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Trace elements in stream bed sediments from agricultural catchments (Gascogne region, S-W France): Where do they come from?

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ABSTRACT

The Gascogne region (SW of France) is cultivated for more than 75% of the area. 83 samples of stream bed sediments were collected in three main Gascogne river basins (Gers, Save and Touch, left tributaries of the Garonne river) to evaluate the impact of agricultural practices on trace elements behavior. Eight potential harmful elements (PHE) (Cr, Co, Ni, Cu, Zn, As, Cd and Pb), four reference elements for normalization (Sc, Cs, Al and Fe) and four major elements (Mn, Ca, Mg and P) were considered. The average trace element concentrations in the fine fractions (<63 μm) are in the decreasing order: Zn>Cr>Ni>Pb>Cu>Co>As>Sc>Cs>Cd. Geochemical investigations and an original approach combining regression analysis and chemical sequential extraction allowed to select the most adequate reference material (regional molasse) and reference element (Cs) for normalization procedure. The enrichment factor (EF) is generally lower than 2.5, particularly for Cr, Ni, Cu, As, Zn; however, 23% of the sampling stations are more contaminated (2.5<EF<4.5), particularly for Cd, Pb and Co. The PHE in the Gascogne river sediments are mainly originated from natural weathering processes; nevertheless, anthropogenic contribution could represent up to 34% of the total sediment content. For lead, geochemical and isotopic methods gave very similar anthropogenic contributions (24% and 22%, respectively).

The enrichment of Cu, Pb, Zn, Co, As, Ni, Cr was mainly related to global and local atmospheric deposition of industrial emissions and gasoline combustion, and was associated to forested catchments. All PHE's are controlled by clay and oxi-hydroxides minerals. Cd was the only PHE enriched downstream cultivated catchments and this enrichment was linked to Ca and P. This indicates a major origin of Cd from fertilizer inputs and a main control by carbonate minerals.

1. Introduction

Continental surfaces are the place of ceaseless transfer and exchange of matters through global biogeochemical cycles: rock weathering — riverine transport — sedimentation — diagenesis. The development of industrial, agricultural and urban activities, lead to disturbance of the biogeochemical cycle of many elements, particularly trace elements. Because of their very low abundance, trace elements are particularly sensitive to surrounding environmental conditions, which influence their physico-chemical speciation and their behavior in the ecosystems. Among these elements, oligoelements (Cu, Zn, Ni, Cr, Co,
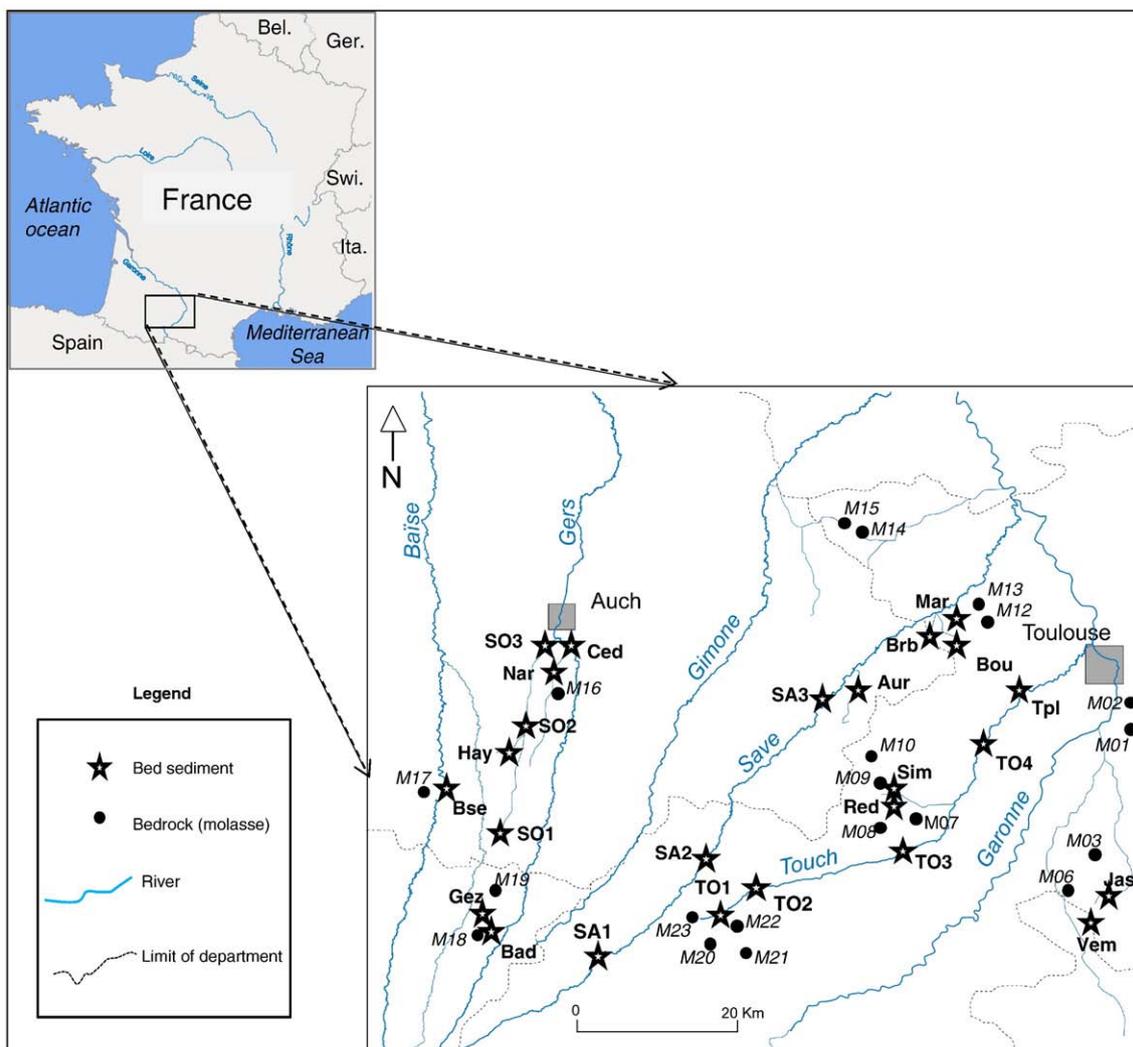
Fig. 1 – Location of the study area showing the stream bed sediments and bedrock sampling sites.

Fe, Mn, V, Mo, Sn) are essential to biological activity, within acceptable concentrations. Other trace elements such as Pb, Cd, As and Hg do not present any biological function and they are particulary toxic and harmful for living organisms (Sigg et al., 2006). These elements, also called "Potential Harmful Elements" (PHE, Plant et al., 1997; Salvarredy-Aranguren et al., 2008), originate from natural processes (rock weathering, volcanic eruption) but also from various anthropogenic activities (mining, industrial emissions, domestic effuents and agriculture…, Hutchinson and Rothwell, 2007). Fertilizers (Senesi et al., 1999), manures (Gomez et al., 1992) and pesticides spreadings (Kabata-Pendias and Pendias, 1984) are the main sources of PHEs supplied by agricultural pratices. As an example, according to Avril (1992), application of 50 kg ha^{-1} phosphate fertilizer brings 70 mg kg^{-1} of cadmium to soils; the « bouillie bordelaise » (composed of a mixture of lime and copper sulfate) used to treat the vineyards, brings significant amounts of copper to soils (reaching 500 mg·kg^{-1} Cu, Robert and Juste, 1997). The spreading of heat-dried sludge from water plant treatment stations is a current and increasing practice in agriculture for decades. After treatment by sludge from water plant treatment stations, soils might content 98 to 369 mg kg^{-1} of Zn and 26 to 44 mg kg^{-1} of Pb

(Anderson and Nilsson, 1972). Soil irrigation and drainage networks might also influence the behavior of PHEs leaching in agricultural soils.

Most of PHE transfer from soil to river systems are associated with physical erosion processes and subsequent riverine transport of particulate matter, notably under high water pH conditions (Liu et al., 2003; Rothwell et al., 2008). Stream bed sediments originate from suspended matter transported during storm events and deposited in the main channel during recession periods of discharge. Analysis of stream bed sediments, particularly the finest fraction (<63 μm), is a good way to get an integrative view of chemical composition of suspended matter transported by rivers (Gaiero et al., 2003). In catchments, the composition of stream bed sediments can be considered on average as representative of PHEs in soils they originate. These sediments represent an important reservoir of natural and anthropogenic PHE, which can be accumulated or released according to hydrological and physicochemical conditions.

To evaluate the ecological risk of PHE in the environment, it is today, widely-admitted that determination of their total concentration is not sufficient. Chemical speciation, distribution,

partitionning of PHEs between dissolved and particulate matter, and the sediment, are essential to understand their availability and toxicity (Förstner, 1993). Unfortunately for river sediments, little information is available for these processes and parameters, particularly in agricultural catchments.

The objectives of this study are:

(i) to evaluate the enrichment of PHE in stream bed sediments from agricultural catchments in the Gascogne region;
(ii) to determine the anthropogenic contribution to PHE concentration using geochemical and isotopic methods, with special emphasis on the choice of the reference element for EF calculation. For that purpose, a statistical analysis and a sequential extraction procedure have been used;
(iii) finally, to discuss the origin and the behaviour of PHEs in relation to chemical characteristics of sediments, to land cover and to regional environmental conditions.

The Garonne river basin has been investigated for major element behaviour (Probst, 1983, 1986), for trace elements (Leleyter et al., 1999; Coynel et al., 2007) and global impact of agriculture on weathering (Semhi et al., 2000; Perrin et al., 2008); nevertheless, no study concerns the PHE contamination in the Gascogne area, which is the most intensively cultivated area in the Garonne basin drained by small streams. The PHE of concern are Cr, Co, Ni, Cu, Zn, As, Cd and Pb.

2. Study area

The Gascogne region (4200 km^2), located in the South-West part of France, West to Toulouse (Fig. 1), is part of the Garonne river basin (52,000 km^2 at the station of Lamagistère). This area is bordered on the Eastern and Northern part by the Garonne river, third French river (discharge 630 m^3 s^{-1}, 523 km). Its source is in Spain (Aran Valley close to the Maladeta massif) at the foot of the Aneto Mountain; it joins the Dordogne river close to Bordeaux.

The Gascogne area is drained by 5 main rivers of which sources are at the foot of the Lannemezan Plateau (from West to East: Baïse, Gers, Gimone, Save and Touch). They join the Garonne river on the left side, between Marmande and Toulouse. Agriculture is the main activity in this area, with more than 75% of arable land, primarily dominated by cereal cultures. This region is classified among the sensitive zones to eutrophication risk by the French Water Agency of the Adour-Garonne Basin (1994).

The Gascogne area is covered by a molassic bedrock (detrital formation of the Tertiary, resulting from physical erosion of the Pyrénées mountains), which is characterized by disparities of facies (more or less carbonated) (Brunet, 1965). On this substrate, two main types of soils (Cavaille, 1969; Revel, 1982) have developed: (i) the "terreforts" (dominated by clay-silt) characterized by a compact texture, weakly permeable and thus, very vulnerable to surface runoff; (ii) the "boulbenes" (soils of alluvial terraces), which are siliceous soils or light soils easy to work and characterized by a rather deep permeability.

The valleys of the Gascogne rivers are characterized by a slope asymmetry: eastern slopes are very steep and covered by "terrefort" soils and western slopes are very smooth and covered by "boulbènes" soils (Ribeyreix-Claret, 2001). Western slopes are mainly cultivated with corn, whereas eastern slopes are forested or cultivated by wheat and sunflower. The northern part of the study area is characterized by the average terraces of the Garonne river and the slopes of Lomagne, slightly broken, mainly occupied by great pieces of cultures and the forest of Bouconne. On the south-western part, forest cover is relatively more important than in the rest of the area.

The climate is oceanic with average precipitations and mean annual temperatures ranging between 600 mm and 700 mm and 13 °C to 14 °C, respectively (Brunet, 1965). The hydrological regime of the rivers is mainly pluvial with low water period from July to November and high water flows between December and May (Probst and Tardy, 1985). The low water period can be very dry, and during that period the Gascogne river discharges are supported by the Neste Channel, which is supplied by water coming from the Pyrénées mountains.

All these environmental characteristics make the slopes of the Gascogne area vulnerable to surface runoff and erosion processes, which might contribute to supply rivers with pollutants. Average mechanical and chemical erosion (Probst, 1983, 1986) in this area is estimated at 27 t km^{-2} an^{-1} (with river suspended matter primarily composed of silica, aluminium, iron and titanium) and 70 t km^{-2} an^{-1}, respectively (with total dissolved solids mainly composed of calcium, magnesium, sodium and carbonates).

3. Materials and methods

3.1. Sampling and pre-treatment of the samples

Stream bed sediments and molasses were collected at about thirty and twenty sampling stations, in 2004 (February, May and July) and July 2005, respectively. The sampling strategy followed these criteria:

(1) Samples were collected in streams belonging to three main tributary basins (Gers, Save and Touch) of the Garonne river basin, which are representative of the Gascogne region. In these small rivers, sediment accumulation (less than 10 cm) is limited to areas of lower hydrodynamic regime. Because of remobilisation and deposition due to frequent storm events, sediments are supposed to represent present-day soil erosion.
(2) For each basin, longitudinal transects were considered from upstream to downstream on the main rivers (Save and Touch) and on a main tributary of the Gers river (Sousson).
(3) Finally, for each river basin, streams draining limited areas were sampled to be representative of a spatial distribution of sediments, according to agricultural practices and forest cover.

Sediments samples were taken in the first centimeters of stream bed sediments using plastic tube of 180 ml and molasse samples were taken at approximately 30 cm depth into the bedrock to avoid surface contamination by anthropogenic inputs.

The samples were thereafter air-dried and stored in a cold room. After being dried, samples were carefully homogenized in an agate mortar, quartered, and separated to obtain 3 fractions: a fine fraction (<63 μm); a coarse fraction (63 μm–2 mm) and finally the fraction >2 mm.

Before sampling, plastic materials (tins, tubes, pliers, washing bottles, nylon sieve, brace sieve etc.) were washed with 1.0 M HCl during 48 h, then rinsed 3 times with Milli-Q water to limit the risks of contamination during sampling and sample treatment.

3.2. Chemical treatments and analysis

Mineralisation was performed on the fine fraction (<63 μm) of sediments because PHE are known to be preferentially associated to (Salomons and Förstner, 1980; Probst et al., 1999). Sediment and molasses samples were digested with a HNO_3–HF–H_2O_2 mixture following a procedure described by Marin (1998). In a savillex (teflon bottle) about 100 mg sample (sediment or molasse) was digested with a mixture of concentrated HNO_3 (0.6 ml) and HF (0.5 ml) at 90 °C overnight. Afterwards, the solution was evaporated and about 2 ml of H_2O_2 was added to remove organic matter. Generally, after 2 to 3 nights the reaction is complete. Finally after evaporation, 15 ml HNO_3 2% was added.

A sequential extraction procedure was applied (following Leleyter and Probst, 1999) to determine the PHE concentrations associated to sediment fractions. Six successive steps corresponding to a specific reagent and with decreasing pH, were performed. The filtrate was acidified with HNO_3 for analysis, while the residue was rinsed by de-ionized water and underwent a new reagent adding. After the ultimate step, the residue was dissolved following the same mineralisation procedure as for total sample.

PHE concentrations and Pb isotopes (^{206}Pb, ^{207}Pb and ^{208}Pb) were determined by inductively coupled plasma-mass spectrometry (ICP-MS Perkin-Elmer ELAN 6000) at the Laboratoire des Mécanismes de Transferts en Géologie (LMTG, Toulouse, France). Detection limits (DL) vary according to the elements (Cd<Co=Cs=Pb<Cu<As<Ni) between 10^{-3} and 10^{-2} μg l^{-1}. For Cr, Sc and Zn, DL is 0.049, 0.167 and 0.187 μg l^{-1}, respectively.

Major element (Al, Fe, Ca, Mg and P), concentrations were analysed by inductively coupled plasma-optic emission spectrometry (ICP-OES Thermo IRIS INTREPID II XDL) at the Laboratoire d'Ecologie Fonctionnelle (EcoLab, Toulouse, France). The DL was 0.2 μg l^{-1}.

The analytical data quality was checked by using simultaneously the STSD-2 certified standard (to verify accuracy and reproducibility of the mineralisation procedure for PHE determination), and by calculating the average relative error (to control analytical precision). For most elements, the recovery (QA/QC) ranges between 80% and 110%, except for Cr (77%) and Cd (for which no certified value was available). The weaker recovery for Cr might be due to its refractory characteristic, which implies a strong adsorption onto siliceous materials (Tam and Yao, 1998; Liaghati et al., 2003). For each element, the Relative Standard Deviation (RSD) was lower than 5%, except for Cd (9.8%), as already shown by other authors (Roussiez et al., 2005; Pekey, 2006).

In addition, the accuracy of sequential extraction procedure was checked by comparing the cumulative PHEs concentrations of the different fractions with the concentration of the bulk sample. The recovery was 94–109%.

For Pb isotopes, the measured ^{206}Pb/^{207}Pb for NIST-SRM-981 was 1.0925 compared to the reference value of 1.0933. The average deviation of ^{206}Pb/^{207}Pb and ^{208}Pb/^{206}Pb varies from 0.3 to 0.6% and from 0.2 to 0.5%, respectively.

3.3. Calculation of enrichment factor and of anthropogenic contribution

PHE in stream bed sediments originate mainly from soil/bedrock weathering and anthropogenic sources. The concept of "enrichment factor" (EF) was developed in the seventies (Chester and Stoner, 1973) to evaluate the anthropogenic contribution. Originally applied to atmosphere and sea water, EF was gradually extended to continental environments, such as soils (Hernandez et al., 2003) or river sediments (Tam and Yao, 1998). It is defined as the concentration ratio of a considered element to a reference element in a given sample, divided by the same ratio in earth's crust (Chester and Stoner, 1973).

$$EF = \frac{(X/Y)_{sample}}{(X/Y)_{reference\ material}} \qquad (1)$$

With X = concentration of the considered element; Y = concentration of the reference element.

The anthropogenic contribution is thus calculated as follows:

$$\%X_{anthropogenic} = \frac{[X]_{sediment} - [Y]_{sediment} \times [X/Y]_{reference\ material}}{[X]_{sediment}} \times 100. \qquad (2)$$

3.4. Statistical analysis

Principal Components Analysis (PCA) is generally considered as an effective tool (Tessier and Bonté, 2002; Liu et al., 2003) to exhibit the main factors controlling geochemical data contained in a matrix. This statistical technique was used to identify relationships between the different PHE (variables) on the one hand, and between PHE and the stations (observations), on the other hand. The "Kaiser criterion" (Kaiser, 1961) recommended to consider significant components with an average explained variance (λ) at least equal to 1. The contribution of each variable in the inertia of a principal component is considered only if loading is >0.5.

4. Results and discussion

4.1. Major and trace element concentrations

Table 1 presents the average and the range of variations for major and trace elements concentrations in the local bedrock (molasse, this study) and in the Gascogne stream bed sediments (this study) compared with data for PAAS (Taylor and Mc Lennan, 1985) and UCC (Wedepohl, 1995).

Concerning major elements, Fig. 2 shows that the sediment chemical composition varies from a non carbonate end-

Elements	Gascogne stream sediments (<63 μm)			Gascogne bedrock (Molasse)	UCC[a]	PAAS[b]
	Min.	Max.	Mean	Mean		
Major (mg g⁻¹)						
Al	31.87	98.17	52.99	46.53	77.44	189
Ca	2.01	104.50	29.18	48.85	29.45	13
Fe	17.63	60.09	28.59	28.43	30.89	72
Mg	1.64	8.76	4.36	3.6	13.5	22
Mn	0.36	2.41	1.05	0.55	0.53	1.1
P	0.24	0.94	0.5	–	0.66	1.6
Trace (μg g⁻¹)						
Sc	6.30	21.88	12.97	14.48	7.0	16.0
Cr	33.49	84.98	52.98	57.56	35.0	110.0
Co	8.15	33.16	14.43	12.19	11.6	23.0
Ni	17.01	43.92	28.20	26.73	18.6	55.0
Cu	11.25	29.62	18.86	18.04	14.3	50.0
Zn	55.46	140.59	81.73	80.96	52.0	85.0
As	8.77	27.48	15.14	17.19	2.0	–
Cd	0.11	0.79	0.30	0.20	0.10	–
Cs	2.24	5.97	4.95	5.50	5.8	15.0
Pb	16.52	41.94	24.90	21.45	17.0	20

–: nd; Min: minimum; Max: maximum.
[a] Wedepohl (1995).
[b] Taylor and Mc Lennan (1985).

the highest content are for Zn and Cr (140.59 and 84.98 μg g⁻¹, respectively). For other elements, concentrations vary between 6.30 μg g⁻¹ (Sc) and 43.92 μg g⁻¹ (Ni). As a whole, the order of abundance is Zn>Cr>Ni>Pb>Cu>Co>As>Sc>Cs>Cd. Mean element concentration does not vary very much from one station to another regardless of the sampling period. However, the concentrations are slightly higher during summer, except for Cd. This geochemical pattern of trace elements in the sediments is very similar to molasse bedrock (Fig. 3). Consequently, natural and anthropogenic processes weakly influence the global geochemical pattern of sediments. Nonetheless, these data do not give any information about the origin and the respective contributions of natural and anthropogenic sources of elements in sediments.

4.2. Enrichment calculation

4.2.1. Selection of the reference material
To normalize trace element concentrations, the authors often used the earth crust as a reference material (Soto-Jiménez and Paez-Osuna, 2001; Pekey, 2006) since it is generally accepted by the scientific community. This normalization is quite correct for large river basins like the Amazon or the Congo river (Gaillardet et al., 1995), where there are various rock outcrops, but for small catchments it did not reflect local bedrock chemical composition (Reimann and De Caritat, 2005). Indeed, some authors have tried to circumvent this handicap by using local background values and by comparing to calculation using earth crust reference (Hernandez et al., 2003). But, the composition of regional bedrocks is rarely known. As seen in Fig. 4a, the ratio between trace element concentration in sediment and in upper continental crust (UCC: Wedepohl, 1995), indicates that sediment concentrations always present a significant enrichment for all elements (particularly As and Cd), except Cs. On the opposite, normalisation to local molasse bedrock indicates no important anomaly, except

member (Ca<15%) towards a carbonate end-member (Ca around 60%). But the respective abundance of Al and Fe+Mn remains the same whatever the sediments.

For trace elements (Fig. 3), Cd and Cs present the lowest mean concentrations (0.11 and 2.24 μg g⁻¹, respectively), while
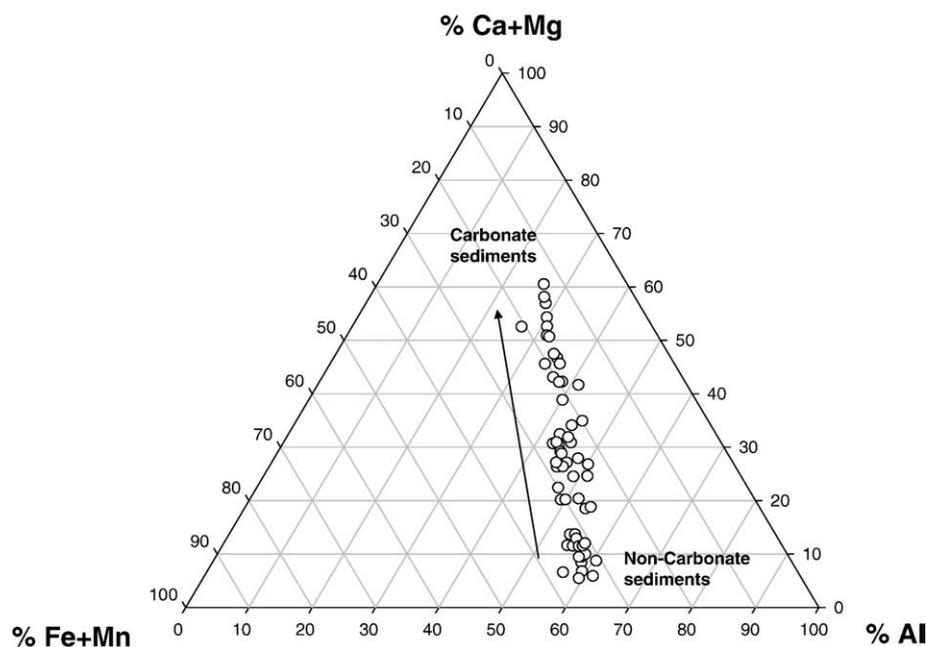
Fig. 2 – Ternary diagram for major elements in the Gascogne stream bed sediments.
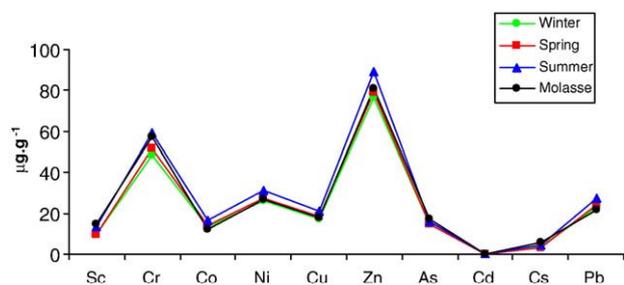
Fig. 3 – Patterns of mean trace element concentrations ($\mu g \ g^{-1}$) in the Gascogne stream bed sediments for three seasonal periods compared to the mean bedrock composition.

Cd, Co and Pb. Consequently, it is more appropriate to normalize Gascogne stream sediments to regional bedrock (molasse) rather than to UCC because most of the elements (except Cs and Co) are enriched in Miocene molassic deposits compared to UCC.

4.2.2. Selection of the normalizer element

The choice of the reference element is constrained by some requirements (Luoma, 1990): (1) the occurence of a linear relationship between this reference element and the PHE; (2) this element must be stable and not submitted to biogeochemical processes such as reduction/oxidation, adsorption/desorption, and diagenetic processes that may alter its concentration (i.e. it must be mainly located in the residual fraction); and finally, (3) it must be of natural origin and its concentration ratio with PHE must be conservative during weathering processes.

In the literature, Al (Windom et al., 1989), Li (Loring, 1990), Cs (Ackermann, 1980; Roussiez et al., 2005), Sc (Grousset et al., 1995; Hernandez et al., 2003), Fe (Schiff and Weisberg, 1999) and even organic matter content (Hissler and Probst , 2005), have been used as reference elements, leading to various results from an element to another. The choice of a reference element is thus not universal and depends on geological and physicochemical characteristics of the study area (Reimann and De Caritat, 2005). Some authors have tried to select the most appropriate element by using some statistics or sequential extraction methods (Loring, 1991; Summer et al., 1996; Tam and Yao, 1998; Aloupi and Angelidis, 2001; Liu et al., 2003; Roussiez et al., 2005).

In our case study, for example, EF calculated for a riverine sediment (SA1) using Sc and Cs as reference elements, indicates rather different results (Fig. 4b). EF calculated using Sc is equal or lower than 1.5, whereas the values always exceed 1.5 using Cs. It is thus obvious that the reliability of the results, as regard to enrichment, depends on the choice of the reference element.

For that purpose, the choice of a reference element can not be arbitrary and must be defined by a combination of two independent scientific methods such as statistics and chemical extractions. The first one aims to check the significant relationship between reference element and PHE of natural origin whereas the second one allows to verify that the reference element is mainly located in the residual fraction (i.e mainly of natural origin).
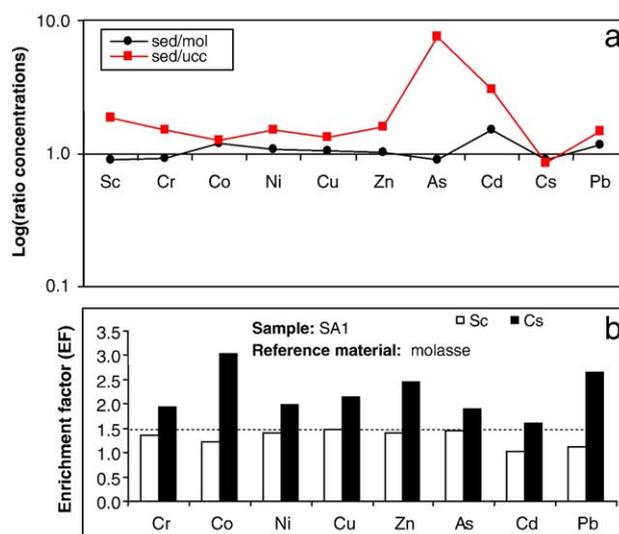
Fig. 4 – a. Comparison of trace element concentrations in the stream bed sediments normalized to UCC (sed/UCC) and to local bedrock concentrations (sed/mol). mol: molasse; sed: sediment; UCC: upper continental crust (Wedepohl, 1995).
b. Comparison of EF for different PHE in the Gascogne stream bed sediment (SA1) using Sc (white bar) and Cs (black bar) as reference elements.

To select the most appropriate reference element, most of the authors used a step by step regression method (Loring, 1991; Summer et al., 1996; Tam and Yao, 1998; Roussiez et al., 2005) in the sediments since they do not have access to the bedrock material. In our case study, the composition of the bedrock material has been analysed. In the molasse, Cs and Fe are the reference elements, which show the best relationships with most of PHE (except Cd) (Table 2). Indeed, Fe is both associated with oxides and clay minerals (Summer et al., 1996; Sterckeman et al., 2002) and Cs is mainly found in the lattice of clay minerals (Roussiez et al., 2005). Fe can thus be mainly controlled by changes in situ of physico-chemical processes and a small Fe fraction in sediments may represent anthropogenically induced Fe sulfides and Fe oxides (Summer et al., 1996). In consequence, Cs may be more suitable as a reference element to calculate PHE enrichment in these clay-enriched studied sediments.

Moreover a sequential extraction applied to the fine fractions ($<63 \ \mu m$) of the sediments, indicates for each reference element

Table 2 – Pearson correlation coefficients (r^2) between the concentration of reference elements (Cs, Sc, Al and Fe) and PHE in the Gascogne bedrock (molasse)

PHE	Reference element			
	Cs	Sc	Al	Fe
Cr	0.72	0.57	0.51	0.93
Co	0.71	0.21	0.55	0.67
Ni	0.83	0.43	0.75	0.84
Cu	0.81	0.37	0.62	0.86
Zn	0.84	0.51	0.64	0.76
As	0.6	0.63	0.51	0.9
Cd	0.02	0.09	0.03	0.002
Pb	0.5	0.5	0.28	0.5
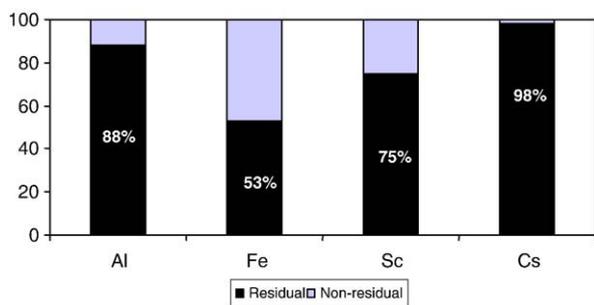
Fig. 5 – Proportion of residual (black) and non residual (grey) fractions of reference elements (Al, Fe, Sc and Cs) usually used as normalizers. The non residual fraction represents the sum of the element measured in the different sequential extraction steps: water leachable, exchangeable, acido-soluble (carbonates), reducible fraction (Mn oxides, amorphous and crystalline Fe oxides), oxidizable (organic matter). The residual fraction represents the remaining fraction at the end of the procedure and corresponds to the element included in the mineral lattice.

the proportion linked to the non-residual and residual fractions, respectively (Fig. 5). 98% of Cs belong to the residual fraction, whereas only 53, 75 and 88%, respectively for Fe, Sc and Al. This result confirms the detrital origin of Cs, its main association with fine fractions and its conservative character. These results are the essential arguments for geochemical normalization. This reference element has been already selected by Roussiez et al. (2005) for fluvial sediments deposited in the Gulf of Lions by Mediterranean rivers.

Considering the above arguments, in the present study, Cs was also retained for normalization of the set of PHE. The natural geochemical background average ratios between the different PHE and Cs in sedimentary bedrock (molasse), are the following: Cr/Cs (10.46), Co/Cs (1.99), Ni/Cs (4.89), Cu/Cs (3.29), Zn/Cs (14.71), As/Cs (3.12) and Pb/Cs (3.74).

One can notice in Table 2 that Cd is not correlated to Cs, but either with the other potential normalizer elements in the bedrock. Some authors have already observed the same result

using several other reference elements (Summer et al., 1996; Mil-Homens et al., 2006) and for interpretation, they recommanded to simply use the concentration without normalization. Thus, to evaluate Cd enrichment in Gascogne sediments, we simply used the ratio between Cd in the sediment and in the reference material (molasse).

4.2.3. PHE enrichment in the Gascogne stream bed sediments

The geochemical natural background ratios (X/Cs) of the different PHE (X) (see previous section) allowed to calculate the enrichment factors (EF).

It is generally accepted that EF<2 reflects natural variability of the sample mineralogical composition (Sutherland, 2000; Hernandez et al., 2003); beyond 2, a significant enrichment is suspected. The use of local geochemical background as a reference in EF calculation allows to decrease the EF threshold to 1.5 (Soto-Jimenez and Paez-Osuna, 2001; Roussiez et al., 2005).

The average results obtained in Fig. 6 show that only three PHE (Cd, Co and Pb) present EF higher than 1.5, the other PHEs remaining within the range of supposed natural variability. The EF spatial distribution (Fig. 7a,b) indicates a significant variability among the samples for all PHEs. All the elements are generally more enriched in sediments located upstream of the main river basins (Baïse, Gers, Save, south-western part of the study area), except Cd for which EF is higher (1.5<EF<4.5) in sediments located downstream of the Garonne tributary basins (Save, Touch and Ariège, eastern part of the region). Among the PHE, Cr, Ni, Cu, Zn (7b) and As (7a) present a similar moderate (1.5<EF<2) spatial enrichment distribution, with the highest EF in the upper part of the Gers and the Save river basins. Pb and Co present as a whole a same enrichment pattern (Fig. 7a), with higher EF values (1.5<EF<3.5) than the previous group, particularly decreasing downstream the Baïse, the Gers and its main tributary, the Sousson.

It is worth to notice that the stations Gez, SA1 and Bad (close to Lannemezan city) present the highest EF values for all elements except Cd (Fig. 7a and b), and that these stations are located on streams draining catchments partially or completely covered by forest. On the other hand, Cd is particulary enriched in sediment samples from stations located in cultivated areas
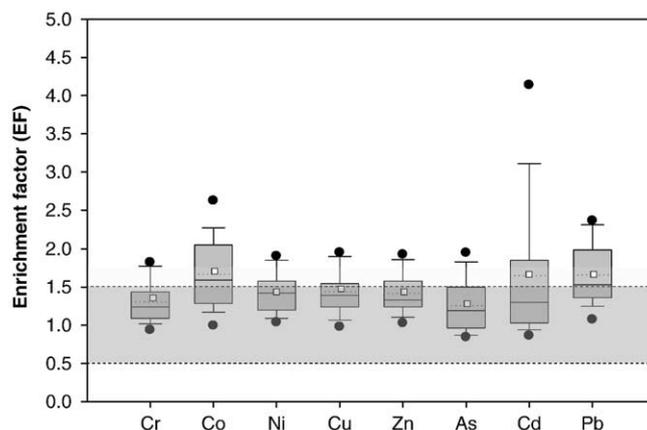
Fig. 6 – Enrichment factor (EF) for trace elements in Gascogne stream bed sediments using the local background (molasse) and Cs as normalizer. Light grey area (0.5<EF<1.5) indicates that elements are almost provided from local bedrock weathering. Box of the plot (dark grey) extends from the lower quartile (25%) to the upper quartile (75%), covering the median (line) and the mean (dotted line) values; black points above and below the box indicate 90th and 10th percentiles. Vertical bars represent the error.
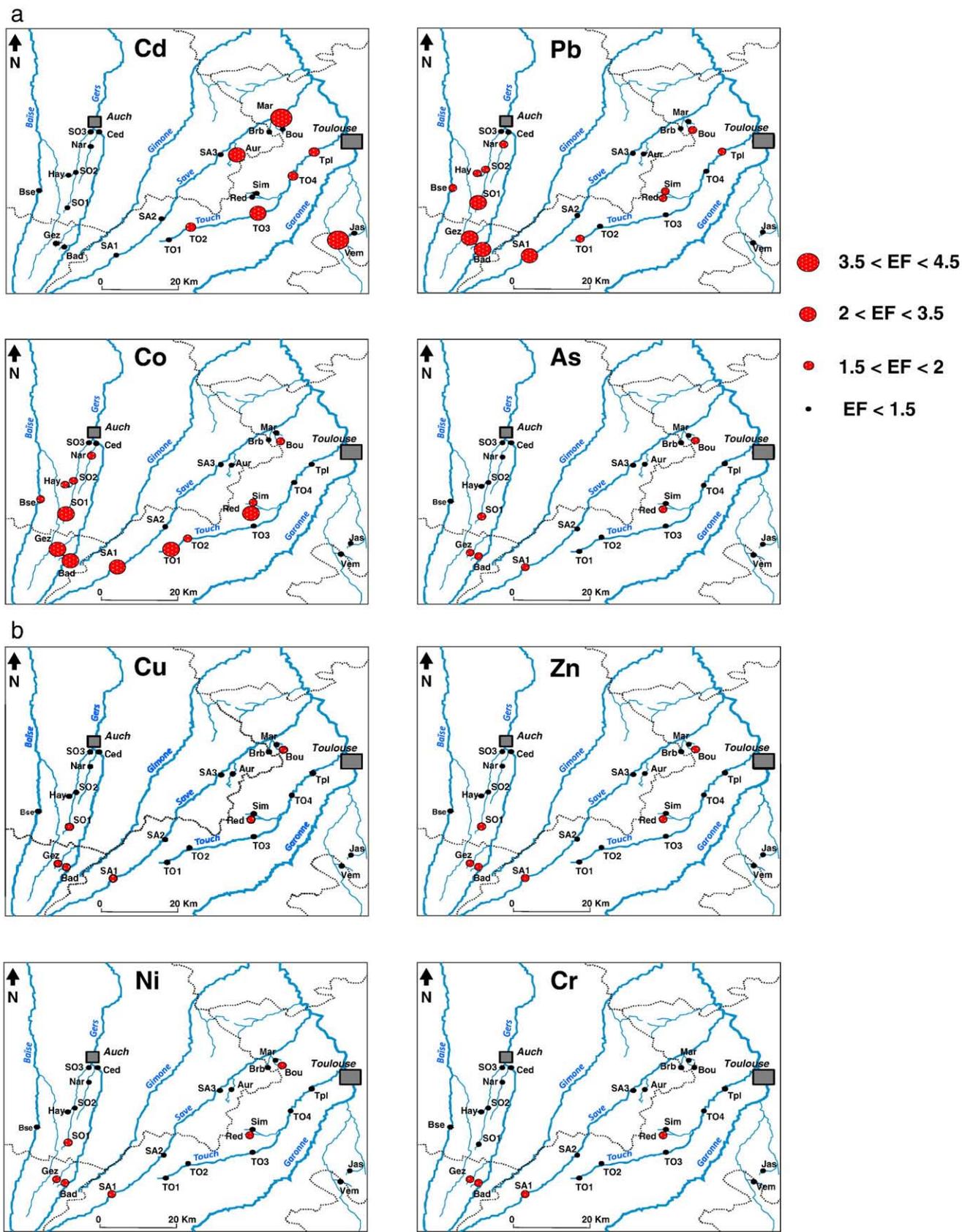
Fig. 7 – Spatial variation of PHE enrichment factors in the Gascogne stream bed sediments: (a) Cd, Pb, Co and As; (b) Cu, Zn, Ni, Cr. The size of the circles is proportionnal to EF range values.

Table 3 – Lead isotope ratios with precision values in the different stream bed sediments of the Gascogne catchments			
Stations	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{206}Pb$	$^{208}Pb/^{207}Pb$
SO2	1.176±0.008	2.127±0.031	2.482±0.036
SO3	1.186±0.021	2.121±0.003	2.476±0.004
SO1	1.173±0.014	2.140±0.011	2.484±0.015
T1	1.177±0.013	2.130±0.019	2.473±0.022
Bad	1.180±0.014	2.125±0.008	2.480±0.011
Mar	1.189±0.016	2.113±0.016	2.479±0.017
Ced	1.177±0.010	2.126±0.019	2.478±0.021
SA1	1.175±0.021	2.135±0.017	2.482±0.018
Gez	1.179±0.014	2.128±0.010	2.482±0.013
T3	1.190±0.015	2.107±0.024	2.480±0.029
Nar	1.176±0.009	2.131±0.018	2.479±0.022
T2	1.178±0.018	2.124±0.018	2.489±0.019
SA2	1.179±0.012	2.124±0.016	2.479±0.017
SA3	1.192±0.010	2.107±0.023	2.488±0.030
T4	1.183±0.010	2.116±0.022	2.484±0.027
Bou	1.184±0.020	2.126±0.014	2.482±0.017

(Vem, Mar and Aur). This observation lets suppose that Cd has an origin or a behavior different from the other PHEs in the Gascogne area. Cadmium is generally associated to carbonate minerals (Davis et al., 1987; Martin-Garin et al., 2002), whereas Co and Pb (for example) are controlled by iron and manganese oxides (Baize, 1997; Sterckeman et al., 2002). In addition, fertilizers are often identified as significant sources of cadmium contamination in agricultural areas (Avril, 1992; Micó et al., 2006), while Pb was mentioned to be partly of atmospheric origin in main river sediments (Elbaz-Poulichet et al., 1986).

According to the classification proposed by Sutherland (2000), EF indicates a moderate enrichment if ranging between 2 and 5, a significant enrichment between 5 and 20, a very high enrichment between 20 and 40 and an extreme enrichment >40. As a whole, we can observe that Gascogne stream bed sediments are slightly or moderately contaminated since EF are generally lower than 2.5 (77% of sampling stations). For Cd, Pb and Co, some stations (SA1, Gez, Mar and Vem, in particular) are however more contaminated with EF between 2.5 and 5 (23% of sampling stations).

The average anthropogenic contribution in the Gascogne stream bed sediments, calculated using Eq. (2) (except Cd see Section 4.2.2), indicates that PHE contamination is lower than 35%, but it depends on the PHE: Cd (34%), Co (24%), Pb (22%), Cu (14%), Zn (11%), Ni (10%), As (2%), Cr (2%). For Co, Pb and Cd, the anthopogenic contamination of Gascogne stream sediment is obvious, whereas the other PHEs mainly originate from natural weathering processes.

4.3. Origins of PHE enrichment in stream sediments

The main objective of this section is to relate EF spatial distribution observed previously with PHE origin using two different methods, particularly lead isotope measurements and a principal component analysis. The results will be discussed according to the potential anthropogenic sources in the study area.

4.3.1. Lead isotope ratios in the sediments

According to Gulson (1986), lead is composed of four isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb). Only ^{204}Pb is not radiogenic i.e. it does not result from desintegration of a radioactive isotope and thus its abundance did not evolve since bedrock formation. Conversely, the other three are produced continuously with time by desintegration of radioactive isotopes (^{238}U, ^{235}U and ^{232}Th, respectively).

Lead isotopic ratios in the environment depend both on age and U/Pb and Th/Pb ratios of the reservoir sources. The factors controlling isotopes fractionation (differences in atomic weight and in behavior) do not play a significant role in the case of lead (Keinonen, 1992). This characteristic gives on lead a capacity to trace various anthropogenic and natural sources (Chow et al., 1975; Elbaz-Poulichet et al., 1986; Monna et al., 1997; Liu et al., 2003; Roussiez et al., 2005).

The different lead isotopic ratios measured in stream sediment samples are summarized in Table 3. $^{206}Pb/^{207}Pb$, $^{208}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$, respectively comprise between 1.173±0.014 and 1.192±0.010, 2.473±0.022 and 2.489±0.019, 2.107±0.023 and 2.140±0.011. On Fig. 8a, we plotted $^{206}Pb/^{207}Pb$ vs $^{208}Pb/^{207}Pb$ for sediments and molasses samples, and for some anthropogenic sources and natural materials from the litterature: lead anthropogenic ratios of leaded gasolines (Monna et al., 1997), metallurgical industries (Véron et al., 1999), fertilizers (NPK, Bur et al., submitted for publication), and natural pre-industrial sediments (Elbaz-Poulichet et al., 1986). The Gascogne stream bed sediments are located close to molasses and pre-industrial sediments, and are distant from the isotopic values of gasoline (Monna et al., 1997). This result indicates a major contribution of geogenic lead and a lesser contribution from anthropogenic sources.

On Fig. 8b, we plotted $^{206}Pb/^{207}Pb$ as a function of 1/EF rather than 1/Pb as it is classically used in the litterature to determine the mixture of various sources of potential contamination (Hernandez, 2003; Roussiez et al., 2005). The authors generally used 1/Pb because anthropogenic contribution is often significant (more than 50%). When this contribution is low (<30%), we propose to use 1/EF since in such conditions, 1/EF is more sensitive to Pb variations. It comes out that $^{206}Pb/^{207}Pb$ is very well related to 1/EF ($r^2 = 0.82$, $n = 16$), showing that EF variations are controlled by one or a mixture of anthropogenic sources of which $^{206}Pb/^{207}Pb$ ratios are indicated on Y axis (Fig. 8b). We can use this graph to determine the anthropogenic contribution: when 1/EF tends to zero, the average $^{206}Pb/^{207}Pb$ equals 1.168. This value indicates that Pb contamination of the Gascogne stream sediments corresponds most probably to a mixing of industrial emissions (Monna et al., 1997; Véron et al., 1999) and of ancient gasolines (Chow et al., 1975) since fertilisers and recent gasoline are far from this intercept value. This result, representative of the Gascogne streams, is in agreement with the data (1.17) obtained for costal sediments supplied by French Mediterranean rivers into the Gulf of Lions (Roussiez et al., 2005). Thus, the anthropogenic lead found in the Gascogne stream sediments results as a whole from a regional non-point atmospheric influence rather than from a local point pollution of agricultural origin.

The percentage of anthropogenic contribution can be calculated from the isotopic ratio of the total sample and of
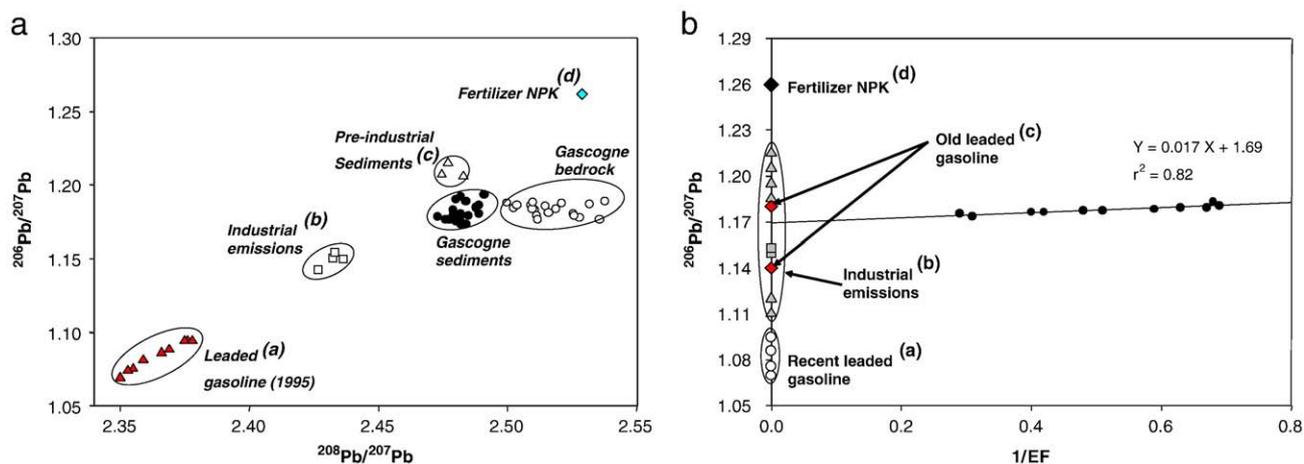
Fig. 8 – a. Diagramm $^{206}Pb/^{207}Pb$ vs $^{208}Pb/^{207}$ for Gascogne stream bed sediments and local bedrock samples (this study). Other anthropogenic and natural samples are from the litterature: [(a), (b)] **Monna et al. (1997);** [(c)] **Elbaz-Poulichet et al. (1986),** [(d)] **Bur et al. (submitted for publication). b.** Plot of $^{206}Pb/^{207}Pb$ ratios vs 1/EF for Gascogne stream bed sediments (this study), from leaded gasoline and incinerator ashes ((a) and (b), respectively, **Monna et al., 1997**), lead gasoline ((c) **Chow et al., 1975**), and Fertilizer ((d) **Bur et al., submitted for publication**).

different sources (1.184 for natural geochemical background *i.e.* molasse and 1.168 for average anthropogenic contribution) by the following equation:

$$Pb\,anthropic\,(\%) = \frac{\left[^{206}Pb/^{207}Pb\right]_{sample} - \left[^{206}Pb/^{207}Pb\right]_{natural}}{\left[^{206}Pb/^{207}Pb\right]_{anthropogenic} - \left[^{206}Pb/^{207}Pb\right]_{natural}} \times 100 \tag{3}$$

The average value calculated using Eq. (3) is 24%. This value is in the same range as the value (22%) calculated previously (see Section 4.3.3) using the geochemical method. Moreover, the ratio Pb/Cs (3.90) calculated using lithogenic Pb (estimated from the isotopic method) is pretty close to the ratio (3.74) calculated using the geochemical method. Consequently, the isotopic method can be used to determine Pb lithogenic background and Pb enrichment, even if there is no relationship between Pb and a normalizer element, like Cs.

4.3.2. Principal Component Analysis (PCA)

The principal component analysis was performed on the average values of the different samplings for each station. The input data were enrichment factors (EF) for PHE and major elements, except P for which we used the total concentration in the sediment. The inertia of the principal axes was expressed in % of variance. The results reported in Table 4 shows that, two components (Comp 1 and Comp 2) present eigenvalues >1 and represent 63.9 and 18.3% of the total explained variance, respectively. All variables can be mainly expressed by these two principal components (Fig. 9). Cr, Ni, Zn, Cu, Co, As, Al and Fe are well related to Comp 1 (loading >0.8). Whereas, Cd, Ca and P are associated to Comp 2 (loading >0.6). The high loading of Al and Fe with Comp 1, highlights the influence of clay minerals and iron oxides in the distribution of PHE in Gascogne stream bed sediments, except Cd which is more associated to carbonates (high correlation between Ca and Comp 2). Several studies (Davis et al., 1987;

Table 4 – Results of Principal Component Analysis (PCA): percentage of variance for each component (initial eigenvalues) and correlation coefficients (component matrix) of each element with component 1 and 2

Component	Initial eigenvalues			Component matrix		
	Total	Variance%	Cumulative variance (%)	Element	Comp 1	Comp 2
1	7.66	63.9	63.9	Cr	−0.94	0.21
2	2.19	18.3	82.2	Co	−0.86	−0.17
3	0.77	6.4	88.7	Ni	−0.87	0.32
4	0.51	4.3	92.9	Cu	−0.83	0.45
5	0.28	2.3	95.2	Zn	−0.9	0.33
6	0.22	1.8	97.1	As	−0.91	0.02
7	0.16	1.3	98.4	Cd	0.16	0.86
8	0.09	0.8	99.2	Pb	−0.83	−0.25
9	0.05	0.4	99.6	Al	−0.91	−0.28
10	0.03	0.3	99.8	Ca	0.22	0.62
11	0.01	0.1	99.9	Fe	−0.95	−0.04
12	0.01	0.1	100.00	P	0.32	0.7
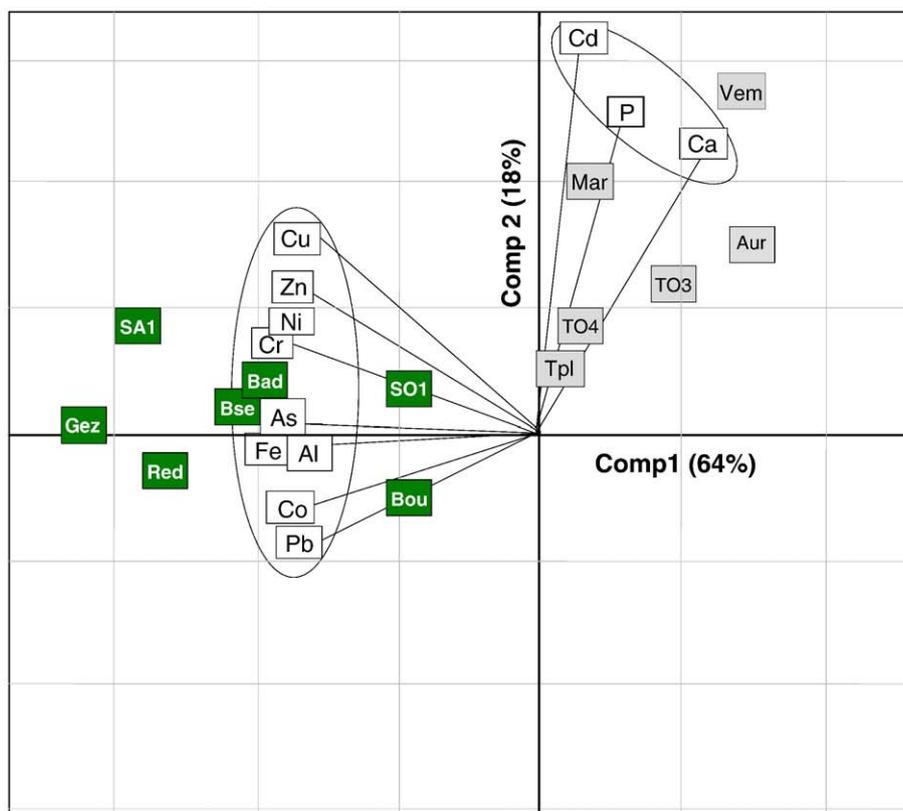
Fig. 9 – Loading plots (component 1 and 2) from a PCA of major and trace elements (white rectangle) compared to sampling stations (green and grey rectangles) of the Gascogne stream bed sediments. The variance percentage of each component is mentionned in Table 4.

Martin-Garin et al., 2002) observed the same association between Cd and carbonate minerals. According to these authors such an association indicates that Cd distribution is mainly controlled by the initial concentration in bedrock, but also by chemical precipitation of Cd with carbonates. Ca and Cd have a close ionic ray (0.100 Nm and 0.095 Nm, respectively) and Cd^{2+} tends to replace Ca^{2+} in carbonate minerals depending on pH (Pickering, 1983; Papadopoulos and Rowell, 1988).

Concerning the sampling stations, Fig. 9 shows that Comp 1 gathers the cluster of samples SA1, Gez, Bad, Red, SO1, Bou corresponding to catchments with forest areas. Whereas, Vem, Aur, Mar, TO3, representing cultivated catchments, are associated to Comp 2.

In Gascogne stream bed sediments, all PHE contents are mainly linked to molasse weathering, but two groups of elements can be distinguished according to anthropogenic sources:

(i) Pb, Cu, Zn, Co, As, Ni, Cr are enriched by contributions of atmospheric deposition from industrial emissions and gasoline combustion, particularly evidenced for Pb. Moreover, these elements are chiefly concerned with forested catchments because atmospheric deposition trapping is enhanced by canopees (Hernandez et al., 2003). Under the action of wind, exogenic Pb coming from automobile traffic and industry (urban incinerators, metallurgical industries or foundries) can be found in a, more or less, significant rating on a regional scale. The highest enrichment for Pb and Co in upper part of the river basins (see Fig. 7) can be related to local industrial sources such as ARKEMA (since 1917) and Pechiney (since 1937) at Lannemezan city, COGNIS France at Boussens, and Ciment Lafarge at Marthe Tolosane (close to Boussens), which are known to emit (or have emitted) these elements into the atmosphere.

(ii) Cd is enriched by fertilizer inputs and is associated to Phosphorus. Fertilizers are known to be significantly enriched in Cd associated to phosphates (Avril, 1992; Micó et al., 2006). Cd enrichment in Gascogne stream sediments mainly concerns agricultural catchments and downstream stations, except western and northern parts of the study area where molasse bedrock and stream bed sediments are not carbonated. The highest enrichment of Cd downstream the Save and Touch rivers and their tributaries can be related to fertilizer inputs to soils developed on carbonated molasse in these intensively cultivated basins.

5. Conclusions

The main results obtained in this study show that:

- The concentrations of the different PHE (Potential Harmfull Element) in sediments eroded from the soils of Gascogne

catchments and transported by the streams are relatively low in such a cultivated area and they present low seasonal variations. The order of abundance is as follows: Zn>Cr>Ni>Pb>Cu>Co>As>Sc>Cs>Cd.

- Nevertheless, an enrichment factor (EF) could be calculated by comparing these concentrations with those measured in a regional reference material (the molasse bedrock). We clearly show that this comparison is more accurate than to compare PHE concentrations in the Gascogne stream bed sediments with references classically used in the literature, such as PAAS or UCC. For the whole set of PHE (except for Cd for which a concentration ratio between sediment and molasse was used), the most appropriate normalizer element to calculate EF, was Cs because: (i) it is mainly located in the residual fraction of the sediments (98% of total); (ii) it is significantly correlated with PHE; (iii) it is not introduced by agricultural inputs.
- Enrichment was relatively low (<2.5) to moderate (<5) for all PHE. This indicates as a whole a rather low anthopogenic impact of PHE inputs from agriculture pratices to soils, of which stream sediments originate. However, Cd, Co and Pb, presented the highest EF values and are the most frequently enriched PHE.
- The EF spatial distribution indicates a higher enrichment for all PHE (except Cd) in sediments located in the upper parts of the streams, particularly where forest cover is more important. On the opposite, Cd is more enriched downstream of the rivers draining large cultivated and carbonated areas, indicating a different origin.
- PHE in the sediments are mostly from natural weathering origin, nevertheless the anthropogenic contribution is not negligeable. It is estimated to represent up to 34% of the total sediment. Cu, Pb, Zn, Co, As, Ni, Cr, are enriched by atmospheric deposition of industrial emissions and gasoline combustion, particularly Pb (as confirmed by lead isotopes), mainly in catchments with forest cover because atmospheric deposition is more significantly trapped by canopees. All these PHE are controlled by clay and oxi-hydroxides minerals (as shown by PCA).
- The Pb isotopic method allows us to estimated the average $^{206}Pb/^{207}Pb$ value for natural geochemical background (Miocène molassic deposits) and for average regional anthropogenic sources to 1.184 and 1.168, respectively. Pb anthropogenic contribution was estimated on average to 24%, which is consistent with the value obtained using the geochemical method (22%).
- Concerning Cd, the enrichment downstream of cultivated catchments and the link to Ca and P confirm its major origin from fertiliser inputs and its major control by carbonates.

Finally, as a whole, the main anthropogenic influence of agricultural pratices on stream sediments can be observed for Cd, whereas global and regional atmospheric pollution contributes to enrich other PHE such as Pb, particularly in the upper forested catchments. This confirms the results already obtained particularly for lead on French forest soils (Hernandez et al., 2003; Probst et al., 2003). Indeed, as a complementary approach the availability of these elements in the sediments would be important to evaluate the potential toxicity risks towards living organisms.

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