The dissolved load of the Loire river: natural inputs and anthropogenic activities contributions

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The Loire river, one of the largest watersheds in France, has been monitored just outside of the city of Orleans from 1994 to 1996 and 150 km downstream Orleans, in the village of Brehemont from 1996 to 1998. The sampling frequency ranged between 2 days and 2 weeks according to the river flow. The location of the sampling point at Orleans represents 34% of the total Loire watershed with 76% silicate rocks and 24% carbonate rocks. The second location at Brehemont represents 26% more of the total watershed, draining only additional carbonate rocks.

This study reports on the temporal distributions of major and trace elements and Sr isotopic measurements on the dissolved load of the Loire river at these two points of the watershed. Natural and anthropogenic inputs to the dissolved load have been distinguished and the exportation rates due to rocks weathering and anthropogenic inputs can also be compared.

The temporal fluctuations of major and trace elements in the dissolved load can be divided into 3 types of geochemical behaviour. They exhibit characteristics of mixed waters as shown by the positive correlation between discharge and $^{87}Sr/^{86}Sr$ ratio. The first kind, present during the low flow, is concentrated in major and trace element and is characterised by a low isotopic Sr ratio. It may be related to groundwaters inputs and anthropogenic activities. The second kind, present during high flow, is more diluted and may be related to rain water and weathering inputs.

The mass-balance approach (Meybeck, 1983; Drever and Hurcomb, 1986) shows that the dissolved load is composed by the mixing of atmospheric inputs, rock weathering and human activities. In order to estimate each component contribution, the rain water influence is subtracted from the river water composition, using chloride as the atmospheric reference (Meybeck, 1983) and using the rain water database collected between 1997 and 1998 near the second sampling location. The atmospheric inputs range from 3 $\pm$ 1% for Mg^{2+} and Ca^{2+} species to 33 $\pm$ 9% for Na^{+} specie. All residual chloride amounts in these atmospheric corrected samples have an anthropogenic origin because there is no evaporitic rock on the Loire watershed.

The atmospheric corrected samples were plotted in X *vs* Cl^{-} diagrams (where X represents other major elements) in order to determine rock weathering and anthropogenic activities signatures in the dissolved

TABLE 1. Mean percent of each end-member inputs in the dissolved load at Orleans station during low flow

	Na^{+}	K^{+}	Mg^{2+}	Ca^{2+}	HCO_3^{-}
Atmospheric end-member	19	8	3	3	0
Anthropogenic end-member 1	29	17	28	7	2
Anthropogenic end-member 2	28	25	33	33	21
Silicate end-member	12	27	17	33	26
Carbonate end-member	12	23	19	24	51

TABLE 2. Mean percent of each end-member inputs in the dissolved load at Orleans station during high flow

	Na^+	K^+	Mg^{2+}	Ca^{2+}	HCO_3^-
Atmospheric end-member	33	12	4	4	0
Anthropogenic end-member 1	8	4	19	<1	8
Anthropogenic end-member 2	13	28	11	36	24
Silicate end-member	23	35	34	39	26
Carbonate end-member	23	21	32	21	42

load. Waters, sampled on silicate monolithologic sub-catchments of the upper Loire watershed (Négrel, 1997; 1998; Négrel and Deschamps, 1996) and on carbonate ones (Négrel, personal communication) are used for the rock signature. Local sewage waters, industrial waters (this work) and fertilizers (Négrel and Deschamps, 1997) represent anthropogenic activities. All the samples are scattered within the silicate and carbonate fields and 2 different anthropogenic components are needed to explain the dispersion of the samples. The first one is characterised by a residual chloride close to 1200 µmoles/l and the second by 500 µmoles/l and higher amounts of dissolved species. So, each geochemical end-member could be characterised and the proportional inputs of the chemical species carried by each end-member were calculated (Table 1 and 2). Generally, the contributions of the different end-members to the dissolved load vary strongly for each specie all over the hydrological cycle. The anthropogenic end-members always give the lowest contributions, excepted during the low flow.

The exportation rates due to rock weathering and anthropogenic are also approached at the 2 sampling points. Concerning Orleans site, the ratio of weathering rates/anthropogenic rates ranges between 0.5 and more than 4. During the low flow, the anthropogenic rates are higher than the rock weathering rates and anthropogenic inputs are the main origin of the dissolved load of the Loire during this period.

The specific dissolved rate/specific particulate rate is 5 at Orleans and 3 at Brehemont. The specific exportation rate for each lithology was calculated for the dissolved transport and was mainly of the same order of magnitude as for other watersheds in same climatic areas.

References

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