Inorganic Chemistry in the Mountain Critical Zone: Are the Mountain Water Towers of Contemporary Society Under Threat by Trace Contaminants?

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INTRODUCTION

It has been established that the water cycle in mountain areas is likely to be impacted by climate change and by local pressure from humans, and if so, the same impacts will apply to the cycles of inorganic contaminants that are intrinsically associated with human activities. The current export and future of inorganic contaminants is related to future changes in hydrology as well as to geochemical processes directed by natural processes and mankind currently at work on mountain watersheds.

Mountains are not only impacted by enhanced deposition of inorganic contaminants but many of them are also the place of past and present mining activities that have increased the level of available contaminants in soils, sediments, and watersheds. Despite environmental improvements such as protocols of the "Clean Air Act," or prohibition of the use of leaded petrol in most countries of the world, pollution from potentially harmful trace elements (PHTEs), such as trace metals, is still an environmental problem. In particular, the energy demand in emerging countries such as China is inducing higher emissions of trace metals due to coal power plants. Other activities, such as the dysfunctional recycling of household electronics or the use of PHTE in nanotechnologies, also induce PHTE environmental emissions. Biogeochemical cycles of metals are still highly disturbed by humans. This has an impact, not only on ecosystem health and human health, but also unexpected effects in the dispersal of these metals. For example, Cziczo et al. (2009) showed that aerosols enriched in anthropogenic lead were better nucleation nuclei than aerosols containing no lead.

The critical zone is defined as the outer Earth's skin, from the treetops down to the maximal extent of groundwater (Brantley et al., 2007). The *mountain critical zone* has specificities including first its high topographic variability. Other particularities (Table 3.1), such a short vegetation growing season or a high snow cover have an impact in mountainous areas, not only on the water cycle but also on the fate of the PHTEs.

WHY GOING INTO THE FIELD TO INVESTIGATE MOUNTAINS

If remote sensing or real-time monitoring tools have been rising sharply for several years and allow for a nearly continuous observation of basic watershed parameters, the study in the field of the atmosphere−soil interface (deposition) and further export of PHTEs in the mountain critical zone is still needed to feed the models and improve spatial and temporal predictions of contaminant availability. This is especially true in remote areas of major research centers and in hard-to-reach areas such as mountains. These are crucial because they are extremely sensitive to environmental change zones: they are anthropically limited, with a short growing season and low warmth. These areas are also

TABLE 3.1 Main Characteristics of the Mountain Temperate Critical Zone for Potentially Harmful Trace Elements (PHTE)

Mountain Critical Zone	Features	Impacts on the Ecogeochemistry
Atmosphere	Orographic phenomena	Higher atmospheric deposition than expected
Weather	High seasonality	Snow deposition, snowmelt, heavy storm rains, and spring floods
Geology	Potential complexity of the geological features, discrete mineralizations, "young terranes"	Potential microscale natural sources of PHTE for the watershed, erodible mining wastes from abandoned ancient mines and potential mines in the future
Topography	High variability, large slopes	Increasing the risk of extreme hydrogeochemical events
Soils	Young soils, thin and fragile soils, presence of potential deep histosoils	Easily erodible, presence of organic matter
Vegetation	Specific mountain-boreal vegetation	Highly impacted by climate variability ("frontier ecosystem")
Forests	A mix between human and natural management — presence of invasive species (spruces)	Soil acidification and impoverishment in limited-resource soils
Grasslands	Grasslands: altitude dependent	Impacted by mining and pastoralism
Headwater catchments	Large incisions, snow dependent, highly seasonal	Erosion and transport of PHTE with suspended matter
Aquatic mountain ecology	High-altitude "white" lakes in the past	Introduction of invasive species, modification of the biogeochemical cycles of PHTEs

subject to specific atmospheric mechanisms compared to the temperate plains. They induce higher atmospheric deposition, but it is more difficult to quantify because few are localized in easily accessible areas (Lovett, 1994; Weathers et al., 2000). The ecological functions and services of these areas are as important as freshwater reserves, as carbon stocks, or by their biological diversity. Up to now, remote sensing and real-time monitoring tools are limited due to the harsh climatic conditions in high mountain areas. The winter season

is quite often less monitored due the unstable climatic conditions, with ice, fog, and snow making a hard life for scientific instruments. Shadow areas due to the topography are limiting remote sensing, and also wireless signal transmission.

A need thus exists to go in the field (Fig. 3.1) to verify the validity of online measurements if there are some, or to complete lower altitude measurements by highest points of measurements.

POTENTIALLY HARMFUL TRACE ELEMENTS

At present, anthropogenic fluxes of up to 62 chemical elements surpass their corresponding natural fluxes, i.e., the contribution of human activities to the atmospheric cycles of these elements far exceeds that of natural contributions (Sen and Peucker-Ehrenbrink, 2012). Among these elements many are considered as PHTEs, which hold limited to no known biological function, such as lead (Pb), arsenic (As), antimony (Sb), or mercury (Hg). Combined, the concentration of these elements constitutes less than 0.1% of the Earth's crust. Several studies have clearly shown that the contamination of PHTEs is widespread and that PHTEs can be found even in remote areas that are far distant from contamination sources. For instance, Rosman et al. (1997) showed that Pb contamination, as recorded in Greenland ice cores, can be dated as far back as 500 BC, which is further supported by numerous studies on lake-sediment cores (Cooke and Bindler, 2015). Even in such a remote area as the Arctic, contamination of Pb and Sb has been shown to occur as far back as

FIGURE 3.1 Photo of a winter field trip in the Bassies area, Central Pyrenees, France to investigate trace metal deposition in snow.

Roman times (Gabrielli and Vallelonga, 2015 and references therein). The occurrence and distribution of PHTEs on both geographical and temporal scales are thus widespread, and mountain areas are no exception.

Sources

Natural Sources

PHTEs are naturally present at low concentrations in rocks and in bedrock, and as a result of physical and chemical weathering, they are thus also naturally present in soil and surface waters. Various natural processes therefore enable their dispersal throughout the environment (Colbeck, 2008; Nriagu et al., 1988; Pacyna and Pacyna, 2001), and from a global point of view the following sources can be distinguished:

- *Terrigenous or lithogenic sources*: dispersal from wind erosion of rocks and soils (i.e., >20% of natural derived Cu, Ni, Pb, Sb, and Zn in the environment).
- *Volcanic sources*: dispersal through volcanic activities discharging emission of a significant amount of PHTEs (i.e., ~20% of As, Cd, Cr, Cu, Hg, Ni, Pb, and Sb) up to the stratosphere.
- *Sea spray*: dispersal through suspending marine water droplets that contributes to about 10% of total PHTEs emissions.
- *Biogenic sources*: biomass fires driven either by natural or anthropogenic processes acts as point sources of PHTEs.

Anthropogenic Sources

Anthropogenic sources of PHTEs are mainly due to high-temperature combustion activities resulting in volatilization of trace elements or their release in the form of very fine aerosols (<μm). In the case of erosion or dust emission, without any underlying high-temperature process, emissions tend to be much more localized (i.e., mining activities). Broadly speaking, the activities can be categorized into the following different sources/activities (De Traubenberg et al., 2013; Pacyna and Pacyna, 2001):

- *Energy production by combustion*: the dominating anthropogenic source of PHTEs emission, entailing burning of wood, coal, and oil (As, Cd, Cu, Hg, Ni, Pb, Sb, Se, V, and Zn),
- *The metallurgical industry*: emission of dust near the extraction and point of exploitation, high-temperature processing of ores emit aerosols rich in trace elements (Cd, Cu, Ni, Pb, V, and Zn). The proportion of individual elements emitted in the aerosols depends on the type of ore processed.
- *Other industrial processes*: high-temperature processing and manufacturing (As, Cr, Cu, Ni, Pb, and Zn)
- *Transport*: road traffic (Cd, Cu, Fe, Ni, Pb, and Zn), erosion of brake pads (Cu, and Sb), erosion of train rails (Cu)

- *Waste treatment*: incineration of household waste (As, Cr, Cu, Ni, Pb, Sb, Se, V, and Zn)

The responsibility of humans regarding the dispersion of aerosols and PHTEs by anthropogenic activities is undeniable, but mankind also holds a strong responsibility in the intensification of natural dispersal processes. For example, the burning of biomass, i.e., forest fires, have been naturally occurring as a part of plant development and ecological renewal for more than 400 million years, yet these fires are now mainly driven and controlled by humans (Andreae and Rosenfeld, 2008). Similarly, desertification of semiarid lands and the intensification of agriculture on bare soil also helps to accelerate the natural suspension of dust (Rauch and Pacyna, 2009) and thus also the dispersal of PHTEs.

Transport

The atmospheric boundary layer is located between 0 and 1−2 km altitude above ground level (Fig. 3.2). Below the boundary layer, contaminant transport is dominated by vertical transport and PHTEs bound to fine particles are subjected to turbulence transport. PHTEs could accumulate in this boundary layer if not washed out by rainfall. They could also be transported in the free troposphere where lateral transport is more dominant. Aerosols and related inorganic contaminants can therefore be transported long distances.

The atmosphere thus has a significant role in the dispersion of PHTEs in the environment, whether they occur in particulate form (solid or liquid aerosols), or as gas (e.g., certain forms of Hg). Because long-distance transport is borderless, contaminants can be transported thousands of kilometers before being deposited, sometimes reaching the most remote areas of the globe (Gabrielli and Vallelonga, 2015; Lee et al., 2008b). The transport of particles, and the distance they may travel, depends not only on their size but also on their reactivity.

The reactivity and particle size determine the residence time (τ) of the compounds in the atmosphere and can be divided into:

- *Compounds and chemical speciation with a short residence time ($\tau < 100$ s).* These are commonly the most reactive form of chemical speciation, which tend to deposit fairly quickly after suspension in the air masses. As these particles do not remain airborne for long, deposition therefore occurs in close proximity to the source of emission.
- *Compounds and chemical speciation with a mean residence time (100 s $< \tau <$ 1 year).* If hemispherical mixing occurs, these compounds may remain suspended in the air on a timescale of months. This is, for example, the case for very fine aerosols for which sedimentation is not possible, or chemicals of highly reactive speciation (e.g., gaseous oxidized Hg; Holmes et al., 2010).

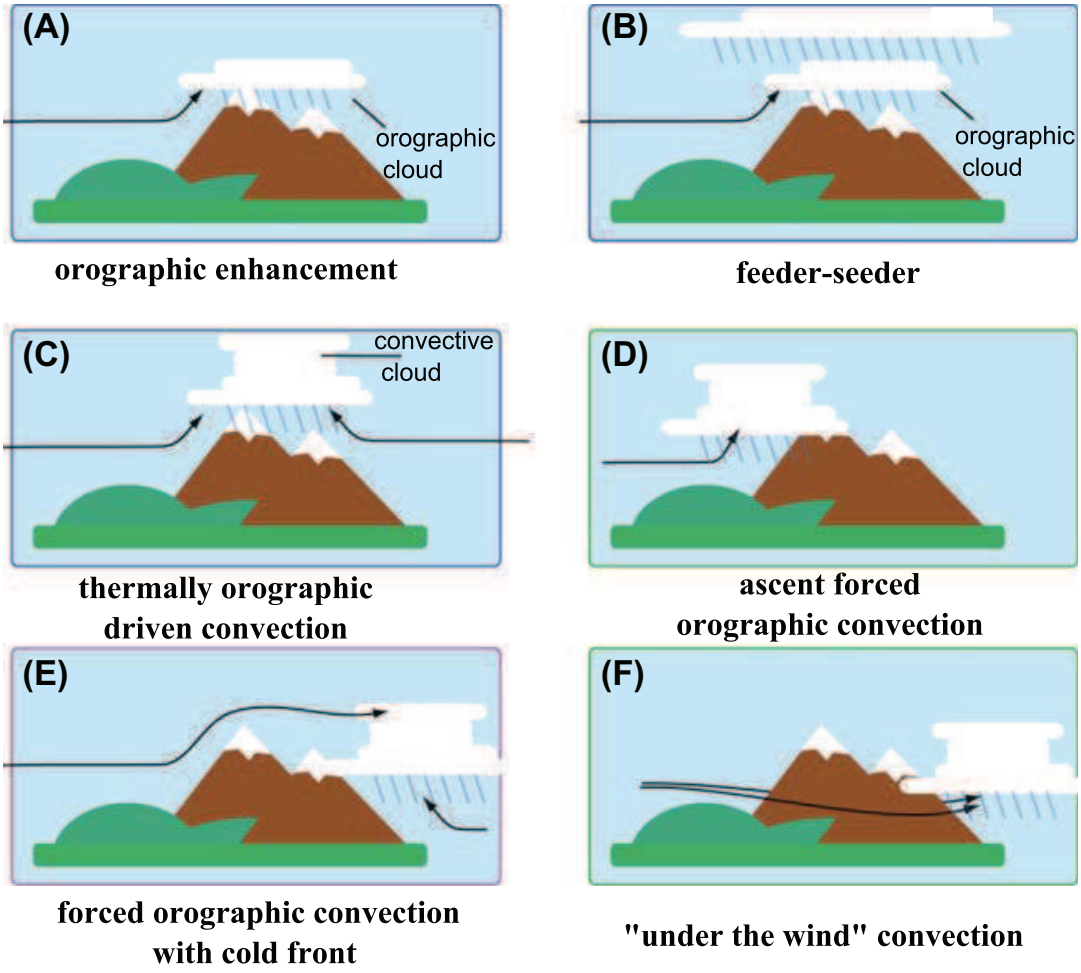

FIGURE 3.2 Schematic representation of different modes of wet precipitation causing differences in precipitation amount and mechanisms of scavenging in mountain areas. Orographic enhancement (A), with "feeder-seeder" effect (B), as well as thermic (C) and forced (D–F) convection leading to rainstorms, are represented.

- *Compounds and chemical speciation with a long residence time ($\tau > 1$ year).* In this case, the interhemispheric mixing becomes possible, as in, for example, the case of gaseous elemental Hg (Holmes et al., 2010), which can thus remain in the atmosphere on a timescale of years.

Deposition

The transport and circulation of PHTEs in the atmosphere, and thus the concentration, can be reduced by deposition which varies depending on weather parameters. Atmospheric deposition that controls the deposited metals onto the ground occurs in the form of:

- *Dry deposition*: aerosols and particle fallout in the absence of precipitation (e.g., rain and snow).
- *Wet deposition*: aerosols and particle fallout driven by precipitation events, either as dissolved in the aqueous phase or in particulate form, physically brought to the ground by the wet precipitation (e.g., rain and snow).

- *Occult deposition*: aerosols and particles are dissolved in aquatic solution with dew and/or mist, i.e., aerosols are present in the water droplets when they are intercepted by a barrier (commonly vegetation).

Dry Deposition

Dry deposition is the process whereby particles are removed from the atmosphere over time due to gravity, and where deposition onto surfaces occurs without involving precipitation (snow, rain, or mist spray; Lovett and Kinsman, 1990; Ruijrok et al., 1995). It essentially depends on the particle size, the concentration, and the reactivity between the deposited particle and the impacted surface (Lindberg et al., 1982). It is considered that the particles with a size of $>0.8\,\mu m$ can easily settle, whereas those with a diameter $<0.08\,\mu m$ tend to track the movement of air masses, and therefore be transported over long distances. The particles of intermediate size (i.e., $0.08-0.8\,\mu m$) thus have a behavior influenced by the two deposition processes (Ruijrok et al., 1995). However, due to changes in physiochemical parameters that occur at the interface of the troposphere and the atmospheric boundary layer, the particles with a size between 0.1 and 1 μm do not easily breach this layer and thus have a tendency to remain in suspension (Weathers et al., 2000).

PHTEs are mainly transported in the form of fine particles (Colbeck, 2008) or, in certain cases, as coarse particles originating from desert or local dust sources, and thus not commonly deposited in the form of dry particulates as wet deposition is the dominating process of removal from atmospheric air masses. The exception to this is mercury in its elemental gaseous form (Hg, gaseous elemental mercury) which may correspond to 50% of the deposit onto continental surfaces (Holmes et al., 2010).

Wet Deposition

As opposed to dry deposition, wet deposition is entirely connected to, and controlled by, wet precipitation events (i.e., rain, snow, and hail). Due to their size, which limits their suspension in the air masses and therefore their atmospheric residence time, the majority of aerosols are primarily deposited through wet deposition. However, fine size particles and aerosols that normally would be deposited through dry deposition can also be effectively leached and/or washed out of the atmosphere during wet precipitation events (Montoya-Mayor et al., 2013), and thereby reducing their atmospheric concentration. Such leaching can be divided in two separate phenomena (Bourcier, 2009; Engelmann, 1965; Ishikawa et al., 1995), which include the following:

- *Scavenging in the cloud (within cloud scavenging and/or rainout)* where condensation forms around one or more aerosols that serve as a core (nucleation).

- *Scavenging below the cloud (below cloud scavenging and/or washout)* where particles in the air column below the cloud are incorporated into droplets due to impaction.

These two phenomena may occur either separately or together, as a function of the concentration of aerosol in and under the cloud at the time of precipitation.

The striking topographical changes that occur in mountains interact with precipitation processes, often resulting in precipitation events, thus leading to a higher degree of wet deposition rather than dry. Roe (2005) described the phenomena specific to these environments with pronounced reliefs, which may cause peculiarities in precipitation patterns, as "orographic enhancement" (or orographic increase).

However, the phenomenon of orographic increase can be more complex locally and result in inhomogeneous deposition on a local level. Examples of precipitation phenomena in Fig. 3.2 show the process that may lead to differences in precipitation patterns in mountain areas. The topography can cause the formation of an orographic cloud as pressure decreases when rising air masses are gaining altitude. The formation of an orographic cloud by rising air masses can lead to the following two phenomena (Fig. 3.2):

- Droplets are formed around a condensation nuclei until they reach a level of saturation and precipitate (Fig. 3.2A).
- The orographic cloud droplets are impacted by rainwater from a higher altitude cloud (Fig. 3.2B). This is the "feeder-seeder" effect, which enhances below cloud scavenging and/or washout under the orographic cloud.

In both cases, the deposition will be more intense at altitude than in the adjacent valley.

Other phenomena, although less frequent, can also occur. During calm weather conditions, air masses heated by the sun can rise up the mountain-sides from the valley by means of convection and cause localized thunder-storms and rain (Fig. 3.2C). During these events, the cloud is located as in Fig. 3.2A but it is a high-altitude cloud that can wash out several atmospheric layers at the same time. In the case of side convection alone, the stormy cloud can be on the same side (Fig. 3.2D). In the case of winds being lower on the opposite slope, either due to a cold air front (Fig. 3.2E) or due to topographic circumvention (Fig. 3.2F), the cloud could form on the opposite slope as well. More details on orographic processes and modeling are given in Roe (2005).

In these different cases of enhanced deposition, aerosols and the fallout of bound PHTEs are increased locally. Some examples of this, with, PHTE or ^{210}Pb (a natural radionuclide tracer of aerosol), are discussed in the following text.

On the scale of several mountain ranges in France (Alps, Puy-de-Dôme, Corsica), a relationship exists between annual rainfall, altitude, and the amount of fine aerosols that are washed out and deposited. The results obtained by Le Roux et al. (2008) show that the amount of ^{210}Pb (proxy of fine particles) stored in mountain soils increases with altitude and annual rainfall. By using a mass-balance approach, they conclude that 50% of ^{210}Pb is derived due to the leaching from low atmospheric layers, or as occult deposition of aerosols. Measures of bioaccumulated PHTEs in moss show a clear increase with altitude for Pb, Zn, and Cd bioaccumulation along several altitudinal transects in the Alps (Zechmeister, 1995).

Precipitation models predict an increase of 0.4–0.9 mm/m year based on an annual precipitation of 1000 mm (Lovett and Kinsman, 1990; Ollinger et al., 1993). This would lead to a contaminant deposition proportionate to precipitation. However, this is not the case. Examples in Fowler et al. (1998) show that for a 30% increase in rainfall, increased aerosol deposition may be as high as 150% (based on inventories of ^{210}Pb) within an 800 m difference in altitude, which is well above forecasts. The work of Le Roux et al. (2008) highlights the scavenging of aerosols from low atmospheric layers, which potentially could have a higher concentration of aerosols, as an explanation of the observed phenomenon.

In cases where significant sources of PHTEs emissions are local (e.g., occurring only on one side of the mountain) and weather conditions are stable, aerosols can accumulate at the top of the upper level of the atmospheric boundary layer. If the boundary layer is located below the highest levels of the surrounding mountains, the deposition of aerosols and contaminants will not be more intense at higher altitude, due to scavenging from the lower layers of the atmosphere. This is a common occurrence in, for example, California (Munger et al., 1983).

Deposition by Cloud or Fog Interception: Occult Deposition

Another deposition, such as cloud or fog interception, is generally called *occult deposition* because of the difficulties in the ability to accurately measure it using classical instruments such as rain gauges. This type of deposition is intermediate between the dry and the wet deposition. As wet deposition, aerosols are integrated into water droplets, and as dry deposition, the main mechanisms of deposition are driven by turbulent transport, impaction onto surfaces, and sedimentation due to gravity (Lovett and Kinsman, 1990). Cloud or fog interception falls within both of these categories. For instance, studies in different ecosystems of the world have shown the importance of such deposition by cloud or fog interception (Lovett, 1994), where concentrations of ions in rainwater deposited in mountains (Weathers et al., 1988) are one to two degrees of magnitude greater than the ion concentration in rainwater deposited in the forest (Lindberg et al., 1982).

PHTEs Deposition and Accumulation Along Altitudinal Gradients

Artificial Radionuclides

Artificial radionuclides, for example ^{137}Cs, plutonium isotopes, or ^{241}Am, are specific contaminants as they are radioactive and emitters of alpha, beta, and gamma particles that all could affect biological processes (Fig. 3.3). Artificial radionuclides are produced by various human activities, including the following:

- Locally around nuclear reactors and nuclear waste-treatment plants,
- Broadly in the past by the nuclear weapon tests (NWT) and the fallout of a Soviet satellite,
- Point sources in the form of accidents in nuclear plants.

Among the radionuclides that are important from an environmental point of view, ^{137}Cs is the one that has a very similar behavior to many inorganic contaminants: It is associated with aerosols in the atmosphere and its greater fallout in mountain areas is due to similar air mechanisms as inorganic contaminants. Because of the low amount of potential anthropogenic sources, ^{137}Cs behavior at the atmosphere–soil interface in mountains is easier to interpret than other PHTEs. ^{137}Cs has also a long half-life (30 years) that makes its impact measurable several years after its deposition.

It has been shown that for NWT and Chernobyl-derived ^{137}Cs, this radionuclide is enhanced by different atmospheric processes:

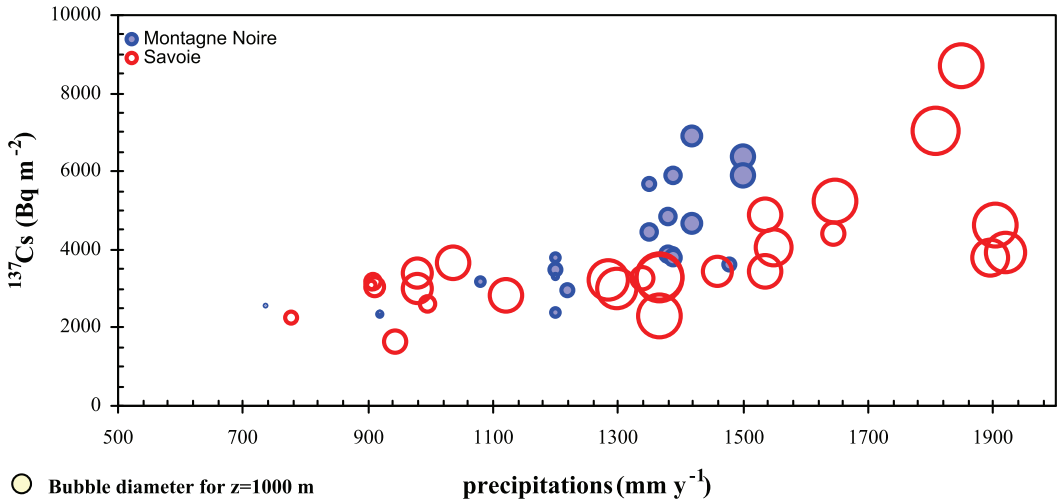

FIGURE 3.3 Bubble chart showing the relationship between ^{137}Cs total soil inventories and annual precipitations in Savoie (*empty red circles* (gray in print versions)), in Montagne Noire (*full blue circles* (dark gray in print versions)) with altitude as a third parameter corresponding to the diameter of the bubble. *Data from Le Roux, G., Duffa, C., Vray, F., Renaud, P., 2010. Deposition of artificial radionuclides from atmospheric Nuclear Weapon Tests estimated by soil inventories in French areas low-impacted by Chernobyl. Journal of Environmental Radioactivity 101, 211–218. http://dx.doi.org/10.1016/j.jenvrad.2009.10.010.*

1. A larger probability that radionuclides transported by air mass will be washed out by rain during orographic events,
2. Orographic deposition is enhanced by processes such as the feeder-seeder effect or fog interception (Le Roux et al., 2010; Fig. 3.4),
3. Enhanced in the watershed by retention in different mountain substrates such as wetlands or forest soils (Pourcelot et al., 2003). Similar conclusions can also be drawn for americium and plutonium isotopes that were transported in the atmosphere.

The accident at Fukushima Daiichi Nuclear Power Plant (FDNPP), Japan, released micron-sized, radioactive particles to the atmosphere. These particles contain different artificial radionuclides including ^{137}Cs. Hososhima and Kaneyasu (2015) showed that enhanced radioactive deposition in the Nikko Mountain National Park, connected to the nuclear plant accident at FDNPP, is related to the altitude and that it is surely also caused by orographic-deposition phenomena. A similar deposition pattern, connected to altitude, has also been shown in the United States. For example, an enhanced transfer of ^{137}Cs and ^{90}Sr from NWT to fish (i.e., trout) at high-altitude (>2500 m) Colorado sites compared to low-altitude sites was shown by Whicker et al. (1972). Persistency of ^{137}Cs can be relatively high as demonstrated by a long-term study of a Norwegian mountain arctic lake (Brittain and Gjerseth, 2010).

PHTEs and Altitudinal Dependency

The different orographic deposition processes can enhance long-range transported contaminant deposition in mountains as previously seen for artificial radionuclides or as evidenced using ^{210}Pb inventories in altitudinal gradients (Fowler et al., 1998; Le Roux et al., 2008). Zechmeister (1995) showed that PHTE concentrations (Pb, Cd, and Zn) in lichens in the Alps are correlated

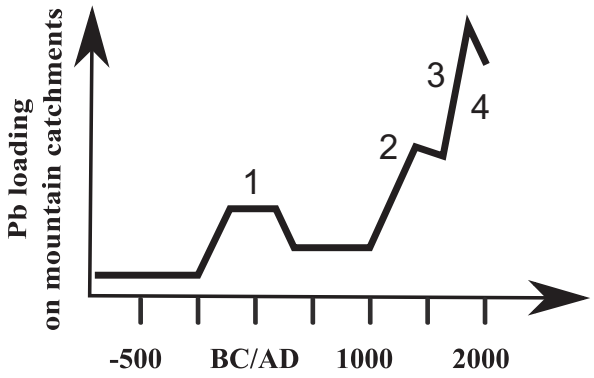

FIGURE 3.4 Typical Pb loading on mountainous environment that occurs in Western European and Mediterranean mountains. (1) Antiquity, (2) Middle Ages, (3) Industrial Revolutions, and (4) use of leaded gasoline and ban of its use in the 1990s.

with altitude. Based on a similar approach using mosses, Gerdol and Bragazza (2006) found a different pattern with higher concentrations at mid-altitude that could be related to higher occult deposition. Altitudinal dependency of PHTE inventories in soils is not obligatorily found in snow precipitations (Bacardit and Camarero, 2010; Yeo and Langley-Turnbaugh, 2010). This can reflect the influence of other parameters (air mass origin, vegetation interception, etc.) on short-time deposition over long-term orographic phenomenon. This emphasizes the need of long-term studies of precipitation along altitudinal transects to reconcile results from soils and mosses with results from orographic precipitations and occult deposition. Orographic phenomenon, such as the feeder-seeder effect or occult deposition, could enhance PHTE deposition, stock and release in mountain soils, wetlands, and sediments due to higher scavenging of aerosols-carrying anthropogenic PHTEs. It has been suggested that additionally to vegetation interception and enhanced orographic aerosol deposition, PHTE altitudinal soil accumulation (Ag, Cd, Pb, and Sb) could also be due to cold trapping on the higher Tibetan plateau (Bing et al., 2016).

Mercury is one of the most investigated PHTEs, but a fraction of Hg is present in a gaseous form in the atmosphere making this PHTE different from metals and metalloids such as Pb or Sb. It has been largely investigated in Arctic areas, and the mercury biogeochemical cycle in the Arctic shares some similarities with the Hg cycle in mountain areas. Hg soil accumulation increases with the elevation (and decreasing temperature) in mountainous areas (Zhang et al., 2013) due to cold trapping of gaseous mercury. Another driver of terrestrial retention of Hg includes air−vegetation gas exchanges (Demers et al., 2013; Enrico et al., 2016). These drivers are interrelated and could be difficult to distinguish, especially in an elevation gradient followed by a vegetation change (Blackwell and Driscoll, 2015).

LEGACY POLLUTION IN MOUNTAIN ENVIRONMENTS

Although we largely associate impacts from anthropogenic activities on the surrounding environment with the industrial era and its advancements in technology, the emission and spread of pollutants has a millennial-scale history in many parts of the globe, characteristically leaving a lasting imprint on the environment. Pollution from preindustrial times caused by mining activities such as ore exploitation and processing, when there were few if any environmental controls, could be substantial (Brännvall et al., 1999; Cortizas et al., 2002; Monna et al., 2004). As mining also entailed widespread land use that included forest disturbance and agriculture, the small-scale but generally widespread mining activities thus amounted to a geographically large-scale impact on the landscape (Bindler et al., 2012; Jouffroy-Bapicot et al., 2007; Monna et al., 2004). It is especially the case in mountain areas where geological features made metallic ores easily available for preindustrial miners.

Environmental Archives: Example of Pb Pollution

Cores derived from natural archives, such as ice cores, lake-sediment cores, and peat cores, allow us to study the aspects of past environmental conditions, such as the net accumulation of elements, deposition, and atmospheric cycling, on time-scales much longer than the information available from contemporary monitoring programs or written records. The magnitude of historical PHTE deposition, and its changes over time, can therefore be reconstructed using such natural archives.

An example of this is the reconstruction of Pb pollution and its global dimension through history. Initially shown by the groundbreaking work of Clair Patterson et al. (Murozumi et al., 1969; Settle and Patterson, 1980; Shirahata et al., 1980), then further refined by Jerome Nriagu (1996), the pollution legacy of Pb has now been reproduced in numerous publications on a world wide scale using both ice and snow records (Gabrielli and Vallelonga, 2015; Hong et al., 1994; Rosman et al., 1997), lake-sediment records (Abbott and Wolfe, 2003; Cooke and Bindler, 2015; Lee et al., 2008a; Renberg et al., 1994), and peat records (Aaby and Jacobsen, 1978; Bao et al., 2015; De Vleeschouwer et al., 2010 and references therein; Jensen, 1997; Lee and Tallis, 1973; Shotyk et al., 1998; Weiss et al., 1999).

Studies of trace metal pollution using natural archives have not only reconstructed contamination history but, more importantly, also have been able to shown that preindustrial pollution and its impact on the environment on a local-scale commonly surpasses the impact of contemporary pollution (Forel et al., 2010; Le Roux et al., 2005; Monna et al., 2004; Weiss et al., 1999). Specifically, reconstructed contamination records obtained in mountain areas, linked to nearby ancient metallurgical activities, show that the preindustrial contribution could exceed that of the last 200 years, especially for Pb and Sb (Camarero et al., 1998; Forel et al., 2010; Le Roux et al., 2005).

Fig. 3.4 shows the general chronological pattern of past Pb loads in Western/Southern Europe. This pattern is highly variable, and especially so in mountain areas, due to local activities such as mining or metallurgical workshops; yet it is commonly found in environmental records from, for example, the Pyrenees and the Alps. On other continents, the PHTE load in the past is less investigated (Marx et al., 2016); however, some chronologies of pollution patterns that follow the developments of large civilizations can also be found. Some examples of this are the increasing pollution in the Andes during the Incas period (Cooke and Bindler, 2015; De Vleeschouwer et al., 2014) or in Central China during the early Han dynasty (Lee et al., 2008a) or Southern China during the Yuan period(Hillman et al., 2015).

Reconstructions of Other Trace Elements

Publication records show that in terms of pollution reconstructions, Pb is by far the most well-documented trace element, much ado to the assumption of Pb being relatively stable (Shotyk et al., 1997) and thus yielding a well-preserved

signal stored in natural archives (Catalan, 2015; Catalan et al., 2013; Hansson et al., 2015; Shotyk and Le Roux, 2005). However, Pb is not the only trace element that has been successfully reconstructed using environmental archives. For example, other studies using peat and lakes as archives have shown the pollution record of As, Cu, Cr, Hg, Ni, Sb, and Zn (Catalan, 2015; Hansson et al., 2015 and references therein). Yet a comprehensive reconstruction of trace elements other than Pb can still be considered restricted, based on the limited geographical coverage. The majority of studies on pollution history have focused on European sites, and even fewer on mountainous areas. A need for further investigations of PHTEs on both spatial and temporal scale, and in mountain areas specifically, still resides (Catalan and Rondón, 2016).

ECOLOGICAL IMPACT OF PHTES IN THE MOUNTAIN ENVIRONMENT

Release of Inorganic Pollutants Into the Mountain Watersheds

One key aspect of mountains is the presence of buffer zones that include organic soils, forests, and wetlands (Bacardit et al., 2012; Gandois et al., 2010; González et al., 2006; Fig. 3.5). Not only do these buffer zones retain and store contaminants, but their alteration or destruction can lead to profound disturbances in the biogeochemical functioning of the mountain critical zone. As identified by Gurung et al. (2012), the current global change research in mountains focus mainly on studying climate change and its impact on mountain ecosystems. Yet, there is an urgent need to understand additional drivers (such as local human activities like mining or hydroelectricity) and disentangle their cascading impacts on, and disturbances of, mountain ecosystems. Gurung et al. also stated that to detect such impacts and attribute them to specific drivers of change, suitable indicators need to be identified. Long-term monitoring is therefore necessary both to understand which drivers are concretely involved and to quantify the associated consequences on biogeochemical processes in the mountain critical zone. Few critical zone observatories (CZO) in Northern America and Europe are located in mountain environments (i.e., Southern Sierra CZO in Unites States and Strengbach-Vosges Mountains in France) and even fewer are actively monitoring and investigating ecogeochemical processes in mountain watersheds. This is despite the fact that many studies have demonstrated a mining PHTE legacy in remote areas and their resulting current impact on the environment (Bindler et al., 2012; Camizuli et al., 2014; Mariet et al., 2016; Monna et al., 2011). Additionally, mountain areas can be geologically enriched in PHTEs (i.e., As; González et al., 2006; Zaharescu et al., 2009), and these PHTEs can be remobilized and released in the watershed due to environmental modifications such as melting of glaciers or dehydration of wetlands.

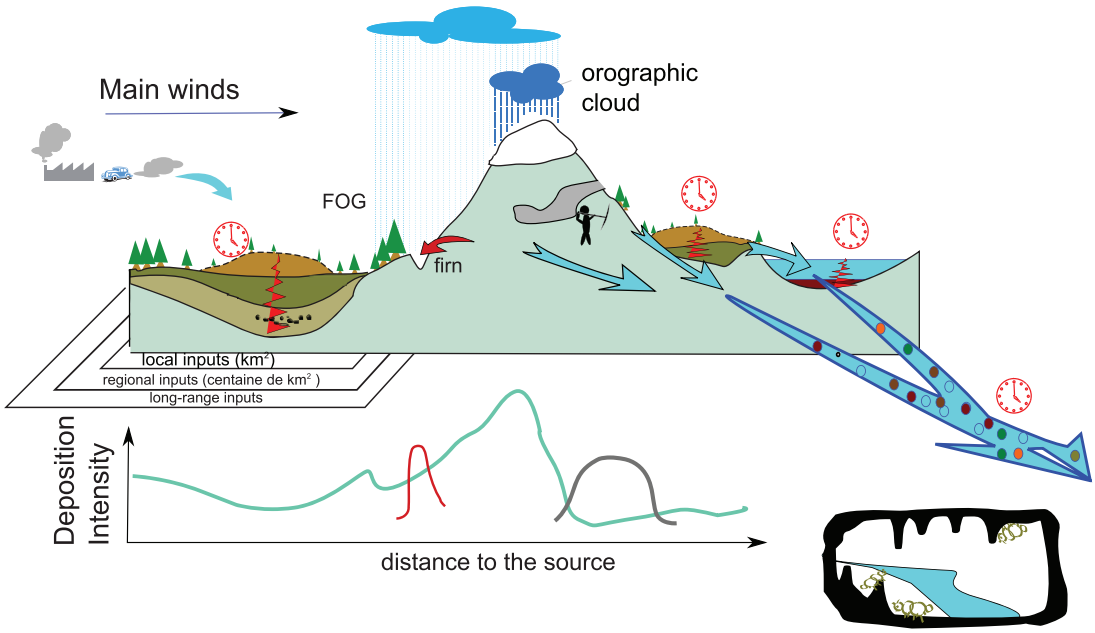

FIGURE 3.5 Atmosphere−soil−water in mountain ecosystems: the mountain critical zone. *Clocks* indicate environmental archives but also potential reservoir compartments for anthropogenic potentially harmful trace element (PHTE). The *arrows with dots* indicate that different PHTE will have different chemical fates, depending on their time and manner of deposition. The inset shows an example of PHTE deposition (accumulation intensity) in soil with deposition enhanced by canopy edge interception and orographic deposition (blue (light gray in print versions)) but also local activities such as mining (gray). Microtopography plays also a role in PHTE accumulation by concentrating snow in winter. A key compartment not discussed in this chapter is caves that are highly sensitive to environmental changes and that are frequently present in mountainous environments.

Potential Impacts

Because of higher concentrations in a localized area, it has been shown that former and present mining mountain areas have a clear impact on the transfer and effect of PHTEs in mountain-living organisms (Camizuli et al., 2014; Mariet et al., 2016; Qu et al., 2010). A key impact is that PHTE bioavailability is enhanced in high mountain areas where the chemical buffering capacity is limited, such as in clear soft water lakes (Köck and Hofer, 1998). Altitudinal ecological impact of enhanced deposition of PHTE is less clear since not only trace metal accumulation drives their transfer to the living organisms. Blais et al. (2006) observed an increase of Hg in fish with altitude in the Pyrenees as well as some organic contaminants. This is similar to a pattern that was observed for Pb in chamois from the Tatras mountains by Janiga (2008). On the other hand, no clear evidence exists of a gradient impact of Hg transfer in amphibians from the Sierra Nevada. Also no evidence occurs of hot spots of mercury concentrations in tadpoles in the Sierra Nevada due to the transportation of atmospheric Hg from the nearby San Joachim valley (Bradford et al., 2012).

Although the ecological impacts and effects of PHTEs on biota could constitute an entire chapter of its own, we believe that a brief summary example for one PHTE: Hg is still beneficial with specific references to mountain areas and therefore it is included below. We would like to remark however, that this summary is not conclusive, and we therefore encourage readers to turn to the literature listed below, and references therein for further information on the matter. For Cd and Pb, the readers are encouraged to consult Köck and Hofer (1998).

As mentioned previously, many PHTEs hold few to no biological functions and are often considered highly toxic. This applies not only to humans but to other biota as well. In the case of, for instance Hg, many studies have focused on the connection between Hg contamination in food webs and the potential effect on fish (Gantner et al., 2009; Mason et al., 2000; Tsui et al., 2014, 2012). Unlike mammals and birds, that can to some extent excrete Hg and thus reduce the internal concentration of Hg through either digestion or shedding of hair, fur, or feathers, fish have no clear possibility to reduce their internal concentration of Hg. Instead, the Hg is bioaccumulated within the individual thus leading to a biomagnification up the food chain (Mason et al., 1996; Power et al., 2002). Some of the effects as seen by an increased concentration of PHTEs in fish are: reproductive difficulties such a reduced sperm mobility (Dietrich et al., 2010) or maternal transfer from female to egg (Hammerschmidt et al., 1999; Hammerschmidt and Sandheinrich, 2005; Sackett et al., 2013), reduced growth length (Simoneau et al., 2005), impairment in the feeding behavior (Fjeld et al., 1998), and histological changes in livers and kidneys (Rhea et al., 2013) to name a few. Sanches-Galan et al. (1998) even showed that increased concentrations of metals (e.g., Hg) could lead to a higher abundance of micronuclei in fish blood, that is a mutation on the cellular level where the cell division is not functioning properly and an "extra" micronuclei is formed within the blood cell (Blais et al., 2006).

CONCLUSION AND FUTURE OUTLOOK

Despite several decades of research on PHTEs in mountains, many questions remains due to the complexity of mountainous areas. PHTE dispersion has varied in its form through time and in the past it was dominated by local human activities but it has been influenced by long-range transportation of pollution from urban and industrial centers. Additionally to legacy pollution, mountain environments are still impacted by PHTE atmospheric deposition. Higher inputs in the environment could be expected in the future for some PHTE such as Hg emitted by coal combustion. New forms and pathways of PHTE dispersion can also be expected because of the use of nanomaterials and emerging trace elements. The quote written by Weathers et al. (2000) is thus still relevant: "Our results suggest that consideration of variation in deposition

across such landscape features as forest edges and gaps, elevation, aspect, and vegetation type should be considered in future modeling efforts. In areas with a long mining history, the pollution legacy should also be considered."

Environmental changes, including climate change (Janiga, 2008), are likely to produce unexpected cascading impacts between PHTE biogeochemical cycles and mountainous ecosystems (including water quality). It is therefore urgent to further investigate the feedbacks between metals and impaired functioning of the mountain critical zone.

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