

Changes in chemical and $^{87}\text{Sr}/^{86}\text{Sr}$ signature distribution patterns of suspended matter and bed sediments in the upper Loire river basin (France)

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Abstract

The mineralogy of the suspended particulate matter (SPM) transported by the upper Loire river consists mainly of quartz and K-feldspar during periods of high river flow, with an increase in calcite concentration during periods of low flow. Concurrently, large fluctuations are observed in the levels of CaO and Fe₂O₃, the main oxides present in the SPM along with SiO₂. The analysed trace elements also fluctuate significantly. The bed sediments (BS) have a similar oxide content to the SPM, but lower Zn and Pb levels and higher Zr levels. Fluctuations in the chemical-element concentrations with river discharge are related to fluctuation in the mineral assemblages present in the SPM. Thus K, Ti and Rb levels increase with increasing in K-feldspar abundance during high flow, and Ca and Sr levels decrease with increasing discharge due to a decrease in calcite abundance. These mineralogical and chemical variations relate to different sources of sediments under different flow conditions—sources that can be distinguished by Sr isotopic study. The Sr isotopic composition fluctuates according to the rate of river discharge; i.e., the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio increases with increasing discharge and reaches a maximum with peak flow, and vice versa. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio also increases with the combined increase in K-feldspar abundance and decrease in calcite abundance. These similarities suggest the existence of at least two particulate-matter reservoirs, one with detrital silicates and the other with carbonates. Finally, the relationship between the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the suspended and dissolved loads suggests the coexistence of authigenic calcite in the carbonate reservoir. The SPM flow is related to a specific mechanical erosion rate over the whole Loire watershed ranging from 9 to 23 t km⁻² yr⁻¹. During the survey at Orleans, the SPM flow of the Loire river was $37 \cdot 10^4$ t yr⁻¹, providing an estimate of the specific erosion rate of around 9.8 t km⁻² yr⁻¹. From the shift in the SPM flux between the sampling point and the mouth of the Loire river and the divergence in the mean annual discharge, a calculation was made of the input of solid matter by the tributaries and by supplementary erosion processes along the river. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Loire river; Suspended matter; Bed load; $^{87}\text{Sr}/^{86}\text{Sr}$; Authigenic calcite

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1. Introduction

Residual products from chemical and mechanical weathering are carried by rivers and streams to the ocean (Garrels and Mackenzie, 1971; Berner and Berner, 1987; Drever, 1988) as suspended load, typically smaller than a few microns in diameter, and as bed load representing the coarser fraction that moves along the river bottom by a process of saltation. The weathering, transportation and deposition processes are all controlled by environmental factors. Transportation in rivers is usually in the form of solid matter (Berner and Berner, 1987), which is also an important transporting vector in the movement of trace metals within the hydrological cycle through adsorption and precipitation processes. The flux of suspended matter reaching the oceans is close $13\text{--}18 \cdot 10^9 \text{ t yr}^{-1}$ (Miliman and Meade, 1983), whereas that of bed sediments is thought to be only about 10% of this value (Meade et al., 1990).

The chemical composition of bed sediments in small catchments has been reported for various lithologies (Albarède and Semhi, 1995; Négrel and Deschamps, 1996). However, a chemical analysis of the sediments alone, without reference to the petrography and sources of solid matter within a catchment area, can lead to an overestimation of natural and/or anthropogenic contributions (Prohic and Juracic, 1989). Consequently, an estimate of the natural level of the sediments' chemical composition is required.

Trace-metal contamination has been intensively studied in small watersheds containing contaminated industrial wasteland (Bird, 1987; Brook and Moore, 1988; Voutsinou-Taliadousi and Varnavas, 1995). Moreover, Sinclair et al. (1989) have shown that the solid load can be more significant in the transport of pollutants than the dissolved load; many pollutants are virtually insoluble and tend to adsorb onto sediment load or organic matter (Hem et al., 1990). Few studies, however, have focused on both the suspended matter and bed sediments within the same river system, and previous investigations of the two show differences in the chemical composition of their solid phases (Stallard, 1988; Gaillardet et al., 1995; Dupré et al., 1996).

The aim of the present work was to study the temporal distribution of chemical species in the suspended matter (SPM) and bed sediments (BS) of the

Loire watershed, using the geochemical behaviour of soluble and insoluble elements, as well as of inert or 'reactive' elements, to determine the role of these materials in relation to their capacity to transport pollutant elements. Other objectives were to identify particle sources and weathering mechanisms, to investigate and quantify the natural and anthropogenic elemental concentrations, and to calculate the solid load transport.

2. Location and description of the Loire watershed

The Loire river in central France is 1010 km long and drains an area of 117,800 km² characterized by varying topographies (Fig. 1). In the upstream basin, the Loire and Allier rivers flow in a roughly south to north direction, join near Nevers and continue as the Loire up to the city of Orleans, 650 km from the source (Fig. 1). Here the Loire river turns to follow a general east to west direction to the Atlantic ocean. The bedrock composition in the upstream section of the watershed encompasses older plutonic rocks (granite, gneiss and mica schist; 500 to 300 Ma) and a large volcanic area which represent 46% of the total basin surface (BRGM, 1996). In the intermediate part of the watershed, the sedimentary series of the Paris Basin (200 to 6 Ma) drained by the Loire river consist primarily of carbonate deposits.

The Loire river carries one of the principal European riverine inputs to the Atlantic ocean ($26 \cdot 10^9 \text{ m}^3 \text{ yr}^{-1}$) with a mean annual discharge of $850 \text{ m}^3 \text{ s}^{-1}$ (Figueres et al., 1985). The solid load output ranges from 10^6 t yr^{-1} (Figueres et al., 1985) to $4.3 \cdot 10^6 \text{ t yr}^{-1}$ (Négrel, 1997), and the suspended load represents 3% of the total suspended sediment load for rivers draining western Europe based on the weighted average of the Seine, Oder, Vistula, Rhine and Garonne (Miliman and Meade, 1983). Near the city of Orleans, large variations in water discharge can be observed between the summer low stage (around $50 \text{ m}^3 \text{ s}^{-1}$) and that of winter high stage ($> 1000 \text{ m}^3 \text{ s}^{-1}$). The Rhône river (Jansen et al., 1979; Meybeck and Ragu, 1996) with a similar drainage area has twice the discharge of water and a

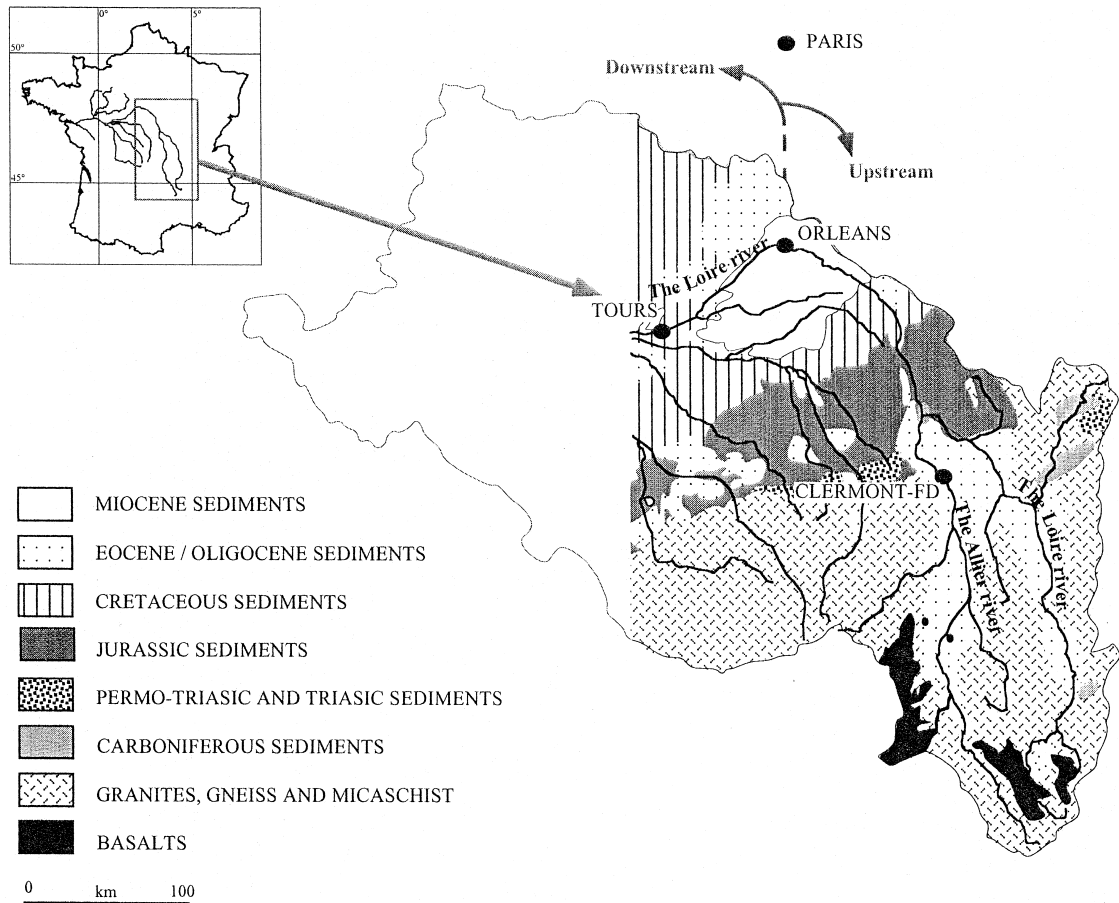


Fig. 1. Simplified geological map of the Loire river basin. The location of the sampling points is in town of Orleans.

much higher suspended sediment discharge ($31 \cdot 10^6$ t yr⁻¹).

3. Sampling and analysis

3.1. SPM and BS sampling

Sampling of the SPM in the Loire river waters was carried out at two locations separated by a distance of about 10 km without any major intermediate tributaries (Fig. 1). The load thus represents the contribution of 34% of the total Loire catchment and corresponds to a drainage area of $40 \cdot 10^3$ km², including the entire silicates basement of the Massif Central and about 24% of the sedimentary forma-

tions. The sampling strategy was divided into two periods. During the first period, from May 1994 to November 1995, the river was sampled at 'monthly' intervals, after which the sampling frequency was increased to a 'daily' interval (in reality between 2 days and 1 week, depending on the river discharge) from May 1995 to March 1996. Each sample was collected from the centre of the main river channel.

Total SPM masses (in mg l⁻¹) were determined by weight differences between dried filters before and after the filtration of 1 l of water through acetate cellulose membranes (0.22 μm). Two procedures were used for the collection of particulate matter: (1) for the 'monthly' survey, 60 l of Loire water were filtered using an ultrafiltration technique (Pellicon® Cassette System; 0.22 μm PVDF membrane by

Table 1

Major-element (wt.% of dried sediment at 70°C) and trace-element (ppm) concentrations and mineralogical composition of the SPM collected during the 'daily' survey (jlo samples) and 'monthly' survey (L samples); the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were determined on the L samples

Sample name	Date	SPM concentration (mg/l)	Discharge (m ³ /s)	SiO ₂ (wt.%)	K ₂ O (wt.%)	CaO (wt.%)	TiO ₂ (wt.%)	Fe ₂ O ₃ (wt.%)
jlo 1	20/05/95	35.0	433	56.43	2.38	2.86	0.99	7.55
jlo 2	24/05/95	22.6	341	57.51	2.63	2.58	0.95	7.55
jlo 3	28/05/95	20.7	272	59.33	2.40	6.15	0.77	5.65
jlo 4	30/05/95	26.4	197	64.81	2.26	8.89	0.74	5.55
jlo 5	12/06/95	17.8	128	51.00	1.84	> 17	0.64	3.91
jlo 6	23/06/95	22.3	122	55.34	2.09	> 17	0.60	3.05
jlo 7	29/06/95	17.1	101	49.34	2.05	11.19	0.53	4.18
jlo 8	03/07/95	17.5	91	36.59	2.23	> 17	0.68	3.62
jlo 9	20/07/95	45.5	71	34.42	1.88	> 17	0.57	2.69
jlo 10	25/07/95	45.8	56	29.69	1.86	> 17	0.62	3.17
jlo 11	03/08/95	60.9	71	16.00	1.67	> 17	0.77	3.18
jlo 12	11/08/95	25.0	53	18.18	1.60	> 17	0.68	2.75
jlo 13	18/08/95	32.8	55	34.38	1.78	> 17	0.75	3.49
jlo 14	27/08/95	25.3	59	56.53	1.59	> 17	0.56	2.49
jlo 15	05/09/95	56.0	108	31.73	1.51	> 17	0.69	2.92
jlo 16	14/09/95	41.0	121	33.93	1.73	> 17	0.74	3.99
jlo 17	25/09/95	51.5	307	47.18	2.27	16.05	0.90	5.77
jlo 18	02/10/95	27.8	177	49.24	2.31	14.41	0.90	6.07
jlo 19	09/10/95	36.8	239	53.93	2.26	13.37	0.91	5.84
jlo 20	16/10/95	20.8	168	54.94	2.45	11.88	0.93	6.59
jlo 21	23/10/95	20.3	137	47.27	2.21	12.17	0.81	5.96
jlo 22	09/11/95	10.5	96	54.04	1.71	7.33	0.61	2.82
jlo 23	27/11/95	4.8	152	50.57	2.11	8.25	0.73	5.96
jlo 24	03/12/95	40.1	251	56.72	2.29	4.77	1.00	6.99
jlo 25	12/12/95	5.3	174	55.08	2.50	4.20	0.91	7.02
jlo 26	17/12/95	3.3	165	52.55	2.29	4.06	0.86	3.14
jlo 27	03/01/96	57.4	760	51.82	2.43	3.27	1.10	7.11
jlo 28	05/01/96	82.2	935	55.82	2.71	3.22	1.09	7.68
jlo 29	07/01/96	55.4	920	55.60	2.77	3.05	1.17	7.79
jlo 30	09/01/96	65.1	965	55.61	2.62	3.32	1.06	7.57
jlo 31	11/01/96	48.0	935	55.96	2.68	2.90	1.11	7.73
jlo 32	14/01/96	52.9	1040	56.23	2.68	3.08	1.10	7.50
jlo 33	16/01/96	60.4	1050	59.89	2.99	2.84	1.20	7.98
jlo 34	18/01/96	34.4	830	58.28	3.01	3.37	1.25	8.37
jlo 35	21/01/96	25.1	620	54.64	3.02	3.13	1.18	8.46
jlo 36	22/01/96	22.3	560	54.77	2.63	3.44	1.14	8.05
jlo 37	26/01/96	25.1	525	53.99	2.56	2.59	1.15	8.34
jlo 38	29/01/96	26.3	605	53.99	2.74	2.60	1.22	8.00
jlo 39	01/02/96	24.4	500	52.97	2.69	3.28	1.17	7.84
jlo 40	06/02/96	24.0	460	54.56	2.58	2.48	1.11	8.00
jlo 41	12/02/96	31.6	450	52.33	2.47	2.70	1.10	7.37
jlo 42	15/02/96	100.1	860	56.74	2.35	2.96	1.12	6.82
jlo 43	19/02/96	34.0	700	56.11	2.46	2.06	1.11	8.64
jlo 44	22/02/96	58.8	735	56.57	2.39	1.88	1.08	8.49
jlo 45	27/02/96	13.2	510	53.96	2.29	2.57	1.08	8.67
jlo 46	08/03/96	25.9	515	54.22	2.37	2.16	1.08	9.17
jlo 47	18/03/96	11.6	341	53.39	2.47	3.13	0.99	7.32
L1	05/94	16.3	433	58.03	2.43	2.01	0.99	7.70
L2	06/94	18.1	341	58.74	2.42	2.08	1.00	7.64

Table 1 (continued)

Sample name	Date	SPM concentration (mg/l)	Discharge (m ³ /s)	SiO ₂ (wt.%)	K ₂ O (wt.%)	CaO (wt.%)	TiO ₂ (wt.%)	Fe ₂ O ₃ (wt.%)
L3	07/94	21.3	272	61.58	1.20	> 17	0.73	4.27
L4	08/94	22.5	197	54.94	1.28	15.41	0.57	3.69
L5	09/94	44.7	128	56.89	1.33	> 17	0.56	2.57
L6	10/94	34.3	122	50.07	2.49	8.90	1.03	6.68
L7	11/94	84.2	101	56.27	2.60	2.83	1.14	8.02
L8	12/94	21.3	91	48.25	2.51	7.99	1.05	7.75
L9	01/95	40.1	71	53.42	2.84	3.31	1.09	8.11
L10	02/95	80.5	56	55.43	2.66	2.00	1.12	7.89
L11	03/95	24.9	71	52.62	2.54	3.40	1.03	7.53
L12	04/95	18.7	53	54.66	2.79	7.20	0.92	7.01
L13	05/95	22.2	55	56.80	2.57	3.99	0.94	6.85
L14	06/95	28.0	59	62.04	2.24	3.17	0.79	6.40
L15	07/95	39.8	108	34.17	2.04	> 17	0.69	3.75
L16	08/95	24.7	121	25.00	2.08	> 17	0.62	2.80
L17	09/95	30.2	307	32.73	1.35	> 17	0.58	2.37
L18	11/95	5.1	177	55.09	1.83	10.65	0.66	4.78

Sample name	Date	Zn (ppm)	Pb (ppm)	Rb (ppm)	Sr (ppm)	Zr (ppm)	⁸⁷ Sr/ ⁸⁶ Sr
jlo 1	20/05/95	323	91	187	174	210	n.d.
jlo 2	24/05/95	361	107	179	159	164	n.d.
jlo 3	28/05/95	366	94	131	236	146	n.d.
jlo 4	20/05/95	323	73	110	180	112	n.d.
jlo 5	12/06/95	229	55	70	269	89	n.d.
jlo 6	23/06/95	232	37	71	316	73	n.d.
jlo 7	29/06/95	1141	74	68	169	60	n.d.
jlo 8	03/07/95	341	55	78	344	65	n.d.
jlo 9	20/07/95	261	68	60	382	58	n.d.
jlo 10	25/07/95	300	42	73	375	98	n.d.
jlo 11	03/08/95	229	34	67	477	118	n.d.
jlo 12	11/08/95	218	28	59	421	100	n.d.
jlo 13	18/08/95	281	51	70	397	126	n.d.
jlo 14	27/08/95	308	41	51	312	65	n.d.
jlo 15	05/09/95	196	36	62	461	100	n.d.
jlo 16	14/09/95	263	52	83	397	124	n.d.
jlo 17	25/09/95	279	75	135	329	180	n.d.
jlo 18	02/10/95	340	68	134	306	158	n.d.
jlo 19	09/10/95	365	73	129	281	145	n.d.
jlo 20	16/10/95	387	99	133	252	137	n.d.
jlo 21	23/10/95	400	122	94	186	91	n.d.
jlo 22	09/11/95	222	109	37	57	28	n.d.
jlo 23	27/11/95	369	108	103	201	78	n.d.
jlo 24	03/12/95	409	135	177	222	193	n.d.
jlo 25	12/12/95	439	141	86	99	59	n.d.
jlo 26	17/12/95	252	135	29	37	22	n.d.
jlo 27	03/01/96	334	103	198	198	197	n.d.
jlo 28	05/01/96	326	125	223	218	221	n.d.
jlo 29	07/01/96	311	121	227	241	228	n.d.
jlo 30	09/01/96	284	102	216	209	218	n.d.
jlo 31	11/01/96	475	115	222	199	207	n.d.
jlo 32	14/01/96	450	114	218	204	217	n.d.

Table 1 (continued)

Sample name	Date	Zn (ppm)	Pb (ppm)	Rb (ppm)	Sr (ppm)	Zr (ppm)	⁸⁷ Sr/ ⁸⁶ Sr
jlo 33	16/01/96	390	100	225	222	211	n.d.
jlo 34	18/01/96	338	109	225	248	197	n.d.
jlo 35	21/01/96	357	117	202	227	167	n.d.
jlo 36	22/01/96	354	101	203	228	171	n.d.
jlo 37	26/01/96	339	101	217	216	182	n.d.
jlo 38	29/01/96	260	88	211	273	188	n.d.
jlo 39	01/02/96	275	99	188	242	172	n.d.
jlo 40	06/02/96	299	102	210	206	173	n.d.
jlo 41	12/02/96	304	115	207	195	189	n.d.
jlo 42	15/02/96	222	90	191	188	227	n.d.
jlo 43	19/02/96	348	114	257	199	220	n.d.
jlo 44	22/02/96	306	104	250	184	221	n.d.
jlo 45	27/02/96	318	175	220	198	193	n.d.
jlo 46	08/03/96	403	128	218	214	177	n.d.
jlo 47	18/03/96	323	128	102	104	75	n.d.
L1	05/94	343	90	154	153	131	0.712298
L2	06/94	370	95	155	151	127	0.715295
L3	07/94	203	44	89	307	121	0.712316
L4	08/94	321	47	74	259	76	0.711784
L5	09/94	294	54	53	326	55	0.711603
L6	10/94	424	135	164	327	187	0.712813
L7	11/94	275	61	203	220	210	0.713835
L8	12/94	752	200	153	224	194	0.713066
L9	01/95	334	95	231	194	174	0.716257
L10	02/95	248	82	237	180	194	0.716691
L11	03/95	287	79	208	202	173	0.714055
L12	04/95	257	86	144	226	135	0.711929
L13	05/95	512	169	187	222	197	0.714964
L14	06/95	1669	97	134	131	110	0.714086
L15	07/95	421	181	87	338	111	0.712228
L16	08/95	186	29	69	416	86	0.712029
L17	09/95	271	38	46	377	74	0.711505
L18	11/95	499	159	56	109	42	0.711256
Sample name	Date	Quartz (%)	K-feldspar (%)	Plagioclases (%)	Illite (%)	Kaolinite (%)	Calcite (%)
jlo 1	20/05/95	35	19	19	5	10	12
jlo 2	24/05/95	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
jlo 3	28/05/95	27	17	15	12	13	16
jlo 4	20/05/95	18	9	11	7	8	47
jlo 5	12/06/95	6	3	4	4	3	80
jlo 6	23/06/95	8	16	6	3	3	64
jlo 7	29/06/95	13	14	7	6	5	55
jlo 8	03/07/95	8	6	4	3	4	75
jlo 9	20/07/95	4	6	2	4	4	80
jlo 10	25/07/95	6	4	21	2	3	64
jlo 11	03/08/95	8	6	3	2	3	78
jlo 12	11/08/95	8	4	3	3	3	79
jlo 13	18/08/95	13	12	12	11	–	52
jlo 14	27/08/95	–	18	15	–	–	67
jlo 15	05/09/95	6	8	4	6	–	76

Table 1 (continued)

Sample name	Date	Quartz (%)	K-feldspar (%)	Plagioclases (%)	Illite (%)	Kaolinite (%)	Calcite (%)
jlo 16	14/09/95	5	11	9	4	4	67
jlo 17	25/09/95	13	11	13	9	7	47
jlo 18	02/10/95	10	15	14	8	8	45
jlo 19	09/10/95	13	13	12	8	8	46
jlo 20	16/10/95	13	13	13	13	11	37
jlo 21	23/10/95	12	14	15	10	7	42
jlo 22	09/11/95	13	23	30	9	8	17
jlo 23	27/11/95	20	20	15	5	8	32
jlo 24	03/12/95	13	20	33	11	9	14
jlo 25	12/12/95	19	20	15	18	18	10
jlo 26	17/12/95	17	17	18	19	15	15
jlo 27	03/01/96	15	26	27	13	13	6
jlo 28	05/01/96	21	33	19	13	14	–
jlo 29	07/01/96	15	22	26	17	20	–
jlo 30	09/01/96	22	22	17	16	16	7
jlo 31	11/01/96	28	25	14	14	13	6
jlo 32	14/01/96	24	24	18	15	11	8
jlo 33	16/01/96	25	24	25	9	11	6
jlo 34	18/01/96	22	24	21	13	13	7
jlo 35	21/01/96	20	21	20	16	17	6
jlo 36	22/01/96	28	19	19	13	14	7
jlo 37	26/01/96	20	24	22	12	14	8
jlo 38	29/01/96	14	20	23	20	16	7
jlo 39	01/02/96	17	17	31	17	12	6
jlo 40	06/02/96	24	18	18	12	19	9
jlo 41	12/02/96	25	20	16	18	13	8
jlo 42	15/02/96	28	22	21	11	12	6
jlo 43	19/02/96	24	21	21	13	14	7
jlo 44	22/02/96	33	19	18	8	15	7
jlo 45	27/02/96	27	23	21	12	10	7
jlo 46	08/03/96	19	30	23	13	15	–
jlo 47	18/03/96	18	27	25	10	13	7
L1	05/94	30	–	20	10	10	30
L2	06/94	40	20	–	20	15	5
L3	07/94	10	10	–	10	10	60
L4	08/94	10	15	–	10	5	60
L5	09/94	5	5	10	–	–	80
L6	10/94	20	15	5	5	5	50
L7	11/94	10	27	–	26	10	27
L8	12/94	25	20	–	5	10	40
L9	01/95	30	30	10	10	10	10
L10	02/95	32	32	11	10	10	5
L11	03/95	20	30	–	20	20	10
L12	04/95	20	30	–	20	10	20
L13	05/95	25	40	–	25	10	–
L14	06/95	25	25	–	25	25	–
L15	07/95	5	–	5	5	5	80
L16	08/95	10	–	10	5	5	70
L17	09/95	5	5	10	–	–	80
L18	11/95	5	20	5	–	–	70

n.d. = non-determined value. For the mineralogical composition of the SPM, semi-quantitative percents were obtained for each mineral by calculating the ratio of the height of its most intense peak against the sum of all the most intense mineral peaks.

Millipore). The SPM samples obtained in this way are referred to in the results section as L_x , where x represents the different samples; (2) for the 'daily' survey, 60 to 90 l of Loire water were collected in precleaned polypropylene containers and left to settle over several days. The efficiency of this separation, tested through replicate filtrations of 1 l samples of water after settling, showed that between 0.5 and 3 mg l^{-1} of the SPM were lost by this procedure, with between 800 and 3500 mg l^{-1} being collected. The SPM samples obtained in this way are referred to in the results as jlo_x , where x represents the different samples.

With both procedures, the SPM samples were oven-dried at 70°C, powdered and dry-sieved through a 165 μm nylon mesh to extract fresh coarse organic matter (wood, etc.) prior to analysis.

Recent BS samples were collected with plastic spatulas at the river bank and stored in polypropylene containers to avoid contamination. The samples were oven-dried at 70°C, homogenized, quartered and dry-sieved through a 165 μm nylon mesh, without the use of a dispersion agent so as to avoid contamination and modification of the samples. A similar analysis of BS from the Allier River was performed on 17 samples taken over a 15-month study period (May 1994 to August 1995) near Clermont-Ferrand (Négrel et al., 1997).

3.2. Major- and trace-element determination and isotopic measurements

The analytical procedures and analysis methods are described in detail by Négrel and Deschamps (1996) and Négrel (1997). All sediment samples were analysed for major and trace elements by X-ray fluorescence energy dispersive spectrometry (XRF) using a Syrano 2/501. Two certified reference materials (GBW 07311; GBW 07306) were run to verify the calibration. Analytical accuracy was monitored by the repeated analysis of an in-house standard of similar mass and physical conditions as the experimental samples—precision was between 2 and 10%.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were measured on the SPM samples collected during the monthly survey. Following standard acid-dissolution procedures of the SPM samples, Sr isotopic ratios were determined

using a Finnigan MAT 262 mass spectrometer after chemical separation using a cation exchange column (Dowex AG50X8; 2 N HCl as the eluant). The total blank for Sr was less than 1 ng for the entire chemical procedure. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios obtained were normalized to an $^{88}\text{Sr}/^{86}\text{Sr}$ of 0.1194. The reproducibility of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio measurements were tested by duplicate analysis of the NBS 987 standard, with a mean value close to $0.710227 \pm 17 \cdot 10^{-6}$ (2σ ; $n = 70$).

3.3. Mineral phases and clay determination

Each bulk SPM sample was homogenized by hand-crushing with an agate mortar, following which 5 mg of crushed powder were mixed with 3 ml of distilled water and placed on glass slides. Thereafter, the suspensions were dried in air for 3 h. The mineralogical composition of the SPM sample was determined by X-ray diffraction using a Rigaku analyser, Cu-K_α ray with a Ni-K_β filter. Qualitative mineralogical analyses were carried out by identifying diffraction spectra (Brown, 1961). Semi-quantitative percents were obtained for each mineral by calculating the ratio of the height of its most intense peak against the sum of all the most intense mineral peaks (Hotzapffel, 1985).

4. Results and discussion

4.1. Variations in SPM concentrations

The relationship between SPM and discharge for large or moderate drainage basins usually follows clockwise loops (hysteresis curves) (Wood, 1977; Meade, 1985; Probst and Bazerbachi, 1986; Olivry et al., 1988; Sinclair et al., 1989; Zhang, 1990). However, the SPM concentrations of the Loire river collected over the two study periods varied widely from 3.3–5 mg l^{-1} to 80–100 mg l^{-1} (Table 1 and Fig. 2) and show neither a linear relationship (correlation coefficient = 0.40) nor a cyclical relationship with river flow; only a weak correlation of increasing SPM concentration with increasing river discharge could be identified.

This lack of relationship between SPM and discharge can be explained by the large human occupation in the Loire watershed and the exploitation of

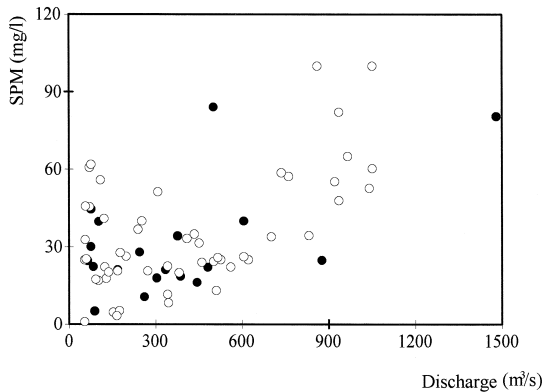


Fig. 2. Evolution of SPM concentration with discharge for the daily (open circles) and monthly (filled circles) samples; analytical errors are represented by the size of the circles.

the river. Multiple developments (dredging for gravel extraction, etc.) have led to significant changes to the channel morphology and are responsible for a constant degradation of the river banks, resulting in both storage and transport of fine particles irrespective of the discharge level of the river. Furthermore, one of the most pervasive influences on the SPM load is due to the large number of dams and reservoirs that have been built on the rivers of the Loire watershed (e.g., six major dams along the Loire and Allier rivers; 30 hydroelectric reservoirs over the entire catchment area). These man-made structures interrupt the down-river flow of sediments, with much of the solid load being trapped in the reservoirs (Meade et al., 1990). The existence of dams along the Loire river implies that, whereas the suspended particles originate from the natural erosion of the watershed, the suspended load could be controlled by non-natural processes.

4.2. Mineralogical composition

A semi-quantitative XRD analysis of the SPM shows that quartz (5–40%), K-feldspar and plagioclase (0–40%) and calcite (0–80%) represent the main mineral phases (Table 1). The quartz and K-feldspar contents increase with increasing discharge and are the dominant minerals present during high flow; during low flow, their contents fall to 5–10% (Fig. 3). By contrast, the calcite concentration varies significantly from 0% during high river flow to 80%

during periods of low flow (Fig. 3). Both illite and kaolinite are dominant clay minerals (0–25%), but only the illite content seems to fluctuate with river discharge. Similar mineralogical associations were found by Manickam et al. (1985) in the SPM of the Loire river just upstream of the estuary.

In the Allier and Loire rivers, the main gravel and sand components of the BS are of granitic–gneissic and basaltic origin from the Massif Central; carbonates from the Limagne d'Allier can also be a source of material. Quartz, feldspar, calcite, biotite and clays are the main phases, and augite, hornblende, olivine, and zircon are the main heavy accessory minerals (Brossé, 1979; Macaire, 1985; Kroonenberg et al., 1988; Roger, 1988).

4.3. Chemical composition: main feature and variations with the Loire river flow

The chemical data for the Loire river SPM and BS are summarized in Table 1 (SPM) and Table 2 (BS). Major-element compositions are expressed in terms of weight percentage (wt.%) and trace-element abundances in parts per million (ppm).

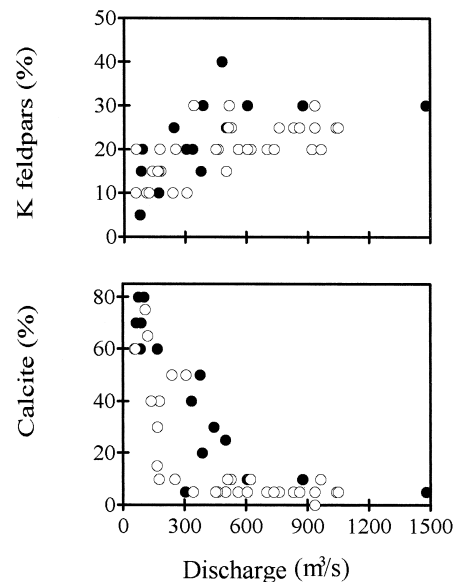


Fig. 3. Evolution of calcite and K-feldspar abundances with river discharge. (Symbols identical to those in Fig. 2.)

Table 2

Major-element (wt.% of dried sediment at 70°C) and trace-element (ppm) concentrations of bed sediments collected from the Loire and Allier rivers

Sample name	Date	SiO ₂ (%)	K ₂ O (%)	CaO (%)	TiO ₂ (%)	Fe ₂ O ₃ (%)		
<i>Loire bed sediments</i>								
BSL1	03/94	61.79	2.63	4.34	1.07	5.94		
BSL2	04/94	57.62	1.86	10.61	0.92	5.64		
BSL3	05/94	64.68	2.76	3.79	0.90	4.98		
BSL4	08/94	60.01	1.67	16.47	0.72	3.68		
BSL5	09/94	59.17	2.05	11.52	0.98	4.89		
BSL6	10/94	51.91	2.10	13.59	0.94	4.96		
BSL7	11/94	53.41	2.40	10.22	0.99	5.70		
BSL8	12/94	61.68	2.49	4.01	0.78	3.01		
BSL9	01/95	63.38	2.80	4.54	1.00	4.94		
BSL10	03/95	64.76	2.57	3.94	0.88	4.08		
BSL11	03/95	63.94	2.69	3.70	0.74	3.66		
BSL12	03/95	64.35	2.63	3.82	0.81	3.87		
BSL13	05/95	58.57	2.61	4.21	0.93	5.23		
BSL14	06/95	58.82	2.50	4.43	0.98	6.94		
BSL15	06/95	59.43	2.58	4.79	1.02	6.94		
BSL16	07/95	49.25	2.24	15.06	0.92	4.47		
BSL17	08/95	60.68	2.59	7.95	0.63	3.11		
<i>Allier bed sediments</i>								
BSA1	03/94	55.60	2.73	1.95	1.06	5.64		
BSA2	04/94	56.93	2.97	1.71	0.94	5.32		
BSA3	05/94	57.03	2.33	2.78	1.05	5.37		
BSA4	06/94	56.26	2.38	2.84	1.03	5.61		
BSA5	08/94	52.50	1.94	2.91	1.26	7.12		
BSA6	09/94	48.86	2.10	2.74	1.28	8.24		
BSA7	10/94	61.43	2.39	2.43	0.80	4.29		
BSA8	10/94	61.10	2.49	2.35	0.77	4.22		
BSA9	11/94	54.32	2.82	2.72	1.25	7.38		
BSA10	11/94	54.30	2.70	3.18	1.35	7.16		
BSA11	12/94	56.53	2.46	2.46	1.01	4.96		
BSA12	01/95	51.17	2.70	2.05	1.16	6.79		
BSA13	05/95	59.08	2.55	2.35	1.15	6.20		
BSA14	05/95	60.97	2.68	1.86	0.97	5.48		
BSA15	05/95	57.86	2.77	2.05	1.20	7.01		
BSA16	08/95	59.53	2.37	1.98	1.09	6.52		
BSA17	08/95	60.16	3.05	0.94	0.91	5.69		
Sample name	Date	Zn (ppm)	Pb (ppm)	Rb (ppm)	Sr (ppm)	Zr (ppm)	Sn (ppm)	Ba (ppm)
<i>Loire bed sediments</i>								
BSL1	03/94	196	76	188	243	312	16	805
BSL2	04/94	191	52	147	261	269	17	556
BSL3	05/94	140	61	181	245	338	15	817
BSL4	08/94	118	43	136	326	278	21	739
BSL5	09/94	102	53	143	289	418	22	765
BSL6	10/94	188	61	155	333	284	22	682
BSL7	11/94	220	48	162	310	280	22	448
BSL8	12/94	86	60	152	256	334	9	823
BSL9	01/95	133	67	180	260	313	9	804

Table 2 (continued)

Sample name	Date	Zn (ppm)	Pb (ppm)	Rb (ppm)	Sr (ppm)	Zr (ppm)	Sn (ppm)	Ba (ppm)
<i>Loire bed sediments</i>								
BSL10	03/95	80	74	157	243	414	15	786
BSL11	03/95	116	62	168	257	292	12	849
BSL12	03/95	98	68	163	250	353	14	818
BSL13	05/95	186	81	185	226	363	16	739
BSL14	06/95	307	104	192	198	263	27	621
BSL15	06/95	327	107	190	203	250	25	611
BSL16	07/95	143	76	142	285	536	48	673
BSL17	08/95	96	77	154	268	345	54	745
<i>Allier bed sediments</i>								
BSA1	03/94	112	55	191	251	233	19	804
BSA2	04/94	114	68	185	245	226	20	771
BSA3	05/94	106	48	145	286	445	10	831
BSA4	06/94	102	45	161	308	461	13	788
BSA5	08/94	181	37	150	324	477	20	628
BSA6	09/94	262	57	175	330	314	20	600
BSA7	10/94	70	41	153	305	220	6	844
BSA8	10/94	72	46	145	298	145	7	825
BSA9	11/94	126	56	185	291	362	13	835
BSA10	11/94	146	51	176	315	413	12	850
BSA11	12/94	82	48	157	303	252	11	826
BSA12	01/95	138	69	196	251	393	17	793
BSA13	05/95	123	81	156	271	437	13	832
BSA14	05/95	106	73	151	275	337	17	915
BSA15	05/95	152	76	195	293	547	17	705
BSA16	08/95	125	66	127	269	> 900	38	741
BSA17	08/95	115	100	181	194	647	70	1042

The order of abundance in the SPM was similar during the two hydrological cycles ($\text{SiO}_2 > \text{CaO} > \text{Fe}_2\text{O}_3 > \text{K}_2\text{O} > \text{TiO}_2$). The larger fluctuations are observed for Fe_2O_3 (34%) and CaO (a factor of 10); all the trace-element concentrations fluctuate significantly. The mean values agree with those published by Manickam et al. (1985). Binary correlations, illustrated by the correlation coefficients R (Table 3a; bold R are statistically significant), show good relationships between chemical elements usually associated with silicates (Ti, K, Zr, Rb). Iron, partitioned between minerals and clays (Price and Calvert, 1973), shows good R coefficients with these elements. CaO and Sr associated within silicate and calcareous phases show good correlation with each other and a strongly negative correlation with Ti, K, Zr and Rb. The trace elements, apart from a few exceptions, do not correlate with each other. Similar relationships

have been measured in other main French rivers (Meuse, Rhine, Rhône, Garonne; Martin and Meybeck, 1978; Probst and Bazerbachi, 1986; Nolting et al., 1989).

The BS (Table 2) show similar orders of major-oxide abundance and variations as the SPM, although Fe_2O_3 and CaO are less concentrated. Similarly, Zn and Pb are less concentrated than in the SPM whereas Zr concentration is higher and Sr, Rb are similar.

The CaO content in the Allier BS is 30% lower than in the Loire BS, although the levels of other major oxides and trace elements are similar for both rivers. The chemical composition of the Allier terraces (Kroonenberg et al., 1988) is in agreement with our measurements, apart from the lower Fe_2O_3 , Zn, Pb, Rb and Zr values. The changes in inter-element correlations in the BS (Table 3b and c) can be

Table 3

Pearson correlation coefficients obtained between the nine elements measured for the Loire SPM over the two periods studied (a), and obtained for the 13 elements measured in the BS of the Loire river (b) and Allier river (c)

(a) Loire SPM <i>n</i> = 67	SiO ₂	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	Zn	Pb	Rb	Sr	Zr				
K ₂ O	0.41	1.00								0.00				
CaO	-0.65	-0.79	1.00											
TiO ₂	-0.30	-0.81	-0.77	1.00										
Fe ₂ O ₃	0.63	0.82	-0.90	0.83	1.00									
Zn	0.21	0.07	-0.16	-0.12	0.11	1.00								
Pb	0.41	0.51	-0.59	-0.41	0.59	0.29	1.00							
Rb	0.52	0.77	-0.81	0.85	0.91	-0.01	0.42	1.00						
Sr	-0.76	-0.49	0.77	-0.33	-0.62	-0.33	-0.62	-0.39	1.00					
Zr	0.36	0.64	-0.63	0.81	0.76	-0.09	0.32	0.92	-0.15	1.00				
(b) Loire BS <i>n</i> = 17	SiO ₂	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	Zn	Pb	Rb	Sr	Zr	Sn	Ba	La	Ce
K ₂ O	0.51	1												
CaO	-0.73	-0.87	1											
TiO ₂	-0.27	0.10	-0.09	1										
Fe ₂ O ₃	-0.27	0.04	-0.10	0.84	1									
Zn	-0.36	0.03	-0.07	0.61	0.91	1								
Pb	0.04	0.49	-0.47	0.29	0.50	0.60	1							
Rb	0.32	0.73	-0.74	0.49	0.62	0.60	0.68	1						
Sr	-0.47	-0.63	0.80	-0.23	-0.41	-0.40	-0.79	-0.75	1					
Zr	-0.20	0.03	0.19	-0.06	-0.37	-0.51	-0.03	-0.39	0.11	1				
Sn	-0.52	-0.17	0.46	-0.24	-0.06	0.09	0.28	-0.27	0.15	0.37	1			
Ba	0.68	0.39	-0.41	-0.37	-0.58	-0.66	-0.06	0.05	-0.14	0.28	-0.31	1		
La	0.10	0.09	0.04	-0.43	-0.60	-0.63	0.09	-0.41	-0.02	0.84	0.41	0.51	1	
Ce	0.05	-0.01	0.16	-0.48	-0.60	-0.63	0.05	-0.48	0.07	0.82	0.52	0.45	0.98	1
(c) Allier BS <i>n</i> = 17	SiO ₂	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	Zn	Pb	Rb	Sr	Zr	Sn	Ba	La	Ce
SiO ₂	1													
K ₂ O	0.31	1												
CaO	-0.45	-0.64	1											
TiO ₂	-0.75	-0.20	0.49	1										
Fe ₂ O ₃	-0.75	-0.15	0.29	0.92	1									
Zn	-0.76	-0.36	0.25	0.75	0.88	1								
Pb	0.25	0.66	-0.79	-0.03	0.14	0.07	1							
Rb	-0.45	0.60	-0.24	0.32	0.37	0.28	0.35	1						
Sr	-0.34	-0.74	0.89	0.36	0.24	0.31	-0.77	-0.31	1					
Zr	0.08	0.03	-0.21	0.30	0.39	0.20	0.42	-0.22	-0.25	1				
Sn	0.14	0.35	-0.71	0.08	0.14	0.14	0.69	0.11	-0.70	0.63	1			
Ba	0.61	0.65	-0.49	-0.50	-0.52	-0.66	0.45	0.02	-0.63	0	0.36	1		
La	0.33	0.05	-0.45	-0.04	0.09	-0.01	0.47	-0.37	-0.43	0.90	0.75	0.20	1	
Ce	0.34	0.05	-0.46	-0.05	0.09	-0.02	0.47	-0.37	-0.43	0.90	0.76	0.20	1	1

R coefficients in bold are statistically representative (SPM: *R* > 0.5, *n* = 67; BS: *R* > 0.7, *n* = 17).

explained by the fact that the Loire drains mainly carbonates between the Allier and the sampling points near Orleans.

Although the above results appear to show no linear trend between the SPM concentration and water discharge (Fig. 2), relationships do exist be-

tween the chemical species in the SPM. Plotted against the hydrological regime of the river, the chemical elements can be classified into three groups.

In the first group, K_2O , TiO_2 , Fe_2O_3 , Si, Zr and Rb concentration levels increase with increasing dis-

charge, showing a logarithmic trend (Fig. 4). In the second group, CaO levels decrease sharply with increasing discharge up to around $300\text{ m}^3\text{ s}^{-1}$, although with a significant scattering of the data (especially for Sr); thereafter, the fluctuations remain low

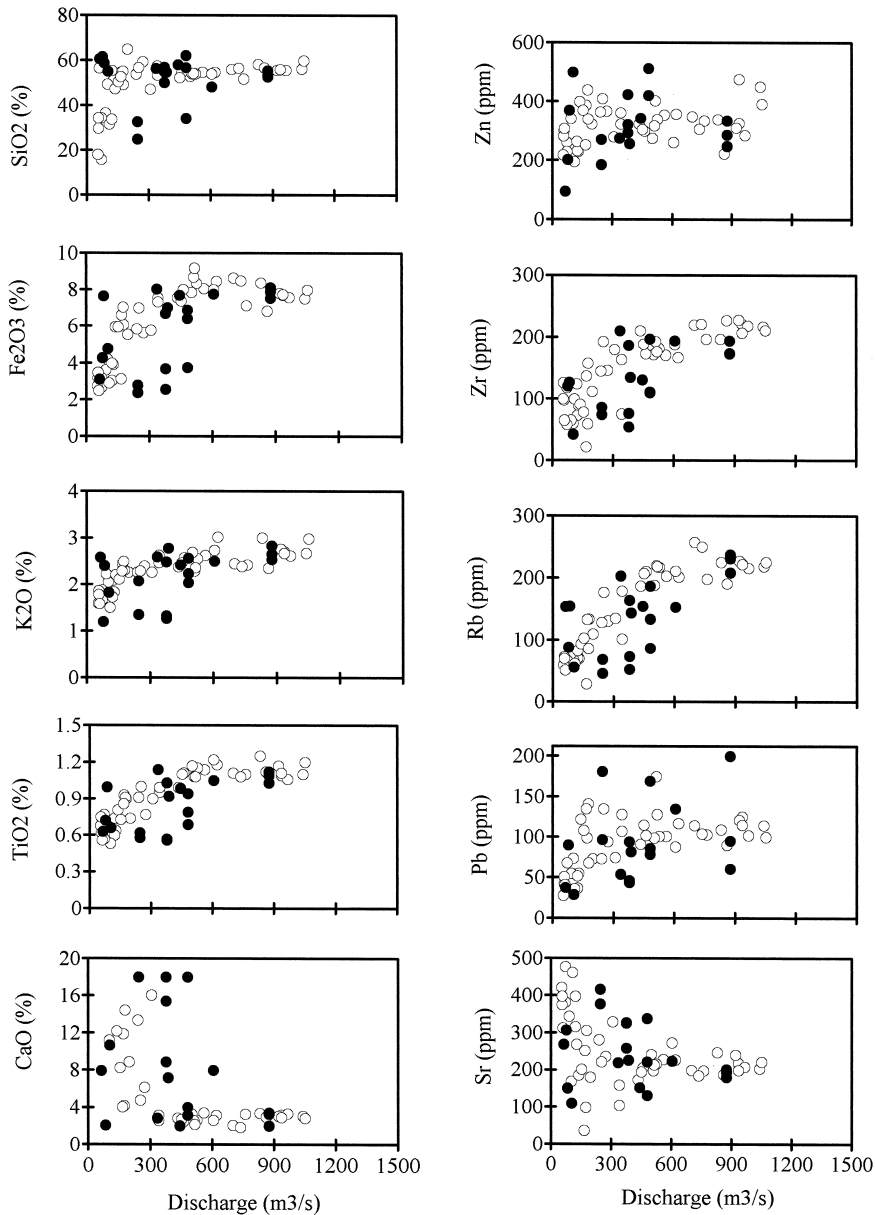


Fig. 4. Evolution of major- and trace-element concentrations with discharge. (Symbols identical to those in Fig. 2.)

up to the maximum discharge. In the last group, Pb and Zn fluctuations cannot be easily related to the discharge.

Because the SPM consists of a wide range of mineralogical phases, the concentrations of chemical species can be related to fluctuations in the mineralogical assemblages. The logarithmic tendencies can be explained either by the presence of at least two mineral-bearing phases, one with high and the other with low elemental concentrations, or by fluctuations in the abundance of the mineral phase that contains most of the element. K-feldspar and illite are the main carriers of both K and Rb, and can also contain significant amounts of Ti, Fe and Zr (Clauer et al., 1993). These minerals are more abundant in the SPM during high flood (Fig. 3). Thus, elevated levels of K, Rb and Ti during high flow and their decrease with attenuating discharge can be related to the abundance of illite and K-feldspar. The levels of silica, Fe and Zr can also be explained in this way.

The decrease in Ca and Sr with increasing discharge can be related to the change in the abundance of the Ca–Sr-bearing phase, for which the two main carriers are calcite and plagioclase. Plagioclase alone does not fluctuate noticeably with the level of river discharge (see Section 4.2), unlike the calcite abundance which reaches a maximum during low flow (Fig. 3). Thus, it appears that the fluctuation of Ca–Sr concentrations in the SPM must be related to the abundance of calcite (correlation coefficient between percent calcite and $[Sr]$ is 0.71).

As Pb and Zn in the SPM cannot be related to fluctuations of a specific mineral, their variations in concentration at similar rates as those in river discharge may be due to an adsorption of dissolved Pb and Zn onto particles.

The large increase in calcite abundance at the sampling stations, and the associated fluctuations in chemical-element concentrations, can be related to different chemical and mineral sources that can be determined under different flow conditions through an isotopic tracing of the SPM.

4.4. Isotope systematics: presence of authigenic calcite in the SPM of the Loire river

The Sr isotopic composition ($^{87}Sr/^{86}Sr$) of the SPM shows large fluctuations of more than $5 \cdot 10^{-3}$, which is higher than the analytical errors for the

procedure ($2 \cdot 10^{-5}$). The $^{87}Sr/^{86}Sr$ ratio varies from 0.71126–0.71193 to 0.71626–0.71669; it correlates neither with the SPM concentration nor with pH of the water, but nevertheless follows the river discharge fluctuations (Fig. 5). The $^{87}Sr/^{86}Sr$ ratio increases and decreases rapidly with increasing and decreasing river discharge and reaches a maximum at peak flow and a minimum at low flow. The link between $^{87}Sr/^{86}Sr$ and discharge implies the existence of at least two main reservoirs of particles that control the isotopic signature of the SPM. Such a link has already been shown by Négrel and Dupré (1995) in SPM carried by the Oubangui river in Central Africa, and might also exist for other rivers; however, as few studies have attempted to examine the temporal variation in SPM isotopic signatures, this phenomenon is not yet well known.

Considering the mineralogical phases present in the SPM of the Loire river, the lower $^{87}Sr/^{86}Sr$ ratio may correspond to plagioclase and calcite, while the higher $^{87}Sr/^{86}Sr$ ratio may be related to K-feldspar and clay minerals. Because K-feldspar and calcite are the most variable mineral phases present in relation to the river discharge, it is not unlikely that the fluctuations in the $^{87}Sr/^{86}Sr$ ratio of the SPM are related mostly to changes in the abundance of these two phases. Thus an increase of the $^{87}Sr/^{86}Sr$ ratio with increasing K-feldspar abundance and, conversely, a decrease in the $^{87}Sr/^{86}Sr$ ratio with increasing calcite abundance (see Fig. 6). Furthermore, the relationship between $^{87}Sr/^{86}Sr$ and Rb/Sr ratios (not shown) yields a regression line fitted by the relation $^{87}Sr/^{86}Sr = 0.71083 + 0.0036 Rb/Sr$, with a correlation coefficient of $R = 0.84$. Compared to

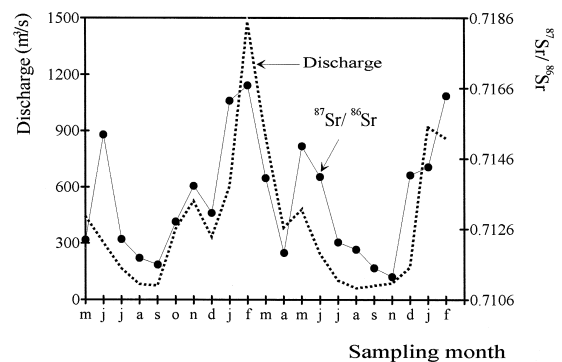


Fig. 5. Fluctuations in $^{87}Sr/^{86}Sr$ and discharge of the Loire river as a function of month of the year.

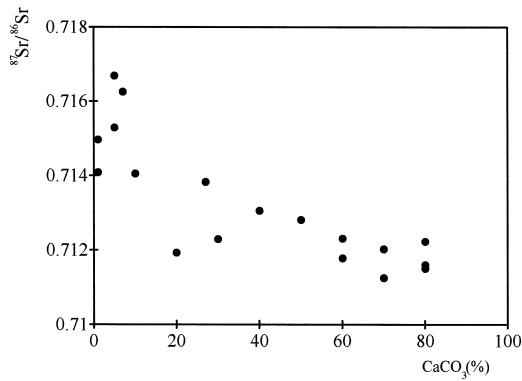


Fig. 6. Relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and calcite abundance in the suspended particulate matter of the Loire river.

Sr, Rb is weakly incorporated into calcite, such that the Rb/Sr ratio of calcite is low, and is abundant in K-feldspar where high Rb/Sr ratios are observed (Faure, 1986). Because the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio fluctuates accordingly to the inverse fluctuation of calcite and K-feldspar with river discharge, the relationship between the $^{87}\text{Sr}/^{86}\text{Sr}$ and Rb/Sr ratios clearly indicates binary mixing between the calcite and K-feldspar end-members.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.71083 could be close to the ratio of the calcite reservoir, which may originate from the mechanical erosion of Jurassic to Oligocene deposits in the ‘Limagne’ (Allier and Loire rivers, before their confluence) and/or from the Jurassic to Cretaceous deposits located between the ‘Limagne’ and the sampling points. As calcite contains strontium whose $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is identical to that of the sea water from which the calcite precipitated (Faure, 1986), the sea-water $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is an indirect indicator of the isotopic signature of the detrital calcite in the SPM. Several investigators have reported systematic variations in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of calcium carbonates and barites from the Jurassic to the Neogene (Clauer, 1981; Elderfield, 1986; Hess et al., 1986; Paytan et al., 1993; Jones et al., 1994) ranging from 0.7069 to 0.7088, but always lower than 0.71083. This implies that the Sr isotopic signature for calcite in the SPM (see Fig. 6) is not only from a detrital source because it includes a component with a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio greater than 0.71083. Our hypothesis is that the relatively high calcite isotopic signature in the Loire SPM reflects a coexistence of

the detrital calcite reservoir with authigenic calcite having a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio close to that of the dissolved load. This is supported (a) by the possible occurrence of calcite precipitation in the lower Loire at the end of the fluvial zone, as suggested by Manickam et al. (1985), and (b) by the calculation of the calcite saturation index for waters of the Loire river (Grosbois et al., in preparation).

Fig. 7 illustrates the relationship between the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the SPM of the upper Loire river (this study) and that of the dissolved load (DL) (Grosbois et al., in preparation). The two ratios are well correlated ($R = 0.66$). The lower ratios in the SPM are close to the lower ratios in the DL, with points for both plots lying close to the 1:1 line. Thereafter, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the SPM increase significantly, whereas the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in DL fluctuate only slightly. Similarities between the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios near the 1:1 line confirm the existence of authigenic calcite in the SPM and imply the considerable abundance of this phase primarily during low river flow. The increase in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the SPM is linked to the corresponding increase in K-feldspar abundance.

4.5. Estimation of solid matter flow

Solid matter flow by suspension reflects the amount of SPM within a hydrological cycle. For this study, the flux Φ , calculated according to Eq. (1)

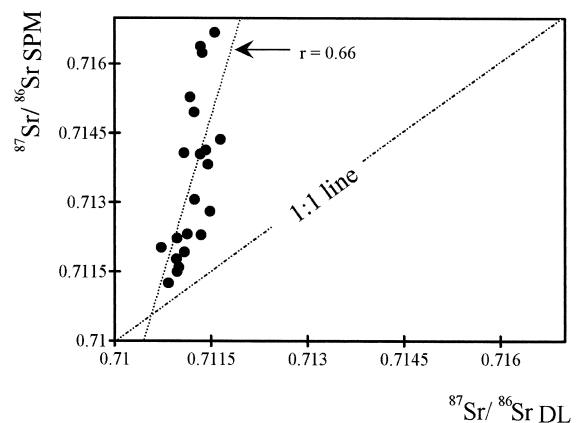


Fig. 7. Relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the suspended particulate matter and of the dissolved load.

following Meybeck (1992), can be converted into an erosion rate when it is extrapolated back to the area of the watershed.

$$\Phi = Q(\Sigma Q_i[\text{SM}]) / (\Sigma Q_i) \quad (1)$$

where Q is the mean discharge over the whole hydrological cycle (m^3/s), Q_i is the daily discharge (m^3/s), $[\text{SM}]$ is the daily SM concentration (mg l^{-1}).

The lower measured flow of solid matter at the Loire river mouth, given by Figueres et al. (1985) and Manickam et al. (1985), ranges from 1.0 to $1.5 \cdot 10^6 \text{ t yr}^{-1}$ and the higher measured flow ranges from $2.7 \cdot 10^6 \text{ t yr}^{-1}$ (given by the Agence de l'eau Loire-Bretagne (personal communication) to $4.6 \cdot 10^6 \text{ t yr}^{-1}$ (given by Négrel, 1997). However, in the study of Négrel (1997), 53% of the flux was related to fluvial sediments, while the remaining 47% was related to particulate matter produced in situ in the estuary; this reduces the solid matter flux calculation to $2.3 \cdot 10^6 \text{ t yr}^{-1}$. Therefore, the specific mechanical erosion rate over the whole Loire watershed ranges from 9 to $23 \text{ t km}^{-2} \text{ yr}^{-1}$. This rate is very low in comparison to other rates observed for large watershed around the world (summarized by Berner and Berner, 1987). With respect to other watersheds in France, this rate is similar to that observed for the Garonne (Probst and Bazerbachi, 1986) and lower than those observed for the Rhône (Jansen et al., 1979).

During the 'daily' survey at Orleans from May 1995 to March 1996, the suspended solid matter flow was $37 \cdot 10^4 \text{ t yr}^{-1}$, resulting in a specific erosion rate of around $9.5 \text{ t km}^{-2} \text{ yr}^{-1}$. At this sampling location, the watershed is composed mainly of silicate terrains (76%). When compared with other major rivers draining silicate areas, such as the Yen and Lena (Berner and Berner, 1987) and the Congo (Olivry et al., 1988), the specific erosion rate of the Loire river is at the same order of magnitude.

The shift in SPM flux between the sampling point ($37 \cdot 10^4 \text{ t yr}^{-1}$) and the mouth of the Loire (range from 1 to $2.7 \cdot 10^6 \text{ t yr}^{-1}$) corresponds to $6.3 \cdot 10^5$ to $2.3 \cdot 10^6 \text{ t yr}^{-1}$, while the variation in the mean annual discharge is around $500 \text{ m}^3 \text{ s}^{-1}$ ($1.6 \cdot 10^{10} \text{ m}^3 \text{ yr}^{-1}$). This variation in discharge corresponds to the input of water from tributaries of the Loire river. The increase in SPM fluxes corresponds to the input

of solid matter by the tributaries of the Loire, as well as to supplementary erosion processes along the river (banks and streambed).

The average SPM concentration transported by the tributaries of the Loire can be calculated using differences in the various reported SPM fluxes (Figueres et al., 1985; Manickam et al., 1985; Négrel, 1997; Agence de l'eau Loire-Bretagne, personal communication) and the river discharge. The lower value obtained from this calculation is 40 mg l^{-1} and the upper value is 146 mg l^{-1} . Observations provided by Manickam et al. (1985) over a complete hydrological cycle give rise to a range of SPM concentrations from 20 to 120 mg l^{-1} , with a mean of $46 \pm 24 \text{ mg l}^{-1}$. Results provided by the Agence de l'eau Loire-Bretagne, personal communication) suggest an average value of 100 mg l^{-1} , whereas an estimate of the input of tributaries corresponds to 50 mg l^{-1} (Agence de l'eau Loire-Bretagne, personal communication). All of these data are in general agreement, with the increase in the SPM flux between the location of our study and the mouth of the river corresponding to mechanical erosion processes within the watershed.

The large increase in SPM fluxes can be related to an increase in the specific erosion rate between the sampling point and the mouth of the river. This increase, by a factor 3 to 7, is due mainly to the drainage of carbonate terrains, which are more sensitive to erosion than silicate terrains. However, these mechanical erosion rates could be overestimated by the existence of authigenic calcite stemming from the chemical dissolution of carbonates.

5. Conclusion

This study reports on the temporal distribution of major- and trace-element concentrations and Sr isotopic ratios in suspended particulate matter transported by the upper Loire river. The sampling site integrates 34% of the total Loire watershed and represents the drainage of the entire igneous and metamorphic basement and 24% of sedimentary formations. Two different experimental surveys were carried out, with measurements of the suspended matter concentration ranging from 3 mg l^{-1} to 100 mg l^{-1} , but showing only a weak link with the rate of river discharge. One hypothesis to explain the

weak of relationship between SPM concentration and discharge rate could be the existence of numerous dams located in the upper basin.

The mineralogy of the suspended matter consists mainly of quartz and K-feldspar during high river flow, with a rise in calcite levels during periods of low river flow. SiO₂, CaO and Fe₂O₃ are the main oxides in the SPM, with larger fluctuations seen in the CaO and Fe₂O₃ concentrations. The concentrations of trace elements, which are present in noticeable quantities, fluctuate extensively. Bed-sediment contents are similar to those in the suspended matter for SiO₂, K₂O and TiO₂, lower for CaO, Fe₂O₃, Zn and Pb, and higher for Zr.

In the suspended matter, fluctuations in elemental concentrations with discharge levels can be related to the fluctuation of the contained mineral assemblages. The concentrations of K, Ti and Rb increase along with the increase in K-feldspar abundance at high flow, whereas the concentrations of Ca and Sr decrease with increasing discharge due to a decrease in calcite abundance.

The Sr isotopic composition fluctuates with the discharge of the river. The ⁸⁷Sr/⁸⁶Sr ratio increases when discharge increases and reaches a maximum corresponding to high flow and vice versa. This relationship implies the existence of at least two reservoirs of particulate matter; one with a high ⁸⁷Sr/⁸⁶Sr ratio and the other with a lower ratio. This fluctuation also reflects variations in mineral assemblages. The ⁸⁷Sr/⁸⁶Sr ratio also increases when both K-feldspar abundance increases and calcite level decreases. This was confirmed by the relationship between the ⁸⁷Sr/⁸⁶Sr and Rb/Sr ratios. However, the ⁸⁷Sr/⁸⁶Sr ratio of the calcite pool, given by the relationship between ⁸⁷Sr/⁸⁶Sr and Rb/Sr, is higher than the signature that can be provided by the detrital calcite reservoir. Moreover, the relationship between the ⁸⁷Sr/⁸⁶Sr ratios in the suspended and dissolved load enables one to postulate the coexistence of authigenic calcite with a ⁸⁷Sr/⁸⁶Sr ratio similar to that of the dissolved load.

The solid matter flow by suspension enabled a specific mechanical erosion rate to be calculated for the entire Loire watershed, which ranged from 9 to 23 t km⁻² yr⁻¹. During the survey at Orleans, the solid suspended matter flow of the Loire river by suspension was 37 · 10⁴ t yr⁻¹, giving a specific

erosion rate of around 9.5 t km⁻² yr⁻¹. The shift in SPM flux between the sampling point at Orleans and the mouth of the Loire river, together the divergence in the mean annual discharge rate, allowed the input of solid matter by the tributaries of the Loire river and supplementary erosion processes along the river (banks and streambed) to be calculated. The lower value obtained by this calculation was 40 mg l⁻¹, and the upper limit corresponded to 146 mg l⁻¹. The large increase in SPM fluxes can be related to an increase in the specific erosion rate between the sampling point and the mouth of the river. This increase, by a factor 3 to 7, is due mainly to the drainage of carbonate terrains, which are more sensitive to weathering than silicated terrains.

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