mountain lake catchments in the Central Pyrenees: apportioning anthropogenic and natural contributions

M. Bacardit, M. Krachler, and L. Camarero, 2010. Geochimica et Cosmochimica Acta, accepted

Figure 8. Panoramic views of the three Pyrenean lake catchments located along an altitudinal gradient (by L. Camarero): Vidal d'Amunt (2684 m a.s.l.; above), Plan (2188 m a.s.l.; central) and Légunabéns (1655 m a.s.l.; below).

Whole-Catchment Inventories of Trace Metals in Soils and Sediments in Mountain Lake Catchments in the Central Pyrenees: Apportioning the Anthropogenic and Natural Contributions

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Abstract

We measured the concentrations of Pb, Zn, Cd, Cu and Ni in rocks, soils, sediments and plants from three catchments in the Central Pyrenees, with the aim of producing whole-catchment inventories for these trace metals and apportioning natural and anthropogenic fractions. We used Pb isotopes to distinguish between natural and contaminant Pb, and compared the results to apportioning based on reference element ratios (e.g. Pb/Ti) in order to validate this second method. Both methods gave similar results, except in one of the catchments where soils presented a highly organic upper horizon with a different geochemistry. Because of this, specific element ratios had to be used for the organic horizon that were different from those used for the mineral horizon, in order to obtain the correct apportioning as estimated by the Pb isotope method. Taking this into account, we then calculated inventories for the other metals for which isotopic methods are not available. Previous studies have shown that Pb contamination started in the area as early as the 1st century BCE. In the present study, the earliest indication of Pb contamination in lake sediments was dated ~1250 CE and has continued until the present. During the 19th century, there was a change in the source of anthropogenic Pb as indicated by its isotopic composition. The estimated inventories of anthropogenic trace metals for the whole catchments were ~1 g m^{-2} of Pb and Zn, ~0.1-0.2 g m^{-2} of Ni and Cu, and ~0.01 g m^{-2} of Cd. The Pb and Zn inventories are similar to those for other mountainous and rural areas in northern and eastern European locations, whereas Ni, Cu and Cd inventories were lower in the Pyrenees. The anthropogenic trace metals accumulated in Pyrenean catchments were three orders of magnitude higher than the current yearly atmospheric deposition over the area. This indicates the potential of sediments and soils as sources of a delayed contamination caused by the remobilisation of anthropogenic trace metals accumulated over the course of time.

1. Introduction

Evidence of widespread, long-term trace metal contamination related to humankind is provided by natural archives as diverse as snow, firn and ice (Zheng et al., 2007) peat (Shotyk et al., 1998), soils (Klaminder et al., 2008), marine (Alfonso et al., 2001) and lacustrine sediments (Renberg et al., 1994; Camarero et al., 1998), corals (David, 2003) and tree-rings (Bindler et al., 2004a). Such contamination of the environment, which often involves potentially toxic metals, is possibly the oldest large-scale, human driven impact on Earth (Nriagu, 1996).

This contamination legacy affects even the remotest areas, represented in the European context by high mountain and arctic areas. Because of the lack of direct local impact, alpine and arctic catchments are qualified as excellent sensors of diffuse background contamination (Camarero et al., 1995). In particular, high mountain lakes are seen as valuable sentinel ecosystems, providing signals that reflect this anthropogenic long-range chemical pollution together with many other aspects related to global environmental change (Williamson et al., 2009). A pan-European survey of several trace metals and metalloids in alpine and arctic lake sediments provided an extensive record of diffuse atmospheric contamination at a continental scale (Camarero et al., 2009). Together with lake sediments, mountain soils are an important store of polluting elements (Bacardit and Camarero, in press) that could eventually be remobilised (Klaminder et al., 2006a).

In order to produce an accurate inventory of the trace metal contamination in soils and sediments, it is necessary to apportion the total element burden to either anthropogenic or natural contributions (i.e., derived from the bedrock). One approach frequently used is to calculate enrichments relative to some reference value, normalised by an element with an exclusively natural origin, i.e., element ratios in contaminated and uncontaminated substrates are compared to establish the enrichment factors (Blaser et al., 2000). However, this method has the shortcoming that it is not always easy to establish a reliable reference value, as there can be several natural sources with diverse elemental compositions. Also, natural processes may cause differential fractionation of elements from the original source (Reimann and De Caritat, 2000).

Another approach is to use the isotopic signature of an element to distinguish between natural and contaminating fractions. However, this approach has been restricted to the study of Pb, which has the particular property of being present in the environment as a mixture of four isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb) in a proportion that varies depending on the source. Lead has been a key metal in the history of contamination from ancient times to the present (Settle and Patterson, 1980), and Pb isotope analysis has become a useful tool in many contamination studies (Bindler et al., 2008). By contrast, few studies have addressed the history of deposition or inventoried the contaminant supply of other trace elements. Atmospheric Pb contamination in antiquity was caused by the smelting of Pb sulphide ores, but these deposits are commonly associated with several other trace elements, such as Cu, Zn, Ag, Cd, Sb, Tl and As (Krachler et al., 2009). In modern times, various industrial and waste treatment processes result in a cocktail of diverse, potentially hazardous, elements that are eventually emitted into the atmosphere.

In previous studies, we have shown that atmospheric deposition of contaminating trace elements occurs in the Pyrenees (Bacardit and Camarero, 2009) with local and regional contributions that vary with altitude (Bacardit and Camarero, 2010). This atmospheric contamination is detectable in the sediments of most Pyrenean lakes (Camarero, 2003) and in soils even at the highest altitudes (Bacardit and Camarero, in press). In the case of Pb, we have shown that such contamination has existed since ancient times (Camarero et al., 1998). In the present study, we aimed to gain insight into this large-scale, historical contamination process for other trace elements besides Pb, as well as to obtain more accurate estimates of the importance of the anthropogenic input by producing an inventory of trace elements using a whole-catchment approach. Here, we focus on soils and lake sediments in three high mountain catchments, as major geochemical stores of atmospherically transported trace metals. We determine total inventories of Ni, Cu, Zn, Cd and Pb in the selected catchments, and apportion anthropogenic and natural contributions. While the difficulty in the inventorying of elements simply consisted of taking into account the spatial physiographic and geochemical variability within each catchment and determining the trace metal inventories in all compartments, apportioning anthropogenic and natural contributions required more careful consideration for the above-mentioned reasons. Thus, we first compared the results of the isotopic composition of Pb in the lake sediments to those of the enrichment with respect to both Ti and Al as reference elements. Sediments have the advantage that deep layers not affected by contamination provide reliable reference values for both the element ratios and isotope composition, as old sediments integrate all the natural processes within the catchment that may modify the original composition of the primary sources. We examined the consistency of the two approaches and assigned the natural and anthropogenic fractions of Pb on this basis. Then, we used these results to: 1) discuss the validity of enrichment factors based on element ratios as a method to estimate the anthropogenic fraction of other elements for which isotopic techniques are not available; and 2) evaluate the measurements made in soils, which are not a chronological record and are therefore more difficult to interpret than sedimentary records.

The results presented here show the extent of long-distance contamination in the three catchments over the course of time. To our knowledge, this is the first study assessing the impact of historical, long-range contamination of several trace metals in a mountainous area in southern Europe at a whole-catchment scale.

2. Materials and Methods

2.1. Study Sites

The catchments were selected to lie in an altitudinal gradient so we could assess differences with altitude. In order to avoid variability induced by differences in lithology, all the sites chosen were on granitic bedrock (the most extended lithology in the Pyrenees). The catchments where chosen so as to have simple, comparable settings in order to facilitate representative whole-catchment inventories: they were of a relatively similar small size, and held a single lake covering a significant proportion of the total area. The catchments had to be free of any direct impact (e.g., mining, constructions). The selected sites were Légunabens (LEG, 42° 45' 21" N 1° 25' 56" E, 1655 m a.s.l.) in the French Pyrenees, and Plan (PLA, 42° 37' 21" N

Table 1. Physiographic characteristics of the catchments studied.

Code	**Site**	**Region**	**Country**	**Latitude**	**Longitude**	**Altitude m a.s.l.**	**A_C ha**	**A_L ha**	**A_c / A_L**	**z_{max} m**
LEG	Légunabens	Ariège	France	42º 45' 21" N	1º 25' 56" E	1655	10.7	1.1	10.1	10
PLA	Plan	Catalonia	Spain	42º 37' 21" N	0º 55' 51" E	2188	22.0	5.4	4.1	11
VAM	Vidal d'Amunt	Catalonia	Spain	42º 31' 56" N	0º 59' 50" E	2684	9.7	2.1	4.6	18

A_C: catchment area; A_L: lake area; Z_{max}: maximum lake depth

0º 55' 51" E, 2188 m a.s.l.) and Vidal d'Amunt (VAM, 42º 31' 56" N 0º 59' 50" E, 2684 m a.s.l.) in the Spanish Pyrenees. LEG belongs to Bassiés granitic batholith and PLA and VAM lie in Maladeta batholith (Zwart, 1979; Arranz, 1997). Because they are in the headwaters, they present a relatively small catchment/lake surface ratio. Table 1 shows their basic physiographic properties.

The vegetation reflects the altitudinal gradient. In LEG, the vegetation consists mainly of heathlands of *Calluna vulgaris* and shrubs of *Rhododendron ferrugineum.* In PLA, the vegetation is comprised mostly of *Festuca eskia* and *Nardus stricta* alpine meadows. In VAM the main vegetation is *Festuca airoides, Festuca eskia* and *Nardus stricta* alpine meadows, but a high proportion of the catchment is covered by scree and bare rock. Aquatic macrophytes are abundant in LEG (*Carex rostrata, Menyantes trifoliata, Isoetes setacea, Sparganium angustifolium, Juncus bulbosus*) and PLA (*Isoetes lacustris, Myriophyllum angustifolium*) in the littoral belt down to 3-4 m depth, whereas in VAM there are no macrophytes.

2.2. Sampling

For soil sampling, different soil units were delimited according to the different plant communities in the catchment. At least one soil profile was sampled from each major (in extension) unit, thus covering >90% of the total area. In the largest units, more profiles were sampled when differences in aspect or slope were marked.

For sediment sampling, sediment units were defined according to the type of macrophyte communities inhabiting the lake and depth. According to visual inspection by diving, sediment accumulation areas were those with slopes <20%. Sediment cores were taken in a stratified way: at the deepest points (including sub-basins), at accumulation areas in intermediate depths and at each of the macrophyte units in the shallowest areas. The ARC-GIS 9.0 software (ESRI, Redlands, CA, USA) was used to produce digital maps of the soil and sediment units sampled (Figs. 1 to 3) and to process the spatial information.

Soil samples were taken from undisturbed sites representative of each soil unit. Between 5 and 9 profiles were taken from each catchment. Pits were dug until the bedrock was reached and the soil profile was described (depth, soil horizons and vegetation species). Soil profiles were cored using a sharpened PVC tube of 6.8 cm inner diameter introduced from the top and 5 cm layers were sectioned as separate samples. From each sample, a sub- sample was kept inside acid-cleaned polypropylene containers for major and trace element, Pb isotope ratios and organic content analyses. The remaining sample was kept in separate bags for the bulk density and fine earth (i.e., the soil fraction with grain size <2 mm) content determination.

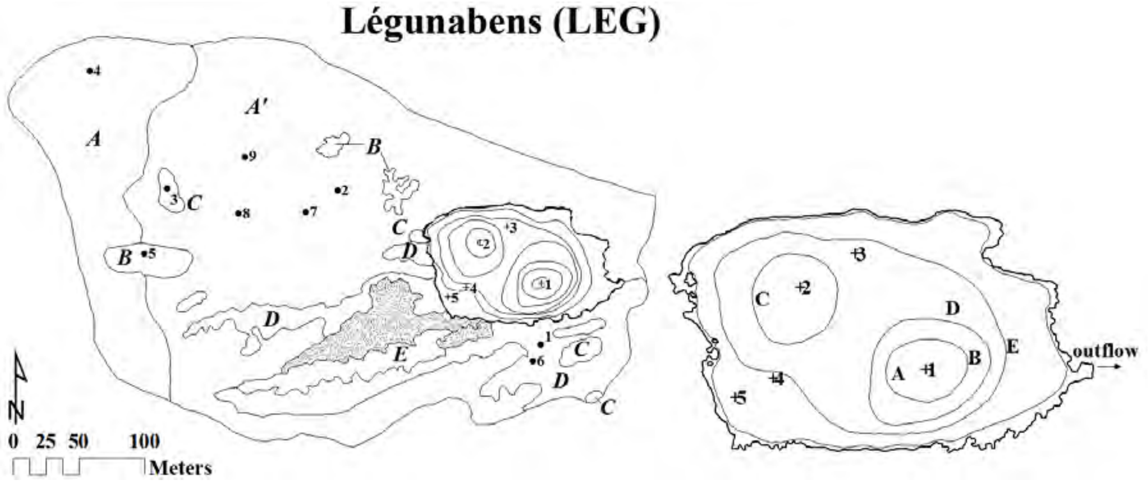

Figure 1. Map of Légunabens (LEG) catchment and lake, with indication of soil and sediment units (in capital letters), sampling sites of soils (●) and sediments (+). Dotted areas are siliceous scree and rocks. Lake bathymetry is presented as isolines every two metres. Legend of soil units: *A* - *Calluna vulgaris* heath (60%) + *Festuca eskia* grassland (40%); *A'* - *Calluna vulgaris* heath (90%) + *Festuca eskia* grassland (10%); *B* -*Rhododendron ferrugineum* heath; *C* - *Sphagnum* sp. peat bog; *D* - *Rhododendron ferrugineum* (80%) + *Calluna vulgaris* (15%) heath + *Nardus stricta* (5%) grassland; *E* - *Rhododendron ferrugineum* heath + alpine scree. Legend of sediment units: *A* - bottom eastern basin (depth > 8 m); *B* - medium depth eastern basin (depth = 6-8 m); *C* - western basin (depth > 6 m); *D* - plateau between basins (depth 4-6 m); *E* - macrophytes belt, with *Carex rostrata*, *Menyanthes trifoliata Isoetes echinospora*, *Sparganium angustifolium* and *Juncus bulbosus* (depth < 4 m).

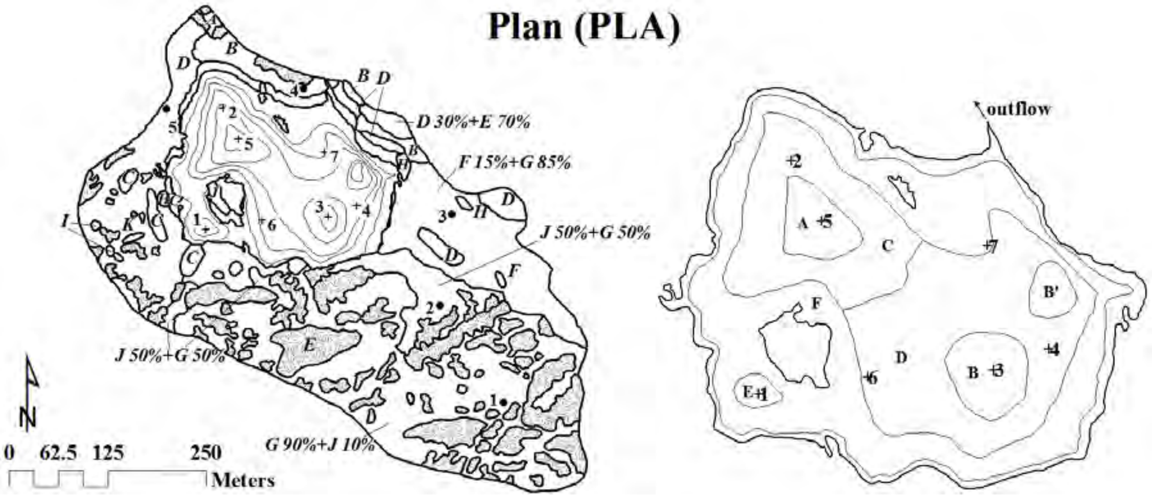

Figure 2. Map of Plan (PLA). Symbols as in Fig. 1. Soil units: *A* - *Pinus uncinata* + *Arctostaphylos uva-ursi* bearberry mountain pine forest; *B* - *Festuca paniculata* sward; *C* - *Nardus stricta* hygrophile mat-grass sward; *D* - snow-patch community with *Festuca eskia*; *E* - siliceous scree with *Pinus uncinata*, 70%; *F* - *Scirpus caespitosum* bog deer-grass; *G* - *Nardus stricta* sward, 85%; *H* - *Carex rostrata* fen; *I* - *Carex nigra* fen; *J* - *Rhododendron ferrugineum* heath; *K* - tall herb community. Sediment units: *A* - northwestern basin (depth > 8 m); *B* - south eastern basin (depth > 8 m) ; *B'* - northeastern basin (depth > 8 m); *C* - northwestern plateau (depth = 4-8 m); *D* - southeastern plateau (depth = 4-8 m); *E* - southwestern basin (depth > 4 m) with *Isoetes lacustris* and *Myriophyllum alterniflorum*; *F* - macrophytes belt, majoritarily composed of *I. lacustris* and *M. alterniflorum* (depth < 4 m).

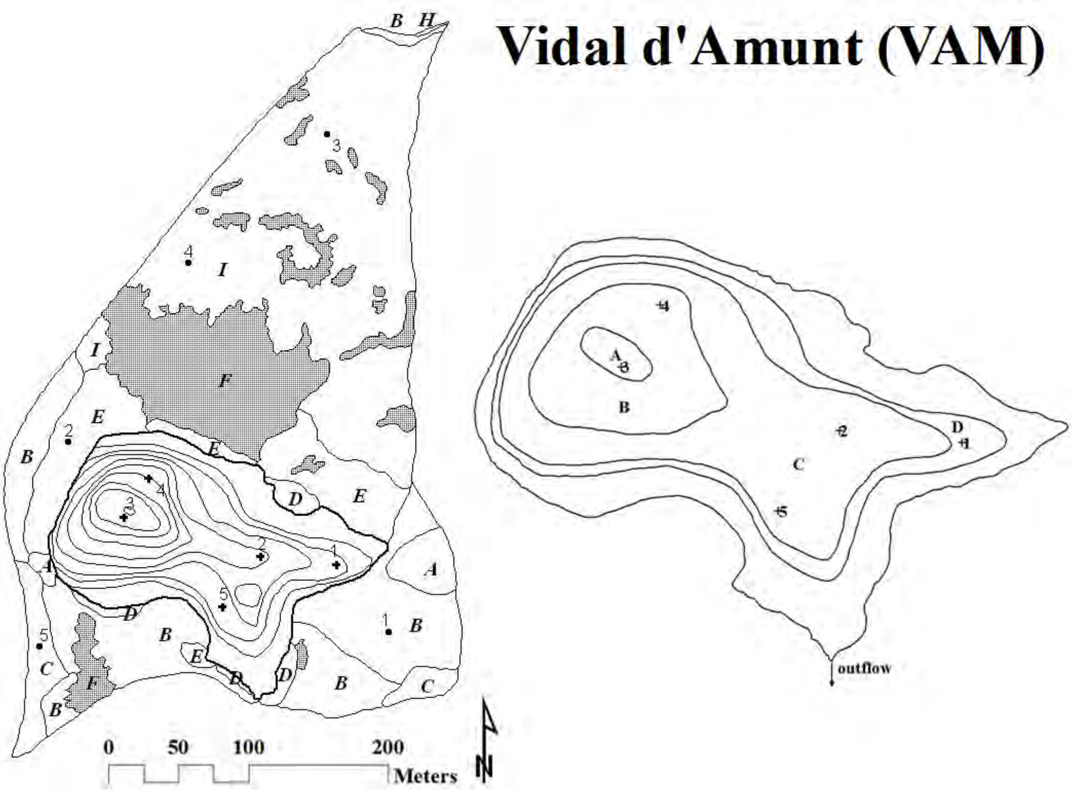

Figure 3. Map of Vidal d’Amunt (VAM). Symbols as in Fig. 1. Soil units: *A* (stony snow-patch); *B* (*Festuca airoides* grassland); *C* (exposed ridge with *Vaccinum uloginosum* dwarf shrub); *D* (*Nardus stricta* hygrophile mat-grass sward); *E* (sub-nival *Festuca eskia* snow-patch community); *E + F* (chaotic siliceous boulder field with *Festuca eskia* snow-patch community); *H* (*Festuca borderi* sward); *I* (*Festuca eskia* meadows on steep slopes). Sediment units (single basin lake without macrophytes, units defined according to depth): *A* - depth > 16 m; *B* - depth = 10-16 m; *C* - depth = 6-10 m; *D* - depth = 4-6 m.

Sediments were sampled using a gravitational corer (UWITEC, Mondsee, cm for the first eight samples, every 2.4 cm for the next eight samples and every 5 cm until the bottom of the core. From each sample, a sub-sample was stored in acid-cleaned polypropylene vials for major and trace element, Pb isotope ratios, organic content and radiocarbon dating analyses. The remaining fraction was kept inside self-sealing polyethylene bags for bulk density determination.

Samples from the dominant species of the terrestrial and aquatic plant communities at each of the sites were collected (both roots and aerial parts), washed with high-purity water produced with a Milli-Q system (Millipore, Billerica, MA, USA)

Austria). At each lake, 5-7 sediment cores were taken, extruded and sliced every 1.2 and kept inside acid-cleaned self-sealing polyethylene bags. Bedrock samples were taken from three different areas chosen randomly within the whole extension of each of the catchments, 100-200 m distant from each other. Large rocks were broken to obtain about 500 g of fragments that had not been exposed to weathering.

All sampling was conducted between August and November 2005.

2.3. Sample Preparation and Analyses

Soil and sediment sub-samples and plant samples for trace metals and Pb isotopes were kept frozen until analysis. Just before analysis, the materials were firstly freeze-dried with a Telstar Cryodos-50 freeze-drier (Telstar, Terrassa, Spain) at 7×10^{-3} mbar and -50ºC for 72 h. The soils were then sieved using a 2 mm acid-cleaned plastic mesh to remove gravel and roots from the fine earth. Metal analyses were performed on the fine earth fraction of the soils and on bulk sediments.

About 50-100 mg of the freeze-dried material was extracted with 2 ml 65% HNO_3 and 1 ml H_2O_2 in closed Teflon beakers at 95ºC for 16 h. The extracts were then diluted by adding 30 ml of Milli-Q water. The mineral residue was allowed to settle and the supernatant carefully poured into polypropylene bottles. Two extraction blanks were produced within every batch of thirty extractions. All extracts were kept at 4ºC until analysis. This extraction method is very similar to the US EPA Method 3050b for sediment and soil samples. It consists of a strong acid digestion that is intended to dissolve the fraction of elements that could become "environmentally available" but does not release the elements from the most resistant mineral fraction (i.e., aluminosilicates) as these are not usually mobile in the environment (EPA, 1996). In this work, we focus on the former, relatively labile fraction.

Bedrock samples from each of the catchments were homogenised and mixed together with a standard WC ring mill and subjected to total digestion. The total digestion procedure is an optimised multi-step protocol consisting of a relatively mild initial extraction of 100 mg of the milled rock samples with 2.5 ml HNO_3 and 2.5 ml H_2O_2 mixture, followed by a strong extraction with 2 ml HNO_3 and 5 ml HF in closed Teflon beakers at 90ºC. The contents are transferred into Teflon vessels with 2 ml $HClO_4$ and heated on a sand bath until almost complete evaporation of the acid occurs. This step is repeated with 2 ml $HClO_4$ and then with 5 ml H_2O and 2.5 ml HNO_3 heated below the boiling point. The final solution was brought up to 50 ml with deionised water.

Concentrations of major elements (Al, Ti) and trace elements (Ni, Cu, Zn, Cd and Pb) were determined at the Scientific-Technical Facilities of the University of Barcelona. The major elements were measured by Inductively Coupled Plasma-Optic Emission Spectrometry (ICP-OES) using a Perkin Elmer 3200 RL instrument , and trace elements by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) using a Perkin Elmer ELAN 6000 instrument. In every ICP-MS run, six standard solutions were prepared for calibration and an Rh internal standard was added to the samples. For the determination of Ni, ^{60}Ni was measured, and possible interferences from Ca were corrected for by determining a correction factor using a 200 ppm Ca standard, and then monitoring the presence of Ca in each sample and applying the corresponding factor. For the determination of Zn, ^{66}Zn was measured, and checked against differences with ^{64}Zn and ^{68}Zn to rule out polyatomic mass interferences.

Similarly, Cu was measured as ^{63}Cu and the absence of mass interferences checked using ^{65}Cu. As for Cd, ^{114}Cd was measured and corrected by the isobaric interference of ^{114}Sn, and ^{111}Cd used to rule out other mass interferences. Lead was measured as ^{208}Pb. Analytical quantification limits expressed as concentrations in analysed extracts were (in µg l^{-1}) 5.0 for Al, 0.5 for Ti, 0.20 for Ni and Zn, and 0.05 for Cu, Cd and Pb.

Table 2. Total and acid-extractable trace metal concentrations of six soil test samples. Coefficients of variation (percentage) for repeated measurements are indicated in brackets.

	Al		**Ti**		**Ni**		**Cu**		**Zn**		**Pb**	
sample	**Total**	**Extract.**	**Total**	**Extract.**	**Total**	**Extr.**	**Total**	**Extr.**	**Total**	**Extr.**	**Total**	**Extr.**
	(g kg^{-1})		**(g kg^{-1})**		**(mg kg^{-1})**		**(mg kg^{-1})**		**(mg kg^{-1})**		**(mg kg^{-1})**	
1	87.3 (<1)	26.5 (5)	4.3 (<1)	1.1 (16)	23 (25)	26 (7)	23 (2)	20 (6)	142 (3)	137 (4)	49(7)	51 (5)
2	91.8 (<1)	33.1 (6)	4.4 (<1)	1.4 (7)	31 (<1)	31 (4)	30 (8)	24 (8)	192 (1)	161 (5)	55 (1)	52 (6)
3	70.5 (<1)	24.3 (10)	3.9 (<1)	1.4 (8)	10 (18)	18 (9)	12 (6)	10 (15)	87 (9)	98 (6)	43 (2)	45 (3)
4	74.8 (<1)	26.6 (10)	3.7 (<1)	2.0 (7)	10 (19)	20 (6)	10 (12)	9 (8)	70 (15)	92 (9)	31 (6)	26 (3)
5	74.4 (<1)	22.3 (5)	3.5 (<1)	0.7 (14)	11 (32)	12 (10)	14 (<1)	10 (6)	75 (12)	77 (8)	53 (4)	55 (5)
6	86.2 (<1)	23.9 (8)	3.7 (<1)	0.8 (9)	3 (33)	12 (9)	11 (20)	7 (9)	53 (2.2)	61 (8)	28 (9)	26 (10)

Measured concentrations in the extracts were corrected by subtracting the corresponding blanks and were expressed on a dry weight basis.

The proportion of trace metals in the fraction extracted with our acid extraction was compared with the total content analysed with an energy-dispersive multielement analyser (EMMA) miniprobe XRF analyser (Cheburkin and Shotyk, 1996) in several test soil samples (Bacardit and Camarero, in press). Total Al and Ti were measured by conventional XRF at the University of Heidelberg analytical services. The results of the comparison are shown in Table 2, with the exception of Cd, which cannot be determined by EMMA-XRF. Nickel, Zn, Cu, and Pb were completely solubilised with our extraction method, whereas Al and Ti (used as conservative reference elements) in the extracts were only a fraction of the total content.

The Pb isotope ratio ($^{206/207}$Pb) in sediment, soil and bedrock samples from each site was determined at the University of Heidelberg by Sector Field-Inductively Coupled Plasma-Mass Spectrometry (SF-ICP-MS) with an Element 2-Thermo Finnigan instrument (Krachler et al., 2004). The isotopic standard reference material NIST 981 was analysed before and after each sample to correct for mass discrimination effects during analysis.

For the purpose of dating, ^{14}C was determined in the bottom layer from a selected sediment core at each site by Compact 1 Mv Accelerator Mass Spectrometry (AMS) at the National Accelerators Centre, CSIC in Seville (Spain). The radiocarbon date was calibrated (Stuiver and Reimer, 1993; software may be downloaded from Stuiver and Reimer, 2005), and then corrected for the C reservoir effect (Hua, 2009) by subtracting the apparent age of the uppermost sediment layer measured in the same way.

Organic matter content was estimated from the freeze-dried fine earth by loss on ignition (LOI) for 4 h at 550ºC (Heiri et al., 2001).

The remaining fraction of the soil samples was dried at room temperature until constant weight, and then sieved through 20 and 2 mm sieves to determine the percentage of stones (>20 mm), gravels (2-20 mm) and fine earth (<2 mm). The remaining fraction of the sediment samples was dried at 80ºC for 5 days to measure percentage dry weight. The bulk density of sediments and the fine earth content of the soil samples were calculated from the dry weight and the volume of each sample.

2.4. Calculations

Total inventories (I_T) of single soil and sediment profiles were determined by integrating the trace metal content in the *n* layers of a profile as follows:

$$I_T = \sum_{i=1}^{n} BD_i \times [TM]_i \times 10^{-3} \times S_i \qquad (1)$$

where I_T is the total inventory (in g m^{-2}), BD_i refers to the bulk density in layer *i* (in kg m^{-3}), $[TM]_i$ to the measured trace metal concentration (in mg kg^{-1}), S_i to the layer thickness (in m) whereas *n* is the total number of sampled sections. The whole-catchment inventories (wcI_T, in g m^{-2}) were then calculated. They were averaged weighting by the area of the *m* soil and sediment units within the catchment, (including areas without soil or sediment where $I_T = 0$), but using the real area (a_R, i.e., corrected for the slope) in the numerator and the projected area (a_P, i.e., the map area) in the denominator:

$$wcI_T = \sum_{j=1}^{m} (I_{T_j} \times a_{R_j}) / \sum_{j=1}^{m} a_{P_j} \qquad (2)$$

The whole-catchment inventories calculated in this way are directly comparable between catchments in terms of a hypothetical vertical atmospheric flux of contaminants. The same calculation was performed for the lake and terrestrial part of the catchment separately in order to obtain areal inventories for both compartments.

The anthropogenic (I_A) and natural (I_N) inventories were calculated similarly using the anthropogenic or natural trace metal concentrations ($[\mathrm{TM}]_A$ or $[\mathrm{TM}]_N$). $[\mathrm{TM}]_A$ and $[\mathrm{TM}]_N$ were calculated on the basis of the natural reference ratios using the equation:

$$[TM_A]_i = [TM]_i - [R]_i \times \frac{[TM]_b}{[R]_b} \qquad (3)$$

where $[TM_A]_i$ is the anthropogenic trace metal concentration in layer *i* (in mg kg^{-1}), $[TM]_i$ is the total trace metal concentration, $[R]_i$ denotes the concentration of a reference element, and $[TM]_b / [R]_b$ is the background natural ratio between the concentration of the trace metal and that of the reference element (in mg kg^{-1}) in the lowest section of each individual profile. Multiplying this quotient by $[R]_i$ thus accounts for the natural trace metal concentration ($[TM_N]$)$_\mathrm{i}$ in layer *i*, where the natural ratio is used to correct for changes in the supply caused by varying weathering rates. We reconstructed the natural and anthropogenic trace metal concentrations on the basis of both Al and Ti as reference elements, because anthropogenic sources of these two elements can be neglected and their behaviour is conservative.

An Isotopic Composition Mixing Model was used to estimate the isotopic composition of anthropogenic Pb in sediments, as expressed by the equation:

$$({}^{206}Pb/{}^{207}Pb)_T = \frac{({}^{206}Pb/{}^{207}Pb)_N \times [Pb]_N + ({}^{206}Pb/{}^{207}Pb)_A \times [Pb]_A}{[Pb]_N + [Pb]_A} \qquad (4)$$

where the subscripts *N* and *A* denote the natural and anthropogenic fractions, and *T* the total. In this equation, the only unknown variable was the anthropogenic Pb isotope ratio, whereas the natural fraction was that of a reference uncontaminated sample, and the total ratio was that measured for each sample. The natural and anthropogenic Pb concentrations were estimated from the natural Pb/Al ratios (reconstructed profiles were practically the same using either Al or Ti). The equation was solved to find the anthropogenic Pb isotopic signature for each layer sampled.

Table 3. Concentrations (mean ± sd, in mg kg^{-1}) of trace metals in bedrock, soils and sediments from the three study catchments.

	Ni	**Cu**	**Zn**	**Cd**	**Pb**
Bedrock					
LEG	18.1 ± 9.6	11.3 ± 1.2	96.5 ± 15.5	0.11 ± 0.01	26.2 ± 2.3
PLA	10.5 ± 1.4	10.8 ± 1.5	114.3 ± 3.2	0.14 ± 0.01	45.2 ± 2.3
VAM	10.0 ± 0.4	4.5 ± 0.2	80.5 ± 1.9	< 0.11	19.8 ± 0.2
Soils					
LEG	3.8 ± 1.4	4.6 ± 2.4	36.3 ± 16.2	0.34 ± 0.40	63.5 ± 26.2
PLA	6.6 ± 2.1	5.7 ± 2.3	58.0 ± 22.7	0.07 ± 0.19	25.9 ± 12.8
VAM	4.3 ± 1.2	2.6 ± 1.3	60.3 ± 15.2	0.02 ± 0.07	18.5 ± 11.7
Sediments					
LEG	15.1 ± 3.6	20.6 ± 6.2	226.9 ± 116.1	1.90 ± 1.30	162.3 ± 49.9
PLA	19.5 ± 4.3	18.5 ± 3.1	115.8 ± 39.6	0.81 ± 0.52	90.9 ± 62.2
VAM	15.9 ± 2.0	13.0 ± 2.8	88.5 ± 17.6	0.37 ± 0.28	81.4 ± 46.1

Once this was established, the same equation was used to estimate the natural and anthropogenic Pb contributions in soils. In this case, the equation takes the form:

$$[Pb]_A = \frac{[Pb]_T \times \left({}^{206/207}Pb_T - {}^{206/207}Pb_N\right)}{\left({}^{206/207}Pb_A - {}^{206/207}Pb_N\right)} \quad (5)$$

Atmospherically deposited trace metals (including Pb) may be subjected to vertical migration from top to bottom within the soil profile. Therefore, the Pb isotopic signature within the soil profile is likely to be a mixture of historical Pb fluxes with distinct isotopic signatures. For this reason, we used the average anthropogenic Pb isotopic signature estimated from the sediment records to reconstruct the anthropogenic and natural Pb contributions in the soil records, but not the other way round.

3. Results and Discussion

3.1. Trace Metal Concentrations in Bedrock, Soils and Sediments

Average trace metal concentrations were higher in lake sediments than in soils (Table 3). Trace metal concentrations are less comparable between rocks and either soils or sediments, because the latter have a high organic content (LOI ranges between 20% and 80%) in addition to the mineral fraction. Bearing this in mind, a rough comparison (Table 2) shows that Ni, Cu and Zn concentrations in the bedrock were generally similar to those in sediments and higher than in soils. In the case of Cd and Pb, their concentrations in the bedrock resembled those in soils and were clearly lower than in sediments, except LEG soils, which also presented high Cd and Pb concentrations. Presumably, the concentration differences between soils and sediments were mostly caused by a particle size effect. Sediments in these alpine lakes are fine grained, with most (>95%) particles being <63 µm (Catalan et al., 2002), whereas the fine earth fraction of soils is coarser, with ~60% of particles <63 µm, and belonging to the USDA texture class of loams (Garcia-Pausas et al., 2007).

The sediment profiles generally showed an increase in the concentration of all trace metals from the lower to the upper layers (Fig. 4) consistent with an increased contamination in more recent times. Overall, the concentrations in the upper sediment layers decreased with the altitude of the catchments, indicating higher contaminating inputs to the lakes at lower altitudes. Lead is the element that showed the larger increase from lower to upper sediments in all lakes, whereas Ni increased only slightly. As for Cu, Zn and Cd, the relative increase seemed to depend on the altitude, with slight increases, similar to that of Ni, in the highest lake (VAM), large increases, similar to that of Pb, in the lowest lake (LEG) and PLA in an intermediate situation. While all sediment profiles within a lake generally showed the same pattern of increasing concentrations towards the upper part, the depth at which this increase started and the peak trace metal concentration may differ from core to core. This was not unexpected, and relates to the spatial heterogeneity in the sediment deposition rates within the lake basin.

Although there was also a certain tendency in soils to present higher trace metal concentrations in the upper layers, it was not as clear as in sediments (Fig. 5). A number of soil profiles presented variable trace metal concentrations with depth. The most consistent trends were seen for all metals in LEG, and for Cd and Pb in all three catchments. Regarding altitudinal trends, mean concentrations of Pb and Cd (LEG > PLA ≈ VAM) and Cu (LEG ≈ PLA > VAM) significantly decreased with altitude, and the opposite (LEG < PLA ≈ VAM) was true for Zn. Nickel concentrations were, as in the case of sediments, higher in PLA than in the other lakes. All these differences were significant at $p < 0.01$.

3.2. Distinguishing Between Anthropogenic and Natural Pb in Sediments

In order to assess the anthropogenic contribution to the total Pb inventory in sediments, we determined the $^{206/207}$Pb isotopic ratio in the cores from the deepest part of the lakes (cores LEG1, PLA3 and VAM3). The sediments in the deepest zone of a lake are expected to be the least disturbed and most representative record. These three cores showed an increase in Pb concentration from bottom to top that was mirrored by a shift from higher to lower $^{206/207}$Pb values (Fig. 6, white circles). This is consistent with Pb contamination from mining in the surrounding areas (and also from leaded gasoline in more recent times), which typically exhibits a lower $^{206/207}$Pb isotopic signature (Camarero et al., 1998) than the Pb in the granite bedrock (Fig. 6, dashed vertical lines). The bottom sediment sample was assumed to be uncontaminated. In the case of LEG, this is supported by a $^{206/207}$Pb of sediment very similar to that of the bedrock. In the case of PLA and VAM, the isotopic ratio in the bottom sediment departed from that of the bedrock towards higher values. However, this cannot be attributed to contamination, because the Pb concentration profiles are clearly flat in the lower part, with minimum Pb concentrations very close to that of the bedrock. In addition, the sediments at the bottom of the core were much older in PLA (910±30 CE) and VAM (445±40 CE) than in LEG (1595±30 CE). It seems likely that a natural fractionation of the Pb isotopes occurs during the weathering of rocks (Shirahata et al., 1980; Graney et al., 1995) at a different intensity that seems to be related to altitude: the departure of $^{206/207}$Pb in sediments from that of the bedrock increased with altitude, perhaps reflecting differences in weathering. We therefore assumed that the $^{206/207}$Pb in the bottom sediment from the cores was the natural isotopic ratio of Pb released from the bedrock.

According to this reasoning, we also assumed that Pb/Ti and Pb/Al in the bottom sediment samples were the natural

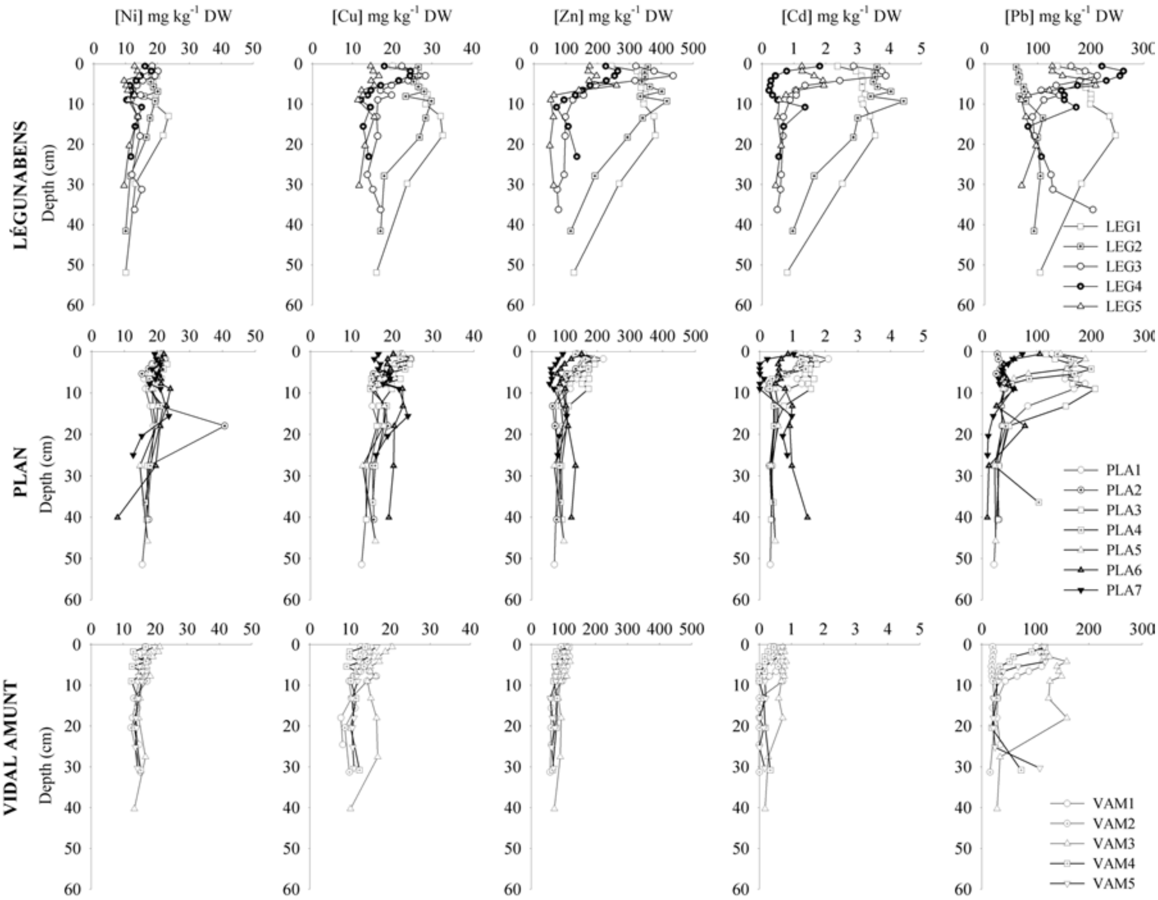

Figure 4. Total extractable trace metal concentrations in all sediment cores from each study site. LEG 1-5, PLA 1-7 and VAM 1-5 denote core names for Légunabens, Plan and Vidal d'Amunt respectively.

ratios derived from weathering in the acid extractable fraction, which virtually represents the total content of the trace elements analysed here (as mentioned in the Methods section). We used these ratios as reference ratios in equation (3) to compute the natural Pb contributions in our cores (Fig. 6, white squares and diamonds). There was little difference between the estimates based on Ti and Al, and in all three cases the natural supply of Pb was rather low and constant throughout the core.

Using these estimates, we applied equation (4) to calculate the isotopic ratios of the anthropogenic Pb (Fig. 6, shaded circles). In each of the three lakes we detected anthropogenic Pb from at least two sources with different isotopic signatures. In LEG, the $^{206/207}$Pb ratio was 1.16 at 30 cm depth, and ranged between 1.13-1.15 in the upper 19 cm. In PLA, the $^{206/207}$Pb ratio was 1.17 between 6-10 cm and 1.15 in the upper 4 cm, with a progressive transition zone in between. In VAM, the $^{206/207}$Pb ratio was 1.17 between 5-19 cm and 1.15 in the upper 1 cm, also with a progressive transition zone in between. Assuming that the sedimentation rates have remained constant during the last 1500 years - this is commonly found in paleolimnological studies of Pyrenean lakes (Camarero et al., 1998; Larrasoaña et al., 2009) - we can assign approximate dates to each

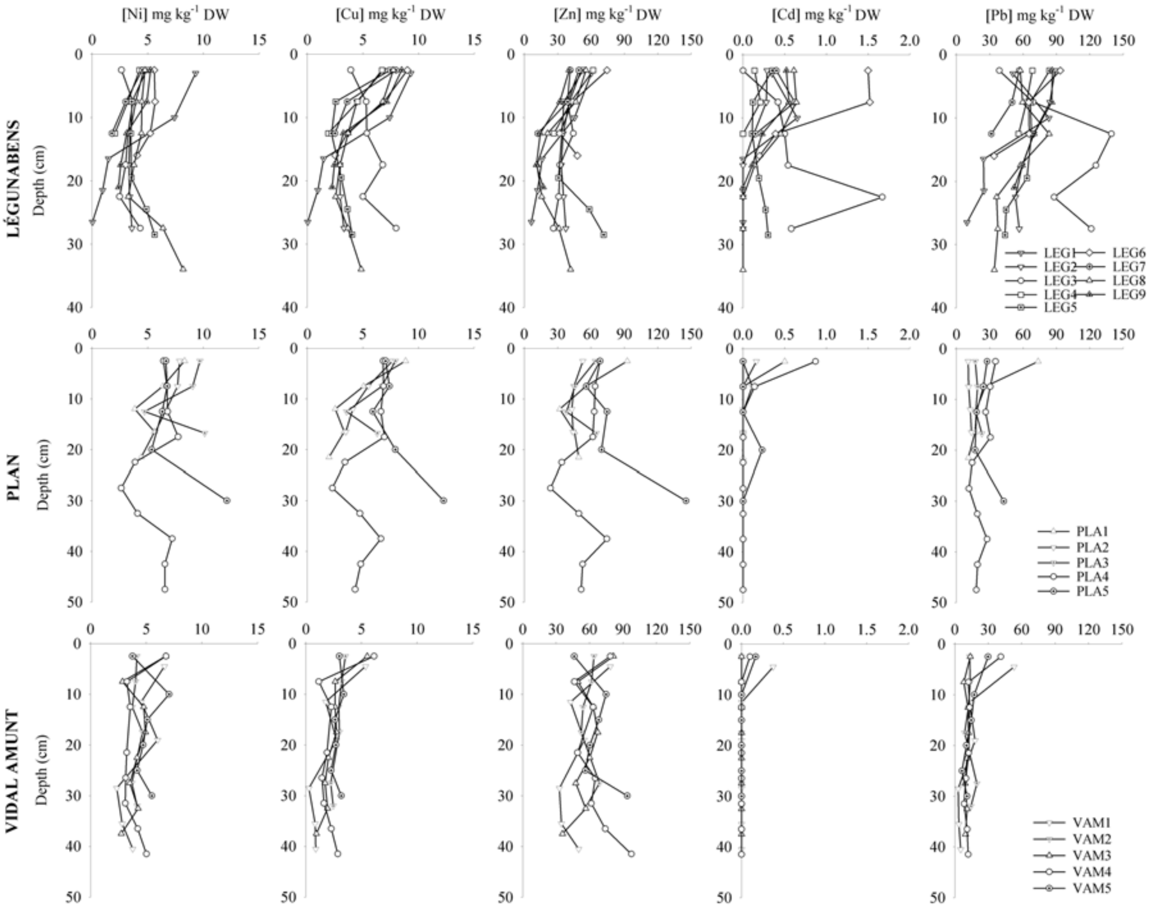

Figure 5. Total extractable trace metal concentrations in all soil profiles from each study site. LEG 1-9, PLA 1-5 and VAM 1-5 denote profile names for Légunabens, Plan and Vidal d'Amunt respectively.

depth (Fig. 6, horizontal dashed lines). It should be noted that our main purpose when dating the sediments was not to establish an accurate chronology, but just to set the time frame for the whole inventories based in the bottom dated sediments. Thus, the interpolated dates have to be taken with caution. In LEG, the first period of contamination went from ~1700 to 1800 CE, and the second was from then to present, with a relatively large uncertainty (added to that mentioned above) in these time boundaries because the samples were more spaced out in the lower part of the core. In PLA, the first period started in ~1700 CE, the transition indicating the introduction of a second contamination source (or a different mixture of sources) started in ~1800 CE and lasted until ~1900 CE, when the isotopic signal became constant up to the present day. In VAM, the first period of contamination started as early as ~1250 CE (or even earlier), and the introduction of Pb with a new isotopic composition started in ~1800 CE.

3.3. Distinguishing Between Anthropogenic and Natural Pb in Soils

We determined the $^{206/207}$Pb ratio in the three soil profiles corresponding to the largest (and hence most representative in terms of catchment area) soil unit from each of the catchments (profiles LEG8, PLA1 and VAM3). As in the case of the sediments, these ratios decreased from the bottom to the top soil layers (Fig. 4, white

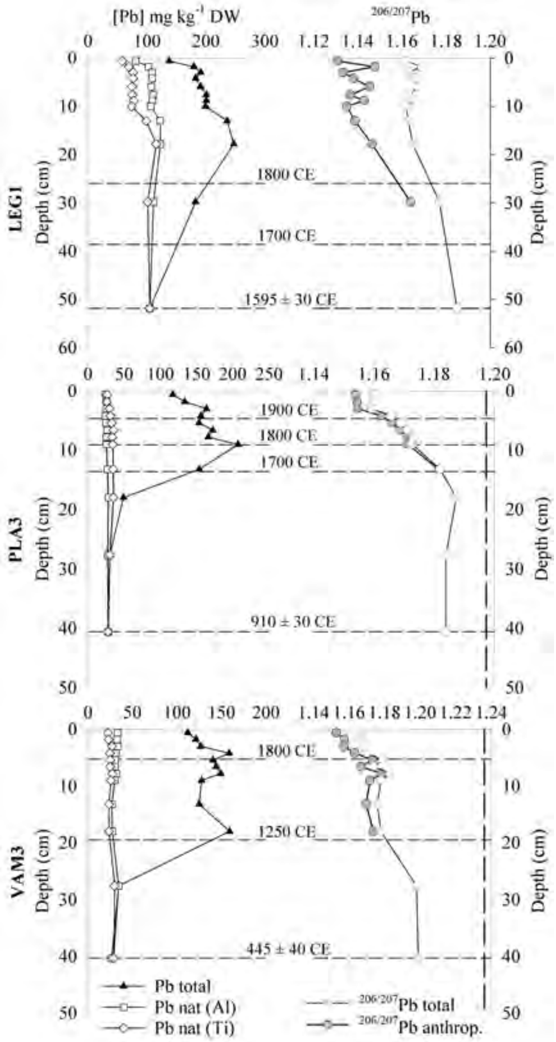

Figure 6. Pb in sediment cores LEG1, PLA3 and VAM3 from the deepest part of the lakes. Left: total Pb (black triangles) versus natural Pb concentrations estimated using Al (white squares) or Ti (white diamonds) as reference element. Right: measured total $^{206/207}$Pb isotope ratios (white circles) and estimated anthropogenic $^{206/207}$Pb values (shaded circles). Vertical dashed lines represent the $^{206/207}$Pb in the bedrock. Horizontal dashed lines are approximate dates based on ^{14}C measurements.

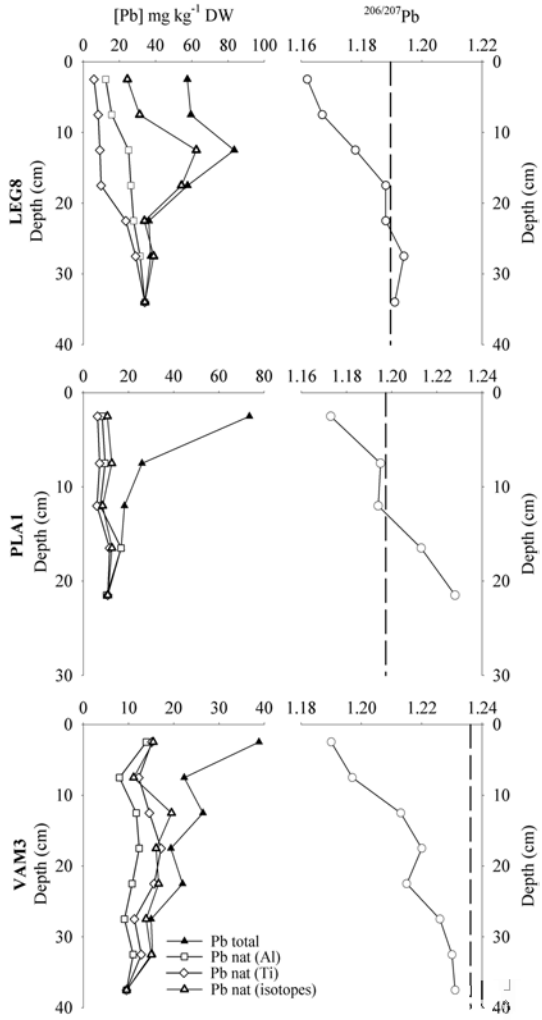

Figure 7. Pb in soil profiles LEG8, PLA1 and VAM3 corresponding to the most extended soil unit from each of the catchments. Left: total Pb (black triangles) versus natural Pb concentrations estimated using Al (white squares), Ti (white diamonds) and isotopes (white triangles). Right: total measured $^{206/207}$Pb isotope ratios (white circles). Vertical dashed lines represent the $^{206/207}$Pb in the bedrock.

circles). The $^{206/207}$Pb ratios in the bottom soil layers matched those of the bedrock well (Fig. 7, vertical dashed lines) in LEG and VAM, but in PLA, $^{206/207}$Pb in the bottom soil layers was markedly higher than in the bedrock.

We have no convincing explanation for this different behaviour. We can only hypothesise that the rocks at the particular soil sampling site had an ano-malous Pb isotopic composition with respect to the rest of the catchment. This means that while for LEG and VAM the isotopic

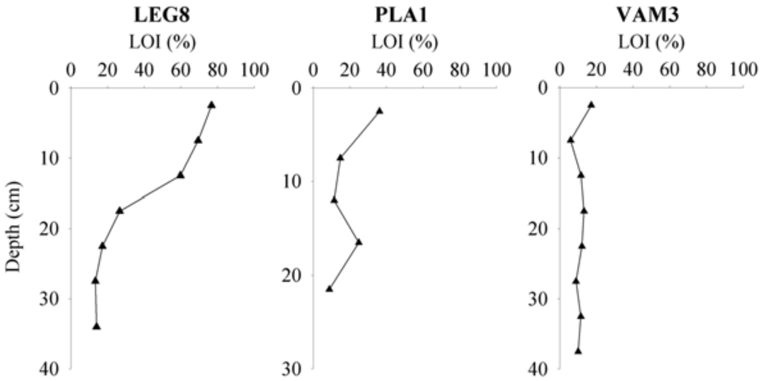

Figure 8. LOI content in soil profiles LEG8, PLA1 and VAM3.

ratio measured either in the bedrock or in the bottom soils could be used indistinctly as the natural reference ratio, for the PLA1 soil profile we had to assume that the reference value was that of the bottom soil layer.

We calculated the natural fraction of Pb in the soils using both equations (3) (element ratios) and (5) (isotopic composition). We used both Pb/Al and Pb/Ti in the bottom soil as reference ratios in equation (3) to compute the natural Pb fraction (Fig. 7, white squares for Pb/Al and white diamonds for Pb/Ti). In equation (5) we used $^{206/207}$Pb in the bottom soil sample as the natural reference ratio and the average of the different $^{206/207}$Pb anthropogenic ratios calculated from the sedimentary record of each catchment.

The estimates using the two methods were almost coincident in the case of PLA, very similar for VAM (with a greater similarity between the estimates based on Ti and Pb isotopes), but different for LEG. Here, the differences were in the upper 20 cm of the soil profile, coinciding with a dramatic change in the soil organic content (as shown by the LOI) which is distinctive of LEG (Fig. 8). Remarkably, the Pb concentration in the 15-20 cm layer increased with respect to deeper layers, but without a change in its isotopic ratio. This feature strongly suggested an accumulation of natural Pb in the upper organic soil layer, which was further enhanced by anthropogenic Pb efficiently retained in the upper 15 cm. The difference in organic content presumably makes differences in the geochemistry of the two soil layers. For this reason, we recalculated the natural Pb fraction for the upper 20 cm using the element ratios and isotopic signature measured at the base of this organic layer (Fig. 9). Doing so, the estimates matched better, especially those based on Al and isotopes.

3.4. Inventories of Natural and Anthropogenic Trace Metals

The previous results indicated that the element ratios measured at the bottom of our sediment and soil cores are a valid reference to calculate the anthropogenic and natural fractions of Pb, with the exception of soils in LEG. Here, the upper organic part has to be treated as the accumulating zone with a different geochemistry and the reference element ratios used to apportion the natural and anthropogenic contributions are those of the base of the organic horizon. That allowed for, the inventories of anthropogenic Pb in the soil profiles LEG8, PLA1 and VAM3 calculated using equation (1) with the anthropogenic fraction calculated using both element ratios and isotopes, agreed well. Anthropogenic Pb inventories derived from the Ti natural ratios were (in g m^{-2})

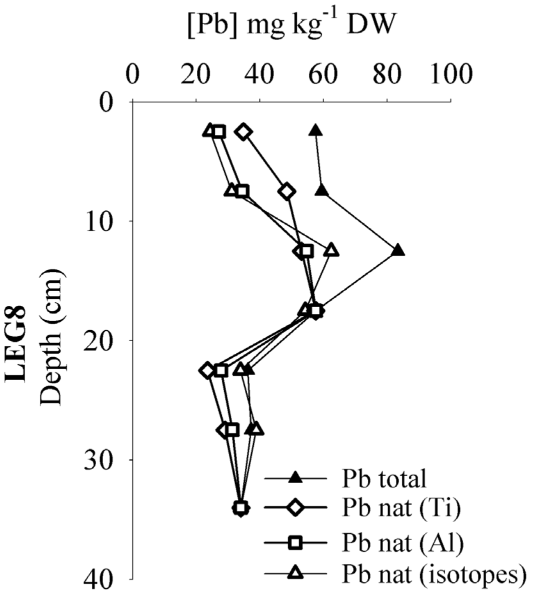

Figure 9. Pb in the soil profile LEG8. Natural concentrations estimated as in Fig. 7, but using Pb/Al and Pb/Ti at the base of the 20 cm upper layer as the reference ratios for the organic horizon.

0.9 in LEG8, 2.1 in PLA1 and 2.1 VAM3, whereas the same inventories reconstructed from the Pb isotopes were 1.0 in LEG8, 1.8 in PLA1 and 1.8 in VAM3.

According to the results of the anthropogenic Pb inventories using element ratios, we attempted to apply the same approach for the other trace metals for which isotopic methods are not available. This step requires the assumption that all metals behave in a similar way in our soils. However, while plant uptake and recycling plays a minor role in the Pb biogeochemistry in soils (Klaminder et al., 2005), Ni, Cu and Zn are essential elements taken up by plants (Kabata-Pendias and Kabata-Pendias, 2000) and most plants do not discriminate between Zn and Cd (Kabata-Pendias and Kabata-Pendias, 2000; Brekken and Steinnes, 2004) so the latter might also be taken up. Therefore, two aspects need to be taken into account regarding the effects of vegetation. First, plants may act as a biological pump (Reimann et al., 2008) and the upper soil horizons may result enriched in some metals, and hence, anthropogenic inventories could be overestimated. Second, plants may represent a significant trace metal store for certain metals in the terrestrial catchment, and therefore the inventories may be underestimated if the vegetation compartment is neglected.

Both processes seemed to have minor effects in our soils. On the one hand, there were significant correlations between Pb and the rest of trace metal concentrations (Table 4), suggesting that there were no great differences in their overall distributions that could have been caused by distinct processes.

Table 4. Correlation coefficients (r) between Pb and other trace metal concentrations in soil profiles from each of the catchments. Symbols ** and * denote a statistical significance at p<0.01 and p<0.05 levels, respectively.

	LEG	PLA	VAM
Zn	0.3809*	0.5948**	0.3797*
Ni	0.3224*	0.6034**	0.5385*
Cu	0.6066**	0.7088**	0.8359**
Cd	0.4936**	0.5033**	0.6226**

On the other hand, the trace metal content in the terrestrial vegetation (per unit area) was two or three orders of magnitude lower than in soils (Table 5). Also aquatic plants represented an insignificant part of the trace metal inventories in comparison to the sediments (Table 5). Estimates of trace metal inventories for the major plant species were obtained using the trace metal concentrations we measured in plants, and standing biomass data(integrating both above-ground and below-ground biomass) for the corresponding communities compiled from the literature (Chapman et al., 1975; Gacia et al., 2009; Remon and Alvera,

Table 5. Trace metal inventory ranges (in mg m^{-2}) in terrestrial and aquatic plant biomass and in their corresponding soil and sediment units. The area of each soil unit is expressed as a percentage of the terrestrial part of the catchment. Area of the sediment units as percentage of the lake area.

site	compartment	soil-sediment unit(s) / core(s) #	area (%)	species / substrate	Zn	Ni	Cu	Cd	Pb
LEG	terrestrial								
		B, D, E 1, 5, 6	17	*R. ferrugineum*	18 – 29	0.5 – 0.8	4 – 7	<0.08	0.7 – 1.1
				soil	2.4 – 5.2×10^3	318 – 499	274 – 411	24 – 41	3.8 – 7.8×10^3
		A, A’ 2, 4, 7, 8, 9	82	*C. vulgaris*	24 – 108	1.0 – 3.9	5 – 24	<0.13	1.5 – 9.0
				soil	1.5 – 3.8×10^3	143 – 715	209 – 563	7 – 31	2.2 – 8.4×10^3
	aquatic								
		E 4, 5	41	*C. rostrata*	76	0.7	3	0.29	23.3
				M. trifoliata	69	0.1	1	0.03	0.8
				I. echinospora	8	0.2	1	0.06	3.9
				sediment	2.3 – 2.6×10^3	242 – 346	288 – 406	12 – 20	2.7 – 2.8×10^3
PLA	terrestrial								
		G+J, J, J+G 1, 2	27	*R. ferrugineum*	19 – 32	0.1 – 0.3	5 – 9	<0.07	0.9 – 1.5
				soil	2.8 – 5.7×10^3	427 – 595	331 – 455	3 – 10	1.6 – 3.0×10^3
		D, D+E 5	20	*F. eskia*	101 – 224	0.3 – 0.7	7 – 16	0.10 – 0.20	0.9 – 2.0
				soil	8.0×10^3	720	790	5	2.6×10^3
		B 4	6	*F. paniculata*	71	0.7	6	0.3	6.1
				soil	16.4×10^3	1.8×10^3	1.7×10^3	40	7.3×10^3
		C, F+G, G+J, J+G 1, 2, 3	65	*N. stricta*	124 – 269	2.3 – 5.0	7 – 15	1.2 – 2.4	3.7 – 6.9
				soil	2.8 – 5.7×10^3	427 – 906	331 – 655	3 – 10	1.6 – 3.2×10^3
	aquatic								
		F 7	12	*I. lacustris*	19	0.6	1	0.23	9
				sediment	1.3×10^3	318	322	8	522
		E 1	15	*M. alterniflorum*	13	0.3	1	0.16	1.1
				sediment	2.3×10^3	457	396	15	1.5×10^3
VAM	terrestrial								
		E, E+F, I 2, 3	70	*F. eskia*	125 – 275	0.4 – 0.8	5 – 12	0.40 – 0.90	2.2 – 4.9
				soil	8.5 – 18.5×10^3	0.6 – 1.3×10^3	416 – 771	0 – 3	3.7 – 6.6×10^3

1989; Pornon et al., 2007). We assumed then that the way to proceed for determining anthropogenic Pb inventories using element ratios was also valid for the other trace metals for which isotopic methods are not available. Thus, inventories distinguishing natural and anthropogenic contributions for both terrestrial and aquatic compartments can be reliably estimated for Ni, Cu, Zn and Cd with equations (1) and (2), using the element ratio method according to

Table 6. Total and anthropogenic trace metal inventories (in g m^{-2}) for the whole catchment, and for the terrestrial catchment and the lake separately. Anthropogenic inventories calculated using natural ratios relative to Ti.

Trace element	Site	Whole catchment		Terrestrial catchment		Lake	
		Total	Anthrop.	Total	Anthrop.	Total	Anthrop.
Ni	VAM	0.52	0.15	0.59	0.27	0.25	0.06
	PLA	0.47	0.17	0.52	0.31	0.31	0.13
	LEG	0.35	0.09	0.36	0.04	0.24	0.09
Cu	VAM	0.31	0.15	0.34	0.26	0.19	0.05
	PLA	0.40	0.18	0.44	0.31	0.29	0.07
	LEG	0.37	0.10	0.38	0.10	0.32	0.10
Zn	VAM	6.84	0.95	8.36	1.75	1.34	0.27
	PLA	3.87	1.31	4.64	2.21	1.47	0.56
	LEG	3.08	0.61	3.13	0.59	2.60	1.41
Cd	VAM	0.002	0.001	0.001	0.001	0.003	0.001
	PLA	0.007	0.006	0.006	0.009	0.009	0.006
	LEG	0.020	0.012	0.020	0.013	0.020	0.014
Pb	VAM	2.19	0.98	2.58	1.74	0.79	0.43
	PLA	1.85	1.03	2.19	1.68	0.80	0.61
	LEG	5.45	0.87	5.78	0.92	2.40	1.15

equation (3). Table 6 shows the results of the total inventories and the anthropogenic contributions obtained from these calculations using, in this case, the element ratio relative to Ti. Overall, Pb and Zn inventories were one order of magnitude higher than those for Cu and Ni, and two orders higher than those for Cd. The anthropogenic inventories were similar for all metals in all catchments, suggesting that they are indicative of a regional contamination load. These anthropogenic inventories are a more reliable estimate of true contamination fluxes than concentrations alone.

Thus, the altitudinal concentration gradients in sediments and soils described above should be interpreted more to be a result of some properties of the catchments related to their altitude than an indication of higher inputs at lower altitude. Previous work in mountainous areas reported both increased trace metal deposition at altitude linked to interception-enhanced rainfall (McGee & Vallejo, 1996; Farmer et al., 2005) and the opposite, i.e., higher deposition at low altitude caused by higher contaminating inputs from the bottom of the valleys (Veysseyre et al., 2001; Gabrielli et al., 2006; Bacardit & Camarero, 2010, in press). However, none of these processes seem to have a marked effect on our inventories.

Lower concentrations in the sediments at higher altitude can be related to a lower transfer from the terrestrial catchment. The terrestrial catchment was clearly the largest reservoir, storing 63-96% of the whole-catchment inventories. Except for Cd, the anthropogenic trace metal inventories per unit area in PLA and

VAM were larger in the terrestrial catchments than in the lakes. This is remarkable: one would expect what was found in LEG, i.e., the inventories to be similar or greater in the lakes as they receive the same atmospheric load as soils plus a contribution from the terrestrial catchment. The lower than expected inventories in lakes mean that in PLA and VAM not all the contaminating load entering the lakes reaches the sediments. A possible mechanism involved is a washout of the contaminants stored in the winter ice and snow cover of the lakes during the early thaw before the melting water can enter the lake. At the altitude of these lakes, the snow cover may last for more than 6 months and accumulate half of the yearly precipitation before thawing. This effect may be less marked at LEG because of the lower altitude. Also, the transfer of metals from soils to lake in LEG could be favoured by the complexation and solubilisation of metals with dissolved organic matter (Bergkvist et al., 1989) derived from the highly organic soils in LEG. Dissolved organic carbon (DOC) in LEG is much higher than in the other lakes (Bacardit, 2006). The production of DOC can in addition be enhanced by higher temperatures in the LEG catchment.

Most of the previous studies in diverse mountainous and rural areas found in the literature comparable to ours (Table 7) focus on the anthropogenic Pb in soils, peat and sediments. By contrast, few studies have attempted to estimate the cumulative atmospheric anthropogenic inputs for other trace metals. The cumulative input of anthropogenic Pb estimates in the soils and sediments studied here are in good agreement with previous estimates from other Pyrenean sites, and are comparable to those in other rural and relatively remote sites across the northern hemisphere. Most contaminating Pb estimates are ~1-2 g m^{-2}, with some higher values up to ~5-10 g m^{-2}. Regarding the other trace metals, results for comparison are fewer in number. Where available, figures for Zn are close to those for Pb, whereas inventories for Cu, Cd and Ni tend to be lower in the Pyrenees than in other northern and eastern locations.

The cumulative anthropogenic inventories of all trace metals in soils and sediments analysed here are three orders of magnitude higher than the current yearly atmospheric deposition in the area (Table 7; Bacardit and Camarero, 2009). This difference gives an indication of the potential of sediments and soils as sources of a delayed contamination if environmental changes (e.g. possible higher soil organic matter decomposition caused by warming) favour the remobilisation of anthropogenic trace metals accumulated over the course of time.

Acknowledgments. This study was supported by the EU funded project Euro-Limpacs (GOCE-CT-2003-505540), and the Spanish MEC projects TRAZAS (CGL2004-02989) and GRACCIE (CSD2007-00067). M. Bacardit was awarded a Spanish Scientific Research Council (CSIC) I3P pre-doctoral grant. We thank Prof. W. Shotyk for kindly providing access to the analytical facilities of the Institute of Earth Sciences (Univ. of Heidelberg) and making valuable comments on an early version of the paper. We thank E. Ballesteros (Centre d'Estudis Avançats de Blanes, CSIC) for field assistance and drawing the vegetation maps, A. Padró (Serveis Científico-Tècnics, Univ. of Barcelona) for trace element analysis, B. Kober (Institute of Earth Sciences, Univ. of Heidelberg) for assistance with the digestion of rocks and comments on Pb isotope results, and S. Rheinberger (Institute of Earth Sciences, Univ. of Heidelberg) for his support with the Pb isotope analysis. We also thank K. Johannesson and two anonymous

Table 7. Anthropogenic trace metal inventories in soil and sediment profiles across the northern hemisphere, and current yearly atmospheric deposition of trace metals in the Central Pyrenees. All data in g m^{-2}.

Study Site	Archive	Chronology (sampling year)	Method*	Pb	Zn	Cu	Cd	Ni
Vidal d'Amunt, Pyrenees, Spain[a]	alpine soil	total profile (2005)	1	1.74	1.75	0.26	0.001	0.27
Plan, Pyrenees, Spain[a]	alpine soil	total profile (2005)	1	1.68	2.21	0.31	0.009	0.31
Légunabens, Pyrenees, Spain[a]	alpine soil	total profile (2005)	1	0.92	0.59	0.10	0.013	0.04
Redon, Pyrenees, Spain[b]	alpine soil	top 8 cm, since 1850 (2000)	2	0.96 - 1.32	0.38 - 0.78	0.06 - 0.12	0.008 - 0.009	
L'adové, Tatras, Slovakia[b]	alpine soil	top 8 cm, since 1850 (2000)	2	2.30 - 3.55	1.41 - 1.63	0.12 - 0.17		
Lochnagar, UK[c]	alpine peat	since 1860 (1997)	3	2.41				
Southern Sweden[d]	forest soil	total profile (1997)	4	2.04 - 3.05				
Northern Sweden[e]	forest soil	total profile (1996, 1997)	4	1.5 - 3.1				
Northern Sweden[f]	forest soil	total profile (2001, 2003)	4	1.5 -1.9				
Northern Sweden[g]	peat bog	past 110 years (2003)	4	0.9 - 1.7				
Switzerland[h]	peat bog	total core (1991)	5	1.0 - 9.7				
Southern Ontario, Canada[i]	peat bog	total core, past 8000 years (2000)	5	1.0 - 2.4				
Myrarnar, Faroe islands, Denmark[j]	peat bog	total core	5	1.9				
Stoby Mose, Denmark[j]	peat bog	total core	5	3.1				
Southern Sweden[k]	forest soil, peat bog and lake sediments	total profile/core (late 90's, prior to 2000)	4	2-3				
Vidal d'Amunt, Pyrenees, Spain[a]	lake sediments	since 445 (2005)	1	0.43	0.27	0.05	0.001	0.06
Plan, Pyrenees, Spain[a]	lake sediments	since 910 (2005)	1	0.61	0.56	0.07	0.006	0.13
Légunabens, Pyrenees, Spain[a]	lake sediments	since 1595 (2005)	1	1.15	1.41	0.10	0.014	0.09
Redon, Pyrenees, Spain[b]	lake sediments	since 1850 (2000)	1	0.42				
L'adové, Tatras, Slovakia[b]	lake sediments	since 1850 (2000)	1	1.34		0.03	0.019 - 0.020	
Lochnagar, UK[c]	lake sediments	since 1860 (1997)	3	1.55				
Lochnagar, UK[l]	lake sediments	since 1860 (1999)	3	1.35	0.40	0.05	0.008	0.030
Loch Chon, UK[l]	lake sediments	since 1860 (2000)	3	4.19	3.51	0.54	0.090	0.324
Loch Grannoch, UK[l]	lake sediments	since 1860 (2000)	3	4.97	6.42	1.10	0.093	0.120
Burnmoor Tarn, UK[l]	lake sediments	since 1860 (2000)	3	0.76	1.75	0.18	0.089	0.139
Llyn Llagi, UK[l]	lake sediments	since 1860 (2000)	3	2.98	3.33	0.46	0.071	0.412
Redó, Pyrenees, Spain[m]	bulk deposition	2004 – 2006		$1.2 – 1.5\times10^{-3}$	$6 – 21\times10^{-3}$	$0.8 – 1.2\times10^{-3}$	$0.03 – 0.07\times10^{-3}$	$0.5 – 0.7\times10^{-3}$

[a]This study; [b]Plöger, 2004; [c]Yang et al., 2002; [d]Bindler et al., 1999; [e]Brännvall et al., 2001; [f]Klaminder et al., 2006a and Klaminder et al., 2006b; [g]Bindler et al., 2004; [h]Shotyk et al., 2000; [i]Givelet et al., 2003; [j]Shotyk and Le Roux, 2005; [k]Renberg et al., 2000; [l]Yang and Rose, 2005; [m]Bacardit and Camarero, 2009. *Method to apportion anthropogenic and natural contributions: 1: element ratio relative to Ti; 2: average of element ratio relative to Al, Ti and Fe and simple background method; 3: simple background concentration; 4: Isotopic composition mixing model; 5: element ratio relative to Sc and/or Zr.

reviewers for their scientific and editorial comments. This study is a result of the activities of the Limnological Observatory of the Pyrenees (LOOP), a joint initiative of the Centre d'Estudis Avançats de Blanes, CSIC and the Centre de Recerca d'Alta Muntanya, Univ. of Barcelona.

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Paper VI. Modelling Pb, Zn and As transfer from terrestrial to aquatic ecosystems during the ice-free season in three Pyrenean catchments

M. Bacardit and L. Camarero, 2010. Science of the Total Environment, 408, doi:10.1016/j.scitotenv.2010.07.088

Figure 9. Water column sampling for trace element analyses at Lake Légunabens, Central Pyrenees (by C. Lluch).

M. Bacardit and Ll. Camarero. “Modelling Pb, Zn and As transfer from terrestrial to aquatic ecosystems during the ice-free season in three Pyrenean catchments”. *Science of the total environmental*. Vol. 408, issue 23 (1 November 2010) : p. 5854-5862 Special Section: Integrating Water and Agricultural Management Under Climate Change

http://www.sciencedirect.com/science/article/pii/S0048969710008296

http://dx.doi.org/10.1016/j.scitotenv.2010.07.088

Received 28 May 2010; revised 30 July 2010; accepted 31 July 2010.
Available online 24 September 2010.

Abstract

Long-range atmospheric trace element contamination affecting natural systems has occurred since early historical times in the Northern Hemisphere. In relatively remote sites, soils are the largest reservoir of these airborne contaminants. Trace elements stored in soils can later be remobilised and thus soils are a potential delayed, long-lasting source of contamination for the aquatic ecosystems. Here we measured the atmospheric deposition and in-lake fluxes in order to model the transfer of Pb, Zn and As from terrestrial to aquatic ecosystems during the snow- and ice-free season in three mountain catchments in the Central Pyrenees. According to the model, there was a net export of Pb and As from the catchments. We postulate that accumulated anthropogenic Pb contamination and the weathering of As-rich rocks are the most likely sources. In contrast, Zn was largely retained in the catchment. For Pb and As, the terrestrial inputs were > 91% and for Zn were ~ 71% of the total inputs to the lakes. Nearly all Pb entering the lakes was retained in the sediments whereas 5–38% of As and Zn was lost through the outflow. We were unable to adjust the model for Zn for one of the lakes. The uptake by macrophytes could be a considerable sink for Zn, which was not considered in our transport model.

Keywords: Long-range contamination; Trace element cycling; Mountain catchment; Contamination legacy; Remobilisation of contaminants; Pyrenees

Summary of the Results

Figure 10. Figure 10. Pyrenean lake catchments. Lake Redon on a clear autumn day (above left, by M. Bacardit); Lake Plan with the first snow in late autumn (above right, by L. Camarero); water column sampling at Lake Légunabens (below left, by C. Lluch); Lake Vidal at the end of the summer (below right, by J. A. Luque).

In this section, we present a summary of the main results from each of the research articles included in this thesis.

Fluxes of Al, Fe, Ti, Mn, Pb, Cd, Zn, Ni, Cu and As in monthly bulk deposition over the Pyrenees (SW Europe): the influence of meteorology on the atmospheric component of trace element cycles and its implications for high mountain lakes (Paper I)

In this study, the atmospheric bulk (wet plus dry) deposition of a suite of major and trace elements was measured monthly at Lake Redon (2240 m above sea level, Central Pyrenees, Spain) in 2004–2006.

Total (dissolved plus particulate) concentration ranges were (in mg L-1): 10-2591 for Al, 6-1936 for Fe, 0.2-30.2 for Ti, 0.5-38.1 for Mn, 0.1-3.1 for Pb, <0.05-0.50 for Cd, 1.1-82.4 for Zn, <0.2-2.6 for Ni, 0.2-3.1 for Cu and <0.1-0.3 for As. Selenium was not detected in almost all cases. Trace element concentrations in this study were comparable to the composition found in previous studies at remote sites. Results show that Al, Ti, Fe, Mn and As were part of the dust carried from the Iberian Peninsula and North Africa. These elements were highly co-distributed, presented low enrichment factors (EF) and occurred (except Mn) mainly as particles. By contrast, Pb, Zn, Cd and Cu appeared to be contaminating. These elements were moderately correlated or independent from the first group of elements, their EF were clearly above those caused by natural fractionation processes and they were found in variable, though always large proportions, as soluble forms. Nickel had properties that were between those of these two groups of elements. This suggests that it came from a balance of both natural and contaminant sources. Enrichment factors were lower when using the Maladeta granite (MDT) and Western Sahara soils (WS) than when the upper continental crust (UCC) was used as a reference. The solubility of Mn, Zn, Cu and Pb showed a positive, significant dependence on precipitation pH. Most element concentrations were not influenced by the precipitation volume, which indicates that dry deposition had a minor weight in the total deposition.

Annual variations in major and trace element deposition were related to the prevailing meteorological conditions. Deposition of dust particles containing terrigenous elements (i.e. Al, Fe, Ti and Mn), and elements with more affinity for particles (i.e. Pb, Ni and Cd) was higher during the year in which a larger proportion of precipitation came from the Iberian Peninsula–North Africa and followed low-altitude trajectories. By contrast, N Atlantic air-masses with a high altitude trajectory favoured the deposition of more soluble elements (i.e. Zn and Cu).

On a seasonal scale, fluxes of terrigenous elements and Pb were higher in warm months (June–November) than in cold months (December–May). The same arguments as for inter-annual changes explain these differences in deposition: air masses with an Iberian-North African component occurred during warm months, whereas Atlantic trajectories predominated during cold months. Furthermore, thermal inversion episodes occurred over central and southern Europe for several days and weeks during cold months, which limited the dispersion of atmospheric contaminants from the lowland source areas to mountain receptor areas.

Atmospherically deposited trace elements in the winter snowpack along a gradient of altitude in the Central Pyrenees: the seasonal record of long-range fluxes over SW Europe (Paper II)

Here we analysed Al, Ti, Mn, Fe, Ni, Cu, Zn, As, Se, Cd and Pb in the 2004-05 winter snowpack in the Central Pyrenees, at an altitude range of 1820-3200 m a.s.l.

Total (particulate plus dissolved) element concentration ranges were (in mg L-1): <5-51.1 for Al, <0.5-2.9 for Ti, 0.03-1.70 for Mn, <10-53.1 for Fe, <0.05-0.39 for Cu, 0.02-17.78 for Zn and 0.10-17.51 for Pb. Nickel, As, Se and Cd were not detected in most cases. The concentrations of the remaining elements were comparable to those found in other high mountain areas in Europe and North America and higher than those in polar areas.

The major ion chemistry of the snow indicated three possible origins of the solutes: terrigenous dust, aerosols of marine origin (i.e. sea salt spray) and contaminating S and N aerosols. We found no association between Cu, Zn and Pb and any of these possible sources.

On the basis of the proportion of soluble forms, the elements were divided into three groups: highly soluble (Mn, Zn and Pb), moderately soluble (Cu) and non-soluble (Al, Ti and Fe). A high content of soluble species indicates an anthropogenic nature (except Mn), whereas the predominance of insoluble forms is consistent with terrigenous origins. The EF results also suggest that Al, Ti, Fe and Mn had terrigenous origins, but provided evidence of a contaminating component for Cu, Zn and Pb.

Single measurements of concentrations and snow accumulation were subject to considerable spatial variability, which could be attributable to strong wind drift and other post-depositional processes. More interpretable patterns were observed when concentrations were integrated over the whole snowpack and averaged for each altitude. Snow collected at altitudes of up to 2050 m a.s.l. presented higher concentrations of several elements than snow above this altitude, thereby indicating a local influence. Snow collected above 2300 m a.s.l. was therefore more representative of broad regional inputs over SW Europe.

Atmospheric trace element contamination in European mountain catchments, as determined from direct bulk deposition records (Paper III)

In this paper, atmospheric bulk deposition samples were collected periodically over a two-year period (May 2004 – May 2006) in six remote mountain sites in the Pyrenees, Alps, Tatras and Grampian Mountains.

Amongst the sites surveyed, major metals (Al, Fe, Ti and Mn) were found in higher concentrations (and fluxes) in the Central Pyrenees. These four elements appeared to be highly co-distributed, with low enrichments with respect to the average composition of the Earth’s crust (UCC). They were also predominantly in particulate forms (except Mn), which indicates their lithologic origins and association with eventual Saharan dust intrusions that affect this mountain range in particular. Selenium was mostly not detected at the sites. By contrast, Pb, Zn, Ni, Cu, As and Cd were found in higher concentrations in the Tatra Mountains, Ticino and Piemonte. Lower concentrations occurred in the Tyrol, and intermediate values appeared in the Pyrenees and Grampian Mountains. These trace elements were variably co-distributed, with intermediate to high enrichments and a high proportion in dissolved forms, which can be interpreted as a variable component of both natural and anthropogenic sources. Precipitation pH and the nature of element sources appeared as determinant factors in the dissolved and particulate phase distribution of selected elements. Low pH values and intermediate to high enrichment values were significantly related to moderately soluble elements, which are thus more bioavailable for biota and may have greater potential toxicity for receiving ecosystems.

Seasonal patterns of depositional fluxes were observed at all sites. There were higher fluxes during the warm months of a year (June – November) than during the cold months (December – May). To assess the potential ecotoxicological risk of atmospheric trace element fluxes over European mountain catchments, the annual trace element fluxes were compared with predicted critical loads (CL). Annual Zn and Pb fluxes exceeded (or were close to) the estimated CL in the Canton Ticino, Pyrenees and Tatra Mountains. The same occurred for Ni in the Grampian Mountains. Annual Pb and Cd inputs in European mountain ranges were compared with modelled deposition maps provided by EMEP: discrepancies between modelled and measured deposition levels were found at all sites. Data series including previous measurements of trace element concentration in precipitation showed a general decreasing trend over European mountain ranges during the last decade, which reflects the continuous reduction of trace element emissions in Europe over the last 40 years.

Major and trace elements in soils in the Central Pyrenees: high altitude soils as a cumulative record of background atmospheric contamination over SW Europe (Paper IV)

Here, several major metals (Al, Ti, Mn and Fe) and trace elements (Ni, Cu, Zn, As, Cd, Pb and Zr) were measured in soils along an altitudinal transect (1520-2880 m a.s.l.) in the Cregüeña valley, Central Pyrenees. Total and acid-extractable elemental concentrations for the soil samples were analysed by X-ray fluorescence and inductively coupled plasma spectrometry, respectively.

Total major element concentration averages were higher than the respective acid-extractable concentrations. By contrast, total and acid-extractable concentrations of Cu, Zn, As and Pb matched well. In the samples with the lowest concentrations, the values of acid-extractable Ni were higher than the total Ni determinations.

Total major element concentration ranges were (in g kg^{-1}) 48.4-91.8 for Al, 3.1-5.0 for Ti, 0.18-2.20 for Mn and 26.6-66.1 for Fe. The distribution patterns of these major metals correlate with those of the underlying rocks. Total trace element concentration ranges were (in mg kg^{-1}, inventories in g m^{-2} between parenthesis) <2-58 (0.5-6.6) for Ni, 6-30 (0.2-3.4) for Cu, 38-236 (1.6-32.4) for Zn, 6-209 (0.2-12.8) for As, 0.02-0.64 (<0.04) for Cd, and 28-94 (0.6-13.0) for Pb. Trace element concentrations in Cregüeña soils were in general comparable to those recorded in soils from other European mountainous areas, with the exception of As, which showed remarkably higher concentrations as a result of the natural abundance of this element in the Pyrenean lithology. These concentrations in soils in the Pyrenees were in several cases above the environmental protection and phytotoxicity thresholds recommended by the local authorities.

None of the storage capacity properties examined in soils (i.e. complexation and sorption potentials determined by the organic matter content and the size of the clay-silt exchange complex, the stone content as an indicator of well drained soils favouring leaching of elements, pH and C/N as factors determining the mobility of trace elements) were determinant of the differences in elemental concentrations along the altitude gradient. Thus, we propose that these concentrations are more dependent on the supply of the elements, whether from natural or contaminant sources. Moreover, trace element concentrations in soils were generally ~2-4 times higher than in the rocks. Thus, in this case, concentrations in the bedrock cannot account for concentrations in soils. Hence, an additional source to that provided by the parent minerals must account for the recorded Ni, Cu, Zn and Pb concentrations.

The highest trace element concentrations were found at lower altitudes, which indicates that local contamination has an effect up to ~2300 m a.s.l. The local road, which is relatively busy in the summer time, and the nearby village appear to be the most likely close sources. In addition, the fact that the local tree-line almost coincides with the ~2300 m a.s.l. limit may enhance deposition of atmospherically transported elements at lower altitudes. Trace elements in soils can only be considered representative of background contamination levels above the altitude of ~2300 m a.s.l. Enrichment factors (EF) were used to assess the extent of this contamination. Nickel, Cu, As and Pb showed a ~2- to 5-fold increase over the average concentration of the local dominant lithology. Enrichment of As was most probably caused by localised As-bearing veins in the area, while Ni, Cu and Pb enrichment reflected the regional and global background of atmospheric contamination.

The patterns of the inventories for all trace elements were very similar, and were fundamentally determined by soil accumulation (depth), which overrides any difference in concentration. There was no evidence of higher accumulation of contaminating trace elements in soils at higher elevations that could indicate increased deposition with altitude, as reported in previous studies.

Whole-catchment inventories of trace metals in soils and sediments in mountain lake catchments in the Central Pyrenees: apportioning anthropogenic and natural contributions (Paper V)

In this study, we measured the concentration of Pb, Zn, Cd, Cu and Ni in rocks, soils, sediments and plants from three catchments in the Central Pyrenees, to estimate whole-catchment inventories for these trace metals and apportion between the natural and anthropogenic fractions. Furthermore, we used Pb isotopes to distinguish between natural and contaminant Pb, and compared the results to the apportioning based on reference elemental ratios to validate this second method.

The sediment profiles generally showed an increase in the concentration of all trace metals from the bottom to the top layers, which was consistent with increased contamination in more recent times. The soil profiles also tended to present higher trace metal concentrations in the upper layers. However, this was not as clear as in the sediments.

Both methods (Pb isotopes and reference elemental ratios) gave similar results, except in one of the catchments in which soils presented a highly organic upper horizon with differentiated geochemistry. These soils required a specific treatment to obtain good agreement between both methods of estimation. Taking this into account, anthropogenic inventories for the other metals for which isotopic methods are not available were calculated using the element ratio method. Previous studies have shown that Pb contamination started in the area as early as the first century BC. In the present study, the earliest indication of Pb contamination in lake sediments was dated ~1250 AD and continued until the present. During the nineteenth century, there was a change in the source of anthropogenic Pb, as indicated by its isotopic composition.

The estimated inventories of anthropogenic trace metals for the whole catchments were ~1 g m^{-2} of Pb and Zn, ~0.1-0.2 g m^{-2} of Ni and Cu and ~0.01 g m^{-2} of Cd. Lead and Zn inventories were similar to those in other mountainous and rural areas in northern and eastern European locations, whereas Ni, Cu and Cd inventories were lower in the Pyrenees.

The anthropogenic trace metal inventories per unit area in the two highest sites were larger in the terrestrial catchments than in the lakes. One mechanism that could be involved is a washout of trace metals retained in the winter ice and snow cover of lakes during the early thaw before the melting water can enter the lake. This effect could be less marked at the lowest site.

The cumulative anthropogenic inventories of all trace metals in the soils and sediments analysed here are three orders of magnitude higher than the current yearly atmospheric deposition in the area.

Modelling Pb, Zn and As transfer from terrestrial to aquatic ecosystems during the ice-free season in three Pyrenean catchments (Paper VI)

Here we measured the inputs (atmospheric deposition to lake and transport from the catchment) and the outputs (sedimentation and losses through the outflow) of Pb, Zn and As over the snow and ice-free season for three high mountain lake catchments in the Central Pyrenees.

Our results, which were based on a mass transport model for the lake and its catchment, show that there was a net export of Pb and As from the catchments. We propose that accumulated anthropogenic Pb contamination and the weathering of As-rich rocks are the most likely sources. By contrast, Zn was largely immobilised in the catchment. We suggest that saturation of the catchments can make them a source of Zn contamination. The terrestrial inputs for Pb and As were >91% and for Zn they were ~71% of the total inputs to the lakes. Nearly all of the Pb entering the lakes was retained in the sediments, whereas 5-38% of As and Zn was lost through the outflow.

We were unable to adjust the model for Zn for one of the lakes. On the basis of concentration measurements in aquatic plant species inhabiting the lakes, we hypothesize that the uptake by macrophytes (which was not accounted for by the model) could be a considerable sink for dissolved Zn in the lake water. By contrast, there is no evidence of such uptake in the budgets for Pb and As.

General Discussion

"The essential is invisible to the eyes."

Antoine de Saint Exupéry in The Little Prince (1943)

In this section, the results of the articles in each part of the thesis are discussed to highlight the main findings and relate them to the idea that high mountain lake catchments are valuable sentinels of long-range contamination, and to many other aspects of global environmental change.

The extent, sources and potential implications of regional/global contamination of trace elements in high mountain areas

The concentrations of atmospherically deposited major and trace elements in the Pyrenees were in agreement with previous results from other high mountain areas (Fowler et al., 2006; Douglas and Sturm, 2004; Gabrielli et al., 2006; Kang et al., 2007; Plöger, 2004; Veysseyre et al., 2001; Yang et al., 2002a and 2002b). Moreover, concentrations in Central Pyrenean soils were, in general, comparable to those recorded in soils from other European mountainous areas (Plöger, 2004; Hernandez et al., 2003; Blaser et al., 2000; Kubica et al., 2002; Yang et al., 2002a; Bacon et al., 2005; Starr et al., 2003). Our measurements from bulk deposition, snow and soil samples can thus be considered representative of the background contamination levels of remote natural areas in Europe. By contrast, the same concentrations were higher than previous results from polar areas (Barbante et al., 2003; Hur et al., 2007; Berg et al., 1994), which can be used to define a global background.

Our analyses of the winter snowpack and soils along gradients of altitude in the Central Pyrenees revealed higher trace element concentrations up to ~2100-2300 m a.s.l., which suggests that atmospheric deposition from this altitude range may be subject to local influences. The same feature was observed by Veysseyre and collaborators (2001) in fresh snow collected along two alpine valleys in the French Alps and by Gabrielli and collaborators (2006) in fresh snow in the Italian Eastern Alps. By contrast to previous studies in Pyrenean soils (McGee and Vallejo, 1996), there was no increase in accumulation of contaminating trace elements in soils at higher elevations due to greater deposition (i.e. precipitation) with altitude.

The altitude transect approach thus evidenced spatial differences in the composition and origin of deposited elements. Therefore, we propose that only the trace element composition in snow, bulk deposition, soils or any other atmospheric deposition record collected above ~2100-2300 m a.s.l. in the Central Pyrenees can reliably be used as a signature of the background long-range fluxes in SW Europe. This altitude coincides with the local tree-line.

Case studies dealing with deposition of atmospheric major and trace elements in high altitude sites are insufficient. This is because mountains and polar areas have often been neglected in considerations of the impact of toxic compounds. It is also due to the logistic constraints of sampling in such isolated sites.

Our atmospheric deposition measurements in the Central Pyrenees and in the Alps, the Tatras and the Grampian Mountains represent an effort to gain insight into the global dispersal of trace elements. Overall, the trace element concentrations in atmospheric bulk deposition showed a general decreasing trend over European mountain ranges during the last decade. This was particularly marked for Pb and reflects the continuous reduction of trace element emissions in Europe over the last 40 years (Pacyna et al., 2007). By contrast, the critical load (CL) exceedance with respect to measured atmospheric trace element fluxes still highlights the evidence of considerable, ubiquitous background atmospheric contamination of trace elements in Europe. Moreover, the discrepancies between modelled and measured deposition levels accentuate the need for further long-term monitoring and improved modelling in remote mountain areas.

We established a relationship between the atmospheric major and trace element fluxes and the prevailing meteorological conditions in the Central Pyrenees, both seasonally and annually. Dust deposition containing terrigenous elements (Al, Fe, Ti, Mn, and As) and elements with a higher affinity for particles (Pb, Ni and Cd) increased during warm months (June–November), when most precipitation came from the Iberian Peninsula and North Africa following low-altitude trajectories. Likewise, dust deposition and associated elements prevailed during a year in which most of the precipitation events were influenced by Iberian and African air-masses. Conversely, the lowest major and trace element fluxes occurred in winter (December–May), and also during a year in which air-masses with an Atlantic component were predominant. Our observation is consistent with previous works based on the major chemistry in precipitation from the Central Pyrenees (Camarero and Catalan, 1996).

Due to its border position between the Atlantic and Mediterranean climatic regimes, the Pyrenees is a mountain range that is especially sensitive to potential global climate effects in SW Europe. In particular, possible changes in the general atmospheric circulation patterns as a result of climate change may cause a shift in the proportion of air masses from different locations. According to our results, such changes may influence the atmospheric fluxes of both major and trace elements in receiving ecosystems. An increasing trend of African dust over 49 years was recently observed in the eastern Mediterranean. This has serious implications for public health and for air transportation in the entire Mediterranean and European regions (Ganor et al., 2010).

We inferred the sources of atmospherically deposited major and trace elements on the basis of three chemical features: the co-distribution of various elements, the partitioning between soluble and insoluble fractions (i.e. the partition coefficient, Cp), and their enrichments (i.e. enrichment factor, EF) with respect to natural sources of reference. Thus, elements with a natural origin tend to correlate consistently with each other, which indicates a broad common origin. By contrast, contaminant elements are variably (or not at all) associated with each other, depending on the site-specific contamination sources. The former tend to occur in particulate forms and present low EF, whereas the later are more soluble and exhibit higher EF. On the basis of these three properties, we conclude that the Pyrenees receive higher inputs of Al, Fe, Ti, Mn and As associated with dust of a natural lithologic origin than the other European sites. As for the remaining elements, Pb, Zn, Ni, Cu, As and Cd originate from a variable contribution of both natural and anthropogenic sources in atmospheric bulk deposition from the six European mountain ranges surveyed. According to the above considerations, we suggest the following ranking of elements on a lithological–anthropogenic origin gradient for the Pyrenees: Al, Fe, Ti, Mn, As > Ni > Cu, Pb > Zn and Cd.

The solubility of the studied elements in precipitation from the Central Pyrenees was the most influenced by the acidity of the precipitation and the element sources, whereas the solubility of trace elements in the precipitation from the Tatra Mountains and the Tyrol showed lower dependence on these two factors. This result is in good agreement with the fact that atmospheric major and trace element deposition in the Central Pyrenees is highly related to particulate forms and dust inputs, in contrast to the deposition that occurs in other central and northern European high mountain ranges.

Episodes of dust deposition in Europe originate from North Africa, which is one of the largest dust producing regions in the world. However, North African dust intrusion events occur more frequently and have a greater impact in southern Europe than in central and northern Europe (Mattson and Nihlén, 1996). Moreover, since dust of Saharan origin represents a significant input of ions and nutrients, it is responsible for the greatest differences in precipitation chemistry (Psenner, 1999), in terms of both acid-base balance and chemical composition, as evidenced by our data on major and trace element deposition in different European mountain ranges.

Enrichment factors (EF) are a widely used approach to identify lithologic versus anthropogenic element sources in air, atmospheric dust and precipitation (Atteia, 1994; Berg et al., 1994; Boutron, 1979; Garcia et al., 2006; Lawson and Windchester, 1979; Veysseyre et al., 2001). Usually, element concentrations are normalised to an average crustal reference to identify and quantify human interference with global element cycles. However, caution must be used in the interpretation of the EF relative to an average crustal reference in environmental geochemistry (Reimann and de Caritat, 2005) for several reasons. The composition of the Earth's crust in different areas is spatially variable in relation to the global average continental crust, and natural fractionation of elements may occur during near-surface processes. Consequently, anomalously high enrichment factors may be due to natural rather than anthropogenic sources, as suggested by Duce and collaborators (1975) when the EF concept first emerged. To avoid disregarding these important biogeochemical processes that influence elemental cycles and the interpretation of their sources, we calculated EF of major and trace elements for the deposition records in the Central Pyrenees using three different natural references: the upper continental crust (UCC), the Maladeta granite (MDT) and the Western Sahara soil (WS). There were differences in the EF calculated using UCC, MDT and/or WS as background references. For the terrigenous elements, EF_{MDT} and EF_{WS} were closer to the expected value of 1 than EF_{UCC}, which indicates that MDT and WS may be more appropriate references than UCC. Furthermore, according to our results, the use of a local background reference like MDT offer a more meaningful basis for calculating EF than average crust, whereas the EF calculated with the "allochthonous" WS reference shows the importance and prevalence of Saharan dust in Pyrenean atmospheric deposition. By contrast, the enrichment level as an indicator of the anthropogenic contribution of trace elements to atmospheric deposition in the Central Pyrenees may be overestimated when UCC is used.

We identified three distinct origins for the major chemical compounds in the winter snowpack in the Central Pyrenees: terrestrial dust, sea salt spray and S and N contaminating aerosols. However, trace elements were not preferentially bound to any particular kind of aerosol. This suggests that in the meteorological conditions recorded during winter, none of these kinds of aerosols carried contaminating trace elements in a preferential way. The trace element content and structure of the winter snowpack was complex because of the interference of several contributions from different sources, in addition to several meteorological variables and atmospheric transport processes. This is in good agreement with the study of atmospheric trace elements in Alpine snow (Gabrielli et al., 2006).

The possible fate of atmospherically deposited major and trace elements in receiving lake catchment ecosystems can be assessed in terms of their potential mobility and bioavailabiltiy, properties that are largely controlled by their solubility. In this sense, we present a ranking based on the potential mobility and bioavailability of trace elements, as indicated by their C_p values: Zn > Cu > Ni > Pb > Cd in atmospheric bulk deposition samples and Zn > Pb > Cu > Ni in the snowpack.

However, what are the long-term implications of atmospheric trace element fluxes for Pyrenean lake ecosystems? Historically, such atmospheric fluxes have caused high concentrations of several trace elements in Pyrenean catchment soils and lake sediments at a level which may be of ecotoxicological relevance (Camarero, 2003). In our study, the trace element concentrations examined along an altitudinal soil transect in the Central Pyrenees were in many cases above the threshold recommended for ecosystem protection by Catalan and European environmental authorities. Moreover, Pyrenean high mountain soils showed a two- to five-fold enrichment in Pb, Ni and Cu as a result of long-range, long-term contamination.

In particular, Pb is the trace element that may have caused the greatest impact in the Pyrenean lake ecosystems (Camarero et al., 1998). The predominance of Pb as a contaminating trace element in the lake sediments contrasts with the present-day deposition fluxes in the Central Pyrenees: Zn deposition is currently one order of magnitude higher than Pb deposition, and Cu and Ni deposition is only slightly lower than Pb deposition. By contrast, Pb shows only moderate enrichment in atmospheric deposition, while Zn and Cd exhibit high enrichment. This is consistent with a decline in Pb deposition, owing to the reduction in European emissions (Pacyna et al., 2007). The actual composition of deposition also indicates a greater ecotoxicological concern for other metals, particularly for Zn. However, we should not neglect the potential significance of the historically stored Pb and other trace elements in both catchment soils and lake sediments as a future source for the lake ecosystems. This is the main focus of Part II of this thesis.

Lastly, we detected very low As concentrations in present-day atmospheric deposition in the Pyrenees in comparison to the high As levels in Pyrenean soils and sediments. Arsenic in bulk and snow samples was highly correlated with other crustal (i.e. terrigeneous) elements. It was present mostly as insoluble forms and showed low enrichment using MDT as a reference. This confirms the theory that localised arsenopyrite veins included in catchment rocks are the major source of As in Pyrenean soils and lake sediments (Camarero, 2003).

The importance of a contamination legacy: the fate of long-term deposited trace elements in high mountain lake catchments

In lake catchment systems, contaminants might be transported, stored and eventually redistributed through the different terrestrial and aquatic compartments after atmospheric deposition. Such dynamics may have delayed effects on the ecosystems. Our results provide insight into this issue.

In the terrestrial catchment, the trace element inventories along an altitudinal soil gradient in the Central Pyrenees were basically dictated by the total soil depth at each site. Furthermore, we found that none of the altitude-related physicochemical properties of soils examined were determinant factors that affected the accumulation of major metals and trace elements along the transect.

To date, only a few studies have attempted to estimate the cumulative atmospheric anthropogenic inputs for trace metals other than Pb at an ecosystem scale. To bridge this methodological gap, we used Pb isotopes to distinguish between natural and contaminant Pb. Our aim was to check the apportioning based on reference elemental ratios and, by extension, to validate this second method for the other trace metals for which no isotopic methods are available.

The estimated Pb and Zn inventories of anthropogenic trace metals for the three whole catchments were in good agreement with those found in other mountainous and rural areas in northern and eastern European locations. By contrast, Ni, Cu and Cd inventories were lower in the Pyrenean sites (Plöger, 2004; Yang et al., 2002b; Bindler et al., 1999; Brännvall et al., 2001; Klaminder et al., 2006a; Klaminder et al., 2006b; Bindler et al., 2004; Shotyk et al., 2000; Givelet et al., 2003; Shotyk and Le Roux, 2005; Renberg et al., 2000; Yang and Rose, 2005). The two lake catchments at higher altitudes presented anthropogenic inventories in their sediments that were smaller than the anthropogenic inventories in the terrestrial part of the catchment. This was unexpected, since part of the atmospheric flux deposited on the catchment may be transported into the lake, in addition to the fallout that enters the lake directly via atmospheric deposition. This may be due to the washout of the contaminants stored in the winter ice and snow cover of the lakes during the early thaw before the melting water can enter the lake. This effect could be less marked at the lowest site, thus evidencing climatic differences with altitude amongst sites.

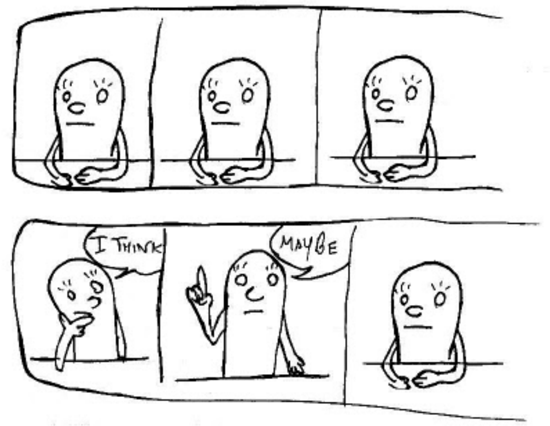
The cumulative anthropogenic trace metal inventories in the Pyrenean lake catchments are three orders of magnitude higher than the current yearly atmospheric deposition in the area. Our result highlights the potential of sediments and soils as sources of delayed, long-lasting contamination if environmental changes (e.g. higher soil organic matter decomposition caused by warming, increased soil erosion, etc.) favour the remobilisation of anthropogenic trace metals accumulated over the course of time.

In fact, the present-day biogeochemical cycling of potentially polluting trace elements in the three lake catchments studied in the Central Pyrenees show that there is a net export of Pb and As from catchment to lake, whereas Zn is largely retained in the catchment. This demonstrates how accumulated trace element contamination in the terrestrial ecosystems of remote natural areas may have a delayed effect on aquatic ecosystems, as shown in previous studies from other remote mountain and boreal ecosystems (Klaminder et al., 2008; Yang et al., 2002). Our study and previous research reinforce the view that terrestrial catchments are transient pools of recent and past atmospheric trace element contamination that occurred in remote, natural areas. After acting as effective sinks over a certain period of time, catchment soils may become sources of contaminants, and thus potential pollutants, as explained by processes such as saturation of specific complexation sites of organic matter in soils (Nriagu et al., 1998), increased C mineralisation enhanced by global warming (Drewnik, 2006), increased soil erosion (Rothwell et al., 2008; Yang et al., 2001) or changes in the water table level (Klaminder et al., 2006a).

An unsolved question raised by the modelling results is the unaccounted sink for Zn. This missing sink could be uptake by macrophytes. Although our measurements are not conclusive, they show that this is possible for Zn, but unlikely for Pb and As. This possible effect of natural biological purification deserves further investigation.

In general, this research illustrates how mountain lake catchments can be employed as sentinels of long-range contamination. Our results reveal the current remobilisation of Pb deposited in the past, and highlight the threat of Zn, which it is still being accumulated in the catchments. Moreover, the study emphasises concerns about how the trace elements in aquatic ecosystems may respond to the hypothesized, continuous release from the terrestrial catchment. For instance, the consequences of trace element fluxes on biota (both terrestrial and aquatic) may be relevant in the net budgets (at least, for Zn), as suggested by our results.

Conclusions and Further Remarks



The main outcomes of this thesis are summarised as follows:

1. Concentrations of atmospherically deposited major and trace elements in the Central Pyrenees were consistent with previous results from other high mountain areas. Our measurements can thus be considered representative of background contamination levels in remote areas of Europe.

2. Only the trace element composition in any atmospheric deposition record collected above ~2100-2300 m a.s.l. in the Central Pyrenees can reliably be used as a signature of the background long-range fluxes in SW Europe.

3. In the Central Pyrenees, Al, Ti, Fe, Mn and As were part of the dust carried from the Iberian Peninsula and North Africa. By contrast, Pb, Zn, Cd and Cu showed a more contaminating nature.

4. Annual and seasonal variations in atmospheric major and trace element deposition were related to the prevailing meteorological conditions: deposition of dust particles which contain terrigenous elements (Al, Fe, Ti, Mn and As) and elements with a higher affinity for particles (Pb, Ni and Cd) occurred during the year and/or during warm months (June–November) in which most precipitation came from the Iberian Peninsula and North Africa, and air-masses followed low-altitude trajectories.

5. Atmospheric bulk deposition of major and trace elements from six European mountain sites revealed regional differences in dust influence and atmospheric contamination. Aluminium, Fe, Ti and Mn were found in higher concentrations in the Central Pyrenees. By contrast, Pb, Zn, Ni, Cu, As and Cd were found in higher concentrations in the Tatra Mountains, Ticino and Piemonte. Lower concentrations occurred in the Tyrol, and intermediate values appeared in the Pyrenees and the Grampian Mountains.

6. Trace element concentrations in Pyrenean soils were comparable to those recorded in soils from other European mountainous areas and were, in many cases, above the threshold recommended for ecosystem protection by regional and European environmental authorities.

7. Pyrenean high mountain soils revealed a ~2- to 5-fold increase in Pb, Ni and Cu as a result of long-term, long-range atmospherically transported contamination. Enrichment of As was also found, but most probably caused by localised As-bearing veins in the area.

8. Cumulative whole-catchment inventories of anthropogenic trace metals in soils and sediments for three Pyrenean lake catchments were ~1 g m-2 of Pb and Zn, ~0.1-0.2 g m-2 of Ni and Cu, and ~0.01 g m-2 of Cd.

9. Lead and Zn inventories were in good agreement with those of other mountainous and rural areas in northern and eastern European locations, whereas Ni, Cu and Cd inventories were lower in the Pyrenees.

10. Trace metal inventories were three orders of magnitude higher than the current yearly atmospheric deposition in the Central Pyrenees, which highlights the potential of sediments and soils as sources of delayed, long-lasting contamination if environmental changes favour the remobilisation of anthropogenic trace metals accumulated over the course of time.

11. A mass transport model for the three lake catchments during the snow- and ice-free season showed net export of Pb and As from the catchments, whereas Zn is largely retained.

12. Delayed release of previously accumulated anthropogenic Pb contamination and the weathering of As-rich rocks are the most likely sources of these two elements. The eventual saturation of Zn in the catchments could also make them a source of Zn contamination.

13. The Zn model for one of the lakes could not be adjusted. Hence, uptake by macrophytes could be a considerable sink for dissolved Zn in the lake water.

Finally, several points that are raised in this thesis require further research, as discussed below.

There are currently insufficient sites for monitoring atmospheric major and trace element deposition in remote natural areas. Several aspects of concern warrant further long-term atmospheric deposition monitoring in a high number of background sites. These include: possible changes in general atmospheric circulation as a result of climate change may influence atmospheric trace element fluxes, in particular those forms associated with particles and dust; although there has been a reduction in atmospheric trace element deposition inputs in recent decades, the current annual deposition fluxes measured for some trace elements in European high mountains still exceed the predicted critical loads for ecosystems and human health protection; actual atmospheric deposition and the measurements for some trace elements in European high mountain sites are in disagreement with estimated atmospheric fluxes obtained from modelled deposition maps of Europe, which are obtained from emission and meteorological data. In this regard, continuous direct measurements are needed to verify the modelling results, as this would allow entire spatial coverage of the considered region.

Remote natural areas, such as mountains and the poles, appear to be much more affected by long-range contamination than usually thought. Consequently, concern is growing about the long-term impact of the continuous release of potentially toxic trace elements from the terrestrial to the aquatic ecosystems. In upland catchments, lateral transport of soil water is substantial and contributes to the quality of surface waters. Moreover, mobilisation and export of contaminants may be favoured by several biogeochemical processes in catchment soil, which are closely related to global warming. Therefore, integrated, long-term monitoring of atmospheric deposition, stream and lake water transport, sediment fluxes and vegetation uptake is also required in as many case study sites as possible.

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