



An Overview of Dissolved and Suspended Matter Fluxes in the Loire River Basin: Natural and Anthropogenic Inputs

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Abstract. The spatial and temporal distributions of major elements were investigated in the surface waters and in associated suspended matter at two sites of the upper Loire basin (Orleans and Brehemont) between 1995 and 1998.

According to geochemical and isotopic patterns, the dissolved load appears to result from a process of mixing rainwater inputs, weathering processes of carbonate and silicate bedrock, and agricultural and urban inputs. Natural inputs influence 60% of water chemical composition at both sites. Annual dissolved fluxes were estimated to be $1300 \cdot 10^3$ t/y at Orleans and $1620 \cdot 10^3$ t/y at Brehemont. Major elements are transported mainly in the dissolved fraction. After correcting for atmospheric and anthropogenic inputs, the silicate specific export rate was calculated to be 11 t/y/km^2 throughout the basin and the carbonate specific export rate to be from 47 t/y/km^2 at Orleans to 23 t/y/km^2 at Brehemont.

The suspended load appears to result from at least two particle reservoirs: a silicate reservoir and a carbonate reservoir. The silicate reservoir has a detrital origin, mainly during periods of high flow, while the carbonate reservoir has a detrital origin during periods of high flow and an authigenic origin during periods of low flow. Of the total annual flow of suspended matter, this authigenic material represents 16% at Orleans, 25% at Brehemont and 37% in the fluvial part of the estuary. After correcting authigenic inputs, the specific export rate due to mechanical weathering was estimated to be 8 t/y/km^2 throughout the Loire basin.

Key words: anthropogenic inputs, authigenic calcite, dissolved load, flux calculation, Loire River, natural inputs, suspended matter

1. Introduction

Chemical weathering supplies the dissolved load to the rivers whereas mechanical erosion supplies the solid load. The products of both chemical and mechanical alteration are transported by rivers from continents to oceans. The total fluxes,

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carried by the largest rivers in the world, are estimated to be $5.6 \cdot 10^9$ t/y of dissolved substances (Martin and Meybeck, 1979) and range from $15.5 \cdot 10^9$ t/y (Martin and Meybeck, 1979) to $20 \cdot 10^9$ t/y (Milliman and Syvitski, 1992) of suspended matter. Major river basins have been individually studied to estimate weathering and mechanical erosion rates (Reeder et al., 1972; Stallard and Edmond, 1983; Meybeck, 1979, 1987; Zhang et al., 1990; Négrel et al., 1993; Gaillardet et al., 1995). Only natural inputs should be considered in calculating the weathering and mechanical erosion rates. The contributions of human activities such as industries, agriculture and domestic inputs, become more and more significant in the chemical composition of the dissolved load (Van Der Weidjen and Middelburg, 1989; Dojlido and Best, 1993; Thibert, 1994; Berner and Berner, 1987; Meybeck, 1998; Roy et al., 1999). The particulate load may also contain secondary mineral phases and authigenic minerals, and its spatial distribution may be influenced by the presence of dams, deforestation and the cultivation of lands (Milliman and Meade, 1983; Collier et al., 1996).

The aim of this study was to identify and to quantify the different inputs to the dissolved and particulate loads, to describe the spatial evolution of weathering and mechanical erosion rates of the Loire river basin in order to calculate annual natural and anthropogenic fluxes. A first sampling site, located in the middle of the basin, has already been described in Négrel and Grosbois (1999) and in Grosbois et al. (2000). For the purpose of this study, another systematic sampling of waters and suspended matter has been performed to characterise temporal fluctuations over the whole basin.

2. The Loire Basin Characteristics

The Loire river basin (1010 km long, $117,800 \text{ km}^2$) is composed of three parts: the upper basin that includes the Allier and Loire rivers from their sources in the Massif Central to Nevers; the middle basin that includes the Cher, the Indre and the Vienne tributaries from Nevers to the Maine confluence; and the lower Loire that includes the Maine river to the estuary (Figure 1). Detailed descriptions can be found in Négrel and Grosbois (1999) and in Grosbois et al. (2000). In the upper basin, bedrock composition encompasses older plutonic rocks (granite, gneiss and mica schist, from 500 to 300 My) superimposed by a volcanic area, together representing 46% of the basin surface (28120 km^2 , BRGM, 1996). In the middle basin, the Loire River drains the sedimentary series of the Parisian Basin (from 200 to 6 My), while in the lower basin, the Loire River drains the granite basement of the Massif Armoricaïn.

The Loire River discharge presents a number of variations during each hydrological cycle and across all hydrological cycles (Figure 2). The mean 1990–1993 interannual discharge varies between $180 \text{ m}^3/\text{s}$ below the Allier–Loire junction to $870 \text{ m}^3/\text{s}$ just before the estuary (RNDE, 1994) and carries one of the principal European riverine inputs to the Atlantic ocean.

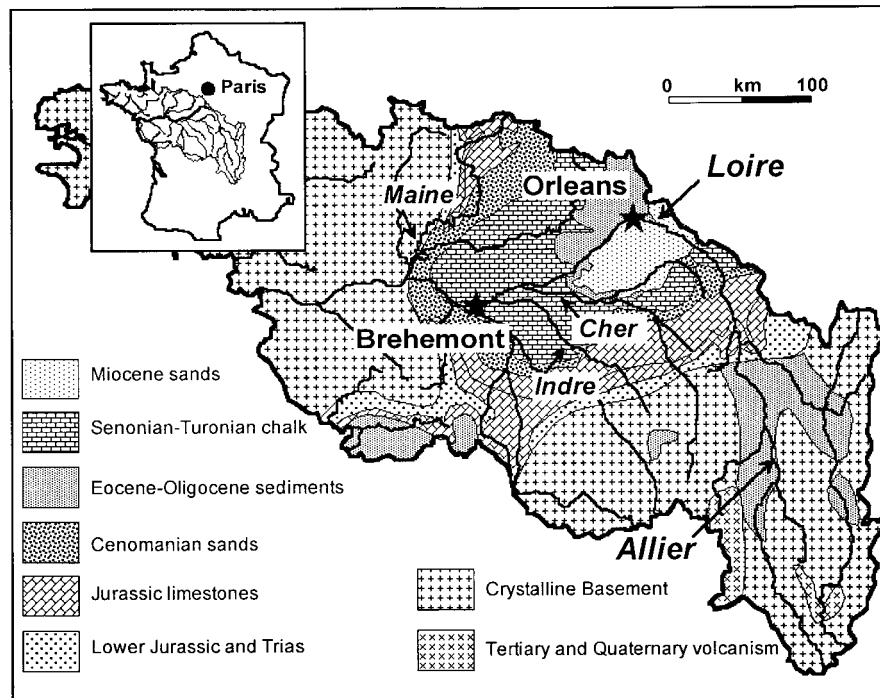


Figure 1. General location map of the Loire River basin and location of the sampling points.

3. Sampling Sites and Analytical Methods

Two sampling sites are located in the middle part of the basin. The first sampling point, located at Orleans (37,000 km², 31% of the basin surface) was studied between 1994 and 1996. The geochemistry of the dissolved load was presented in Grosbois et al (2000), that of suspended load in Négrel and Grosbois (1999) and Négrel et al. (2000). The second sampling site is located 150 km downstream from Orleans, at Brehemont, about 10 km after the confluence of the Cher and the Loire rivers. At this site, 56,600 km² and 53% of the basin are considered that include 50% of carbonates and 50% of silicates. The sampling frequency at Brehemont was bimonthly during the 1996–1998 survey and weekly or daily during each flood of the river.

The water and suspended matter sampling methods that were applied at Orleans are described in Négrel and Grosbois (1999) and in Grosbois et al. (2000). At Brehemont, all waters were collected in the middle of the main channel at mid depth, using Nalgene bottles and filtered through 0.45 μm cellulose acetate filters using a precleaned Nalgene filter apparatus. For each sample, electrical conductivity, pH and water temperature were measured using a microprocessor conductivity meter WTW LF96 standardised to 20 °C and calibrated beforehand using standard buffers. For the suspended matter study, about 130 litres of water were collected

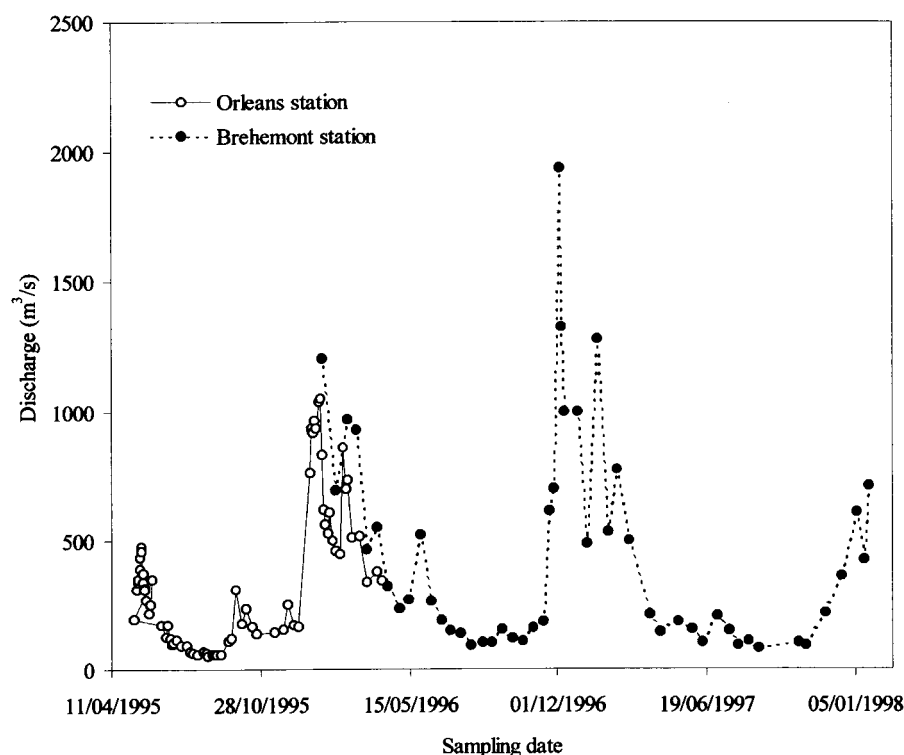


Figure 2. Fluctuations of the discharge during the sampling period at Orleans (open circles) and at Brehemont (filled circles).

in precleaned polypropylene containers. The samples were left to settle for several days and only the bottom 70 litres were centrifuged. The masses of total suspended matter (in $\text{mg}\cdot\text{l}^{-1}$) were determined by the differences in weight between dried filters before and after the filtration of 10 litres of water through the $0.45\ \mu\text{m}$ acetate cellulose membranes.

Chemical analyses of the dissolved load were performed by ion chromatography for major elements, by colorimetry for Si, and by HCl titration and Gran's method for alkalinity. Analytical accuracy, measured at better than 5%, was monitored by the repeated analysis of a fixed sample that had been collected during the flood of 1996. The strontium isotopic composition ($^{87}\text{Sr}/^{86}\text{Sr}$) and Sr contents were determined on six samples. Chemical separation and mass spectrometric procedures for strontium isotopic measurements, ICP-MS procedure for Sr content determination follow the standard method used at BRGM and are described in Négrel and Deschamps (1996), Négrel and Grosbois (1999) and Grosbois et al. (2000). The reproducibility of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio measurements was tested through duplicate analyses of the NBS 987 standard, and the mean value appears to be close to $0.710248 \pm 25 \cdot 10^{-6}$ (2σ , $n = 25$). The determination of major elements in the suspended matter (SPM) was performed by X-ray fluorescence energy dispersive

spectrometer (Négre and Deschamps, 1996, Négre, 1997b). Two certified reference materials (GBW 07311, GBW 07306) were analysed to verify the calibration. Precision of measurements ranged between 2% and 10%.

The determination of mineral phases follows the procedure described in Négre and Grosbois (1999). Suspended matter samples were homogenised by hand-crushing with an agate mortar and 5 mg of the crushed powder were mixed with 3 ml of distilled water and placed on glass slides. These suspensions were dried in air for 3 hours and a preparation of non-oriented particles was obtained. The mineralogical composition of the SPM sample was determined by X-ray diffraction using a Rigaku analyser, Cu-K α ray and two-angstrom slits with a Ni-K β filter. Qualitative mineralogical analyses were carried out by identifying diffraction spectra. Semi-quantitative percentages 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.

4. The Dissolved Load in the Loire River

4.1. MASTER VARIABLES

Ninety-two water samples were collected between May 1994 and July 1996 at Orleans and sixty-eight samples between January 1996 and January 1998 at Brehemont.

During the sampling periods at Brehemont (Table I), the water temperature decreased by a factor of 21 (from 29.6 °C in August 1997 to 1.4 °C in January 1997). By comparison, the range at Orleans is from 27.6 °C in July 1995 to 1.8 °C in February 1996 (factor of 15). The pH of the river water presented wide variations according to season, ranging from 6.47 in January 1996 to 8.28 in May 1995 at Orleans with an annual averaged pH of 7.4 ± 0.7 (Grosbois et al., 2000). At Brehemont (Table I), the pH of the water ranged from 5.98 in November 1996 to 9.83 in May 1997 with an annual averaged pH of 8.4 ± 0.9 .

The total dissolved salts (TDS) ranged from 136 mg/l to 241 mg/l with an annual average equal to 182 ± 25 mg/l at Orleans (Grosbois et al., 2000). At Brehemont, the TDS ranged from 140 mg/l in December 1996 to 291 mg/l in November 1996 with an annual average equal to 197 ± 39 mg/l. It is noteworthy that all geochemical parameters are on the same order of magnitude at the two sampling stations.

4.2. MAJOR ELEMENT CHEMISTRY IN THE LOIRE DISSOLVED LOAD

4.2.1. *Fluctuations of Concentrations*

Major element concentrations are on the same order of magnitude at Orleans and at Brehemont with the exception of chloride (for Orleans station, Grosbois et al., 2000; Table I for Brehemont). Chloride concentrations are 30% higher at Brehemont (annual average = 533 ± 134 μ mole/l) than at Orleans (annual av-

Table 1. Master variables: discharge W (m^3/s), temperature T ($^{\circ}C$), pH, electrical conductivity C ($\mu S/cm$), suspended matter SM (mg/l), suspended matter SM (mg/l). Concentration of dissolved major elements ($\mu mol/l$) in the Loire River at Brehement. n.d.refers to non determined values.

Sample name	Date	W m^3/s	T $^{\circ}C$	pH	C $\mu S/cm$	SM mg/l	HCO ₃ $\mu mol/l$	Cl $\mu mol/l$	SO ₄ $\mu mol/l$	NO ₃ $\mu mol/l$	P $\mu mol/l$	Ca $\mu mol/l$	K $\mu mol/l$	Na $\mu mol/l$	Mg $\mu mol/l$	Si
0186-Loire	01/18/96	1204	6.3	6.74	274	n.d	1462	390	169	257	2.2	918	77	341	156	123
0366-Loire	02/06/96	693	3.8	7.27	310	n.d	1620	355	171	226	2.5	1093	80	381	180	115
0526-Loire	02/21/96	968	2.7	7.29	266	n.d	1487	401	155	237	2.0	978	71	352	155	113
0646-Loire	03/04/96	930	6.8	7.06	296	37	1351	407	142	213	2.1	871	74	397	158	114
0786-Loire	03/18/96	462	9.1	7.92	340	10	1824	445	168	245	2.0	1202	87	483	201	114
0926-Loire	04/02/96	551	8.9	8.07	296	19	1548	450	172	200	1.5	767	67	463	156	n.d
1076-Loire	04/16/96	321	15.5	9.34	271	30	1649	443	182	156	3.1	895	79	457	182	75
1206-Loire	05/02/96	237	15.5	9.21	n.d	35	1346	487	190	111	0.0	688	81	504	190	1
1356-Loire	05/14/96	270	13.3	8.49	n.d	58	1557	462	191	109	0.0	801	83	541	222	25
1506-Loire	05/29/96	522	19.1	8.26	239	35	1500	367	166	129	1.4	728	83	440	163	176
1646-Loire	06/12/96	262	25.9	9.35	253	30	1757	408	175	85	0.9	844	95	468	173	145
1796-Loire	06/27/96	191	19.4	9.22	233	31	1148	535	220	21	0.1	586	90	629	198	77
1916-Loire	07/09/96	150	20.1	8.92	264	55	1450	580	228	63	0.6	673	97	668	238	102
2056-Loire	07/23/96	137	25.4	9.61	242	17	1263	552	215	38	0.1	564	102	666	178	196
2196-Loire	08/06/96	92	23.2	8.95	279	28	1937	750	223	47	0.1	756	130	788	238	130
2356-Loire	08/22/96	102	24.5	9.28	260	42	1426	586	198	13	0.1	642	111	712	274	122
2476-Loire	09/03/96	101	18.3	9.18	254	44	1400	621	203	39	0.0	783	122	915	305	83
2616-Loire	09/17/96	153	17.8	9.20	286	64	1497	686	237	17	0.4	755	113	976	258	34
2766-Loire	10/02/96	120	14.9	8.51	310	45	1743	643	227	62	0.3	802	100	652	267	33
2906-Loire	10/16/96	108	15.6	9.12	290	51	1467	652	233	67	0.3	776	109	890	254	2
3036-Loire	10/29/96	161	14.0	9.12	319	39	1852	589	222	64	0.3	914	97	717	211	52
3186-Loire	11/13/96	184	10.8	8.40	377	36	2424	762	275	143	2.4	1363	99	731	207	96
3256-Loire	11/21/96	611	6.9	7.55	229	108	1251	378	190	179	2.5	730	99	405	157	n.d
3326-Loire	11/27/96	701	5.6	5.98	223	46	1209	430	208	200	0.0	777	95	453	163	212
3396-Loire	12/04/96	1940	7.7	7.03	201	110	1007	347	148	242	2.0	645	88	289	132	n.d

Table I. Continued.

Sample name	Date	W m ³ /s	T °C	pH	C mg/l	SM μmol/l	HCO ₃ ⁻ μmol/l	Cl μmol/l	SO ₄ ²⁻ μmol/l	NO ₃ ⁻ μmol/l	P μmol/l	Ca μmol/l	K μmol/l	Na μmol/l	Mg μmol/l	Si
3426-Loire	12/07/96	1324	7.7	8.13	242	32	924	619	165	247	2.4	723	87	306	136	n.d.
3456-Loire	12/10/96	1000	5.4	7.67	333	21	1019	656	205	318	2.7	823	93	319	155	n.d.
3636-Loire	12/29/96	999	1.9	8.24	216	57	1061	344	142	179	2.0	629	71	310	142	195
0097-Loire	01/09/97	489	1.4	8.00	244	11	1505	419	172	240	2.5	873	112	511	246	229
0247-Loire	01/24/97	1276	6.0	n.d.	233	59	1286	437	172	248	2.2	822	87	419	180	215
0397-Loire	02/06/97	534	6.3	n.d.	277	20	1735	453	189	277	2.3	1031	80	471	196	n.d.
0507-Loire	02/19/97	773	8.8	7.55	253	37	1209	427	191	251	2.5	959	84	425	183	n.d.
0667-Loire	03/07/97	499	13.2	8.21	277	17	1450	427	191	253	2.2	1099	81	509	180	n.d.
0937-Loire	04/03/97	212	16.3	9.15	285	n.d.	2071	573	245	226	0.4	1052	92	754	206	1
1077-Loire	04/18/97	144	14.2	7.81	314	3	2138	648	262	200	0.4	n.d.	n.d.	n.d.	n.d.	n.d.
1327-Loire	05/12/97	185	14.7	8.76	297	n.d.	2108	695	258	138	0.2	1075	116	731	219	36
1497-Loire	05/29/97	154	21.9	9.83	239	36	1899	550	227	81	0.2	818	103	762	189	n.d.
1647-Loire	06/13/97	104	21.7	8.76	277	32	1580	686	236	54	0.3	903	108	853	209	130
1857-Loire	07/03/97	205	17.9	8.41	301	43	2050	571	207	122	0.8	1161	95	705	201	66
1997-Loire	07/18/97	151	22.8	8.43	242	46	1373	572	213	32	0.2	726	103	769	203	78
2127-Loire	07/31/97	93	23.1	8.86	290	29	1511	646	212	26	0.3	774	146	867	274	79
2267-Loire	08/14/97	109	29.6	9.30	287	47	1359	n.d.	n.d.	n.d.	0.2	730	115	898	228	61
2397-Loire	08/27/97	83	23.2	8.81	295	12	1462	979	280	0	0.1	688	122	963	242	69
2937-Loire	10/20/97	105	15.6	8.71	330	31	1833	677	240	70	0.5	957	153	1028	303	6
3037-Loire	10/30/97	92	7.3	9.07	402	n.d.	2465	n.d.	n.d.	n.d.	0.9	1384	156	1018	304	95
3297-Loire	11/25/97	216	9.0	8.22	376	25	2177	546	228	203	3.0	1284	148	785	261	136
3527-Loire	12/18/97	362	5.5	8.00	322	n.d.	1723	490	195	240	2.3	1149	136	696	231	143
0068-Loire	01/06/98	605	7.8	7.89	307	94	1578	599	250	368	2.9	1079	124	597	228	143
0178-Loire	01/17/98	427	7.7	7.86	332	19	1745	472	197	315	2.7	1223	118	597	233	171
0238-Loire	01/23/98	710	3.9	7.86	216	55	1030	360	122	195	2.0	726	93	283	123	178

erage = $380 \pm 74 \mu\text{mole/l}$). Calcium and bicarbonate are the main dissolved species in the Loire River waters. Calcium species represent between 10% and 30% of the TDS, and bicarbonate species between 40% and 70% of the TDS, depending on season. Bicarbonates are twice as concentrated as calcium, in agreement with weathered carbonate lithologies (Buffle and De Vitre, 1994). Moreover, Brehemont, the most downstream station, presents a larger variations in the dissolved major element concentrations.

Three types of relationship are observed between chemical concentrations and discharge at Brehemont (Figure 3) as was shown at Orleans (Grosbois et al., 2000).

1. the first type of relationship is observed for nitrates (Figure 3), silica and phosphates. Their concentrations increase with increasing discharge and they remain consistent during the winter season when the discharge is higher than $1000 \text{ m}^3/\text{s}$.
2. the second type of relationship is observed for most of the major elements (Na^+ , K^+ , Mg^{2+} , SO_4^{2-} and Cl^-). As illustrated for Cl in Figure 3, the highest concentrations occur during the low flow of summertime. Then, their concentrations decrease as flow increases, becoming consistently low when the discharge is above $600 \text{ m}^3/\text{s}$.
3. the third type of relationship is only observed for HCO_3^- and Ca^{2+} (Figure 3). When the discharge is around $300 \text{ m}^3/\text{s}$, HCO_3^- and Ca^{2+} concentrations reach a maximum level. When the discharge is above $300 \text{ m}^3/\text{s}$, concentrations decrease as flow increases while when the discharge is below $300 \text{ m}^3/\text{s}$, concentrations decrease sharply. At the end of the summer, dissolved HCO_3^- and Ca^{2+} concentrations are as low as in winter.

4.2.2. *Characterisation of the Different End-members*

As previously described at Orleans station in Grosbois et al. (2000), these three geochemical behaviours may result of mixing process, involving at least two geochemical signatures. The first signature appears during the low flow of the summer and is very concentrated in cations, SO_4^{2-} and HCO_3^- and lower concentrated in silica, nitrates and phosphates. The second signature appears during the high flow of the winter. It is characterised by low concentrations of cations, SO_4^{2-} and HCO_3^- and high concentrations of silica, nitrates and phosphates. However, as stated by Grosbois et al. (2000), each geochemical signature must be related to several end-members.

At Orleans, the use of the Sr isotopic composition (Grosbois, 1998; Grosbois et al., 2000) allow to identify the different end-members. Figure 4 illustrates the repartition of the data in a classical $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $1/\text{Sr}$ contents diagram for the Loire river at Orleans (Grosbois et al., 2000) and at Brehemont (Table II). The Sr isotopic composition and Sr contents at Brehemont correlates well with that measured at Orleans and all data are scattered between the 5 end-members which are rain waters, silicate weathering, carbonate weathering, agricultural inputs and urban inputs. For this latter, Grosbois et al. (2000) evidenced a similar $^{87}\text{Sr}/^{86}\text{Sr}$ ra-

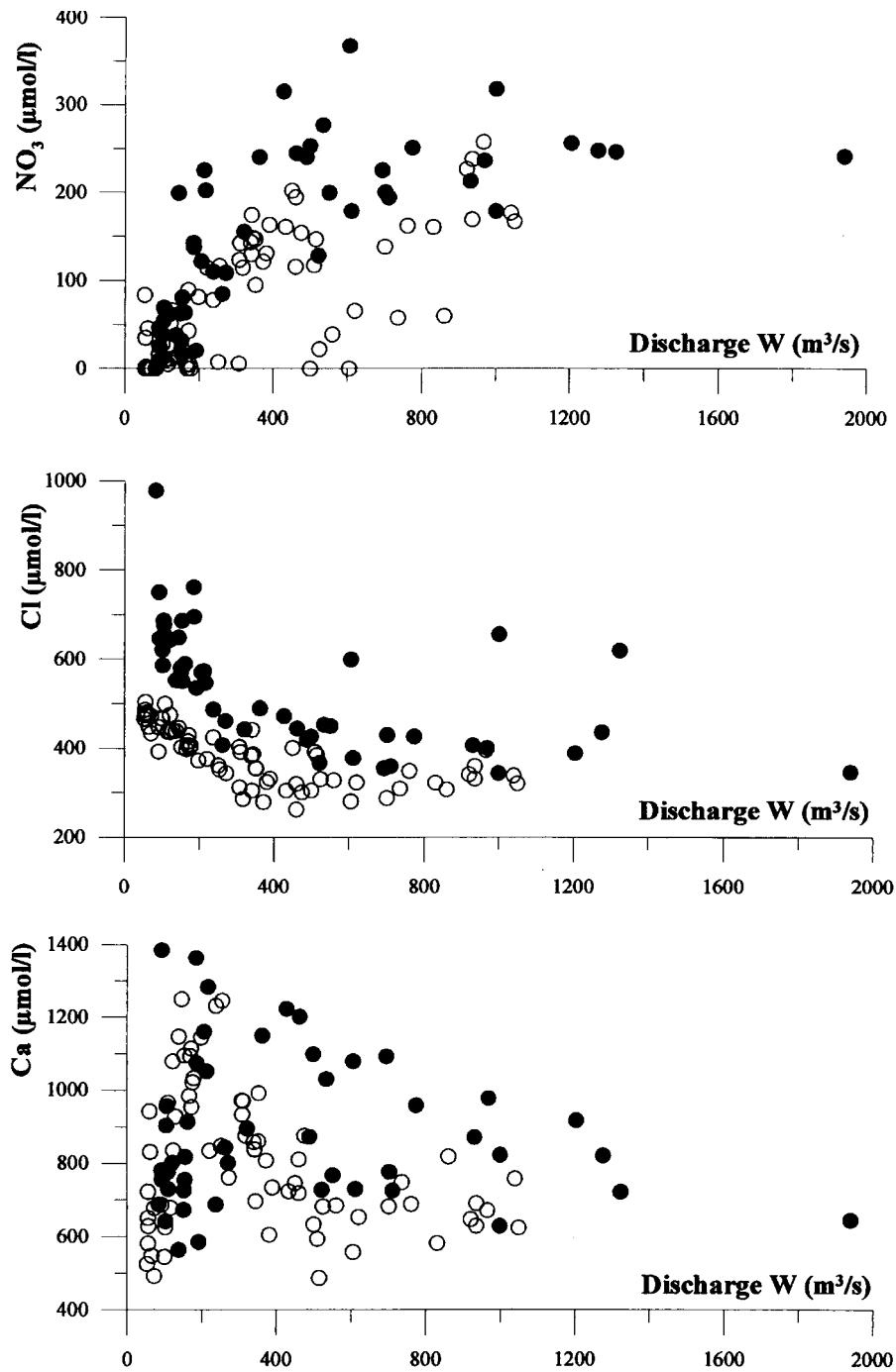


Figure 3. Evolution of element concentrations (nitrate, chloride and calcium) with discharge in the dissolved load (Symbols are identical to those in Figure 2).

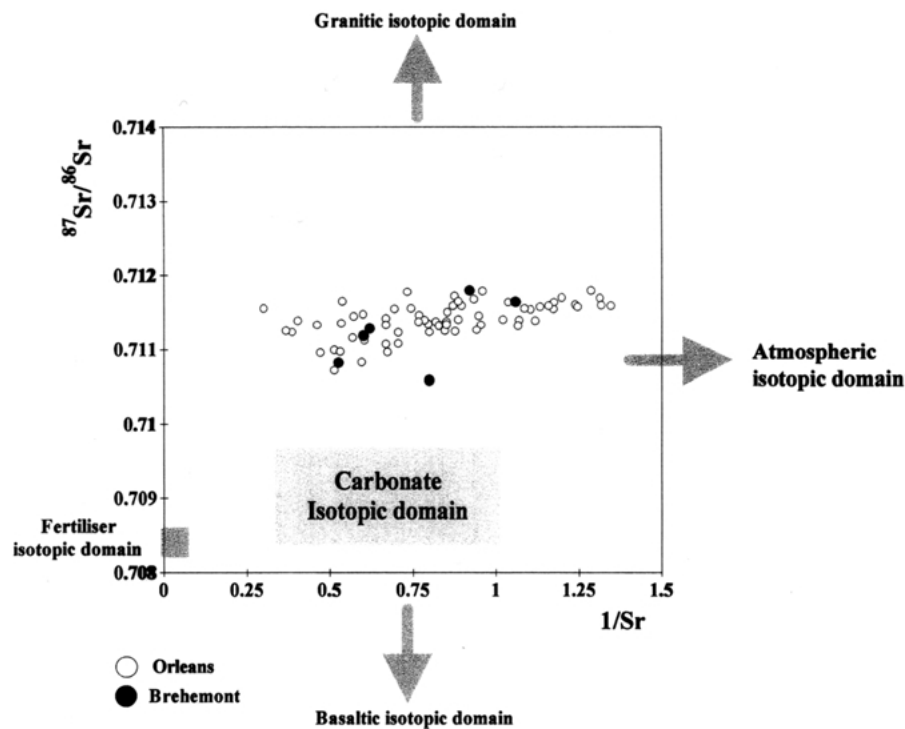


Figure 4. Relationship between the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the dissolved load and the $1/\text{Sr}$ ratio at Orleans (open circles) and at Brehemont (filled circles). Arrows indicate the isotopic and chemical domains of the dissolved load in waters from small watersheds: granitic (Négrel, 1999), basaltic (Négrel and Deschamps, 1996; Négrel, 1997a) and atmospheric domain (i.e., rainwater, Négrel and Roy, 1998) The fertilisers domain (Négrel and Deschamps, 1996) and carbonate watershed domain (Grosbois et al., 2000) and were also indicated.

tio than that of the Loire river, mainly because urban waters originate mainly from pumping of the Loire groundwaters and treatment do not modify the Sr isotopic composition.

The same geochemical patterns and Sr isotopic signature observed at Orleans (Grosbois et al., 2000) and Brehemont (this study) implies that these five end-members can be considered at Brehemont to explain the two geochemical signatures. Inputs from rainwaters and bedrock weathering may be present mainly during the periods of high flow due to the oceanic weather and large runoff, respectively. These inputs can explain the low cations, chlorides and sulfates concentrations, and high silica concentrations in the high flow signature. Moreover, agricultural disturbance (fertilisers application, lack of nutrient, consumption by algae during winter ...) have to be considered during the high flow to explain the high concentrations of nitrates and phosphates.

On the other hand, during the low flow, mainly carbonate (ground or surface water) and sewage water inputs could explain the high concentrations of cations

Table II. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr concentration ($\mu\text{mol/l}$) in selected samples from the Loire River at Brehemont.

Sample name	Date	Sr $\mu\text{mol/l}$	$^{87}\text{Sr}/^{86}\text{Sr}$
1076-Loire	04/16/96	1.25	0.710582
1206-Loire	05/02/96	1.61	0.711286
2056-Loire	07/23/96	1.66	0.711186
2906-Loire	10/16/96	1.90	0.710823
3326-Loire	11/27/96	1.09	0.711793
3636-Loire	12/29/96	0.95	0.711645

and sulfates. Low silica concentrations could be explained by the diatom bloom occurring during this period whereas the low nitrates and phosphates concentrations could be related both to algae consumption and to the non bioavailability of these chemical species in soils.

However, an additional process is needed to explain HCO_3^- and Ca^{2+} behaviour. As previously revealed at Orleans (Négre and Grosbois, 1999; Négre et al., 2000), an authigenic component (i.e., an authigenic calcite mechanism during the low flow) might have a direct impact on dissolved calcium and carbonate species. We will focus on this mechanism in the section dedicated to the geochemistry of the suspended matter.

4.3. THE DISSOLVED FLOW IN THE LOIRE RIVER BASIN

4.3.1. *The End-member Chemical Compositions*

In order to evaluate end-member contributions to the chemical composition of the Loire River waters throughout hydrological cycles, the end-member chemical compositions need to be constrained. At Orleans, they have been characterised by plotting major elements, corrected from atmospheric inputs, against residual chloride concentrations. The method for atmospheric inputs correction follows Meybeck (1979, 1983) and was described precisely in Grosbois et al. (2000). The residual chloride, when salty rocks are not present in the watershed, is seen to be due only to punctual and diffusive pollution sources in the basin (Négre and Deschamps, 1996; Négre, 1999; Grosbois et al., 2000). At Brehemont, the correction of atmospheric inputs was performed (Grosbois, 1998) and Figure 5 illustrates the relationships in corrected Ca and SO_4 vs. residual Cl.

To constrain the chemical composition of the silicate end-member, three small watersheds in the upper part of the Loire River basin were used (Négre and Deschamps, 1996; Négre, 1997a, 1999). They drain granitic and basaltic bedrocks

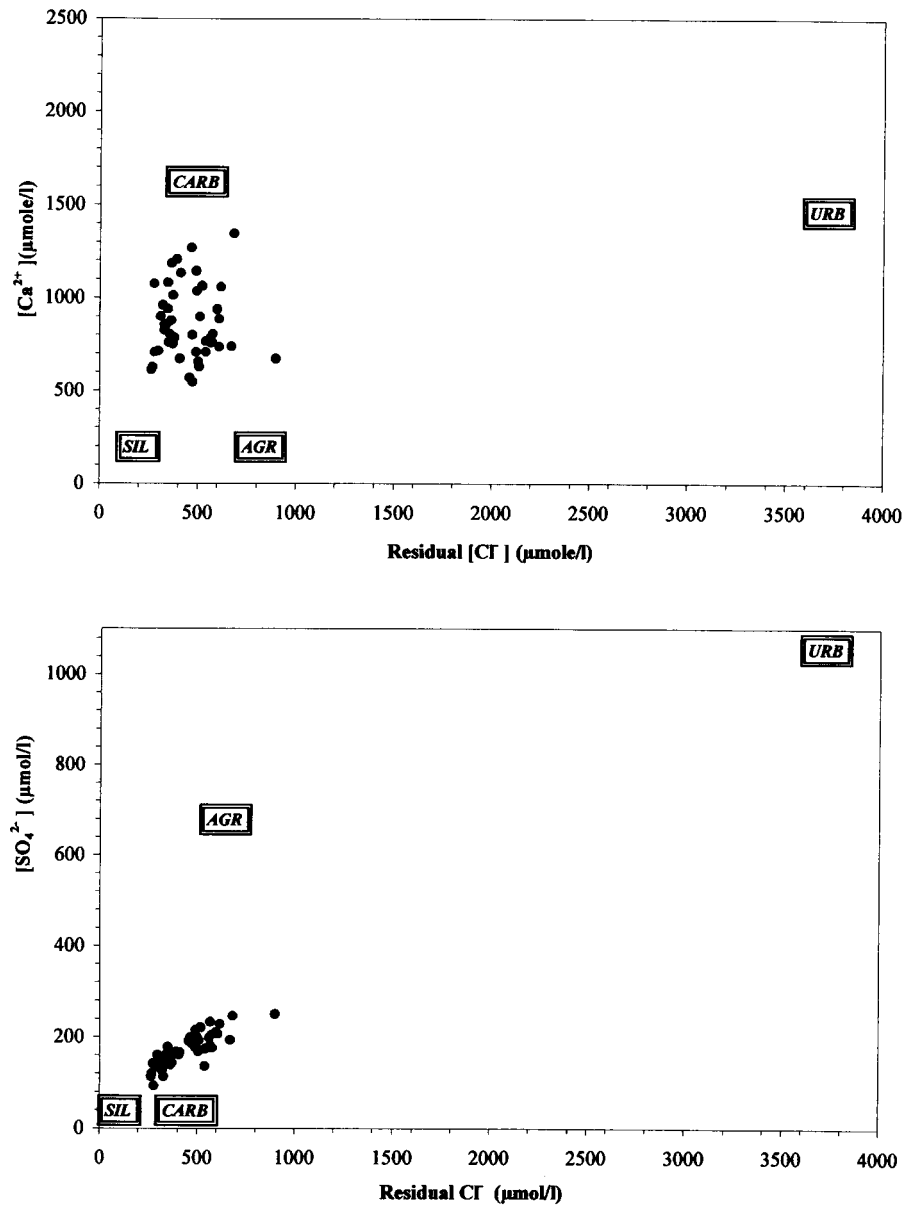


Figure 5. Relationships between residual chloride and Ca and SO₄ in the dissolved load of the Loire River at Brehemont and waters from small watersheds. SIL represents the silicate end-member (Négre and Deschamps, 1996; Négre, 1997a, 1999), CAR the carbonate end-member (black cross, Meybeck, 1986; Grosbois, 1998) URB the urban end-member (open and filled triangles, open and filled squares, this study and Grosbois et al., 2000) and AGR the agricultural end-member (this study, Négre and Deschamps, 1996; Oubelkasse and Grimaud, 1997; Oubelkasse, 1998; Négre and Roy, 1998; Grosbois et al., 2000). Calculation procedure is in annexe.

Table III. Chemical composition of the silicate (Négre and Deschamps, 1996; Négre, 1997a, 1999), carbonate (Meybeck, 1986; Grosbois, 1998), agricultural (this study, Négre and Deschamps, 1996; Oubelkasse and Grimaud, 1997; Oubelkasse, 1998; Négre and Roy, 1998; Grosbois et al., 2000) and urban (this study and Grosbois et al., 2000) end-members at Orleans and Brehemont (in $\mu\text{mol/l}$). n.d.refers to non determined values.

	Urban		Agricultural		Silicate	Carbonate	
	Orleans	Brehemont	Orleans	Brehemont		Orleans	Brehemont
Cl^-	1100	3700	500	880	100	300	500
SO_4^{2-}	n.d.	1100	n.d.	660	n.d.	n.d.	10
NO_3^-	n.d.	600	n.d.	500	n.d.	n.d.	10
HCO_3^-	100	10	100	10	200	4000	3000
Ca^{2+}	2500	1500	500	10	70	2000	1500
Na^+	750	4000	1200	1200	60	20	20
Mg^{2+}	250	450	500	400	75	100	100
K^+	300	300	75	150	35	125	120

and the composition of this end-member, summarised in Table III and in Figure 5, shows very low amounts in comparison with other end-members.

The chemical composition of the carbonate end-member (Table III), was determined by using data from unpolluted rivers draining carbonate rocks (Meybeck, 1986) and the data from groundwater in carbonate aquifers (provided by the *Environment Department* of Tours, in Grosbois, 1998). The carbonate end-member summarised in Table III and in Figure 5 shows the highest concentrations of calcium and bicarbonates and the lowest concentrations of sodium and potassium.

The chemistry of the urban end-member was estimated with Orleans and Tours sewage station surveys (Grosbois, 1998). Sewage waters are processed to remove nitrogen and phosphorus and they are 3 to 4 times more concentrated than the Loire River waters (Table I). The urban end-member shows the highest concentration in chlorides, sulphates and sodium (Table III and Figure 5). It is noteworthy that the chemistry of carbonate groundwater is close to the chemical composition of sewage waters and may already be influenced by anthropogenic inputs.

The agricultural end-member is the most difficult to appreciate because agricultural activities are diffusive and seasonally effective. The study of the Negron River basin (Oubelkasse and Grimaud, 1997; Oubelkasse, 1998) and the chemistry of fertilisers (Négre and Deschamps, 1996; Négre and Roy, 1998) were used to determine the composition of the agricultural end-member. While it shows high concentrations of sulphates, nitrates, sodium and magnesium (Table III), it is still less concentrated than the urban end-member.

The chemical composition of each end-member, defined previously at Orleans (Grosbois et al., 2000), was compared to the ones determined at Brehemont (Table III). Because of same geological features, the chemical composition of silicate

end-member is similar at both sites whereas that of carbonate end-member differs slightly. The agricultural end-member is similar, with the exception of chloride, calcium and bicarbonate species. This may be due to the use of different fertilisers or/and crops. The urban end-member is particularly different for chloride, sodium and calcium. The different possible urban sources studied at Brehemont show that the urban end-member can vary widely, certainly depending on several parameters like number of inhabitants, etc.

Each end-member may present spatial and temporal variations in its chemical composition because of local inputs, but potential fluctuations are not easily evaluated. They concern mainly the agricultural end-member composition because of the seasonal use of fertilisers. Temporal variations are less important for the urban end-member because of the constancy of sewage water composition (Grosbois, 1998). From these observations, and according to Grosbois et al. (2000), the assumption was made that the end-member chemical composition held constant during a hydrological cycle and therefore fluxes of each end-member were calculated only during low and high flows.

4.3.2. *Dissolved Fluxes at Brehemont*

By using the mass balance equations, the contributions of the different end-members are calculated in each water sample for each chemical specie (see Annexe).

At Brehemont, the annual dissolved flux is equal to $1620 \cdot 10^3$ t/y during 1996–1997 (Table IV). The weathering of carbonate bedrock provided the highest dissolved flux, which represents 41% of the total annual dissolved flux. However, authigenic calcite formation, as evidenced during the summertime in the Loire river (Grosbois, 1998; Négrel and Grosbois, 1999; Grosbois et al., 2000), removes dissolved calcium and bicarbonate from the dissolved load and may contribute to an underestimation of the carbonate contribution during the summer period. It is noteworthy that the carbonate flux increases by 12% at Orleans and by 17% at Brehemont when solid authigenic carbonate fluxes are added to dissolved carbonate fluxes (see §5.2).

The other natural dissolved flux due to weathering of silicate bedrock represents 20% of the total annual dissolved flux. The silicate flux is half the carbonate flux. The resistance of silicate bedrock against chemical weathering may explain this.

The two anthropogenic fluxes together represent 39% of the total dissolved flux of the Loire River at Brehemont. The agricultural flux is always higher than the urban one (up to 20%) throughout the hydrological cycle. At the beginning of the high flow in winter, the agricultural flux is very high because of chemical specie mobilisation from fertilisers not used by plants during the summertime and not yet trapped in the soil structure. During the summer, agricultural and urban daily fluxes are similar.

Table IV. Results of the Loire river dissolved fluxes calculation for each end-member (a) at Orleans and (b) at Brehemont. See text and Annexe for procedure calculation.

Orleans	Urban flux	Agricultural flux	Silicate flux	Carbonate flux	Number of days
Low flow 95/96 (t/d)	213	567	483	676	217
High flow 95/96 (t/d)	434	1891	1736	1927	147
Annual flux (t/y)	110 10 ³	401 10 ³	360 10 ³	430 10 ³	1300 10 ³
Annual percent (%)	8	31	28	33	
Brehemont	Urban flux	Agricultural flux	Silicate flux	Carbonate flux	Number of days
Low flow 96/97 (t/d)	425	548	499	1284	235
High flow 96/97 (t/d)	1395	1812	1540	2757	130
Annual flux (t/y)	281 10 ³	364 10 ³	317 10 ³	660 10 ³	1620 10 ³
Annual percent (%)	17	22	20	41	

4.3.3. Dissolved Fluxes Throughout the Basin: Comparison between Orleans and Brehemont

At Orleans, the survey was done a year before (Grosbois et al., 2000) and the comparison of fluxes at the two sampling sites, summarised in Table IVa and b, shows that the total annual dissolved flux is 20% lower at Orleans (1300 10³ t/y) than at Brehemont. Higher fluxes at Brehemont can be correlated with the increase of weathered carbonate (35% more) and by the Cher tributary inputs (430 10³ t/y, Grosbois, 1998). Carbonate fluxes increase between Orleans and Brehemont but the specific export rate due to carbonates weathering decreases from 47 t/y/km² at Orleans to 23 t/y/km² at Brehemont. This implies that the increase of the carbonate flux is not as great as it should be with respect to the increase of the weathered carbonate surface. One way to explain this deficiency of carbonate fluxes is to consider a Ca²⁺ and HCO₃⁻ consumption process such as the formation of authigenic calcite. Silicate fluxes are similar at the two sampling points inducing a specific export rate for silicate bedrock constant and equal to 11 t/y/km².

Anthropogenic fluxes represent 40% of the total annual dissolved flux at both sites. However, the agricultural impact is more evident in the Orleans area with a ratio of the agricultural/urban flux ratio of 3.6 while this ratio is close to 1.3 at Brehemont. A larger agricultural area is present in the vicinity of Orleans and it may explain the higher ratio. At Brehemont, the urban impact is more marked because of urban waste inputs (i.e., city of Tours) upstream of Brehemont site and inhabitants of the Cher basin (455 10³ inhabitants).

5. The Suspended Matter Flux in the Loire Basin: Results and Calculations

5.1. CHEMICAL, MINERAL AND MORPHOLOGICAL VARIATIONS OF THE SUSPENDED MATTER

The mineralogical and chemical composition of suspended matter is similar at the two sampling sites as well as their variations with discharge (Grosbois et al., 2000 for Orleans station; Table V for Brehemont). As discharge increases, the concentration of major oxides (Al_2O_3 , Fe_2O_3 , K_2O , MgO and SiO_2) and the percentage of silicate mineral (mostly quartz and feldspars) increase logarithmically, as illustrated by the Figure 6 for Fe_2O_3 at Brehemont. The logarithmic tendencies were explained by Négrel and Grosbois (1999) 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.

However, during the low flow (i.e. $<300 \text{ m}^3/\text{s}$), higher SiO_2 concentrations are noticed at Brehemont (Table V). According to the phytoplankton study in the Loire River (Agence de l'eau Loire-Bretagne, 1996), the Brehemont site is the most algae productive area in the Loire catchment and the algae consists mainly as diatoms. In river water just upstream to Brehemont, about 69,000 algae/ml were measured during May to July 1996 whereas at the same time, only 46,000 algae/ml of water were measured at Orleans. The larger diatom concentration may induce high SiO_2 concentrations in suspended matter.

The second kind of relationship is observed for CaO (Figure 6). CaO concentrations decrease sharply from 40% to 5% when the discharge increases up to $300 \text{ m}^3/\text{s}$, and therefore concentrations are very low and constant during the high flow. The main Ca bearing phases are plagioclases and calcite. However, the amount of plagioclases does not fluctuate greatly with discharge whereas the amount of calcite does. This may imply that CaO variations are related to calcite variations. BEM observations show two types of carbonates. The carbonates sampled during the winter period have a regular rhomboedric shape (Figure 7a) and are very small (less than $10 \mu\text{m}$ long). These do not look eroded by shocks as quartz grains show. Conversely, the carbonates that were sampled during the summer period are larger (between 20 and $40 \mu\text{m}$ long) and have a very specific shape that shows an authigenic polynuclear crystalline growth (Figure 7b). A lot of these carbonate grains present diatoms in their center, which might serve as a nucleus for the authigenic growth (Suarez, 1983; Mucci and Morse, 1983). During the summertime, the formation of authigenic calcite in the Loire River is an important contributor to the suspended load. At Brehemont, the authigenic calcite precipitation period occurs from April 1996 to the end of October 1996 and from May 1997 to the end of November 1997. At Orleans, most of the suspended matter flux during summer is due only to authigenic calcite. The calculation of the solid export rate should only consider the detrital suspended matter in the framework of determining the rate of mechanical erosion. In the last part of this study, calculations of solid fluxes were

Table V. Major element concentrations (%wt of air-dried sediments) and mineralogical composition of the suspended matter collected at Brehement. n.d. refers to non determined values.

Sample name	Date	W (m ³ /s)	SiO ₂	P ₂ O ₅	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	NaO	K ₂ O	TiO ₂	MnO	Ill	Kao	Q	K F	Pla	Cal
0186-Loire	01/18/96	1204	83.3	1.0	19.0	7.4	n.d.	2.0	1.0	2.9	1.1	0.6	n.d	n.d	n.d	n.d	n.d	n.d
0366-Loire	02/06/96	693	67.3	0.5	10.2	4.1	13.7	1.1	0.5	1.6	0.6	0.2	n.d	n.d	n.d	n.d	n.d	n.d
0526-Loire	02/21/96	968	5.9	0.2	5.6	2.2	11.2	0.5	0.3	0.9	0.3	0.1	n.d	n.d	n.d	n.d	n.d	n.d
0646-Loire	03/04/96	930	66.1	0.4	18.0	7.4	1.9	1.8	0.5	2.6	1.1	0.2	10	15	30	15	20	10
0786-Loire	03/18/96	462	69.1	0.7	16.0	6.5	2.2	2.0	0.5	2.0	0.9	0.2	0	15	25	25	25	0
0926-Loire	04/02/96	551	70.2	0.7	15.7	6.1	2.0	1.7	0.5	2.1	0.9	0.2	15	20	20	15	15	10
1076-Loire	04/16/96	321	66.8	0.4	4.4	1.9	24.5	0.5	0.5	0.7	0.2	0.1	0	0	0	0	0	100
1356-Loire	05/14/96	270	59.9	0.3	3.6	1.7	32.5	0.6	0.5	0.6	0.2	0.1	0	0	0	0	0	100
1506-Loire	05/29/96	522	72.5	0.6	13.8	5.9	2.2	1.4	0.4	2.2	0.9	0.2	15	15	16	25	15	5
1646-Loire	06/12/96	262	78.0	0.9	11.3	4.5	1.4	0.9	0.4	1.8	0.6	0.2	15	15	25	20	25	0
1796-Loire	06/27/96	191	70.1	0.4	4.6	1.8	21.0	0.6	0.4	0.7	0.3	0.1	10	0	0	10	0	80
1916-Loire	07/09/96	150	61.6	0.2	2.6	1.0	33.0	0.6	0.4	0.4	0.1	0.1	0	0	0	0	0	100
2196-Loire	08/06/96	92	72.0	0.6	7.4	3.0	13.7	0.9	0.4	1.3	0.5	0.3	10	10	10	10	10	50
2356-Loire	08/22/96	102	62.6	0.5	3.4	1.7	29.9	0.7	0.4	0.5	0.2	0.2	0	0	0	0	0	100
2476-Loire	09/03/96	101	63.6	0.4	2.2	0.9	31.3	0.6	0.4	0.4	0.1	0.1	0	0	0	0	0	100
2616-Loire	09/17/96	153	62.1	0.4	4.4	1.8	29.2	0.6	0.4	0.7	0.2	0.2	2	3	6	4	3	80
2766-Loire	10/02/96	120	68.4	0.2	7.7	1.6	17.8	0.6	1.0	2.5	0.3	0.1	0	4	6	6	6	78
2906-Loire	10/16/96	108	63.3	0.3	2.4	1.0	31.0	0.5	1.0	0.3	0.1	0.1	0	0	16	2	2	80
3036-Loire	10/29/96	161	52.2	0.3	4.2	1.7	38.6	0.8	1.0	0.8	0.2	0.2	0	0	7	2	3	88
3186-Loire	11/13/96	184	66.1	0.5	5.8	2.4	22.3	0.7	1.0	0.8	0.3	0.2	0	2	6	8	0	84
3216-Loire	11/17/96	790	62.1	0.4	8.0	3.4	22.7	1.0	0.6	1.3	0.5	0.2	3	4	8	6	4	75
3236-Loire	11/19/96	804	64.1	0.5	14.0	5.7	10.2	1.5	0.6	2.5	0.8	0.2	7	6	14	22	15	36
3256-Loire	11/21/96	611	63.6	0.5	16.6	6.9	6.1	1.8	0.6	2.9	0.9	0.2	11	11	13	13	24	28
3326-Loire	11/27/96	701	65.7	0.5	16.5	6.7	4.4	1.6	0.7	2.8	1.0	0.3	11	15	16	19	13	25
3376-Loire	12/02/96	1527	66.5	0.3	16.7	6.7	4.0	1.5	0.6	2.6	1.0	0.2	8	13	21	21	17	20

Table V. Continued.

Sample name	Date	W (m ³ /s)	SiO ₂	P ₂ O ₅	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	NaO	K ₂ O	TiO ₂	MnO	Ill	Kao	Q	KF	Pla	Cal
3396-Loire	12/04/96	1940	65.3	0.4	17.2	6.6	3.9	1.6	1.0	2.8	1.0	0.2	6	11	22	29	23	9
3426-Loire	12/07/96	1324	66.1	0.4	17.4	6.8	2.6	1.7	0.9	2.9	1.0	0.2	8	10	22	28	24	8
3456-Loire	12/10/96	1000	66.4	0.4	16.6	6.7	3.3	1.7	0.8	2.8	1.0	0.2	8	10	23	27	25	7
3636-Loire	12/29/96	999	65.3	0.4	19.0	7.1	3.4	1.3	0.3	2.3	0.8	0.2	9	12	21	15	13	30
0097-Loire	01/09/97	489	65.7	0.5	16.3	6.5	4.5	1.7	0.9	2.7	1.0	0.2	11	8	21	23	23	15
0247-Loire	01/24/97	1276	65.9	0.5	17.7	7.2	2.0	1.8	0.8	2.9	1.1	0.2	11	15	33	15	17	8
0397-Loire	02/06/97	534	65.5	0.5	16.3	6.9	4.0	1.8	1.0	2.8	1.1	0.2	9	11	23	22	20	16
0507-Loire	02/19/97	773	66.8	0.4	17.3	6.9	2.5	1.6	0.6	2.7	1.1	0.2	8	11	29	23	22	7
0667-Loire	03/07/97	499	67.7	0.4	16.4	6.5	3.5	1.4	0.6	2.4	0.9	0.2	0	8	17	19	25	31
0937-Loire	04/03/97	212	69.5	0.5	5.1	2.2	20.5	0.7	0.2	0.9	0.3	0.1	0	0	16	4	4	76
1077-Loire	04/18/97	144	83.3	0.7	7.3	3.0	2.5	0.9	0.4	1.2	0.4	0.3	0	11	27	40	12	10
1327-Loire	05/12/97	185	74.5	0.8	6.6	2.6	13.1	0.8	0.2	1.0	0.4	0.1	0	0	8	5	6	81
1647-Loire	06/13/97	104	76.9	0.9	6.8	2.8	9.4	0.9	0.5	1.2	0.4	0.2	6	5	13	10	14	51
1857-Loire	07/03/97	205	62.6	0.6	7.9	3.2	23.0	0.9	0.2	1.0	0.4	0.2	0	4	6	4	4	82
1997-Loire	07/18/97	151	65.5	0.6	5.2	2.1	24.4	0.8	0.2	0.8	0.3	0.1	0	0	8	3	3	86
2127-Loire	07/31/97	93	72.9	0.7	8.7	3.7	10.1	1.1	0.5	1.4	0.5	0.4	0	0	15	5	11	69
2267-Loire	08/14/97	109	76.1	0.8	7.3	2.7	10.3	0.9	0.2	1.2	0.5	0.1	0	5	12	5	9	69
2397-Loire	08/27/97	83	81.6	1.0	7.1	3.0	4.0	0.9	0.3	1.2	0.4	0.6	0	0	28	18	15	40
2937-Loire	10/20/97	105	70.5	0.8	3.8	1.9	21.2	0.7	0.2	0.6	0.2	0.2	0	3	5	0	93	
3297-Loire	11/25/97	216	60.6	0.5	7.5	3.6	24.7	1.0	0.2	1.2	0.4	0.4	0	0	0	0	0	100
3527-Loire	12/18/97	362	62.9	0.6	10.0	4.6	18.0	1.2	0.3	1.6	0.6	0.3	0	3	8	3	3	83
0068-Loire	01/06/98	764	65.2	0.4	13.7	5.5	10.7	1.2	0.4	2.0	0.8	0.2	4	7	16	13	7	54

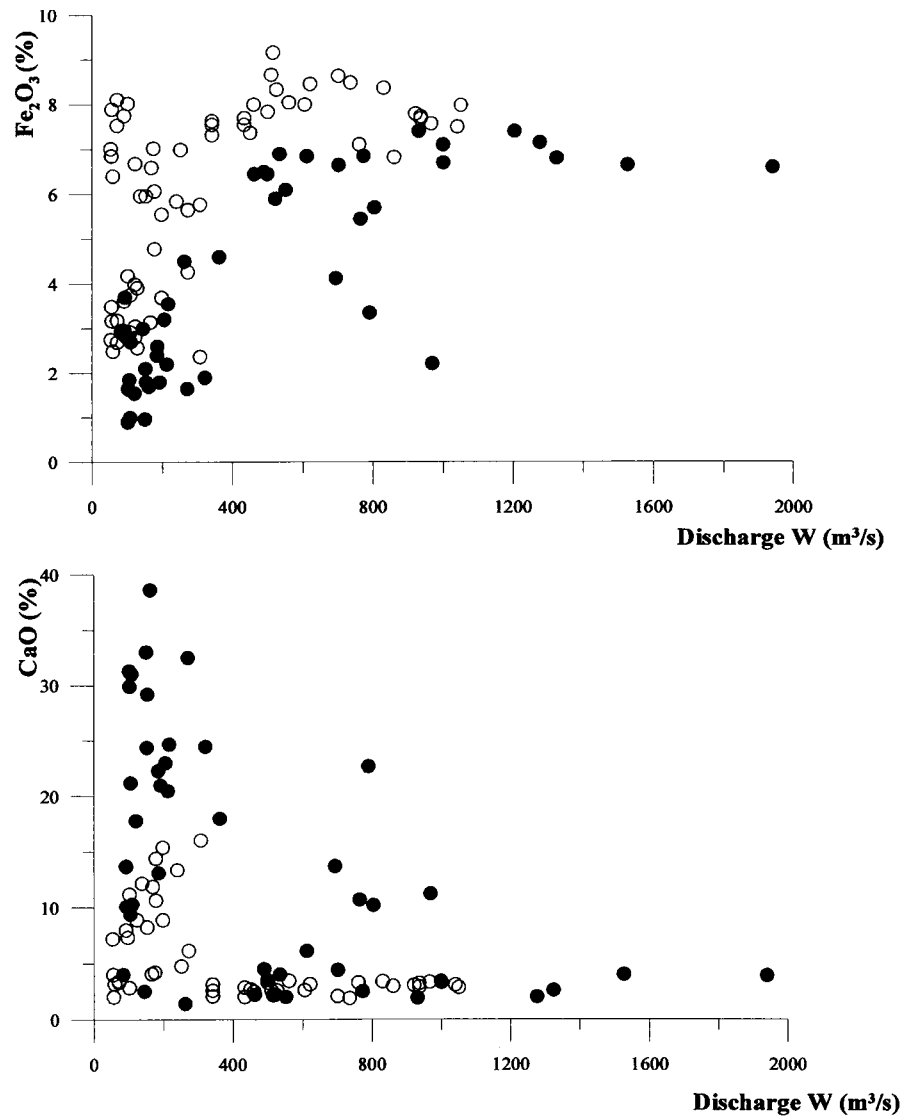


Figure 6. Evolution of Fe₂O₃ and CaO concentrations in suspended matter with river discharge at Orleans and at Brehemont. (Symbols identical as in Figure 2).

done for different hydrological periods in order to distinguish between authigenic and detrital material and to observe the spatial distribution of authigenic calcite throughout the Loire basin.

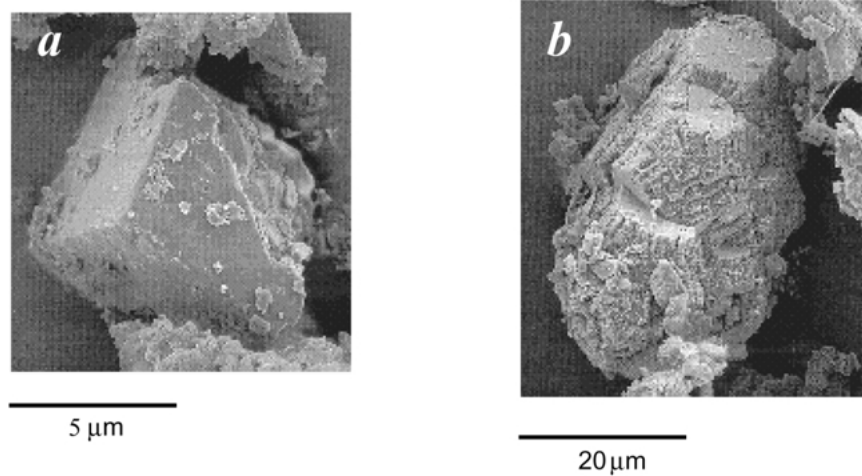


Figure 7. Carbonate particles sampled at Brehemont (a) during the high flow and (b) during the low flow.

5.2. THE SUSPENDED MATTER FLUX IN THE LOIRE BASIN

5.2.1. *Suspended Matter Fluxes*

The method to determine the suspended matter flux is the same as for the dissolved load (see Annexe). Suspended matter fluxes show an increase from Orleans to Brehemont (Table VIa and b). At Orleans, the annual solid flux represents $370 \cdot 10^3$ t/y, including 16% of authigenic carbonates for 1995–1996 (Négre and Grosbois, 1999). At Brehemont, the annual solid flux represents $525 \cdot 10^3$ t/y for 1996–1997 and $490 \cdot 10^3$ t/y for 1997–1998. Authigenic carbonates corresponds to 25 and 10% of annual solid flux, respectively. The decrease of the proportion of authigenic calcite during 1997–1998 at Brehemont may be explained by the two different hydrological conditions existing in 1996–1997 and in 1997–1998. The increase in the proportion of authigenic material throughout the Loire River basin may be due to the degradation of water quality and the increasing dystrophy during the summer.

5.2.2. *Specific Export Rate in the Loire Basin*

The specific export rate calculated at Orleans is close to $9.5 \text{ t/km}^2/\text{y}$ (Négre and Grosbois, 1999), its value ranged from 6.9 to $7.7 \text{ t/km}^2/\text{y}$ at Brehemont. This specific export rate appears to be roughly homogeneous in this part of the Loire basin.

With regard to these values, a specific export rate of around $8 \text{ t/km}^2/\text{y}$ can be estimated between Orleans/Brehemont and the estuary of the Loire river. This specific export rate agrees with that determined by Manickam et al. (1985) in the fluvio-estuarine part of the Loire river ($8.7 \text{ t/km}^2/\text{y}$ during 1981–1982).

Table VI. Results of the Loire river suspended matter fluxes (a) at Orleans (results from Négrel and Grosbois, 1999) and (b) at Brehemont.

Orleans	Total suspended matter	Including authigenic CaCO ₃
Low flow 95/96	314 t/d during 190 days	314 t/d during 190 days
High flow 95/96	1800 t/d during 173 days	
Total annual flux 95/96	370 10 ³ t/y	including 60 10 ³ t/y
Brehemont	Total suspended matter	Including authigenic CaCO ₃
Low flow 96/97	621 t/d during 235 days	600 t/d during 222 days
High flow 96/97	2940 t/d during 129 days	
Low flow 97/98	346 t/d during 273 days	249 t/d during 201 days
High flow 97/98	2529 t/d during 156 days	
Total annual flux 96/97	525 10 ³ t/y	including 133 10 ³ t/y
Total annual flux 97/98	490 10 ³ t/y	including 50 10 ³ t/y

This specific export rate also agrees with that measured on the Seine River basin (9 t/km²/y, Meybeck and Ragu, 1996, 6 t/km²/y at Paris, Roy et al., 1999) but is lower than in the Rhine River basin (15 t/km²/y, Meybeck and Ragu, 1996) and in the Garonne River basin (20 t/km²/y, Probst and Bazerbachi, 1986).

6. Conclusions

This study report on the temporal and spatial variations of major elements in the dissolved and the suspended matter loads, transported throughout the Loire basin. The objectives of this study were to describe the transport of major elements in the dissolved and suspended load and to define the different inputs that contribute to the Loire River water chemistry in order to estimate dissolved and solid fluxes.

Two sampling sites were monitored: one at Orleans, draining 34% of the total basin surface (Négrel and Grosbois, 1999; Grosbois et al., 2000) and the second one at Brehemont, 150 km downstream, draining 50% of the total basin surface.

According to the geochemical and isotopic patterns, the chemical composition of the Loire River results from a mixing process involving weathering of carbonate and silicate bedrock, inputs from rain water, agricultural and urban inputs. The chemical characterisation of these natural and anthropogenic end-members has been determined in order to calculate their contributions and their respective dissolved fluxes. The highest annual dissolved flux is provided by the weathering of carbonate bedrock. It represents 33% of the annual dissolved flux at Orleans and 41% at Brehemont. The annual silicate flux represents 28% of the total annual dissolved flux at Orleans and 20% at Brehemont. Natural inputs fix very well the

chemical composition of the Loire River with around 60% of the annual dissolved flux provided by the weathering processes of silicate and carbonate bedrock. The remaining 40% of the annual dissolved flux has an anthropogenic origin at both sampling sites. At Orleans, the main anthropogenic inputs are from agriculture because this location is surrounded by farmland. At Brehemont, the main anthropogenic inputs are urban because Brehemont receives all the upstream urban inputs.

The study of suspended matter chemistry and mineralogy suggests the existence of at least two particle reservoirs, one with detrital silicate particles and one with carbonate particles. The carbonate reservoir has a detrital origin during the high flow and an authigenic origin during the low flow. The detrital and authigenic exportation fluxes were calculated at the two sampling sites. At Orleans, the total annual flux is calculated to be $370 \cdot 10^3$ T/y including 16% of authigenic carbonates. At Brehemont, the flux is calculated to be $525 \cdot 10^3$ T/y with a percentage of authigenic carbonate ranging between 10% and 25%. An homogeneous specific erosion rate of 8 t/y/km^2 has been determined at Orleans and Brehemont and also in the fluvial zone of the estuary in agreement with the literature. The percentage of authigenic carbonate increases from upstream to the estuary and might be related to the degradation of the water quality.

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Annexe

The contributions α of the different end-members (hereafter silicate SIL, carbonate CAR, agricultural AGR and urban URB) are calculated in each water sample for each chemical specie X by using the following mass balance equation:

$$[X]_{\text{RIV}} = \alpha_{\text{X,SIL}}[X]_{\text{SIL}} + \alpha_{\text{X,CARB}}[X]_{\text{CAR}} + \alpha_{\text{X,AGR}}[X]_{\text{AGR}} + \alpha_{\text{X,URB}}[X]_{\text{URB}} \quad (1)$$

with $\alpha_{\text{X,SIL}} + \alpha_{\text{X,CARB}} + \alpha_{\text{X,AGR}} + \alpha_{\text{X,URB}} = 1$.

In Equation (1), $[X]_{\text{EM}}$ represents the concentration of the element X of each end-member (EM, in $\mu\text{mole/l}$).

Natural and anthropogenic export fluxes F can be calculated during each hydrological period. This method takes into account only the variations in daily discharge

(Walling and Webb, 1985; Meybeck, 1992). This is illustrated for carbonate end-member by the following equation:

$$\begin{aligned} \Phi_{\text{CARB}} = & W \cdot S (\alpha_{\text{Ca,CARB}} [\text{Ca}^{2+}]_{\text{RIV}} + \alpha_{\text{Mg,CARB}} [\text{Mg}^{2+}]_{\text{RIV}} \\ & + \alpha_{\text{K,CARB}} [\text{K}^+]_{\text{RIV}} + \alpha_{\text{Na,CARB}} [\text{Na}^+]_{\text{RIV}} \\ & + \alpha_{\text{HCO}_3,\text{CARB}} [\text{HCO}_3^-]_{\text{RIV}} + \alpha_{\text{Si,CARB}} [\text{Si}]_{\text{RIV}} \\ & + \alpha_{\text{NO}_3,\text{CARB}} [\text{NO}_3^-]_{\text{RIV}} + \alpha_{\text{SO}_4,\text{CARB}} [\text{SO}_4^{2-}]_{\text{RIV}} \\ & + \alpha_{\text{Cl,CARB}} [\text{Cl}^-]_{\text{RIV}}). \end{aligned} \quad (2)$$

In this Equation (2), Φ is the dissolved flux due to the weathering of carbonate bedrock (in t/d), W the discharge of the river (m^3/s), $[\text{X}]_{\text{RIV}}$ the concentration of the element X in the river (in g/l), and $\alpha_{\text{X,CARB}}$ the proportion of the carbonate end-member. Only the anthropogenic end-members provide nitrates, sulphates and chlorides, and therefore, for carbonate and silicate EM, α_{NO_3} , α_{SO_4} and α_{Cl} are equal to zero. Silicium is supposed to be provided only from the weathering of silicate bedrocks (Berner and Berner, 1987) inducing that $\alpha_{\text{Si,CARB}}$ is equal to zero.

The method to determine the suspended matter flux is the same as for the dissolved load. However, as Négrel and Grosbois (1999) evidenced, extrapolation methods concerning non-sampled days could not be applied in this study because of the lack of a correlation between the concentration of suspended matter and discharge. Therefore, the instantaneous flux $C_i Q_i$ is assumed constant between two sampling dates and soils are considered stationary.

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