# Contaminant Records in Ice Cores

**Paolo Gabrielli and Paul Vallelonga**

**Abstract** Ice cores extracted in polar regions and in high altitude glaciers at low and mid latitudes are important recorders of global to regional changes in climate, ecosystems and human activities (e.g. industry, mining, transport). All of the contaminants found in ice cores are transported through the atmosphere, with the transport mechanism and atmospheric lifetime of these contaminants determining their spatial extent. In this chapter, we consider such ice core impurities as lead, mercury, platinum group elements, other trace elements, black carbon, organic and radioactive species. These contaminants are evaluated over the past few centuries, from the pre-industrial period through the Industrial Revolution and up to the most recent years of atmospheric monitoring, pollutant moratoria and/or abatement technologies. Contamination by most of these compounds is widespread from the higher latitudes of the Northern Hemisphere down to the remotest locations of Antarctica, suggesting that today there are no glaciers on Earth where atmospheric depositions of anthropogenic origin cannot be detected.

**Keywords** Snow accumulation · Alpine glaciers · Ice sheets · Greenland · Antarctica · Industrial Revolution · Anthropogenic emissions · Long range transport · Environmental reconstruction

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## Introduction

Thick ice sheets and glaciers build up over centuries and millennia in areas where snow accumulates at a greater rate than it is lost. Usually this occurs in cold regions at high latitudes, although the highest mountain chains of the tropics and mid-latitudes also contain glaciers. The surface snow layers are gradually compacted by the overlying snow to become dense snow, known as firn, which is then further compacted to form ice. Cold glaciers (characterized by a temperature below the pressure melting point) preserve physical, chemical, and biological evidence of past atmospheric variability, for example changes in stable isotopes (e.g. EPICA community members 2006), soluble and insoluble inorganic impurities (e.g. Thompson et al. 2000) and a multitude of organic species (Grannas et al. 2006), respectively. Ice sheets and alpine glaciers also archive information about the human influence on the past atmosphere retaining contaminants such as, among many others, trace elements (e.g. Boutron et al. 1991), organic compounds (e.g. Legrand et al. 2007) and radionuclides (e.g. Fourré et al. 2006) that are wet- or dry-deposited on the glacier surface (Davis 1991).

Insights into the paleo-environmental information contained in glaciers can be obtained by extracting ice cores. These are ice cylinders of typically ~10 cm diameter that can be recovered by drilling into glaciers hundreds or even thousands of meters thick (EPICA community members 2004). Ice cores extracted from the Antarctic and Greenland ice sheets (N-GRIP-members 2004; Petit et al. 1999) and alpine glaciers (Thompson et al. 1986; Schwikowski 2003) have the potential to provide very detailed information on past atmospheric characteristics, from sub-annual to orbital time scales ($10^5$ years). Ice core studies offer the considerable advantage that multiple physical, chemical and biological records are obtained from the same ice matrix and thus can be compared on exactly the same time scale (except gaseous species). This reduces the relative temporal uncertainty and allows the examination of synchronous interactions between climate, ecosystems and, more recently, human societies.

Nevertheless obtaining an accurate absolute ice core chronology is often a challenge. Where annual snow layers are thick and preservation conditions are favorable (e.g. Thompson et al. 1986; N-GRIP-members 2004), robust dating can be obtained by counting annual ice layers (typically characterized by seasonal variations in stable isotopes, major ions and/or microparticle concentrations) in combination with the use of time markers. These are chemical signals in the ice which can be linked to known events, for instance the ash or acid fallout of major volcanic eruptions, aeolian dust events and atmospheric nuclear bomb tests (e.g. Knüsel et al. 2003). Thinning of the ice layers in glaciers and ice sheets eventually results in annual layers that are too thin to resolve. At low and mid latitudes rare organic fragments embedded in ice cores can be used for dating by determining their ^{14}C content (e.g. Thompson et al. 1998). Particularly promising is also a recent dating technique employing ^{14}C determined in the carbon fraction dissolved in the ice (Jenk et al. 2009; Sigl et al. 2009). In polar areas, ice flow models of varying levels of complexity can be coupled to time markers, such as the stratospheric products

($^{10}$Be) linked to variations in the Earth's magnetic field (Raisbeck et al. 2006), and eventually tuned to other well-dated paleo-records and orbital parameters (Parrenin et al. 2007; Wolff et al. 2010).

The surface of alpine glaciers, and to a lesser or negligible extent that of polar ice sheets, are intermittently subjected to summer melting, percolation and refreezing that increase the glacier temperature and create ice lenses that may cause different degrees of perturbation in the records, especially for the most soluble species (Eichler et al. 2001). In a rapidly warming climate, many cold glaciers that were suitable drilling sites until only a few decades ago are now disrupted by percolation of surface meltwater and are rapidly transitioning from a cold to a temperate state (temperatures at the pressure melting point throughout the glacier) (Gabrielli et al. 2012). Under these conditions untapped glacial paleo-environmental archives are being irreversibly obliterated, and their valuable climatic and historical information are lost.

The structure and dynamics of a glacier are very important to the preservation and extraction of a useful ice core record. The continuity of the ice stratigraphy is critical and can be assured only if the snow accumulates throughout the year and if reworking processes at the glacier surface are limited (e.g. wind erosion and re-deposition, summer melting, sublimation and re-condensation) (Schotterer et al. 2004). Ideally, ice core drilling sites should be characterized by minimal horizontal glacier flow, resulting in parallel ice layers that can preserve the depositional sequence. The Greenland ice sheet is characterized by a central ice divide, the highest point along the ice sheet where horizontal flow is minimized, while Antarctica features a number of ice domes with similar ice flow characteristics. However, closer to bedrock the ice flow dynamics are often poorly constrained and phenomena such as ice folding and shearing may hamper the stratigraphy and therefore the interpretation of ice core records (Chappellaz et al. 1997). The weight of the thickest ice sheets can induce pressure-melting at the base of the ice, resulting in the loss of the deepest and oldest sections of the ice core record. However, the basal ice stratigraphy can also be retained in such areas if the liquid water interface between the ice and bedrock limits folding and shearing.

In order to verify the robustness and reproducibility of the local and regional findings obtained from the polar ice sheets and the alpine glaciers, ice core records are often replicated (Jouzel et al. 1989). For this purpose multiple short ice cores (typically up to ~100 m long) have been drilled in alpine glaciers at the same drilling site (Thompson et al. 2002) while several long ice cores (up to 3.6 km long) have been retrieved in different locations located on the same polar ice sheets (Watanabe et al. 2003). Building a network of ice core drilling sites also allows the identification of impacts and sources of atmospheric emissions on regional, hemispheric or global scales. For example, signals from tropical volcanic eruptions are occasionally found in ice cores from Greenland and Antarctica, confirming the global impact of the eruption and allowing ice cores from around the world to be chronologically synchronized by such global markers (Severi et al. 2007).

If an appropriate sample preparation methodology is adopted and sensitive enough analytical techniques are available, the ice core matrix (essentially distilled

seawater with low content of salts and insoluble particles) offers a very low analytical background that allows even small deviations of atmospheric proxies to be detected (e.g. Vallelonga et al. 2010). Depending on the analyte, the process of drilling, handling and transporting ice cores can contaminate the outer surface of the ice cores. Hence strict contamination controls can be a fundamental prerequisite to extracting reliable records from ice cores (Candelone et al. 1994). Trace elements (e.g. lead, zinc, copper, cadmium), biota and organic species are perhaps the most prone to contamination due to their broad diffusion in the modern human environment. During the most recent decades an awareness of the importance of contamination control has increased and thus clean materials, reagents and careful procedures have been developed, allowing pristine and detailed records to be extracted from the ice cores (McConnell et al. 2002a; Candelone et al. 1995).

While polar ice core records can be representative of hemispheric and global atmospheric contamination by humans (Murozumi et al. 1969), alpine ice cores from lower latitudes are in general more indicative of the history of regional or local pollution (Schwikowski et al. 2004; Kaspari et al. 2011). The first striking evidence of an early large-scale human contamination was provided by an ice core extracted at Summit in central Greenland (Hong et al. 1994, 1996). In this core, enrichment of copper and lead relative to the average terrestrial crustal composition was attributed to mining and smelting emissions produced by Roman and Greek civilizations. It is significant that this widespread pollution event occurred well before the beginning of the so-called "Anthropocene" that is commonly attributed to the inception of the Industrial Revolution (Crutzen and Stoermer 2000). Since the beginning of the Anthropocene, the atmosphere has undergone a major change in its chemical composition that, as we will see in detail, is well evidenced by many ice core records extracted from both polar regions and high altitude glaciers.

In this chapter we will review the ice core records that detail the history of atmospheric contamination over the last ~ 300 years, covering the transition from the pre-industrial to the industrial period up to recent years. We will deal in particular with records of trace elements (including lead, mercury and platinum group elements), black carbon, organic species, and radionuclides, and compare them with corresponding records from other sedimentary archives such as lake sediment cores, peat bogs, etc. Table 1 details the species of presumed anthropogenic origin detected in glacial archives covering the time interval of the last ~ 300 years. We acknowledge the many other signals of natural and anthropogenic change that are recorded in ice cores, such as gases and major ions and their linked isotopic or physical properties (e.g. acidity, conductivity), but these are not evaluated in this chapter because they do not have direct counterparts in other paleo-environmental archives, as described in this book.

# Lead

Unquestionably, the pioneer of environmental lead (Pb) analysis is Clair C. Patterson (Flegal 1998). In his attempts to measure Pb isotopic compositions at µg g$^{-1}$ concentrations in meteorites, Patterson inadvertently discovered that the air, water and

**Table 1** List of the species of anthropogenic origin detected in glacial archives covering a time interval that goes from the beginning of the industrial revolution to the present time.

| Species | Location | Reference |
|---|---|---|
| **Pb** | Greenland | Murozumi et al. 1969; Rosman et al. 1993; McConnell et al. 2002b; McConnell and Edwards, 2008 |
| | Alps | Van de Velde et al. 1998; Heisterkamp et al. 1999; Rosman et al. 2000; Schwikowski et al. 2004 |
| | N. America | Shotyk et al. 2005b; Zheng et al. 2007; Osterberg et al. 2008; Shotyk and Krachler, 2010 |
| | Asia | Lee et al. 2011; Eichler et al. 2012 |
| | S. America | Correia et al. 2003; Rosman et al. 2003; Hong et al. 2004 |
| | Antarctica | Wolff and Suttie 1994; Hong et al. 1998; Vallelonga et al. 2002; Planchon et al. 2002b; Planchon et al. 2003; Van de Velde et al. 2005; Burn-Nunes et al. 2011 |
| **Hg** | Greenland | Boutron et al. 1998; Mann et al. 2005; Faïn et al. 2009 |
| | Alps | Jitaru et al. 2003 |
| | N. America | Schuster et al. 2002 |
| | Asia | Wang et al. 2008a; Zhang et al. 2012 |
| **PGEs** | Greenland | Barbante et al. 2001b; Barbante et al. 2003; Gabrielli et al. 2008 |
| | Alps | Van de Velde et al. 2000a; Barbante et al. 2004 |
| | Antarctica | Soyol-Erdene et al. 2011 |
| **Ag** | N. America | Krachler et al. 2008 |
| | S. America | Hong et al. 2004 |
| | Antarctica | Planchon et al. 2002a |
| **As** | N. America | Krachler et al. 2009 |
| | Asia | Hong et al. 2009 |
| | S. America | Correia et al. 2003; Hong et al. 2004 |
| **Bi** | Alps | Barbante et al. 2004 |
| | N. America | Krachler et al. 2009 |
| | Asia | Li et al. 2006; Kaspari et al. 2009; Liu et al. 2011 |
| | S. America | Hong et al. 2004 |
| | Antarctica | Planchon et al. 2002a |
| **Cd** | Greenland | Boutron et al. 1991; Candelone et al. 1995; McConnell and Edwards 2008 |
| | Alps | Van de Velde et al. 2000b; Barbante et al. 2004 |
| | Asia | Liu et al. 2011 |
| | S. America | Correia et al. 2003; Hong et al. 2004 |
| **Co** | Alps | Van de Velde et al. 1999 |
| | S. America | Correia et al. 2003 |

**Table 1** (continued)

| Species | Location | Reference |
|---------|----------|-----------|
| **Cr** | Alps | Van de Velde et al. 1999 |
| | S. America | Correia et al. 2003 |
| | Antarctica | Planchon et al. 2002a |
| **Cs** | Asia | Kaspari et al. 2009 |
| **Cu** | Greenland | Boutron et al. 1991; Candelone et al. 1995 |
| | Alps | Van de Velde et al. 2000b; Barbante et al. 2004 |
| | S. America | Hong et al. 2004 |
| | Antarctica | Wolff et al. 1999; Planchon et al. 2002a; Vallelonga et al. 2004 |
| **Mo** | Alps | Van de Velde et al. 1999 |
| | Asia | Hong et al. 2009 |
| **Ni** | Alps | Barbante et al. 2004 |
| | Asia | Correia et al. 2003 |
| **Sb** | Alps | Van de Velde et al. 2000b |
| | N. America | Krachler et al. 2005; Krachler et al. 2008; Krachler et al. 2009 |
| | Asia | Li et al. 2006; Hong et al. 2009; Liu et al. 2011 |
| **Sn** | Asia | Hong et al. 2009; Liu et al. 2011 |
| **Tl** | Greenland | McConnell and Edwards 2008 |
| | N. America | Krachler et al. 2008 |
| | Asia | Liu et al. 2011 |
| **U** | Alps | Barbante et al. 2001a |
| | Asia | Kaspari et al. 2009 |
| | Antarctica | Planchon et al. 2002a |
| **Zn** | Greenland | Boutron et al. 1991; Candelone et al. 1995 |
| | Alps | Van de Velde et al. 2000b; Barbante et al. 2004 |
| | S. America | Correia et al. 2003; Hong et al. 2004 |
| | Antarctica | Planchon et al. 2002a |
| **PAHs** | Greenland | Masclet et al. 1986; Kawamura et al. 1994; Jaffrezo et al. 1994 |
| | Alps | Gabrieli et al. 2010 |
| | Asia | Wang et al. 2008b |
| | Antarctica | Fuoco et al. 2012 |
| **POPs** | N. Europe | Hermanson et al. 2010; Ruggirello et al. 2010 |
| | Alps | Villa et al. 2001; Villa et al. 2003; Maggi et al. 2006; Kirchgeorg et al. 2013 |

**Table 1** (continued)

| Species | Location | Reference |
|---|---|---|
| | N. America | Gregor et al. 1995; Donald et al. 1999 |
| | Asia | Wang et al. 2008a; Wang et al. 2008b; Wang et al. 2010a; Wang et al. 2010b |
| | Antarctica | Fuoco et al. 2012; Kang et al. 2012 |
| **BC** | Greenland | McConnell et al. 2007 |
| | Alps | Lavanchy et al. 1999; Jenk et al. 2006; Thevenon et al. 2009 |
| | Asia | Kaspari et al. 2011 |
| | Antarctica | Bisiaux et al. 2012 |
| **Radionucl.** | Greenland | Koide et al. 1982; Picciotto and Wilgain 1963 |
| **Radiocact.** | | Merlivat et al. 1973 |
| | Alps | Vincent et al. 1997; Schwikowski et al. 1999; Eichler et al. 2000; Reithmeier et al. 2006; Gabrieli et al. 2011b; Warneke et al. 2002 |
| | Asia | Kehrwald et al. 2008; Thompson et al. 1995b; Liu et al. 2011; Olivier et al. 2004 |
| | S. America | Thompson et al. 1995a; Knusel et al. 2003 |
| | Antarctica | Crozaz, 1969; Jouzel et al. 1979; Koide et al. 1982; Fourré et al. 2006 |

chemicals he used were thoroughly contaminated with Pb from leaded gasoline. He developed techniques for removing Pb from his laboratory, purifying both the lab water by filtration and sub-boiling distillation in quartz vessels and the air by using HEPA filters. In addition he ensured that the filtered clean lab air was over-pressured with respect to external contaminated air. He needed to produce his own lead-free acid and used only polyethylene or stainless steel apparatus that could be cleaned using his own Pb-free acid and water.

Patterson's legacy was to demonstrate just how pernicious the Pb contamination of modern society was. The pinnacle of this work involved the collection and analysis of snow blocks and ice cores from Antarctica and Greenland in order to demonstrate that Pb concentrations in 1960s Greenland snow were up to 300 times greater than they had been 3000 years ago (Murozumi et al. 1969). This record was instrumental in convincing American policy makers to enact the Clean Air Act in 1970, which mandated the removal of Pb from gasoline in the US. By the start of the twenty-first century, most of the countries in the world had switched to unleaded gasoline, thanks in part to Patterson's tireless dedication to science and environmental stewardship.

Following the careful sample collection and preparation techniques pioneered by Patterson, sensitive analytical techniques and instruments are required to accurately determine ultra-low Pb concentrations in environmental matrices. Instruments such as Inductively Coupled Plasma Sector-Field Mass Spectrometers (ICP-SFMS) and

Thermal Ionization Mass Spectrometers (TIMS) are regularly used to study Pb and its isotopic ratios. Pb isotopes are of interest because they can be used to identify Pb pollution sources (Rosman 2001). Three stable isotopes of Pb ($^{206}$Pb, $^{207}$Pb, $^{208}$Pb) are respective end-products of the radioactive decay chains of uranium ($^{238}$U, $^{235}$U) and thorium ($^{232}$Th). When Pb is incorporated into an ore body, it is removed from its parent U and Th and its isotopic composition is fixed. While the isotopic composition of Pb in an ore body is related to its age, its composition in volcanic emissions is dependent upon the crustal material from which the magma was produced (Sun 1980).

Murozumi et al. (1969) produced the first Pb record from snow blocks carved out of the walls of the Camp Century base in Northwestern Greenland. The results showed a tenfold increase in Pb concentrations from the earliest sample (1 pg g$^{-1}$ at 800 BC) to 1750 AD (10 pg g$^{-1}$), which marked the early Industrial Revolution. However, there was a greater than tenfold increase from 1750 to 1965 AD (230 pg g$^{-1}$). This trend was confirmed and further developed by colleagues and students of Patterson over the 1980s and 1990s (Boutron et al. 1991; Ng and Patterson 1981; Sherrell et al. 2000). Candelone et al. (1994) developed an advanced technique for the contamination-free sampling of ice cores which involved the use of a plastic lathe in a clean-air bench located in a cold room. Acid-washed stainless steel chisels were used to scrape away 4 to 6 layers of the external, contaminated, layers of ice. The pristine inner sections were isolated in acid-cleaned polyethylene bottles, then melted and analyzed. The chiseled outer layers were also analyzed to demonstrate the successful removal of external contamination.

Hong et al. (1994) identified a fourfold Pb enrichment in Greenland ice between 500 BC and 300 AD resulting from ancient mining and smelting activities during the height of the Greco-Roman empires. Pb isotopic analysis enabled Rosman et al. (1997) to attribute this Pb to smelters in two regions of southern Spain, with 70 % of Pb pollution originating from the Rio Tinto mines between 150 BC and 100 AD. Post-Roman Pb enrichment in ice occurred after 500 AD with the development of mining and smelting in the Harz Mountains of Germany. Pb isotopes were also used to study twentieth-century Pb deposited in Greenland (Rosman et al. 1993). These authors were able to distinguish between Pb additives used in the USA ($^{206}$Pb/$^{207}$Pb 1.21) from those used in European refineries ($^{206}$Pb/$^{207}$Pb~1.14), thus resolving the mixture of US and European gasoline Pb deposited in Greenland from 1968 to 1988. The data showed a change from US to European sources after the introduction of clean air legislation in the US in 1970 AD. A more recent study of Pb pollution in Greenland resulted from another leap in analytical capability in which McConnell et al. (2002b) developed a technique to continuously melt ice core sections on an acid-cleaned heated plate. The meltwater was pumped continuously to an ICP-SFMS for determination of Pb concentrations. They were able to report sub-annual variations in Pb concentrations from central and southern Greenland over the past 250 years, thus detailing the history of industrial development at unprecedented high resolution (McConnell and Edwards, 2008; McConnell et al. 2002a).

Alpine records of Pb have been used to reconstruct regional variability in industrial development. Several studies of Pb concentrations and isotopic compositions (Heisterkamp et al. 1999; Rosman et al. 2000; Schwikowski et al. 2004; Van de Velde et al. 1998) have featured snow and ice cores from the Alpine glaciers of
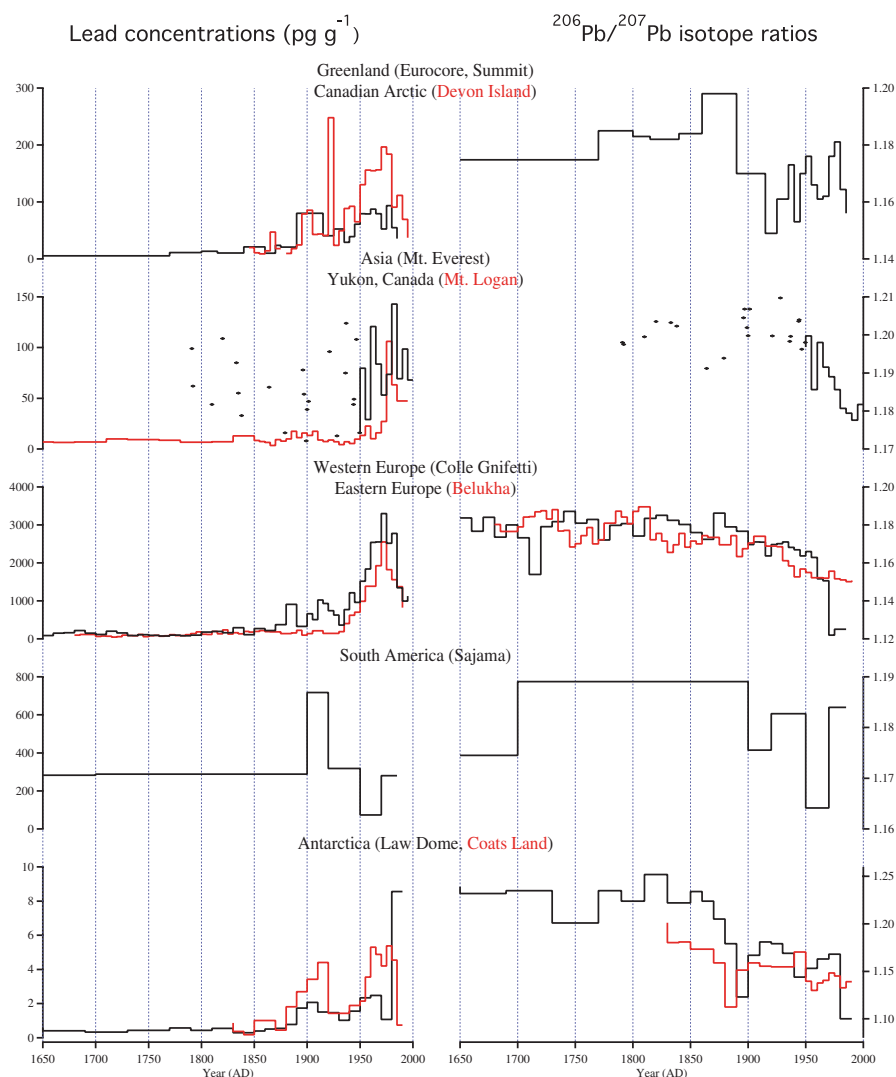
**Fig. 1** Lead concentrations (*left column*) and $^{206}Pb/^{207}Pb$ ratios (*right column*) in ice cores from Greenland (Eurocore, Rosman, pers. comm. and Summit, Rosman et al. 1993) and Devon Island (Shotyk et al. 2005b); Mt. Everest (Lee et al. 2011) and Mt. Logan (Osterberg et al. 2008); Colle Gnifetti (Schwikowski et al. 2004) and Belukha (Eichler et al. 2012); Sajama (Rosman et al. 2003) in South America; Law Dome (Vallelonga et al. 2002) and Coats Land (Planchon et al. 2003) in Antarctica

central Europe to report the development of atmospheric Pb pollution, particularly in Europe during the twentieth century. For example, Schwikowski et al. (2004) reported that Pb concentrations increased from ~0.2 ng g$^{-1}$ in 1800 AD to ~3 ng g$^{-1}$ by the 1970s (Fig. 1). Abundances of industrial Pb emissions from coal burning, mining and smelting were overwhelmed by the emissions from leaded gasoline in

the 1960s and 1970s. Through the measurement of Pb isotopes, it was determined that the Pb added to gasoline originated from various mines, including Broken Hill, in Australia, and the Mississippi Valley ore complex in the USA. The findings of these studies corroborate well with lake sediment (Farmer et al. 1996), moss (Rosman et al. 1998) and peat bog records (Kylander et al. 2005; Shotyk et al. 1998) across Europe. However, while these Pb records may agree in the general trends observed, the magnitude of the post-industrial increases in Pb pollution recorded in non-glacial archives remain uncertain as, for example, changes in catchment detrital input or scavenging of metals by organic matter may "magnify" the apparent metal inputs from the atmosphere. This should be kept in mind also when comparing other trace metals recorded in different archives.

Other records of Pb pollution have been reported from glaciated areas of North America, and these generally agree with the Greenland ice cores (i.e. peak Pb concentrations in the 1970s and 1980s followed by sharp decreases in concentration during the last two decades). Records have been reported from ice cores from Devon Island in Northeast Canada (Shotyk et al. 2005b; Zheng et al. 2007) and a peat bog record from Eastern Canada (Shotyk and Krachler 2010). Despite indications of recent lower atmospheric Pb concentrations over continental North America, Pb isotope ratios suggest that air here is still contaminated with Pb from the Asian continent (Shotyk and Krachler 2010; Shotyk et al. 2005b), and one record from Mt. Logan (Yukon, Canada) shows a strong increase of Pb concentrations attributed to the transport of pollutants across the Pacific Ocean from Asia since the 1980s (Osterberg et al. 2008). Recent work by Shotyk and colleagues (e.g. Shotyk and Krachler 2010) highlights the varying responses of different terrestrial compartments to decreasing anthropogenic Pb contributions; Pb is preferentially removed from lake basins, leading to lower enrichments compared to transport media such as streams, or fixed deposition sites such as ice, sediments and peat bogs.

Ice cores have been retrieved from various sites across Asia, from the Siberian Altai to the Himalayas and in the South American Andes. The most coherent Pb record is from the Siberian Altai (Eichler et al. 2012), spanning from 1680 to 1995 AD and demonstrating the influence of leaded gasoline and mining emissions from Russia between the 1940s and 1980s. Pb concentrations decreased after 1995 AD due to post-communist economic collapse. Lee et al. (2011) reported Pb concentrations and isotopic compositions in ice cores from the Himalayan East Rongbuk glacier at an altitude of 6518 m above sea level. The pollution record showed relatively constant Pb concentrations of about 50 pg g$^{-1}$ before 1959 AD, then higher concentrations (70–111 pg g$^{-1}$) between 1960 and 2002 AD. The data demonstrate the influence of leaded petrol from South Asia (predominantly India) until it was phased out in 1997 AD. Samples from 1997 to 2002 AD still showed high Pb levels which were attributed to fossil fuel combustion and non-ferrous metal production. Two ice core records of Pb pollution have been reported from Bolivian glacier archives. Hong et al. (2004) reported Pb concentrations in the Sajama glacier from 22,000 years ago until 1988 AD. When normalized to mineral dust inputs, Pb showed a clear enrichment from the start of the twentieth century which was approximately six times over pre-industrial levels. Lead isotope ratios, reported by Rosman et al. 2003 (Fig. 1), confirm that this enrichment was anthropogenic in origin. Correia

et al. (2003) investigated a suite of heavy metals in an ice core from the Nevado Illimani glacier also in Bolivia, finding that the concentrations and enrichment of heavy metals with respect to mineral dust inputs was seasonally dependent, with the preferential deposition of anthropogenically-emitted pollutants during the dry season (June to August). A well-resolved record of Pb concentrations and isotopic compositions covering the past few 1000 years' atmospheric deposition is still lacking from South America. Nevertheless, Cooke et al. (2008) reconstructed the distribution and intensity of metallurgical and industrial activity over the past 4000 years, from lake sediment records obtained in Peru and Bolivia. These records showed changes in the location and intensity of Pb emissions over the successive periods of Tiwanaku/Wari, Inca, Colonial and modern industrial culture.

A detailed history of Pb pollution in the Southern Hemisphere has been compiled from Antarctic snow and ice cores. Wolff and Suttie (1994) sampled an 8.3 m snow pit, the record from which shows Pb concentrations varying between 2–4 pg g$^{-1}$ from 1920 to 1950 AD, with a peak of ~7 pg g$^{-1}$ in the late 1970s and slightly lower values during the 1980s. Despite the possibility of contamination from overflights in the 1970s, their results agreed with reconstructions of southern hemisphere gasoline consumption. Vallelonga et al. (2002) produced a 500 year record of Pb concentrations and isotopic compositions from Law Dome. They found concentrations of ~0.4 pg g$^{-1}$ and $^{206}Pb/^{207}Pb$~1.22 until the onset of anthropogenic Pb pollution at about 1890 AD. Pb isotopic compositions observed at Law Dome around 1900 AD ($^{206}Pb/^{207}Pb$~1.12) clearly pointed to contamination from the Broken Hill Pb/Ag mine ($^{206}Pb/^{207}Pb$~1.04) in Southeastern Australia. Since the 1950s, Pb isotopic compositions have been consistent with inputs of products of combustion of gasoline added with Pb extracted in Australia, potentially emitted into the atmosphere of both hemispheres and deposited globally. Subsequent studies of Pb isotopes from other Antarctic coastal locations (Burn-Nunes et al. 2011; Hong et al. 1998; Planchon et al. 2003, 2002b; Van de Velde et al. 2005) have demonstrated similar pollution histories across the Antarctic continent, suggesting that the Antarctic cryosphere accurately archives Pb emitted from the continental landmasses of the Southern Hemisphere before the 1950s while afterwards it may also reflect Pb isotopic composition from global transport emission.

# Mercury

Gaseous elemental mercury (Hg$^0$) is the predominant atmospheric mercury (Hg) species, with an estimated residence time of ~1 year which allows long-range transport and inter-hemispheric mixing. However, the discovery at high latitudes of so-called "Atmospheric Mercury Depletion Events" (Schroeder et al. 1998) and post-depositional re-emission of Hg$^0$ from the snow pack (Durnford and Dastoor 2011) suggests that the residence time of Hg in the atmosphere is more difficult to define. Likewise, understanding to what extent Hg is deposited and preserved in the ice sheets and glaciers is complicated and mostly depends on the specific Hg form retained in the snow. Particulate Hg is intimately linked to the insoluble matrix and
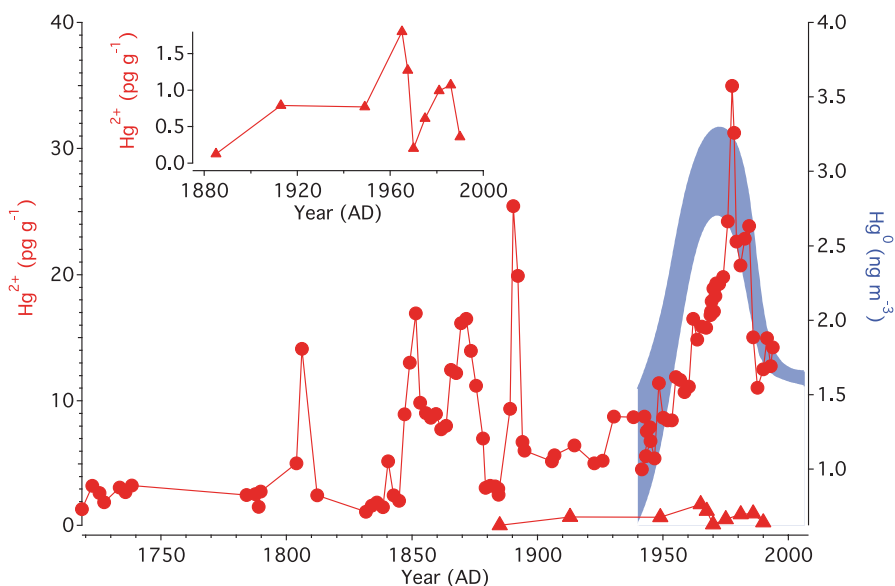
**Fig. 2** $Hg^{2+}$ concentrations in ice cores from Wyoming (*dots*, from Schuster et al. 2002) and the Western Alps (*triangles*, also in inset, from Jitaru et al. 2003) are compared with $Hg^0$ concentrations as recorded in interstitial air from Greenland firn (*shaded area*, indicating a range of maximum and minimum values, from Faïn et al. 2009)

is the most stable species found in glaciers (Jitaru et al. 2009), while $Hg^{2+}$ can react quickly to form $Hg^0$ and is re-emitted from the snow into the atmosphere (Ferrari et al. 2004). Taking all these processes into account, records of total Hg (here defined as particulate $Hg + Hg^{2+}$) within snow and ice layers in the Antarctic and Greenland ice sheets may provide some constraints in answering the long standing questions on Hg origin (natural vs. anthropogenic) in the modern atmosphere and whether its deposition is due to local, regional or global sources.

Only a few ice core records reliably report Hg concentrations during modern times. This is mainly due to the fact that most of the early records were affected by contamination during field sampling and/or laboratory analysis. An ice core time series of Hg is available from Greenland (Fig. 2), covering a 40 year period from 1949 to 1989 AD (Boutron et al. 1998). This record basically provides $Hg^{2+}$ concentrations because particulate Hg was not detectable by means of the extraction technique used. In this core $Hg^{2+}$ concentrations ranged from less than 0.05 to 2 pg g$^{-1}$. Although these values are very low and do not represent total Hg, they could not be explained in terms of a natural contribution alone. Therefore it was suggested that Hg deposition to the Greenland ice sheet was influenced by the anthropogenic input from the North Hemisphere, possibly linked to coal and solid waste combustion. A recent report, however, emphasizes gold mining as an important global source of atmospheric Hg (UNEP 2013). A successive study from a firn shallow core extracted from the same Greenland site confirms Hg concentrations to fall within the range previously determined (Mann et al. 2005).

It is noticeable that the Boutron et al. (1998) Greenland record shows an apparent peak in $Hg^{2+}$ concentration between the late 1940s to the mid 1960s. Similarly, a recent study found that $Hg^0$ concentrations determined in the interstitial air of the Greenland firn (Fig. 2) started to increase in the 1940s and reached a peak of 3 ng m$^{-3}$ around 1970 AD, subsequently decreasing and stabilizing around 1995 AD (Faïn et al. 2009). In this context, $Hg^{2+}$ and $Hg^0$ determined in the firn and in its interstitial air, respectively, appear to be correlated to some extent, suggesting that $Hg^{2+}$ determined in firn and ice cores may be linked to atmospheric $Hg^0$ concentrations. Accordingly both US and Europe sediment and peat record reconstructions show higher deposition of atmospheric Hg during the 1970s (Pirrone et al. 1998; Bindler 2003), which is also broadly simultaneous with the 1970s peak in worldwide production on the order of $10^7$ kg y$^{-1}$ (USGS 2006). While Arctic sediment records of $Hg^{2+}$ show a similar global trend (Biester et al. 2007; Muir et al. 2009), it is not clear whether these can be affected by climate-driven biophysical processes, which could modify the recorded history of atmospheric Hg deposition (Goodsite et al. 2013).

A mid-latitude Hg ice core record was also reconstructed from the Upper Fremont Glacier in Wyoming, North America (Schuster et al. 2002). This glacier is temperate and thus is more prone to post depositional processes. However, the low solubility of the Hg compound detected ($Hg^{2+}$) might have reduced the impact of melting processes on this record, which shows some features that broadly resemble that from the Greenland ice sheet (Fig. 2) and global Hg production. According to the Upper Fremont Glacier record $Hg^{2+}$ concentrations started to rise during the 1950s and peaked during the 1970s and 1980s (20–25 pg g$^{-1}$), followed by an abrupt decrease in the 1990s (10–15 pg g$^{-1}$). The 5-fold increase in the $Hg^{2+}$ depositional rate from pre-industrial times to the mid-1980s is consistent with the corresponding increases determined in sediment records from North America (Pirrone et al. 1998), and is perhaps linked to the proximity of this site to industrial sources. A low-resolution $Hg^{2+}$ and methylmercury (MeHg) record was also obtained from an ice/snow core drilled at an altitude of 4250 m in the Col du Dome glacier on Mont Blanc, France (Jitaru et al. 2003). In this case, at the beginning of twentieth century an increase in $Hg^{2+}$ was observed with a maximum six-fold increase at 1965 AD (1.80 pg g$^{-1}$) compared to 1885 AD (Fig. 2). Here we argue that the large difference in absolute $Hg^{2+}$ concentration between the Upper Fremont Glacier and Mont Blanc ice cores, in addition to the different potential source areas for these regions, could be largely ascribed to the different fractions analyzed by means of the two analytical methods used.

Altogether, the few existing ice and firn records support the hypothesis that a recent deposition of anthropogenic Hg has occurred on a large (continental to hemispheric) spatial scale. The rapid industrial development in the Northern Hemisphere may have caused an increase in atmospheric Hg levels after World War II. Conversely, the decline observed since the 1970s is likely a response to the Clean Air Act of 1970 and similar European regulations. It is now imperative to determine Hg in ice cores from the Himalaya and the Tibetan Plateau glaciers. If regional Hg transport is predominant, records from these ice cores would indeed be well suited

to reflect the recent continental increase in Hg emissions due to the rapid ongoing industrialization in this part of the world (Pirrone et al. 2010). So far Hg has been determined in this region only in snow pit samples, yielding results that are indicative of modern deposition in the Himalayan and Tibetan Plateau regions (Zhang et al. 2012; Wang et al. 2008a). In this case concentrations were found to be on the same order as those recorded in the snow and firn records from the other glaciers around the world, perhaps supporting the view of a large scale transfer and deposition of Hg. A ~700 years record of Hg in eggshells from Guangjin Island (South China Sea) indicates a rapid increase in Hg deposition since ~1800 AD (Xu et al. 2011). In other records obtained from Tibetan plateau lake sediment, the most significant increase in Hg pollution was shown to occur since the 1970s, followed by a further marked increase in the 1990s (Yang et al. 2010). This is also consistent with a three-fold increase in atmospheric Hg deposition since the advent of the Industrial Revolution as recorded in Alaskan lake sediments (Fitzgerald et al. 2005).

## Platinum Group Elements

Platinum Group Elements (PGEs) are constituted by rhutenium (Ru), palladium (Pd), rhodium (Rh), osmium (Os), platinum (Pt) and iridium (Ir). These metals are depleted in the upper terrestrial crust (0.05–0.4 ng g$^{-1}$) (Wedepohl 1995) and enriched in the terrestrial mantle and in meteorites (Anders and Grevesse 1989). Since the mid-1970s Pt, Pd and Rh have been widely employed as catalysers to reduce the emissions of unburned hydrocarbons (HC), carbon monoxide (CO), and nitrogen oxides (NOx) from automobile traffic. The first vehicles equipped with catalytic converters adopting Pt, Pd and Rh were constructed in the mid-1970s in North America and Japan and, beginning in the 1980s, in Europe, particularly Germany. This resulted in a well documented decrease in HC, CO and NOx emissions and indirectly a decrease in environmental Pb pollution (Boutron et al. 1991) because the new catalytic converters required the use of unleaded gasoline. However, the increasing use of Pt and particularly Pd and Rh by the automobile industry raised some concerns about their possible toxicity for humans and the environment.

Several studies have demonstrated that urban and roadside PGEs concentrations are higher than in rural areas as a result of automobile emissions (Rauch et al. 2005, 2006; Rauch and Fatoki 2013). However, few studies have shown a temporal increase in PGEs concentrations. Ice cores provide an opportunity to reconstruct such trends. A methodology aimed at determining Pt, Pd and Rh in snow and ice at the pg g$^{-1}$ level by ICP-SFMS was developed by Barbante et al. (1999). Using this procedure Pt, Pd and Rh were determined in the Dome de Goûter ice core which was extracted from Mt. Blanc (French-Italian Alps) and covered the 1778–1991 AD time intervals (Van de Velde et al. 2000a). Pd and Rh concentrations were found to be about two times higher during the second half of the twentieth century than in ancient ice, with values ranging up to 10 and 0.2 pg g$^{-1}$, respectively. A parallel study, conducted in the Swiss-Italian Alps at Colle Gnifetti, substantially confirms the results obtained for the Mt. Blanc core and also suggests a two-fold increase

in Pt concentrations with values up to 0.8 pg g$^{-1}$ (Barbante et al. 2004). Relatively high levels of Pt, Pd and Rh were determined in shallow snow and firn samples from central Greenland dated from the last few decades and were interpreted to be mainly a consequence of hemispheric pollution by these metals due to emissions from vehicles equipped with catalytic converters during the 1990s (Barbante et al. 2001b, 2003).

However, in a more recent study (Gabrielli et al. 2008), Pt was determined a second time in these same 1990s Greenland samples by means of a more sensitive technique which extends detection to the sub fg g$^{-1}$ level (Gabrielli et al. 2004). In this case, only a few Pt spikes were found, with concentrations ranging from 37 fg g$^{-1}$ to 90 fg g$^{-1}$, 5–15 times higher than the background but lower by about one order of magnitude than the Pt concentrations previously determined. This suggests that the supposed load of anthropogenic Pt to the northern Arctic latitudes was lower than previously assumed. These more recent Pt data, while still suggestive of a hemispheric Pt contamination, re-evaluated the concept of the hemisphere-scale diffusion of atmospheric Pt. Aside from this research, significant recent Pt enrichments were found in the Northern Hemisphere only in urban sediments where a 40-fold increase was observed over the pre-1975 background (Rauch and Hemond 2003; Rauch et al. 2004).

In Greenland snow sampled during the 1990s, low background concentrations of Ir (1–2 fg g$^{-1}$) were concomitant with the few Pt spikes, possibly reflecting that only traces of Ir were present in the majority of the catalytic converters at that time and that the natural atmospheric budget of Ir was not perturbed at hemispheric spatial scales (Gabrielli et al. 2008). Ir was in fact widely used only in small quantities by chemical and electrochemical industries, and in electronics. Only more recently Ir was included in new generation automobile catalysts but it remains unclear to what extent all these human activities might affect the Ir natural budget. Only a few other sediment studies have attempted to evaluate the recent deposition of Ir and only in the urban environment. For example Ir was found to increase by up to 5 times in Northern Hermisphere lake sediments near Boston (USA), following the introduction of automobile catalysts (Rauch et al. 2004).

Recently Soyol-Erdene et al. (2011) determined Pt, Ir and Rd in snow samples collected from two pits excavated in Queen Maud Land, East Antarctica and covering the 1957–2000 AD period. The average 50-year concentrations in Antarctic snow were: 7 fg g$^{-1}$ (4.7–76 fg g$^{-1}$) for Pt, 0.12 fg g$^{-1}$ (0.05–0.34 fg g$^{-1}$) for Ir, and 0.71 fg g$^{-1}$ (0.12–8.8 fg g$^{-1}$) for Rh. These records illustrate the recent natural (volcanic) and anthropogenic contribution to the Antarctic continent for these trace elements. Significant enrichment in Pt and perhaps in Rh suggested large scale pollution since the 1980s for these two metals (Fig. 3). This was possibly due to anthropogenic sources such as automobile catalysts (introduced in 1987 AD in Australia and 1996 AD in Brasil-Argentina) and metal production processes (South Africa is the single largest PGEs producer). In contrast, no detectable Ir enrichment was observed. The possible anthropogenic Pt enrichment and negligible Ir in Antarctic firn are consistent with the preliminary information from the Greenland snow pit record (Gabrielli et al. 2008), perhaps suggesting a recent and detectable global Pt contamination concomitant with a negligible large scale diffusion of anthropogenic Ir.
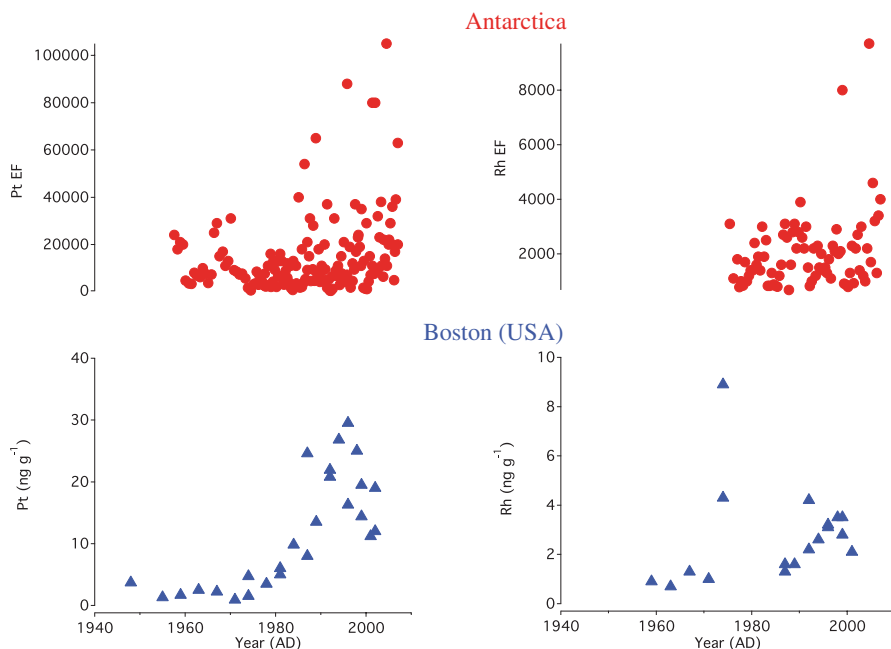
**Fig. 3** Crustal enrichment factors of Pt (*top left*) and Rh (*top right*) from two snow pits in Central Antarctica (*dots*; from Soyol-Erdene at al. 2011) and concentrations of Pt (*bottom left*) and Rh (*bottom right*) in two sediment cores from the urban area of Boston, USA (*triangles*; from Rauch et al. 2004)

## Other Trace Elements

Investigations on many other trace elements started in the polar ice sheets and are now extending to lower latitudes with the study of firn and ice collected from high altitude glaciers. In central Greenland a recent increase in trace element concentrations in snow and ice dated between 1773 AD and the 1960–1970 AD was found for cadmium (Cd; 8 times), copper (Cu; 4 times) and zinc (Zn; 5 times) (Candelone et al. 1995), indicating hemispheric contamination of the atmosphere for these trace elements (Cu and Zn are displayed in Fig. 4). As a result of the policy initiatives aimed at limiting atmospheric pollution in the USA and Europe, Cd and Zn concentrations have decreased by a factor of ~2 in Greenland snow between the end of the 1960s and the beginning of the 1990s (Boutron et al. 1991). The crustal enrichment factors, or EFc (a comparison of trace element mass ratios determined in the ice and in the terrestrial crust, typically using aluminum as a normalizing factor) of Cd and Zn decreased respectively from 186 and 19 in 1967 AD, to 58 and 6.3 in 1989 AD, suggesting a large scale reduction in the anthropogenic component of these two trace elements that are typically emitted during combustion of fossil fuels, nonferrous metal production, steel and iron manufacturing and incineration
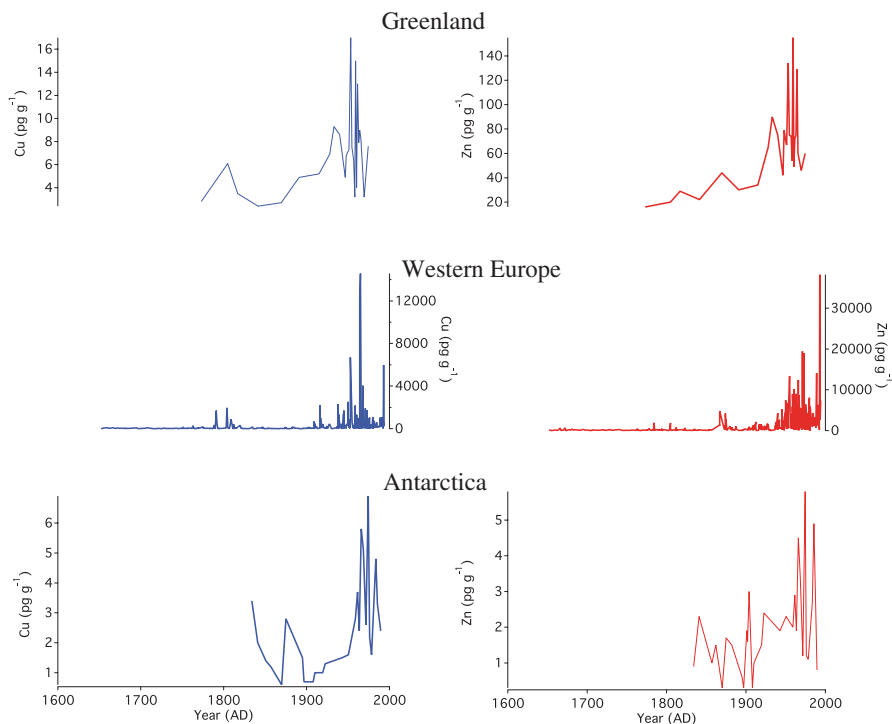
**Fig. 4** Cu (*left column*) and Zn (*right column*) concentrations in a Greenland ice core (from Candelone et al. 1995), in a Western Alps ice core (from Barbante et al. 2004) and in Antarctic firn (from Planchon et al. 2002a)

of refuse (Nriagu and Pacyna 1988). In contrast, a significant decrease in Cu concentration was not found (Candelone et al. 1995), probably due to its still relatively important natural emission sources of windborne mineral dust.

The advent of the continuous flow analysis technique coupled to ICP-SFMS allowed more detailed investigation of the history of trace element pollution in the Northern Hemisphere. Cd and thallium (Tl) which were determined in Greenland snow and ice showed that atmospheric deposition for these elements was high by the early 1900s, with a tenfold increase from preindustrial levels (McConnell and Edwards 2008). The levels found at the beginning of the last century were 2–5 times higher than during recent decades. This early increase occurred after 1860 AD and was attributed to coal burning in North America and Europe. In this study the different signature of sources of trace elements emissions over time, from coal-dominated industrial (1860–1940 AD) to oil-dominated industrial (1940–2003 AD) was also distinguished. A Tl peak, indicating a marked enrichment at the beginning of the last century, was also recorded in a Swiss peat bog (Shotyk and Krachler 2004).

In the Canadian High Arctic Tl, and silver (Ag) were determined in snow and ice collected from Devon Island indicating a predominant recent anthropogenic

contribution for these metals (Krachler et al. 2008b). In this core also antimony (Sb) was studied showing concentrations increasing 6–8 times during the last century and peaking during the 1950–1960 AD time period, reflecting contamination from industrialization, the economic growth that followed World War II, as well as the introduction of flue gas filter technologies (Krachler et al. 2008a, 2005). The modern Sb EFc (referenced to scandium) was ~25 and may have resulted from Asian production of Sb sulfides such as stibnite ($Sb_2S_3$) and as a by-product of Pb and Cu smelting. Starting perhaps several thousands of years ago, the Devon Island ice core suggests a 5-fold enrichment above the natural background for Sb, arsenic (As) and bismuth (Bi), which was attributed to mining and smelting emissions as a co-product of ancient Pb sulphide ores (Krachler et al. 2009). As noted before, Pb emissions from mining activities during the Greek and Roman periods were detected in Greenland (Hong 1994, Rosman 1998). Additional evidence of large scale Sb contamination during the Roman and also the Medieval Period was provided through analyses of peat samples from various bogs in Europe (Shotyk et al. 2005a, and references therein).

In the western European Alps Cd, Cu and Zn were determined in snow and ice from Dome de Goûter, Mt. Blanc (Van de Velde et al. 2000b). Concentrations were constant until the end of the nineteenth century and then they increased 10, 15 and 30 times for Cu, Cd and Zn, respectively, until the 1970s. During the following two decades Cd and Zn concentrations decreased while Cu continued to increase. Cobalt (Co), chromium (Cr), molybdenum (Mo), and Sb were also determined in this core. Concentrations in recent firn were found to be generally higher than in ice dated from before the middle of the nineteenth century. Mo displays the strongest increase (16 times), followed by Sb (5), Co (2–3) and Cr (2–3) (Van de Velde et al. 1999). In this latter study it was suggested that enrichments in Co, Mo, and Sb were due to contributions from oil and coal combustion while Cr originated from Fe, steel, and Fe-alloy industries. In this core from Mt. Blanc a significant increase factor (3) was found also for U in post-World War II layers and was attributed to tropospheric transport of dust emitted during extensive mining and milling operations, mainly in the former German Democratic Republic (Barbante et al. 2001a).

In the western Alps trace elements were also determined in another ice core extracted from the glacier saddle of Colle Gnifetti, Monte Rosa at 4450 m of elevation, and with a time scale spanning from 1650 to 1994 AD. Higher concentrations were found during the second half of the twentieth century than in the seventeenth and eighteenth centuries. The highest increase were observed for Cd (36 times), Zn (19), Bi (15), Cu (11), and nickel (Ni; 9), suggesting a significant input of these trace elements to the central European atmosphere (Fig. 4 displays trends for Cu and Zn) (Barbante et al. 2004). Consistent with the ice core results, Cu, Zn and Cd were also found to increase until about 1960 AD in sediment cores from Lake Zurich (Switzerland) (von Gunten et al. 1997). However, Cu and Cd decreased sharply afterwards in the sediment records, in accordance with the trend registered in the Mt. Blanc ice core. In the eastern European Alps only a few trace element data are available from a snow pit dug on Mt. Ortles in 2009 at 3830 m of elevation. These suggest a pollution source in the adjacent Po' Valley in Italy (Gabrieli et al. 2011a).

The first trace element data from the high altitudes of Central Asia were extracted from a firn/ice core drilled at an elevation of 7010 m near the top of Muztagh Ata glacier, east Pamirs, which was dated from the mid-1950s to 2000 AD. Increases in concentrations were observed for Sb (three times) and perhaps Bi (two) from the mid-1960s to the beginning of the 1990s (Li et al. 2006). In another study in Central Asia, trace elements were quantified in an ice core recovered from the Miaoergou glacier in the eastern Tien Shan, spanning the period 1953–2004 AD. Also in this case only slight enhancements in concentrations were observed for Cd (2.7), Sb (1.8), Bi (1.5), Tl (1.2), and tin (Sn) (1.6) during the 1953–2004 AD time period, perhaps due to enhanced anthropogenic emissions from activities such as metal smelting, mining, stationary fossil fuel combustion, and combustion of gasoline in Eurasia, particularly Xinjiang in northwestern China, Russia, and Kazakhstan (Liu et al. 2011).

In the high-altitude Himalayan glaciers trace elements from 1650 to 2002 AD were determined in a Mount Everest ice core drilled at 6518 m elevation. Bi, U, and cesium (Cs) concentrations and EFc's were found to have increased since the 1950s. The likely sources for the enrichment of Bi included mining, metal smelting, oil and coal combustion, as opposed to mining and refinement as the sources for U and Cs (Kaspari et al. 2009). As, Mo, Sn, and Sb were determined over the period from 1205 to 2002 AD in another high-altitude ice core from Mt. Everest. Compared to the pre-1900 period, increases in concentrations and EFc were observed after the 1970s, with the highest increase in EFc for Sn (2.6) and the lowest for As (1.4) in the 1995–2002 AD period (Hong et al. 2009). The increases in these elements were attributed to increased anthropogenic emissions from stationary fossil fuel combustion and nonferrous metals production, likely in India.

Few trace element data are available from tropical high altitude glaciers in the Southern Hemisphere. The 137 m ice core drilled at the summit of Nevado Illimani (6350 m) in the eastern Bolivian Andes was analyzed for various trace elements from the section dated from 1919 to 1999 AD. Significant increases were observed for the concentrations of several species such as Cu (2–6 times), As (2), Zn (2–4), Cd (2–4), Co (2–15), Ni (2–10) and Cr (2–5) (Correia et al. 2003). Other ice core sections from a snow/ice core drilled at an altitude of 6542 m on the Sajama ice cap in Bolivia were also analyzed for various trace elements. In this case increasing trends were observed for Cu, Zn, As, Ag, Cd and Bi during the nineteenth and twentieth centuries (Hong et al. 2004). In this period an increase of EFc values was found for As (5), Bi (7), Cu (2), Zn (4), Ag (5) and Cd (5). The notable excesses in Cu, Zn, Ag and Cd were attributed to metal production activities, especially in Peru, Chile and Bolivia where a continuous increase in production occurred during the twentieth century.

In the most remote sites of the Southern Hemisphere, recent enrichments of trace elements in Antarctic snow and ice were detected with more difficulty than in the Arctic due to the lower concentrations and the greater isolation of Antarctica from emission sources in the Southern Hemisphere. Measured concentrations of Cd, Cu and Zn in snow from Adelie Land in East Antarctica were initially found not to have significantly increased during the time period 1940–1980 AD (Görlach and Boutron

1992). In a core from Law Dome in East Antarctica, enrichments of Cu concentrations during the twentieth century were observed to be greater by a factor of 1.5 than during earlier centuries, consistent with increasing anthropogenic emissions for Cu over that period (Vallelonga et al. 2004). In another study conducted on samples collected from a deep snow pit dug in Coatsland in West Antarctica, Cu showed a 2-fold increase (from ~2 to ~4 pg g$^{-1}$) during the period from 1923 to 1986 AD (Wolff et al. 1999). This increase of Cu in Antarctic snow was suggested to originate from South American smelters emissions that are advected relatively far to the south compared to other Southern Hemisphere emissions. Analysis of samples from the same snow pit also found pronounced enhancements after the mid 1940s for Cr (2–4), Zn (2–4), Cu (~4), Ag (~7), Bi (~10) and U (~5) (Planchon et al. 2002a) (Cu and Zn are displayed in Fig. 4). The enrichments were attributed to emissions from human activities in Southern America, Southern Africa and Australia, especially from non-ferrous metal mining and smelting in Chile, Peru, Zaire, Zambia and Australia. Interestingly an enrichment peak in Cr, Bi and perhaps U was found in this Antarctic snow pit at the beginning of the twentieth century, similar to the corresponding trace element enrichment found in the Arctic at about the same time (McConnell and Edwards 2008).

## Organic Compounds

Environmental monitoring of organic pollutants in snow and ice started only recently and has led to regional studies of pesticide exposure (Ruggirello et al. 2010) as well as the investigations of other types of human related activity, such changes in fuel use (Gabrieli et al. 2010). The delay in the relatively recent development of these studies was also due to the challenging techniques required to determine organic compounds in the environment. Some of them, such as polycyclic aromatic hydrocarbons (PAHs) and persistent organic pollutants (POPs), require pre-concentration on compound-specific solid phase extraction columns coupled to separation devices such as high pressure liquid chromatographs or gas chromatographs. In addition, the sensitivity required to detect and quantify very low concentrations of organic compounds in polar ice and snow could be achieved with the latest generation of mass spectrometers, such as ion trap or triple-quadrupole mass spectrometers (Gambaro et al. 2008).

The first category of organic pollutants detected in ice cores was PAHs, a class of relatively non-reactive organic compounds. PAHs are by-products of the incomplete combustion of various fossil fuels, including fuel oil, gasoline and coal, as well as biomass burning. PAHs are of interest because they are a threat to human health: they have been identified to have carcinogenic and mutagenic properties and have been listed by the US Environmental Protection Agency (USEPA) as a "priority pollutant". PAHs were first studied in ice cores in the 1990s in central Greenland where Kawamura et al. (1994) reported a 400-year ice-core record that demonstrated a 50-fold increase from pre-1800 background concentrations (2.3 pg g$^{-1}$)

to late twentieth century values (103 pg g$^{-1}$). Jaffrezo et al. (1994) investigated 13 PAHs in a Summit snow pit corresponding to 4 years of deposition. They reported average total PAHs concentrations of 1360 fg g$^{-1}$ and observed a distinct seasonal cycle of summer minima, elevated winter concentrations and spring peaks. These observations were reproduced and refined by Masclet et al. (1986) with a second Summit snow pit record covering the period from 1993 to 1996 AD. They found that total PAHs concentrations correlated well with black carbon concentrations (with an average PAHs/carbon ratio of 0.1%). Concentrations of fluoranthene and pyrene, indicators of coal and fuel-oil combustion sources, were found to be well correlated with sulfate, a byproduct of coal combustion. High concentrations of retene, an indicator of boreal forest fires, were not always coincident with high ammonium concentrations.

Gabrieli et al. (2010) presented a record of PAHs concentrations over the past 300 years in the Alpine ice core from Colle Gnifetti on Mt. Rosa which demonstrated the overwhelming increase of PAHs in Europe since the nineteenth century. Total concentrations increased from 2 pg g$^{-1}$ before 1875 AD to peak values of 32 pg g$^{-1}$ between 1945 and 1955 AD, followed by decreasing levels since the 1970s. A different industrial development history for Asia is reflected by the PAHs record from the East Rongbuk glacier in the Himalayas (Wang et al. 2008b), where fluxes increased continuously to 8 ng cm$^{-2}$ y$^{-1}$ in the late 1990s. This history suggests a predominantly Indian source for the emissions transported to the Himalayas, with PAHs co-deposited with excess sulfates. Accordingly, a lake sediment record from the Northeastern Tibetan Plateau (Wang et al. 2010b) shows total PAH fluxes at about 0.3 ng cm$^{-2}$ y$^{-1}$ in 1860 AD, and increasing greatly after 1960 AD to approximately 14 ng cm$^{-2}$ y$^{-1}$, reflecting the somewhat earlier development of industry in China (Fig. 5). In this latter case, fluxes of the 16 USEPA-listed priority PAHs similarly varied from 0.2 ng cm$^{-2}$ y$^{-1}$ in 1860 AD to 11 ng cm$^{-2}$ y$^{-1}$ after 1960 AD.

A second category of organic pollutants that has been studied in ice cores involve POPs, which is an umbrella term that refers to bio-accumulative, long-lived organic compounds that present a public or environmental health threat, such as polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs, including aldrin, DDT, and dieldrin). Since the 1970s many of these compounds have been regulated or banned in some way, and the Stockholm Convention on POPs in 2004 enforced the prohibition of the production and use of 16 of these compounds in 151 countries. Glaciers have great potential for the study of POPs because they act as "cold condensers", i.e., concentrating POPs by removing them from the atmosphere (Daly and Wania 2004). Unfortunately, the very glaciers that accumulate POPs are the same ones that provide drinking and irrigation water to highly populated areas and are now rapidly melting due to climate change. Schmid et al. (2010) conducted a compelling study of the release of POPs into downstream freshwater systems decades after being first used as pesticides.

In a series of papers (Maggi et al. 2006; Villa et al. 2001, 2003), Villa and colleagues reported historical profiles of PCBs since the 1950s from the Lys Col, next to Mt. Rosa in the Western Alps. They found that hexachlorocyclohexane (HCH) concentrations peaked at 20 pg g$^{-1}$ in the 1970s and then decreased and stabilized
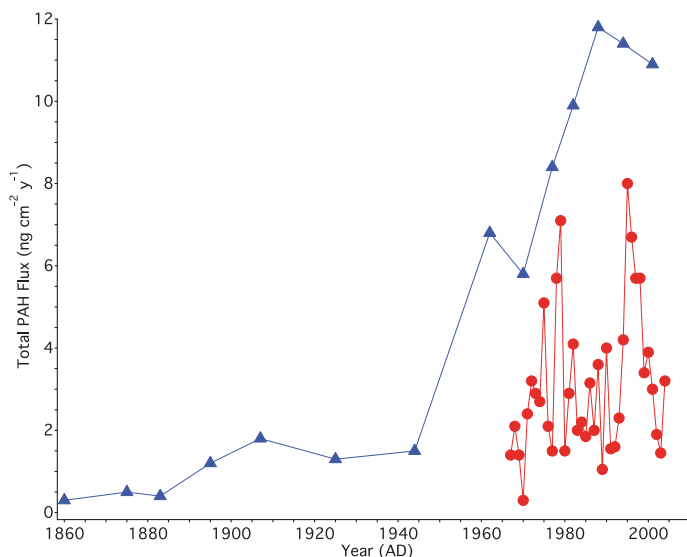
**Fig. 5** Total PAH fluxes determined from an ice core from the Dasuopu glacier in the central Himalayas (*circles*, from Wang et al. 2008b) and from a sediment core from Qinghui Lake on the Tibetan Plateau (*triangles*; from Wang et al. 2010b)

at 0.5 pg $g^{-1}$ after 1980 AD. In contrast, DDT concentrations steadily increased from 1 pg $g^{-1}$ in 1965 AD to 10 pg $g^{-1}$ in 1996 AD; this trend was attributed to a local factory that produced DDT as a precursor to difocol pesticide. These findings were confirmed by similar DDT trends in the sediments of nearby Lake Maggiore (Guzzella et al. 1997). First Hermanson et al (2005) and then Ruggirello et al. (2010) provided a comprehensive evaluation of current and past pesticide concentrations in snow and ice from Svalbard, a remote polar island which has no history of pesticide use. The latter demonstrated the persistent and extensive distribution of POPs like HCH, chlordane, DDE (a DDT byproduct) and dieldrin, most of which had decreasing flux trends. Chlordane fluxes decreased from ~15 pg cm$^{-2}$ y$^{-1}$ in 1990 AD to ~5 pg cm$^{-2}$ y$^{-1}$ in 2000 AD and dieldrin had steadily decreased from 55 pg cm$^{-2}$ y$^{-1}$ in 1950 AD to 5 pg cm$^{-2}$ y$^{-1}$ after 1995 AD.

Studies of North American glaciers reveal a similar history of accumulation of POPs in ice long after being banned. Donald et al. (1999) reported concentrations of DDT, chlordane and dieldrin in a temperate glacier in western Canada, observing that peak values (2.6 pg $g^{-1}$ for DDT, 0.05 pg $g^{-1}$ for dieldrin, 0.07 pg $g^{-1}$ for chlordane) occurred in the 1980s and 1990s, a decade or more after being phased out in the US. While evaluating the release of PCBs from a snowpack in Banff National Park, Blais et al. (2001) found that at least 10 % of the summer glacial melt contained PCBs which had been deposited between 1950 AD and 1970 AD. Comprehensive studies of POPs in lake sediments, soils and aerosols have also been conducted in North American watersheds (e.g. Hornbuckle et al. 2006), generally demonstrating post-1970s peaks in POPs concentrations and, more recently, slowly

declining concentrations. However, at the Agassiz Ice Cap (Ellesmere Island, Canadian Arctic) no evidence of a consistent long-term trend PCB deposition was found for the period 1963–1993 (Gregor et al. 1995).

Extensive studies of POPs have also been conducted in Himalayan glaciers (Wang et al. 2010a, 2010b, 2008b), in which it was shown that DDT concentrations peaked at about 2 pg g$^{-1}$ in the 1970s and then decreased sharply to 0.2 pg g$^{-1}$ after being banned in India in 1989 AD. HCH concentrations similarly peaked at about 6 pg g$^{-1}$ in the early 1970s but dropped to about 1 pg g$^{-1}$ after 1980 AD. These trends further confirmed the dominant Indian source of pollutants to the East Rongbuk Glacier. A study of POPs in the Dasuopu Glacier demonstrated a strong winter enhancement of those PAHs related to the use of heating fuel, with total concentrations below 26 pg g$^{-1}$ and DDT concentrations at about 0.2 pg g$^{-1}$. Concentrations of all PAHs in the Dasuopu Glacier have been steadily decreasing from their highest values at ~2000 AD (Wang et al. 2008a).

Studies of organic pollutants in Antarctica have been limited. Fuoco et al. (2012) recently reported PAHs and PCBs levels in snow and ice from Talos Dome in coastal East Antarctica. They found a sharp increase in PCBs since 1930 AD with occasional spikes related to volcanic eruptions. PAH concentrations increased by 50% and PCBs by 200% after 1930 AD. Kang et al. (2012) studied OCP deposition in surface snow over a traverse from the coast to Dome Fuji in central East Antarctica. Although they did not sample older snow or ice, they observed that Antarctic concentrations of HCH were 2 to 20 times lower than concentrations found in glaciers in Norway and Svalbard.

An emerging new field of research concerns brominated flame retardants (BFRs). These are a class of compounds used to slow the diffusion of flame in residential and commercial indoor fabric, foam, and electronic products in the industrialized world. An atmospheric BFR deposition history was identified in an ice core extracted in the Svalbard including including hexabromocyclododecane (HBCD), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), decabromodiphenyl ethane (DBDPE), pentabromoethylbenzene (PBEB), and 15 polybrominateddiphenyl ether congeners (PBDE). It was found that the greatest inputs were HBCD and BDE-209, 910, and 320 pg cm$^{-2}$ year$^{-1}$ from 1995 to 2005 (Hermanson et al. 2010). Finally, polybrominated diphenyl ethers (PBDEs) and Perfluoroalkyl substances (PFASs) were detected in a 1997–2007 AD shallow firn core from Colle Gnifetti in the Alps (Kirchgeorg et al. 2013).

## Black Carbon

Several findings and developments have recently been reported regarding the environmental impacts of another important organic compound. Elemental carbon (EC) or black carbon (BC) (see Rose and Ruppel, this volume), which is commonly called soot, is primarily emitted from the combustion of biomass and coal, thus making it a proxy related to both natural combustion processes and industrial

development (Ramanathan and Carmichael 2008). An important consideration regarding the emission of BC is its highly refractory nature; it is a strong absorber of solar energy and thus has a very strong radiative forcing effect (McConnell 2010). Because the accumulation of BC on glacier ice reduces the albedo while BC in the atmosphere may also amplify the current warming trends at high altitudes (Ramanathan and Carmichael 2008), reduction of anthropogenic emissions can be an effective measure for inhibiting melt. The study of BC has been accelerated by the development of the Single Particle Soot Photometer, an instrument that is field-portable, has sufficient sensitivity to study BC in aerosols as well as in polar ice, and can be coupled to continuous flow analysis systems commonly used for analysis of ice cores at high resolution. Highly-resolved records of BC deposition describing the industrial development of the Northern Hemisphere have been produced from Greenland ice. There was a seven-fold increase in BC concentrations from 1.7 ng g$^{-1}$ before 1850 AD (the start of the industrial era) to peak concentrations of about 12 ng g$^{-1}$ in 1910 AD, with lower concentrations of 2.3 ng g$^{-1}$ since 1955 AD (McConnell et al. 2007). Kaspari et al. (2011) reported a three-fold increase in BC concentrations in the East Rongbuk Glacier, from background levels of 0.2 ng g$^{-1}$ from 1860 to 1975 AD up to 0.7 ng g$^{-1}$ between 1975 and 2000 AD. In the Alps BC concentrations were determined in an ice core from Colle Gnifetti and were found to vary between 7 and 128 ng g$^{-1}$ increasing by a mean factor of 3.7 between preindustrial (1755–1890 AD) and modern times (1950–1975 AD) (Lavanchy et al. 1999). These results were essentially confirmed by further analyses from another Colle Gnifetti core, although with lower maximum concentrations (20 ng g$^{-1}$), during modern times (Thevenon et al. 2009). These studies are also consistent with EC analyses (in a range of 6–50 ng g$^{-1}$) performed in the alpine core from Fiescherhorn glacier (Switzerland) (Jenk et al. 2006). A recent study of BC deposition at two Antarctic sites from 1850 to 2000 AD indicates that any anthropogenic contribution to Antarctic BC fluxes is minimal (Bisiaux et al. 2012). These results may be due to a hemispheric gradient in anthropogenic biomass burning emissions, with greater emissions in the Northern Hemisphere than in the Southern Hemisphere.

## Radionuclides

After the detonation of the first atomic bombs, radionuclides started to be deposited and can be detected in ice strata dated to 1945 AD (Kudo et al. 1998). The intentional release or accidental loss of radioactive materials to the environment has been closely monitored (Carter and Moghissi 1977). The earliest atomic bombs operated on the same principle as fission nuclear reactors. After 1952 AD, thermonuclear weapons were developed, involving combined fission-fusion reactions and resulting in much greater energy yields and radionuclide production. Atmospheric testing of nuclear weapons was not regulated until the signing of the 1963 AD "Limited Test Ban Treaty", after which an additional 64 above-ground tests were conducted until 1980 AD, when all such tests were banned (Norris and Arkin 1988). The

most serious cases of accidental release of radionuclides involve nuclear power plant accidents, such as Chernobyl (Ukraine 1986 AD) and Fukushima (Japan 2011 AD). The presence of radioactive material in snow and ice is quantified either by β-radioactivity or specific detonation byproducts including tritium ($^3$H) and isotopes of chlorine ($^{36}$Cl), iodium ($^{129}$I), cesium ($^{137}$Cs) and plutonium ($^{239}$Pu). In this section we explore three applications of glaciological studies of radionuclides: the reconstruction of past atmospheric bomb tests; the use of well-dated atomic bomb horizons in the ice layers for developing core chronologies; and the study of atmospheric chemistry and dynamics.

The study of radionuclides in ice and snow has enabled an accurate reconstruction of the regional and global extent of nuclear weapons' testing as well as accidental radioactivity releases. Picciotto and Wilgain (1963) were the first to identify a 5–10-fold increase in β-activity in Greenland as a result of the first above-ground thermonuclear bomb tests from 1952 to 1955 AD. Later studies continued to monitor the evolution of radionuclide deposition in Greenland as well as to extend the research to Antarctica (Crozaz 1969). In particular, monitoring focused on $^3$H, which has both natural and anthropogenic production sources. In addition to being formed by nuclear weapon detonations, $^3$H (half-life 4500 days) is formed in the upper atmosphere from interaction with cosmic radiation and is rapidly incorporated into water molecules to form tritiated water (HTO). As such, HTO becomes diffused in the hydrological cycle, being precipitated as rain or snow, and eventually is incorporated into the considerably larger oceanic reservoir. A number of investigators (Jouzel et al. 1979; Koide et al. 1982; Merlivat et al. 1973) reported concentrations of $^3$H in Greenland and Antarctica, focusing on the two bomb peaks in the late 1950s and early 1960s. $^3$H concentrations corresponding to the 1963 AD bomb peak were approximately 500 times greater than background levels in Greenland (Koide et al. 1982) and approximately 100 times greater in Antarctica (Fourré et al. 2006). Fourré et al. (2006) demonstrated that $^3$H concentrations in Greenland snow and ice have consistently decreased since the 1960s, as would be expected from natural decay and dilution into the oceans, whereas levels remained higher than background in central Antarctica due to the more frequent incursion of stratospheric air through the more persistent polar vortex. $^3$H levels in central Antarctica were 2–3 times greater compared to lower-altitude coastal zones.

By the late 1970s, detection of radioactivity peaks from nuclear bomb tests had become a common stratigraphic dating tool for ice core studies (Hammer et al. 1978) and is still routinely employed (Eichler et al. 2000; Kehrwald et al. 2008; Knusel et al. 2003) also at high resolution such as in the case of tritium determined in the alpine core from Fiescherhorn glacier (Schwikowski et al. 1999). Gabrieli et al. (2011b) reported a high-resolution record of $^{239}$Pu concentrations in the Alpine Colle Gnifetti ice core from Mt. Rosa, demonstrating that Pu concentrations remain approximately twice that of pre-1952 AD concentrations during the 1970s and return to background levels by 1980 AD (Fig. 6). Histories of radionuclide deposition have also been reported from other mountain glaciers at middle and low latitudes around the world, including Huascarán in the Andes of Peru (Thompson et al. 1995a), Guliya in the Kunlan Shan of China (Thompson et al. 1995b), Miaoergou
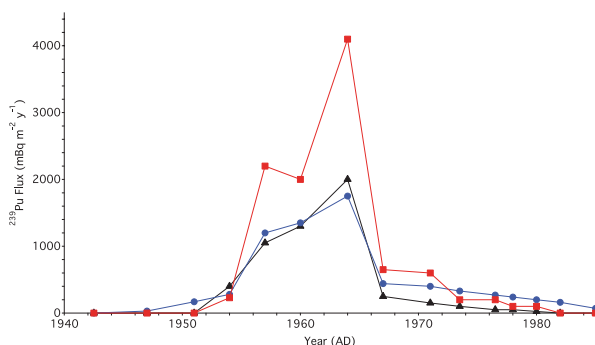
Glacier in the Tien Shan of China (Liu et al. 2011) and Belukha in the Siberian
Altai (Olivier et al. 2004). These studies consistently demonstrate two radioactivity
peaks: the first, relatively low and wide, in the mid- to late 1950s (β, $^3$H, $^{36}$Cl, $^{137}$Cs,
$^{239}$Pu) and the second, relatively high and narrow between 1962 and 1964 AD (β,
$^3$H, $^{137}$Cs, $^{239}$Pu).

The explosion at the Chernobyl nuclear power plant in April, 1986 AD led to
a resurgence of interest in detection of the released radionuclides. Particularly
high levels of activity were recorded in the Alps (10–20 Bq kg$^{-1}$) and in Svalbard
(1–9 Bq kg$^{-1}$) whereas radioactivity levels in Northern Greenland and North Amer-
ica were consistently below 1 Bq kg$^{-1}$ (Pourchet et al. 1988). The fact that nuclear
disasters, such as that at Chernobyl, are essentially discrete, well-recorded atmo-
spheric releases of radionuclides has resulting in such events being utilized for gla-
ciological studies. Vincent et al. (1997) measured $^{137}$Cs in ice and snow at various
locations over the Dome du Goûter on Mt. Blanc in the Western Alps and demon-
strated the effect of wind scouring on surface accumulation across the dome. $^{137}$Cs
concentrations were found to vary from 10 Bq m$^{-2}$ at the dome summit to 25 Bq m$^{-2}$
at a drilling site 30 m away, and up to 3000 Bq m$^{-2}$ at a second drilling site over
100 m distant. This phenomenon was only observed for the thin layer of accumula-
tion associated with the Chernobyl disaster. For the 1950s and 1960s bomb peaks,
the deposition of radionuclides was more extensive over time and hence less subject
to surface scouring, so all three sites at the Dome du Goûter had similar $^{137}$Cs con-
centrations of 2000–3000 Bq m$^{-2}$.

The emission, distribution and deposition of radionuclides to ice sheets and gla-
ciers have also been employed to investigate atmospheric circulation and aerosol
deposition processes. Heikkilä et al. (2009) compiled $^{36}$Cl flux histories from a
global suite of eight ice cores, demonstrating the existence of a broad peak from
1955 to 1964 AD. They employed this network of ice core-based $^{36}$Cl deposition to
validate an advanced climate model of global stratospheric and tropospheric aerosol
and precipitation transport, called ECHAM5-HAM. The history of $^{36}$Cl emission is
unique because this species results from neutron activation of $^{35}$Cl in sea salts, and
hence was exclusively produced by nuclear bomb testing on Pacific Ocean atolls or
islands. The largest tests occurred in 1954 AD (producing 112 kg $^{36}$Cl) with smaller
tests in 1958 AD (producing 71 kg $^{36}$Cl) and 1962 AD (producing 54 kg $^{36}$Cl).

Similarly, releases of $^{129}I$ due to nuclear bomb tests, accidents and reprocessing (the extraction of fissionable Pu from spent nuclear fuel material) have been detected in an ice core (Reithmeier et al. 2006) and allowed the improvement of models of atmospheric chemistry and circulation (Reithmeier et al. 2010). The March 2011 AD Fukushima nuclear power plant disaster has already become a topic of study (Hsu et al. 2012), and is likely to be included as a chronological tiepoint in future glaciological studies.

## Conclusions and Perspectives

We have shown how ice and firn cores provide a broad suite of information on the occurrence of anthropogenic contaminants in the past and present atmosphere. The advent of highly sensitive analytical techniques based on mass spectrometry allows the detection of anthropogenic impacts of these contaminants on firn and ice extracted from the remotest glaciers and ice sheets of the planet. The Arctic and Antarctic firn and ice records have provided a global perspective of the contamination from toxic elements such as Pb, Cu, Cd, Zn and various radionuclides. Other contaminants such as Hg, PGEs, BC and organic species such as, POPs and PAHs need to be further investigated to better understand their diffusion to the remotest locations of the Earth.

Knowledge of the dispersion of some anthropogenic toxic species has proven to be extremely important for policy makers as the attempt to take action to preserve terrestrial and aquatic ecosystems and protect human health. During the last few decades it has become apparent how studies on toxic contaminants in ice cores have the capability to influence political decisions to mitigate the diffusion of such species. For instance, knowledge of the global impact of atmospheric Pb emissions was an instrumental contribution to the decision to ban leaded gasoline. Subsequently, ice core analyses documented the effectiveness of this decision as Pb concentrations in polar snow were found to slowly decrease by the 1980s.

In this context, starting with the 1980s other inorganic (Zn, Cd) and organic (PCBs and POPs) species were observed to decrease in Arctic firn thanks to the technological advances forced by policies focused on reducing the impact of these toxic species in the atmosphere. Nevertheless, massive regional industrialization such as that occurring in Asia today is resulting in new and potent sources of anthropogenic contaminants into the atmosphere. The few mid and low latitude ice core records in existence do not provide coherent indications of the regional trends of atmospheric contamination. In this context, policymakers, governmental agencies, and public resource administrators require novel and more precise insights into short-term regional changes in the composition of the atmosphere. Studies on *fluxes* of targeted species to ice sheets and high altitude glaciers may provide a guide for prioritizing which anthropogenic emissions need to be regulated at regional levels. Ice cores still appear to be not only suitable but also convenient archives to conduct diffuse monitoring operations, typically lasting decades.

We note that most of the ice and firn records report only concentration data. While often the largest part of the concentration variability is influenced by the atmospheric input of the studied species, still a significant part of the variability is influenced by changes in snow accumulation rate. In cases of dry deposition of contaminants, snow accumulation significantly modulates the concentration of the species in the ice. In this context, in order to refine the modeling of transport and deposition of these species, it is also important to evaluate carefully the accumulation rate in order to assess fluxes (concentration × water equivalent accumulation rate). Nevertheless, we acknowledge that snow accumulation rate cannot always be obtained precisely from ice cores, especially when the seasonality of the signal is not pronounced and ice thinning deviates from conventional linear models at greater depths in the glaciers and ice sheets.

Another emerging difficulty to monitoring modern changes in regional atmospheric contamination by means of ice and firn cores is linked to the increasing widespread post-depositional effects due to the ongoing rapid climate change that is causing significant surface snow ablation and obliteration of the signal through melt water percolation. Modern ice core and firn records will need to be extracted at the highest latitudes and even higher elevations to guarantee that an accurate environmental signal is preserved. Especially at low latitudes, global climatic change is already limiting the paleoenvironmental potential of locations that were entirely suitable drilling sites until only a few decades ago.

# References

Anders E, Grevesse N (1989) Abundances of the elements: meteoritic and solar. Geochim Cosmochim Acta 53:197–214

Barbante C, Cozzi G, Capodaglio G, Van de Velde K, Ferrari C, Veysseyre A, Boutron CF, Scarponi G, Cescon P (1999) Determination of Rh, Pd, and Pt in polar and alpine snow and ice by double-focusing ICPMS with microcentric nebulization. Anal Chem 71:4125–4133

Barbante C, Van de Velde K, Cozzi G, Capodaglio G, Cescon P, Planchon F, Hong S, Ferrari C, Boutron CF (2001a) Post-World War II uranium changes in dated Mont Blanc ice and snow. Environ Sci Technol 35:4026–4030

Barbante C, Veysseyre A, Ferrari C, Van de Velde K, Morel C, Capodaglio G, Cescon P, Scarponi G, Boutron CF (2001b) Greenland snow evidence of large scale atmospheric contamination from platinum, palladium, and rhodium. Environ Sci Technol 35:835–839

Barbante C, Boutron CF, Morel C, Ferrari C, Jaffrezo JL, Cozzi G, Gaspari V, Cescon P (2003) Seasonal variations of heavy metals in central Greenland snow deposited from 1991 to 1995. J Environ Monit 5:328–335

Barbante C, Schwikowski M, Döring T, Gäggeler HW, Shotterer U, Tobler L, Van de Velde K, Ferrari C, Cozzi G, Turetta A, Rosman K, Bolshov MA, Capodaglio G, Cescon P, Boutron CF

(2004) Historical record of European emission of heavy metals to the atmosphere since the 1650s from alpine snow/ice cores drilled near Monte Rosa. Environ Sci Technol 38:4085–4090

Biester H, Bindler R, Martinez-Cortizas A, Engstrom DR (2007) Modeling the past atmospheric deposition of mercury using natural archives. Environ Sci Technol 41(14):4851–4860. doi:10.1021/es0704232

Bindler R (2003) Estimating the natural background atmospheric deposition rate of mercury utilizing ombrotrophic bogs in southern Sweden. Environ Sci Technol 37(1):40–46. doi:10.1021/es020065x

Bisiaux MM, Edwards R, McConnell JR, Curran MAJ, Van Ommen TD, Smith AM, Neumann TA, Pasteris DR, Penner JE, Taylor K (2012) Changes in black carbon deposition to Antarctica from two high-resolution ice core records, 1850–2000 AD. Atmos Chem Phys 12(9):4107–4115. doi:10.5194/acp-12-4107-2012

Blais JM, Schindler DW, Muir DCG, Sharp M, Donald D, Lafrenière M, Braekevelt E, Strachan WMJ (2001) Melting glaciers: a major source of persistent organochlorines to subalpine Bow Lake in Banff National Park, Canada. Ambio 30(7):410–415. doi:10.1043/0044-7447-30.7.410

Boutron CF, Görlach U, Candelone JP, Bolshov MA, Delmas RJ (1991) Decrease in anthropogenic lead, cadmium and zinc in Greenland snow since the late 1960s. Nature 353:153–156

Boutron CF, Vandal GM, Fitzgerald WF, Ferrari C (1998) A forty year record of mercury in central Greenland snow. Geophys Res Lett 25:3315–3318

Burn-Nunes LJ, Vallelonga P, Loss RD, Burton GR, Moy A, Curran M, Hong S, Smith AM, Edwards R, Morgan VI, Rosman KJR (2011) Seasonal variability in the input of lead, barium and indium to Law Dome, Antarctica. Geochim Cosmochim Acta 75:1–20. doi:10.1016/j.gca.2010.09.037

Candelone JP, Hong S, Boutron CF (1994) An improved method for decontaminating polar snow and ice cores for heavy metal analysis. Anal Chim Acta 299:9–16

Candelone J-P, Hong S, Pellone C, Boutron CF (1995) Post-industrial revolution changes in large-scale atmospheric pollution of the northern hemisphere by heavy metals as documented in central Greenland snow and ice. J Geophys Res 100(D8):16605–16616. doi:10.1029/95jd00989

Carter MW, Moghissi AA (1977) Three decades of nuclear testing. Health Phys 33(1):55–71

Chappellaz J, Brook E, Blunier T, Malaizé B (1997) $CH_4$ and $\delta^{18}O$ of $O_2$ records from Antarctic and Greenland ice: a clue for stratigraphic disturbance in the bottom part of the Greenland Ice core project and the Greenland Ice sheet project 2 ice cores. J Geophys Res 102(C12):26547–26557. doi:10.1029/97jc00164

Cooke CA, Abbott MB, Wolfe AP (2008) Late-Holocene atmospheric lead deposition in the Peruvian and Bolivian Andes. Holocene 18(2):353–359

Correia A, Freydier R, Delmas RJ, Simoes JC, Taupin JD, Dupré B, Artaxo P (2003) Trace elements in South America aerosol during 20th century inferred from a Nevado Illimani ice core, Eastern Bolivian Andes (6350 m asl). Atmos Chem Phys 3:1337–1352

Crozaz G (1969) Fission products in Antarctic snow, an additional reference level in January 1965. Earth Planet Sci Lett 6:6–8

Crutzen P, Stoermer EF (2000) The "Anthropocene". Glob Change Newslett 41:12–13

Daly GL, Wania F (2004) Organic contaminants in mountains. Environ Sci Technol 39(2):385–398. doi:10.1021/es048859u

Davis RE (1991) Links between snowpack physics and snowpack chemistry. In: Davies TD, Tranter M, Jones HG (eds) Processes of chemical change in snowpacks. Springer, Berlin, pp 115–139

Donald DB, Syrgiannis J, Crosley RW, Holdsworth G, Muir DCG, Rosenberg B, Sole A, Schindler DW (1999) Delayed deposition of organochlorine pesticides at a temperate glacier. Environ Sci Technol 33(11):1794–1798. doi:10.1021/es981120y

Durnford D, Dastoor A (2011) The behavior of mercury in the cryosphere: a review of what we know from observations. J Geophys Res 116(D6):D06305. doi:10.1029/2010jd014809

Eichler A, Schwikowski M, Gäggeler HW, Furrer V, Synal HA, Beer J, Saurer M, Funk M (2000) Glaciochemical dating of an ice core from upper Grenzgletscher (4200 m a.s.l.). J Glaciol 46(154):507–515

Eichler A, Schwikowski M, Gaeggeler HW (2001) Meltwater-induced relocation of chemical species in Alpine firn. Tellus B 53:192–203

Eichler A, Tobler L, Eyrikh S, Gramlich G, Malygina N, Papina T, Schwikowski M (2012) Three centuries of Eastern European and Altai lead emissions recorded in a Belukha ice core. Environ Sci Technol 46(8):4323–4330. doi:10.1021/es2039954

EPICA Community Members (2004) Eight glacial cycles from an Antarctic ice core. Nature 429(6992):623–628

EPICA Community Members (2006) One-to-one coupling of glacial climate variability in Greenland and Antarctica. Nature 444:195–198

Faïn X, Ferrari CP, Dommergue A, Albert MR, Battle M, Severinghaus J, Arnaud L, Barnola J-M, Cairns W, Barbante C, Boutron C (2009) Polar firn air reveals large-scale impact of anthropogenic mercury emissions during the 1970s. Proc Natl Acad Sci U S A 106(38):16114–16119

Farmer JG, Eades LJ, Mackenzie AB, Kirika A, Bailey-Watts TE (1996) Stable lead isotope record of lead pollution in Loch Lomond sediments since 1630 A.D. Environ Sci Technol 30(10):3080–3083. doi:10.1021/es960162o

Ferrari C, Dommergue A, Boutron CF, Jitaru P, Adams FC (2004) Profiles of Mercury in the snow pack at Station Nord, Greenland shortly after polar sunrise. Geophys Res Lett 31(3). doi:10.1029/2003GL018961

Fitzgerald WF, Engstrom DR, Lamborg CH, Tseng C-M, Balcom PH, Hammerschmidt CR (2005) Modern and historic atmospheric mercury fluxes in northern Alaska: Global sources and Arctic depletion. Environ Sci Technol 39(2):557–568

Flegal AR (1998) Clair Patterson's influence on environmental research—introduction. Environ Res 78A(2):65–70

Fourré E, Jean-Baptiste P, Dapoigny A, Baumier D, Petit J-R, Jouzel J (2006) Past and recent tritium levels in Arctic and Antarctic polar caps. Earth Planet Sci Lett 245(1–2):56–64. doi:10.1016/j.epsl.2006.03.003

Fuoco R, Giannarelli S, Onor M, Ghimenti S, Abete C, Termine M, Francesconi S (2012) A snow/firn four-century record of polycyclic aromatic hydrocarbons (PAHs) and polychlorobiphenyls (PCBs) at Talos Dome (Antarctica). Microchem J 105:133–141. doi:http://dx.doi.org/10.1016/j.microc.2012.05.018 (SI)

Gabrieli J, Vallelonga P, Cozzi G, Gabrielli P, Gambaro A, Sigl M, Decet F, Schwikowski M, Gäggeler HW, Boutron CF, Cescon P, Barbante C (2010) Post-17th-Century changes of European PAHs emissions recorded in high-altitude alpine snow and ice. Environ Sci Technol 44:3260–3266. doi:10.1021/es903365s

Gabrieli J, Carturan L, Gabrielli P, Kehrwald N, Turetta C, Cozzi G, Spolaor A, Dinale R, Staffler H, Seppi R, dalla Fontana G, Thompson LG, Barbante C (2011a) Impact of Po Valley emissions on the highest glacier of the Eastern European Alps. Atmos Chem Phys 11:8087–8102

Gabrieli J, Cozzi G, Vallelonga P, Schwikowski M, Sigl M, Eickenberg J, Wacker L, Boutron C, Gäggeler H, Cescon P, Barbante C (2011b) Contamination of Alpine snow and ice at Colle Gnifetti, Swiss/Italian Alps, from nuclear weapons tests. Atmos Environ 45(3):587–593. doi:10.1016/j.atmosenv.2010.10.039

Gabrielli P, Varga A, Barbante C, Boutron CF, Cozzi G, Gaspari V, Planchon F, Cairns W, Hong S, Ferrari C, Capodaglio G (2004) Determination of Ir and Pt down to the sub-femtogram per gram level in polar ice by ICP-SFMS using preconcentration and a desolvation system. J Anal At Spectrom 19(7):831–837

Gabrielli P, Barbante C, Plane JMC, Boutron CF, Jaffrezo JL, Mather TA, Stenni B, Gaspari V, Cozzi G, Ferrari C, Cescon P (2008) Siderophile metal fallout to Greenland from the 1991 winter eruption of Hekla (Iceland) and during the global atmospheric perturbation of Pinatubo. Chem Geol 255(1–2):78–86

Gabrielli P, Barbante C, Carturan L, Cozzi G, Dalla Fontana G, Dinale R, Draga G, Gabrieli J, Kehrwald N, Mair V, Mikhalenko VN, Piffer G, Rinaldi M, Seppi R, Spolaor A, Thompson LG, Tonidandel D (2012) Discovery of cold ice in a new drilling site in the Eastern European Alps. Geogr Fis Dinam Quat 35(1):101–105

Gambaro A, Zangrando R, Gabrielli P, Barbante C, Cescon P (2008) Direct determination of levoglucosan at the picogram per milliliter level in Antarctic ice by high-performance liquid chromatography/electrospray ionization triple quadrupole mass spectrometry. Anal Chem 80:1649–1655

Goodsite ME, Outridge PM, Christensen JH, Dastoor A, Muir D, Travnikov O, Wilson S (2013) How well do environmental archives of atmospheric mercury deposition in the Arctic reproduce rates and trends depicted by atmospheric models and measurements? Sci Total Environ 452–453:196–207. doi:10.1016/j.scitotenv.2013.02.052

Görlach U, Boutron CF (1992) Variations in heavy metals concentrations in Antarctic snows from 1940 to 1980. J Atmos Chem 14(1–4):205–222. doi:10.1007/bf00115234

Grannas AM, Hockaday WC, Hatcher PG, Thompson LG, Mosley-Thompson E (2006) New revelations on the nature of organic matter in ice cores. J Geophys Res 111(D4):D04304. doi:10.1029/2005jd006251

Gregor DJ, Peters AJ, Teixeira C, Jones N, Spencer C (1995) The historical residue trend of PCBs in the Agassiz Ice Cap, Ellesmere Island, Canada. Sci Total Environ 160–161:117–126. doi:10.1016/0048-9697(95)04349-6

Guzzella L, Patrolecco L, Pagnotta R, Langone L, Guilizzoni P (1997) DDT and other organochlorine compounds in the Lake Maggiore sediments: a recent point source of contamination. Fresenius Environ Bull 7:79–89

Hammer CU, Clausen HB, Dansgaard W, Gundestrup N, Johnsen SJ, Reeh N (1978) Dating of Greenland ice cores by flow models, isotopes, volcanic debris, and continental dust. J Glaciol 20(82):3–26

Heikkilä U, Beer J, Feichter J, Alfimov V, Synal HA, Schotterer U, Eichler A, Schwikowski M, Thompson L (2009) 36Cl bomb peak: comparison of modeled and measured data. Atmos Chem Phys 9(12):4145–4156. doi:10.5194/acp-9-4145-2009

Heisterkamp M, Van de Velde K, Ferrari C, Boutron CF, Adams FC (1999) Present century record of organolead pollution in high altitude alpine snow. Environ Sci Technol 33(24):4416–4421. doi:10.1021/es990612n

Hermanson MH, Isaksson E, Forsström S, Teixeira C, Muir DCG, Pohjola VA, van de Wal RSV (2010) Deposition history of brominated flame retardant compounds in an ice core from Holtedahlfonna, Svalbard, Norway. Environ Sci Technol 44(19):7405–7410. doi:10.1021/es1016608

Hong S, Candelone JP, Patterson CC, Boutron CF (1994) Greenland ice evidence of hemispheric lead pollution two millenia ago by Greek and Roman civilization. Science 256(5180):1841–1843

Hong S, Candelone JP, Patterson CC, Boutron CF (1996) History of ancient copper smelting pollution during Roman and medieval times recorded in Greenland ice. Science 272(5259):246–249

Hong S, Boutron CF, Edwards R, Morgan VI (1998) Heavy metals in Antarctic ice from Law Dome: initial results. Environ Res 78(2):94–103. doi:10.1006/enrs.1998.3849

Hong S, Barbante C, Boutron CF, Gabrielli P, Gaspari V, Cescon P, Thompson LG, Ferrari C, Francou B, Maurice-Bourgoin L (2004) Atmospheric heavy metals in tropical South America during the past 22,000 years recorded in a high altitude ice core from Sajama, Bolivia. J Environ Monit 6:322–326

Hong S, Lee K, Hou S, Hur SD, Ren J, Burn LJ, Rosman KJR, Barbante C, Boutron CF (2009) An 800-year record of atmospheric As, Mo, Sn, and Sb in central Asia in high-altitude ice cores from Mt. Qomolangma (Everest), Himalayas. Environ Sci Technol 43(21):8060–8065

Hornbuckle K, Carlson D, Swackhamer D, Baker J, Eisenreich S (2006) Polychlorinated biphenyls in the Great Lakes. In: Hites R (ed) Persistent organic pollutants in the Great Lakes. The handbook of environmental chemistry, vol 5N. Springer, Berlin, pp 13–70. doi:10.1007/698_5_039

Hsu S-C, Huh C-A, Chan C-Y, Lin S-H, Lin F-J, Liu SC (2012) Hemispheric dispersion of radioactive plume laced with fission nuclides from the Fukushima nuclear event. Geophys Res Lett 39(1):L00G22. doi:10.1029/2011gl049986

Jaffrezo JL, Clain MP, Masclet P (1994) Polycyclic aromatic-hydrocarbons in the polar ice of Greenland: geochemical use of these atmospheric tracers. Atmos Environ 28(6):1139–1145

Jenk TM, Szidat S, Schwikowski M, Gäggeler HW, Brütsch S, Wacker L, Synal HA, Saurer M (2006) Radiocarbon analysis in an Alpine ice core: record of anthropogenic and biogenic contributions to carbonaceous aerosols in the past. Atmos Chem Phys 6(12):5381–5390. doi:10.5194/acp-6-5381-2006

Jenk TM, Szidat S, Bolius D, Sigl M, Gäggeler HW, Wacker L, Ruff M, Barbante C, Boutron CF, Schwikowski M (2009) A novel radiocarbon dating technique applied to an ice core from the Alps indicating late Pleistocene ages. J Geophys Res 114. doi:10.1029/2009JD011860 (D14305)

Jitaru P, Infante HG, Ferrari C, Dommergue A, Boutron CF, Adams FC (2003) Present century record of mercury species pollution in high altitude alpine snow and ice. J Phys IV France 107(Pt 1):683–686

Jitaru P, Gabrielli P, Marteel A, Plane JMC, Planchon FAM, Gauchard PA, Ferrari CP, Boutron CF, Adams FC, Hong S, Cescon P, Barbante C (2009) Atmospheric depletion of mercury over Antarctica during glacial periods. Nature Geosci 2(7):505–508

Jouzel J, Merlivat L, Pourchet M, Lorius C (1979) A continuous record of artificial tritium fallout at the South Pole (1954–1978). Earth Planet Sci Lett 45(1):188–200. doi:10.1016/0012-821×(79)90120-1

Jouzel J, Raisbeck G, Benoist JP, Yiou F, Lorius C, Raynaud D, Petit JR, Barkov NI, Korotkevich YS, Kotlyakov VM (1989) A comparison of deep Antarctic ice cores and their implications for climate between 65,000 and 15,000 years ago. Quat Res 31:135–150

Kang J-H, Son M-H, Do Hur S, Hong S, Motoyama H, Fukui K, Chang Y-S (2012) Deposition of organochlorine pesticides into the surface snow of East Antarctica. Sci Total Environ 433:290–295. doi:http://dx.doi.org/10.1016/j.scitotenv.2012.06.037

Kaspari S, Mayewski PA, Handley M, Osterberg E, Kang S, Sneed S, Hou S, Qin D (2009) Recent increases in atmospheric concentrations of Bi, U, Cs, S and Ca from a 350-year Mount Everest ice core record. J Geophys Res 114(D4):D04302

Kaspari SD, Schwikowski M, Gysel M, Flanner MG, Kang S, Hou S, Mayewski PA (2011) Recent increase in black carbon concentrations from a Mt. Everest ice core spanning 1860–2000 AD. Geophys Res Lett 38(4):L04703. doi:10.1029/2010gl046096

Kawamura K, Suzuki I, Fujii Y, Watanabe O (1994) Ice core record of polycyclic aromatic hydrocarbons over the past 400 years. Naturwissseschaften 81(11):502–505. doi:10.1007/bf01132682

Kehrwald N, Thompson LG, Yao T, Thompson EM, Shottered U, Alfimov V, Beer J, Eikenberg J, Davis M (2008) Mass loss on Himalayan glacier endangers water resources. Geophys Res Lett 35(L22):503. doi:10.1029/2008GL035556

Kirchgeorg T, Dreyer A, Gabrieli J, Kehrwald N, Sigl M, Schwikowski M, Boutron C, Gambaro A, Barbante C, Ebinghaus R (2013) Temporal variations of perfluoroalkyl substances and polybrominated diphenyl ethers in alpine snow. Environ Pollut 178:367–374. doi:10.1016/j.envpol.2013.03.043

Knüsel S, Ginot P, Schotterer U, Schwikowski M, Gggeler HW, Francou B, Petit JR, Simoes JC, Taupin JD (2003) Dating of two nearby ice cores from the Illimani, Bolivia. J Geophys Res 108(D6):4181. doi:10.1029/2001jd002028

Koide M, Michel R, Goldberg ED, Herron MM, Langway CC (1982) Characterization of radioactive fallout from pre-moratorium and post-moratorium tests to polar ice caps. Nature 296(5857):544–547

Krachler M, Zheng J, Koerner RM, Zdanowicz C, Fisher DA, Shotyk W (2005) Increasing atmospheric antimony contamination in the northern hemisphere: snow and ice evidence from Devon Island, Arctic Canada. J Environ Monit 7(12):1169–1176. doi:10.1039/b509373b

Krachler M, Zheng J, Fisher D, Shotyk W (2008a) Atmospheric Sb in the Arctic during the past 16,000 years: Responses to climate change and human impacts. Glob Biogeochem Cycles 22(1):GB1015. doi:10.1029/2007gb002998

Krachler M, Zheng J, Fisher D, Shotyk W (2008b) Atmospheric inputs of Ag and Tl to the Arctic: comparison of a high resolution snow pit (AD 1994–2004) with a firn (AD 1860–1996)

and an ice core (previous 16,000 yr). Sci Total Environ 399(1–3):78–89. doi:http://dx.doi.org/10.1016/j.scitotenv.2008.03.006

Krachler M, Zheng J, Fisher D, Shotyk W (2009) Global atmospheric As and Bi contamination preserved in 3000 year old Arctic ice. Glob Biogeochem Cycles 23(3):GB3011. doi:10.1029/2009gb003471

Kudo A, Zheng J, Koerner RM, Fisher DA, Santry DC, Mahara Y, Sugahara M (1998) Global transport rates of $^{137}$Cs and $^{239+240}$Pu originating from the Nagasaki A-bomb in 1945 as determined from analysis of Canadian Arctic ice cores. J Environ Radact 40(3):289–298. doi:10.1016/S0265-931X(97)00023-4

Kylander ME, Weiss DJ, Martínez CA, Spiro B, Garcia-Sanchez R, Coles BJ (2005) Refining the pre-industrial atmospheric Pb isotope evolution curve in Europe using an 8000 year old peat core from NW Spain. Earth Planet Sci Lett 240(2):467–485. doi:10.1016/j.epsl.2005.09.024

Lavanchy VMH, Gäggeler HW, Schotterer U, Schwikowski M, Baltensperger U (1999) Historical record of carbonaceous particle concentrations from a European high-alpine glacier (Colle Gnifetti, Switzerland). J Geophys Res 104(D17):21227–21236. doi:10.1029/1999jd900408

Lee K, Do Hur S, Hou S, Burn-Nunes LJ, Hong S, Barbante C, Boutron CF, Rosman KJR (2011) Isotopic signatures for natural versus anthropogenic Pb in high-altitude Mt. Everest ice cores during the past 800 years. Sci Total Environ 412:194–202. doi:10.1016/j.scitotenv.2011.10.002

Legrand M, Preunkert S, Schock M, Cerqueira M, Kasper-Giebl A, Afonso J, Pio C, Gelencsér A, Dombrowski-Etchevers I (2007) Major twentieth century changes of carbonaceous aerosol components (EC, WinOC, DOC, HULIS, carboxylic acids, and cellulose) derived from alpine ice cores. J Geophys Res 112(D23):S11. doi:10.1029/2006JD008080

Li Y, Yao T, Wang N, Li Z, Tian L, Xu B, Wu G (2006) Recent changes of atmospheric heavy metals in a high-elevation ice core from Muztagh Ata, east Pamirs: initial results. Ann Glaciol 43(1):154–159. doi:10.3189/172756406781812186

Liu Y, Hou S, Hong S, Do Hur S, Lee K, Wang Y (2011) High-resolution trace element records of an ice core from the eastern Tien Shan, central Asia, since 1953 AD. J Geophys Res 116(D12):D12307. doi:10.1029/2010jd015191

Maggi V, Villa S, Finizio A, Delmonte B, Casati P, Marino F (2006) Variability of anthropogenic and natural compounds in high altitude-high accumulation alpine glaciers. Hydrobiologia 562(1):43–56. doi:10.1007/s10750-005-1804-y

Mann J, Long S, Shuman C, Kelly WR (2005) Determination of mercury content in a shallow firn core from Greenland by isotope dilution inductively coupled plasma mass spectrometry. Water Air Soil Pollut 163(1–4):19–32. doi:10.1007/s11270-005-7607-y

Masclet P, Mouvier G, Nikolaou K (1986) Relative decay index and sources of polycyclic aromatic-hydrocarbons. Atmos Environ 20(3):439–446. doi:10.1016/0004-6981(86)90083-1

McConnell JR (2010) New directions: historical black carbon and other ice core aerosol records in the Arctic for GCM evaluation. Atmos Environ 44(21,22):2665–2666. doi:10.1016/j.atmosenv.2010.04.004

McConnell JR, Edwards R (2008) Coal burning leaves toxic heavy metal legacy in the Arctic. Proc Natl Acad Sci U S A 105(34):12140–12144

McConnell JR, Lamorey GW, Hutterli MA (2002a) A 250-year high-resolution record of Pb flux and crustal enrichment in central Greenland. Geophys Res Lett 29(23):2130. doi:10.1029/2002GL016016

McConnell JR, Lamorey GW, Lambert SW, Taylor KC (2002b) Continuous ice-core chemical analyses using inductively coupled plasma mass spectrometry. Environ Sci Technol 36(1):7–11

McConnell JR, Edwards R, Kok GL, Flanner MG, Zender CS, Saltzman ES, Banta JR, Pasteris DR, Carter MM, Kahl JDW (2007) 20th-Century industrial black carbon emissions altered Arctic climate forcing. Science 317(5843):1381–1384. doi:10.1126/science.1144856

Merlivat L, Ravoire J, Vergnaud JP, Lorius C (1973) Tritium and deuterium content of the snow in Greenland. Earth Planet Sci Lett 19(2):235–240. doi:10.1016/0012-821×(73)90121-0

Muir DCG, Wang X, Yang F, Nguyen N, Jackson TA, Evans MS, Douglas M, Koeck G, Lamoureux S, Pienitz R, Smol JP, Vincent WF, Dastoor A (2009) Spatial trends and historical deposi-

tion of mercury in eastern and northern Canada inferred from lake sediment cores. Environ Sci Technol 43(13):4802–4809. doi:10.1021/es8035412

Murozumi M, Chow TJ, Patterson C (1969) Chemical concentrations of pollutant lead aerosols, terrestrial dusts and sea salts in Greenland and Antarctic snow strata. Geochim Cosmochim Acta 33:1247–1294

N-GRIP-Members (2004) High-resolution record of Northern Hemisphere climate extending into the last interglacial period. Nature 431(7005):147–151. doi:10.1038/nature02805

Ng A, Patterson CC (1981) Natural concentrations of lead in ancient Arctic and Antarctic ice. Geochim Cosmochim Acta 45:2109–2121

Norris R, Arkin W (1998) Known nuclear tests worlwide 1945–1998. Bull Atomic Sci 54:65–67

Nriagu JO, Pacyna JM (1988) Quantitative assessment of world-wide contamination of air, water and soils by trace metals. Nature 333(6169):134–139

Olivier S, Bajo S, Fifield LK, Gäggeler HW, Papina T, Santschi PH, Schotterer U, Schwikowski M, Wacker L (2004) Plutonium from global fallout recorded in an Ice Core from the Belukha Glacier, Siberian Altai. Environ Sci Technol 38(24):6507–6512. doi:10.1021/es0492900

Osterberg E, Mayewski P, Kreutz K, Fisher D, Handley M, Sneed S, Zdanowicz C, Zheng J, Demuth M, Waskiewicz M, Bourgeois J (2008) Ice core record of rising lead pollution in the North Pacific atmosphere. Geophys Res Lett 35(5):L05810. doi:10.1029/2007/GL032680

Parrenin F, Barnola JM, Beer J, Blunier T, Castellano E, Chappellaz J, Dreyfus G, Fischer H, Fujita S, Jouzel J, Kawamura K, Lemieux-Dudon B, Loulergue L, Masson-Delmotte V, Narcisi B, Petit JR, Raisbeck G, Raynaud D, Ruth U, Schwander J, Severi M, Spahni R, Steffensen JP, Svensson A, Udisti R, Waelbroeck C, Wolff E (2007) The EDC3 chronology for the EPICA Dome C ice core. Clim Past 3(3):485–497

Petit JR, Jouzel J, Raynaud D, Barkov NI, Barnola JM, Basile-Doelsch I, Bender M, Chappellaz J, Davis M, Delaygue G, Delmotte M, Kotlyakov VM, Legrand M, Lipenkov VY, Lorius C, Pépin L, Ritz C, Saltzman E, Stievenard M (1999) Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica. Nature 399(6735):429–436

Picciotto E, Wilgain S (1963) Fission products in Antarctic snow, a reference level for measuring accumulation. J Geophys Res 68(21):5965–5972

Pirrone N, Allegrini I, Keeler GJ, Nriagu JO, Rossmann R, Robbins JA (1998) Historical atmospheric mercury emissions and depositions in North America compared to mercury accumulations in sedimentary records. Atmos Environ 32(5):929–940. doi:10.1016/s1352-2310(97)00353-1

Pirrone N, Cinnirella S, Feng X, Finkelman RB, Friedli HR, Leaner J, Mason R, Mukherjee AB, Stracher GB, Streets DG, Telmer K (2010) Global mercury emissions to the atmosphere from anthropogenic and natural sources. Atmos Chem Phys 10(13):5951–5964

Planchon F, Boutron CF, Barbante C, Cozzi G, Gaspari V, Wolff EW, Ferrari C, Cescon P (2002a) Changes in heavy metals in Antarctic snow from Coats Land since the mid-19th to the late-20th century. Earth Planet Sci Lett 200(1–2):207–222

Planchon F, Boutron CF, Barbante C, Cozzi G, Gaspari V, Wolff EW, Ferrari CP, Cescon P (2002b) Short-term variations in the occurrence of heavy metals in Antarctic snow from Coats Land since the 1920s. Sci Total Environ 300(1–3):129–142

Planchon F, Van de Velde K, Rosman K, Wolff EW, Ferrari C, Boutron CF (2003) One hundred fifty year record of lead isotopes in Antarctic snow from Coats Land. Geochim Cosmochim Acta 67(4):693–708

Pourchet M, Pinglot JF, Reynaud L, Holdsworth G (1988) Identification of Chernobyl fall-out as a new reference level in Northern Hemisphere glaciers. J Glaciol 34(117):183–186

Raisbeck GM, Yiou F, Cattani O, Jouzel J (2006) [10]Be evidence for the Matuyama-Brunhes geomagnetic reversal in the EPICA Dome C ice core. Nature 444(7115):82–84

Ramanathan V, Carmichael G (2008) Global and regional climate changes due to black carbon. Nature Geosci 1(4):221–227

Rauch S, Fatoki OS (2013) Anthropogenic platinum enrichment in the vicinity of mines in the Bushveld Igneous Complex, South Africa. Water Air Soil Poll 212(1):1–8. doi:10.1007/s11270-012-1395-y

Rauch S, Hemond HF (2003) Sediment-based evidence of platinum concentration changes in an urban lake near Boston, Massachusetts. Environ Sci Technol 37(15):3283–3288. doi:10.1021/es034162h

Rauch S, Hemond FH, Peucker-Ehrenbrink B (2004) Recent changes in platinum group element concentrations and osmium isotopic composition in sediments from an urban lake. Environ Sci Technol 38(2):396–402

Rauch S, Hemond HF, Peucker-Ehrenbrink B, Ek KH, Morrison GM (2005) Platinum group element concentrations and osmium isotopic composition in urban airborne particles from Boston, Massachusetts. Environ Sci Technol 39(24):9464–9470

Rauch S, Peucker-Ehrenbrink B, Molina LT, Molina MJ, Ramos R, Hemond HF (2006) platinum group elements in airborne particles in Mexico City. Environ Sci Technol 40(24):7554–7560

Reithmeier H, Lazarev V, Rühm W, Schwikowski M, Gäggeler HW, Nolte E (2006) Estimate of European $^{129}$I Releases Supported by $^{129}$I Analysis in an Alpine Ice Core. Environ Sci Technol 40(19):5891–5896. doi:10.1021/es0605725

Reithmeier H, Lazarev V, Rühm W, Nolte E (2010) Anthropogenic $^{129}$I in the atmosphere: Overview over major sources, transport processes and deposition pattern. Sci Total Environ 408(21):5052–5064. doi:10.1016/j.scitotenv.2010.07.015

Rosman KJR (2001) Natural isotopic variations in lead in polar snow and ice as indicators of source regions. In: Caroli S, Cescon P, Walton DWH (eds) Environmental contamination in Antarctica: a challenge to analytical chemistry. Elsevier Science B.V., New York, pp 87–106

Rosman KJR, Chisholm W, Boutron CF, Candelone J-P, Görlach U (1993) Isotopic evidence for the source of lead in Greenland snows since the late 1960s. Nature 362(6418):333–334

Rosman KJR, Chisholm W, Hong S, Candelone J-P, Boutron CF (1997) Lead from Carthaginian and Roman Spanish mines isotopically identified in Greenland ice dated from 600 B.C. to 300 A.D. Environ Sci Technol 31(12):3413–3416

Rosman KJR, Ly C, Steinnes E (1998) Spatial and temporal variation in isotopic composition of atmospheric lead in Norwegian moss. Environ Sci Technol 32(17):2542–2546. doi:10.1021/es9710215

Rosman KJR, Ly C, Van de Velde K, Boutron CF (2000) A two century record of lead isotopes in high altitude Alpine snow and ice. Earth Planet Sci Lett 176:413–424

Rosman KJR, Hong S, Bulion G, Burn L, Boutron CF, Ferrari CP, Thompson LG, Maurice-Bourgoin L, Francou B (2003) Pb and Sr isotopes from an ice-core provides evidence for changing atmospheric conditions at the Sajama icecap, South America. J Phys IV France 107(1):1157–1160

Ruggirello RM, Hermanson MH, Isaksson E, Teixeira C, Forsström S, Muir DCG, Pohjola V, van de Wal R, Meijer HAJ (2010) Current use and legacy pesticide deposition to ice caps on Svalbard, Norway. J Geophys Res 115(D18):D18308. doi:10.1029/2010jd014005

Schmid P, Bogdal C, Blüthgen N, Anselmetti FS, Zwyssig A, Hungerbühler K (2010) The missing piece: sediment records in remote mountain lakes confirm glaciers being secondary sources of persistent organic pollutants. Environ Sci Technol 45(1):203–208. doi:10.1021/es1028052

Schotterer U, Stichler W, Ginot P (2004) The influence of post-depositional effects on ice core studies: examples from the Alps, Andes, and Altai. In: Cecil LD, Green JR, Thompson LG (eds) Earth paleoenvironments: records preserved in mid- and low-latitude glaciers. Developments in paleoenvironmental research, vol. 9. Kluwer Academic, Dordrecht, pp 39–59

Schroeder JP, Anlauf KG, Barrie LA, Lu JY, Steffen A, Schneeberger DR, Berg T (1998) Arctic springtime depletion of mercury. Nature 394(6691):331–332

Schuster PF, Krabbenhoft DP, Naftz DL, Cecil LD, Olson ML, Dewild JF, Susong DD, Green JR, Abbott ML (2002) Atmospheric mercury deposition during the last 270 years: a glacial ice core record of natural and anthropogenic sources. Environ Sci Technol 36(11):2303–2310. doi:10.1021/es0157503

Schwikowski M (2003) Reconstruction of European air pollution from Alpine ice cores. In: Cecil LD, Green JR, Thompson LG (eds) Earth Paleoenvironments: Records preserved in Mid- and Low Latitude Glaciers. Develvolments in Paleoenvironmental Research, vol. 9. Kluwer Academic, Dordrecht, pp 95–119

Schwikowski M, Brutsch S, Gaeggeler HW, Shottered U (1999) A high-resolution air chemistry record from an Alpine ice core: Fiescherhorn glacier, Swiss Alps. J Geophys Res 104(D11):13709–13719

Schwikowski M, Barbante C, Döring T, Gäggeler HW, Boutron CF, Schotterer U, Tobler L, Van de Velde K, Ferrari C, Cozzi G, Rosman K, Cescon P (2004) Post-17-century changes of European lead emissions recorded in high-altitude Alpine snow and ice. Environ Sci Technol 38(4):957–964

Severi M, Becagli S, Castellano E, Morganti A, Traversi R, Udisti R, Ruth U, Fischer H, Huybrechts P, Wolff E, Parrenin F, Kaufmann P, Lambert F, Steffensen JP (2007) Synchronisation of the EDML and EDC ice cores for the last 52 kyr by volcanic signature matching. Clim Past 3:367–374

Sherrell RM, Boyle EA, Falkner KK, Harris NR (2000) Temporal variability of Cd, Pb, and Pb isotope deposition in central Greenland snow. Geochem Geophys Geosyst 1:1002. doi:10.1029/1999GC000007

Shotyk W, Krachler M (2004) Atmospheric deposition of silver and thallium since 12370 $^{14}$C years BP recorded by a Swiss peat bog profile, and comparison with lead and cadmium. J Environ Monit 6(5):427–433

Shotyk W, Krachler M (2010) The isotopic evolution of atmospheric Pb in central Ontario since AD 1800, and its impacts on the soils, waters, and sediments of a forested watershed, Kawagama Lake. Geochim Cosmochim Acta 74(7):1963–1981. doi:10.1016/j.gca.2010.01.009

Shotyk W, Weiss D, Appleby PG, Cheburkin AK, Frei R, Gloor M, Kramers JD, Reese S, Van der Knaap WO (1998) History of atmospheric lead deposition since 12,370 $^{14}$C year BP from a peat bog, Jura Mountains, Switzerland. Science 281(5383):1635–1640. doi:10.1126/science.281.5383.1635

Shotyk W, Chen B, Krachler M (2005a) Lithogenic, oceanic and anthropogenic sources of atmospheric Sb to a maritime blanket bog, Myrarnar, Faroe Islands. J Environ Monit 7(12):1148–1154

Shotyk W, Zheng J, Krachler M, Zdanowicz C, Koerner RM, Fischer D (2005b) Predominance of industrial Pb in recent snow (1994–2004) and ice (1842–1996) from Devon Island, Arctic Canada. Geophys Res Lett 32(21):L21814. doi:10.1029/2005GL623860

Sigl M, Jenk TM, Kellerhals T, Szidat S, Gaggeler HW, Wacker L, Synal HA, Boutron CF, Barbante C, Gabrieli J, Schwikowski M (2009) Intruments and methods towards radiocarbon dating of ice cores. J Glaciol 55(194):985–996

Soyol-Erdene T-O, Huh Y, Hong S, Do Hur S (2011) A 50-year record of platinum, iridium, and rhodium in Antarctic snow: volcanic and anthropogenic sources. Environ Sci Technol 45(14):5929–5935. doi:10.1021/es2005732

Sun SS (1980) Lead isotopic study of young volcanic rocks from mid-ocean ridges, ocean islands and island arcs. Philos Trans R Soc Lond Series A 297(1431):409–445

Thevenon F, Anselmetti FS, Bernasconi SM, Schwikowski M (2009) Mineral dust and elemental black carbon records from an Alpine ice core (Colle Gnifetti glacier) over the last millennium. J Geophys Res 114 (D17):102. doi:10.1029/2008JD011490

Thompson LG, Mosley-Thompson E, Dansgaard W, Grootes PM (1986) The Little Ice Age as recorded in the stratigraphy of the tropical Quelccaya ice cap. Science 234(4774):361–364

Thompson LG, Mosley-Thompson E, Davis ME, Lin P-N, Henderson KA, Cole-Dai J, Bolzan JF, Liu K-B (1995a) Late glacial stage and Holocene tropical ice core records from Huascarán, Peru. Science 269(5220):46–50

Thompson LG, Mosley-Thompson E, Davis ME, Lin PN, Dai J, Bolzan JF, Yao TD (1995b) A 1000 year climate ice-core record from the Guliya ice cap, China: its relationship to global climate variability. Ann Glaciol 21:175–181

Thompson LG, Davis ME, Mosley-Thompson E, Sowers T, Henderson KA, Zagorodnov VS, Lin PN, Mikhalenko VN, Campen RK, Bolzan JF, Cole-Dai J, Francou B (1998) A 25,000-year tropical climate history from Bolivian ice cores. Science 282:1858–1864. doi:10.1126/science.282.5395.1858

Thompson LG, Yao T, Thompson EM, Davis M, Henderson KA, Lin PN (2000) A high-resolution millennial record of the South Asian Monsoon from Himalayan ice cores. Science 289:1916–1919

Thompson LG, Mosley-Thompson E, Davis ME, Henderson KA, Brecher HH, Zagorodnov VS, Mashiotta TA, Lin PN, Mikhalenko VN, Hardy DR, Beer J (2002) Kilimanjaro ice core records: evidence of Holocene climate change in tropical Africa. Science 298(5486):589–593

UNEP (2013) Global Mercury Assessment 2013: Sources, Emissions, Releases and Environmental Transport UNEP Chemicals Branch, Geneve, Switzerland

USGS (2006) Mercury Statistics. US Geological Survey. http://minerals.usgs.gov/ds/2005/140/mercury.pdf. Accessed 25 Dec 2012.

Vallelonga P, Van de Velde K, Candelone JP, Morgan VI, Boutron CF, Rosman KJR (2002) The lead pollution history of Law Dome, Antarctica, from isotopic measurements on ice cores: 1500 AD to 1989 AD. Earth Planet Sci Lett 204(1–2):291–306

Vallelonga P, Barbante C, Cozzi G, Gaspari V, Candelone JP, Van de Velde K, Morgan VI, Rosman KJR, Boutron CF, Cescon P (2004) Elemental indicators of natural and anthropogenic aerosol inputs to Law Dome, Antarctica. Ann Glaciol 39:169–174

Vallelonga P, Gabrielli P, Balliana I, Wegner A, Delmonte B, Turetta C, Vanhaecke F, Rosman KJR, Hong S, Boutron CF, Cescon P, Barbante C (2010) Lead isotopic compositions in the EPICA Dome C ice core and Southern Hemisphere potential source areas. Quat Sci Rev 29(1–2):247–255

Van de Velde K, Boutron CF, Ferrari C, Bellomi T, Barbante C, Rudnev S, Bolshov MA (1998) Seasonal variation of heavy metals in the 1960s Alpine ice: sources versus meteorological factors. Earth Planet Sci Lett 164(3–4):521–533

Van de Velde K, Ferrari C, Barbante C, Moret I, Bellomi T, Hong S, Boutron CF (1999) A 200 year record of atmospheric cobalt, chromium, molybdenum, and antimony in high altitude Alpine firn and ice. Environ Sci Technol 33(20):3495–3501

Van de Velde K, Barbante C, Cozzi G, Moret I, Bellomi T, Ferrari C, Boutron CF (2000a) Changes in the occurrence of silver, gold, platinum, palladium and rhodium in Mont Blanc ice and snow since the 18th century. Atmos Environ 34(19):3117–3127

Van de Velde K, Boutron CF, Ferrari C, Moreau AL, Delmas RJ, Barbante C, Bellomi T, Capodaglio G, Cescon P (2000b) A two hundred years record of atmospheric cadmium, copper and zinc concentrations in high altitude snow and ice from the French-Italian Alps. Geophys Res Lett 27(2):249–252

Van de Velde K, Vallelonga P, Candelone J-P, Rosman KJR, Gaspari V, Cozzi G, Barbante C, Udisti R, Cescon P, Boutron CF (2005) Pb isotope record over one century in snow from Victoria Land, Antarctica. Earth Planet Sci Lett 232(102):95–108. doi:10.1016/j.epsl.2005.01.007

Villa S, Maggi V, Negrelli C, Finizio A, Bolzacchini E, Vighi M (2001) Historical profile of polychlorinated biphenyls (PCBs) in an alpine glacier. Fresenius Environ Bull 10(9):711–716

Villa S, Vighi M, Maggi V, Finizio A, Bolzacchini E (2003) Historical trends of organochloride pesticides in an Alpine glacier. J Atmos Chem 46(3):295–311

Vincent C, Vallon M, Pinglot JF, Funk M, Reynaud L (1997) Snow accumulation and ice flow at Dome du Gouter (4300m), Mont Blanc, French Alps. J Glaciol 43(145):513–521

von Gunten HR, Sturm M, Moser RN (1997) 200-year record of metals in lake sediments and natural background concentrations. Environ Sci Technol 31(8):2193–2197. doi:10.1021/es960616h

Wang X, Yao T, Wang P, Wei Y, Tian L (2008a) The recent deposition of persistent organic pollutants and mercury to the Dasuopu glacier, Mt. Xixiabangma, central Himalayas. Sci Total Environ 394(1):134–143. doi:10.1016/j.scitotenv.2008.01.016

Wang X, Xu B, Kang S, Cong Z, Yao T (2008b) The historical residue trends of DDT, hexachlorocyclohexanes and polycyclic aromatic hydrocarbons in an ice core from Mt. Everest, central Himalayas, China. Atmos Environ 42(27):6699–6709. doi:10.1016/j.atmosenv.2008.04.035

Wang X, Gong P, Zhang Q, Yao T (2010a) Impact of climate fluctuations on deposition of DDT and hexachlorocyclohexane in mountain glaciers: evidence from ice core records. Environ Pollut 158(2):375–380. doi:10.1016/j.envpol.2009.09.006

Wang X, Yang H, Gong P, Zhao X, Wu G, Turner S, Yao T (2010b) One century sedimentary records of polycyclic aromatic hydrocarbons, mercury and trace elements in the Qinghai Lake, Tibetan Plateau. Environ Pollut 158(10):3065–3070. doi:10.1016/j.envpol.2010.06.034

Warneke T, Croudace IW, Warwick PE, Taylor RN (2002) A new ground-level fallout record of uranium and plutonium isotopes for northern temperate latitudes. Earth Planet Sci Lett 203(3–4):1047–1057. doi:10.1016/s0012-821×(02)00930-5

Watanabe O, Jouzel J, Johnsen S, Parrenin F, Shoji H, Yoshida N (2003) Homogeneous climate variability across East Antarctica over the past three glacial cycles. Nature 422(6931):509–512

Wedepohl KH (1995) The composition of the continental crust. Geochim Cosmochim Acta 59(7):1217–1232

Wolff EW, Suttie ED (1994) Antarctic snow record of Southern Hemisphere lead pollution. Geophys Res Lett 21:781–784

Wolff EW, Suttie ED, Peel DA (1999) Antarctic snow record of cadmium, copper, and zinc content during the twentieth century. Atmos Environ 33(10):1535–1541. doi:10.1016/s1352-2310(98)00276-3

Wolff EW, Chappellaz J, Blunier T, Rasmussen SO, Svensson A (2010) Millennial-scale variability during the last glacial: the ice core record. Quat Sci Rev 29(21–22):2828–2838. doi:10.1016/j.quascirev.2009.10.013

Xu L-Q, Liu X-D, Sun L-G, Chen Q-Q, Yan H, Liu Y, Luo Y-H, Huang J (2011) A 700-year record of mercury in avian eggshells of Guangjin Island, South China Sea. Environ Pollut 159(4):889–896

Yang H, Battarbee RW, Turner SD, Rose NL, Derwent RG, Wu G, Yang R (2010) Historical reconstruction of mercury pollution across the Tibetan Plateau using lake sediments. Environ Sci Technol 44(8):2918–2924

Zhang Q, Huang J, Wang F, Mark L, Xu J, Armstrong D, Li C, Zhang Y, Kang S (2012) Mercury distribution and deposition in glacier snow over western China. Environ Sci Technol 46(10):5404–5413. doi:10.1021/es300166x

Zheng J, Shotyk W, Krachler M, Fisher DA (2007) A 15,800-year record of atmospheric lead deposition on the Devon Island Ice Cap, Nunavut, Canada: natural and anthropogenic enrichments, isotopic composition, and predominant sources. Global Biogeochem Cycles 21(2):GB2027. doi:10.1029/2006gb002897