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Pb isotopes and Pb, Zn and Cd concentrations in the rivers feeding a coastal pond (Thau, southern France): constraints on the origin(s) and flux(es) of metals

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Abstract

The aim of this study was to identify the various sources and the behaviour of Pb, Zn and Cd in the watershed of the Thau pond (southern France), using Pb isotopes and Pb, Zn and Cd contents. The study was carried out at two different sites. The first (sub-watershed of the Vène river) presents a high density of potential sources of anthropogenic pollution (liquid urban wastes, road traffic, industries) coupled with a karstic-type water supply. The second (Pallas zone) is located in a mainly agricultural area distant from industrial activities. Several main sources of lead pollution are distinguished using the $^{206}Pb/^{207}Pb$ ratio: lead from gasoline (1.109–1.111), natural lead leached out of rocks and soils (1.198–1.200) and lead from treated or untreated urban wastes (1.147–1.162). The transfer of gasoline lead to the rivers occurs essentially during rainfall; in the Vène area, the urban anthropogenic lead component dominates while the 'rock-derived' lead is the main source in the rural area of the Pallas. Relationships existing between Pb concentrations, Pb/Zn ratios and $^{206}Pb/^{207}Pb$ ratios make it possible to determine the various transfer cycles of these different elements. Metal concentrations in water remain very low: Pb < 9 ppb ($\mu g/l$), Zn < 35 ppb and Cd < 0.4 ppb, much lower than the norms accepted for drinking water.

Keywords: Lead pollution; Zinc pollution; Cadmium pollution; Lead isotopes; Thau basin, southern France

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1. Introduction

Assessment of lead, zinc and cadmium contamination worldwide, of anthropogenic or natural origin, have been the subject of several studies during the last decade (Jaworowski et al., 1981; Patterson, 1983; Nriagu, 1988, 1989). These metals have been intensively used in industry especially in the northern hemisphere, but their global emission in the atmosphere has been decreasing since 1975 (Nriagu, 1988). This decrease has been observed in Greenland ice (Boutron et al., 1991), freshwaters from the Mississippi river (Trefry et

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al., 1985) and pond sediments (Thomas et al., 1984), and is related to the worldwide overall reduction in particulate emission by industries and anti-knock lead in gasoline. In spite of this recent improvement, the study of heavy metals remains a crucial problem, particularly in fragile ecosystems such as lagoons in urban or industrial areas.

The measurement of lead isotopic compositions coupled with the use of 'heavy' metals (Pb, Zn, etc.) can be a powerful tool to evaluate the effects of pollution and also to trace their origin(s) (Patterson, 1963), as lead retains the signature of the source from which it is derived. Lead consists of four isotopes, ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb, of which the first, ^{204}Pb, is the only one which is not radiogenic. The other isotopes (^{206}Pb, ^{207}Pb and ^{208}Pb) are produced by radioactive decay of ^{238}U, ^{235}U and ^{232}Th, respectively. Usually environmental scientists prefer to discuss ^{206}Pb/^{207}Pb ratio because its measurement presents the lowest analytical error. With this method, it is possible to identify various lead sources, provided they have a distinct isotopic 'signature', although some details may be obscured by not using ^{206}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios. Several earlier studies have already proved the effectiveness of this approach for seawater samples (Stukas and Wong, 1981), freshwater (Flegal et al., 1989; Erel et al., 1991), human tissues (Keinonen, 1992), atmosphere (Maring et al., 1987; Sturges and Barrie, 1987; Hamelin et al., 1989), sediment (Petit, 1974; Hamilton and Clifton, 1979; Shirahata et al., 1980; Hamelin et al., 1990).

The Thau basin, located along the Mediterranean Sea (Fig. 1), was chosen for this study because it presents many potential sources of pollution: industries (Sète harbour and neighbouring industries), agricultural area (e.g. fertilisers, Cu sulphate used in the treatment of vineyards), heavy road traffic, urban wastes (untreated sewage, output of water treatment plants) and an inherent natural component present in soils and rocks. Moreover, it is intensively used for the rearing of mussels and oysters in which heavy metals concentrate (Jensen and Bro-Rasmussen, 1992).

We have attempted to combine the use of Pb isotopes with metal concentrations to trace different sources of lead pollution (and possibly other metals) in the rivers feeding the Thau pond, to assess the level of pollution in Pb, Zn and Cd and to discuss the processes of their mobilisation.

2. Study site

The Thau basin is located at 43°20′ North and 3°35′ East (Fig. 1) and about 20 km south of Montpellier, Southern France. This lagoon is 19.5 km in length with a maximum width of 4.5 km. Its watershed covers 280 km^2. Several rivers feed the pond on its northern border, while a narrow offshore bar separates it from the Mediterranean Sea.

The Vène is the major stream feeding the basin, and is 12 km in length; its sub-watershed covers 70 km^2, representing 25% of the total watershed of the basin. It receives the output of three water treatment plants located near the villages of Montbazin, Gigean and Poussan (Fig. 1). The Vène runs mainly on a karstic surface and has a retention time of a few days. It may occasionally be fed by a karstic source, and also by a water catchment located in the Jurassic limestone (Issanka spring) which serves Sète for drinking water. Its flow rate, like most of the streams under a Mediterranean climate, depends heavily on rainfall, resulting in a very irregular discharge. Its hydrodynamic behaviour is influenced by both a strong slope (2%) and an irregular karstic feeding. Recently, the L.H.M.[1] has installed a gauging station equipped with a rectangular overflow near the Vène estuary (Station 1) in order to estimate the relationship between rainfall and discharge.

The Pallas has a sub-watershed of nearly 51 km^2, (representing 18% of the total watershed) formed by Cretaceous terrain and a small part of sealed Jurassic limestone; it has a retention time of several days (Tournoud et al., 1991). A water treatment plant, located at Villeveyrac village feeds it, but the output from the plant is lost

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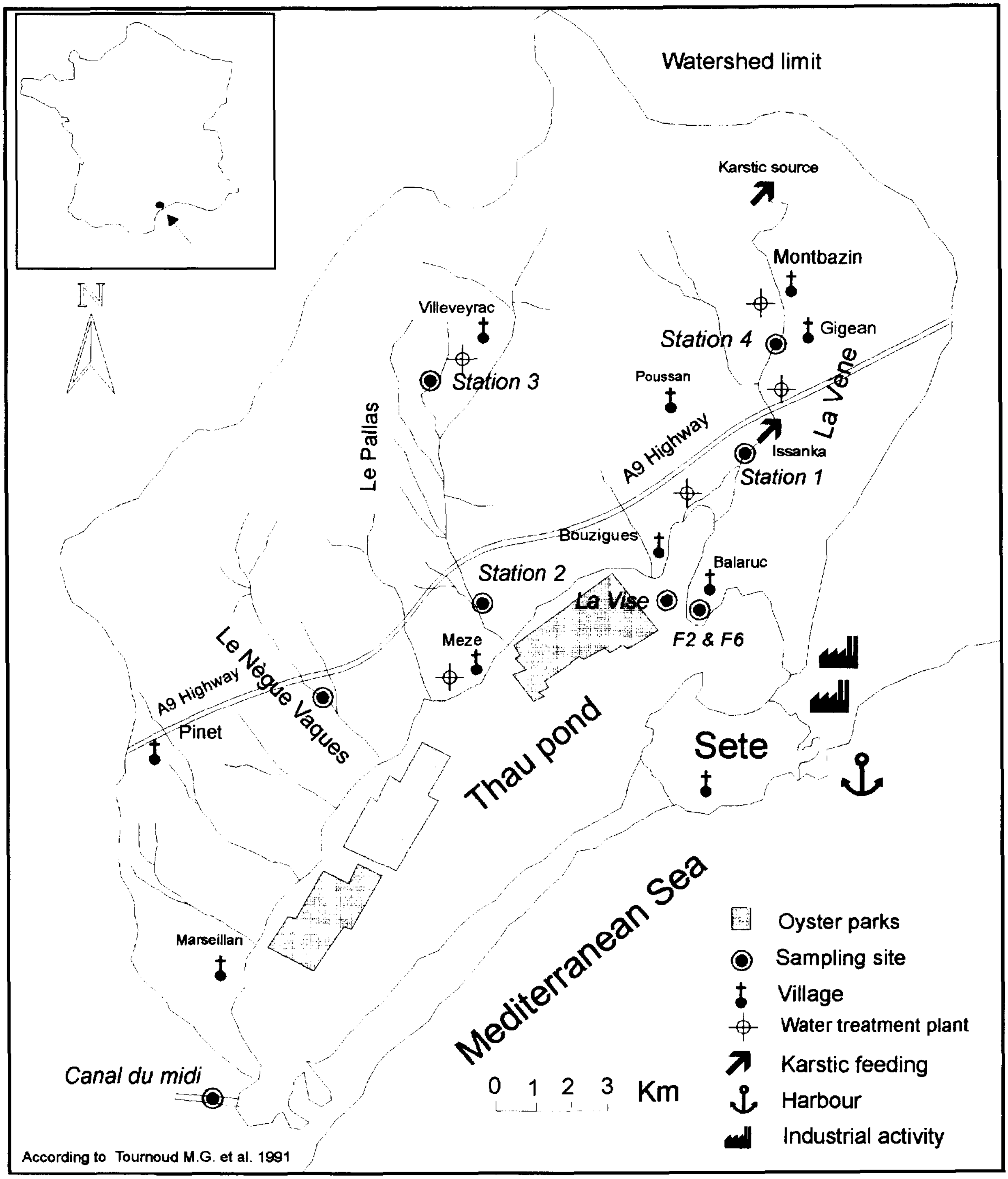

Fig. 1. The map of the Thau pond and its watershed.

before arriving at the pond (the Pallas is dry all year, except during strong rainfall).

The Languedoc is not a heavily industrialised region, but the Sète area presents a local network of industrial activities: cement plant, oil refinery, paper plant located mainly around the basin and harbour facilities. Most of the pollutant emissions are discharged directly into the basin or into the atmosphere, rather than into the rivers of the watershed. A previous study (Picot et al., 1987; Pena, 1989) showed high concentrations of heavy metals ($20.2 < \mathrm{Pb\ ppm} < 116.2$; $0.08 < \mathrm{Cd\ ppm} < 1.42$; $9.6 < \mathrm{Cu\ ppm} < 144.8$; $24.2 < \mathrm{Cr\ ppm} < 62.3$, Hg and Zn) in the superficial sediments deposited in the northern part of the pond, demonstrating the impact of industrial activities located around Sète. In addition, the watershed is crossed by a dense road complex especially on the north-east, near the Vène, and by the A9 highway, used by 37000 cars per day (annual average) with a significant increase during the summer (67000 cars per day in August). Along the highway several filtration tanks, filled with sand and vegetation, collect the rainwater which streams onto the road, before rejecting it into the rivers.

3. Sampling and analysis

Rainwater sampling was accomplished with a Teflon funnel at the University and near the Thau basin, far from human activity. River water and waste water samples were collected just beneath the surface in high density polyethylene bottles. Sampling from the Vène has been mainly targeted at station 1 (Fig. 1) because it is equipped with a rectangular overflow which allows measurement of the discharge. Bottles, washed in aqua-regia for 2 days then rinsed three times with ultra-pure deionised water (DIW) and soaked for 2 days in sub-distillation 5% HCl were rinsed again in DIW and soaked for a further 2 days in sub-distillation 5% HNO_3, then finally rinsed several times. Bottles were rinsed several times with the sample before filling. The samples (0.5 or 1 litre) were immediately acidified with 5 ml sub-distillation 15 N HNO_3 and kept at 4°C as quickly as possible. They were evaporated at 80°C until almost dry and the digestion of the residue was accomplished with a mixture of 6 N HCl, 6 N HF and 15 N HNO_3 in a Teflon beaker. Some water samples were filtered to separate particulate and dissolved phases using 0.45-μm acid-cleaned filters (Gelman Sciences). For freshwater samples, the chromatographic separation of Zn, Pb, and Cd was achieved on an anion exchange resin Bio-Rad AG1 X 4 using the appropriate eluting agents: 0.25 N HBr, 6 N HCl and 1 N HNO_3, respectively (Strelow, 1978; Savary et al., 1992). Lead separation and purification for isotopic composition measurement was made following the same method.

Concentrations were measured using isotopic dilution with three tracers enriched in ^{111}Cd, ^{66}Zn and ^{207}Pb, respectively (these spikes were regularly calibrated with a ^{208}Pb spike and with Cd and Zn standards). Lead isotopic ratios and Pb, Zn, Cd concentrations were determined on a VG SECTOR mass spectrometer, under computer control, loading on a single Re filament using the silica-gel/phosphoric acid method (Cameron et al., 1969). Results for isotopic compositions were corrected for mass fractionation by systematic NBS 981 measurements before each series of analyses, yielding a value of 1.2‰ per atomic mass unit. Blanks were measured for many sets of samples for correction. The results show that blanks are very acceptable compared to the amounts usually analysed (Table 1) for Pb and Zn

Table 1
Analytical blanks

Measurements	*n*	Blank (ng)	Poll%
Concentration measurements			
Zn	6	7.86	2.7
Cd	8	0.15	8.9
Pb	10	0.28	1.1
Filtering			
Zn	1	4.89	0.1
Cd	1	0.11	0.6
Pb	1	0.34	0.2
Isotope measurements (separation and purification)			
Pb	4	0.48	0.4

n, number of analysis; Blank, pollution in ng; Poll%, part of pollution under amount analysed (mean).

and to a lesser extent for Cd because of its low content (sometimes < 10 ppt).

This method (isotopic dilution and mass spectrometry) makes it possible to measure very low concentrations (< 0.01 ppb) with good precision ($< 5\%$) except for low Cd content (maximum error of 20%). Most of the isotopic compositions are measured with a precision better than 1‰ for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios and better than 0.6‰ for $^{206}Pb/^{207}Pb$ ratios.

4. Results and discussion

4.1. Characterisation of potential sources by their Pb isotopic composition and heavy metal content

Lead isotopic compositions (Table 2) and heavy metal contents (Table 3) were first measured at the outlet of the potential sources of pollution to study their respective contributions in the river waters. Isotopic data are reported in a $^{206}Pb/^{204}Pb$ versus $^{206}Pb/^{207}Pb$ diagram (Fig. 2) and define the three following fields: non-radiogenic lead from gasoline (1.109–1.111), radiogenic lead from rocks of the watersheds (1.198–1.200), and intermediate lead from treated and untreated urban wastes (1.147–1.161).

Lead from gasoline. Most of the anthropogenic Pb in the environment, originates from automotive exhausts and is added as an anti-knock agent in gasoline ($0.25\ g \cdot l^{-1}$ maximum in France). About 30% is retained by motor oil, and most of the remainder is deposited in a band 200 m wide, along roads and highways or is carried away in the atmosphere (Joumard et al., 1983). Other sources of metal pollution are also derived from wear and tear on the automobiles, such as Cd and Zn from tyre wear (Akhter and Madany, 1993).

The Pb isotopic composition of tetraethyl and tetramethyl lead additives depends directly on the geological source of the Pb ores used in its manufacture. This situation is often complicated by frequent changes in the origin of the supplies. Fortunately, in France, only one company, (Octel Co.), supplies the market for anti-knock lead additives. Today, nearly 90% of its lead comes from Australia, Canada, Morocco, and Zimbabwe (Hamelin et al., 1989). This lead must necessarily contain amounts of low Bi and the main sources are from the Mt. Isa and Broken Hill complexes (Australia) and British Columbia (Canada). They have low $^{206}Pb/^{207}Pb$ isotopic ratios (1.04–1.10) reflecting old deposits, while Mesozoic French ores possess higher signatures (close to 1.20).

Some data on French anti-knock lead are available. In 1966, $^{206}Pb/^{207}Pb$ measured in petrol from Paris was ~ 1.162 (Chow et al., 1975). A few years later, a grass sample from near a Parisian motorway yielded, for the same ratio, a value of 1.122 (Petit, 1974). In 1986, a study on aerosols from a parking site provided ratios ranging from 1.101 to 1.105 (Elbaz-Poulichet et al., 1986). Recently, Grousset et al. (submitted) noted a small decrease in this ratio (1.09) on filtered air samples in Lyon.

In this study, three 0.45-μm filters were used to extract the automotive exhausts during 24 h, in the centre of the city of Montpellier or near a car park. The $^{206}Pb/^{207}Pb$ values for these aerosols (1.109–1.111) are homogeneous for all three different sites studied in Montpellier and are similar to those found by Elbaz-Poulichet et al. (1986) in Paris and Grousset et al. (submitted) in Lyon.

Dust removed from a filter at the University of Montpellier provided a $^{206}Pb/^{207}Pb$ ratio (1.139) higher than the tetraethyl lead value found above. The same type of shift was observed by Elbaz-Poulichet et al. (1986) between suburban aerosol in Paris and dust extracted in the laboratory. Besides a recent change in isotopic composition as proposed by these authors, this difference could also reflect a natural lead contribution from soils which would increase the $^{206}Pb/^{207}Pb$ ratio. Indeed, as noted below, local natural source of lead is characterised by more radiogenic values.

Lead from rocks of the watershed. This has radiogenic $^{206}Pb/^{207}Pb$ values of 1.200 (Miocene siltstones) and 1.198 (Jurassic limestones). It is the more radiogenic end-member and despite the limited number of samples, we can assume that it somewhat reflects the natural lead signature within the Thau pond environment. It also falls in the field of pre-industrial sediment discharged by the major French rivers, as defined by Elbaz-Poulichet et al. (1986) of 1.197–1.206.

Table 2
Lead isotope ratios

Samples	Date	$^{206}\text{Pb}/^{204}\text{Pb}$	2σ	$^{207}\text{Pb}/^{204}\text{Pb}$	2σ	$^{208}\text{Pb}/^{204}\text{Pb}$	2σ	$^{206}\text{Pb}/^{207}\text{Pb}$	2σ
Water treatment plants									
Montbazin	22 Sept 1992	18.113	0.007	15.646	0.008	38.207	0.021	1.1600	0.0001
Duplic. Mtb.	22 Sept 1992	18.093	0.026	15.629	0.022	38.184	0.059	1.1609	0.0002
Montbazin	24 Jan 1993	18.174	0.014	15.706	0.013	38.315	0.033	1.1600	0.0001
F Montbazin	12 May 1993	18.140	0.021	15.661	0.020	38.176	0.049	1.1613	0.0001
Poussan	23 Mar 1992	18.027	0.010	15.611	0.010	38.025	0.028	1.1547	0.0001
F Poussan	12 May 1993	18.071	0.005	15.635	0.005	38.146	0.016	1.1585	0.0001
Villeveyrac/in tank	22 Sept 1992	17.860	0.011	15.587	0.011	37.822	0.028	1.1476	0.0001
Duplic. Villev./in tank	22 Sept 1992	17.906	0.023	15.577	0.020	37.904	0.051	1.1494	0.0003
Villeveyrac/output	22 Sept 1992	17.808	0.012	15.543	0.011	37.618	0.028	1.1479	0.0001
F Villeveyrac	12 May 1993	18.027	0.005	15.606	0.005	38.023	0.014	1.1578	0.0001
F Gigean	12 May 1993	18.038	0.006	15.620	0.006	38.011	0.016	1.1577	0.0001
Untreated urban outputs									
Montbazin	24 Mar 1992	17.871	0.021	15.585	0.017	37.743	0.043	1.1468	0.0001
Montbazin	22 Sept 1992	17.896	0.006	15.580	0.006	37.813	0.016	1.1505	0.0001
Montbazin	12 May 1993	18.078	0.006	15.597	0.006	38.067	0.016	1.1623	0.0001
Highway filtration tanks									
Output	24 Mar 1992	17.457	0.010	15.524	0.009	37.200	0.022	1.1249	0.0001
Input	22 Sept 1992	17.590	0.004	15.600	0.004	37.498	0.013	1.1298	0.0001
Output	9 Feb 1993	17.693	0.009	15.586	0.009	37.556	0.023	1.1379	0.0001
Dust									
USTL Laboratory	Dec 1992	17.739	0.018	15.610	0.016	37.678	0.041	1.1392	0.0002
Centre of Montp. St 1	3 Sept 1987	17.385	0.044	15.663	0.039	37.471	0.101	1.1093	0.0004
Centre of Montp. St 1	2 Sept 1987	17.270	0.003	15.556	0.004	37.172	0.011	1.1102	0.0001
Centre of Montp. St 3	3 Sept 1987	17.332	0.029	15.603	0.027	37.306	0.064	1.1108	0.0003
Rainwater									
Montpellier 22:00–00:00 h	2–3 Dec 1992	17.925	0.006	15.625	0.007	37.947	0.024	1.1495	0.0002
Montpellier 14:00–17:00 h	8 Feb 1993	17.992	0.007	15.653	0.019	38.047	0.019	1.1525	0.0001
Montpellier 17:00–20:00 h	8 Feb 1993	18.248	0.004	15.627	0.004	38.303	0.012	1.1708	0.0001
Montpellier 20:00–00:00 h	8 Feb 1993	18.266	0.005	15.683	0.006	38.445	0.018	1.1680	0.0001
Duplic. Mtp. 20:00–00:00 h	8 Feb 1993	18.200	0.007	15.645	0.007	38.274	0.019	1.1663	0.0001
Balaruc 17:00 h	9 Feb 1993	18.069	0.006	15.622	0.006	37.999	0.015	1.1596	0.0001
Vène									
Station 1/ 1	9 Nov 1991	18.457	0.032	15.707	0.030	38.443	0.076	1.1750	0.0001
2	15 Jan 1992	18.084	0.022	15.658	0.022	38.046	0.057	1.1542	0.0001
Duplic. 2	15 Jan 1992	18.033	0.005	15.587	0.006	37.914	0.017	1.1592	0.0002
4	4 Feb 1992	18.281	0.060	15.647	0.051	38.199	0.129	1.1678	0.0001
5	20 Feb 1992	17.664	0.022	15.604	0.020	37.662	0.060	1.1324	0.0001
6	25 Feb 1992	17.793	0.010	15.653	0.010	37.867	0.029	1.1364	0.0002
8	24 Mar 1992	17.896	0.042	15.639	0.038	37.788	0.097	1.1436	0.0002
9	25 May 1992	17.726	0.007	15.575	0.006	37.543	0.015	1.1374	0.0002
10	22 Sept 1992	17.886	0.010	15.609	0.009	38.834	0.025	1.1478	0.0002
11	18 Oct 1992	17.970	0.013	15.568	0.013	37.852	0.033	1.1566	0.0002
12	26 Oct 1992	18.136	0.045	15.668	0.040	38.191	0.098	1.1599	0.0004
13	30 Oct 1992	18.116	0.014	15.573	0.013	38.057	0.031	1.1656	0.0002
14	1 Nov 1992	17.960	0.029	15.611	0.025	37.950	0.067	1.1523	0.0004
15	15 Nov 1992	17.991	0.020	15.530	0.018	37.815	0.047	1.1615	0.0003
16	30 Nov 1992	17.968	0.014	15.593	0.013	37.876	0.036	1.1552	0.0002
17	6 Dec 1992	18.180	0.018	15.638	0.017	38.221	0.047	1.1654	0.0003
18	13 Dec 1992	18.263	0.016	15.682	0.015	38.345	0.039	1.1676	0.0002
19	19 Dec 1992	17.898	0.014	15.590	0.013	37.804	0.033	1.1512	0.0002
20	3 Jan 1993	18.080	0.020	15.658	0.016	38.119	0.042	1.1580	0.0003

Table 2 (*continued*)

Samples	Date	$^{206}Pb/^{204}Pb$	2σ	$^{207}Pb/^{204}Pb$	2σ	$^{208}Pb/^{204}Pb$	2σ	$^{206}Pb/^{207}Pb$	2σ
21	17 Jan 1993	18.119	0.008	15.612	0.008	38.121	0.024	1.1634	0.0002
22	7 Feb 1993	18.105	0.009	15.631	0.009	38.210	0.030	1.1602	0.0001
23	9 Feb 1993	17.813	0.007	15.612	0.007	37.822	0.020	1.1441	0.0001
24	10 Feb 1993	17.932	0.010	15.646	0.010	38.032	0.025	1.1494	0.0002
25	9 May 1993	18.262	0.022	15.698	0.019	38.332	0.048	1.1660	0.0002
F 25	9 May 1993	18.130	0.008	15.597	0.008	38.062	0.021	1.1652	0.0001
26	12 May 1993	18.055	0.008	15.596	0.009	37.975	0.022	1.1612	0.0001
Duplic. 26	12 May 1993	18.079	0.013	15.615	0.012	38.058	0.030	1.1611	0.0001
Pallas									
Station 2/1	15 Jan 1991	18.070	0.024	15.685	0.022	38.224	0.059	1.1521	0.0002
Duplic. 1	15 Jan 1991	17.956	0.007	15.598	0.007	37.918	0.019	1.1535	0.0001
2	20 Feb 1991	18.130	0.057	15.640	0.050	38.015	0.125	1.1588	0.0001
3	24 Mar 1992	18.153	0.020	15.723	0.019	38.443	0.076	1.1751	0.0001
4	9 Feb 1993	18.363	0.004	15.679	0.004	38.464	0.014	1.1744	0.0001
Duplic. 4	9 Feb 1993	18.345	0.007	15.647	0.007	38.404	0.019	1.1747	0.0001
5	10 Feb 1993	18.288	0.019	15.634	0.017	38.285	0.045	1.1730	0.0002
F 6	12 May 1993	18.271	0.0061	15.616	0.006	38.202	0.017	1.1728	0.0001
Other specific places									
Canal du midi	9 Nov 1991	18.346	0.005	15.622	0.005	38.294	0.013	1.1737	0.0008
Duplic. Canal du midi	9 Nov 1991	18.387	0.013	15.658	0.012	38.453	0.031	1.1743	0.0001
F6 water catchment	24 Jan 1992	18.071	0.033	15.712	0.030	38.098	0.078	1.1494	0.0001
Negue Vaques	9 Nov 1991	18.125	0.014	15.706	0.013	38.249	0.037	1.1534	0.0001
Rocks and soils									
Jurassic limestone		19.094	0.024	—	—	—	—	1.1984	0.0028
Miocene		18.743	0.002	15.657	0.008	38.785	0.021	1.2002	0.0001

F, Filter analysis; the isotopic ratios were measured by VG Sector mass spectrometer using multicollection and were corrected from mass discrimination (1.2‰ ± 0.2) using numerous NBS 981 measurements.

Lead from urban areas. This is composed of both the untreated output from the villages, discharged directly into the rivers (in the present study, the Vène) and the sewage from water treatment plants.

The Vène river flows through Montbazin village (Fig. 1), but it is usually dry above this village, hence, we can assume that the water sampled at the exit of the village, before the output of the water treatment plant, reflects the untreated urban contribution. Lead contents and isotopic compositions are very irregular. $^{206}Pb/^{207}Pb$ ratios range from 1.146 to 1.162 while lead concentrations range from 1.28 to 27.5 ppb, which indicates several sources. However, higher values correspond to the more anthropogenic signature, that is to say the lower ratio.

Treated water is characterised by low heavy metal contents: $Pb < 1$ ppb, $Zn < 15$ ppb and $Cd < 60$ ppt in total, except for the Poussan station where Pb content is close to 2 ppb. Nearly 70% of the measured elements are trapped between the input and the output of the water treatment plant (compare with Villeveyrac, 22 Sept 1993). The $^{206}Pb/^{207}Pb$ values range from 1.147 to 1.161 similar to urban values, but each station has individually a rather constant ratio through time. This constancy is probably due to the importance of the residence time (more than 2 months) in the treatment basins which is responsible for an 'averaging effect'. Lead isotopic values reflect a mixing between several end-members: industrial lead entering in the composition of domestic products, and to a lesser degree, the rain and the dust deposited directly in the basins. These ratios plot in the domain of lead used in

Table 3
Heavy metal concentrations in ppb

Samples/ (label)	Date	Pb	2σ	Zn	2σ	Cd	2σ	Pb/Zn	Q (l/s) ±20%
Water treatment plants									
Montbazin	22 Sept 1992	0.67	0.05	3.43	0.07	—	—	0.195	≈ 2–3
Montbazin	24 Jan 1993	0.74	0.02	7.01	0.18	0.056	0.004	0.106	≈ 2–3
Montbazin	12 May 1993	0.29	0.01	4.20	0.16	0.011	0.001	0.070	≈ 2–3
Poussan	12 May 1993	1.83	0.05	11.02	0.25	0.058	0.001	0.166	≈ 2–3
Gigean	12 May 1993	0.79	0.02	4.26	0.09	0.023	0.001	0.185	≈ 2–3
Villeveyrac/in tank	22 Sept 1992	1.91	0.04	23.09	0.73	—	—	0.083	≈ 2–3
Villeveyrac/output	22 Sept 1992	0.57	0.02	7.84	0.18	—	—	0.073	≈ 2–3
Dupl. Vill./output	22 Sept 1992	0.52	0.02	7.22	0.19	—	—	0.072	≈ 2–3
Villeveyrac	12 May 1993	0.92	0.03	13.75	0.31	—	—	0.067	≈ 2–3
Untreated	**urban outputs**								
Montbazin	20 Feb 1992	1.46	0.01	10.10	0.11	0.054	0.002	0.145	< 1
Montbazin	24 Mar 1992	27.50	0.20	87.57	2.25	—	—	0.314	< 1
Montbazin	22 Sept 1992	15.07	0.35	64.78	3.52	0.303	0.014	0.233	< 1
Montbazin	12 May 1993	1.28	0.04	8.66	0.19	—	—	0.148	< 1
Highway filtation tanks									
Output	24 Mar 1992	2.24	0.02	9.17	0.14	0.057	0.002	0.244	—
Stagnant	22 Sept 1992	22.9	1.8	362	24	0.518	0.052	0.063	—
Duplic. stagnant	22 Sept 1993	23.4	1.2	352	10	0.506	0.012	0.067	—
Output	9 Feb 1993	2.04	0.21	6.30	0.24	—	—	0.324	—
Rainwater									
Montpellier	2–3 Dec 1992	21.26	0.73	39.7	1.1	0.555	0.015	0.535	—
Dupl. Montpellier	2–3 Dec 1992	23.55	1.19	39.5	5.3	0.612	0.024	0.596	—
Montpellier 20:00 h	8 Feb 1993	39.56	1.41	36.8	1.2	0.222	0.016	1.073	—
Balaruc 17:00 h	9 Feb 1993	9.77	0.34	21.65	0.87	0.205	0.018	0.451	—
Vène									
Station 1/ 1	9 Nov 1991	0.41	0.01	24.19	0.34	0.082	0.004	0.017	20
2	15 Jan 1992	1.31	0.18	11.21	0.17	0.048	0.002	0.117	5
3	24 Jan 1992	1.56	0.06	8.06	0.12	0.232	0.008	0.193	21
4	4 Feb 1992	0.84	0.06	4.41	0.07	0.332	0.006	0.191	7
5	20 Feb 1992	0.93	0.01	3.69	0.04	0.059	0.002	0.252	4
6	25 Feb 1992	2.16	0.02	5.26	0.6	0.051	0.002	0.410	40
7	23 Mar 1992	0.13	0.01	0.75	0.01	—	—	0.169	22
8	24 Mar 1992	—	—	0.77	0.01	0.022	0.002	—	26
9	25 May 1992	0.66	0.01	2.74	0.05	0.030	0.002	0.242	6
10	22 Sept 1992	0.59	0.02	1.85	0.05	0.048	0.004	0.317	21
Duplic. 10	22 Sept 1992	0.57	0.02	1.74	0.05	0.079	0.002	0.327	21
11	18 Oct 1992	0.43	0.02	1.49	0.03	0.011	0.002	0.291	7
12	26 Oct 1992	0.38	0.02	1.45	0.03	—	—	0.264	16
Duplic. 12	26 Oct 1992	0.36	0.01	1.52	0.06	—	—	0.237	16
13	30 Oct 1992	0.21	0.01	0.55	0.02	—	—	0.385	6
14	1 Nov 1992	0.61	0.03	2.50	0.06	—	—	0.245	10
15	15 Nov 1992	0.18	0.01	0.83	0.04	0.007	0.002	0.221	7
Duplic. 15	15 Nov 1992	0.21	0.02	—	—	0.005	0.002	—	7
16	30 Nov 1992	0.35	0.01	1.06	0.03	0.006	0.002	0.331	7
17	6 Dec 1992	0.25	0.01	2.00	0.05	0.006	0.002	0.125	8
18	13 Dec 1992	0.32	0.01	1.28	0.04	0.008	0.002	0.251	6
19	19 Dec 1992	0.49	0.02	1.93	0.08	0.013	0.002	0.254	8
20	3 Jan 1993	0.34	0.01	1.98	0.05	0.012	0.002	0.172	9
21	17 Jan 1993	0.33	0.01	2.08	0.06	0.026	0.002	0.159	7
22	7 Feb 1993	0.27	0.01	1.33	0.03	0.011	0.002	0.199	7
23	9 Feb 1993	5.52	0.13	13.78	0.32	0.055	0.004	0.401	28

Table 3 (*continued*)

Samples/ (label)	Date	Pb	2σ	Zn	2σ	Cd	2σ	Pb/Zn	Q (l/s) ±20%
Duplic. 23	9 Feb 1993	5.49	0.17	13.48	0.39	—	—	0.407	28
24	10 Feb 1993	1.84	0.05	6.62	0.16	0.032	0.002	0.278	11
25	9 May 1993	0.16	0.01	1.49	0.04	0.024	0.001	0.107	100
Duplic. 25	9 May 1993	0.16	0.01	—	—	—	—	—	100
26	12 May 1993	0.26	0.01	2.24	0.06	0.019	0.001	0.117	60
Station 3/ 1	20 Feb 1992	0.93	0.01	6.96	0.07	0.028	0.005	0.134	—
2	24 Mar 1992	0.76	0.02	6.39	0.10	0.030	0.002	0.119	—
Pallas									
Station 2/ 1	15 Jan 1991	2.07	0.2	28.2	0.4	—	—	0.073	—
2	20 Feb 1991	0.44	0.01	3.76	0.04	0.083	0.002	0.117	—
3	24 Mar 1992	0.56	0.01	3.57	0.08	0.041	0.002	0.157	—
4	9 Feb 1993	8.76	0.22	34.9	1.5	0.084	0.006	0.251	—
5	10 Feb 1993	0.43	0.02	3.36	0.08	0.013	0.002	0.128	—
6	12 May 1993	0.43	0.02	2.42	0.06	0.014	0.001	0.178	—
Other specific places									
Canal du midi	9 Nov 1991	1.36	0.04	3.88	0.07	0.028	0.002	0.351	—
F6 water catchment	24 Jan 1992	0.35	0.01	10.1	0.2	0.143	0.004	0.035	—
F2 water catchment	24 Jan 1992	1.41	0.03	43.7	1.1	—	—	0.033	—
La Vise	24 Jan 1992	0.04	0.01	1.34	0.02	—	—	0.030	—
Negue Vaques	9 Nov 1991	0.58	0.01	4.03	0.04	0.004	0.004	0.144	—
Rocks[a]									
Upper Jurassic	#1	0.81	0.03	7.95	0.22	0.261	0.009	0.102	—
Upper Jurassic	#2	0.31	0.02	4.07	0.11	—	—	0.075	—

[a] Concentrations in ppm.

industry ($1.130 < {}^{206}Pb/{}^{207}Pb < 1.170$, Elbaz-Poulichet et al., 1984, 1986) which reflects a wider range of origin of ores than in the case of anti-knock lead.

The other sources are thought to derive mainly from the previous end-members already identified.

Rainwater. We observed that total metal concentrations in rain collected before it reaches the ground are similar to those found by other authors (Table 4). ${}^{206}Pb/{}^{207}Pb$ ratios in rainwater present a wide range of values from 1.149 to 1.170. We followed the evolution of Pb isotopic composition during a single rainfall at Montpellier on 8 February 1993. At the beginning, the ${}^{206}Pb/{}^{207}Pb$ ratio was 1.152, then it stabilised around 1.170 after 3 h, until the end of the rainy episode. We consider that a large part of the local aerosols is scavenged at the beginning of the rain event and is responsible for the low lead isotopic ratios, or that the small anthropogenic particles are first affected by the nucleation (B. Dupré, personal communication). After a few hours, the Pb isotopic composition of rainwater may reflect the 'true' composition of the particles remaining in the clouds.

Leachate of roads. To describe the remobilisation of dry automotive deposition by rainwater on the tarred roads, we targeted the sampling at the output of a rainwater collector along the highway. This allowed us to assess the impact of the car traffic on the Vène and to avoid external contamination such as the weathering of the soil since the water exclusively flows on the asphalt. We observed (Table 3) that after streaming on the highways and flowing through filtration tanks, the lead concentration decreases considerably (2.04 ppb for 9 February 1993) compared to rainwater before it reaches the ground (9.8 ppb for the same day). An important part must be taken up on sand and vegetation in filtration tanks along the highway proving its efficiency.

Table 4
Intercomparison of wet precipitation concentration (μg/l)

	Pb	Zn	Cd
Rural region			
Yerseke NDL[a]	7.95–12.9	8.88–20.0	0.14–0.37
FRG[a]	4.27–14.1	6.93–33.4	0.10–0.30
Mean of Camargue	Particulate		Particulate
Tour du Valat[b]	0.06–20.9		0.01–0.50
	Dissolved		Dissolved
	0.1–15.9		0.02–2.03
This study (total)	9.77	21.65	0.21
Urban region			
FRG[a]	14.3–47.0	16.6–264	0.24–0.92
This study (total)	21.3–39.6	36.9–39.7	0.22–0.55
Average for southern France[c]	16		

[a] Nguyen et al. (1990).
[b] Guieu et al. (1990).
[c] Servant and Delapart (1979).

Measured ^{206}Pb/^{207}Pb ratios (1.125–1.137) are higher than those of the additive lead found on aerosols in Montpellier, but it is not surprising if we consider that our samples correspond to a mixing between lead from automotive exhaust and a more radiogenic lead brought by rainwater.

4.2. *Transfer in the rivers*

Now that we have characterised isotopically the several possible sources of pollution, we now examine their interaction with the surficial water, in the two cases of the Vène and the Pallas streams.

The Vène case. Our water data from the Vène river (labelled points) are illustrated in two diagrams, along with data from leach of highway, rainwater, water plants and untreated urban feeding (stippled domains). The first diagram (Fig. 3) represents Pb concentration versus ^{206}Pb/^{207}Pb ratios, whereas the second one (Fig. 4) integrates Zn data, plotting the Pb/Zn ratio versus ^{206}Pb/^{207}Pb. The use of the Pb/Zn ratio makes it possible to compare two different waters avoiding the variations in concentration linked to the discharge. The temporal variations of this parameter indicate that Pb and Zn are not mobilised in the same proportions during all events. Metal concentrations are summarised in Table 4. In Figs. 3 and 4, four domains, representing four different hydrodynamic episodes, are distinguished.

Domain A: dry periods. This field represents water sampled several days after the last rainfall in the absence of karstic feeding. It is quite small and presents low Pb and Zn contents, < 0.5 ppb and 3 ppb, respectively. ^{206}Pb/^{207}Pb ratios range from 1.155 to 1.167. There are two potential contributions, treated and untreated urban sewage, but the impact of this last one is very weak due to its low discharge when compared to the somewhat constant flux from water treatment plants. Most samples are located close to the domain defined by the water treatment plants of Montbazin and Gigean (0.29–0.79 ppb and ^{206}Pb/^{207}Pb near 1.160). However, one point (no. 5) possesses a ^{206}Pb/^{207}Pb ratio, which is much too low to be interpreted as a water treatment plant output alone and up to now remains unexplained.

It is also possible to estimate the pollutant impact of these two plants on the pond, measuring metal flux at station 1 assuming the other sources are negligible. We obtain a discharge around 8 l/s and a metal flux of Pb = 2.9 ± 1.6 μg/s (n = 13), Zn = 13.0 ± 7.8 μg/s (n = 13) and Cd = 0.08 ± 0.04 μg/s (n = 9) eliminating one value of Cd flux which seems erroneous (2.32 μg/s).

Domain B: during the rainfall. A strong content in lead (> 2 ppb), high Pb/Zn ratio (0.40–0.41) and rather low lead isotopic values ranging from

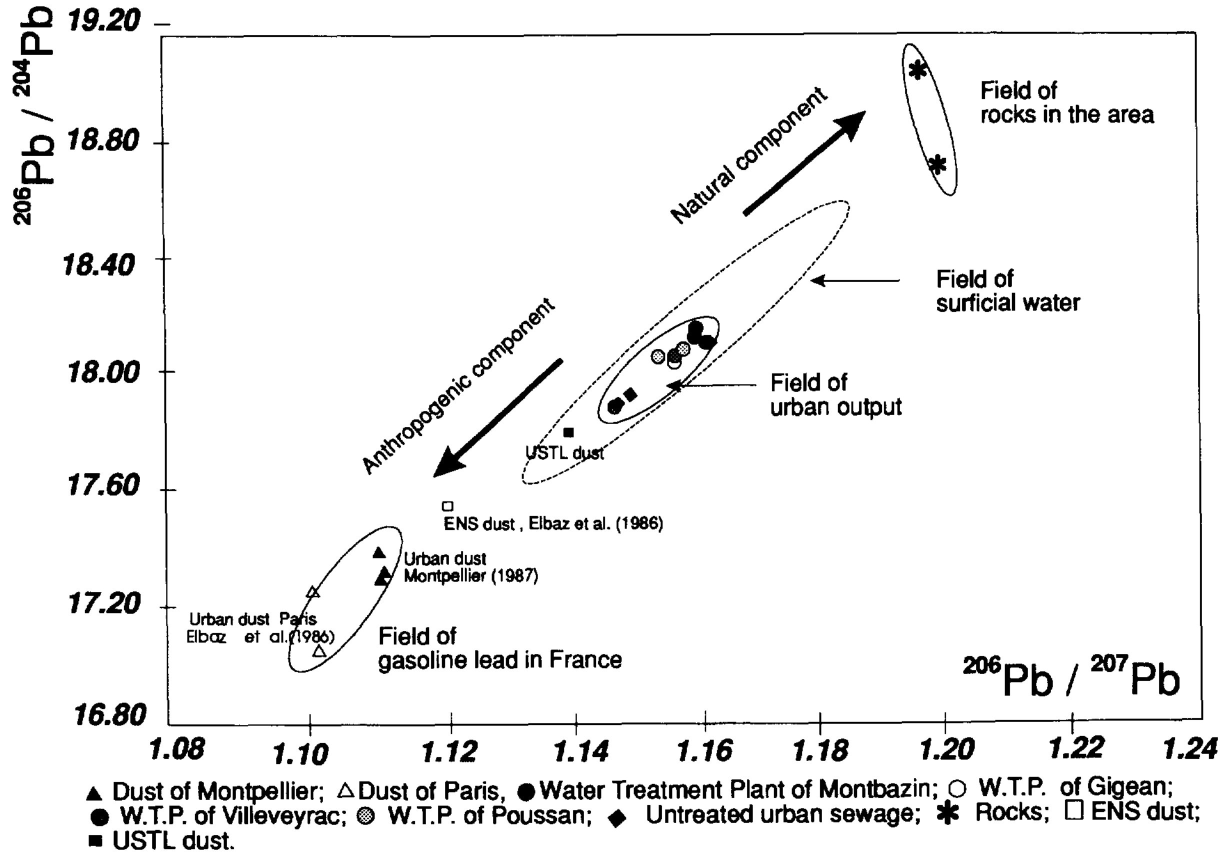

Fig. 2. Lead isotopic compositions.

1.136 to 1.144 were measured. These values can result from the leachate of paved surfaces, to the weathering of soils and rocks or to a contribution purely contained in the rainwater. It is very difficult to quantify each source, yet, the water from Vène shows a ^{206}Pb/^{207}Pb ratio having an anthropogenic signature; the natural Pb is not dominant. To explain the Pb content in the Vène water being lower than in the rainwater, we can invoke a strong trapping by the soil according to Servant and Delapart (1979), who estimated that 87% of lead is fixed by the superficial layer of the soil.

Domain C: during the drop in the level. For samples taken during the drop in level, 1 or 2 days after the end of rainfall, Pb concentrations decrease ranging from 1.84 to 0.49 while the ^{206}Pb/^{207}Pb ratio increases, ranging from 1.137 to 1.154. During this stage, the discharge declines and the contribution from water treatment plants becomes more important. Points shift significantly to a lower Pb content field with higher lead isotope compositions.

These three stages (A, B, C) have been followed during a single rainfall event over 4 days. The arrow between the points 22 (7 February 1993) and 23 (9 February 1993) illustrates the evolution during the rainy event while the arrow between the points 23 and 24 (a day after the rainfall) represents the drop in the level.

Domain D: karstic contribution. Some days after the rainy event, if only the water from treatment plants fed the river then samples are located in the domain A (see below), but sometimes this process can be modified by a karstic contribution. In this last case, the waters originate either from the natural spring of the Vène, or from karstic water pumped out at Issanka, of which a part is

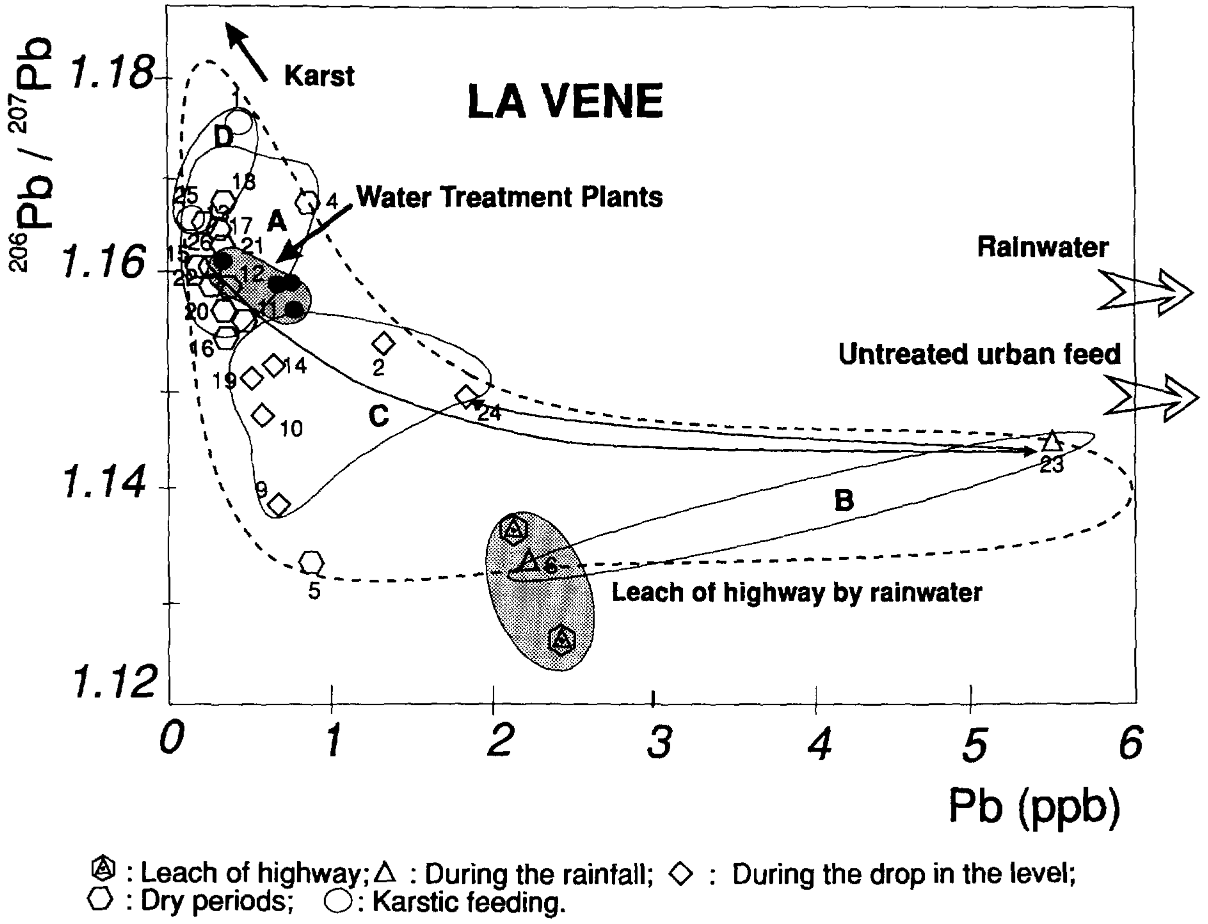

Fig. 3. Pb concentration versus ^{206}Pb/^{207}Pb.

released into the river at the beginning of a pumping period.

They contain a very low lead content (0.10–0.41 ppb) and high lead ratios (1.166–1.174) reflecting a natural contribution. Pb/Zn ratios range from 0.017 to 0.08. Similar values are found at the karstic springs of the Vise (0.029), at F2 water catchment (0.032) and in whole rock of Jurassic limestone (0.075–0.101). Nevertheless, in the case of F6 water catchment, though the Pb/Zn ratio is low (0.035) and close to the karstic signature, its lead isotopic composition (1.149) does not record a predominant karstic influence. One explanation of this high isotopic composition could be pollution by the pipes and/or the pump.

In Fig. 4 (Pb/Zn vs. ^{206}Pb/^{207}Pb), the shape of these fields are a mixing zone between several end-members which play a more or less important role in relation to the hydrologic conditions. This diagram would suggest that the increase in the Pb/Zn ratio is associated with a decrease in the ^{206}Pb/^{207}Pb ratio when there is an anthropogenic contribution.

The Pallas case. The shape of the domain defined by the Pallas waters in the same diagram (Pb/Zn vs. ^{206}Pb/^{207}Pb, Fig. 5) is very different. The rainy episode is characterised by a smaller Pb/Zn ratio (0.25 vs. 0.40 for the Vène, the same day) and by a much higher isotopic composition (1.174 vs. 1.144). When the drop in the level begins, the Pb/Zn and ^{206}Pb/^{207}Pb ratios decrease to approach the water treatment plant

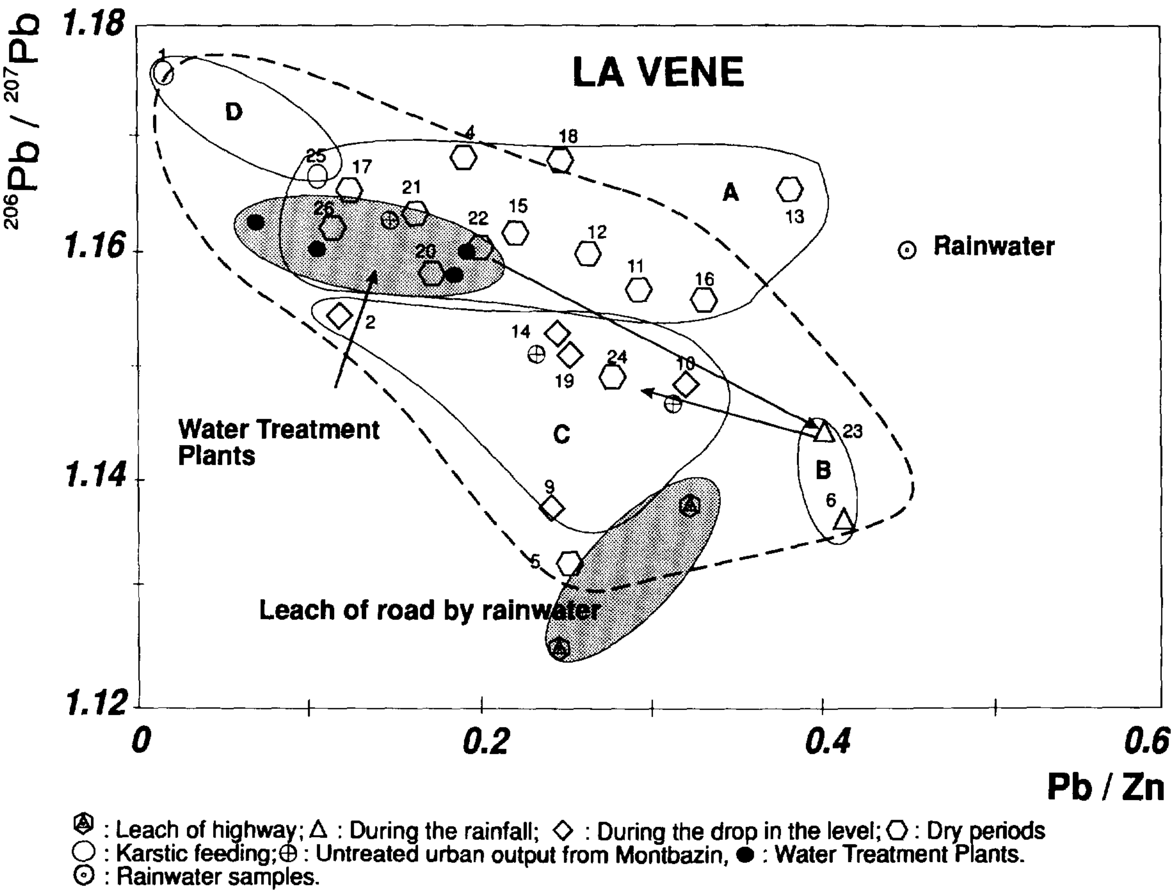

Fig. 4. Pb/Zn ratio versus ^{206}Pb/^{207}Pb (Vène).

domain of Villeveyrac (see the arrow illustrating the drop in the level between 9–10 February). In the case of the Pallas, there is no measurement corresponding to several days after the rain event. Indeed, during the dry periods, the water from the plant at Villeveyrac is lost by infiltration before arriving at the estuary.

The water of 9 February 1993, a rainy day, presents the same partition coefficients for Pb and Zn in particulate and dissolved phases (80% is associated with the particulate phase). In addition, a high isotopic signature (1.174) seems to indicate a dominant natural contribution (removal of unpolluted superficial soils). The anthropogenic component present within the Vène during rainfall is not detected here. This could be the result of the subwatershed of the Pallas having less dense car traffic and being more distant from major human activity than the subwatershed of the Vène.

Finally, in the Vène and the Pallas rivers, the ^{206}Pb/^{207}Pb ratio of the dissolved and particulate phases shows no significant difference (Table 5) which could indicate a rapid isotopic homogenisation of both phases. Cd content does not really correlate with the other metals, but remains very low and near the detection limit.

Inputs to the pond from other streams were also examined (Fig. 1). The Negue Vaques is comparable to the Pallas and has similar concentrations and isotopic composition. The Canal du Midi connects the Thau pond with the Herault

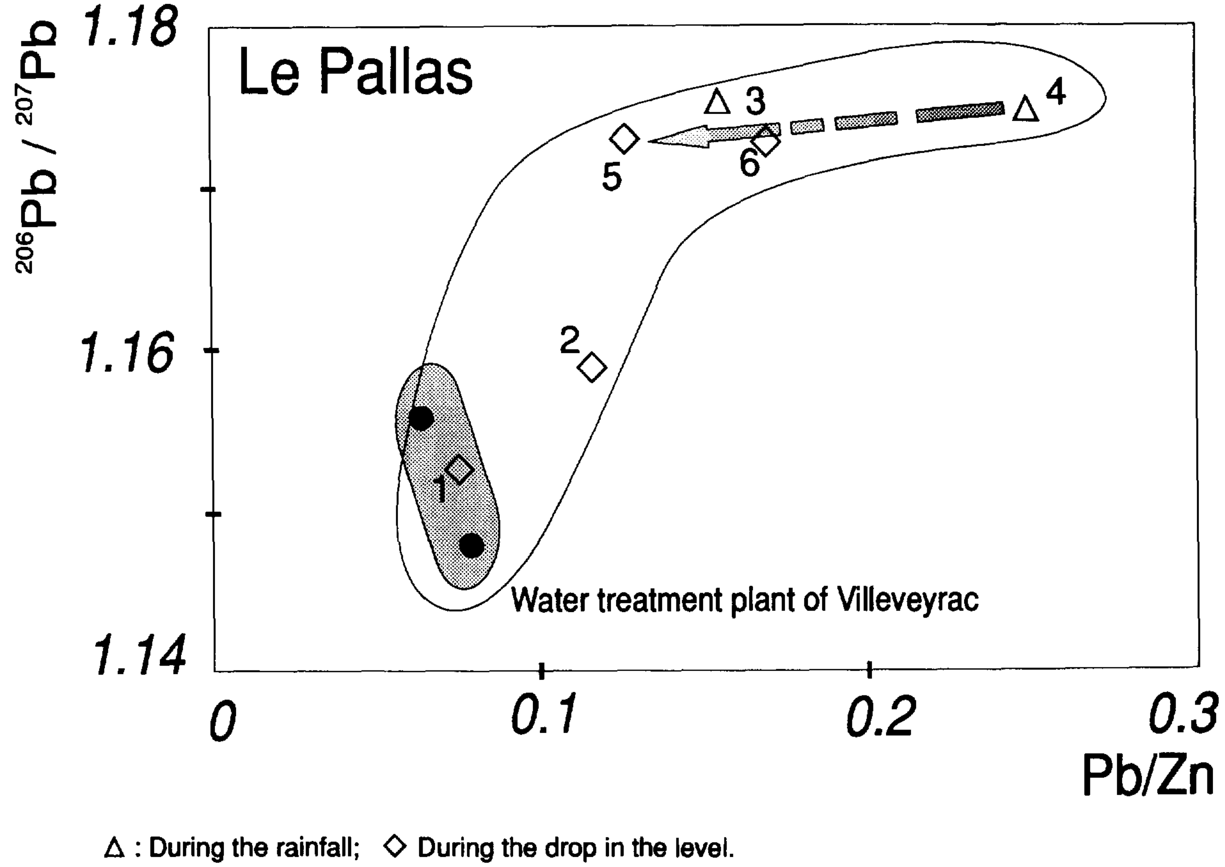

Fig. 5. Pb/Zn ratio versus ^{206}Pb/^{207}Pb (Pallas).

(an important river to the west of the pond) which receives the effluent from the Pb-Zn Malines mine which has recently closed. The concentrations encountered are Pb = 1.4 ppb, Zn = 3.9 ppb and Cd = 0.03 ppb whereas the lead isotopic compositions (^{206}Pb/^{207}Pb = 1.174) can be attributed

Table 5
Particulate and dissolved phases and lead isotopes

	^{206}Pb/^{207}Pb			Pb %		Zn %	
	> 0.45 μm	< 0.45 μm	Total	> 0.45 μm	< 0.45 μm	> 0.45 μm	< 0.45 μm
Vène 9 Feb 1993	1.1425	1.1452	1.1441	47.5	52.5	30.5	69.5
Vène 9 May 1993	1.1652	—	1.1660	—	—	—	—
Pallas 9 Feb 1993	1.1710	1.1732	1.1744	81.7	18.3	79.8	20.2
W.T.P. Montbazin	1.1613	1.1655	1.1623	—	—	—	—
12 May 1993		1.1635 (dupl.)					
W.T.P. Poussan 12 May 1993	1.1585	1.1551	—				
W.T.P. Villeveyrac 12 May 1993	1.1578	1.1573	—				
W.T.P. Gigean 12 May 1993	1.1577	1.1518	—				

W.T.P., water treatment plant.

to the ore deposit (1.175, Le Guen et al., 1991; Savary et al., 1992) or by a leaching of soils on the watershed of the Herault.

5. Conclusions

The use of lead isotopes allowed the identification of three main end-members for lead pollution: lead from gasoline (1.109–1.111), natural lead from rocks (1.198–1.200), and liquid urban output (1.146–1.162). Two other end-members, resulting from a complex mixing between various components, are also identified: rainwater (1.149–1.170) and leach from roads by rainwater (1.125–1.137).

It appears that the maximum 'pollution' flux occurs directly during rainfall. Rainwater drains the aerosols from the air. In the Vène case, once it reaches the soil, it washes out the dry deposition which presents an anthropogenic signature and a smaller fraction of natural material by weathering and streaming. If this rainfall is important enough, the karstic store fills up and feeds the Vène. Pb isotopes then move to a natural signature (increase in $^{206}Pb/^{207}Pb$). For the Pallas, far from industrial activity and roads, the contribution of the anthropogenic component is less important. In this area, Pb isotopes indicate an important removal of natural material.

The rivers studied are not important enough to note variations on a seasonal scale, as has been shown in a remote mountain stream (Erel et al., 1991). Nevertheless, in the Vène case, a similar kind of variation is observed, but on a shorter time scale due to the nature of the stream and to the exceptional character of its karstic feeding. Finally, the concentrations of heavy metals still remain very low in these streams, below the drinking water norms: Pb $<$ 9 ppb, Zn $<$ 35 ppb and Cd $<$ 0.4 ppb.

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