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Predicting the impact of land use on the major element and nutrient fluxes in coastal Mediterranean rivers: The case of the Têt River (Southern France)

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Abstract

This study presents a detailed discrimination between the natural and anthropogenic sources of dissolved major elements in the Têt River, a typical small coastal river in the south of France. The main objectives were to quantify the materials that were released by human activities in the basin, and to determine the specific element inputs for the major land use forms. The dissolved material fluxes were estimated by weekly monitoring over a hydrological year (2000–2001) along the major water gauging stations, and the flux relationships were examined in the context of anthropogenic and natural basin characteristics as determined by a Geographical Information System (GIS). Intensive agricultural land use in the form of fruit tree cultures and vineyards has a strong control on the dissolved element fluxes in the river. Area specific element releases for these cultures are greatest for SO_4, with an estimated average of about 430 ± 18 keq km^{-2} a^{-1}. This is $\geqslant 11$ times the natural SO_4 release by rock weathering. Also for K, NO_3, PO_4 and Mg, the specific releases were $\geqslant 6$ times the natural weathering rates (respectively about 44, 60, 4 and 265 keq km^{-2} a^{-1}). Waste-waters are the other major source of anthropogenic elements in the river. They have an important role for the fluxes of inorganic P and N, but they are also a considerable source of Cl and Na to the river. For example, the average annual release of Cl is around 150 moles/inhabitant in the rural basin parts. Further downstream, however, where population density strongly increases, industrial effluents can enhance this value (>300 moles/inhabitant). The waste-waters contribute more than 70% of the dissolved inorganic N export to the sea, although their contribution to the average DOC export is almost negligible (3%).

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1. Introduction

Dissolved major elements in river water are generally considered to strongly reflect water–rock interactions in its catchment area, giving them an

important role in the study of chemical weathering rates (Meybeck, 2003). As geochemists became aware of the close coupling between the chemical weathering of rocks and the atmospheric CO_2 content, and hence global climate, many studies have focussed on the global controls of chemical weathering rates, and the evaluation of major element fluxes in world rivers remains still a common approach for this purpose (e.g. Probst et al., 1994; Amiotte Suchet and Probst, 1996; Gaillardet et al., 1997, 1999; Millot et al., 2003; Mortatti and Probst, 2003).

Major elements are released to surface waters from various sources, and using them as proxies for weathering rates requires first of all the identification of their different origins. Also human activities can strongly modify the abundance of major elements in natural waters. At present, for nutrient fluxes, e.g. the fluxes of dissolved inorganic N, several modelling approaches exist that allow calculating the nutrient export by a given catchment as a function of anthropogenic parameters, among which population density or fertilizer spreads are the most important (e.g. Seitzinger and Kroeze, 1998; Smith et al., 2003; Harrison et al., 2005). This is because in populated areas, nutrient levels are almost exclusively controlled by human activities, and natural levels can only be found in pristine watersheds. For other compounds, however, such as Cl, SO_4 and/or Na, such approaches are missing and the distinction between natural and pollution levels remains difficult.

The purpose of this study is to establish a detailed quantitative assessment of the different sources that contribute to the dissolved loads in the Têt River, to identify the materials that are released by human activities, and to examine whether they can be related to land use practices or other anthropogenic activities in the basin. The approach is built on mass budget calculations from data of a high frequency sampling during one complete hydrological year along the major gauging stations of the river, together with a GIS-based determination of the basin characteristics. Due to its moderate basin size, the river can be easily sampled within 1 day from its uppermost headwaters down to its mouth, which allows good data comparability between the different stations. Another advantage is that the major material sources can be clearly identified. In its upper course, population density is very low and the river chemistry is almost exclusively controlled by natural processes. In the

middle part, agriculture leaves its fingerprints in the water chemistry, whereas the lowest part is strongly impacted by urban wastewater releases.

2. Data and methods

2.1. Sampling and water fluxes

The Têt River is a typical small Mediterranean river that drains the eastern part of the French Pyrenees in a WSW-ENE direction. Its basin area is about 1400 km^2 and the river length is about 120 km. The uppermost basin parts reach up to elevations of >2500 m and are regularly snow-covered during winter. From there, the river descends on a rather steep gradient down to sea level, passing rapidly through various climate and vegetation zones before entering the sea in the SW part of the Gulf of Lions.

The river was sampled weekly between September 2000 and September 2001, and monthly between October 2001 and May 2002 at its major water gauging stations. This was done manually from bridges in the central part of the river. High frequency sampling (hourly) during one major flood at the downstream stations and seasonal sampling of the major tributaries (at least one sample per season) completed the survey. Fig. 1a shows the locations of the sampling stations at the main river and Table 1 lists the corresponding hydroclimatic characteristics in the corresponding basin parts.

The sampling stations St1–St4 are situated in the mountainous part of the basin, whereas stations St5–St7 lie in the much flatter alluvial plain. The last water gauging station corresponds to St5 in the town of Perpignan, just a few meters above the confluence of its last tributary (the Basse tributary), which is gauged separately. The combination of both records determines the total water flux of the river. Two additional sampling stations (St6 and St7) downstream of St5 were introduced in order to catch the wastewater inputs from Perpignan (St6), and from a smaller wastewater station further downstream (Sainte-Marie, St7). In the 1970s, a reservoir was constructed between St3 and St4 for flood control (Vinça reservoir: 24.6 Mm^3). It is maintained at very low levels during late autumn and early winter, when the risk of flash-floods is maximal, and allowed to be filled during spring and summer in order to sustain irrigation in the basin. There is also a reservoir upstream St1 (Bouillouse reservoir: 17.5 Mm^3) for hydroelectric power
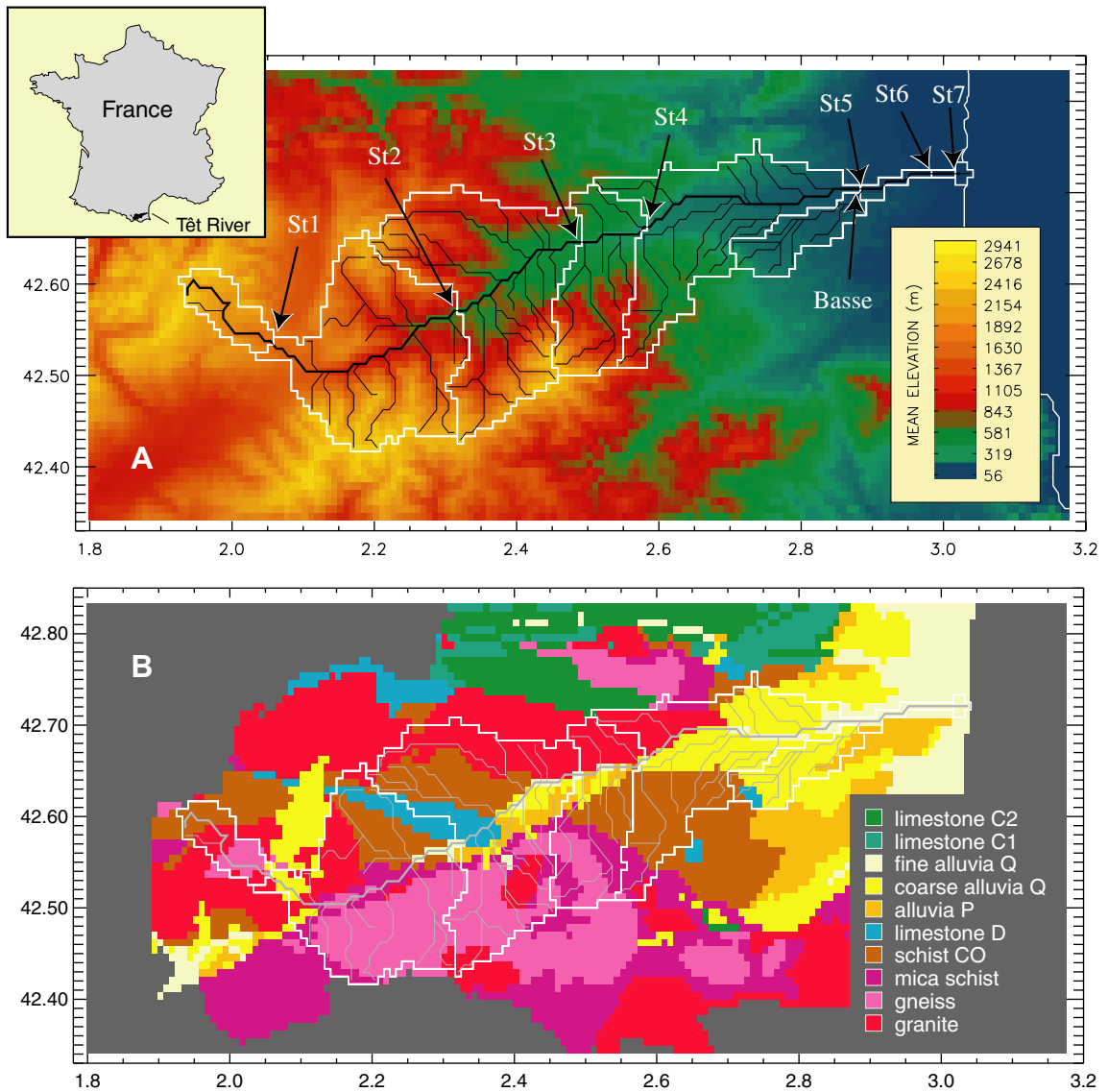
Fig. 1. Morphology, location of the sampling stations (both map A), and lithology (map B) in the basin of the Têt River (after USGS (2000) and Salvayre (1974)). The capital letters in B denote Cambrian (C), Ordovician (O), Devonian (D), Cretaceous (C1, C2), Pliocene (P), and Quaternary (Q) ages. Note that the Devonian limestone is dolomitic.

generation. As the water flow of the Têt River is low at St1, its impact on the material transport in the river is much less important compared to the Vinça reservoir.

Water flow is complex because of anthropogenic water extraction at many places along the river course. Irrigation channels can be found almost everywhere along the basin. This means that the average discharge values that are recorded at the gauging stations (Table 1) do not allow a conservative budgeting of the surface water flow. Major irrigation channels start from the Vinça reservoir and

from the main river course downstream and extract water for agricultural and urban water use. As a consequence, the average water flow at St5 is often lower than at St4, although tributaries bring additional water to the river between both stations. Also upstream of the reservoir, irrigation channels exist and the water can bypass the gauging stations at several places.

For the above reason, we also include in Table 1 an estimation of the potential water flux at each gauging station that corresponds to the water discharge if no water extraction occurred. These values

Table 1
Average hydroclimatic characteristics of the sampling stations in the Têt basin

Station	Mean T, long term (°C)	Mean T, study year (°C)	Mean P, long term (mm)	Mean P, study year (mm)	Mean Q, long term (mm)	Mean Q, study year (mm)	Model long term Q (mm)
St1	3.7	3.1	1044	962	672	618	692
St2	6.2	5.8	798	754	314	267	450
St3	9.7	10.0	755	684	319	230	338
St4	10.6	11.1	799	766	84	86	300
St5	14.1	14.3	675	678	2	-133	131
St6	15.6	15.7	641	630	311	239	66
St7	15.5	15.4	608	475	0	0	54
St1c	3.7	3.1	1044	962	672	618	692
St2c	5.9	5.4	831	782	361	313	482
St3c	7.7	7.6	795	735	341	274	413
St4c	8.2	8.2	795	740	297	241	393
St5c	9.6	9.7	767	726	227	153	332
St6c	10.0	10.1	758	719	233	159	313
St7c	10.0	10.1	758	718	232	158	312

Average temperature (T), precipitation (P), discharge (Q) and modelled discharge were determined according to Ludwig et al., 2004 (the long-term estimates correspond to the 1980–2000 period); St1–St7 refer to the basin area between two successive sampling stations, whereas St1c–St7c refer to the cumulative basin area.

are 1980–2000 averages established by applying the estimated runoff ratios to the precipitation totals according to Ludwig et al. (2004), who estimated an anthropogenic reduction of the natural water flow of 35% for the entire river.

2.2. Analytical methods and flux calculations

After measuring pH and temperature in the field, 10 L samples were collected in plastic containers and stored in the laboratory at 4°C before filtration, using 0.4 μm *Millipore* polycarbonate filters for major element, and pre-ashed 0.7 μm *Whatman* GFF glass fibre filters for dissolved organic C (DOC) analysis. Major cations (Ca, Mg, Na, K, NH$_4$) and anions (Cl, SO$_4$, F, NO$_3$, NO$_2$, PO$_4$) were analysed by HPIC (High Pressure Ionic Chromatography) using cation (*Dionex* CS12) and anion (*Dionex* AS9) columns, coupled to anion (*Dionex* ASRS Ultra) and cation (*Dionex* CSRS Ultra) suppressors, respectively. The sample aliquots for cations were acidified with ultra-pure HNO$_3$ acid to avoid the risk of precipitation. Alkalinity was measured with an automatic titration burette, DOC was analysed with a *Shimadzu* 5000 TOC analyser, and dissolved silica was measured spectrophotometrically by comparing the samples with standard solutions according to Mortlock and Froelich (1989). All methods were thoroughly tested for accuracy and reproducibility prior to sample analyses.

Water discharge data for flux calculations were obtained from the *HYDRO* database hosted at the French Ministry of Environment. Mean annual fluxes for the investigated compounds were calculated by the summation of the partial fluxes between sampling for the entire hydrological year. For a given period j, which lays between the two sampling events i and $i + 1$, the discharge-weighted mean concentration (C_j^*) was determined on the basis of the instantaneous concentration (C_i, C_{i+1}) and discharge values (Q_i, Q_{i+1}):

$$C_j^* = \sum_i^{i+1}(C_i Q_i) / \sum_i^{i+1}(Q_i) \qquad \text{(i)}$$

C_j^* values were then multiplied with the corresponding water discharges during j (Q_j) that were calculated with the daily discharge records, and summing of the fluxes for all periods resulted in the mean annual flux (F_{an}):

$$F_{an} = \sum_{j=1}^{j=n}(C_j * Q_j) \qquad \text{(ii)}$$

Most of the dissolved constituents show significant but non-linear relationships with discharge, and the above method normally gives highly realistic flux estimates (Karakatsoulis and Ludwig, 2004). For some nutrients, such as NO$_3$, concentrations are not clearly linked to discharge, so other methods were tested for more accurate calculations (for a

presentation of different methods, see for example Moatar and Meybeck, 2005). However, in most cases, the resulting mean annual fluxes were not much different from the ones obtained by the above method, and therefore it was decided to apply it uniformly to all dissolved compounds. The relatively high sampling frequency means that for nutrients also, the fluxes determined should be close to reality ($\pm 10\%$).

2.3. Quantification of non-weathering sources

In the absence of evaporite outcrops in the catchment, Cl in rivers can be entirely attributed to non-weathering sources (Meybeck, 1983, 1986). Four major non-weathering sources that supply Cl and other dissolved elements to the river were identified: atmospheric deposits (rain), road salting, urban wastewaters and diffuse agricultural sources (mainly fertilizer use). Once the chemical composition of these sources is known, and the respective parts of the riverine Cl from each of the mentioned sources can be determined, one can then correct the river composition from its non-weathering contribution according to:

$$X_{i,c} = X_i - (Cl_{q,j} R_{i,j}) \qquad (iii)$$

X_i and $X_{i,c}$ are, respectively, the average concentration of a given element i in the river before and after the correction, $Cl_{q,j}$ is the average Cl concentration in the river that comes from the non-weathering source j, and $R_{i,j}$ is the average element over Cl ratio of the element i in the non-weathering source j. $R_{i,j}$ was derived from the literature sources and from differences between two neighbouring river stations when they can be attributed to pollution inputs. $Cl_{q,j}$ was deduced via estimation of the major non-weathering inputs of Cl from upstream to downstream.

2.4. Average rainwater composition

Atmospheric inputs are an important source of dissolved elements in rivers, in particular for coastal rivers where large parts of the catchment are under marine influence (Gibbs, 1970; Stallard and Edmond, 1981; Meybeck, 1983). Rainwater chemistry was not monitored in the study. Compositions can vary considerably, both spatially and temporally, and long-term networks are needed to determine the average composition (Ulrich and Williot, 1993). Major elements in rain over the Têt basin were estimated from previous studies on atmospheric deposition in the south of France, in particular the data on the French network CATAENAT-RENECOFOR (Croisé et al., 2002). The authors mapped the average deposition 1993–1998 by a geostatistical interpolation approach and supplied the data in a 10 by 10 km^2 grid point resolution. They were converted into average concentrations based on the precipitation totals for 1993–1998 over the Têt basin (Table 2, column 1).

Table 2
Different estimates for the average rainwater composition in the Têt Basin (µeq/L)

Station	Ca			Mg			Na		
	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)
St1c	39.3	29.9	22.8	13.9	10.8	7.6	33.6	36.3	18.6
St2c	45.9	33.0	29.4	17.0	12.1	10.4	41.2	40.3	25.2
St3c	45.9	36.4	32.4	16.6	13.4	11.3	40.2	44.9	27.5
St4c	46.2	38.1	34.1	16.7	14.1	11.9	40.4	47.1	28.9
St5c	47.6	46.0	42.5	17.2	17.4	15.1	42.0	57.9	37.0
St6c	48.3	50.6	47.4	17.4	19.4	17.1	42.8	64.4	41.9
St7c	48.4	51.5	48.4	17.5	19.8	17.5	42.9	65.7	42.9
	K			Cl			SO$_4$		
St1c	4.9	2.6	2.3	53.5	39.5	27.2	36.3	36.4	27.7
St2c	5.3	3.0	2.9	65.9	44.4	37.7	39.0	38.3	31.4
St3c	5.2	3.4	3.3	64.2	50.1	41.4	37.6	40.3	31.8
St4c	5.2	3.6	3.5	64.3	52.9	43.9	37.5	41.3	32.5
St5c	5.3	4.6	4.5	66.3	67.0	57.2	37.6	45.2	35.7
St6c	5.4	5.3	5.3	67.1	75.7	65.5	37.8	47.2	37.5
St7c	5.4	5.4	5.4	67.2	77.6	67.2	37.8	47.6	37.8

Data sources and explanations: (1) Croisé et al., 2002; (2) Ladouche et al., 1998; and (3) combination of both (this study): the percentages of the rainwater compositions compared to St7 in (2) were applied to (1) for each station. St1c–St7c refer to the cumulative basin area.
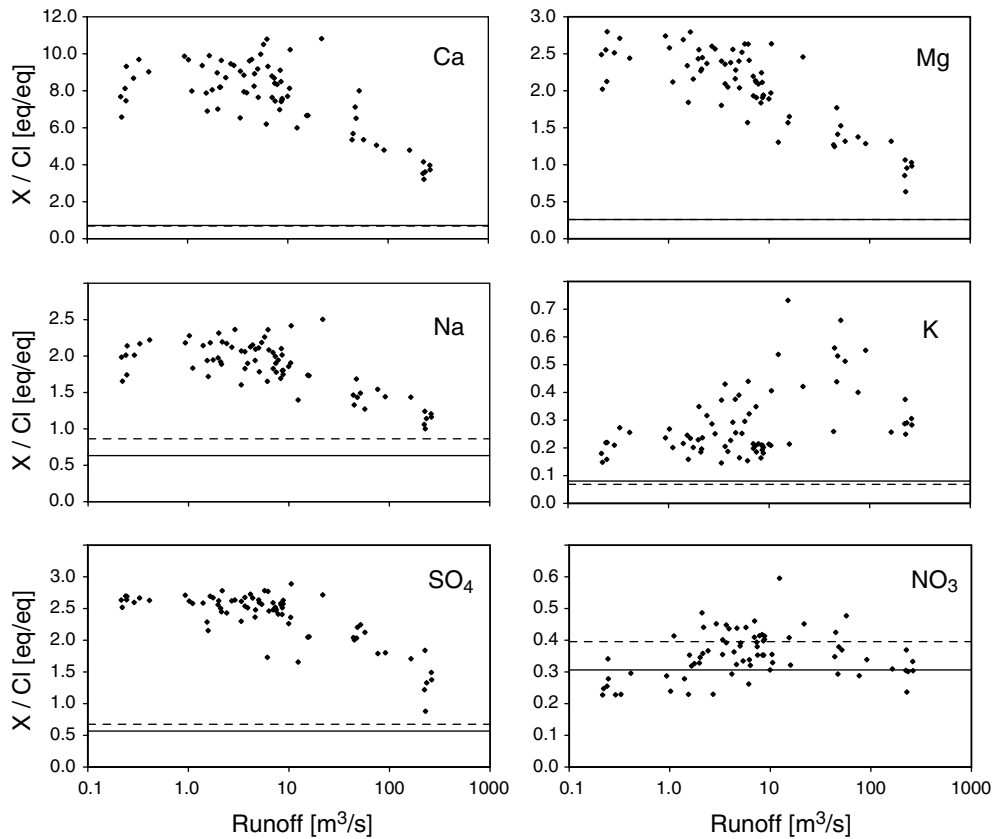
Fig. 2. Evolution of the element over Cl ratios in the Têt River at St5 during floods in comparison with the average rainwater ratios of Croisé et al. (2002) (CATAENAT-RENECOFOR, solid line) and of Ladouche et al. (1998) (dashed line).

These data were combined with a second estimation of the average rainwater composition based on the measurements of the rainwater chemistry in the Hérault basin (Ladouche et al., 1998; Petelet, 1998). The Hérault River is situated about 200 km NE of the Têt River and, as the latter, under the strong influence of Mediterranean air masses. The rainwater chemistry rapidly changes in the hinterlands of the Hérault basin, and highly significant relationships exist between the average concentrations and the elevation of the rain gauge stations for almost all elements (Petelet, 1998). Assuming that these relationships hold for the Têt basin too, they were applied to the digital elevation model (see below) in order to derive an alternative rainwater chemistry data set (Table 2, column 2).

Both data sets are generally in good agreement for the entire Têt basin (St7), except for Na, which is higher in the Hérault data. Validation of these data for the current study was done indirectly by comparing the respective R_i ratios with the element over Cl ratios in the Têt River during flash-floods,

when most of the river water is rain-derived. Although the R_i ratios are very different during normal hydrological conditions for most conservative elements (Na, Ca, Mg, SO$_4$), they tend towards the respective rainwater ratios during floods (Fig. 2). The fit for Na is best with the CATAENAT data and it was concluded that they give the most reliable values for the entire basin. However, because of the higher spatial sampling resolution, it was taken that the upstream to downstream variability is better represented in the Hérault study, and both data sets were combined to derive the best estimate for average rainwater composition in the Têt basin (Table 2, column 3).

3. Results

3.1. Land use and general basin characteristics

For a comparison of the major element fluxes with the general basin characteristics in the corresponding catchments, a Geographical Information

System (GIS) was developed for the Têt basin on the basis of a digital elevation model (USGS, 2000; see also Ludwig et al., 2004). The data layers were taken from available data sets or were digitized from maps in the framework of this study. Table 3 gives the basin averages for the sampling stations with regard to basin morphology, vegetation types and land use, soil C and population numbers. Table 4 summarizes the nature of the main rock types that outcrop in the respective catchments.

The three uppermost basin parts (St1, St2 and St3) are situated in elevated regions with steep morphologies and are only very weakly affected by human activities. Natural vegetation types represent more than 90% of the land cover and agricultural activity is mainly limited to extensive practices like animal farming. Upstream of St3, population density is extremely low. These low values, however, have to be considered with caution since they are based on the existing villages and towns and do not take into account the seasonal influx of tourists. In the catchments of St1 and St2, ski tourism is frequent in winter and many habitations were constructed for this purpose (as indicated by their urban areas in Table 3).

Further downstream, land use practices change. Intensive agricultural land use becomes a dominant pattern in the basin in the form of fruit tree cultures (ca. 80%) and vineyards (ca. 20%). Population density still remains at low levels, at least in the middle part of the basin (St4 and St5). Most of the population is concentrated in the catchment of St6, where the city of Perpignan is located: although this catchment covers only about 7% of the total basin area, more than 70% of the total basin population is concentrated here.

The lithology of the basin is dominated by old plutonic and metamorphic rocks (Fig. 1b), which are weathering resistant. However, in the basin parts of St2 and St3, limestone is present, which can have a strong impact on the water chemistry. Limestone is on average about 20 times more rapidly weathered than granite (Meybeck, 1986; Amiotte-Suchet and Probst, 1993, 1995) and even small areas of limestone can strongly influence the water composition. In the Têt basin, this effect is strongest at St3, where the main river crosses the limestone and hence drains the local karst aquifer that is contained in this formation (Courtois et al., 2001).

After St4, the river enters into its alluvial plain which consists of thick fillings of the erosion prod-

ucts of the upstream rocks that accumulated during Pliocene and Quaternary periods. No sedimentary rocks containing evaporites exist in the basin, which excludes a lithological origin of Cl in the river water.

3.2. Major element fluxes

Table 5 shows the mean annual concentrations and mean specific element fluxes for all dissolved compounds and at all stations. The latter clearly increase from upstream to downstream for most elements. The corresponding downstream evolution of the relative element distribution is shown in the Piper diagram in Fig. 3. Along the three uppermost stations, the water quality evolves toward enrichment in Ca and HCO_3, which are the dominant ions in the Têt. This evolution can be explained by changes in the outcropping rock types (see above), since the dissolution of carbonates releases both elements. Also other changes in the water composition can be directly related to the lithology. For example, F concentrations increase by a factor of >10 from St1 to St2, which reflects the existence of fluorite bearing rocks. This mineral was formerly mined in this region and F concentrations as high as 360 µeq/L could be measured in some small tributaries.

Downstream of St3, however, the water composition changes without any visible connection to the lithology. There are particularly high contributions of SO_4 (St4 and St5) and of Cl (St5, St6 and St7). Sulfate in rivers can be the result of pyrite bearing shale and schist, but it is unlikely that this effect accounts for the downstream increase of SO_4 in the Têt. The geological map of this region shows pyrite facies in the mica schist and schist of the St2 catchment (Guitard et al., 1998), but not in the rocks further downstream.

3.3. pH, alkalinity and pCO_2

When river water is in equilibrium with atmospheric CO_2, pH values are controlled by alkalinity, which directly reflects the water-rock interactions in the watershed. Deviations from the close coupling of both parameters, however, can occur. High pH values are often associated with intense in-situ primary production, which consumes acidity (Stumm and Morgan, 1981; Crouzet et al., 1999), while low values relate to biological respiration of organic matter, which releases CO_2 to the river water. Waste-water effluents, which have been subjected

Table 3
Average basin characteristics of the monitored catchments in the Têt basin

Station	Basin area (km^2)	Mean elevation (m)	Mean slope (°)	Number of inhabitants	Urban and industrial area (%)	Natural vegetation area (%)	Wetlands & water area (%)	Cattle agriculture area (%)	Fruit trees/ vineyard area (%)	Other agriculture area (%)	Carbon content in soils (%)
St1	56	2148	11.1	0	0.3	91.1	6.5	2.1	0	0	9.4
St2	370	1672	17.6	2438	0.5	91.4	0	5	0.2	2.8	6.8
St3	389	1135	15.4	13,940	0.3	90.2	0.6	4.9	2.9	1	4.3
St4	170	856	14.5	3071	0.3	74.5	0.9	9.1	14.9	0.3	4.4
St5	303	314	5.5	23,424	2.2	64.8	0	4.5	21.3	7.2	1.7
St6	95	76	1.3	146,958	16.2	8.5	0	0	31.4	43.8	0.9
St7	8	9	0.5	16,095	9.9	0	0	0	0	90.1	0.7
St1c	56	2148	11.1	0	0.3	91.1	6.5	2.1	0	0	9.4
St2c	426	1735	16.8	2438	0.5	91.4	0.9	4.6	0.2	2.5	7.1
St3c	815	1448	16.1	16,378	0.4	90.8	0.7	4.8	1.5	1.8	5.8
St4c	984	1346	15.8	19,449	0.4	88.0	0.8	5.5	3.8	1.5	5.5
St5c	1287	1103	13.4	42,873	0.8	82.5	0.6	5.3	7.9	2.9	4.6
St6c	1382	1033	12.6	189,831	1.9	77.5	0.5	4.9	9.5	5.7	4.4
St7c	1390	1027	12.5	205,926	1.9	77.0	0.5	4.9	9.5	6.2	4.4

Data sources: Columns 2–4: USGS (2000); column 5: INSEE (2005); columns 6–8, Corine (2000); columns 9–11: total agricultural area according to Corine (2000) and specification of land use type according to AGRESTE (2003); column 12: Jones et al. (2003, 2004); Extraction of the data was done with ArcInfo software tools. St1–St7 refer to the basin area between two successive sampling stations, whereas St1c–St7c refer to the cumulative basin area.

Table 4
Distribution of the different rock types in the Têt basin (in % of basin area)

Station	Granite	Gneiss	Mica schist	Schist CO	Lime-stone D	Alluvium P	Coarse alluvium Q	Fine alluvium Q	Lime-stone C2
St1	34.8	31.5	0.0	32.6	0.0	0.0	1.1	0.0	0.0
St2	17.3	39.5	12.8	16.7	7.5	0.3	4.3	1.5	0.0
St3	30.2	21.0	6.0	21.6	8.0	5.8	5.2	2.3	0.0
St4	21.2	22.3	23.1	20.4	0.0	5.2	5.9	1.9	0.0
St5	15.8	1.0	6.7	31.7	0.0	0.0	38.3	6.2	0.2
St6	0.0	0.0	0.0	5.3	5.3	19.2	54.3	15.9	0.0
St7	0.0	0.0	0.0	0.0	0.0	33.3	0.0	66.7	0.0
St1c	34.8	31.5	0.0	32.6	0.0	0.0	1.1	0.0	0.0
St2c	19.6	38.5	11.1	18.8	6.5	0.3	3.9	1.3	0.0
St3c	24.6	30.1	8.7	20.1	7.2	2.9	4.5	1.8	0.0
St4c	24.0	28.8	11.2	20.2	6.0	3.3	4.7	1.8	0.0
St5c	22.1	22.2	10.1	22.9	4.6	2.5	12.6	2.8	0.0
St6c	20.6	20.7	9.4	21.7	4.6	3.7	15.5	3.7	0.0
St7c	20.5	20.6	9.4	21.6	4.6	3.9	15.4	4.1	0.0

For explanations of the rock type symbols, see Fig. 1b. St1–St7 refer to the basin areas, whereas St1c–St7c refer to the cumulative basin areas.

to intense biological degradation, are therefore often characterized by relatively low pH and elevated pCO_2 levels (e.g. Neal et al., 1998a).

A plot of the annual averages of pH, alkalinity, and excess CO_2 partial pressures ($EpCO_2$) for the 7 water monitoring stations along the Têt (Fig. 4) reveals that pH closely follows alkalinity in the three uppermost stations, whereas this relationship breaks down further downstream. As a consequence, the calculated $EpCO_2$ values are high at these stations. The values of St6 and St7 are not surprising since the water is strongly impacted by the waste-waters from Perpignan. The high $EpCO_2$ at St4 can be related to the Vinça reservoir. Reservoirs are generally known to be sources of CO_2 to the atmosphere (St. Louis et al., 2000).

Fig. 4 shows that $EpCO_2$ values in St1 and St2 are above the atmospheric levels too. Soils are organic rich in these catchments (Table 3) and the drainage waters show elevated DOC concentrations (Table 5). High partial pressures of CO_2 can therefore be explained by the slow in-river respiration of natural organics. Another explanation is that DOC in the upper stations directly contributes to water acidity. The DOC/HCO_3 ratio at St1 is much greater than in all downstream stations. Here, a significant correlation between DOC and most major elements was found, as in particular with dissolved silica ($r^2 = 0.69$, $n = 47$). More recent studies show that this behaviour is common in rivers of cool climates (e.g. Millot et al., 2003), and indicates that DOC is directly involved in the chemical weathering.

4. Discrimination of the major element sources

4.1. Atmospheric inputs

The three uppermost sampling stations in the Têt basin are controlled mainly by natural conditions, whereas the water quality further downstream is increasingly affected by human activities. As a consequence, Cl in the upstream stations should be strongly controlled by atmospheric inputs. This is confirmed when comparing the river fluxes at these stations with the atmospheric deposition based on the reconstruction of the rainwater composition (Fig. 5). Downstream of St4, however, pollution must be an important additional source of Cl.

A quantification of the pollution part can be done by assuming that in unpolluted water where there are no Cl releases from rock weathering, the enrichment of the average Cl concentration in the

Table 5
Mean annual concentrations (C) and specific fluxes (F) of the dissolved elements in the Têt River

C (µeq/L)	St1	St2	St3	St4	St5	St6	St7
Ca	166	456	681	711	1159	1405	1416
Mg	38	106	149	167	295	339	343
Na	68	158	174	183	286	465	477
K	6	15	22	25	45	62	62
NH_4	0	0	1	4	2	102	83
SiO_2[a]	88	140	151	136	148	160	157
F	1	10	10	10	11	11	11
Cl	33	69	74	88	166	354	357
SO_4	51	146	156	193	377	474	482
NO_3	5	17	25	29	61	101	98
HCO_3	184	523	763	790	1115	1295	1319
PO_4	nd	nd	2	2	5	10	8
DOC[a]	194	183	195	243	300	287	296
F (keq km^{-2} a^{-1})	St1	St2	St3	St4	St5	St6	St7
Ca	106	191	226	227	259	300	301
Mg	24	44	49	53	66	72	73
Na	43	66	58	58	64	99	101
K	4	6	7	8	10	13	13
NH_4	0.0	0.0	0.3	1.3	0.4	21.8	17.6
SiO_2[a]	56	59	50	43	33	34	33
F	1	4	3	3	2	2	2
Cl	21	29	25	28	37	76	76
SO_4	32	61	52	62	84	101	102
NO_3	3	7	8	9	14	22	21
HCO_3	117	219	253	252	250	277	280
PO_4	nd	nd	0.7	0.6	1.1	2.1	1.7
DOC[a]	123	76	65	77	67	61	63

Explanations: Average concentrations were calculated as the annual fluxes (Eqs. (ii) and (iii)) divided by the annual water discharge on the basis of the weekly sampling from September 2000 to September 2001. Estimates for the corresponding specific element fluxes were corrected for the effects of water extraction. They were calculated with the average concentrations above, multiplied with the theoretical long-term discharge values in Table 1 (column 8) and with the ratio of the observed study year and long-term discharges (column 7/column 6), and then divided by the basin areas of Table 3.
 nd: not detected.
 [a] Units are (µmoles/L) and (kmoles km^{-2} a^{-1}), respectively.

river (Cl_q) with respect to the average concentrations in rainwater (Cl_r) should reflect the water that is lost by evapotranspiration in the basin. In other words, this ratio is equal to the ratio of precipitation (P) over runoff (Q):

$$Cl_q/Cl_r = P/Q \qquad \text{(iv)}$$

If pollution supplies additional Cl, the Cl_q/Cl_r ratio increases and Eq. (iv) is no longer valid. This increase can be used to distinguish between natural and pollution-derived Cl ($Cl_{q,pol}$) according to:

$$Cl_{q,pol} = Cl_r[(Cl_q/Cl_r) - (P/Q)] \qquad \text{(v)}$$

For some of the upstream stations (St1, St3 and St4), Eq. (v) gives slightly negative values, indicating that the atmospheric inputs are probably overestimated. Moreover, in the calculations, the mean long term precipitation and the modelled long-term runoff val-

ues from Table 1 were used, but the study year was dry and water discharge at St3 was about 20% lower than average. It is also not clear whether one can use the average Cl concentrations determined in the river for long-term flux calculations, as they might be greater during dry years. It is therefore concluded that during the study period, the atmospheric contribution of Cl in the Têt should have been clearly lower than in Fig. 5. Also upstream, many waste water stations discharge to the river and anthropogenic Cl cannot be completely absent.

When reducing the atmospheric inputs by about 20% Eq. (v) does not produce negative values. When reducing them by about 35%, similar average inhabitant releases of Cl from waste-waters were obtained in most basin parts. This can be considered as the best estimate for the rain-derived Cl during the study year. According to Eq. (v), the resulting
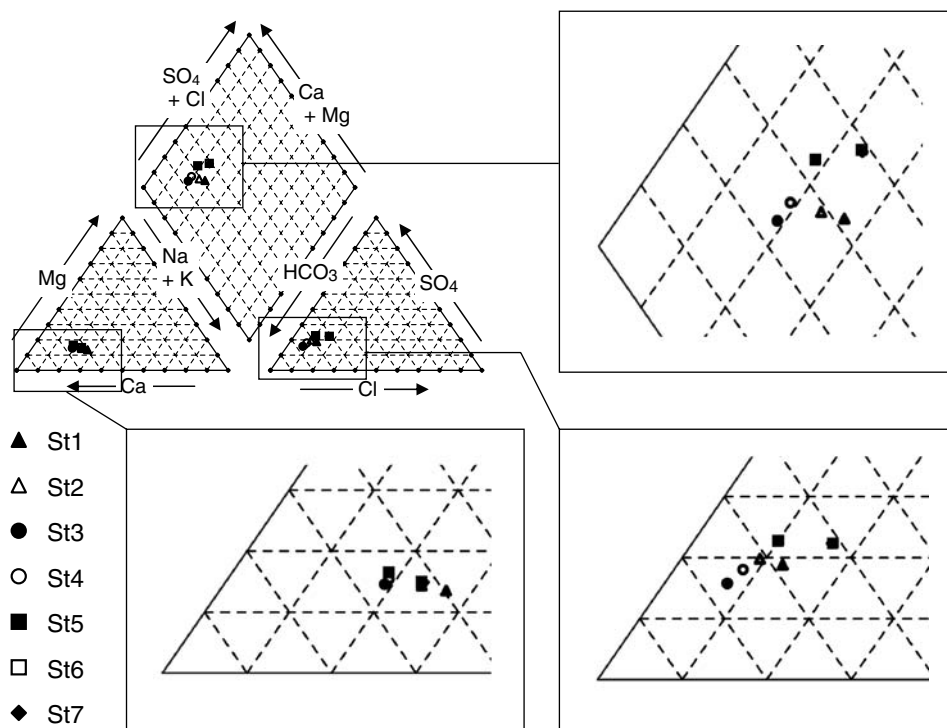
Fig. 3. Distribution of the average water composition (in μeq/L) at the seven sampling stations in the Piper-Diagram. Arrows point to 100% poles for the indicated elements.
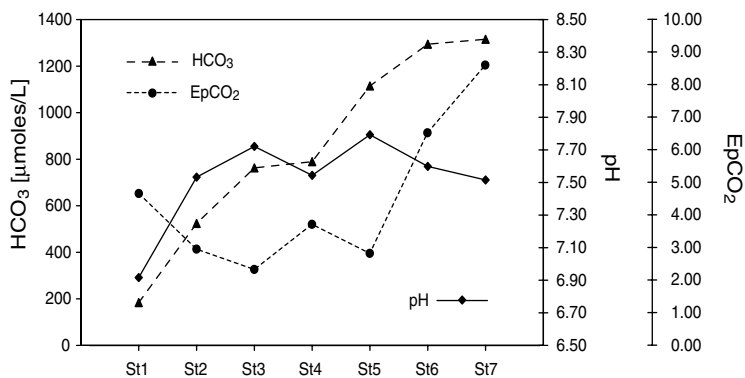

Fig. 4. Mean values of field pH, alkalinity and excess partial pressure of CO_2 (EpCO$_2$) along the seven sampling stations of the Têt River. EpCO$_2$ was calculated according to Eq. (3c) of Neal et al. (1998b) and includes the correction of the atmospheric reference pCO$_2$ as a function of station altitude (Eq. (A-1a) of Neal et al. (1998b)). Averages of pH and EpCO$_2$ were respectively determined as the mean annual fluxes of H$^+$ and CO_2 in the river, divided by the annual discharge (Eqs. (i) and (ii) of this study).

estimates for the pollution part of Cl in the Têt are then 20, 38, 30, 34, 48, 71 and 71% for the stations St1–St7, respectively.

4.2. Road salting

It was unexpected to find a greater share of Cl pollution in St2 than in St3 and St4, although pop-ulation density is very low in this basin part (Table 2). Chloride is only weakly correlated with Na at St2, in contrast with all other stations. This can be attributed to an important contribution of road salting to the Cl transport in the river. Cl/Na ratios are much greater in winter and spring, when they are frequently >0.6, compared to summer and autumn, when they are mostly <0.3 (Fig. 6). Basin
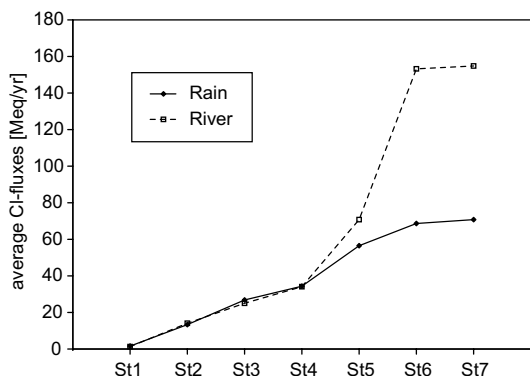
Fig. 5. Comparison of the total amounts of the average atmospheric deposition and the average river fluxes of Cl ions in the monitored catchments of the Têt River. For the flux calculations, the long-term P and modelled long-term Q values of Table 1 were used.
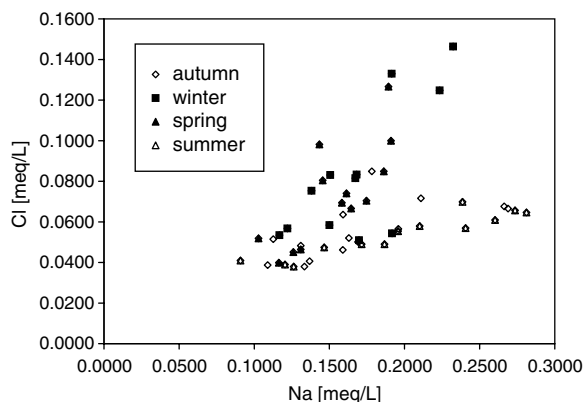

Fig. 6. Seasonal variability of the Cl/Na ratio in the Têt River at St2.

elevation strongly increases above this station and snowfall is frequent in winter.

From the differences in the Cl/Na ratios during the cold and the warm seasons, it is estimated that the additional contribution of Cl from road salting is about 15 μeq/L in the mean annual concentration of St2 (or 22%). This Cl is then transferred further downstream and diluted proportionally to the increase of water discharge. Removing the effect of road salting reduces the pollution part of Cl from other pollution sources to values of 20, 21, 21, 28, 46, 70 and 71% of the total concentrations at St1–St7, respectively. Of course, road salting may also occur in other parts of the basin, but this is probably much less important. The basins of St3–St7 are at elevation levels where snowfall is rare. The basin of St1, however, is often covered by snow. It is

therefore assumed that the effect of road salting in the Têt basin is confined to St2 and St1 and assigned arbitrarily a value of 70% of the pollution inputs at St1 to this source.

Taking the respective parts of Cl that can be attributed to road salting and rainwater inputs ($Cl_{q,rs}$ and $Cl_{q,rw}$), one can hence correct the river composition for both non-weathering sources along all sampling stations (Table 6). For the corresponding element to Cl ratios, $R_{i,rs}$ was fixed according to the average composition of seawater (Berner and Berner, 1987), and $R_{i,rw}$ according to the average rainwater composition in Table 2.

Table 6
Different origins of major components in the Têt River (in %)

		St1	St2	St3	St4	St5	St6	St7
Rain	Ca	13	7	6	6	6	5	5
	Mg	20	11	9	9	8	8	8
	Na	27	18	20	21	19	14	14
	K	36	22	19	18	15	13	13
	Cl	80	62	70	65	52	29	29
	SO$_4$	54	24	25	22	14	12	12
	HCO$_3$	0	0	0	0	0	0	0
Road salting	Ca	0	0	0	0	0	0	0
	Mg	3	3	1	1	0	0	0
	Na	6	8	4	4	2	1	1
	K	1	2	1	1	0	0	0
	Cl	15	22	12	9	4	2	2
	SO$_4$	1	1	1	0	0	0	0
	HCO$_3$	0	0	0	0	0	0	0
Waste-waters[b]	Ca	1	3	2	2	3	17	17
	Mg	1	2	2	1	2	10	10
	Na	2	7	7	6	10	38	38
	K	3	7	6	5	6	29	30
	Cl	5	17	18	14	18	55	56
	SO$_4$	1	3	3	2	3	15	15
	HCO$_3$	1	2	2	1	2	13	13
Agriculture	Ca[a]	0	0	0	2	5	5	5
	Mg	0	0	0	16	40	40	39
	Na	0	0	0	8	22	15	15
	K	0	0	0	18	43	36	36
	Cl	0	0	0	11	25	14	14
	SO$_4$	0	0	0	23	51	46	45
	HCO$_3$	0	0	0	0	0	0	0
Erosion	Ca	85	90	92	89	86	73	73
	Mg	77	84	88	72	50	42	42
	Na	65	67	69	61	47	31	32
	K	60	69	74	59	35	21	21
	Cl	0	0	0	0	0	0	0
	SO$_4$	44	72	71	52	32	26	28
	HCO$_3$	99	98	98	99	98	87	87

[a] Ca was used to balance electro-neutrality.
[b] Including industrial effluents.

4.3. Average waste-water composition

Between St5 and St6, where the waste-waters of Perpignan are discharged, the average Cl concentrations increase by a factor of 2.1. The effluents were not sampled and analysed as they are difficult to access, and the waste-water treatment plant does not monitor the entire major element composition (only N and P compounds). Nevertheless, the water quality has been measured upstream (St5) and downstream (St6), and the waste-water component can be determined indirectly. For this, the inputs of the Basse tributary have to be estimated too, which also joins the river between both stations. This tributary was sampled less frequently ($n = 10$) and its contribution was estimated in the basis of the discharge-weighted average concentrations and the water discharge.

Table 7 shows the derived chemical composition of the effluents. They have an average Cl concentration of about 2.9 meq/L (or 103 mg/L) when referred to the average discharge of the treatment plant (0.44 m^3/s). This is in good agreement with the average Cl concentrations commonly found in urban waste-waters (Pescod, 1992), and with the data of Rabiet et al. (2005) who reported average Cl concentrations of 2.3 ± 1.3 meq/L for waste-waters in the Hérault River basin. The additional Cl inputs to the river are accompanied by relatively high inputs of Na, NH$_4$, Ca and HCO$_3$. Comparing the fluxes with the fluxes of dissolved inorganic N and P that were monitored by the waste-water treatment plant reveals very good agreements between both methods (differences are less than 5%).

4.4. Discriminating between waste-water and fertilizer inputs

In addition, agricultural products can introduce Cl into the river (CA66, 2003). A characterization of the average composition of these inputs is difficult since they correspond to a diffuse pollution source. In the Têt basin, however, it is strongly indicated that the major changes in the average water composition between St3 and St4 are dominated by agricultural inputs. Intensive agricultural practices become a major part of the land use patterns and the greatest flux increases are found for common fertilizers elements, such as SO$_4$, Cl, NO$_3$, K and Mg (Table 5). Assuming that at St3, all of the non-identified Cl comes from urban waste-waters, and that in the additional inputs between St3 and St4 (fluxes at St4 minus fluxes at St3), 60% are of this origin (following the same per-inhabitant release of Cl at both stations), the remaining inputs can be used to calculate the average element to Cl ratios which characterize the agricultural inputs ($R_{i,\mathrm{ag}}$).

The $R_{i,\mathrm{ww}}$ and $R_{i,\mathrm{ag}}$ ratios were used to test whether a given pollution source is either waste-water or fertilizer dominated. This is particularly interesting for St5, where the increase of the average concentrations points to an important chemical input to the river from other sources. Most of the element to Cl ratios of these inputs (fluxes at St5 minus fluxes at St4) lie between $R_{i,\mathrm{ww}}$ and $R_{i,\mathrm{ag}}$, allowing the application of a simple linear mixing model for each element in order to determine the theoretical percentages that come from both sources. For the major elements Na, K, Mg and SO$_4$, agricultural percentages yield to 64, 54, 69 and 66%, respectively. Because of the similarity in these values, it is reasonable to conclude that a dominant contribution from both sources can indeed explain the major changes at St5, and that the additional Cl contribution from agriculture may be estimated to about 63% (arithmetic mean of all four elements). The estimated agricultural contribution for NO$_3$, an important element in fertilizers, is 84%. When the NO$_3$ fluxes at St5 were corrected for the conversion of NH$_4$ to NO$_3$ between St4 and St5, this value reduces to 68%, in good agreement with the estimates above.

For Ca and HCO$_3$, however, the agreement is not as good (agricultural contributions of 88 and 38%, respectively). In these cases, the $R_{i,\mathrm{ag}}$ ratios might

Table 7
Average waste-water composition in the effluents of the city of Perpignan

Ca (meq/L)	Mg (meq/L)	Na (meq/L)	K (meq/L)	Cl (meq/L)	HCO$_3$ (meq/L)	SO$_4$ (meq/L)
3.56	0.51	2.63	0.27	2.89	2.57	1.05
NH$_4$ (meq/L)	NO$_3$ (meq/L)	DIN[a] (meq/L)	PO$_4$ (meq/L)	F (meq/L)	SiO$_2$ (mmoles/L)	DOC (mmoles/L)
1.67	0.68	2.35	0.08	0.01	0.31	0.13

[a] Sum of NO$_3$ and NH$_4$.

be less representative, and the additional inputs of these elements in St5 are probably related to the lithology (see below). Also for DOC, the mixing model does not fit (agricultural contribution of only 2%). The important increase of the fluxes between St3 and St4 might be related to a release to the river by the reservoir through primary production and/or from the organic rich reservoir sediments rather than to agricultural inputs.

For the Basse catchment, an estimate for the agricultural Cl contribution can be obtained in a similar way (about 46%), even if this value is associated with more uncertainty, mainly in relation to the lower sampling frequency here. This finally allows for all stations downstream of St3 to discriminate between fertilizer and waste-water Cl in the remaining riverine Cl loads (after correction for atmospheric deposition and road salting), and to correct the water compositions. The results are given in Table 6. These values integrate, of course, also the pollution inputs that come from the upstream stations, which were diluted proportionally to the increase of water discharge (because of the water extraction, the theoretical water fluxes were used).

4.5. Rock weathering

When corrected for the non-weathering sources, the remaining specific element fluxes should come from rock weathering. While the bulk water shows increasing values especially in the downstream stations for most major elements (Table 5), the corrected values now remain constant or even decrease further downstream (not shown). Peak values occur for St2 (e.g. Na, SO$_4$) and St3 (e.g. Mg), where the outcropping rock types and the climatic conditions may favour higher weathering rates. For Ca and HCO$_3$, the downstream increase at St5–St7 still persists, probably because of the existence of carbonate facies in the alluvial fillings. Also the relative element composition is now in better agreement with the basin lithology. Major changes mainly occur from St1 to St3, where the water composition evolves from a slightly more Na and K dominated composition (silicate weathering) to a stronger dominance of Ca and Mg (carbonate weathering). The relative contribution of Mg is greatest at St3, in agreement with the dolomitic nature of the carbonate rocks here. St2 has a particularly high contribution of SO$_4$, which probably indicates pyrite weathering.

4.6. Nutrient fluxes (Si, N, P)

Nutrients are involved in the biological processes in the river itself, and their fluxes from upstream to downstream do not necessarily follow conservative behaviour. A good example is the SiO$_2$ flux downstream St3, which is reduced by diatom growth in the Vinça reservoir during summer (Fig. 7). Silica retention in reservoirs is a widespread phenomenon (e.g. Humborg et al., 1997). By comparison of the inter-annual variability of the concentrations between SiO$_2$ and more conservative elements (e.g. Ca and F) at St3 and St4, the reduction of the natural SiO$_2$ fluxes was estimated to about 21% during the warm season (April–October), or to about 11% for the entire hydrological year.

Also the inorganic N and P species could be affected by a reduction of the fluxes between St3 and St4. The fluxes of NO$_3$ increase between both stations more or less proportionally to the fluxes of the other fertilizer elements (K, SO$_4$, Cl, Mg), and the linear mixing model for the prediction of the agricultural inputs at St5 (see above) indicates that NO$_3$ retention in the reservoir is not important. For PO$_4$, however, there is strong evidence that this element is retained in the reservoir. The fluxes at St4 are clearly lower than at St3. In order to estimate the respective agricultural contributions of PO$_4$ to the river fluxes downstream of St3 in a similar way as for the other nutrients (Table 8), a theoretical value was attributed to the reservoir retention of about 33% of the fluxes at St4. This value was selected in a way that at St5, the mixing model predicts an additional agricultural PO$_4$ input that
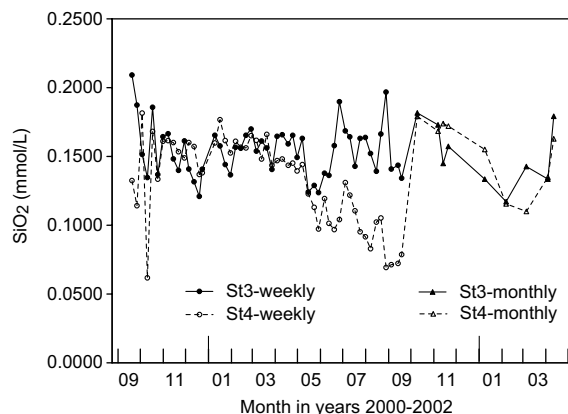

Fig. 7. Evolution of the concentrations of SiO$_2$ at St3 and St4 in the Têt River. In September 2001, sampling frequency switched from weekly to monthly sampling.

Table 8
Different origins of nutrients and dissolved organic C in the Têt River (in %)

		St1	St2	St3	St4	St5	St6	St7
Waste-waters[a]	SiO_2	0	1	1	1	2	13	13
	NO_3	8	16	13	10	12	46	48
	PO_4	nd	nd	15	13	17	52	67
	DOC	0	0	0	0	0	3	3
Agriculture	SiO_2	0	0	0	0	0	0	0
	NO_3	0	0	0	22	46	30	31
	PO_4	nd	nd	0	17	38	21	27
	DOC	0	0	0	0	0	0	0
Erosion	SiO_2	100	99	99	99	98	87	87
	NO_3	92	84	87	68	42	24	21
	PO_4	nd	nd	85	71	45	27	6
	DOC	100	100	100	100	100	97	97

nd : not detected.

[a] Including industrial effluents.

follows the estimate for Cl (see above), but the validity of this value remains, of course, unproved.

4.7. Dissolved organic carbon

Little is known about the human impact on the fluxes of dissolved organic C (DOC) in rivers. Previous studies showed that DOC seems to be mainly of soil origin, although in situ primary production can also contribute significantly to the riverine DOC pool (Ludwig et al., 1996; Ludwig, 1997). Soil derived DOC is chemically rather inert, which makes DOC often follow a conservative transport from the headwaters down to the sea.

The latter is obviously the case in the Têt River, where concentrations of DOC mostly changed simultaneously in the different stations. Seasonality is not very marked, but DOC levels are highly influenced by changes in discharge, especially during floods. One observes a pronounced flushing effect, with clearly greater concentrations during the high-discharge stages (Fig. 8). This flushing is more important in the downstream than in the upstream basin parts. At St1, where soils are the richest in organic C because of the occurrence of bogs (Table 3), DOC concentrations are even negatively correlated with Q, as is often observed in rivers draining wetlands (e.g., Moore and Jackson, 1989).

Waste-waters are known to be enriched in labile organics and might be a potential source of DOC. These inputs, however, can be easily quantified, but they are not a major source for the DOC in the Têt. When comparing the C–Q relationships at St5, St6 and St7 (Fig. 8), the waste-water DOC
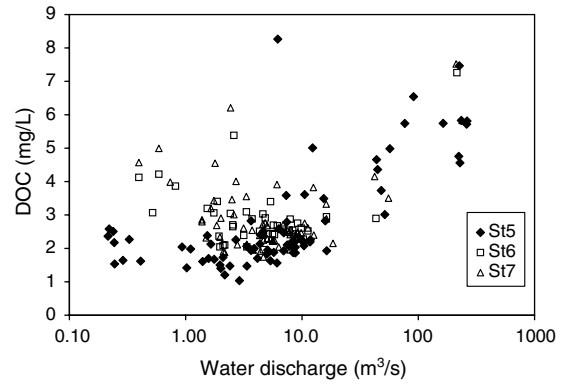

Fig. 8. Relationship between DOC and discharge at stations St5, St6, and St7 in the Têt River.

can be identified for lowest Q values ($\leqslant 3 \text{ m}^3/\text{s}$) through an enrichment of the samples at St6 and St7, compared to St5. At that low water discharge, the urban inputs represent a considerable part of the total discharge and DOC is well correlated with other substances of anthropogenic origin, such as PO_4. However, most of the DOC transport occurs when high discharge coincides with elevated DOC concentrations from the flushing of soil C, and cutting down the high concentrations at St6 and St7 to the values at St5 for low Q values ($\leqslant 3 \text{ m}^3/\text{s}$) would only reduce the total transport by a few percent (see also Table 7).

5. Element releases by human activities

5.1. Agriculture

In the different catchments, the Cl fluxes (Meq/a) from agriculture are well correlated with the agricultural land area, in particular with the areas for fruit tree cultures and vineyards (Table 3): r^2 is 0.97 ($n = 7$). The correlation coefficient holds also for SO_4, Mg, NO_3 and K, as their agricultural inputs were directly derived from constant element to Cl ratios.

One can consequently establish for all elements the area specific releases from these cultures in the Têt basin (Table 9). These values are the average of the specific fluxes in the catchments St4–St6, which have the greatest areas of intensive agricultural land use. Here, the specific fluxes agree well and standard deviations are low. Upstream St4, agricultural use is poorly developed. Some fruit tree cultures and vineyards already exist in the downstream part of St3, but here the main irrigation channel bypasses the sampling station.

Table 9
Specific element releases by agriculture in the Têt basin

	Flux SO_4 (keq km^{-2} a^{-1})	Flux K (keq km^{-2} a^{-1})	Flux Mg (keq km^{-2} a^{-1})	Flux NO_3 (keq km^{-2} a^{-1})	Flux PO_4 (keq km^{-2} a^{-1})	Flux Cl (keq km^{-2} a^{-1})
Agriculture[a]	430	44	265	60	4.3	95
Standard deviation	18	2	11	3	0.2	4
Erosion[b]	37	5	44	7	0.6	–

[a] Average of St4–St6 when only considering vineyards and fruit tree cultures.
[b] Average fluxes at St3 from Table 5, corrected for non-weathering sources (Tables 6 and 8).

Table 9 shows that the element release from agricultural lands is greatest for SO_4. The specific inputs to the Têt River are more than 11 times greater than the specific weathering fluxes. Sulfate is an abundant anion in fertilizers (Vitòria et al., 2004; CA66, 2003). However, vineyards are frequently treated with fungicides ($CuSO_4$), which might be a dominant source for this element too (Van der Weijden and Pacheco, 2006). Also for K and NO_3, the releases from agricultural terrains are clearly more elevated than the natural fluxes (about 8–9 times the average weathering rates). For NO_3, the specific fluxes from soil erosion (bulk fluxes minus anthropogenic fluxes) are rather constant along all stations, varying only between 7–9 kmoles km^{-2} a^{-1}, except for St1 where this value is 3 kmoles km^{-2} a^{-1}. The corresponding average concentrations stretch from 0.07 to 0.34 mg N/L. Such low concentrations are normally found in European rivers that are only weakly affected by human activities (Crouzet et al., 1999), but the values are still greater than the ones commonly attributed to pristine rivers (e.g. 0.05–0.20 mg N/L by Meybeck and Helmer (1989)). Also the moderate agricultural activity in the upstream basin may release some additional NO_3 to the river. For PO_4, the concentrations in the upper two stations were mostly below the detection limit and the flux estimates might be less accurate than for the other elements.

5.2. Waste-waters

Waste-waters are the major source for Cl in the Têt River close to its mouth. Also for Na, they are a dominant source, more important than the amount of Na that is mobilized by weathering (Table 6). The average annual inhabitant release of Cl for the entire river is 311 moles/inhabitant, which is relatively high compared to what has been found elsewhere. For example, Verbanck et al. (1989) reported 237 moles/inhabitant for the Cl inputs from the city of Brussels, Thibert (1994) of 177 moles/inhabitant for the city of Paris, and Caille et al. (1973) of 231 moles/inhabitant for the city of Montreal.

In the individual basin parts, however, considerable differences can be found, indicating that there are also Cl inputs from industrial pollution. The greatest flux of about 368 moles Cl/inhabitant is obtained for the St6 catchment, which corresponds to the drainage basin of the Basse tributary, where the waste-waters of Perpignan come in. But it is also here where the industrial zones are concentrated in the Têt basin (Table 3). Notice that the specific Cl flux in the Basse is about four times greater than the specific Cl fluxes in the Têt at St5, and 1.7 times greater than the fluxes at St6, after the river has received the waste-waters of Perpignan. In the latter, the inhabitant release of Cl is still elevated (276 moles/inhabitant) and some of the industrial pollution also joins the river via the waste-water plant.

Further upstream, the specific Cl inputs per inhabitant are clearly lower. The values in the catchments St3, St4 and St5 are 141, 161 and 201 moles Cl/inhabitant, respectively. As industry is very poorly developed upstream of St4, a value of 150 moles Cl/inhabitant might be representative for the rural populations that live in the major parts of the Têt basin. In the catchment of St2, however, the theoretical per-inhabitant inputs of Cl are about 3.5–5 times greater than in St3–St5. This, of course, has to be taken with caution. As mentioned above, the population densities in Table 3 might be strongly underestimated because of tourism. On the other hand, the rainwater inputs may be underestimated, since it is very difficult to estimate the average rainwater composition in the basin parts >1500 m. It is also possible that some additional sources of Cl at St2 were overlooked, in particular the hydrothermal springs that exist in this basin part.

6. Conclusions

The approach was based on a high frequency sampling from the headwaters to the river mouth, which has not often been done in previous studies. This gives highly reliable budgets and allows a detailed tracking of the different material sources in the basin. At the basin outlet, only the fluxes of DOC, SiO_2, HCO_3 and Ca can be confidently attributed to chemical weathering (97, 87, 87 and 73% of the bulk fluxes), while atmospheric deposition is mainly important for Cl (29%) and, to a lesser extent, also for Na (14%). For most other elements, anthropogenic sources have a strong control on the element fluxes. SO_4, Mg, K, NO_3 and PO_4 are strongly influenced by inputs from agriculture (45, 39, 36, 31 and 27%), and PO_4, Cl, NO_3 and Na are largely controlled by urban waste-water effluents (67, 56, 48 and 38%).

The impact of waste-waters on the water chemistry in the Têt is naturally greatest close to its mouth where the effluents of the agglomeration of Perpignan are discharged into the river. But here, also industrial pollution sources can contribute to the material fluxes. Further upstream, where industrial activity is poorly developed, the data might be more representative for the average Cl release from house-holds, indicating that this value is close to 150 moles/inhabitant. It is interesting to compare this value with the annual food consumption of NaCl in Western Europe and North America, which has been estimated to range between 30 and 120 moles/inhabitant, with an average of 60 moles/inhabitant (WHO, 1979).

The area specific element releases from intensive agricultural land use, on the other hand, are rather constant in the basin and may also hold for other rivers with similar land use patterns. For SO_4, however, the specific inputs are, compared to the natural weathering rates, greater than for the other fertilizer elements NO_3, K, PO_4 and Mg. Sulphate can originate from the use of fungicides on vineyards, which may explain this. Unfortunately, the monitoring approach does not allow distinguishing between the element inputs from the fruit tree cultures and the vineyards in the basin. The latter, which are a widespread land use pattern along the French Mediterranean coast, may be particularly important as anthropogenic sources of SO_4 in many of the coastal rivers.

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