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Review article

Lead isotopes in environmental sciences: A review

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Abstract

Lead (Pb) isotopic analyses proved to be a very efficient tool for tracing the sources of local and global Pb pollution. This review presents an overview of literature published on the use of Pb isotopic analyses of different environmental matrices (atmospheric aerosols, lichens, tree rings, peat deposits, lake, stream, marine sediments, soils, etc.). In order to gain more insight, the isotopic compositions of major sources of Pb in the environment as determined by several authors are described in detail. These include, above all, the former use of leaded gasoline, coal combustion, industrial activities (e.g., metallurgy) and waste incineration. Furthermore, this review summarises analytical techniques (especially ICP-MS) used for the determination of Pb isotopes in environmental samples.

Keywords: Lead; Isotopes; ^{206}Pb/^{207}Pb; Pollution; Atmosphere; Soil; Sediment; Peat deposit; Tree rings

Contents

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1. Introduction

Lead (Pb) is a non-essential and toxic metal whose biogeochemical cycle has been affected by man to a great degree. Lead enters the environment during production (including mining and smelting), use (batteries, pigments, ceramics, plastics), recycling, disposal of Pb compounds, combustion of fossil fuels (coal, former use of leaded gasoline), use of mineral fertilisers and sewage sludge application, etc. (Mihaljevič, 1999; Rieuwerts et al., 1999; Adriano, 2001; Ahlberg et al., 2006). Estimates of the emissions of individual sources of Pb indicate that the atmosphere is the major initial recipient and that the anthropogenic sources are at least 1–2 orders of magnitude greater than natural sources. The contamination of the atmosphere with Pb is estimated to be ~5000 years old when first inefficient smelting technologies were introduced in south-western Asia (processing of sulphides containing Pb–Ag alloys). The world Pb production at that time was estimated to be 200 t year^{-1}. During the era of the Roman Empire the production increased to up to 80000 t Pb year^{-1} (Patterson, 1971; 1972; Adriano, 2001). At the beginning of the 20th century, a further increase (to 1×10^6 t year^{-1}) occurred due to emerging industrial activities together with the introduction of leaded gasoline in the 1940s (Shiharata et al., 1980; Adriano, 2001). In the 1960s and 1970s, alkyllead gasoline additives became the most important sources of atmospheric Pb pollution throughout the world (Nriagu, 1990). The phasing out of leaded gasoline increased the relative contribution of industrial Pb in atmospheric pollution (Nriagu and Pacyna, 1988; Nriagu, 1990; Véron et al., 1999; Bollhöfer and Rosman, 2001).

Knowing only the total concentrations and chemical/mineralogical position of Pb is not sufficient for a precise evaluation of contamination sources. Lead isotopes have thus been introduced as “fingerprints” of environmental pollution. Each source of Pb can have distinct or sometimes overlapping isotopic ratio ranges. The isotopic composition of Pb in soils reflects the mixing of these sources, and source apportionment can be quantified in cases where all potential sources of Pb are characterised and have specific ratios. Lead isotopic studies provide therefore a convenient approach for studying and tracing the sources of Pb pollution in different environmental compartments. The aim of this review is to present an overview of literature published on the use of stable Pb isotopes as tracers of environmental pollution.

2. Basic information about Pb isotopes

Lead is present in the environment as four main isotopes: ^{208}Pb (52%), ^{206}Pb (24%), ^{207}Pb (23%) and ^{204}Pb (1%). While radiogenic isotopes ^{206}Pb, ^{207}Pb and ^{208}Pb are products of radioactive decay of ^{238}U, ^{235}U and ^{232}Th, respectively, ^{204}Pb is the only primordial stable isotope with a constant abundance on Earth in time (Table 1; Long, 1999). The abundance of Pb isotopes in a sample depends thus strictly on the concentrations of primordial Pb, U and Th and the lengths of the decay processes, i.e., half-lives ($t_{1/2}$) of the parent isotopes. The three radioactive isotopes ^{210}Pb ($t_{1/2}$=22 years), ^{212}Pb ($t_{1/2}$=10 h) and ^{214}Pb ($t_{1/2}$=26.8 min) are commonly used in tracing experiments (e.g., Narbutt and Bilewicz, 1998; Sanchez-Cabeza et al., 2007). Furthermore, ^{210}Pb for its convenient half-time is widely used for dating of glacial age, recent sediments and peat deposits (Vile et al., 2000; Shotyk et al., 1996).

The isotopic composition of Pb can be expressed by several means. In Earth and especially environmental sciences, the isotopic composition of Pb is commonly expressed as ratios ^{206}Pb/^{204}Pb, ^{206}Pb/^{207}Pb, ^{208}Pb/^{206}Pb with ^{206}Pb/^{207}Pb being the most preferred because it can be determined precisely analytically and the abundances of these isotopes are relatively important. However, normalisation to ^{204}Pb (^{206}Pb/^{204}Pb, ^{208}Pb/^{204}Pb) yields the largest variability between reservoirs. Furthermore, the abundance of ^{207}Pb has changed very little with time compared to ^{206}Pb because most ^{235}U has already decayed while ^{238}U still has a relatively high abundance on Earth (Erel et al., 2001). For example, while old Pb ores are generally characterised by a low ^{206}Pb/^{207}Pb ratio (1.06–1.10), more recent samples containing more radiogenic Pb (originating from U and Th decay) reflect higher ^{206}Pb/^{207}Pb ratios (>1.18) (Farmer et al., 2000; Bacon, 2002). The isotopic composition of Pb is not significantly affected by physico-chemical fractionation processes; therefore, Pb isotopes provide an efficient tool

Table 1
Pb isotopes and half-times of the decay processes of their parent isotopes

Parent isotope	Pb isotope	Decay half-time of the parent isotope (years)	Decay constant of the parent isotope (years^{-1})
–	^{204}Pb	–	–
^{238}U	^{206}Pb	4.466×10^9	λ_{238U}: 1.552×10^{-10}
^{235}U	^{207}Pb	0.704×10^9	λ_{235U}: 9.850×10^{-10}
^{232}Th	^{208}Pb	1.401×10^{10}	λ_{232Th}: 4.948×10^{-11}

for determining the sources and pathways of Pb pollution (Bollhöfer and Rosman, 2001; Veysseyre et al., 2001).

3. Analyses of Pb isotopes

3.1. Recent analytical techniques used for Pb isotopic ratios measurements

Mass spectrometry, either with thermal ionisation (TIMS) or with inductively coupled plasma as the ion source (ICP-MS), has been successfully applied in Pb isotopic studies. The ICP-MS instruments include those with quadrupole-based (ICP-QMS), sector-based (or sector field) (ICP-SFMS) and time-of-flight-based mass analysers (ICP-TOF-MS). Furthermore, the sector-based techniques can be equipped with single (SC) or multiple collector (MC) detection.

3.1.1. TIMS

TIMS is a reliable analytical technique for precise and accurate determination of Pb isotope ratios in environmental samples (e.g., Weiss et al. 1999). Suitable chemical forms for filament loading, absence of elements used as spike, and minimal analyte contamination are of a great concern during the sample preparation for TIMS measurement. This technique requires separation of Pb from matrix elements, which is performed using dithizone (e.g., Rabinowitz and Wetherill, 1972) or HBr complexes and AG1-X8 ion exchange separation (Manhes et al. 1978; Monna et al. 1997). Extensive chemical treatment and optimisation of vaporisation and ionisation of sample prolong the analytical procedure but permit the determination of Pb isotopes with relative standard deviation (RSD) of 0.00*X* to 0.0*X* % (Thirlwall, 2000).

3.1.2. ICP-QMS

The ICP as an ion source allows easy handling and preparation of samples, fast and simple analyte introduction into the mass spectrometer which result in fast analyses (Montaser, 1998). The accuracy and precision of ICP-QMS are lower (from 0.1–0.5%, e.g., Becker and Dietze, 2000) compared to TIMS (Quétel et al., 1997; Montaser, 1998). This limitation of ICP-QMS is due to the unstable nature of the plasma ion source and analyser parameters. The other drawback is that the masses are not detected simultaneously; therefore, the precision during isotope ratio measurements obtained using single collector configurations is generally lower.

3.1.3. ICP-SFMS

The main advantages of ICP-SFMS are as follows: (i) simplified sample preparation procedures with high sample throughput (Quétel et al., 1997); (ii) measurement time is reduced compared to TIMS. The other advantages of ICP-SFMS compared to ICP-QMS include higher sensitivity, less electronic noise and ability to separate spectral interferences in high resolution mode (Krachler, 2007). In low resolution modes, ICP-SFMS yields isotope ratio precision of $<0.05\%$ (Krachler et al., 2004; Krachler, 2007). The use of other techniques in specific applications, such as time-of-flight inductively coupled plasma mass spectrometry (TOF-ICP-MS), can lead to comparable precision levels as those obtained by ICP-SFMS (Barbaste et al., 2001).

3.2. Factors influencing measurement precision and accuracy

As the masses of Pb isotopes are high, spectral interferences of polyatomic ions are not common. Possible small isobaric interference occurs in TIMS from $BaPO_{2^+}$ (Potts, 1995). The important isobaric interference at *m*/*z* (mass/charge) = 204 (^{204}Hg) (Baker et al., 2004) can be mathematically corrected using the isotope ^{202}Hg (Barbaste et al., 2001) or ^{200}Hg (Dolgopolova et al., 2004). Prior to analyses, some authors recommend to perform matrix separation by co-precipitation to avoid mainly non-spectral interferences (Reuer et al., 2003; Chillrud et al., 2005); by ion exchange chromatography (Yoshinaga, 1996; Monna et al., 1998; Weiss et al., 2004; Hinners et al., 1998) or using the flow injection on-line preconcentration procedure (Benkhedda et al., 2004). These approaches preconcentrate Pb in the samples and thus overcome the isobaric interferences and possible matrix effects. For the same reasons, an external normalisation with matrix-matched standards is strongly recommended (Reuer et al., 2003).

Methods for correcting the behaviour of individual masses in an ion beam (space charge effects) for TIMS and ICP-MS are described by many authors (Woodhead et al., 1995; Thirlwall, 2000; 2001; Xie and Kerrich, 2002; Reuer et al., 2003; Baker et al., 2004). No definitive method exists but the correction using NIST 981 (Common Lead Isotopic Standard) could be possibly applicable directly to all analytical methods used for isotope ratio measurements (Monna et al., 1998). For specific applications other Pb isotopic standards can be used (e.g., NIST 982 — Equal-Atom Lead Isotopic Standard; NIST 983 — Radiogenic Lead Isotopic Standard). The other mass bias correction used for ICP-MS measurements is based similarly on a correction via the internal ^{203}Tl/^{205}Tl (NIST 997 — Isotopic Standard for Thallium) ratio determination and subsequent calculation of the mass discrimination factor (Woodhead et al., 1995; Thirlwall, 2000; Xie and Kerrich, 2002; Reuer et al., 2003).

Counting statistics can be considered as another important parameter limiting the precision when the instrument is operated under optimal conditions (Monna et al., 1998). Improvement of the counting statistics is theoretically possible by (i) increasing the time spent on each isotope; (ii) increasing the number of repetitions and (iii) increasing analyte concentration. However, some limitations to this approach occur: high concentrations reduce rapidly the detector lifetime and, additionally, memory effects could be expected (Monna et al., 1998). Earlier work concerning the optimisation of data acquisition factor to minimise non-random instrumental noise by Pb isotopic ratio determination using ICP-MS was published by Quétel et al. (1997). The factors evaluated in this work were (i) dwell time (period of time spent by the quadrupole on each peak); (ii) number of sweeps/replicate and (iii) number of replicates/analyses. The authors concluded that for accurate and precise analyses (mainly of ^{204}Pb with low relative abundance) it is important to increase the counting time by increasing the number of sweeps together with shortening the dwell time to 20 ms. Monna et al. (1998) recommended for quadrupole-based ICP-MS an external mass bias correction based on measuring a solution of known isotopic composition, e.g., NIST 981 after every 4 or 5 unknown samples and correct isotope ratio by extrapolation. The authors further tested the four schemes of different dwell time settings dedicated to each isotope measurements by ICP-QMS: (i) strictly equal times; (ii) times inversely proportional to abundances; (iii + iv) two intermediate positions corresponding to optimal times computed using Poisson statistics (73% for ^{204}Pb, 10% for each of ^{206}Pb and ^{207}Pb and 7% for ^{208}Pb). Results showed that analysis time can be reduced down to 40% (^{206}Pb, ^{207}Pb) and 20% (^{208}Pb) (Monna et al., 1998); therefore, it should be pointed out that the previous solutions using timings inversely proportional to the abundance are not optimal.

3.3. Quality control and quality assurance of Pb isotopic ratios determination

Standard reference materials used for quality control (QC) and quality assurance (QA) of Pb isotopic analyses are the following: certified rock powders AGV – 2 (andezite) and BCR – 2 (basalt) from the U.S. Geological Survey (USGS, 1998; Woodhead and Hergt, 2000), and the glass wafers (NIST 610) used for laser ablation ICP-MS (Platzner et al., 2001; Walder et al., 1993). Low ash peat material with known Pb isotopic composition is available at the University of Edinburgh (Yafa et al., 2004). Certified values for Pb isotopic composition are available for the wine sample IMEP 16 (Pb in wine) (van Nevel et al., 2001). Other materials with analysed ^{206}Pb/^{207}Pb ratio include NIST 1635 – (Trace elements in coal — subbitumenous) and BCR CRM 40 (Steam coal) (Farmer et al., 1999). Due to the low number of reference materials suitable for QC/QA of Pb isotope ratio analyses, individual laboratories prepared their “in-house reference materials” or provided comparative measurements of identical samples by TIMS (Krachler et al., 2004).

4. Pb isotopic ratios of different anthropogenic sources

While each Pb source has its own specific isotopic composition, it is important to note that separate geochemical reservoirs are linked together and the final isotopic composition of Pb results from mixing of many different sources. The following chapters present an overview of the Pb isotopic compositions (mainly ^{206}Pb/^{207}Pb) of different anthropogenic sources as published in the literature. Table 2 summarises these data.

4.1. Leaded gasoline

The former use of leaded gasoline had represented one of the main sources of global Pb pollution in the period between the 1940s and the 1980s. The knowledge about the origin of gasoline, i.e. about the origin and age of Pb ore used for alkyllead antiknock additives (tetraethyllead $Pb(C_2H_5)_4$ (TEL), tetramethyllead $Pb(CH_3)_4$ (TML)) is vital for a precise identification of Pb originating from leaded gasoline combustion (Shiharata et al., 1980; Monna et al., 1997). The isotopic composition of Pb ores used thus reflects the composition of leaded gasoline. The ^{206}Pb/^{204}Pb and ^{206}Pb/^{207}Pb ratios commonly found in Pb ores throughout the world range between 16.0–18.5 and 1.19–1.25, respectively (Hansmann and Köppel, 2000). Exception to this rule is the commonly used Pb ore from the Broken Hill deposit, Australia, which is characterised by extremely low ^{206}Pb/^{207}Pb ratios (1.03–1.10). On the other hand, Pb originating from the Mississippi Valley ore deposit, USA, exhibits significantly more radiogenic Pb isotopic composition (^{206}Pb/^{204}Pb > 20.0; ^{206}Pb/^{207}Pb = 1.31–1.35) (Doe and Delevaux, 1972). American leaded gasoline reflected therefore significantly higher ^{206}Pb/^{207}Pb ratios compared to European gasoline (Fig. 1). The introduction of the European leaded gasoline around 1945 resulted in a steep decrease of the ^{206}Pb/^{207}Pb ratio of atmospheric Pb (Weiss et al., 1999; data from peat deposits). The isotopic composition of leaded gasoline was to some extent dependent on economical factors, such as the availability and price of Pb ores and has evolved due to the different Pb ores used. For example, Pb used for French leaded gasoline originated from Australian, Moroccan and Swedish ores and the contribution of the separate ores changed during time (Véron et al., 1999). It is therefore indispensable to gather data concerning the origin of gasoline used in studied regions. It is possible to assume that Pb originating from European leaded gasoline has the least radiogenic composition from all anthropogenic sources. While the Pb isotopic composition of gasoline originating from Western Europe was strongly influenced by low ^{206}Pb/^{207}Pb values (~1.03–1.04; Pb imported from Broken Hill, Australia) (Doe and Stacey, 1974; Grousset et al., 1994; Weiss et al., 1999), gasoline used in Central and Eastern Europe reflected slightly higher values (^{206}Pb/^{207}Pb ~ 1.11–1.13) due to petrol additives originating from Eastern Germany and/or Russia (Novák et al., 2003).

4.2. Coal combustion

Coal combustion has been another important anthropogenic source influencing the isotopic composition of Pb for many decades. Lead released during coal combustion can be distinguished from other sources using Pb isotopes because of its different isotopic composition. The ^{206}Pb/^{207}Pb ratio in European coals is not age dependent and ranges between 1.16 and 1.21 (Farmer et al., 1999; Hansmann and Köppel, 2000; Rosman et al., 2000; Novák et al., 2003). Lead isotopic studies in peat deposits proved that coal combustion was the predominant source of Pb in the atmosphere before the introduction of leaded gasoline and air pollution control (APC) policies in thermal plants (Vile et al., 2000; Novák et al., 2003). Coal burning in Central Europe is often difficult to discern from the background source (^{206}Pb/^{207}Pb ~ 1.19), but contributes to the isotopic composition of an “industrial” Pb mixture, which can be detected in recent atmospheric aerosols and yields ^{206}Pb/^{207}Pb values of ~1.15 (Weiss et al., 1999; Novák et al., 2003).

4.3. Metallurgical activities

The isotopic composition of Pb emitted to the atmosphere during pyrometallurgical processes reflects closely the isotopic

Table 2
Examples of Pb isotopic compositions (^{206}Pb/^{207}Pb) of different anthropogenic Pb sources in the environment

Sample	Country (location)	^{206}Pb/^{207}Pb		n [a]	References
		Range	Mean±SD		
Gasoline and vehicular Pb					
Leaded gasoline	United Kingdom	1.059–1.079	1.067±0.007	7	Monna et al. (1997)
Leaded gasoline	France (NW)	1.060–1.100	1.083±0.015	4	Véron et al. (1999)
Leaded gasoline	France	1.069–1.094	1.084±0.009	9	Monna et al. (1997)
Leaded gasoline	Switzerland (Geneva)	1.081–1.132	1.113±0.015	12	Chiaradia and Cupelin (2000)
Road tunnel dust	Switzerland (Milchbuck)	1.109–1.118	1.114±0.004	3	Hansmann and Köppel (2000)
Vehicle exhaust	Switzerland (Milchbuck)	1.086–1.125	1.107±0.012	6	Hansmann and Köppel (2000)
Leaded gasoline	Czech Republic		1.110±0.016	10	Novák et al. (2003)
Road tunnel dust	Czech Republic (Prague)		1.135±0.001	1	Ettler et al. (2004)
Leaded gasoline	Israel (Jerusalem)	1.094–1.119	1.109±0.007	8	Erel et al. (1997)
Unleaded gasoline	Israel (Jerusalem)	1.108–1.146	1.126±0.015	4	Erel et al. (1997)
Leaded gasoline	Mexico	1.202–1.204	1.203±0.001	2	Sañudo-Wilhelmy and Flegal (1994)
Leaded gasoline	Canada	0.920–1.190	1.105±0.086	15	Sturges and Barrie (1987)
Leaded gasoline	USA	1.040–1.390	1.183±0.103	8	Sturges and Barrie (1987)
Leaded gasoline	Russia	1.134–1.149	1.142±0.008	2	Mukai et al. (2001)
Vehicle exhaust (leaded)	China (Shanghai)	1.098–1.116	1.110±0.005	5	Chen et al. (2005)
Vehicle exhaust (unleaded)	China (Shanghai)	1.138–1.160	1.147±0.004	5	Chen et al. (2005)
Coal					
Coal	United Kingdom (England and Wales)	1.172–1.202	1.184±0.006	25	Farmer et al. (1999)
Coal	United Kingdom (Scotland)	1.159–1.213	1.181±0.011	30	Farmer et al. (1999)
Coal	Ireland	1.165–1.307	1.178±0.012	6	Farmer et al. (1999)
Coal	Spain	1.130–1.268	1.191±0.032	24	Diaz-Somoano et al. (2007)
Coal	Poland (Yanowice)		1.177±0.001	1	Farmer et al. (1999)
Coal	Germany (Hambach)		1.174±0.003	1	Farmer et al. (1999)
Coal	Switzerland (Geneva)		1.181	1	Chiaradia and Cupelin (2000)
Coal	Belgium	1.170–1.180	1.176±0.004	10	Walraven et al. (1997)
Coal	Czech Republic		1.190±0.006	7	Novák et al. (2003)
Coal	China (Shanghai)	1.140–1.208	1.163±0.001	23	Chen et al. (2005)
Coke	China (Shanghai)		1.160±0.001	1	Chen et al. (2005)
Coal combustion dust	China (Shanghai)	1.163–1.172	1.167±0.002	3	Chen et al. (2005)
Coal fly ash	China (Shanghai)	1.161–1.170	1.166±0.002	3	Chen et al. (2005)
Coal	USA	1.126–1.252	1.201±0.023	21	Tsaihwa and John (1972)
Coal	Colombia (La Jagua)		1.219±0.004	1	Farmer et al. (1999)
Coal fly ash	Australia (Illawara/Tallawara)		1.211	1	Chiaradia et al. (1997)
Coal	Russia	1.200–1.212	1.206±0.005	3	Mukai et al. (2001)
Coal	South Africa (Reitspruit)		1.206±0.003	1	Farmer et al. (1999)
Metallurgy/smelters					
Aerosol–Fe–Mn metallurgy	France (Nord-Pas de Calais)		1.111±0.005	n.a. [b]	Véron et al. (1999)
Aerosol–Pb smelter	France (Nord-Pas de Calais)		1.133±0.001	n.a.	Véron et al. (1999)
Aerosol–steel metallurgy	France (Nord-Pas de Calais)		1.196±0.015	n.a.	Véron et al. (1999)
Slag — Pb–Zn smelter	France (Noyelles-Godault)		1.104	1	Cloquet et al. (2006b)
Dust from filters — Pb–Zn smelter	France (Noyelles-Godault)	1.127–1.131	1.129±0.002	2	Cloquet et al. (2006b)
Slags from medieval metal workshops	France (Mont-Lozère/Cévennes)	1.175–1.182	1.181±0.001	37	Baron et al. (2005, 2006a,b)
Dust — Zn metallurgical plant	Switzerland (Buchs)		1.143	1	Hansmann and Köppel (2000)
Slag — Pb smelter (ore processing)	Czech Republic (Příbram)		1.165±0.004	1	Ettler et al. (2004)
Slag — Pb smelter (battery processing)	Czech Republic (Příbram)		1.168±0.004	1	Ettler et al. (2004)
Fly ash — Pb smelter (ore processing)	Czech Republic (Příbram)		1.167±0.003	1	Ettler et al. (2004)
Fly ash — Pb smelter (battery processing)	Czech Republic (Příbram)		1.177±0.003	1	Ettler et al. (2004)
Slag — Zn–Pb smelter	Australia (Cockle Creek/New S Wales)	1.139–1.140	1.139±0.001	2	Gulson et al. (2004)
Fume — base metal smelter	Australia (Illawara/Port Kembla)	1.146–1.148	1.147±0.001	3	Chiaradia et al. (1997)
Fume — base metal smelter	Australia (Illawara/Kanahooka)		1.058	1	Chiaradia et al. (1997)
Fume — steel works	Australia (Illawara/Port Kembla)	1.180–1.213	1.196±0.017	2	Chiaradia et al. (1997)

Table 2 (*continued*)

Sample	Country (location)	$^{206}Pb/^{207}Pb$		n[a]	References
		Range	Mean±SD		
Metallurgy/smelters					
Ingots — Pb smelter	USA (Bunker Hill/Idaho)	1.070–1.140	1.095±0.029	4	Rabinowitz (2002, 2005)
Ingots — Pb smelter	USA (Doe Run/Missouri)	1.310–1.340	1.330±0.014	3	Rabinowitz (2002, 2005)
Slags and ingots — Pb smelter	USA (Eagle-Picher/Kansas–Okl.–Missouri)	1.210–1.360	1.282±0.058	6	Rabinowitz (2002, 2005)
Slag — Pb smelter	USA (ILP/Utah)		1.150	1	Rabinowitz (2002, 2005)
Electric-arc furnace dust — Zn smelter	USA (Palmerton, Pennsylvania)	1.206–1.224	1.213±0.055	6	Ketterer et al. (2001)
Cu smelter emissions	Canada (Rouyn-Noranda)	0.920–1.030		n.a.	Gallon et al. (2006), Savard et al. (2006a,b), Hou et al. (2006)
Aircraft-sampled Cu smelter emissions	Canada (Rouyn-Noranda)	1.122–1.167	1.144±0.012	21	Simonetti et al. (2004)
Dust — metallurgy	China (Shanghai)	1.148–1.164	1.157±0.005	5	Chen et al. (2005)
Municipal solid waste incinerators					
Incinerator ash	Switzerland (Geneva)	1.154–1.156	1.155±0.001	2	Chiaradia and Cupelin (2000)
Incinerator fly ash	Switzerland (Zürich/Hinwill)	1.150–1.153	1.151±0.001	6	Hansmann and Köppel (2000)
Incinerator flue gas	France (Metz)	1.154–1.157	1.155±0.002	3	Cloquet et al. (2006a)
Incinerator electrostatic precipitator ash	France	1.150–1.158	1.155±0.002	13	Carignan et al. (2005)
Incinerator filter cake	France	1.156–1.157	1.156±0.001	4	Carignan et al. (2005)
Incinerator scrubber residue	France	1.149–1.155	1.152±0.002	5	Carignan et al. (2005)
Incinerator fly ash	France	1.148–1.151	1.149±0.001	4	Carignan et al. (2005)
Incinerator ash	France (Sète)	1.143–1.155	1.149±0.004	4	Monna et al. (1997)

[a] Number of samples.

[b] n.a. — not available.

composition of the material processed, such as Pb ore or secondary processed materials containing Pb (e.g., Pb batteries) (Ettler et al., 2004). Further information can be obtained from APC residues originating from the smelters which will influence to a great extent the isotopic composition of Pb in atmospheric aerosols and after sedimentation, in soils (Ettler et al., 2005a). The predominant influence of Pb smelters on local contaminations of the atmosphere, soils and sediments has been proved by several Pb isotopic studies (e.g., Ettler et al., 2004; Hou et al. 2006; Komárek et al., 2007).

4.4. Waste incineration

Monna et al. (1997) showed in their work that fly ash originating from waste incinerators can be used as an average industrial source of Pb. All waste products containing Pb are mixed together and burned; the measured Pb isotopic composition thus reflects average values. However, the ratio $^{206}Pb/^{207}Pb$ measured by Monna et al. (1997) in fly ash originating from the incinerator in Sète, France, varied due to the heterogeneity of the wastes and due to the limited number of samples ($^{206}Pb/^{207}Pb = 1.14–1.16$). Carignan et al. (2005) analysed fly ash and flue gas from eight municipal solid waste combustors in France and obtained $^{206}Pb/^{207}Pb$ values ranging from 1.15 to 1.16. Similar results were obtained in other countries: Japan ($^{206}Pb/^{207}Pb = 1.15$) (Mukai et al., 1993) and Germany ($^{206}Pb/^{207}Pb = 1.14–1.16$) (Monna et al., 1997). A recent investigation of Pb isotopic composition of urban waste incineration flue gases from northeastern France showed the $^{206}Pb/^{207}Pb$ values close to 1.155 (Cloquet et al., 2006a).

5. Pb isotopes in different reservoirs

Tracing the sources of transboundary atmospheric pollution using Pb isotopic ratios has been successfully applied in studies dealing with atmospheric aerosols (e.g., Sturges and Barrie, 1987; Monna et al., 1997; Bollhöfer and Rosman, 2000, 2001; Flament et al., 2002), lake sediments (e.g., Farmer et al., 1996; Monna et al., 1999; Renberg et al., 2002), snow and ice samples (e.g., Döring et al., 1996; Rosman et al., 2000; Simonetti et al., 2000), peat deposits (e.g., Shotyk et al., 1996; Weiss et al., 1999; Novák et al., 2003), tree rings (e.g., Watmough et al., 1999; Patrick and Farmer, 2006; Savard et al., 2006a), epiphytic lichens (e.g., Carignan and Gariépy, 1995; Doucet and Carignan, 2001; Kylander et al., 2007), grasses (Bacon et al., 1996), etc.

5.1. Atmospheric aerosols

Atmospheric Pb is mostly present in submicrometric aerosols which can be transported over long distances making thus the interpretation of Pb isotopic data complicated. For example, Erel et al. (2002) found that Pb in atmospheric aerosols sampled in Jerusalem, Israel, was not derived only from local sources, but Pb originating from Turkey, Egypt and Eastern Europe contributed

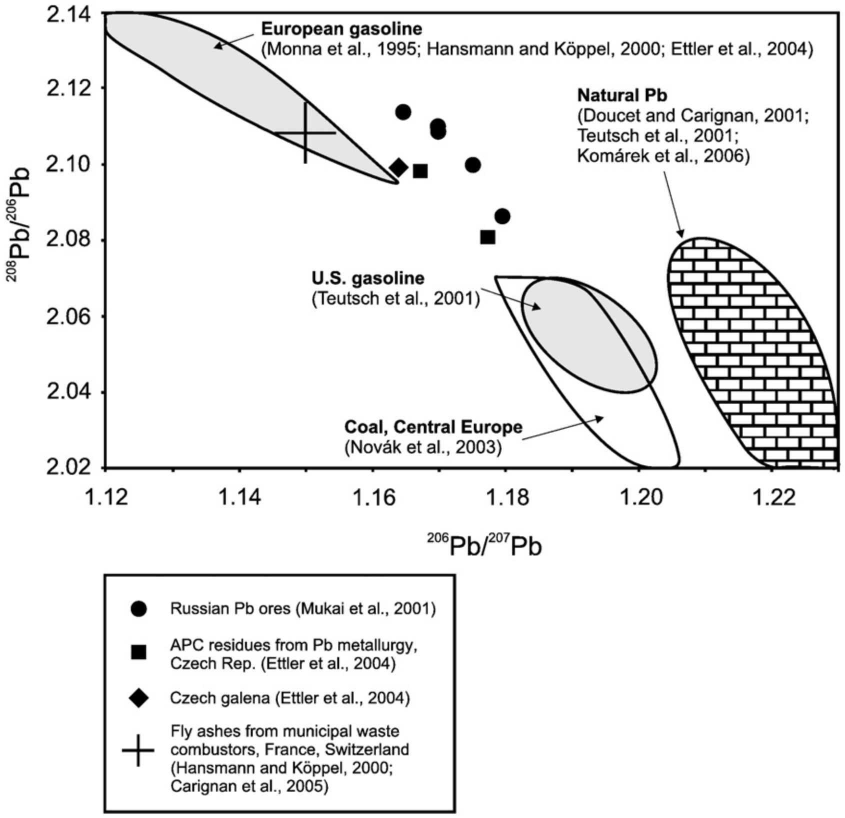

Fig. 1. A schematic three-isotope plot (^{206}Pb/^{207}Pb vs. ^{208}Pb/^{206}Pb) showing the isotopic compositions of different Pb sources.

significantly to the isotopic composition of atmospheric Pb. Doucet and Carignan (2001) proved that even Pb from dust originating from Sahara influences the Pb isotopic composition in European aerosols. A multi-elemental approach using concentrations of other elements (e.g., Zn, Cd, Cu, As, Mn, Al, etc.) or other isotopic ratios (e.g., ^{87}Sr/^{86}Sr) in aerosols can be thus helpful for a precise evaluation of Pb origins (Simonetti et al., 2000; Doucet and Carignan, 2001). The isotopic composition of Pb quickly changes depending on the different inputs of Pb, distances from industrial areas, traffic density, prevailing wind directions, rainfall intensity, etc. (Shiharata et al., 1980; Monna et al., 1997; Simonetti et al., 2000). For example the ^{206}Pb/^{207}Pb ratio in aerosol samples from California, USA, changed from 1.15 (data from 1967) to 1.23 (data from 1977). This increase was associated with the use of gasoline additives containing Pb from Mississippi Valley, USA, ores characterised with a high ^{206}Pb/^{207}Pb ratio (1.28–1.33) (Shiharata et al., 1980). Abandoning Pb originating from Mississippi Valley ores resulted in a decrease of the ^{206}Pb/^{207}Pb ratio in American aerosols in the 1980s down to 1.18 (Erel et al., 1997) and to 1.16 in 1990s (Bollhöfer and Rosman, 2001). As a whole, the isotopic composition of US aerosols changed but it remained relatively heterogeneous, depending on the location of sampling. As an example, Carignan et al. (2002) reported ^{206}Pb/^{207}Pb values obtained from epiphytic lichens originating from northeastern North America to be 1.15–1.21. The evolution of the ^{206}Pb/^{207}Pb ratio in Western European atmosphere, as measured in grasses originating from Southeast of England, reflected a different trend. A significant decrease of the ^{206}Pb/^{207}Pb ratio (from 1.17 to 1.09) was observed from the end of the 19th century to the end of WWII. This decrease can be explained by several means: (i) increased import of ores with less radiogenic ratios, (ii) changes in industrial practices, (iii) combustion of coal originating from different areas (Bacon et al., 1996). The further decrease of the ^{206}Pb/^{207}Pb value was caused by the introduction of leaded gasoline throughout the world. The subsequent increase of the ^{206}Pb/^{207}Pb ratio (to 1.13) in the 1980s reflects the gradual abandoning of leaded gasoline throughout Europe. These changes are associated with decreases of atmospheric Pb concentrations. Similar evolution trends of Pb isotopic ratios and concentrations in European atmosphere were observed by several authors (e.g., Shiharata et al., 1980; Grousset et al., 1994; Hansmann and Köppel, 2000). The opposite evolutions of ^{206}Pb/^{207}Pb ratios in Northern America and Europe are given in Fig. 2.

5.2. Peat deposits

Many studies have used peat deposits as archives of historical Pb pollution and atmospheric Pb deposition. The scientific community using this type of archive is still growing as shown by a number of papers published in recent years (e.g., Shotyk et al., 2003; Bindler et al., 2004a; Monna et al., 2004a; Farmer et al.,

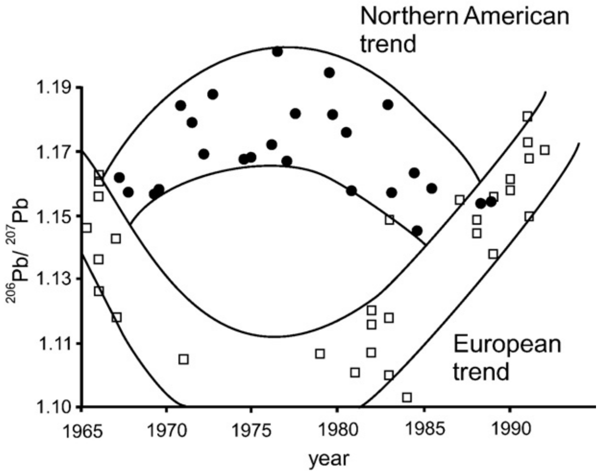

Fig. 2. Different evolution trends of the ^{206}Pb/^{207}Pb ratio in North American and European atmospheric aerosols (redrawn after Grousset et al., 1994).

2005). The ombrotrophic peat bogs are considered as one of the best continental archives, which can be used to reconstruct the historical atmospheric deposition (MacKenzie et al., 1998; Weiss et al., 2002; Shotyk and Le Roux, 2005). Ombrotrophic *Sphagnum*-derived peat bogs are fed only by rain water and efficiently retain metals entering by atmospheric deposition. Minerotrophic peat deposits are also used for this purpose (Monna et al., 2004b; Weiss et al., 1999; Baron et al., 2005; Mihaljevič et al., 2006a); however, being fed not only by atmospheric precipitation, but also by groundwater, the continuity of the atmospheric deposition can be disturbed (MacKenzie et al., 1998).

Lead isotopic studies in peat deposits are often focused on tracing Pb pollution sources during the last ~200 years (since the Industrial Revolution) (Weiss et al., 1999; Novák et al., 2003). However, some deeper peat profiles are used to reconstruct Pb deposition to a larger extent, e.g., a period of more than the last 5000 years on the Faroe Islands (Shotyk et al., 2005), more than 4000 years in England (Le Roux et al., 2004) or the last 4600 years in Spain (Martínez Cortizas et al., 2002). Such studies of long-term Pb isotopic changes can be useful in determining the pre-anthropogenic Pb deposition and specific Pb isotopic fingerprints for periods of Metal Ages, Roman periods and Middle Ages.

The patterns of Pb isotopic changes recorded in peat bogs are strictly dependent on the localities. The Central European studies show that pre-industrial isotopic compositions yielded values close to the value of the continental crust (^{206}Pb/^{207}Pb ~ 1.19–1.22) (Weiss et al., 1999). The most important shift to lower ^{206}Pb/^{207}Pb values can be noticed in peat profiles after ~1930s due to the increase of vehicular Pb. In peat profiles from England and Scotland, anthropogenic Pb mostly derived from car exhausts (^{206}Pb/^{207}Pb ~ 1.11–1.13) is distinguished from the pre-industrial values, which were slightly lower than in continental Europe (^{206}Pb/^{207}Pb ~ 1.16–1.17) (MacKenzie et al., 1998; Weiss et al., 2002; Farmer et al., 2005). In Scotland, a significant decline in ^{206}Pb/^{207}Pb value can be observed after the 1930s with a minimum in 1990s (~1.13) and an increase to 1.16 in very recent years corresponding to a cessation in the use of Pb-containing gasoline (Farmer et al., 2005). This temporal trend can also be observed for other archives used for the reconstruction of changes in Pb pollution sources in UK (Fig. 3). A historical insight into Pb deposition from 2000 BC to 1800 AD (Le Roux et al., 2004) showed a slight decrease in ^{206}Pb/^{207}Pb value with respect to the pre-anthropogenic isotopic composition (1.18–1.17) during the Roman Occupation (43 AD–410 AD), which however still corresponds to the Pb isotopic fingerprints of English Pb ores. Declines in Pb metallurgical activities in England during the epidemics are also indicated by Pb isotopes in English peat cores (Le Roux et al., 2004).

The Spanish peat bog archives showed high values of pre-anthropogenic isotopic compositions (^{206}Pb/^{207}Pb ~ 1.27, 4000 years BP) with an increasing trend until the period of the Roman Empire, which significantly enhanced the mining and smelting of Iberian ores (^{206}Pb/^{207}Pb = 1.18), followed by an increase in ^{206}Pb/^{207}Pb value due to the fate of mining during Middle Ages (Martínez Cortizas et al., 2002). Similarly, the extensive mining/smelting activities were detected in peat archives from French Central Massif (Morvan) in several successive period from Bronze and Iron Ages, Antiquity to Middle Ages using a combination of differences in Pb isotopic composition and Sc-normalised Pb contents (Monna et al., 2004b). As the isotopic compositions of Pb sources in the North America are significantly different and variable, the records from Canadian peat deposits contrast with those from Europe. The pollution sources cannot be often satisfactorily explained

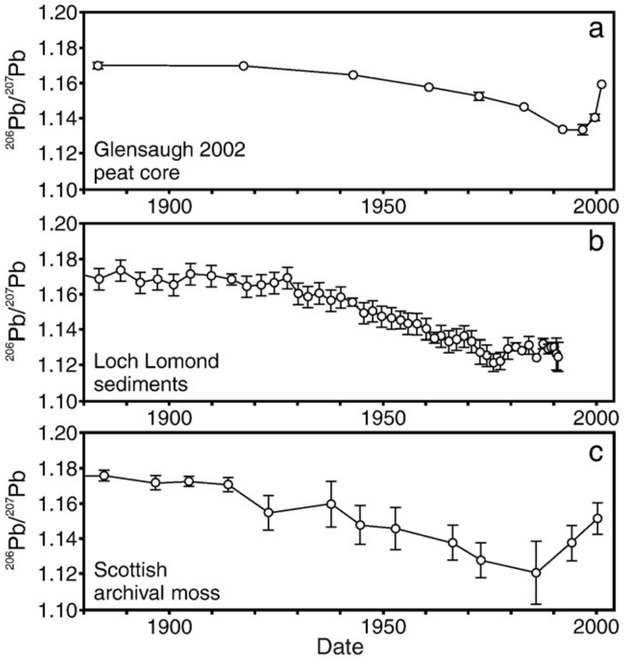

Fig. 3. A comparison of temporal trends in ^{206}Pb/^{207}Pb ratios between different Scottish archives (modified from Farmer et al., 2005): peat core from Glensaugh (north-eastern Scotland) sampled in 2002 (Farmer et al., 2005); Loch Lomond sediment core (Farmer et al., 1996, Eades et al., 2002); Scottish *Sphagnum* moss archive samples (Farmer et al., 2002).

(Weiss et al., 2002). For example, pre-industrial Pb found in deeper peat horizons yields $^{206}Pb/^{207}Pb \sim 1.16$ and the $^{206}Pb/^{207}Pb$ increase up to 1.20, corresponding to modern North American $^{206}Pb/^{207}Pb$ values (Weiss et al., 2002).

5.3. Sediments

5.3.1. Lake sediments

Lake sediments were used as archives of historical Pb contamination to a larger extent since the 1980s (Shiharata et al., 1980; Graney et al., 1995). Lake sediments can give (through feasible slicing in very thin sections) a precise time resolution in Pb deposition and changes in Pb isotopic composition (Farmer et al., 1996). In contrast to deep peat bog profiles, such samples generally yield the record of the last 500 years maximum, showing the Pb isotopic pattern from pre-industrial to recent periods (Farmer et al., 1996; Erel et al., 2001; Eades et al., 2002). Some exceptions, such as studies of deep cores from Swedish lake sediments, show the reconstructions of the last ~11 000 years (Brännvall et al., 2001; Renberg et al., 2002).

The studies of Pb isotopic patterns in lake sediments from continental Europe are mainly studied in Sweden and Switzerland. A ~3500-year record from 31 lake sediment cores in Sweden showed a noticeable peak in $^{206}Pb/^{207}Pb$ value during the Roman Period (~0 AD, $^{206}Pb/^{207}Pb \sim 1.45$), returning to the background value of ~1.15 until the Middle Ages (1000 AD) with small peaks in 1200 and 1530 AD. A further rapid decrease in $^{206}Pb/^{207}Pb$ after World War II (peak in the 1970s, $^{206}Pb/^{207}Pb \sim 1.12$) and a further increase until today's value ~1.13 was observed (Renberg et al., 2002). The variation of $^{206}Pb/^{207}Pb$ ratios is consistent with Pb enrichment factors with respect to the background (Renberg et al., 2002). The Swiss lake sediment profiles are characterised by a background $^{206}Pb/^{207}Pb$ value of ~1.2 and Pb concentration and isotopic peaks in the 1980s and the 1990s ($^{206}Pb/^{207}Pb$ from 1.13 to 1.16, respectively) corresponding to the predominant pollution by gasoline-derived Pb ($^{206}Pb/^{207}Pb \sim 1.04$–$1.10$) (Moor et al., 1996; Kober et al., 1999).

The studies from Britain predominantly attribute the most significant shift in $^{206}Pb/^{207}Pb$ value from background 1.17–1.18 to 1.12 (during 1929 and 1991) to the use of leaded gasoline since the 1920s (Farmer et al., 1996). In general, several different periods can be discerned from the Pb isotopic pattern in lake sediments from northern and central Scotland: (i) pre-1820 $^{206}Pb/^{207}Pb$ ratio close to the local coal (1.18); (ii) 1820–1900, constant $^{206}Pb/^{207}Pb$ value of ~1.17 corresponding to a combination of emissions from coal burning (1.18), indigenous ore smelting (1.17) and use of Australian Pb in south England (1.04); (iii) 1900–1985, decrease in $^{206}Pb/^{207}Pb$ value down to 1.13 due to use of gasoline additives and (iv) increase to $^{206}Pb/^{207}Pb$ value of ~1.145 until the mid 1990s as a consequence of a reduction in car-exhaust emissions (Eades et al., 2002).

A new application of Pb isotopes in lake sediments to trace the atmospheric pollution from Horne smelter (Rouyn-Noranda, Québec, Canada) was recently presented by Gallon et al. (2006). The contribution of the smelter emissions on Pb deposition was calculated using dated sediment cores from four lakes (located 10, 25, 150 and 300 km from the smelter). Lead from the Horne smelter had a Pb isotopic composition ($^{206}Pb/^{207}Pb \sim 0.99$) significantly different from aerosols sampled at remote sites in Eastern Canada ($^{206}Pb/^{207}Pb \sim 1.15$–$1.20$) and USA ($^{206}Pb/^{207}Pb \sim 1.15$–$1.22$) and allowed thus to discern the impact of the smelter. The results showed that the smelter emissions accounted for 89%, 88% and 5–34% of total Pb inventories in lakes located 10, 25 and 150 km from the smelter, respectively. In a distant lake (300 km), the smelter-derived Pb was not isotopically detected.

5.3.2. Stream sediments

Stream (or bottom) sediments and alluvial soils deposited during the flood events represent valuable tools for an assessment of metal contamination dispersal by fluvial systems. Lead isotopes were satisfactorily used to trace the sources and dispersal of Pb in several mining areas (MacKenzie and Pulford, 2002; Ettler et al., 2006). Each polymetallic mining district possesses its characteristic Pb isotopic composition, which helps to discern the degree of contamination downstream from the specific contamination source (mining and milling facilities, tailing ponds, dumps) and to distinguish between the pollution and the geological background. For this purpose, Ettler et al. (2006) used the diagram $^{206}Pb/^{207}Pb$ ratio vs. Al-normalised Pb, which helped to determine the sources of pollution and Pb enrichment with respect to the background (Fig. 4). The degree of pollution generally decreases with the distance from the contamination source, but metals bound to suspended solid particles can travel in the fluvial systems especially during the floods and settle as overbank sediments (alluvial soils) (Monna et al., 2000a). If dated, overbank sediments can be used as a marker of historical Pb deposition during flood events. For example, through Pb isotopic investigations of overbank sediments and possible sources (local ores with variable $^{206}Pb/^{207}Pb$ ratios), Monna et al. (2000a) reconstructed the

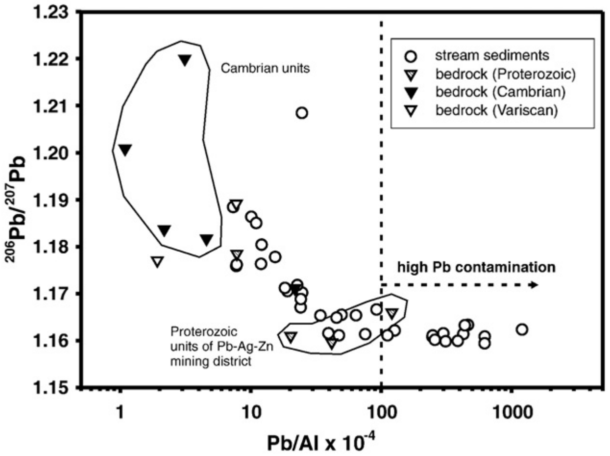

Fig. 4. Diagram $^{206}Pb/^{207}Pb$ vs. Pb/Al showing the sources and degrees of contamination of the stream sediments from the mining/smelting district of Příbram, Czech Republic (modified from Ettler et al., 2006).

history of mining and smelting activities in Harz province, Germany, which began as early as 3500 years ago.

5.3.3. Marine sediments

Relatively few works are dealing with Pb isotopic tracing of pollution in marine sediments. Lead isotopic analyses of surficial pelagic sediments from the North Atlantic identified increased anthropogenic Pb input to marine sediments during the 20th century (Hamelin et al., 1990). Gobeil et al. (2001) used Pb isotopes in sediments underlying boundary currents in the Arctic Ocean to identify pathways of contaminant Pb between the Eurasian basin and the North Atlantic. In their preceding study, Gobeil et al. (1995) used coupled Pb concentration and isotopic data to estimate the depth distribution and the burden of deposited Pb in sediments from the St. Lawrence Estuary, Canada, which is suggested as a globally significant basin for anthropogenic Pb deposition. In another study, Flegal et al. (1989) observed patterns of trace element cycling within coastal waters of the north-east Pacific through Pb isotope analyses.

The study by Hinrichs et al. (2002), focused on Pb pollution pathways in sediments and suspended particulate matter (SPM) in German Bight, shows the differences in Pb isotopic composition between tidal flat sediments (human-unaffected, with geogenic $^{206}Pb/^{207}Pb \sim 1.2$) and nearshore and offshore SPM ($^{206}Pb/^{207}Pb \sim 1.172$ and 1.166, respectively). As the anthropogenic/atmospheric signal corresponds to values $^{206}Pb/^{207}Pb$ ranging from 1.11 to 1.14, the authors calculated that SPM yields $^{206}Pb/^{207}Pb$ values reflecting a mixture of anthropogenic and geogenic Pb.

Coastal ponds communicating with sea water, but fed mainly by rivers represent another type of historical archive of Pb deposition. Several studies of dated sediment cores from Thau coastal pond (southern France) permitted to reconstruct the input and sources of Pb during the last ~150 years (Monna et al., 1995, 2000b). Lead in pond sediments resulted from mixing of three end members: Pb from gasoline used in the area ($^{206}Pb/^{207}Pb$ ranging from 1.10–1.11), natural Pb (1.20) and liquid urban output (1.15–1.17) (Monna et al., 1995). The upper parts of the sediment profiles are characterised by low $^{206}Pb/^{207}Pb$ ratios, corresponding to gasoline-derived Pb (Monna et al., 2000b). In contrast, significant rainfall or storm events are responsible for higher input of geogenic material from karstic areas located north of the coastal pond (Monna et al., 1995).

5.4. Soils

Anthropogenic contamination of soils with metals represents a very serious environmental problem especially in industrial and urban areas (e.g., Adriano, 2001; Mihaljevič et al., 2006b; Komárek et al., 2007). Lead contamination is mainly concentrated in superficial soil horizons depending on organic matter and Fe-, Mn-, Al-(hydr)oxides contents (Ettler et al., 2005b). While the vast majority of heavy metals in soils are derived from anthropogenic sources, Pb isotopic studies proved that increased Pb concentrations can originate from natural processes as well. In general, the isotopic composition of Pb in "uncontaminated" soils is more radiogenic ($^{206}Pb/^{204}Pb \sim 18.5–19.5$) because most Pb is derived from weathered bedrocks and the isotopic composition of Pb is mostly influenced by the decay of ^{238}U to ^{206}Pb. On the other hand, the Pb isotopic composition of Pb ores (with higher Pb/U ratios, due to the separation of Pb from U) will reflect a less radiogenic composition ($^{206}Pb/^{204}Pb \sim 16.0–18.5$) (Hansmann and Köppel, 2000).

Pb isotopic studies have been widely used in soil analyses to evaluate the downward migration of Pb throughout the soil profile (e.g., Puchelt et al., 1993; Ettler et al., 2004). The migration of gasoline-derived Pb was estimated by Erel (1998) using an advection–dispersion model and reached 0.5 cm $year^{-1}$. However, the Pb migration rate is site specific and will depend on many factors (e.g., precipitation, soil organic matter and clay content, etc.) (Ettler et al., 2004; 2005b). Similarly, Klaminder et al. (2006) calculated that Pb deposited in a soil of a small catchment over the past ~4000 years has penetrated below 50 cm down the soil profile. On the other hand, Baron et al. (2006a) in their study involving Pb isotopes and concentrations found no evidence for massive leaching of dissolved Pb through soils at sites contaminated by metallurgical activities. The authors suggest that Pb in such soils is rather dispersed as physical particles (e.g., slag grains).

In some works, sequential extractions preceded Pb isotope analyses in soils. This approach allows to get a more detailed insight on the distribution and origin of Pb in soils (Teutsch et al., 2001; Emmanuel and Erel, 2002; Komárek et al., 2007). For example, Teutsch et al. (2001) proved, via analyses of the Pb isotopic composition in separate soil fractions, that anthropogenic Pb (predominantly derived from leaded gasoline) is concentrated mainly in the exchangeable/carbonate bound and reducible (Fe-(hydr)oxides) fractions. On the other hand, "natural" Pb is mainly associated with the residual silicate fraction. Similar results were obtained in the work of Emmanuel and Erel (2002) with the only exception that anthropogenic Pb was bound predominantly to soil organic matter. Another approach is to use Pb isotopic data obtained from an easily extractable chemical fraction, e.g., 0.05 M EDTA-extractable (Komárek et al., 2006), 0.5–2 M HNO_3-extractable (Hansmann and Köppel, 2000; Teutsch et al., 2001), 0.25 M HCl-extractable (Hou et al., 2006), etc.

Semlali et al. (2001) used a combination of Pb isotopic ratios with Pb/Sc ratios in soils to obtain more detailed information about the distribution of endogenous and exogenous Pb. Moreover, Prohaska et al. (2005) used a combination of $^{207}Pb/^{206}Pb$, $^{87}Sr/^{86}Sr$ and Ti/Zr to trace different lithological processes in soils and subsequent distribution of Pb in a soil profile. Such multi-elemental approaches represent powerful tools for interpreting pedogeochemical processes and Pb distribution in soils. Another very common tool used for distinguishing between separate Pb sources are three isotopes plots (e.g., $^{206}Pb/^{207}Pb$ vs. $^{208}Pb/^{206}Pb$) or Pb isotopes vs. Pb concentrations plots (Figs. 4 and 5). These approaches allow identifying more precisely separate Pb sources (Bacon and Dinev, 2005; Monna et al., 2000a; Ettler et al., 2004). Additionally, several models for assessing the relative contribution of separate Pb sources have been proposed (e.g., Monna et al., 1997; 2000a; Semlali et al., 2004). The most commonly used is the simple binary model that allows calculating the approximate contributions of two end members (i.e., background Pb vs. anthropogenic Pb input) (Monna et al., 1997; Emmanuel and Erel, 2002; Ettler et al., 2004; Hou et al., 2006):

$$X_{\text{sample}} = \frac{\left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_{\text{sample}} - \left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_{\text{background Pb}}}{\left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_{\text{anthropogenic Pb}} - \left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_{\text{background Pb}}} \times 100\% \tag{1}$$

where X_{sample} is the % contribution of anthropogenic Pb in the analysed sample; $(^{206}\text{Pb}/^{207}\text{Pb})_{\text{sample}}$ is the isotopic composition of Pb in the sample; $(^{206}\text{Pb}/^{207}\text{Pb})_{\text{anthropogenic}}$ is the Pb isotopic composition of the contaminant (e.g., gasoline- or smelter-derived Pb); $(^{206}\text{Pb}/^{207}\text{Pb})_{\text{background}}$ is the Pb isotopic composition of background Pb. More complicated mixing models have been introduced by Monna et al. (2000a). These models take into account Pb concentrations in addition to Pb isotopic ratios:

$$\left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_{\text{m}} \approx \frac{\text{Pb}_{\text{A}}\text{Pb}_{\text{B}}\left[\left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_{\text{B}} - \left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_{\text{A}}\right]}{\text{Pb}_{\text{m}}(\text{Pb}_{\text{A}} - \text{Pb}_{\text{B}})} + \frac{\text{Pb}_{\text{A}}\left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_{\text{A}} - \text{Pb}_{\text{B}}\left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_{\text{B}}}{\text{Pb}_{\text{A}} - \text{Pb}_{\text{B}}} \tag{2}$$

where $(^{206}\text{Pb}/^{207}\text{Pb})_{\text{A}}$, $(^{206}\text{Pb}/^{207}\text{Pb})_{\text{B}}$ are the Pb isotopic compositions of two end members (A, B); $(^{206}\text{Pb}/^{207}\text{Pb})_{\text{m}}$ is the resulting value after the mixing; Pb_{A}, Pb_{B} are Pb concentrations in the two end members (A, B) and Pb_{m} the Pb concentration in the mixture.

5.5. Tree rings

Trees growing in areas with temperate climate have visually distinguishable tree rings and those can be precisely dated (Nabais et al., 1999). Retrospective analyses of separate tree rings or bark encapsulated in the xylem are called dendroanalyses or dendrochemistry. Dendroanalyses assume that during growth separate tree rings reflect the composition of the environment (Cutter and Guyette, 1993) and thus reflect the variations in the atmospheric deposition of metallic and non-metallic elements and changes of the chemical composition of the soils and sediments (Watmough, 1999; Bukata and Kyser, 2007). Dendroanalysis is thus often applied in Pb isotopic studies for identifying Pb sources (Bellis et al., 2004; Bellis et al., 2005; Patrick and Farmer, 2006; Watmough, 1999; Bindler et al., 2004b; Mihaljevič et al., in press).

Factors influencing the applicability of a tree species for dendrochemical analyses include: (i) habitat-based factors, (ii) xylem-based factors and (iii) element factors (Cutter and Guyette, 1993). Habitat-based factors (i) influence mainly the occurrence of the tree species, its age, accuracy in the dating, growth habit and soil chemistry. The distribution of separate elements in the xylem (ii) depends on the differences between physiologically active sapwood and mechanically non-functional heartwood. Chemical, anatomical and physical changes in the xylem arise during the transformation from sapwood to heartwood and influence the distribution of several chemical compounds (Cutter and Guyette, 1993; Meerts, 2002). In the case of tree species with a large number of tree rings in the sapwood (e.g., 30–40 annual rings of sugar maple (*Acer saccharum* Marshall.), a possible translocation of compounds via diffusion within the sapwood can occur and results of their uptake by the tree can be misleading. For this reason, such tree species are unsuitable for dendrochemical analyses. Element factors (iii) incorporate differences in element properties that influence the form of uptake by the plant (root uptake, deposition on the foliage, deposition on the bark) and subsequent mobility across ring boundaries.

Lead is a suitable element for isotopic dendroanalyses due to its minimal lateral mobility within the xylem (Watmough, 1999). However, as it is the case for other transition metals, Pb in the xylem sap can be complexed to organic acids. The formed complexes are not strongly bound to cell walls exchange sites and lignin (Nabais et al. 1999); therefore, the concentration of Pb in the xylem is dependent on the amount and composition of the xylem sap during the year (Hagemeyer and Schäfer, 1995). Concentrations and isotopic ratios of Pb were analysed in beech (*Fagus silvatica* L.) (Bellis et al., 2004), sycamore (*Acer pseudoplatanus* L.) (Watmough et al., 1999), oak (*Quercus robur* L.), pine (*Pinus sylvestris* L.) (Watmough and Hutchinson, 2002), spruce (*Picea abies* L.) (Bindler et al., 2004b), nettle tree (*Celtis australis* L.) (Tommasini et al., 2000) and common Pb sources were identified (e.g., lithogenic Pb, Precambrian and Phanerozoic ores, coals, etc.). Bellis et al. (2002) in their study with Japanese oak (*Quercus crispula* Blume) found that Pb concentrations in bark pockets are 10–100-fold higher than in tree rings. Furthermore, bark pockets accumulate Pb originating mainly from dry and wet deposition, Pb in tree rings can originate from the soil via root uptake (Bellis et al., 2004). It is therefore possible to assume that bark pockets, compared to tree rings, are more suitable for Pb dendrochemical analyses used for studies dealing with the evolution of atmospheric pollution. While some works show that Pb isotopic dendrochemistry in combination with analyses of soils or other archives document changes in the deposition of Pb, especially in the vicinities of large local Pb inputs (e.g., Watmough et al., 1999, Savard et al., 2006a), other studies did not prove that selected tree species are suitable for recording the historical Pb deposition, especially due to the accumulation of Pb in heartwood (e.g., Patrick and Farmer, 2006; Bindler et al., 2004b; Watmough and Hutchinson, 2002).

The isotopic composition of Pb in tree ring samples is usually determined using ICP-MS in a conventional configuration. Separate segments of tree rings are mineralised prior to analyses using low temperature ashing (e.g., Watmough et al., 1999) or wet mineralisation using HNO_3 (e.g., Tommasini et al., 2000; Patrick and Farmer, 2006). The determination of the isotopic composition using laser ablation (LA) connected to ICP-MS (e.g., Bellis et al., 2004) is not limited by the use of suitable internal reference material needed for elemental analyses (e.g., Hoffmann et al., 1994; Prohaska et al., 1998; Watmough et al., 1998).

5.6. Other applications

In addition to previously presented Pb isotopic studies, some other applications were recently tested especially in the field of contaminant hydrogeology. Vilomet et al. (2003) used stable Pb isotopes as tracers of a landfill leachate in a shallow groundwater. The landfill plume was monitored to up to 1000 m from the landfill and Pb isotopic data were in a very good agreement with the more conventional method using chloride concentrations. Furthermore, data from piezometers suggested that the contamination by the landfill plume reached more than 4000 m from the landfill. The study by Landmeyer et al. (2003) employed Pb isotopes for tracing the movement of gasoline-contaminated groundwater at several gasoline-release sites. They showed that Pb in gasoline-contaminated groundwater may be derived from the local aquifer material, rather than the gasoline release.

6. Discussion and perspectives

This paper presents a review of the literature published on the use of Pb isotopes in environmental sciences as tracers of global (transboundary) and local pollution. Analyses of Pb isotopic composition were successfully used in studies dealing with atmospheric aerosols, lichens, lake, river and marine sediments, soils, waters, tree rings, etc. Recent anthropogenic activities (fossil fuel combustion, heavy industries, waste disposal and incineration) as well as historical pollution loads at sites, where future dispersal of metallic contamination may occur, can be studied by means of Pb isotopes.

In particular, natural archives are a powerful tool for studying the history of pollution and are of interest especially for evaluation and distinction of pre-anthropogenic and anthropogenic sources of metallic contaminants (e.g., Martínez Cortizas et al., 2002; Monna et al., 2004b). It is known that soils do not serve as ideal natural historical archives of pollution because metals are distributed between anthropogenic and geogenic sources and newer anthropogenic deposition cannot be precisely distinguished from older depositions (Savard et al., 2006b). Therefore, especially tree rings, peat deposits and lake/marine sediments are more suitable archives of pollution history often going thousands of years back (e.g., Renberg et al., 2002; Le Roux et al., 2004; Martínez Cortizas et al., 2002). Although the time evolution of Pb isotopic composition is usually similar in sediments and tree rings, the mode of metal accumulation is different (Savard et al., 2006b). Nevertheless, soil humic horizons together with lake and bay sediments and trees served as efficient receptor media used for identifying cumulative metal pollution (especially when using Pb isotopes analyses) even at sites lying at long distance (>100 km) from the contamination source (Hou et al., 2006; Savard et al., 2006a,b). Therefore, research focused on the combined use of natural archival systems is very important for the evaluation of either cumulative metal pollution or the evolution of pollution history (Savard et al., 2006b).

The higher accessibility of ICP-MS techniques has led to a higher number of Pb isotopic studies in recent years. The rapidity and relatively simple use of ICP-MS for Pb isotopic analyses are still challenging for investigations and applications of the Pb isotopic tracing at contaminated sites. Actual and future developments and spread of more precise analytical techniques (such as MC-ICP-MS) will certainly be useful for more accurate Pb isotopic determinations in many environmental matrices.

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