

Dissolved load of the Loire River: chemical and isotopic characterization

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Abstract

The Loire River, with one of the largest watersheds in France, has been monitored just outside the city of Orleans since 1994. Physico-chemical parameters and major and trace elements were measured between 2-day and 1-week intervals according to the river flow. The sampling site represents 34% of the total Loire watershed with 76% silicate rocks and 24% carbonate rocks.

Elements are transported mainly in the dissolved phase with the ratio of total dissolved salts (TDS) to suspended matter (SM) ranging between 1.6 and 17.4. Chemical weathering of rocks and soils are thus the dominant mechanisms in the Loire waters composition. The highest TDS/SM ratios are due to dissolved anthropogenic inputs. The database shows no link between NO_3^- content and river flow. The Na^+ , K^+ , Mg^{2+} , SO_4^{2-} , and Cl^- concentrations are seen to decrease with increasing discharge, in agreement with a mixing process involving at least two components: the first component (during low flow) is concentrated and may be related with input from the groundwater and sewage station water, the second component (during high flow) is more dilute and is in agreement with bedrock weathering and rainwater inputs. A geochemical behaviour pattern is also observed for HCO_3^- and Ca^{2+} species, their concentrations increase with increasing discharge up to 300 m^3/s , after which, they decrease with increasing discharge. The Sr isotopic composition of the dissolved load is controlled by at least five components — a series of natural components represented by (a) waters draining the silicate and carbonate bedrock, (b) groundwater, and (c) rainwaters, and two kinds of anthropogenic components.

The aim of this study is to describe the mixing model in order to estimate the contribution of each component. Finally, specific export rates in the upper Loire watershed were evaluated close to 12 $\text{t year}^{-1} \text{ km}^{-2}$ for the silicate rate and 47 $\text{t year}^{-1} \text{ km}^{-2}$ for the carbonate rate. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Loire River; Major and trace elements; Sr isotopic ratio; Mixing model; Anthropogenic end-members; Export rate

1. Introduction

Weathering processes dominate the dissolved and suspended loads of most of the world's major rivers.

Specifically, chemical weathering of rocks and soils is one of the essential processes in the geochemical cycling of elements in rivers (Garrels and McEnzie, 1971; compilation in Berner and Berner, 1987; Drever, 1988). The weathering process is affected by the climatic impacts, such as moisture and temperature (Berner and Berner, 1987; Drever, 1988; Hem et

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al., 1990). The natural balance of chemical species is disturbed by anthropogenic additions deriving from the domestic and industrial activities (e.g., fertilizers, sewage waters, road water runoff, etc. (Meybeck, 1979; Etchantu and Probst, 1988).

A river catchment is usually a good area for studying the supply of surface waters through the dissolved load of the river (Edwards, 1973a,b; Likens et al., 1977; Miller and Drever, 1977). The surface waters of the upper Loire drainage basin offer unusual opportunities for the selected geochemical studies because: (a) the Loire drains areas with two main types of bedrock — the silicate basement of the Massif Central and the sedimentary area of the

southern Paris Basin (Fig. 1); (b) the watershed is an inland basin in which atmospheric input can be characterized by local rains; and (c) parts of the watershed are industrialized and parts are agricultural, where anthropogenic activities may contribute in varying degrees to the dissolved load.

Systematic sampling of the river water should enable the identification of different geochemical signatures since the chemical composition of the water appears to be controlled by (a) rainwater inputs, (b) water–rock interactions, and (c) human activities. One aim of the present study was to characterize the chemistry of the dissolved load of the upper Loire with regard to the temporal fluctua-

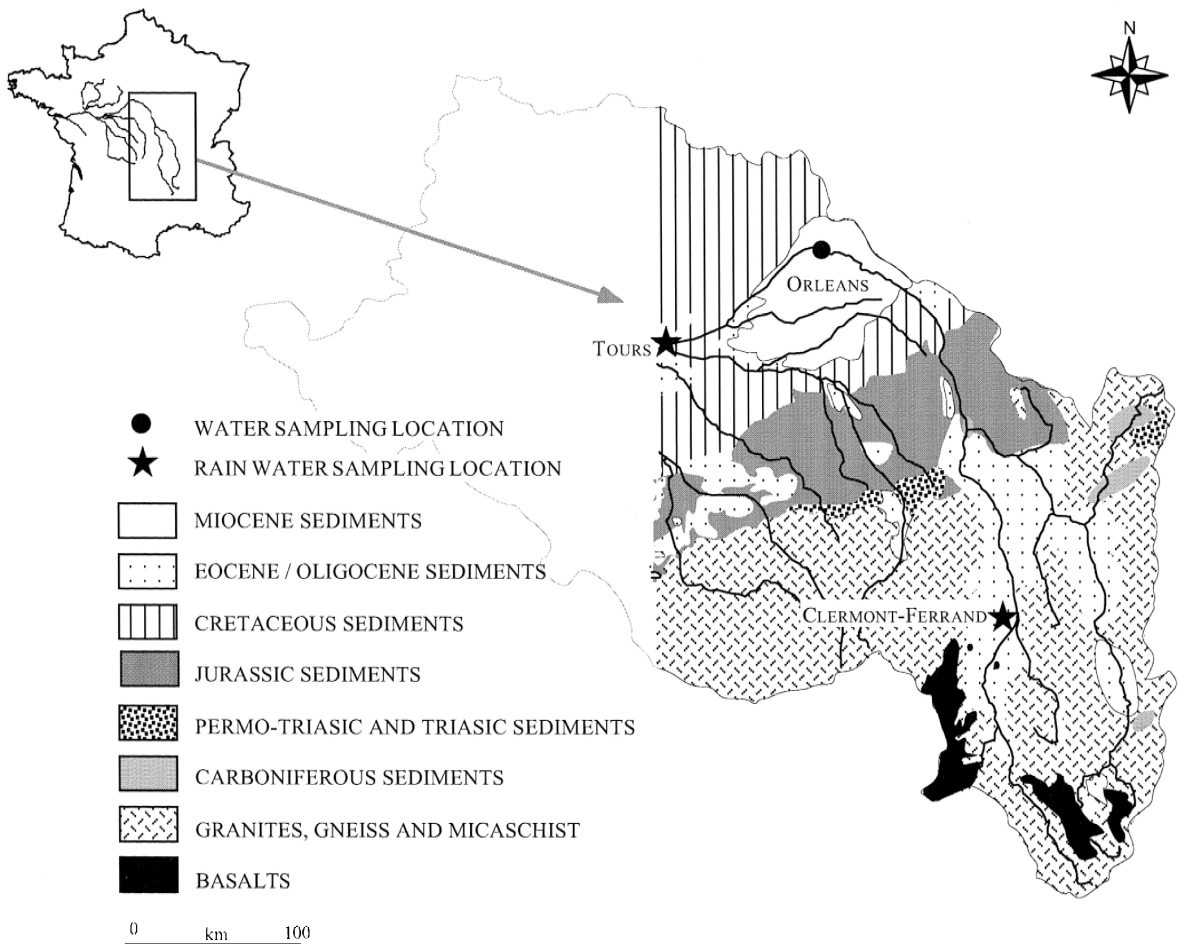


Fig. 1. Simplified geological map of the upper Loire watershed and location of the sampling points for the dissolved load and for rainwater.

tions of the major and trace elements and strontium isotopic ratios. From this, a second aim was to identify and quantify each geochemical signature in order to calculate chemical weathering rates and anthropogenic fluxes.

Major and trace (Rb, Sr) elements associated with the strontium isotopic compositions were investigated, as in many studies on major river basins, in terms of weathering processes and fluxes to the ocean (Sarin et al., 1989; Négrel et al., 1993; Pande et al., 1994; Zhang, 1995; Gaillardet et al., 1995). For the strontium systematic, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio varies according to the Rb/Sr ratio and the age of the material (Faure, 1986). Since any natural processes do not fractionate Sr isotopes, the measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratio differences are due to the mixing of Sr derived from various sources and to different isotopic compositions. Thus, $^{87}\text{Sr}/^{86}\text{Sr}$ ratio variations within an hydrosystem can provide information about the sources of Sr and the different involved mixing processes (Albarède and Michard, 1987; Anderson et al., 1992; Palmer and Edmond 1992; Stueber et al., 1993).

2. Geography, geology and meteorology of the Loire watershed

The Loire River, from its source in the Massif Central to the Atlantic Ocean, is 1010 km long (Fig. 1) and the total basin area is 117 800 km². In the upstream basin, which represents 46% of the total basin surface, the Loire River flows roughly from south to north, draining old plutonic and volcanic rocks (Bureau de Recherche Géologiques et Minières, 1980). Numerous small tributaries are present in this mountainous region (maximum elevation 1500 m).

Then the stream flows westward and its valley stretches toward the Atlantic Ocean. The intermediate part of the basin is underlain by the sedimentary series of the Paris Basin (mainly carbonate deposits, from 200 to 6 Ma). Three major tributaries flow into the Loire River from the left bank (Cher, Indre, and Vienne) and one from the right bank (Maine).

On a Western European scale, the Loire is one of the major fluvial inputs to the Atlantic Ocean with a water discharge of 26 km³/year and a mean annual discharge of 850 m³/s in the estuary (Figueres et al.,

1985). In the middle of the basin, the Loire discharge fluctuated widely, between 53 m³/s (August 1995) and 1480 m³/s (January 1995). The hydrological cycle of the river encompasses three different periods with an annual recurrence. These periods are seasonally marked with: (a) a low flow during two or three warm months in summer, (b) a high flow in winter, generally from December to February with short higher floods, and (c) a smaller high flow, which occurs during the spring and is related to the Massif Central snow melt.

In addition to the physical characterization of the watershed, meteorological parameters are also important for evaluating the rainfall effects. The Loire basin is characterized by its diversity of air-mass trajectories divided into four major origins. One is westerly and originates from the Atlantic Ocean. This west sector is predominant with 52% of the rain events (Jaffrezo, 1987; Colin, 1988). The second sector is northeasterly to northwesterly, still with a marine origin (North Atlantic and North Sea), it passes over Great Britain and the industrialized countries from France to Eastern Europe. The third is easterly with a continental origin; its geochemical signature is different because it passes over polluted countries and a large forested area. The last is southeasterly to southwesterly, originating in the Mediterranean Sea, and carries natural Saharan aerosols and pollution from Spain.

3. Sampling and analytical methodology

3.1. Sampling and analysis of the dissolved load

The water sampling was carried out at two sites about 10 km apart at the inflexion of the Loire River and with no important tributaries between them (Fig. 1). The two sites integrate 34% of the total Loire watershed and correspond to a drainage area of 42 103 km². They represent the drainage of the whole silicate basement of the Massif Central and of about 24% of the sedimentary formations, just before the drainage of the extensive agricultural Beauce area.

The sampling strategy was divided into two periods. From May 1994 to February 1996, the Loire

Table 1

Major and trace element concentrations ($\mu\text{mol/l}$) and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the dissolved load collected during the daily survey (jlo samples, A) and the monthly survey (L samples, B) nd = non-determined values
d.l. = detection limit.

(A)

Sample name	Date	W (m^3/s)	pH ^a	T (°C)	Conductivity ($\mu\text{S}/\text{cm}$)	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	Ca^{2+}	Na^+	K^+	Mg^{2+}	Rb	Sr	$^{87}\text{Sr}/^{86}\text{Sr}$
jlo1	05/16/1995	310	8.28	14.8	235	1860	392.1	190.2	142.9	970.5	491.3	79.2	209.6	0.05	1.44	nd
jlo2	05/17/1995	339	8.21	14.9	227	1590	383.4	177.1	143.9	857.8	473.5	85.4	194.6	0.05	1.30	nd
jlo3	05/18/1995	351	7.79	14.3	221	1560	355.8	165.9	147.3	860.0	416.5	79.2	174.2	0.05	1.15	nd
jlo4	05/19/1995	389	8.05	13.4	229	1700	331.8	169.0	163.5	734.3	407.8	81.8	163.3	0.15	3.99	nd
jlo5	05/20/1995	433	7.51	14.2	222	1770	305.1	159.1	161.1	724.0	360.0	72.1	148.8	0.12	3.13	0.711253
jlo6	05/21/1995	475	7.47	15.7	214	1620	301.1	157.1	154.5	875.8	338.7	75.9	161.3	0.20	5.27	nd
jlo7	05/22/1995	460	7.68	17.0	203	1760	262.5	135.7	115.8	811.0	331.3	63.8	152.5	0.05	1.17	nd
jlo8	05/23/1995	372	7.40	19.4	202	1630	279.2	140.0	121.6	807.8	340.9	66.4	152.9	0.05	1.15	nd
jlo9	05/24/1995	341	7.56	17.8	211	1620	305.1	152.7	130.0	838.5	360.9	70.8	164.2	0.05	1.20	0.711336
jlo10	05/25/1995	317	7.50	18.2	214	1730	286.2	142.2	114.8	875.3	382.6	72.8	174.2	0.05	1.24	nd
jlo11	05/26/1995	308	7.55	19.1	217	1680	312.4	157.8	123.7	933.8	423.9	74.4	187.5	0.05	1.31	nd
jlo12	05/28/1995	272	7.55	21.5	222	1840	344.5	165.9	108.9	761.3	370.4	61.5	161.7	0.05	1.36	0.711262
jlo13	05/31/1995	220	7.50	18.6	244	1860	376.3	177.4	114.8	834.8	420.4	64.6	177.9	nd	nd	nd
jlo14	06/03/1995	254	7.46	17.7	234	1880	352.7	173.9	116.8	1245.8	587.0	103.3	285.8	0.06	1.43	nd
jlo15	06/05/1995	352	7.73	18.1	209	1400	354.6	160.3	95.2	992.0	590.0	87.9	245.4	0.05	1.18	nd
jlo16	05/12/1995	197	7.43	17.7	228	1730	372.7	178.1	81.6	1144.5	629.1	98.5	290.4	0.05	1.40	0.711372
jlo17	06/17/1995	170	7.32	19.1	233	1710	415.8	191.4	89.5	1114.5	699.6	103.6	302.9	0.06	1.50	nd
jlo18	06/23/1995	128	7.29	18.0	225	1530	440.6	202.4	66.3	928.5	736.5	121.0	310.0	0.13	2.85	0.711388
jlo19	06/25/1995	171	7.41	21.5	215	1490	429.9	202.1	43.1	954.3	755.7	117.7	306.7	0.11	2.48	nd
jlo20	06/29/1995	122	7.28	23.3	211	1390	436.9	194.1	51.5	835.5	728.3	135.9	316.3	0.07	1.35	0.711379
jlo21	07/01/1995	99	7.10	24.1	222	1360	468.2	207.3	40.2	545.0	584.3	76.9	303.3	0.10	1.69	nd
jlo22	07/03/1995	101	7.31	24.7	240	1580	466.8	213.2	28.2	625.8	520.0	85.6	212.5	0.13	2.49	0.711334
jlo23	07/06/1995	115	7.11	25.9	226	1400	437.5	190.5	5.2	678.8	719.1	117.4	305.8	0.11	2.05	nd
jlo24	07/12/1995	91	7.26	26.3	213	1540	393.0	173.3	16.5	780.8	630.9	126.9	273.3	0.08	1.38	nd
jlo25	07/20/1995	91	7.01	27.6	227	1390	447.9	192.7	8.7	687.0	704.3	129.7	290.8	0.08	1.39	0.711322
jlo26	07/25/1995	71	6.93	26.0	237	1130	434.1	192.3	0.0	492.8	694.8	131.5	310.4	0.08	1.35	0.711338
jlo27	07/28/1995	61	7.40	22.2	247	1650	474.9	206.5	46.0	831.5	766.1	137.7	314.6	0.08	1.59	nd
jlo28	08/03/1995	56	7.03	28.5	230	1250	503.7	199.8	2.1	629.0	827.8	133.8	306.7	0.08	1.31	0.711246
jlo29	08/11/1995	71	7.22	23.4	224	1450	472.4	197.3	0.0	678.3	828.7	141.5	340.8	0.08	1.44	0.711241
jlo30	08/15/1995	65	7.09	23.9	214	1160	448.5	174.1	0.0	548.0	801.3	156.2	295.0	0.07	1.25	nd
jlo31	08/18/1995	53	7.02	23.4	212	1120	466.8	185.1	83.7	525.5	811.3	139.7	294.6	0.08	1.22	0.711271
jlo32	08/24/1995	55	7.00	24.3	225	1240	474.4	189.2	35.2	581.3	827.8	226.4	317.1	0.08	1.32	nd

jlo33	08/27/1995	55	7.07	21.3	238	1480	478.6	188.9	0.0	723.0	864.3	136.4	338.3	nd	nd	0.711261
jlo34	08/30/1995	55	7.02	18.4	231	1300	486.5	191.4	0.0	651.3	896.1	179.5	368.8	0.07	1.35	nd
jlo35	09/05/1995	59	7.18	15.9	241	1570	480.3	196.5	0.0	942.5	1071.7	173.1	381.3	0.07	1.50	0.711465
jlo36	09/14/1995	108	7.10	15.8	264	1550	499.4	216.0	9.7	966.0	1137.8	152.6	362.9	0.07	1.46	0.711393
jlo37	09/19/1995	121	7.22	17.2	270	1650	474.9	219.2	11.1	1079.3	1124.8	164.1	330.0	0.06	1.31	0.711724
jlo38	09/25/1995	307	8.00	13.8	248	1430	403.4	195.6	6.0	972.3	928.7	157.7	312.5	0.06	1.20	0.711786
jlo39	10/02/1995	177	7.52	15.3	253	1620	405.6	186.7	0.0	1033.3	883.9	129.7	335.0	0.10	2.14	0.711653
jlo40	10/09/1995	237	7.20	17.2	273	1770	424.8	191.3	78.1	1231.5	922.6	153.6	321.7	0.06	1.35	0.711504
jlo41	10/16/1995	168	7.02	19.0	258	1670	407.9	189.3	0.0	1093.8	883.0	179.0	335.0	0.06	1.28	0.711591
jlo42	10/23/1995	137	7.81	12.2	275	1700	439.4	202.0	13.4	1147.0	929.1	166.4	329.6	0.06	1.32	0.711594
jlo43	11/15/1995	145	6.95	19.9	270	2000	445.6	187.8	14.5	1249.5	892.6	157.2	329.2	0.06	1.50	0.711377
jlo44	11/27/1995	152	7.32	6.3	253	1740	402.8	175.6	23.4	1095.0	800.4	152.6	299.2	0.06	1.30	0.711402
jlo45	12/03/1995	251	6.76	6.6	203	1380	362.0	152.4	7.7	847.8	724.3	118.5	257.9	0.06	1.04	0.711543
jlo46	12/12/1995	174	6.70	3.9	227	1620	401.1	163.0	4.8	1021.8	767.0	128.2	288.8	0.06	1.21	0.711455
jlo47	12/17/1995	165	6.65	3.2	222	1530	398.0	158.4	4.4	984.5	763.0	132.1	277.1	0.05	1.13	0.711401
jlo48	01/03/1996	760	6.48	5.6	196	1230	349.3	155.9	162.4	688.8	346.5	82.8	153.8	0.05	0.98	0.711551
jlo49	01/05/1996	935	6.50	5.7	186	1150	331.8	147.3	169.7	629.8	347.4	120.5	223.8	0.05	0.93	0.711606
jlo50	01/07/1996	920	6.51	6.4	184	1200	341.7	147.8	226.9	647.5	354.8	89.2	122.5	0.06	1.23	0.71168
jlo51	01/09/1996	965	6.48	7.1	194	1300	395.8	163.6	257.9	671.8	297.4	103.3	135.0	0.05	1.01	0.711579
jlo52	01/11/1996	935	6.50	7.1	194	1270	360.3	160.7	238.2	691.3	317.4	120.0	124.2	0.07	1.54	0.711556
jlo53	01/14/1996	1040	6.50	7.8	188	1290	339.2	146.9	177.2	758.0	326.1	37.2	138.8	0.04	0.92	0.711579
jlo54	01/16/1996	1050	6.47	6.1	179	1100	320.9	141.1	167.4	624.5	343.5	63.1	119.2	0.04	0.87	0.711696
jlo55	01/18/1996	830	6.51	5.8	182	1190	322.7	145.5	160.9	582.3	281.7	115.6	116.3	0.07	1.57	0.711778
jlo56	01/21/1996	620	6.57	4.5	186	1190	323.1	148.8	65.9	653.5	301.7	88.5	150.8	0.04	0.96	0.71117
jlo57	01/22/1996	560	6.63	5.5	191	1260	328.3	149.9	39.1	685.0	346.1	70.8	177.1	0.04	0.98	0.711641
jlo58	01/26/1996	525	6.99	4.1	198	1120	331.1	152.6	22.4	682.3	357.8	95.1	171.7	0.04	0.99	0.711592
jlo59	01/29/1996	605	7.84	4.7	165	1270	280.5	131.1	0.0	558.3	305.7	82.8	150.0	0.03	0.85	0.711591
jlo60	02/01/1996	500	7.53	3.8	183	1200	305.5	149.8	0.0	633.8	337.8	67.2	166.7	0.00	0.11	0.711558
jlo61	02/06/1996	460	7.02	3.3	204	1500	320.3	156.3	194.8	719.0	338.3	63.8	174.6	0.04	1.03	0.71139
jlo62	02/12/1996	450	6.88	4.7	208	1500	401.1	160.3	202.3	746.0	391.7	69.2	174.6	0.04	1.07	0.711399
jlo63	02/15/1996	860	6.74	3.8	212	1490	307.9	147.3	60.0	819.0	329.6	72.6	161.3	0.04	1.08	0.711325
jlo64	02/19/1996	700	6.68	3.8	189	1270	287.9	127.8	138.7	682.5	317.0	61.5	141.3	0.04	0.87	0.711597
jlo65	02/22/1996	735	6.52	1.8	202	1410	309.6	135.7	57.9	748.8	329.6	66.4	144.6	nd	nd	nd
jlo66	02/27/1996	510	6.61	7.0	200	1440	392.4	148.2	117.6	594.0	417.4	72.8	127.5	0.14	3.83	0.711558
jlo67	03/08/1996	515	6.72	4.5	204	1320	385.1	142.1	147.3	487.3	432.2	69.7	160.0	0.03	0.89	0.711796
jlo68	03/18/1996	341	6.62	7.6	235	1530	441.7	174.9	174.7	837.5	486.5	75.1	205.4	0.04	1.30	0.711652
jlo69	04/02/1996	381	nd	6.6	184	nd	324.2	140.2	131.1	605.5	386.1	65.4	170.0	0.04	0.97	nd
jlo70	04/07/1996	344	nd	10.6	205	nd	387.0	159.7	148.5	696.8	439.1	67.7	198.3	0.04	1.16	nd

(continued on next page)

Table 1 (continued)

(B)																
Sample name	Date	W (m ³ /s)	pH	T (°C)	Conductivity (μS/cm)	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	Ca ²⁺	Na ⁺	K ⁺	Mg ²⁺	Rb	Sr	⁸⁷ Sr/ ⁸⁶ Sr
L1	5/05/94	443	8.20	15.1	189	1394	299.0	157.3	135.5	668.7	335.8	61.6	129.9	0.04	1.26	0.711134
L2	7/06/94	303	8.02	17.8	263	2046	375.2	180.2	154.8	920.7	396.7	71.1	164.5	0.04	1.76	0.711166
L3	4/07/94	167	9.05	23.7	220	1299	358.3	169.8	64.5	553.9	439.3	81.8	153.9	0.08	1.65	0.711127
L4	9/08/94	83	9.03	23.8	234	1662	423.1	188.5	46.8	611.3	465.4	81.8	164.6	0.07	2.12	0.710959
L5	9/09/94	76	8.59	14.9	293	2101	713.7	236.5	d.1	783.4	565.5	87.0	192.1	0.07	1.95	0.710995
L6	3/10/94	376	8.00	15.6	230	1444	434.4	180.2	d.1	648.7	448.0	81.8	239.1	0.05	1.67	0.711478
L7	7/11/94	500	7.37	12.8	223	1686	363.9	156.3	d.1	856.5	381.0	94.6	226.1	0.05	1.75	0.711446
L8	9/12/94	334	8.15	9.5	345	1851	351.8	163.5	43.5	1047.4	461.1	83.6	214.3	0.07	2.59	0.711237
L9	5/01/95	605	8.61	4.3	317	1619	263.2	122.8	175.6	864.5	328.8	77.2	150.6	0.06	1.87	0.711355
L10	30/01/95	1480	7.78	15.2	179	1373	249.4	119.3	69.8	692.9	280.6	74.2	123.7	0.05	1.44	0.711552
L11	10/03/95	875	8.10	8.1	202	1277	261.5	111.3	124.2	790.7	322.7	67.0	147.6	0.03	1.19	0.711329
L12	5/04/95	386	8.07	13.8	236	1696	321.9	136.5	228.7	970.8	394.5	61.4	176.4	0.04	1.42	0.711108
L13	5/05/95	480	9.14	20.3	215	1654	325.8	160.9	91.1	862.0	390.6	73.9	165.7	0.05	1.42	0.711234
L14	9/06/95	244	9.13	19.2	248	1850	283.8	153.1	107.3	1176.1	548.1	92.6	269.3	0.05	1.50	0.711075
L15	10/07/95	102	9.36	28	290	1350	318.2	132.3	87.3	822.9	631.6	108.2	169.4	0.07	1.48	0.710968
L16	9/08/95	63	9.28	21.8	292	2020	405.6	185.3	68.7	648.7	826.4	136.8	213.0	0.08	1.95	0.71072
L17	12/09/95	75	8.28	16.2	309	1770	415.5	204.3	89.0	1153.2	846.0	125.6	288.3	0.49	1.88	0.710969
L18	14/11/95	88	n.d	n.d	n.d	1530	325.8	160.9	91.1	1631.0	863.0	129.4	197.3	0.06	1.68	0.710831
L19	12/12/95	174	6.70	3.9	227	1620	401.7	163.0	4.8	962.1	725.5	121.0	215.8	0.40	1.50	0.711416
L20	7/01/96	920	6.51	6.4	184	1200	342.2	147.8	226.9	697.6	431.1	96.2	136.1	0.26	0.96	0.711641
L21	15/02/96	860	6.74	3.8	212	1490	308.3	147.3	60.0	817.4	329.7	72.4	197.4	0.39	1.50	0.711334
L22	12/04/96	261	n.d	n.d	n.d	1752	413.2	163.4	181.7	706.3	448.5	71.1	169.0	n.d	n.d	0.711244

^a measured in the laboratory.

River was sampled once a month at the Beaugency station (monthly survey). The second period of sample collection (daily survey) was between May 1995 and March 1996 inside Orleans and in the same water mass as at the Beaugency station. The sampling interval ranged between 2 days and 1 week according to the fluctuations of the river discharge.

All of the water samples were collected in polyethylene bottles and filtered through precleaned 0.22 μm Teflon (PVDF) Millipore filters using a pre-cleaned Nalgene filter apparatus. The electrical conductivity, standardized to 20°C, and the water temperature of each sample were measured on site. The pH was measured on site for the monthly survey samples and in the laboratory as soon as possible after the collection for the daily survey samples.

Chemical analyses of the water samples were performed by atomic absorption spectrometry (Ca^{2+} , Na^+ , K^+ , Mg^{2+}), ion chromatography (Cl^- , SO_4^{2-} , NO_3^-), inductively coupled plasma mass spectrometry (Sr and Rb trace elements), HCl titration, and Gran's method for alkalinity. Chemical separation and mass spectrometric procedures for strontium followed the standard method used at BRGM (Négre and Deschamps, 1996). An average internal precision of $\pm 10 \times 10^{-6}$ (2σ) was obtained during this study. 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 $0.710227 \pm 17 \times 10^{-6}$ (2σ , $n = 70$).

The discharge of the Loire River was measured continuously by the Environmental Agency (DIREN-Agence de l'Eau) at a gauging station located in the vicinity of the sampling point. A mean daily value was obtained throughout the hydrological cycle (Table 1).

3.2. Rainwater sampling

Two rainwater samplers were installed in the Loire watershed. One sampling site was near Clermont-Ferrand in the Massif Central, 200 km upstream from Orleans, this was fitted with an automatic sampler (Négre and Roy, 1998) that functioned from March 1994 to March 1995. The second sampling site was at Tours, 110 km downstream from Orleans, and was operated during each rain

event from September 1996 to January 1998. These two collectors enabled a mean geochemical signature of rainwater to be determined for the Loire watershed above Orleans.

4. Results and discussion

4.1. Chemical element distribution and Sr isotopic variation in rain events

4.1.1. The upper part of the watershed: the Massif Central

Thirteen samples of rainwater (970 mm) were collected between March 1994 and March 1995, with one sample representing all the rainwater that fell during a period of 1 month. During the sampling period, the electrical conductivity ranged from 5 (October–November 1994) to 52 $\mu\text{S}/\text{cm}$. (June–July 1994) with an annual mean of 17.2 ± 14.8 $\mu\text{S}/\text{cm}$. The pH of the rainwater was always acid and ranged between 4.3 (March–April 1994) and 6.0 (June–July and September–October 1994) with an annual mean of 5.2 ± 0.6 .

The eight major elements, the trace element Sr, and the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio were analysed, with the results presented and discussed in Négre and Roy (1998). To summarise, the order of cation abundance was $\text{Ca}^{2+} > \text{Na}^+ > \text{K}^+ > \text{Mg}^{2+}$, with the Ca^{2+} and Na^+ species giving a mean weighted concentrations of 17.7 and 14 $\mu\text{mol}/\text{l}$, respectively. The cation concentrations showed large variations during the sampling period: the Na^+ concentration varied 100-fold (from 0.4 $\mu\text{mol}/\text{l}$ in October–November 1994 to 43 $\mu\text{mol}/\text{l}$ in February–March 1995), the Ca^{2+} concentration varied 80-fold, and the K^+ concentration varied 20-fold.

The order of anion abundance is $\text{NO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$, but their mean weighted contents were very similar (26, 23, and 19 $\mu\text{mol}/\text{l}$, respectively). Their variations were less than those of the cations, between 5- and 10-fold. The charge imbalance showed an anionic excess close to 36% in the Massif Central, which is usual for dilute waters (Edmond et al., 1995). The main explanation for this charge imbalance is the absence of NH_4^+ analysis. Actually, NH_4^+ ions were present in all the rainwater samples as a

minor element, supplied from the ammonia atmospheric cycle, essentially due to fertilizer release and biological decay (Sloan et al., 1994; Berner and Berner, 1996).

The trace element Sr varied greatly, but was around 1000 times lower than in the Loire waters. Its concentration in the rainwater ranged from 0.008 (October–November 1994) to 0.121 $\mu\text{mol/l}$ (June–July 1994). The $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio ranged from 0.709198 (September 1994) to 0.71314 (October 1994) with a mean annual average of 0.7097, this ratio increased and decreased several times during the sampling period.

4.1.2. The lower part of the Loire watershed: the city of Tours

An identical survey was carried out in the sedimentary part of the watershed (Fig. 1). Seven samples of rainwater (190 mm) were collected each month in the city of Tours from September 1996 to September 1997. As with the automatic sampler, one sample represented all the rainwater that fell during one month. The pH of the rainwater was again acid, varying between 3.3 (September 1997) and 5.8 (March 1997) with an annual mean of 4.4 ± 1.0 . The electrical conductivity was very low and ranged between 17 (May 1997) and 31 $\mu\text{S/cm}$ (September 1997) with an annual mean of 20.5 ± 0.9 .

The cation abundance was $\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+}$ and K^+ . The mean weighted Na^+ concentration was 203 $\mu\text{mol/l}$, with the mean weighted Mg^{2+} concentration being 30 times lower at 6.7 $\mu\text{mol/l}$ and the mean weighted Ca^{2+} concentration being 2.7 $\mu\text{mol/l}$. The K^+ concentration was often below the detection limit of the analysis (between 5 and 10 $\mu\text{mol/l}$).

The anion abundance was $\text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^- > \Sigma\text{P}$, except for January 1997 when NO_3^- was the most abundant species. The mean weighted Cl^- concentration was 104 $\mu\text{mol/l}$, with the mean weighted SO_4^{2-} concentration being six times lower at 16 $\mu\text{mol/l}$ and the mean weighted NO_3^- concentration being at the same order of magnitude as SO_4^{2-} at 15 $\mu\text{mol/l}$. The inversion of the Cl^- and NO_3^- species abundances was due to different air-mass origins. During January 1997, the dominant wind directions and air-mass trajectories were clearly easterly; they passed over all of the Eastern Euro-

pean forested areas to give dominant NO_3^- . Moreover, during November 1996, the Cl^- concentration varied twofold because of the dominant westerly wind directions with an oceanic origin for the air mass.

The Rb and Sr concentrations were fairly uniform, except for the January 1997 rainwater. Sr concentrations varied from 0.012 (December 1996) to 0.04 $\mu\text{mol/l}$ (January 1997) and the Rb concen-

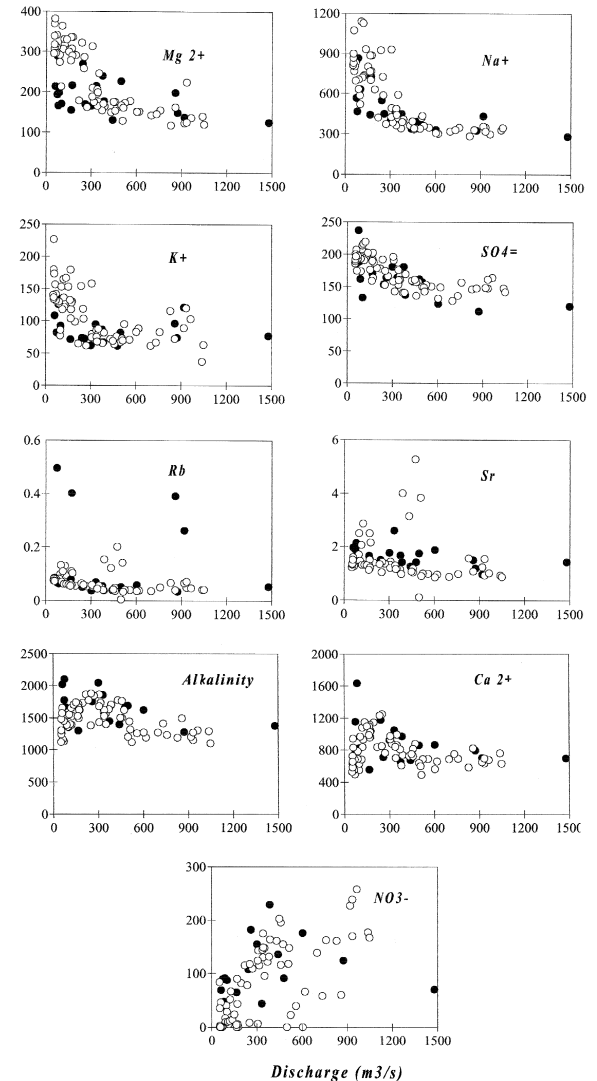


Fig. 2. Evolution of element concentrations with discharge for the daily survey (jlo samples, open circles) and the monthly survey (L samples, filled circles). Analytical errors are in symbols.

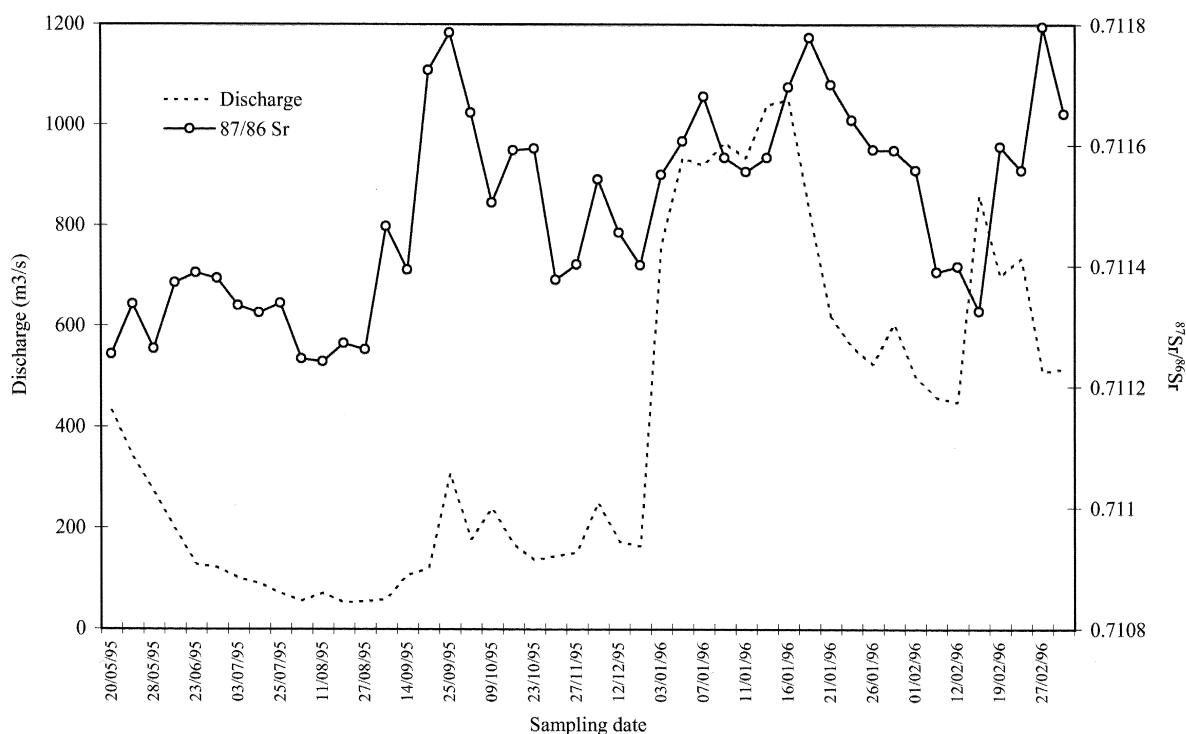


Fig. 3. Fluctuations of $^{87}\text{Sr}/^{86}\text{Sr}$ and discharge in the dissolved load for the daily survey samples.

trations from 0.0009 (June 1997) to 0.0014 $\mu\text{mol/l}$ (March 1997). The $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio ranged between 0.70901 (May 1996) and 0.70106 (March 1997) with a weighted mean of 0.70943, this ratio was very stable during the sampling period.

4.1.3. Comparison of the two surveys

Compared to the rainwater in the Massif Central, the rainwater at Tours was four times more concentrated in chloride species (104 against 26 $\mu\text{mol/l}$)

and 15 times more concentrated in sodium species (204 against 14 $\mu\text{mol/l}$). The marine influence was more marked in the rainwater at Tours than in the Massif Central. Conversely, calcium concentrations were six times more concentrated in the Massif Central (17.7 as against 2.7 $\mu\text{mol/l}$) because of the more marked influence of carbonate wind dust. Sulphates and nitrates were 1.5 times more concentrated. The concentration of magnesium species was of the same order of magnitude at the two sampling

Table 2

Major and trace element concentrations ($\mu\text{mol/l}$) and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the dissolved load collected during July 1988 on monolithologies in the Seine watershed

Locality	Bedrock age	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	Ca^{2+}	Na^+	K^+	Mg^{2+}	Sr	$^{87}\text{Sr}/^{86}\text{Sr}$
Villeneuve	Upper Cretaceous	4000	225	52	2.0	1800	148	16	60	1.2	0.70837
Eglény	Lower Cretaceous	2200	300	132	1.3	900	160	113	100	1.3	0.709548
Migé	Upper Lias	3830	350	168	5.7	1900	115	113	110	1.1	0.708454
Lucy le bois	Lias	2940	435	333	1.7	1500	400	135	158	2.2	0.710022
Vault de lugny		2090	220	106	0.7	650	175	137	183	1.5	0.713715

points, as were the Sr and Rb concentrations. The isotopic ratio of the rainwater was lower at Tours than in the Massif Central (0.70943 and 0.70972, respectively), but the isotopic composition was more constant.

4.2. Major geochemical parameters of the Loire

The total cationic charge ($TZ^+ = Na^+ + K^+ + 2Mg^{2+} + 2Ca^{2+}$) ranged between 1794 (January 1996) and 4207 $\mu\text{eq/l}$ (November 1995) with an annual average of 2753 $\mu\text{eq/l}$. The anionic charge ($TZ^- = HCO_3^- + NO_3^- + Cl^- + 2SO_4^{2-}$) ranged from 1779 (January 1996) to 2836 $\mu\text{eq/l}$ (November 1995) with an annual average of 2250 $\mu\text{eq/l}$.

The database showed a charge imbalance mainly in favour of a positive charge excess or inversely, to a negative charge deficit. A greater imbalance ap-

peared during the low flow period. This deficit of negative charges could be related to the absence of the analysis of organic matter (Sigg et al., 1992; Berner and Berner, 1996), which is mainly produced during spring and summer by biological activities.

The total dissolved salts (TDS) ranged from 136 mg/l at the high stage to 241 mg/l at the end of the low flow with a mean annual value of 181 mg/l. Identical orders of annual average TDS values are observed in other rivers in France, e.g., 174 mg/l for the upstream of the Garonne River (Probst and Bazerbachi, 1986), 461 mg/l for the Seine (Roy, 1996), and 600 mg/l for the Rhine (Meybeck and Ragu, 1996).

The annual flux of dissolved salts, calculated from the daily survey samples, is 13×10^5 t/year at Orleans. This flux is four times greater than the annual transport of suspended matter (SM) of almost 3.5×10^5 t/year (Négré and Grosbois, 1999). The

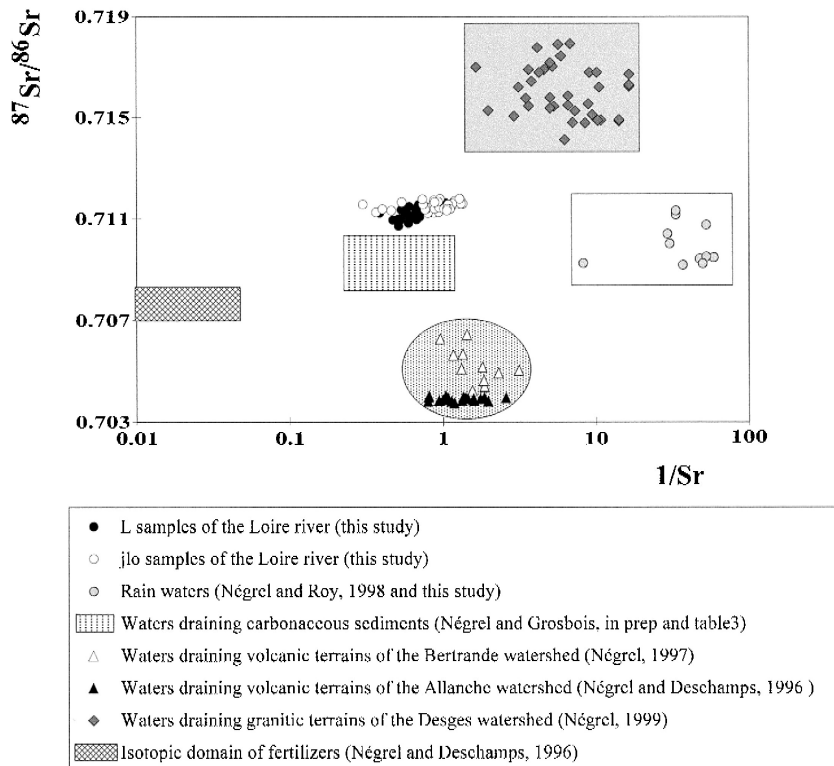


Fig. 4. Relationship between the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the dissolved load in the jlo and L samples and the $1/\text{Sr}$ ratio. Isotopic and chemical domains of the dissolved load in water draining monolithologic watersheds and different French rivers are drawn (see text).

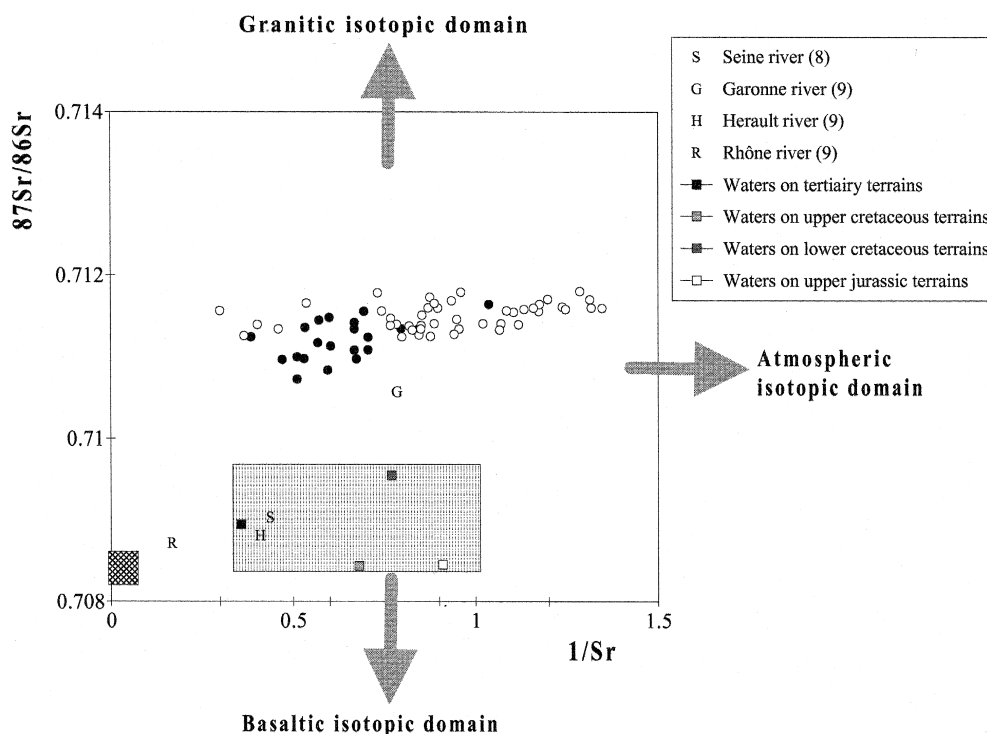


Fig. 4 (continued).

major characteristic of the Loire is that the annual flux of dissolved salts always dominates that of SM, independent of the discharge. However, the dissolved load of the Loire is of the same order of magnitude as those of the Garonne and Seine Rivers ($11.9 \cdot 10^5$ t/year, Probst and Bazerbachi, 1986; and $6.5 \cdot 10^5$ t/year, Roy, 1996). The Rhine dissolved flow ($60.5 \cdot 10^6$ t/year, Meybeck and Ragu, 1996) is 46 times higher than that of the Loire and is the greatest of any river in West Europe.

4.3. Chemical element distribution in the Loire dissolved load

Table 1a and b shows the chemical and isotopic composition of the dissolved load for the daily and monthly survey samples, respectively. The order of cation abundance was $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ and that for anion abundance was $\text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{CO}_3^{2-}$. The Loire waters plot in the calcium bicarbonate field. Calcium and bicarbonate species,

respectively represent between 13% and 33% and between 43% and 58% of the TDS. The concentrations of the bicarbonate ions are strongly related to those of calcium ions, which reflects the carbonate nature of part of the drainage basin.

The seasonal fluctuations of dissolved concentrations compared with those of discharge (Fig. 2) reveal three geochemical behaviour patterns.

The first geochemical behaviour pattern was observed for nitrate, which tends to increase with increasing discharge. The increased river flow during the autumn and winter seasons indicates a larger runoff, and therefore, greater leaching of the watershed soils. The highest inputs of nitrates in the river water originate from leaching because NO_3^- comes mainly from fertilizer applications (Meybeck, 1982; Probst, 1985). Moreover, any NO_3^- consumption by plants or algae could induce a decrease of NO_3^- concentrations.

The second geochemical behaviour pattern applies to most species (Na^+ , Mg^{2+} , K^+ , SO_4^{2-} , Cl^-) with

concentrations being highest during low flow and decreasing with increasing discharge until a stable stage above 400 m³/s. The dissolved element contents reveal two signatures, one dominating during high flow with low concentrations, and the other one, dominating during the low flow with higher concentrations. The high flow signature is in agreement with rock weathering and rainwater inputs (Gibbs, 1970). The summer low flow signature can be related to groundwaters and anthropogenic inputs such as urban sewage and farming waters. Rb and Sr fall into the second geochemical behaviour pattern with several values higher than the trend.

The third geochemical behaviour pattern was more complex because the calcium and bicarbonate concentrations increased only up to an intermediate flow of 300 m³/s. More than two signatures was needed to explain this geochemical behaviour since it is clearly not a binary relation.

It is noticeable that one chemical signature at a hydrological period can encompass several end-members and therefore, the isotopic characteristics were used to differentiate between them.

4.4. Strontium isotopic variations in the Loire dissolved load

Systematic sampling of the dissolved load shows a wide range in the ⁸⁷Sr/⁸⁶Sr ratio with variations clearly greater than the analytical errors — i.e., the strontium isotopic data showed variations around 10⁻³ between the lower value (0.71072) observed in August 1995 and the higher value (0.71196) observed in March 1996, whereas the analytical uncertainties were close to 2.10⁻⁶. The fluctuations of the ⁸⁷Sr/⁸⁶Sr ratio of the dissolved load correlates well with the discharge of the river as illustrated in Fig. 3. The ratio is lowest at low flow and increases with increasing discharge. Each high stage peak exhibits a high ⁸⁷Sr/⁸⁶Sr both in the daily survey samples (0.71179) and in the monthly survey samples (0.71164). When the discharge decreased, the isotopic ratio also decreased. This kind of relationship, previously demonstrated by Négrel and Dupré (1995) on the Oubangui basin in Central Africa, can be related to a mixing model with two signatures. The first, present during high flow, was the highest of the

hydrological cycle and agreed with the geochemical signature of the weathered silicate bedrock of the Massif Central, the second, present during the low flow, was the lowest of the hydrological cycle and agreed with the geochemical signature of weathered carbonate bedrock, carbonate groundwaters, and fertilizers inputs. The decrease in element concentrations cannot be explained simply by a process of rainwater dilution because of the increasing ⁸⁷Sr/⁸⁶Sr ratio during peak discharge. The weighted isotopic composition of rainwater in the upper Loire basin was around 0.70962 (0.70969 in the Massif Central, 0.70943 in the sedimentary part) and was, in every case, lower than the Loire river data.

In order to correlate the geochemical and isotopic signatures, the classical ⁸⁷Sr/⁸⁶Sr vs. 1/Sr contents diagram (Faure, 1986) was used. Natural inputs and anthropogenic additions influence the river water chemistry. Natural inputs were represented by the rainwater of the Massif Central (Négrel and Roy, 1998) and of the Tours (this work) and by the waters weathering carbonate, granitic, and basaltic terrains that were included in small monolithologic watersheds in the headwater of the Loire watershed (Table 2; Négrel, unpublished data, 1997, 1999; Négrel and Deschamps, 1996). The watersheds are polluted mainly by agricultural activities (fertilizers, Négrel and Deschamps, 1996) and by sewage waters from towns and industries. The isotopic signature of each natural and anthropogenic component was determined and plotted in the diagram. The isotopic signature of the dissolved load of the Loire is scattered between all the different isotopic fields (Fig. 4). In detail, the isotopic field of the dissolved load of the Loire plots near the isotopic composition of the Garonne River (Albarède and Michard, 1987). The Seine (Roy, 1996) and Herault (Albarède and Michard, 1987) Rivers plot in the isotopic field of waters draining carbonate terrain. The Rhône River (Albarède and Michard, 1987) plots near the isotopic field of fertilizers. The sewage waters are clearly included in the same isotopic field as the Loire water because they originate mainly from the pumping of the Loire groundwaters. The influence of weathered silicate and carbonate terrains, rainwater, and fertilizers is well marked. The different geochemical signatures, which could contribute to the ⁸⁷Sr/⁸⁶Sr ratio of the dissolved load of the Loire, were composed

with several end-members that made it possible to explain the geochemical behaviour of different dissolved species. In conclusion, the use of the $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $1/\text{Sr}$ systematic revealed the existence of at least five end-members.

The next step will be focused on the different contributions of the different end-member inputs to the total dissolved load since any calculation of the export rate of chemical species of natural or anthropogenic origin requires the quantification of each end-member. An approach using a mass balance calculation can provide answers to this problem.

5. Identification and quantification of natural and anthropogenic inputs

A general mass balance equation for the budget can be written as follows (Meybeck, 1983; Drever and Hurcomb, 1986; Drever and Zobrist, 1992):

$$\begin{aligned} &\text{rock weathering} + \text{atmospheric input} \\ &+ \text{human activities input} \\ &= \text{dissolved load} + \text{solid load} \end{aligned}$$

The mass balance approach requires the determination of an output–input budget (Velbel, 1985; Mast and Drever, 1990) with the determination of element origins. It is commonly accepted that chloride ions come mostly from airborne sea salt (Erickson, 1955; Junge, 1963; Meybeck, 1983) and also, from human activities (Meybeck, 1986). Other chemical species may have several origins, such as sodium species with a marine origin and a silicate weathering origin. The abundance of major and trace elements can be influenced by human activities, thus, the large increase in the concentration of nitrate, sulfate, chloride, and potassium in river water can be related to a marked increase in fertilizer applications (Etchantu and Probst, 1988; Ramos, 1996). Moreover, the mobility of chemical species can be affected by the use of nitrogen fertilizers (Meybeck, 1979; Etchantu and Probst, 1988; Négrel, 1997, 1999; Négrel and Deschamps, 1996) or regulated by biochemical processes (Johnson et al., 1969).

The mass balance approach tries to evaluate the contribution of atmospheric inputs, fertilizer applica-

tions or other anthropogenic impacts, and rock weathering processes.

5.1. Atmospheric inputs correction: methodology and results

Some solutes in rainfall can constitute an important fraction of dissolved species appearing in surface waters (Meybeck, 1983). The aim of the atmospheric input correction is to quantify and subtract the portion of the elements carried by rainwater in the chemical composition of the river water. The quantification of atmospheric input due to rainwater requires knowledge of the chemical composition of the rainfall on the total watershed (Likens et al., 1977; Meybeck, 1983).

The estimation of the mean rainwater input on the whole watershed required the data of the two sampling databases and the meteorological data. The chemical composition of each monthly rainwater sample from the two sampling sites was weighted by the percent of rainfall in the same month.

Rainwater inputs in the dissolved load carried by the Loire had two distinct origins: (a) rainwater falling on the Massif Central, for which the chemical and isotopic characteristics are discussed elsewhere (Négrel and Roy, 1998) and briefly described in Section 4.1; and (b) rainwater falling between the Massif Central and the sampling point, for which the chemical and isotopic characteristics may be approached through the rainwater study near Tours in the sedimentary area (see Section 4.1). The rainwater inputs at the sampling site are approximately 25% rainwater of the sedimentary area (i.e., 9500 km² drained area between Orleans and Tours) and 75% rainwater of the Massif Central type (i.e., 32500 km² drained area between Orleans and the Massif Central).

In precipitation at Orleans station, sodium was the most concentrated species (61 $\mu\text{mol}/\text{l}$), chloride concentration was approximately 41 $\mu\text{mol}/\text{l}$, sulfate and nitrate, around 20 $\mu\text{mol}/\text{l}$, and calcium, 13 $\mu\text{mol}/\text{l}$. Other species (K^+ , Mg^{2+}) were estimated to be approximately 5 $\mu\text{mol}/\text{l}$. For the trace elements, Sr was close to 0.03 $\mu\text{mol}/\text{l}$ and Rb is 10 times lower at 0.04 $\mu\text{mol}/\text{l}$. The Sr isotopic ratio of rainwater inputs at Orleans was close to 0.70962.

Classically (Meybeck, 1983), for any element 'Z' in the river (Z)_r, the correction of atmospheric contribution to a river (r) is estimated by reference to the Cl concentration called (Cl)_{ref} multiplied by the Z/Cl ratios of rainwater (rw):

$$(Z)_{rw} = (Cl)_{ref}^* (Z/Cl)_{rw} \quad (1)$$

$$(Z)_{r,rw \text{ corrected}} = (Z)_{initial r} - (Z)_{rw} \quad (2)$$

Chloride ions in the atmosphere originate from sea salt and human activities. The release of Cl due to rock weathering has not been demonstrated clearly except in the weathering of salt rock (Meybeck, 1979). Furthermore, as chloride ions behave conservatively through the hydrological cycle (Meybeck, 1979), they have been used as a reference of atmospheric inputs in many unpolluted hydrosystems (Meybeck, 1983; Sarin et al., 1989; Négrel et al., 1993; Gaillardet et al., 1997). However, chloride ions can also result from a wide range of human activities (Meybeck, 1986; Sherwood, 1989). For the mass balance equations, the highest concentrations of Cl ions issued from rainwater, termed (Cl)_{ref}, had to be determined. The (Cl)_{ref} was calculated with each mean weighted chloride content for the sampling station at Tours and for the sampling station in the Massif Central, multiplied by the concentration factor *F* of each region. This factor *F* represents the concentration effect of evapotranspiration and is related to the total quantity of rainwater *P* (in mm) and the evapotranspiration process *E* (in mm) by the equation:

$$F = P / (P - E) \quad (3)$$

According to Eq. (3), the *F* value was equal to 1.2 in the Massif Central and to 2.2 in the sedimentary area for the two sampling periods. The general equation to calculate the (Cl)_{ref} was as follows:

$$(Cl)_{ref} = (Cl)_{SA}^* 0.25 * F_{SA} + (Cl)_{MC}^* 0.75 * F_{MC} \quad (4)$$

where (Cl)_{SA} and (Cl)_{MC} correspond to the weighted concentrations of chloride in the sedimentary area and the Massif Central, *F*_{SA} and *F*_{MC} correspond to the concentration factors in the sedimentary area and the Massif Central, and 0.25 and 0.75 correspond to

the respective proportions of sedimentary area and Massif Central area.

The (Cl)_{ref} was estimated at 74 μmol/l and represents the highest chloride concentration in the rainwater input to the river. When the chloride content measured in the dissolved load of the river (Table 1a and b) was lower than the (Cl)_{ref}, the whole chloride content of the river was assigned to atmospheric origin. When the chloride content measured in the dissolved load of the river was higher than the (Cl)_{ref}, the atmospheric correction was applied with (Cl)_{ref} as the rainwater input. The residual chloride (Cl)_{res} in the river was attributed only to human activities.

$$(Cl)_{res} = (Cl)_{measured} - (Cl)_{ref} \quad (5)$$

The estimate of the mean rain input at Orleans was calculated. Because the order of species abundance in the mean rainwater composition was Na⁺ > Cl⁻ > NO₃⁻ > SO₄²⁻ > Ca²⁺ > K⁺ > Mg²⁺, the atmospheric input corrections were important only for sodium and chloride. The main atmospheric correction was for sodium with a mean input of 23 ± 9%, i.e., ranging from 10% (September 1995) to 40% (January 1996), the atmospheric input of sodium varied widely throughout the year. The atmospheric correction for sulfate was of the same order of magnitude close to 20 ± 3% and ranging from 15% (September 1996) to 26% (February 1996). Corrections for chloride and potassium were two times lower than those for sodium (11 ± 2% and 10 ± 3%, respectively). Corrections for magnesium and calcium were similar, close to 3 ± 1%. The samples taken in summer generally presented lower rainwater input than the samples taken in winter because of the fewer rain events.

Note that the atmospheric input of NO₃⁻ in the river water (39 ± 20% and ranging from 16% (January 1996) to 97.7% (June 1995)) could not be calculated with mass balance considerations for 19 samples of Loire water taken in the period between July 1995 and December 1995. Their NO₃⁻ contents were too low relative to the rainwater content and this resulted in a 100% higher atmospheric input in the river. The low NO₃⁻ content in the river water was due to the biological pump of aquatic plants and algae, depending on the water temperature. From

July to December 1995, the water temperature ranged between 23°C and 6°C. After this period, the water temperature was too low for biological functions and the amount of nitrates increased because of no consumption.

For the trace elements, Rb exhibited the highest input by rainwater at $12.2 \pm 4.3\%$ (ranging from 3.5% (May 1995) to 22.1% (March 1996)), and Sr, a lower input at $3.8 \pm 1.1\%$ (ranging from 1% (May 1995) to 6% (January 1996)).

5.2. Budgets of human activities: methodology and results

When the rainwater influence was subtracted from the river water composition, the general mass balance equation showed that the dissolved load carried by the Loire was composed by the mixing of two individualized signatures: rock weathering and human activities. The influence of anthropogenic inputs needed to be quantified in order to evaluate the chemical weathering on the Loire watershed.

Human activities generate both diffuse contamination sources, including atmospheric transport, fertilizer applications, and local contamination sources that include urban and industrial wastewaters. It is well known that phosphorus and nitrogen forms, and potassium and chloride ions are mostly derived from agricultural fertilizers, animal waste, and municipal and industrial sewage (Meybeck, 1986; Dojlido and Best, 1996; Ramos, 1996), these species can be used as an indicator of both population and agricultural impacts. Sulfates are the product of the bacterial oxidation of some industrial products and of the mineralization of organic matter (Mackenzie and Garrels, 1966; Probst, 1986).

In order to identify anthropogenic and rock weathering end-members in the dissolved load of the Loire, atmospheric corrected samples were plotted in X vs. residual Cl^- diagrams, where X represents Na^+ , Ca^{2+} , Mg^{2+} , K^+ and HCO_3^- (Fig. 5a,b,c,d,e). Residual Cl^- in these atmospheric corrected samples has only an anthropogenic origin because there are no evaporitic rocks in the Loire watershed. Other anionic species (NO_3^- , SO_4^{2-}) could not be plotted because of the uncorrected atmospheric data and the lack of data for the different end-members, respectively. Waters of the Desges (Négre, 1999), Al-

lanche (Négre and Deschamps, 1996), and Bertrande watersheds (Négre, 1997) were plotted on the same diagrams to represent silicate weathering end-members. Several samples of water representing the weathering of carbonate monolithologies of the Seine watershed (Négre, unpublished data) were used to represent carbonate weathering end-members. Those of the Loir River, a tributary of the Loire just downstream of Orleans, represent the Tertiary basement of the Loire watershed (Négre and Grosbois, in prep.). Local samples of sewage station and industrial inputs represent waters with an anthropogenic activity origin. All these samples, except the samples of sewage station and industrial inputs, were corrected of rainwater inputs but still showed an anthropogenic influence (agricultural or urban). They cannot be considered as pure end-members, but as a mixing of monolithologic rock weathering and anthropogenic components. Moreover, for this first approach, the geochemical compositions of natural and anthropogenic end-members are considered constant. Seasonal variations in composition could not be evaluated and results will be calculated over the full hydrological cycle 1995–1996.

Thus, in the diagrams of Fig. 5(a,b,c,d,e), all the Loire River samples are scattered within the silicate, carbonate, Tertiary, and anthropogenic component fields. Two different anthropogenic end-members were distinguished to explain the dispersion of points for the Loire: one, called ANT1 (mainly related to sewage station), is characterized by a high residual chloride of over 1000 $\mu\text{mol/l}$ and by low amounts of X chemical species, the other, called ANT2 (related to agricultural activities), is characterized by a residual chloride close to 500 $\mu\text{mol/l}$ and higher amounts of X chemical species than ANT1.

The silicate end-member has the lowest anthropogenic chloride signature ($< 100 \mu\text{mol/l}$). The calcareous end-member has an intermediate anthropogenic chloride content ranging from 200 to 400 $\mu\text{mol/l}$. The variation of residual chloride of the Loire samples ranged between 250 and 450 $\mu\text{mol/l}$.

The inputs of the X chemical species carried by each pure end-member was evaluated by maximizing the highest value of the different end-members in order to encompass the Loire samples. To quantify the silicate signature for each chemical species, the linear regression was used with a residual chloride

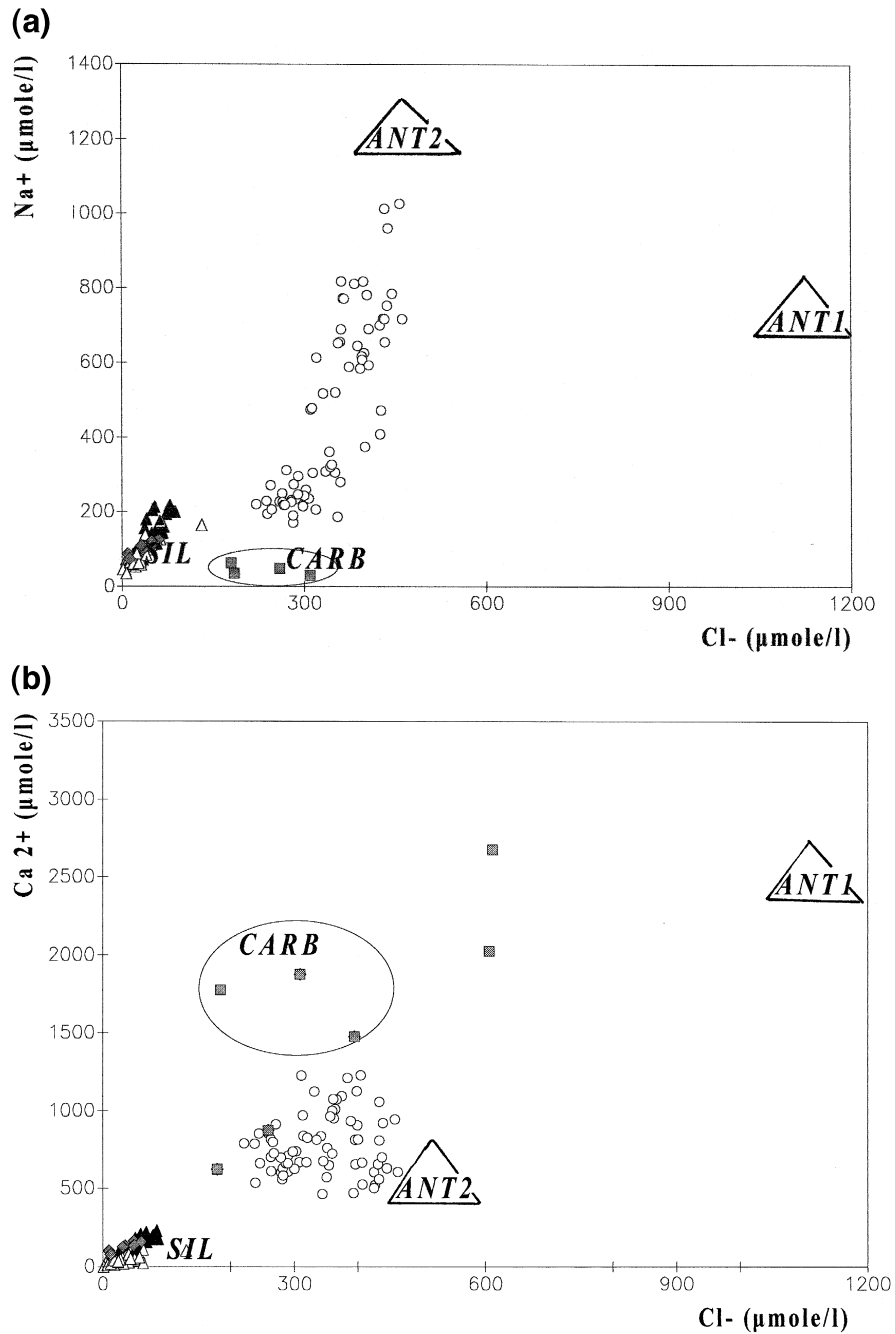


Fig. 5. Relationships between Cl^- and X chemical species in the dissolved load of the daily survey samples and water draining monolithological terrains. X = Na^+ (a), Ca^{2+} (b), K^+ (c), Mg^{2+} (d) and HCO_3^- (e). Symbols and references are identical to those in Fig. 4. The dissolved load was corrected for atmospheric inputs (see text for the calculation procedure). SIL represent the silicated end-member, CAR the carbonate end-member, and ANT1 and ANT2 the two types of anthropogenic end-members.

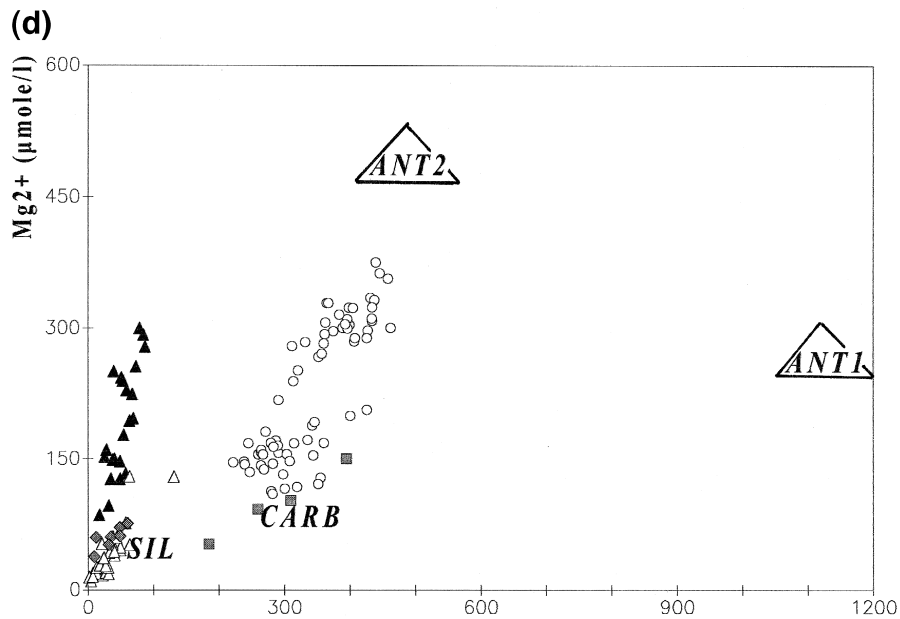
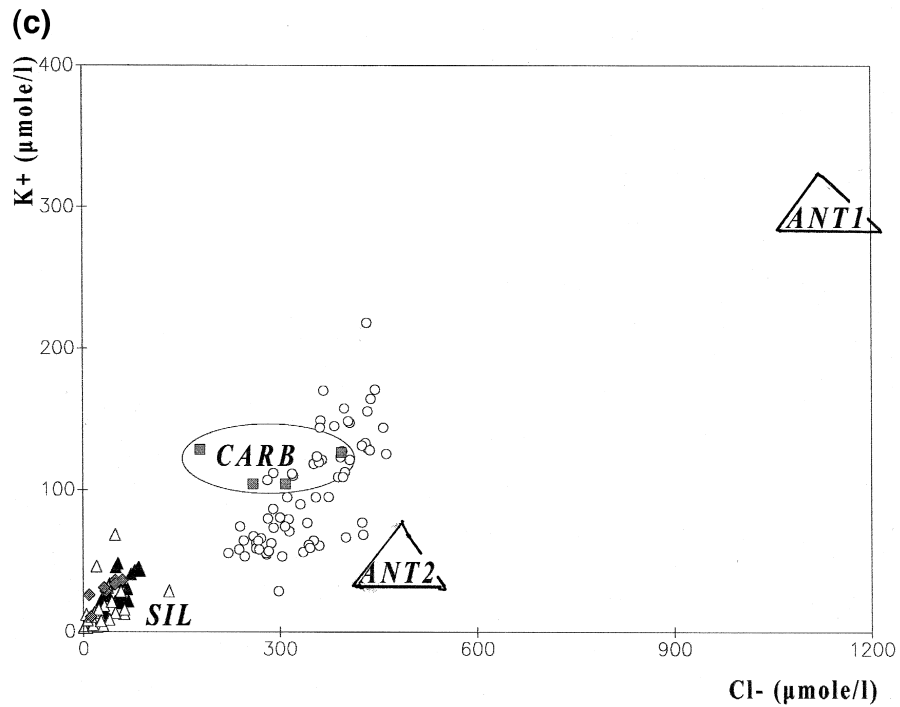


Fig. 5 (continued).

reduced to zero. This estimation showed that for the Na^+ signature of the different reservoirs, the anthro-

pogenic ANT1 reservoir carried $750 \mu\text{mol/l}$, two times lower than ANT2 ($1200 \mu\text{mol/l}$), 20 times

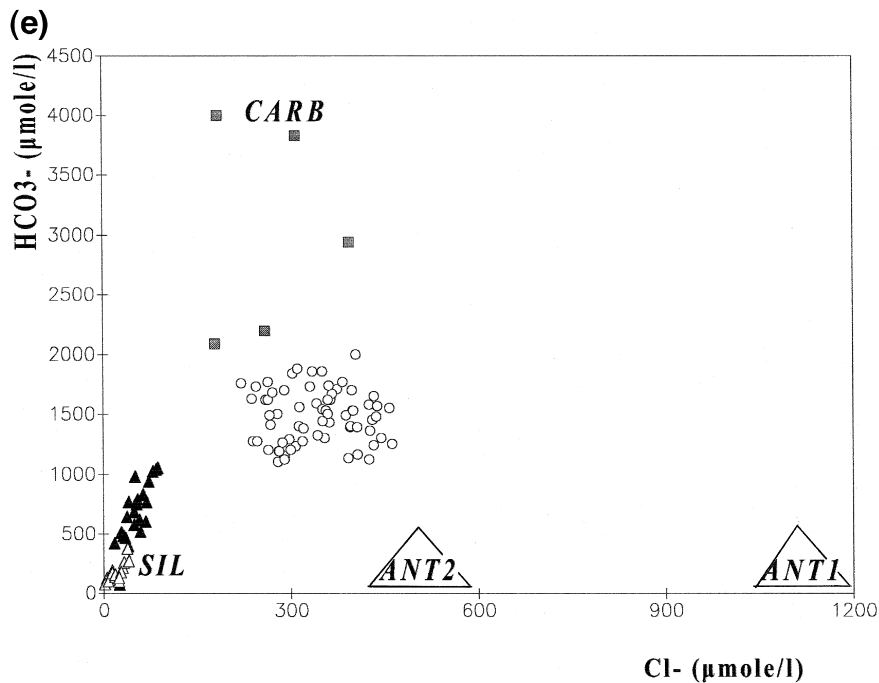


Fig. 5 (continued).

higher than the silicate end-member (60 $\mu\text{mol/l}$) and 60 times higher than the carbonate end-member (20 $\mu\text{mol/l}$).

For the Ca^{2+} signature, the most important reservoirs were the anthropogenic end-member ANT1 (2500 $\mu\text{mol/l}$) and the carbonate end-member (2000 $\mu\text{mol/l}$), which represents both groundwaters inputs and carbonate bedrocks weathering. This is also true for the K^+ signature (respectively, 300 and 125 $\mu\text{mol/l}$). The second anthropogenic end-member, ANT2, carried 500 $\mu\text{mol/l}$ of Ca^{2+} and 75 $\mu\text{mol/l}$ of K^+ . The silicate end-member carried 70 $\mu\text{mol/l}$ of Ca^{2+} and 35 $\mu\text{mol/l}$ of K^+ .

Finally, for the Mg^{2+} signature, the ANT1 end-member was lower (250 $\mu\text{mol/l}$) than the ANT2 end-member (500 $\mu\text{mol/l}$), the carbonate and silicate end-members carried 100 and 50 $\mu\text{mol/l}$, respectively.

The inputs of the different end-members to the dissolved load could be calculated using this estimation of the chemical signature of the pure end-members. For each chemical species, the contributions for the silicate (SIL), carbonate (CAR), and anthro-

pogenic (ANT1, ANT2) end-members were calculated for each sample of Loire water using the following Eq. (6):

$$[\text{X}]_{\text{riv}} = a[\text{X}]_{\text{SIL}} + b[\text{X}]_{\text{CAR}} + c[\text{X}]_{\text{ANT1}} + d[\text{X}]_{\text{ANT2}}, \quad (6)$$

with the condition: $a + b + c + d = 1$, where X represents each cationic species, [X] represents the amounts (in $\mu\text{mol/l}$) of X in the SIL, CAR, ANT1 and ANT2 end-members, and a , b , c , d represent the proportions (%) of each end-member contribution.

The proportions of weathered terrains and anthropogenic contributions resulting from the mass balance calculations show that dissolved Na^+ inputs are dominated by both silicate weathering ($20.8 \pm 1.1\%$) and carbonate weathering ($20.9 \pm 1.2\%$). These two inputs from rock weathering increased with increasing discharge. The anthropogenic inputs of end-members ANT1 and ANT2 were quite similar with a proportion close to $17 \pm 2\%$, they were more impor-

tant during low flow than during high flow, being higher than the rock weathering end-members.

Dissolved Ca^{2+} inputs were controlled both by silicate weathering ($34.6 \pm 3.9\%$) and anthropogenic inputs ANT2 ($34.3 \pm 4.9\%$). This influence of silicate and ANT2 inputs on Ca^{2+} proportions was present over the entire hydrological cycle except during the summer flow. The influence of carbonate weathering was also important ($23 \pm 4\%$). The ANTI proportions had the lowest ($9.5 \pm 6.9\%$) over the hydrological cycle for Ca^{2+} inputs but this end-member ANTI1 was mainly present during low flow, equal to carbonate inputs during this period.

Dissolved K^+ inputs were clearly controlled by silicate weathering ($34.5 \pm 5.2\%$) and its proportion increased with increasing discharge. A large proportion of the dissolved K^+ could be related with the anthropogenic end-member ANT2 ($30.3 \pm 1.2\%$), but this proportion decreased with increasing discharge. The carbonate end-member inputs carried about 23% of total amount of dissolved K^+ . As for the silicate end-member, its proportions increased with increasing discharge. The anthropogenic end-member ANTI1 was preponderant only during the summer period between mid-August and November 1995, outside this period, it was negligible for dissolved K^+ inputs.

The dissolved Mg^{2+} was mainly controlled by silicate and carbonate weatherings ($27.5 \pm 1.2\%$ and $26.7 \pm 8.9\%$, respectively) during the autumn and winter seasons. During the spring and summer seasons, it was controlled by the ANT2 and ANTI end-members ($20.1 \pm 1.5\%$ and $22.6 \pm 0.6\%$, respectively).

Finally, the dissolved HCO_3^- input was controlled by carbonate weathering ($48.2 \pm 7.5\%$) throughout the hydrological cycle. The silicate end-member was still present and constant ($25.6 \pm 0.2\%$). The ANT2 end-member was of the same order of magnitude ($22.3 \pm 4\%$), but decreased during two periods (May 1995 and October–November 1995) while the ANTI end-member increased to almost 15%. Outside of these two periods, the ANTI end-member gave the lowest contribution to the dissolved HCO_3^- input ($3.9 \pm 4.8\%$).

Thus, the contributions to the dissolved load of the different end-members varied greatly. Each end-member was significant at different periods of the

hydrological cycle and had a characteristic geochemical behaviour.

5.3. Natural and anthropogenic export in the upper Loire watershed

The results of the preceding calculation using the mixing Eq. (6) made it possible to determine natural and anthropogenic exports from the upper Loire watershed. The export rates ω (in t/day) due to rock weathering or anthropogenic additions can be calculated for each end-member (SIL, CAR, ANTI1, and ANTI2) and for each hydrological period as follows:

$$\omega = \Sigma(\alpha[\text{Ca}^{2+}] + \alpha[\text{Mg}^{2+}] + \alpha[\text{K}^+] + \alpha[\text{Na}^+] + \alpha[\text{HCO}_3^-] + \alpha[\text{Si}])^* W \quad (7)$$

where $[X]$ represents the concentration expressed in g/l, W represents the discharge (m^3/s) measured at the sampling points during the considered hydrological period, and α represents the proportion of an end-member for the sample i .

The rock weathering and anthropogenic rates were calculated and the results of ω showed different behaviours according to the hydrological period (Table 3). During high flow, the export rate for each end-member is always greater because of the high daily water discharge. This is the main hydrological period for dissolved export and about 71% of dissolved elements with a silicate origin are exported, 69% with an ANTI1 origin, 66% with a carbonate origin, and 58% with an ANT2 origin. On the average, 68% of the total annual dissolved flow is transported during the high flood while this period represented only 40% of the hydrologic year.

The total annual dissolved flow is close to 1300×10^3 t/year. In detail, the carbonate weathering rate is 430×10^3 t/year, about 33% of the total annual dissolved flow (Table 3). The daily rate for carbonate weathering is always the highest, except during the high stage 95/96 when ANTI1 exportation rate is of the same order because of leaching of the cultivated soils and nutrients mobilization.

The export rate for silicate weathering is 360×10^3 t/year, about 28% of the total annual dissolved

Table 3
Dissolved export for each end-member during each hydrological period

	Mean daily discharge (m ³ /s)	Total water volume (t/period)	Duration of the period (d)	ANT1 (t/d)	ANT2 (t/d)	SILICATE (t/d)	CARBONATE (t/d)	% of total annual flow
End of high flow 95	301	7.2 × 10 ⁵	23	1233	157	1285	1908	8
Low flow 95	126	2.1 × 10 ⁶	217	567	213	483	676	32
High flow 95/96	567	5.5 × 10 ⁶	124	1997	481	1810	1926	60
Total annual flow (t/year)	–	–	–	401 × 10 ³	110 × 10 ³	360 × 10 ³	430 × 10 ³	
% of the total annual flow	–	–	–	31	8	28	33	

flow. The ratio of carbonate /silicate weathering rates ranges between 1.2 during the high flood and 1.4 during the low stage. As usual, carbonate rock weathering is more productive for the dissolved load than silicate weathering (Meybeck, 1994), which in comparison, exports more dissolved elements during the high stage than carbonate weathering in the same period.

For exported dissolved elements from anthropogenic origins, ANT1 export (close to 401 × 10³ t/year) is four times higher than the ANT2 export (close to 110 × 10³ t/year) over the hydrological cycle. It represents 31% of the total annual export and it is on the same order with silicate weathering export over the full year. At the Orleans station, about 40% of the total dissolved load have an anthropogenic origin (mainly agricultural) over the hydrological cycle. The ratio of rock weathering/anthropogenic rates is evaluated throughout the sampling period. It ranges from 1.48 during low flow to 1.58 during high flow. Thus, the ratio was around 1.5 implying that the rock weathering processes were the main source of the dissolved load.

The sampling point can be considered as a sub-basin. Therefore, the specific dissolved exportation rates ϖ for silicate and carbonate weatherings (expressed in t year⁻¹ km⁻²) can be calculated from the respective drained areas as follows:

$$\varpi = (\omega)/S, \quad (8)$$

where ω (t/year) is the export rates and S is the drainage area of the sub-basins (km²).

The export rate for silicate rocks is close to 360 × 10³ t/year with a respective specific export

rate close to 12 t year⁻¹ km⁻². The export rate for carbonate rocks is higher than for silicate rocks (430 × 10³ t/year) with a specific export rate close to 47 t year⁻¹ km⁻². This exportation rate is of the same order as the export rate for carbonate terrain in the Seine watershed (42 t year⁻¹ km⁻²; Roy, 1996). The ratio of carbonate/silicate rock export rates is close to 3.9 for the upper Loire watershed. By comparison, this ratio is two times greater in the Seine watershed (Roy, 1996) at close to 7.9.

The total exportation at the sampling point is 1300 × 10³ t/year for the dissolved transport. It has been determined to be close to 370 × 10³ t/year for the SM transport on the same hydrological cycle (Négre and Grosbois, 1999) and close to 1200 × 10³ t/year for bed sediments at Belleville station, 120 km upstream from the Orleans station (study between 1979 and 1994, Hydratec, 1985; Anonymous, 1993). The dissolved export is a factor of 3.5 higher than the SM export for the upper Loire. This ratio is of the same order of magnitude as for the Seine (Roy, 1996) or the Garonne (Probst and Bazerbachi, 1986), and clearly, lower than for the Rhine (close to 17.8; Meybeck and Ragu, 1996). For the Rhône, which is one of the rivers where particulate transport is preponderant, the ratio is close to 0.6 (Meybeck and Ragu, 1996).

The dissolved export is of the same order as solid export when SM and bed sediments are considered. But bed sediments transport values are often unreliable because of their strong variability both in time and space, and remobilization and storage in the mean stream of the river (Meade 1986, Meade et al., 1990).

6. Conclusions

The seasonal fluctuations of dissolved concentrations compared with those of the discharge reveal different geochemical behaviour patterns. The high flow signature is in agreement with rock weathering and rainwater inputs and the low flow signature can be related to groundwaters and anthropogenic inputs, such as urban sewage and farming waters. The correlation between discharge and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio reveals two geochemical signatures. The chemical composition of the Loire water appears to be controlled by rainwater inputs, by silicate and carbonate weathering inputs and by the two kinds of anthropogenic input. Each end-member appears at different periods during the hydrological cycle and has a characteristic geochemical behaviour. The contributions of the different end-members to the dissolved load were calculated with the mass balance approach and vary greatly for each chemical species. The export rates due to rock weathering and anthropogenic additions were also calculated. The ratio of weathering rates/anthropogenic rates ranged between 1.48 and 1.58. Anthropogenic inputs represent 40% of the dissolved load over the full hydrological cycle.

Transport at the Orleans sampling point reached 1300×10^3 t/year for the dissolved transport, a factor of 3.5 higher than the particulate transport (Négrel and Grosbois, 1999). The specific exportation rate for each lithology was generally of the same order of magnitude as for the other watersheds in France. The ratio of carbonate rock/silicate rock export rates is close to 3.9 on the upper Loire watershed.

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