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Distribution and origin of lead in stream sediments from small agricultural catchments draining Miocene molassic deposits (SW France)

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A B S T R A C T

Total Pb concentrations and isotopic composition were determined in stream-bed sediments and bedrock from 29 small agricultural or forested catchments in the Gascogne area (SW France). The contribution of Pb from various natural and anthropogenic sources was investigated in this rural area which is very weakly impacted by industrial or urban emissions. Environmental parameters in catchments (importance of forest cover, organic matter and oxide content in sediments) were considered. A combination of geochemical (enrichment calculation, sequential extraction) and isotopic investigations was performed to constrain the origin of Pb and the distribution of anthropogenic Pb in sediments. Most of the sediments have low total Pb content compared to other agricultural regions more impacted by industrial or urban emissions. The results indicated a moderate but significant Pb enrichment, particularly for catchments draining forested areas. This enrichment was positively related to organic C content in sediment and catchment forest cover, whereas in entirely cultivated catchments it was related to Fe-oxide content.

An average anthropogenic end-member was determined using Pb isotopes, and was supposed to be representative of background atmospheric Pb pollution, with a weak influence of Pb from recent gasoline and local fertiliser spreading. The amount of anthropogenic Pb (Pb_{anthr}) in sediments estimated using a geochemical approach (mean 63.7 ± 20.4%) was higher than that estimated using an isotopic approach (mean 36.6 ± 17.8%), but the same trend was observed among the samples, except for low anthropogenic contributions. The distribution of Pb_{anthr} in sediments from weakly forested catchments indicated a strong affinity for carbonates and Fe-oxides. Amorphous Fe-oxides became preferential trapping compounds as soon as Pb enrichment increased and carbonate content decreased. Finally, in cultivated catchments, organic C was not a main trapping component for Pb_{anthr} in sediments.

1. Introduction

For centuries, anthropogenic use of Pb, mainly linked to metallurgy and industrial activities, has contributed to Pb transfer from lithosphere to atmosphere and biosphere. The local impact of industries like smelting or mining activities has been intensively investigated (Verner et al., 1996; Li and Thornton, 2001; Piatak et al., 2004; Patrick and Farmer, 2007) since they induce high contaminant levels in their neighbouring environments (atmosphere, soil, water, air, fauna, and flora), and consequently they might represent an ecological threat (Singh et al., 1997; Patra et al., 2004).

To enhance crop productivity in cultivated soils, modern agriculture commonly uses chemical inputs (fertilisers, pesticides) which might contain trace metal elements and more particularly Pb (Gimeno-Garcia et al., 1996; Camelo et al., 1997; Abdel-Haleem et al., 2001). Consequently, agriculture might be a potential pathway of non-point pollution in soils and from soils to surface waters, particularly in rural areas. Many investigations have been performed to evaluate the impact of sewage sludge application on trace metal element content of soils (Nicholson et al., 2003; Gavalda et al., 2005), but few studies have dealt with metal enrichment of soils and sediments due to chemical fertiliser inputs.

The Pb atmospheric pathway is one of the main explanations of Pb dispersion into pristine environments. Lead is mainly found in small particles and aerosols (Komarek et al., 2008), which might fall on the earth's surface even very far from their emission source through long range transboundary air transportation (Klaminder et al., 2003). Anthropogenic Pb emissions in France were mainly governed by car exhausts between the late 1950s and the early 1990s. A rapid increase can be noted up to 1970, followed by a sequential decrease due to successive reductions in the Pb concentration in gasoline and the introduction of unleaded gasoline in the early 1990s (Ferrand et al., 1999). In European Union countries, the use of Pb in gasoline has been forbidden since 2000, but almost all soil surface horizons across Europe have been shown to be

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impacted by anthropogenic Pb originating from gasoline or industrial fumes (Bacon et al., 1992; Shotyk et al., 1998; Hernandez et al., 2003; Klaminder et al., 2006; Komarek et al., 2008). The occurrence of global atmospheric non-point Pb pollution is effective, and consequently it is supposed to impact all kind of soils.

Both long range atmospheric deposits (industrial and agricultural emissions, road traffic, etc.) and local farming practices are anthropogenic metal sources for cultivated soils. However, the importance of these respective pollution sources has not been clearly evaluated yet.

Stream-bed sediments originate mainly from physical soil erosion, transportation of suspended matter mainly during storm events, and their deposition in the main channel during recession periods of discharge. In agricultural catchments, soil erosion is particularly important (Govers et al., 1994; Revel and Guiresse, 1995), and stream-bed sediments deposited after each storm event are representative of the soil material from which they originate. Investigation of stream-bed sediments, particularly the finest fraction (<63 μm), is a good way to get an integrative view of the chemical composition of suspended matter transported by the rivers (Gaiero et al., 2003).

The purpose of this study was:

(i) to quantify Pb contamination of stream-bed sediments from cultivated catchments in an intensively agricultural region and to compare the results with those for forested catchments;
(ii) to identify the different Pb sources (natural and anthropogenic), particularly regarding the influence of agricultural inputs;
(iii) to evaluate the role of environmental parameters on Pb content in sediments; and finally,
(iv) to investigate the distribution of Pb among the different geochemical constitutent phases of sediments and to determine where anthropogenic Pb is located.

Here, bed sediments of very small brooks (a few kilometres in length and less than 1 m in width) for which local anthropogenic perturbations are limited, in an intensively cultivated area of SW France, the Gascogne region, are considered. Away from other local stream pollution, sediment metal content might be considered as a proxy for the mean surface soil metal content of the whole catchment. A special emphasis will be placed on the characterisation of chemical and isotopic compositions of the reference material (sedimentary bedrock) and of the anthropogenic Pb sources.

2. Materials and methods

2.1. Description of the sampling area

The study area belongs to the Midi-Pyrénées region, located in the SW of France, and is part of the Garonne river basin (see Fig. 1). The major part of this area is devoted to agricultural activities (around 60%, with forest cover representing only 8%) as it benefits from rich deep clayey soils with low organic matter, mainly developed on detrital material from the Pyrénées Mountains, usually called "molasse". This bedrock is composed of different facies (non-carbonate or more or less carbonated), and was deposited during the Miocene from the Pyrénées Mountains to the left bank (west) of the Garonne river, forming an alluvial fan of about 8000 km^2. This area is characterised by asymmetrical hills with maximum elevation close to 300 m and slopes varying generally between 4% and 10%. Mean elevation decreases from south to north and from east to west. The region is well drained by five main tributaries (the Baïse, Gers, Gimone, Save, and Touch) of the Garonne river. There is no important anthropogenic point source related to mining or industrial activities which could locally contaminate surface waters.

Average precipitation ranges between 600 mm and 700 mm, with annual mean temperatures between 13 °C and 14 °C in the area. The climate is oceanic and the hydrological regime of the rivers is mainly pluvial with a low water period from July to November and high water flows between December and May (Probst and Tardy, 1985).

Eight sampling areas with both forested and agricultural catchments were selected in the region (Fig. 1). Cultivated catchments were representative of the various agricultural practices. For each sampling area, 2–9 small brooks draining very small catchments (from 0.38 to 10.09 km^2) were selected to avoid too wide a variability in bedrock, soil type, and hydrodynamic properties within the catchment. These brooks are characterised by a very low sedimentation rate of fine sediments in the stream channel, which leads to a thin sediment layer (5–10 cm depths). The sediments originate as suspended particulate matter from soil erosion, which is high (20–30 ton km^{-2} a^{-1}, Probst, 1986; Etchanchu and Probst, 1986) in such catchments. The contribution of stream bank erosion to sediment deposition is low (Etchanchu and Probst, 1986). The mean residence time of sediments is estimated to be one or two years (maximum) because they are frequently totally removed during flood events, which are very intense and time limited (a few hours).

Agricultural areas are essentially covered by cultivated crops, mainly corn, wheat and sunflower, and application of N-fertiliser (ammonium nitrate 33.5% N) and P–K fertiliser (25% P, 25% K) is a common practice in this region. For each catchment, the percentage of forest cover was evaluated using aerial photographs.

2.2. Sampling procedure and pre-analysis treatments

Stream-bed sediments and molassic bedrocks were sampled during spring 2002 (following a sampling strategy designed by Dermont, 2002) and summer 2005, respectively. In each sampling area, 1–4 molassic bedrock samples were collected at a minimum depth of 30 cm within the bedrock (to prevent surface contamination) from different outcrop sites in the catchments and analysed for major and trace elements to determine accurate local geochemical backgrounds.

Sediment was sampled using a HCl pre-cleaned plastic container (150 mL) in several stream curves to get a representative sample with a sufficient amount of fine fraction (<63 μm). The latter is known to be metal enriched (Probst et al., 1999; Hernandez et al., 2003; Zhou et al., 2004).

In the laboratory, sediment samples were dried at 40 °C and sieved through an acid cleaned nylon mesh to separate the <63 μm fraction sediment. Molasse samples were crushed using an agate mortar and a representative part was extracted by a quartile separation procedure for analytical work. All samples were referenced using the first three letters of the name of each sampling area, followed by a number and a letter for sediment and molasse samples, respectively (see Fig. 1 and Table 1).

To estimate the regional anthropogenic contribution to Pb content by agricultural inputs, samples of N-fertiliser and P–K fertiliser from a local agricultural cooperative were analysed.

2.3. Sample digestion

Stream-bed sediment and molasse samples were totally digested. About 100 mg of each sample was weighed precisely and placed into a PTFE beaker before adding 1 mL of supra pure concentrated HNO_3 and HF. Samples were ultrasonicated and placed on a hot plate for 12 h. Concentrated H_2O_2 was added (0.5 mL each)

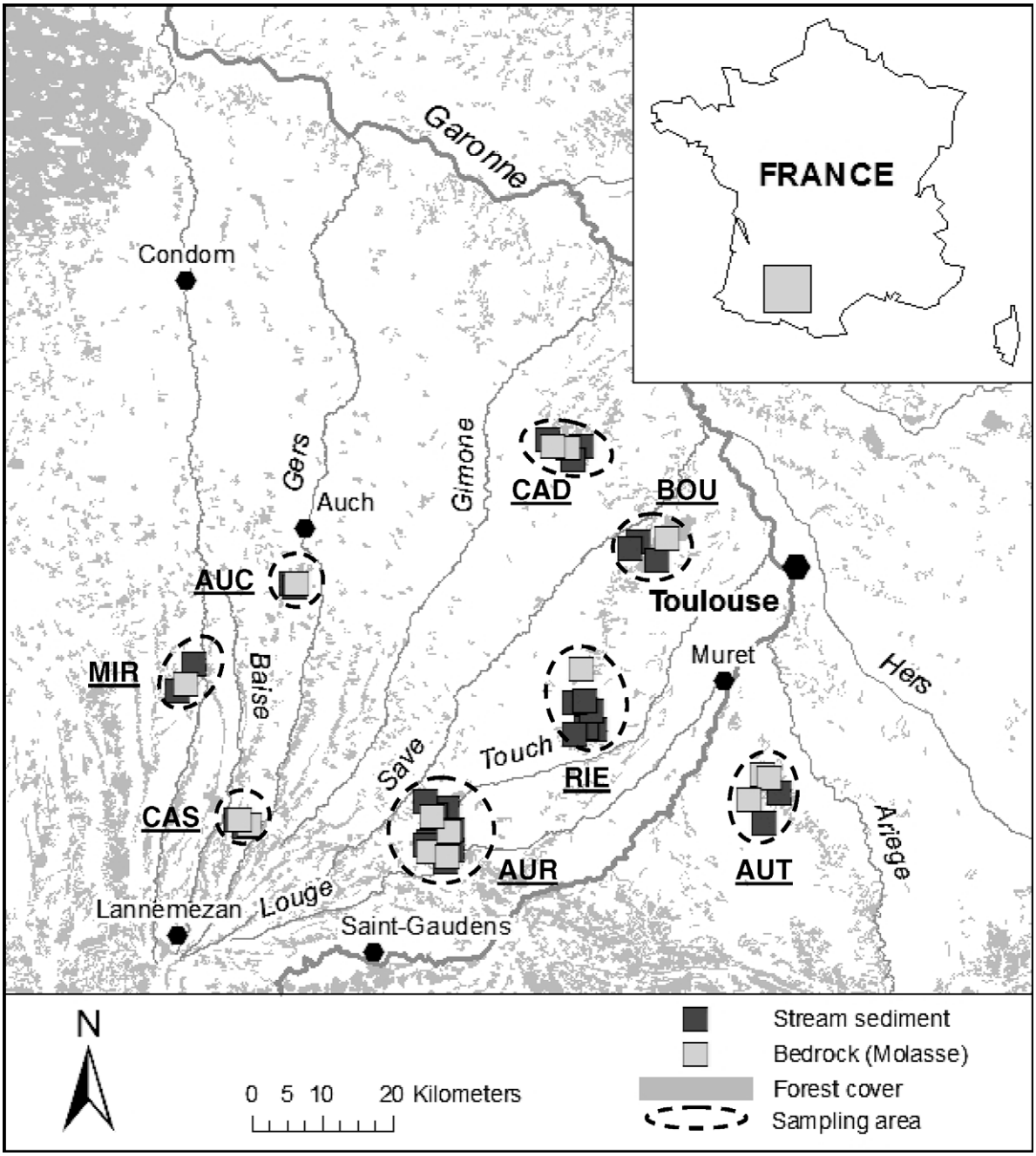

Fig. 1. Sampling site location of sediment (dark grey squares) and molasse samples (light grey squares) in the Midi-Pyrénées region (SW France). Medium grey represents forest areas.

until whole sample dissolution was attained. Each digestion was controlled with procedural blanks and certified standard sediment STSD-2. This procedure has been successfully tested in the laboratory (Hernandez et al., 2003; N'guessan et al., 2009).

2.4. Sequential extraction procedure

Three sediment samples of increasing total Pb content (25.0, 28.2, and 52.3 $\mu g\,g^{-1}$ for CAD-19, AUR-11, and RIE-25, respectively) were selected for chemical sequential extraction. The procedure (Leleyter and Probst, 1999) aimed to separate eight geochemical fractions in river sediment (water soluble, exchangeable, acid-soluble, bound to Mn oxides, amorphous and crystalline Fe oxides, oxidisable and residual fractions). Each fraction was solubilised using specific chemicals, with pH gradually decreasing step by step. This method was chosen from several procedures because it was initially developed for river sediments and checked for selectivity, reproducibility, and repeatability (for details, see Leleyter and Probst, 1999; Leleyter et al., 1999). The procedure was performed in a tight Teflon container under continuous agitation. After each extraction, the residue was separated from the solution by filtration (0.45 μm) and rinsed twice with pure water. The residual fraction remaining after the last extraction step was dissolved by acid digestion as mentioned in Section 2.3. It was possible to compare the sum of Pb contained in all the separated phases with the total Pb content, which was measured independently, to guarantee the quality of the extraction procedure. The results indicate a very good recovery (98–102%). The Pb content in water soluble,

Table 1
Characteristics of the sampling sites.

Sampling area	Molasse reference	Sediment reference	Catchment characteristics	
			Total area (km^2)	Forest cover (%)
Auch	AUC-A	AUC-01	2.09	5
		AUC-02	0.58	5
Aurignac	AUR-B	AUR-03	n.d.	5
	AUR-C	AUR-04	1.18	100
	AUR-D	AUR-05	0.58	5
	AUR-E	AUR-06	2.98	5
		AUR-07	0.49	5
		AUR-08	0.7	100
		AUR-09	3.37	37
		AUR-10	2.31	5
		AUR-11	3.06	5
Auterive	AUT-F	AUT-13	6.86	5
	AUT-G			
	AUT-H			
	AUT-I			
Bouconne	BOU-L	BOU-14	2.04	5
		BOU-15	2.62	48
		BOU-16	1.87	5
Cadours	CAD-M	CAD-17	0.44	100
	CAD-N	CAD-18	2.54	5
		CAD-19	5.14	5
		CAD-20	n.d.	5
Castelnau-Magnoac	CAS-P	CAS-21	1.3	61
	CAS-Q	CAS-22	2.11	16
Mirande	MIR-R	MIR-23	0.85	5
		MIR-24	10.09	27
Rieumes	RIE-V	RIE-25	2.04	46
		RIE-26	0.49	5
		RIE-27	8.8	18
		RIE-28	2.46	10
		RIE-29	1.51	5
		RIE-30	0.38	70

n.d.: not determined.

exchangeable, and Mn oxide fractions was very low (<1%) and thus will not be considered.

2.5. Trace and major element analysis

All the samples (from total digestion and from sequential extraction) were analysed for major elements, Pb and Sc content, Pb isotopes, and organic C content. Lead and Sc concentrations and Pb isotopes were analysed using a Perkin-Elmer ELAN 6000 ICP-MS. Major element contents were measured using a Thermo IRIS INTREPID II XDL ICP-OES. The detection limits were <0.01 and 0.21 $\mu g\,L^{-1}$ and the quantification limits were <0.21 and 0.71 $\mu g\,L^{-1}$ for Pb and Sc, respectively. For major elements, the detection limit was always <0.2 $\mu g\,L^{-1}$. Quality of measurements was controlled by procedural blanks and a standard (STSD-2). Recoveries (the relative difference between certified and measured values of STSD-2 as percentages ± 95% confidence intervals) for Pb and Sc were 7 ± 16% and 7 ± 12%, respectively.

Total organic C determination was performed on decarbonated material using a Carlo Erba NA 2100 protein CHN analyser (detection limit < 0.02%).

2.6. Lead isotopic ratio determination

Lead has four-isotopes: ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb. The radiogenic ^{206}Pb, ^{207}Pb, and ^{208}Pb are produced by radioactive decay of the long-lived radioactive parents ^{238}U, ^{235}U and ^{232}Th, respectively.

Lead isotopic composition was used to identify the different Pb sources and to determine their respective contributions as commonly described in the literature (Erel et al., 1994, 1997; Hansmann and Koppel, 2000; Teutsch et al., 2001; Hernandez et al., 2003; Bacon and Hewitt, 2005; Roussiez et al., 2005). To evaluate the origin and the availability of Pb in stream-bed sediments, chemical sequential extraction was combined with isotopic investigations as already performed for soils (Hernandez et al., 2003; Probst et al., 2003; Bacon and Hewitt, 2005).

Lead isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb) were analysed in bulk and extracted fractions with an ICP-MS Perkin-Elmer ELAN 6000 (Halicz et al., 1996; Aries et al., 2001; Hernandez et al., 2003). The model used to correct mass bias effects was an external mass bias correction (standard-sample bracketing technique) using NBS981 as the reference standard. No Pb isotopic ratios concerning ^{204}Pb were considered in the following because of the low abundance and interferences. For each sample, the 95% confidence intervals for $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ are mentioned in Table 2.

The very good quality of sequential extractions and measurement procedures is attested by the low difference (<0.4%) between the sum of isotopic ratios of the different extracted fractions weighted by their Pb content and the isotopic composition of the bulk sample.

2.7. Calculations of lead anthropogenic contribution

2.7.1. Based on geochemical analyses

Total Pb (Pb_{tot}) measured in sediments was considered to be the sum of Pb originating from the natural lithogenic source (molasse) and Pb from human activities (Eq. 1).

$$Pb_{total} = Pb_{anthropogenic} + Pb_{lithogenic} \quad (1)$$

Table 2
Pb, Sc (μg g^{-1}), major elements (%), organic C content (%) and Pb isotopic composition of stream-bed sediment, molasse, and fertiliser samples.

Sample	Trace elements (μg g^{-1})		Major elements (%)							C_{org} (%)	Pb isotope ratios (±95% confidence interval)	
	Pb	Sc	Al	Ca	Fe	K	Mn	Na	Mg		$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
Sediment												
AUC-01	51.59	15.67	4.90	5.38	2.83	1.40	0.11	0.22	0.35	1.18	1.1758 ± 0.0050	2.4956 ± 0.0104
AUC-02	24.94	7.72	4.45	2.39	1.95	1.39	0.05	0.22	0.32	1.85	1.1802 ± 0.0051	2.4993 ± 0.0109
AUR-03	23.01	4.28	2.39	0.25	2.22	1.24	0.12	0.28	0.22	1.97	1.1824 ± 0.0051	2.5053 ± 0.0111
AUR-04	20.79	3.31	1.87	0.63	2.20	1.17	0.07	0.03	0.17	1.76	1.1851 ± 0.0054	2.5071 ± 0.0108
AUR-05	24.72	5.11	2.79	1.59	2.88	1.35	0.12	0.08	0.22	1.34	1.1798 ± 0.0048	2.5009 ± 0.0108
AUR-06	23.64	3.29	2.17	0.23	2.58	1.28	0.11	0.18	0.24	1.30	1.1771 ± 0.0052	2.4914 ± 0.0104
AUR-07	23.49	7.03	4.31	4.82	2.62	1.22	0.15	0.17	0.32	1.44	1.1805 ± 0.0053	2.4981 ± 0.0114
AUR-08	23.98	2.92	1.83	0.46	3.49	1.52	0.10	0.10	0.27	1.46	1.1817 ± 0.0051	2.5026 ± 0.0111
AUR-09	28.71	8.62	4.62	1.50	3.24	1.59	0.14	0.22	0.44	0.82	1.1766 ± 0.0050	2.4930 ± 0.0104
AUR-10	25.40	9.75	5.42	4.44	3.12	1.55	0.14	0.19	0.47	1.60	1.1799 ± 0.0050	2.5014 ± 0.0108
AUR-11	28.24	5.36	2.96	2.48	2.53	1.25	0.13	0.10	0.22	1.00	1.1793 ± 0.0050	2.4947 ± 0.0109
AUT-13	21.54	6.13	3.45	6.09	2.00	1.59	0.11	0.10	0.81	2.04	1.1922 ± 0.0054	2.5071 ± 0.0113
BOU-14	24.90	8.34	5.00	3.68	2.41	1.45	0.08	0.42	0.54	1.93	1.1869 ± 0.0054	2.4957 ± 0.0119
BOU-15	29.10	6.06	3.82	0.43	2.58	1.43	0.04	0.38	0.39	0.55	1.1904 ± 0.0053	2.5025 ± 0.0109
BOU-16	23.72	6.40	3.52	4.27	2.14	1.42	0.17	0.14	0.47	1.34	1.1901 ± 0.0053	2.5103 ± 0.0113
CAD-17	25.49	2.77	1.90	0.24	3.10	1.62	0.13	0.16	0.31	0.63	1.1899 ± 0.0052	2.5057 ± 0.0111
CAD-18	34.56	7.26	4.27	5.81	1.97	1.31	0.09	0.21	0.45	0.89	1.1840 ± 0.0051	2.4899 ± 0.0109
CAD-19	24.99	6.14	3.45	2.77	2.06	1.35	0.07	0.13	0.37	1.82	1.1863 ± 0.0053	2.4964 ± 0.0106
CAD-20	20.52	2.78	1.72	0.04	1.38	1.21	0.02	0.24	0.20	1.11	1.1860 ± 0.0053	2.5005 ± 0.0113
CAS-21	26.31	6.20	4.22	0.26	2.48	1.20	0.19	0.00	0.24	1.97	1.1755 ± 0.0051	2.4966 ± 0.0109
CAS-22	25.02	2.60	1.35	0.05	2.29	1.19	0.09	0.02	0.15	1.99	1.1791 ± 0.0051	2.4983 ± 0.0110
MIR-23	28.93	6.11	3.19	0.07	2.53	1.29	0.13	0.18	0.19	1.34	1.1776 ± 0.0049	2.5028 ± 0.0107
MIR-24	27.19	8.04	4.41	1.94	2.99	1.31	0.43	0.20	0.25	2.46	1.1787 ± 0.0049	2.4981 ± 0.0104
RIE-25	52.33	3.06	2.13	0.13	1.83	1.14	0.06	0.17	0.19	1.73	1.1584 ± 0.0044	2.4640 ± 0.0092
RIE-26	23.33	6.70	4.36	0.26	1.98	1.17	0.04	0.07	0.28	0.67	1.1893 ± 0.0050	2.5103 ± 0.0104
RIE-27	29.88	10.98	6.26	1.61	3.49	1.87	0.08	0.18	0.77	0.56	1.1842 ± 0.0049	2.4991 ± 0.0104
RIE-28	24.64	4.08	2.40	0.08	1.91	1.22	0.06	0.25	0.29	1.01	1.1847 ± 0.0052	2.5050 ± 0.0113
RIE-29	27.67	2.39	1.37	0.06	2.10	1.37	0.03	0.06	0.24	1.76	1.1850 ± 0.0050	2.4996 ± 0.0107
RIE-30	24.71	2.97	1.19	0.05	2.11	1.31	0.07	0.12	0.24	1.23	1.1877 ± 0.0051	2.5024 ± 0.0109
Mean	27.36	5.93	3.30	1.79	2.45	1.36	0.11	0.17	0.33	1.41	1.1822	2.4991
Std. dev.	7.42	2.99	1.37	2.01	0.52	0.17	0.08	0.10	0.16	0.51	0.0066	0.0085
Molasse												
AUC-A	16.73	12.20	4.93	20.23	2.76	1.31	0.08	0.12	0.60	n.d.	1.1764 ± 0.0072	2.5357 ± 0.0162
AUR-B	14.69	17.75	6.90	6.53	3.75	1.88	0.03	0.16	0.55	n.d.	1.1886 ± 0.0077	2.5379 ± 0.0164
AUR-C	33.24	28.16	4.10	0.12	4.35	1.22	0.06	0.10	0.38	n.d.	1.1765 ± 0.0074	2.5118 ± 0.0156
AUR-D	33.25	28.74	7.69	0.02	5.10	1.35	0.03	0.09	0.31	n.d.	1.1810 ± 0.0072	2.5160 ± 0.0152
AUR-E	18.96	16.54	7.84	8.26	4.14	2.18	0.09	0.19	0.61	n.d.	1.1870 ± 0.0071	2.5319 ± 0.0153
AUT-F	14.87	7.27	4.25	6.40	1.85	1.70	0.04	0.48	0.75	n.d.	1.1859 ± 0.0075	2.5092 ± 0.0163
AUT-G	22.03	10.37	4.57	0.96	2.49	1.81	0.13	0.32	0.59	n.d.	1.1830 ± 0.0070	2.5106 ± 0.0155
AUT-H	12.85	9.48	3.99	14.48	1.26	1.58	0.03	0.31	0.59	n.d.	1.1855 ± 0.0075	2.5147 ± 0.0167
AUT-I	21.35	10.11	5.70	1.56	2.29	2.25	0.03	0.46	0.79	n.d.	1.1787 ± 0.0072	2.5114 ± 0.0156
BOU-L	21.19	9.72	2.43	0.06	2.84	1.30	0.02	0.48	0.39	n.d.	1.1874 ± 0.0063	2.5211 ± 0.0140
CAD-M	26.77	12.58	4.33	0.16	2.48	1.28	0.02	0.35	0.37	n.d.	1.1820 ± 0.0061	2.5098 ± 0.0133
CAD-N	4.58	4.39	1.17	34.87	0.65	0.25	0.10	0.01	0.40	n.d.	1.1956 ± 0.0086	2.5355 ± 0.0190
CAS-P	17.32	21.98	2.80	0.01	3.32	0.71	0.01	0.07	0.16	n.d.	1.1832 ± 0.0078	2.5187 ± 0.0163
CAS-Q	28.45	25.64	4.98	0.01	3.28	1.45	0.22	0.10	0.20	n.d.	1.1786 ± 0.0072	2.5260 ± 0.0154
MIR-R	28.29	33.05	7.35	0.06	4.52	2.19	0.06	0.27	0.49	n.d.	1.1777 ± 0.0068	2.5279 ± 0.0152
RIE-V	21.66	8.53	1.33	0.05	1.88	0.87	0.02	0.28	0.17	n.d.	1.1800 ± 0.0067	2.5255 ± 0.0148
Mean	21.01	16.03	4.65	5.86	2.94	1.46	0.06	0.24	0.46	n.d.	1.1830	2.5215
Std. dev.	7.72	8.85	2.09	9.80	1.23	0.55	0.05	0.15	0.19	n.d.	0.0052	0.0101
Fertiliser												
PK-25-25	1.33	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.2417 ± 0.0151	2.4032 ± 0.0177
PK-25-25	1.55	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.2102 ± 0.0139	2.4083 ± 0.0184

n.d.: not determined.

The Enrichment Factor (EF) was calculated for each stream-bed sediment sample by comparing the sediment to an uncontaminated reference material (here, the molasse bedrock) and by using a reference element which was supposed to be conservative during weathering processes (see Eq. (2)). In this study, Sc was chosen according to the method developed by Roussiez et al. (2005). The principle of this method is to select the reference element which exhibits the higher number of samples with large Pb anthropogenic contributions but exhibits a significant correlation with Pb for other (uncontaminated) samples. Moreover it was observed that the reference element was mainly distributed in the residual fraction like Al, Fe, Cs, and Ti and was weakly affected or unaffected by anthropogenic contributions (Shotyk et al., 2000, 2001; Hernandez et al., 2003; Hissler and Probst, 2006)

$$EF = \frac{(Pb/Sc)_{sediment}}{(Pb/Sc)_{molasse}} \quad (2)$$

The lithogenic Pb content (Pb_{lith}) in sediment is calculated (Eq. (3)) from the Pb/Sc ratio in molasse with the assumption that this natural ratio remains the same in sediment

$$Pb_{lith} = Sc_{sediment} \times \left(\frac{Pb}{Sc}\right)_{molasse} \quad (3)$$

The anthropogenic Pb content is finally calculated from the difference between Pb_{tot} and Pb_{lith}. The anthropogenic contribution can be expressed as a percentage of the total Pb in sediment.

2.7.2. Based on Pb isotopic ratios

The Pb anthropogenic contribution to total Pb content of sediment was estimated by an independent isotopic approach, which can be compared to the geochemical approach detailed above.

The molasse bedrock has been considered as the only natural source of Pb contained in sediments. The isotopic composition of the anthropogenic source was determined on the basis of the $^{208}Pb/^{207}Pb$ ratio as detailed in Section 4.2.2. For each sample, the contribution of natural and anthropogenic sources was estimated using a simple mixing model (Eqs. (4) and (5)), where c is the contribution of each source and δ is the isotopic composition of a source or a sample

$$\delta_{\text{sample}} = c_{\text{Nat}} \times \delta_{\text{Nat}} + c_{\text{Anthr}} \times \delta_{\text{Anthr}} \quad (4)$$

$$c_{\text{Nat}} + c_{Anthr} = 100\% \quad (5)$$

3. Results

3.1. Pb and Sc contents in stream sediments, molasse and fertilisers

A relatively large range of values – equivalent for the two materials – is observed for Pb and Sc content in bedrock (molasse) and sediments (Table 2). Higher Pb values are observed in sediments (Mann–Whitney test $P = 0.01$), whereas molasse samples are more concentrated in Sc ($P < 0.001$).

The observed wide range of Pb and Sc concentrations might be the result of the large diversity in mineral composition of the detrital bedrock (molasse), which is a mixture of quartz, feldspar, mica and carbonates, all consolidated by a marly cement (Crouzel, 1957). Lead and Sc contents follow a normal distribution in molasse samples only (Shapiro test, $P = 0.77$ and $P = 0.09$, respectively).

For both molasse and sediment samples, mean Pb values (Table 2) are higher than the mean Upper Continental Crust (UCC) content (14 $\mu g\ g^{-1}$, Wedepohl, 1995), whereas mean Sc values are lower for sediment samples only (16 $\mu g\ g^{-1}$, Wedepohl, 1995). This indicates that local geochemical background must be considered in order to proceed to a relevant estimation of anthropogenic impact, particularly for EF calculations (see Section 2.7.1 for more details and N'guessan et al., 2009).

The Pb content in N-fertilisers frequently used in the study area is very low (<0.5 $\mu g\ g^{-1}$, Table 2). But P–K fertiliser samples have a higher mean Pb content (1.44 ± 0.11 $\mu g\ g^{-1}$, see Table 2), which is within the range of other P–K fertilisers used in France (SOGREAH, 2007).

3.2. Major element and organic matter contents in molasse and sediment

As shown in Table 2, about 38% of sediment samples are enriched in carbonate (more than 2% Ca, i.e. ~5% $CaCO_3$, AFES, 1995) and 17% contain less than 0.1% Ca. Sediments are enriched in Al and Fe compared to molasse. In the molasse, a few samples have very significant Ca contents (up to 35% Ca) and 62% of samples contain less than 2% Ca, indicating a greater heterogeneity than for sediments. The contents of other major elements are quite homogeneous among the different samples, but Al is more enriched in bedrock than in sediment (Student test for normal distribution, $P = 0.03$), and the reverse is observed for Mn (Mann–Whitney test for non-normal distribution, $P = 0.003$). Total organic C content (TOC%) of sediments is very low (mean 1.4%) and has a normal distribution. It is within the lower range of similar sediments in the Seine river flood plain (Grosbois et al., 2006).

The ternary diagrams (Fig. 2) represent the relative percentages of Ca + Mg, Fe + Mn, and Al (the sum of the three end-members equals 100%) in stream-bed sediment (a) and molasse (b) samples. Two groups of sediments (A and B) can be identified with respect to the "Ca + Mg" proportion. Group A (corresponding to carbonate enriched sediments, Fig. 2a) has low variation in the relative proportions of Al and Fe + Mn. In contrast, the non-carbonate sediments (Group B, Fig. 2a) are more spread between Al and Fe + Mn end-members. Regarding Ca and Mg, the variability is less important for sediment (Fig. 2a) than for molasse (Fig. 2b). In contrast, the variability of the relative "Fe + Mn" and Al contents is more important for sediment than for molasse samples.

3.3. Pb isotopes in molasse, sediments, and fertilisers

The $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios were considered to characterise the isotopic composition of sediment samples and only the $^{208}Pb/^{207}Pb$ ratio was used to quantify the respective contributions of natural and anthropogenic end-members. The ratios, presented in Table 2, range from 1.176 to 1.196 and from 2.509 to 2.538 in molasse ($n = 16$), 1.158 to 1.192 and 2.464 to 2.510 in sediments ($n = 30$), and 2.210 to 2.242 and 2.403 to 2.408 in fertiliser samples ($n = 2$), for $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$, respectively.

3.4. Total concentration and isotopic composition of lead in residual and non-residual fractions of sediments

Because the risk assessment of metal pollution depends on metal availability, it is important to know where anthropogenic Pb is located in sediments, and particularly to which geochemical fractions it is associated.

Chemical sequential extractions were performed on three sediment samples (CAD-19, AUR-11, RIE-25) selected for their various total Pb contents (25, 28, and 52 $\mu g\ g^{-1}$, respectively). The results indicated (Fig. 3) that the residual fraction is the dominant Pb-bearing phase (37% and 41% for AUR-11 and CAD-19, respectively), except for RIE-25 (18%). Among the non-residual fractions, acid-soluble, oxidizable, and Fe-oxide are the dominant fractions for CAD-19, AUR-11 and RIE-25, respectively. A significant increase in Pb linked to acid-soluble and Fe-oxide fractions with increasing total Pb content (AUR-11 < CAD-19 < RIE-25) is generally observed.

The $^{206}Pb/^{207}Pb$ ratio of the different fractions varies between 1.1668 and 1.1900 for AUR-11 and CAD-19 samples and between 1.1419 and 1.1885 for RIE-25, whereas the $^{208}Pb/^{207}Pb$ ratio varies between 2.4749 and 2.5088 for AUR-11 and CAD-19 samples and between 2.3826 and 2.5153 for RIE-25.

For all samples, the residual fraction is always the most radiogenic whereas the acid-soluble fraction is the least radiogenic. The exception is RIE-25, for which the amorphous oxide fraction is the least radiogenic with respect to the $^{208}Pb/^{207}Pb$ ratio.

4. Discussion

4.1. Lead contamination in Gascogne stream sediments

The Pb content of stream-bed sediments measured in this study (20.5–52.3 $\mu g\ g^{-1}$) is within the range of values given by Audry et al. (2004a) and Masson et al. (2006) for uncontaminated bed sediments in the Garonne river and one of its tributaries, the Lot river (respectively, 26.3–87.4 $\mu g\ g^{-1}$ and 43.6–46 $\mu g\ g^{-1}$). Nevertheless, bed sediments from sites which are contaminated (by mining, smelting, and industrial activities, Grousset et al., 1999) located along these two rivers may have Pb contents of 105–523 $\mu g\ g^{-1}$ (Audry et al., 2004b); that is 2–10 times higher than the highest Pb concentration measured in the present study.

The study area has some similarities with the Seine River Basin since an important part of this basin is dedicated to agriculture as

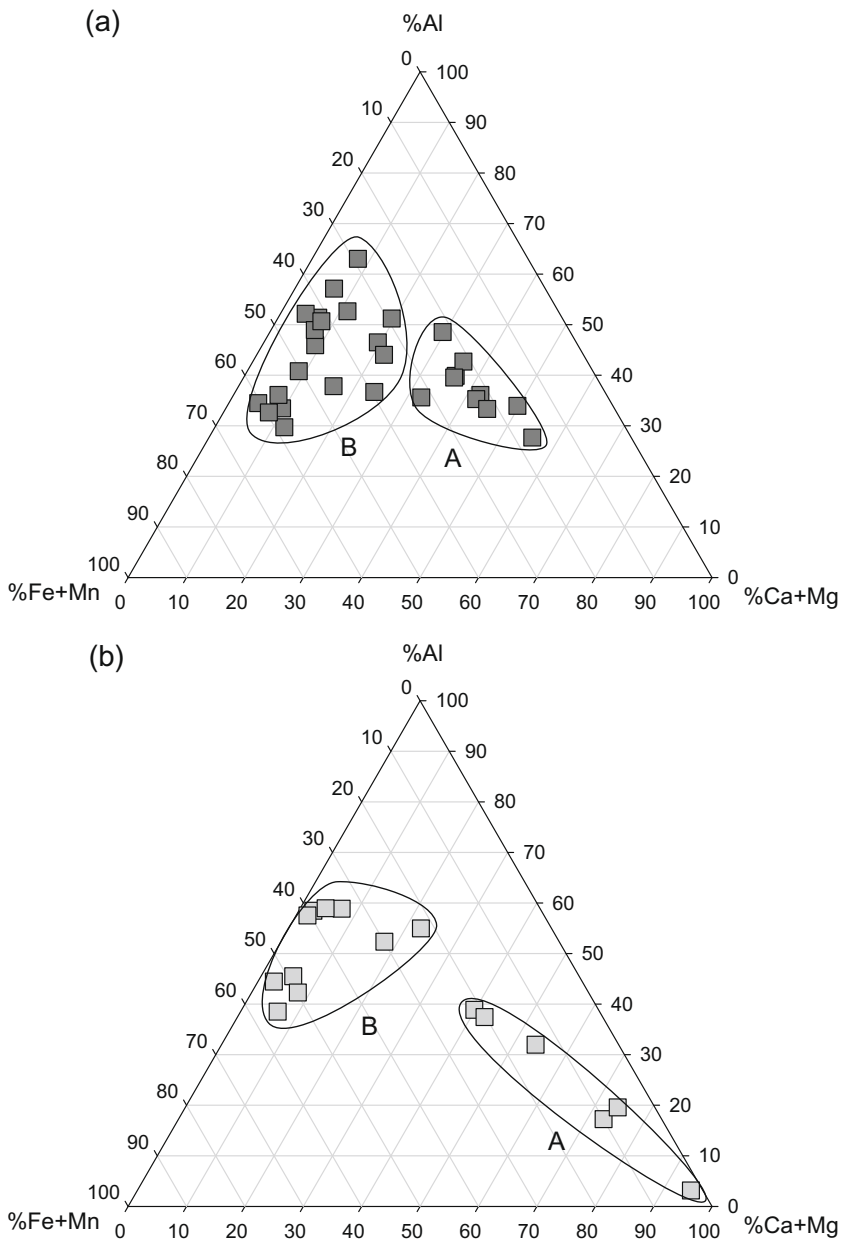

Fig. 2. Ternary diagrams of major elements for sediment (a) and molasse samples (b). Group A represents carbonate samples (Ca content > 2%, Table 2) and group B represents poorly or non-carbonate samples (Ca content < 2%, Table 2).

well, and the geological substratum is mainly composed of sedimentary and carbonate bedrock. In this area, the natural geochemical background for Pb is $20 \pm 3\ \mu g\ g^{-1}$ (Grosbois et al., 2006), which is very close to the value for the Gascogne molasse bedrock ($21 \pm 8\ \mu g\ g^{-1}$). However, Pb concentration in the Seine sediments from the agricultural (upper) part of the basin is higher (54 ± 4–$94 \pm 34\ \mu g\ g^{-1}$, Grosbois et al., 2006) than in the Gascogne sediments. This difference might be related to other Pb anthropogenic sources like urban wastes or atmospheric deposition (as shown by Garban et al., 1996) since the Seine basin is more intensively urbanised and industrialised than the Gascogne area.

Indeed, the Gascogne area was expected to be contaminated only by non-point pollution sources. In such cultivated areas, mainly inorganic fertilisers are spread. They are known to be a potential source of Pb (Nicholson et al., 2003) in soils, particularly superphosphates which contain high amounts of trace elements (Camelo et al., 1997; Nicholson et al., 2003). However, these kinds of fertilisers are not commonly applied in the studied region (less than 10% of P fertilisation, UNIFA, 2007) and those used have low Pb contents (Table 2). Finally, in the studied area, agricultural lands presently receive significantly higher Pb inputs from atmospheric deposits (around $10\ g\ ha^{-1}\ a^{-1}$) than from synthetic manure (around $0.3\ g\ ha^{-1}\ a^{-1}$; SOGREAH, 2007).

Consequently, non-point anthropogenic sources might contribute to higher Pb concentrations in stream-bed sediments compared to molasse (Table 2). It is thus important to evaluate the intensity of Pb contamination and to determine and quantify the contributions of the different sources. For this purpose, two independent methods based respectively on geochemical and isotopic approaches were investigated.

4.2. Anthropogenic lead contribution

4.2.1. Geochemical approach

Most authors (e.g. Chester and Stoner, 1973; Shotyk et al., 2000) usually determine trace element anomalies by comparison with

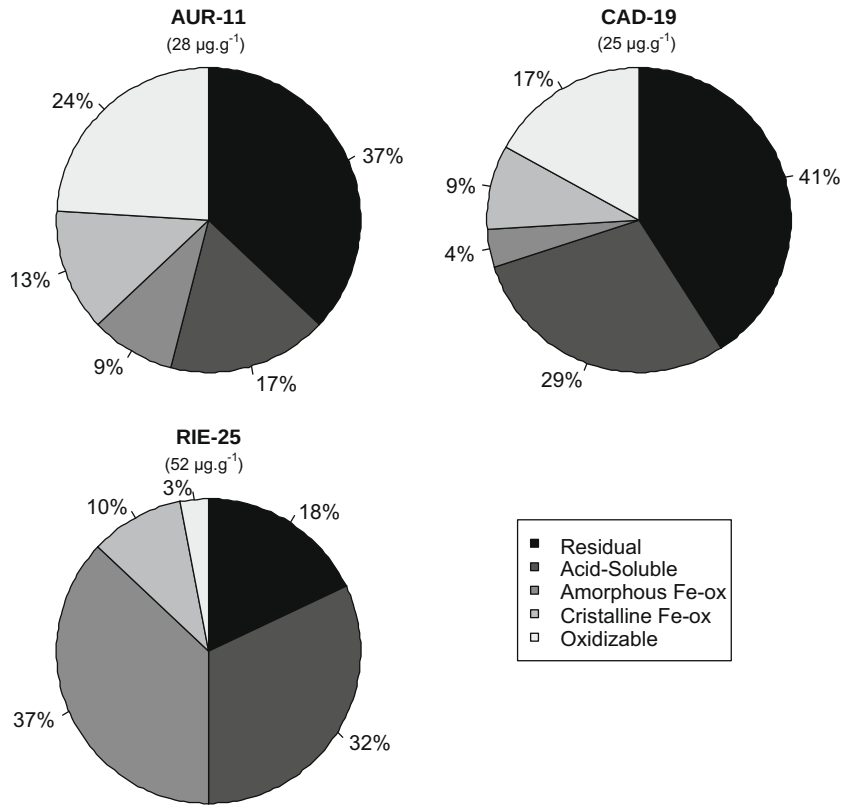

Fig. 3. Relative percentage of Pb in the different sediment fractions, extracted using a chemical sequential procedure (after Leleyter and Probst, 1999). The samples considered have been selected for their increasing total Pb content. CAD-19: 25 μg g^{-1}, AUR-11: 28 μg g^{-1}, and RIE-25: 52 μg g^{-1}.

values from uncontaminated reference material such as UCC or Post-Archean Australian Shale (PAAS) (Wedepohl, 1995). Nevertheless, this kind of normalisation is too rough to be used to estimate a regional level of contamination. In this case, the studied material must be compared to the local geochemical background (N'guessan et al., 2009). In the case study, taking the mean UCC values (Pb = 14 μg g^{-1}; Sc = 16 μg g^{-1}) as the uncontaminated reference instead of molasse bedrock (Pb = 21 ± 8 μg g^{-1}; Sc = 16 ± 9 μg g^{-1}) led to a mean overestimation of Pb EF in sediments (by around 50%), as also shown by Covelli and Fontolan (1997) and Hernandez et al. (2003).

Molasse and sediment samples were classified into two groups (Fig. 2a and b) according to their carbonate content, taking 2% Ca as the limit between carbonate and non-carbonate samples. Each sediment sample has been normalised to the molasse of the same carbonate feature (Fig. 2, Table 2) in the corresponding sampling area (Fig. 1, Table 1) to estimate the most accurate EF.

EF (Eq. (2), Table 3) varies between 1.1 and 10.1 with a mean of 3.7 (std. dev. = 2.1), which corresponds (according to Eqs. (1) and (3)) to an anthropogenic Pb contribution ($Pb_{anthr\text{-}geo}$) of 2–44.6 μg g^{-1}, that is 7–90% of the total Pb content of sediment. An anthropogenic impact is usually diagnosed when EF rises above 1.5–2 because of uncertainties (Vertacnik et al., 1995; Hernandez et al., 2003). In the study, EF exceeds two for more than 75% of the samples. The mean $Pb_{anthr\text{-}geo}$ calculated for the whole study area is 63.7 ± 20.4%.

4.2.2. Isotopic approach

The relationship $^{208}Pb/^{207}Pb$ *vs.* $^{206}Pb/^{207}Pb$ indicates that isotopic compositions of gasoline (old gasoline, i.e. 1966, and more recent gasoline, i.e. 1995), aerosols, pre-industrial sediments and UCC taken from the literature are almost aligned (Fig. 4), as abundantly previously described (Monna et al., 1997; Ferrand et al., 1999; Veron et al., 1999; Hansmann and Koppel, 2000; Haack et al., 2004; Millot et al., 2004; Komarek et al., 2008). In the present study, the molasse samples representing the local natural Pb end-member are not located on this line as they have a higher $^{208}Pb/^{207}Pb$ ratio. The molasse isotopic composition is significantly different from that of UCC (student's *t*-test: $P = 0.049$ for $^{206}Pb/^{207}Pb$; $P = 0.137$ for $^{208}Pb/^{207}Pb$) and isotopic compositions of pre-early sediments (from Monna et al., 1997). Indeed, some studies on molassic bedrock have also shown this pattern (Clift et al., 2001). The sediment samples plot between the molasse end-member and the "literature data line" described previously, but they are closer to the molasse isotopic composition than to the other end-members, indicating a major Pb contribution of natural local lithic origin. Molasse and sediment isotopic compositions are very close with respect to the $^{206}Pb/^{207}Pb$ ratio, but they differ significantly for $^{208}Pb/^{207}Pb$ (Mann–Whitney, $P < 0.001$).

The isotopic composition of P–K fertiliser (see inset Fig. 4) has the highest $^{206}Pb/^{207}Pb$ value, which is very far from all the other isotopic compositions reported in Fig. 4. Thus, this end-member does not significantly influence the sediment Pb isotopic composition, and consequently will not be taken into account in the following.

Regarding the present data, a global mixed atmospheric contamination influence is expected (as already shown by Ferrand et al., 1999, for example). To identify the average anthropogenic end-member isotopic composition, $^{208}Pb/^{207}Pb$ was plotted against 1/Pb in sediments (Fig. 5). A significant relationship can be observed ($R^2 = 0.47$, $n = 29$, $P < 0.001$), indicating that sediment isotopic composition is influenced by an anthropogenic Pb source with an average $^{208}Pb/^{207}Pb$ value of 2.466 ± 0.013. This value is located close to that of old gasoline, some aerosols, and pre-early sediments. The anthropogenic end-member is weakly influenced by aerosols from recent leaded gasoline. No significant relationship

Table 3
Total Pb content, estimations of Enrichment Factor (EF), proportion of anthropogenic Pb (%), and anthropogenic Pb content ($\mu g\ g^{-1}$) using the geochemical approach ($Pb_{anthr\text{-}Geo}$) and using the isotopic approach ($Pb_{anthr\text{-}Iso}$) for each sediment sample.

Sample	Pb Tot ($\mu g \cdot g^{-1}$)	EF	Pb_{anthr} Geo		Pb_{anthr} Iso	
			(%)	($\mu g \cdot g^{-1}$)	(%)	($\mu g \cdot g^{-1}$)
AUC-01	51.59	2.4	58	30.12	58	29.68
AUC-02	24.94	2.4	58	14.36	52	13.04
AUR-03	23.01	4.6	78	18.01	18	4.11
AUR-04	20.79	5.4	81	16.92	14	2.94
AUR-05	24.72	4.1	76	18.75	27	6.73
AUR-06	23.64	6.1	84	19.79	47	11.10
AUR-07	23.49	2.9	65	15.27	33	7.75
AUR-08	23.98	7.0	86	20.57	24	5.67
AUR-09	28.71	2.9	65	18.63	44	12.50
AUR-10	25.40	2.2	55	14.00	26	6.61
AUR-11	28.24	4.5	78	21.98	40	11.32
AUT-13	21.54	1.7	40	8.55	9	1.87
BOU-14	24.90	1.4	27	6.72	46	11.45
BOU-15	29.10	2.2	55	15.90	34	9.80
BOU-16	23.72	1.7	41	9.78	20	4.65
CAD-17	25.49	4.3	77	19.60	9	2.38
CAD-18	34.56	2.2	55	19.12	45	15.70
CAD-19	24.99	1.9	48	11.92	31	7.68
CAD-20	20.52	3.5	71	14.60	21	4.38
CAS-21	26.31	4.5	78	20.43	46	12.03
CAS-22	25.02	10.1	90	22.55	43	10.66
MIR-23	28.93	5.5	82	23.70	41	11.75
MIR-24	27.19	4.0	75	20.30	48	13.09
RIE-25	52.33	6.7	85	44.55	100	52.33
RIE-26	23.33	1.4	27	6.30	26	5.97
RIE-27	29.88	1.1	7	1.99	44	13.25
RIE-28	24.64	2.4	58	14.26	35	8.50
RIE-29	27.67	4.6	78	21.60	44	12.04
RIE-30	24.71	3.3	70	17.17	39	9.61
Mean	27.36	3.7	64	17.41	37	10.01
Std. dev.	7.42	2.1	20	1.51	18	1.32

n.d.: not determined.

between $^{206}Pb/^{207}Pb$ and 1/Pb could be observed; hence only the $^{208}Pb/^{207}Pb$ value was used to determine the respective anthropogenic and natural contributions of Pb in sediments.

Consequently, according to Eqs. (4) and (5) and using the $^{208}Pb/^{207}Pb$ average anthropogenic end-member and the natural molasse end-member of each sampling area, the anthropogenic Pb contribution to sediment varies between 14 and 58% of total Pb content, except in 3 sediments (9% in CAD-17 and AUT-13, and 100% in RIE-25) (Table 3).

4.2.3. Comparison of the two methods

The anthropogenic Pb in sediments is quite significant (36.6 ± 17.8% or 63.7 ± 20.4% as means of total Pb, for isotopic and geochemical approaches, respectively). The soils originating sediments are influenced by an average regional Pb pollution whose isotopic composition is close to that of old gasoline Pb. For the highest anthropogenic Pb concentrations, the results are comparable between both methods, whereas for the lowest values they differ more significantly due to the poorer method sensitivity of the geochemical approach.

These values are also slightly higher than those found in another sampling set studied in the same area (N'guessan et al., 2009), but in this case the considered sediments belonged to larger rivers. This supports the idea that sediments from upper stream catchments are more influenced by anthropogenic Pb.

As a whole, Pb isotopes indicate the significant influence of an average anthropogenic end-member on stream sediments (Fig. 4). The exception is for the particular sediment RIE-25, whose isotopic composition approximates the value of the calculated anthropogenic end-member. This indicates the contribution of a less radiogenic Pb source which may originate from car traffic (recent gasoline, i.e. the lowest $^{208}Pb/^{207}Pb$) close to this sampling site.

4.3. Environmental parameters influencing lead enrichment

4.3.1. Role of bedrock weathering

The Spearman correlation coefficients (ρ) between organic C content and major and trace elements are given in Table 4 for sediment (a) and molasse samples (b). Lead is not significantly correlated with major elements in sediments, whereas it is linked positively to Fe and negatively to Ca in molasse (Table 4b). Scandium is only significantly positively correlated with Fe and Al in molasse samples, whereas it is related to Al, Ca and Mg in sediments. In molasse, the weak variation in Sc content whatever the carbonate content explains the absence of any relationship with Ca (Table 4b).

Lead content of molasse varies significantly (average 21 ± 8 $\mu g\ g^{-1}$) and is partly controlled by carbonate content since the Pb concentration in carbonate-rich molasse is significantly lower than in non-carbonate material (medians of 15 and 24 $\mu g\ g^{-1}$, respectively; Mann–Whitney test, $P < 0.001$). The carbonate feature may thus be a major controlling factor of Pb content as carbonate minerals are generally less Pb enriched than certain silicate minerals that are more resistant to weathering (Erel et al., 2004). An important variability is also observed for Pb isotopic composition, particularly with respect to $^{208}Pb/^{207}Pb$. The variability is less important when considering samples with an equivalent carbonate content and collected in the same area. This indicates that the geological features (age, lithology) and the local environmental factors have influenced the Pb concentration and isotopic composition during molasse deposition and weathering/erosion processes. The correlations between Sc and major elements are different for sediments and molasse (Table 4), confirming the roles of these processes.

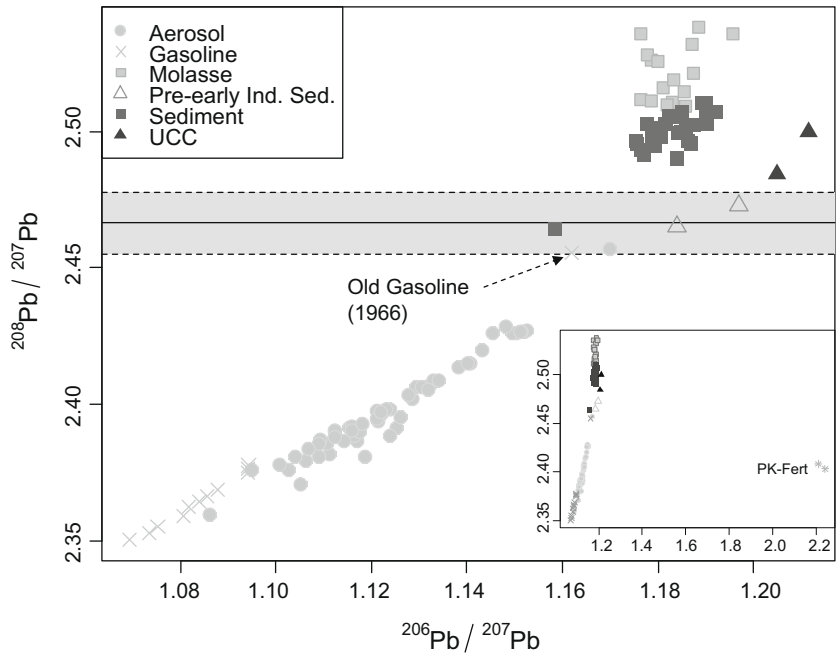

Fig. 4. ^{208}Pb/^{207}Pb *versus* ^{206}Pb/^{207}Pb diagram for studied sediments (dark grey squares) and molasse samples (light grey squares). Literature data on potential natural or anthropogenic sources are mentioned: gasoline (Monna et al., 1995, 1997), aerosol (Monna et al., 1997; Ferrand et al., 1999; Veron et al., 1999; Hansmann and Koppel, 2000), pre-early sediments (Monna et al., 1997), UCC (Millot et al., 2004). Notice that data for fertilisers (this study) are represented by grey stars in the inset. See text and Fig. 5 for details on the determination of the average anthropogenic end-member represented by the horizontal grey area (solid line: mean value; dotted line: 95% confidence interval).

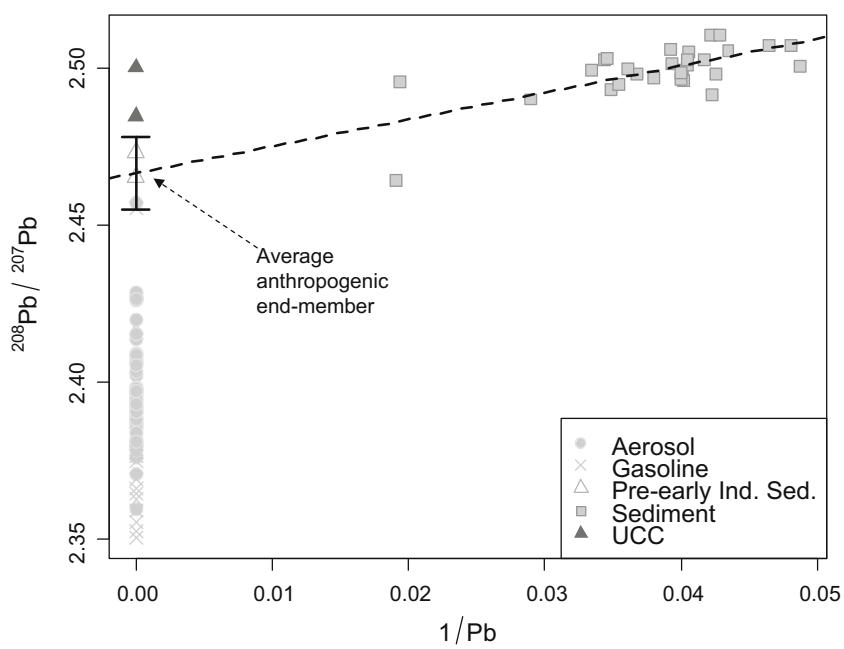

Fig. 5. Relationship between ^{208}Pb/^{207}Pb and 1/Pb (with Pb in μg g^{-1}) for stream sediment samples. The dotted line represents the linear regression adjusted to the cluster of points ($Y = 0.856\times + 2.466$, $R^2 = 0.47$, $n = 29$, $P < 0.001$). The intercept value (2.466 ± 0.013) represents the average anthropogenic end-member which was used to estimate the Pb anthropogenic contribution. The same data as in Fig. 4 (possible natural or anthropogenic sources) are mentioned (see references for Fig. 4), but for ^{208}Pb/^{207} Pb only.

In molasse, Pb is significantly related to Ca and Fe contents, but no relationship can be observed in sediment. This difference in behaviour can be explained: (i) by carbonate dissolution, which greatly decreases Ca + Mg content and variability in sediments compared to molasse (Fig. 2); (ii) by the addition of anthropogenic Pb to sediment samples. These processes modify the natural geochemical pattern between Pb and major elements, as observed in molasse. Consequently, it is very important to consider the local geochemical background to evaluate the origin and behaviour of Pb in weathering products.

4.3.2. Role of land use

Average EF is higher for catchments totally covered by forest than for catchments with less than 10% forest cover (mean EFs of 5.6 and 3.1, respectively, Table 3 and Fig. 6). For cultivated catchments with less than 10% forest cover, a large range of EF values

Table 4
Correlation coefficients ρ (Spearman) for trace and major elements in sediments (a, $n = 29$) and molasse samples (b, $n = 16$). Italic values: $P < 0.05$ and bold values: $P < 0.01$.

	Sc	Al	Ca	Fe	K	Mn	Na	Mg	C_{org}
Panel (a)									
Pb	*0.30*	0.32	0.09	0.27	0.24	0.08	0.16	0.12	−0.25
Sc		**0.97**	**0.75**	*0.28*	*0.36*	0.35	0.38	**0.68**	−0.06
Al			**0.71**	*0.31*	*0.40*	0.31	0.40	**0.71**	−0.10
Ca				0.22	0.43	0.38	0.13	**0.70**	0.08
Fe					**0.51**	***0.60***	−0.02	0.20	−0.17
K						0.18	0.26	**0.75**	−0.21
Mn							−0.12	0.13	*0.20*
Na								0.37	−0.22
Mg									−0.20
Panel (b)									
Pb	**0.66**	0.36	**−0.71**	**0.59**	0.05	0.09	−0.05	−0.44	
Sc		*0.63*	−0.54	**0.92**	0.20	0.08	−0.43	−0.35	
Al			−0.01	**0.63**	**0.76**	0.28	−0.03	0.34	
Ca				*−0.48*	0.20	0.31	0.11	0.76	
Fe					0.21	0.06	−0.37	−0.27	
K						0.24	0.44	**0.69**	
Mn							−0.28	0.31	
Na								*0.46*	

from 1.4 to 6.1 is observed. Moreover, a significant positive relationship between the EF and the percentage of forest cover is observed for catchments with more than 10% forest cover (Fig. 6, $R^2 = 0.63$, $n = 10$, $P = 0.006$), excluding two samples, CAS-22 and RIE-25, which have abnormally elevated EFs (Fig. 6). These two peculiar samples are located close to main roads (RD929 and RD58a, respectively), which might explain a higher local anthropogenic Pb impact. The significant influence of forest cover on EF value led to agricultural catchments being considered separately from those covered by some forest.

4.3.2.1. Forest land and organic matter in sediments. Compared to cultivated catchments which receive agricultural inputs, forest areas are *a priori* often considered as slightly impacted by anthropogenic activities. However, forests are known to enhance atmospheric particle capture because they have a larger leaf area than crops do, which leads to increased atmospheric metal inputs to soils (Kozlov et al., 2000; Hernandez et al., 2003; Steinnes et al., 2005). Lead content is generally greater in the upper soil horizons enriched in organic matter and this enrichment originates from atmospheric anthropogenic Pb from gasoline (Emmanuel and Erel, 2002; Hernandez et al., 2003; Steinnes et al., 2005; Steinnes and Friedland, 2006). Since upstream sediments are the result of soil erosion processes, their Pb contents should be increased indirectly by atmospheric deposition.

For forested catchments, a positive but weakly significant relationship is observed between the EF and TOC in sediments ($R^2 = 0.37$, $n = 12$, $P = 0.03$), indicating that sediment enriched in organic matter might preferentially trap anthropogenic Pb. No significant relationship could be observed between the percentage of forest cover and TOC content in sediments, but the importance of forest cover was found to be an efficient control parameter of Pb content (Fig. 6). Nevertheless, combining the percentage of catchment forest cover and sediment organic C content allows accurate prediction of Pb enrichment in sediment:

$$\begin{aligned} &EF_{Pb} = 2.1\ C_{org} + 0.03\ FC - 0.1 \\ &R^2 = 0.72; \quad P = 0.01; \quad n = 10 \end{aligned} \tag{6}$$

where EF_{Pb} is the Pb enrichment factor, C_{org} is organic C (%) in sediment, and FC is the percentage of forest cover (as a percentage of the total catchment area).

4.3.2.2. Cultivated land and iron oxides in sediment. Compared to forest catchments, sediments originating from cultivated areas are less enriched in anthropogenic Pb because (i) Pb atmospheric deposition is lower since crops are seasonal and partly harvested; (ii) Pb in sediments is less controlled by TOC since soils are poorly enriched in organic matter (Table 2); and (iii) cultivated soils are mechanical worked every year, which homogenises the topsoil and mixes deeper and less impacted particles with those of the surface layer.

In sediments from cultivated catchments, organic matter is low but Fe-oxides are frequent (Table 2). They are known for their affinity for Pb (Mosser and Gense, 1979; Dong et al., 2000; Liu and Huang, 2003). In Table 2, Fe content (%) can be considered as the sum of Fe contained in Fe oxides and in clay minerals. The association of Fe-oxides with anthropogenic Pb was evidenced by the relationship between EF and total Fe content, corrected for Fe contained in clay minerals. To determine the Fe associated with clay minerals, Al content (here, mainly associated with clay minerals, Revel, 1982) has been introduced in a multiple regression:

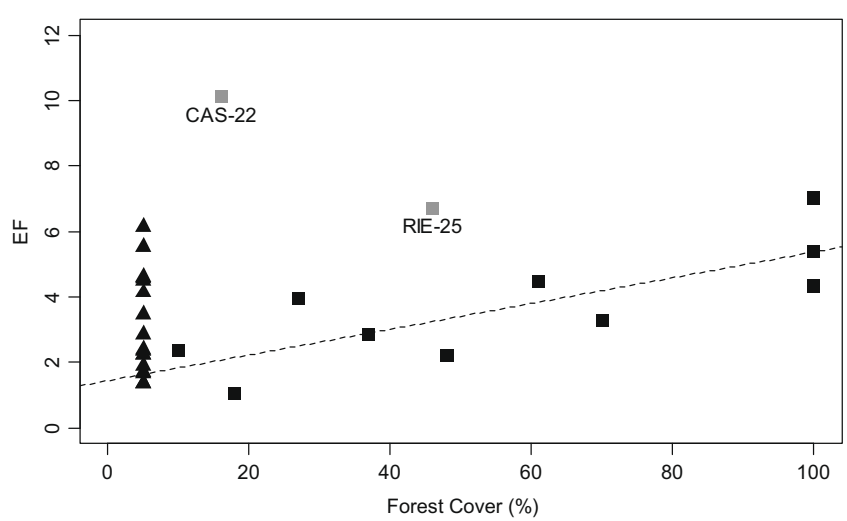

Fig. 6. Relationship between Pb Enrichment Factor (EF) in sediments and catchment forest cover. The dash line represents the linear relationship (EF = 0.04 × %Forest + 1.44; $R^2 = 0.63$; $P = 0.006$; $n = 10$) for catchments with a significant forested cover (squares), excluding samples CAS-22 and RIE-25. The local environment of these two sites (particularly the proximity of a main road) may explain the abnormally high EF values. Cultivated catchments (triangles) are not considered in the relationship since their forest cover is always lower than 10%.

$$EF_{Pb} = 1.96\ Fe - 1.16\ Al + 2.67$$
$$R^2 = 0.75; \quad P < 0.001; \quad n = 17 \tag{7}$$

where EF_{Pb} is the Pb enrichment factor, Fe is the total Fe content (%), and Al is the total Al content (%) in sediments.

The trapping role of Fe-oxides for anthropogenic Pb has already been shown (Lee et al., 1997; Wong et al., 2002; Probst et al., 2003; Bacon and Hewitt, 2005), particularly in low organic matter containing materials.

4.4. Location of anthropogenic lead in sediments

The combination of sequential extraction and Pb isotope investigations allowed determination of the behaviour of anthropogenic Pb in three selected sediment samples, classified according to their increasing anthropogenic Pb content: $\%Pb_{anthr}$·(CAD-19) < $\%Pb_{anthr}$·(AUR-11) < $\%Pb_{anthr}$·(RIE-25) (Table 5).

Fig. 7 shows $^{208}Pb/^{207}Pb$ *vs.* $^{206}Pb/^{207}Pb$ for the different sediment fractions extracted by chemical sequential extraction. The isotopic compositions of the different fractions are as a whole aligned above the data from the literature as previously mentioned (see also Fig. 4). For each sediment, as expected from the mass balance, the bulk sample always plots in between the different fractions. Generally, the isotopic ratio of the different fractions differs greatly from that of the bulk sample. The cluster of points spreads between the residual fraction (circle) and the average anthropogenic end-member (Fig. 7), except for RIE-25, for which the acid-soluble and oxide fractions are less radiogenic than the average anthropogenic end-member. For this more contaminated sample, the spread of the different fractions is more important than for the other two samples, indicating that anthropogenic Pb is not equally distributed among the different fractions.

The results of sequential extraction showed that total anthropogenic Pb and Pb associated with Fe-oxides increased in a similar way in the studied samples (Table 5). It indicates that Fe-oxides are a predominant component in fixation of anthropogenic Pb, particularly Pb from recent gasoline for RIE-25. Moreover, the fraction order of increasing $^{206}Pb/^{207}Pb$ ratios (acid-soluble > oxides > oxidizable) suggests that anthropogenic Pb is enriched in carbonate and oxides fractions. These fractions are thus essential trapping components for anthropogenic Pb. Indeed, secondary carbonate precipitation has been observed in soils and stream channels at these high pH conditions (Perrin et al., 2008).

For the three studied samples, non-residual Pb (the sum of Pb contents in non-residual fractions) was compared to anthropogenic Pb estimated by isotopic and geochemical approaches (Table 5). Despite the differences in anthropogenic Pb estimates obtained using the two methods, an increase was observed in non-residual Pb with increasing anthropogenic Pb content in both cases. This confirms that anthropogenic Pb is mainly adsorbed onto labile

Table 5
Pb content and anthropogenic Pb content estimated by both geochemistry and isotopes in the three sediment samples used for the sequential extraction procedure. The concentrations of Pb contained in residual and in non-residual fractions, as well as associated to Fe oxides, are given.

Sample	Total	Anthropogenic		Residual	Non-residual	Associated to Fe oxides
		Estimated using geochemical approach	Estimated using isotopic approach			
CAD-19	24.99	11.92	7.68	10.31	14.68	3.36
AUR-11	28.24	21.98	11.32	10.2	18.04	6.22
RIE-25	52.33	44.55	52.33	8.97	43.36	24.41

All values are in $\mu g\ g^{-1}$.

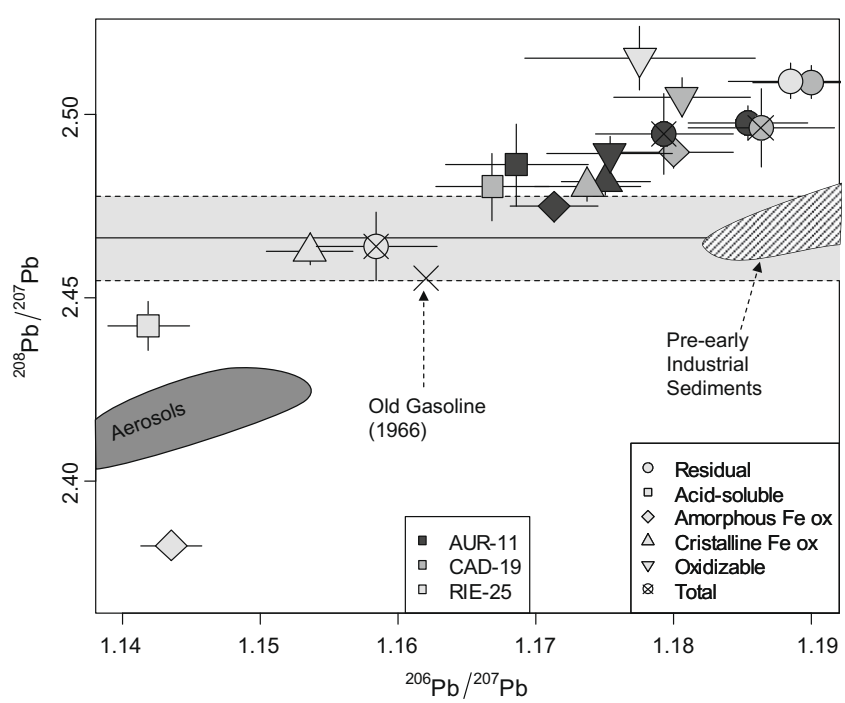

Fig. 7. $^{208}Pb/^{207}Pb$ *vs.* $^{206}Pb/^{207}Pb$ diagram for the bulk sediments and the different fractions extracted by performing chemical sequential extraction on three selected sediment samples (CAD-19, AUR-11, and RIE-25; see also Fig. 3). The isotopic composition of non-residual fractions spread from the residue to the average anthropogenic end-member, except for RIE-25, whose labile fractions are influenced by a less radiogenic anthropogenic end-member. The average anthropogenic end-member is represented by the horizontal grey area (solid line: mean value; dotted line: 95% confidence interval).

fractions of sediments, as already shown for soils (Teutsch et al., 2001; Bacon and Hewitt, 2005). The amorphous Fe-oxide fraction often has a high affinity for anthropogenic Pb and consequently, it is a favourite anthropogenic Pb trapping component. This is corroborated by: (i) the positive relationship between total Pb associated with amorphous Fe oxides and Pb_{anthr} (Table 5), and (ii) the observation that the higher the Pb enrichment, the lower the $^{208}Pb/^{207}Pb$ isotopic ratio in sediment (Table 5 and Fig. 7).

For the peculiar RIE-25 sample, the position of the Fe-oxides under the isotopic line (formed by aerosols, gasoline and pre-early industrial sediment, Fig. 7) suggests contamination by a mixture of Pb from fertilisers and aerosol (influenced by recent gasoline), with amorphous oxides and carbonate being the main fractions concerned. The contributions of Pb from residue, recent gasoline, and P–K fertiliser in the amorphous Fe-oxide fraction were estimated at 14%, 82% and 4%, respectively, using a three end-member isotopic mixing model. The affinity order of anthropogenic Pb content in this sample is as follows: amorphous Fe oxides > acid-soluble > crystalline Fe oxides > oxidizable > residue.

Finally, in this environment, anthropogenic Pb has a weak affinity for the oxidizable fraction. From the results, it can be deduced that the less important the carbonates, the more important the Fe-oxides (particularly the amorphous fraction) are for anthropogenic Pb trapping. These results are consistent with other studies of various soils, where a decreasing Pb affinity could be evidenced for Fe-oxides, carbonates, and organic matter (Teutsch et al., 2001; Emmanuel and Erel, 2002; Probst et al., 2003).

5. Conclusions

The purpose of this study was to determine the Pb sources and their contributions to Pb content in stream-bed sediments of the French Gascogne region, which is mainly cultivated and weakly impacted by urban and industrial activities. Geochemical and isotopic approaches were originally associated with chemical sequential extraction. This allows quantification of the intensity of sediment contamination, to discriminate between natural (bedrock weathering) and anthropogenic Pb, and to determine the distribution of anthropogenic Pb among the residual and non-residual fractions of the sediment. The more important findings are:

- There is a relatively low total concentration and a moderate enrichment of Pb in sediments, except for some samples, signifying a low but significant regional contamination level in relation to non-point pollution sources.
- The correlations between Sc, Pb and major elements are different for sediments and molasse: the geological features and the local environmental factors have influenced the Pb concentration and isotopic composition during molasse deposition and weathering/erosion processes. It is thus important to consider the local background in order to accurately determine Pb contamination in sediments.
- There is an influence of an average anthropogenic Pb source, which is characterised by an isotopic composition close to the values of the most radiogenic aerosols and old gasoline, rather than more recent leaded gasoline, except for one sample. A negligible Pb contamination associated with fertiliser spreading was evidenced.
- In the area, the mean contribution of anthropogenic Pb is 63.7 ± 20.4% and 36.6 ± 17.8%, as estimated by geochemical and isotopic approaches, respectively. A higher anthropogenic Pb was estimated using the geochemical approach, but both estimations are in the same direction, except for weakly contaminated samples.
- Pb enrichment in stream sediments is positively related to catchment forest cover and increasing organic C content, whereas it is strongly linked with Fe-oxide content in cultivated catchments.
- As confirmed by three independent approaches (sequential extraction, geochemical, and isotopic investigations), in this low organic C containing material, anthropogenic Pb is clearly associated with carbonates and Fe-oxides (preferentially amorphous fraction). Iron oxides become the most efficient anthropogenic Pb trapping component as soon as the carbonate content is reduced and Pb enrichment increases, whereas organic mater is always weakly involved.

These results also show the importance of the choice of both a normaliser element and local reference material (as also shown in N'guessan et al., 2009) for estimating the anthropogenic Pb content.

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