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Long-term changes in water physicochemistry in the Adour–Garonne hydrographic network during the last three decades

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This study details a trend analysis covering a 30-year period (1975–2004), for 19 physicochemical parameters at 45 surface water sites in the Adour–Garonne basin, south-west France. To perform statistical analysis, we used the annual average of each variable. The analysis revealed sites affected by strong patterns of temporal variation and sites with weak or imperceptible changes of water quality. More than half the studied sites were affected by chemical changes. Trends were generally clearest in the River Garonne continuum, but similar tendencies could also be identified in tributaries. The overall trends indicated the onset of an increase of water temperature starting about 20 years ago and partial recovery from eutrophication during the last decade. As expected, the strongest trend affected the temperature regime of the hydrosystems, there being a more significant warming during the second decade of the study (1984–1994). Additionally, at many sites nutrient loads were lower between 1995 and 2004. This confirms a downward trend in eutrophication status resulting from more stringent control of sewage treatment despite the constant increase of anthropic pressure. Sites that did not present any trends are extreme sites located at each end of the river gradient: headwater and downstream sites under tidal influence. Other sites not affected by changes are those strongly perturbed by human activities showing a high level of degradation.

1. Introduction

Clean water is a question of vital importance for the well-being of human societies. Damage caused to inland hydrosystems is one of the most serious environmental problems of the last century. Historically, rivers have been considered as a drainage channel for dilute pollutants and this behaviour has led to an inevitable increase of pollutant load. Water shortages are increasingly common and likely to become more severe in the future. Water shortages and poor water quality are linked since contamination reduces the supply of water and increases the cost of treating water for use (Carpenter et al., 1998). There is a growing body of evidence that long-term changes are occurring in surface water chemistry in Europe and North America (Jenkins et al., 2001). As a response to these environmental concerns, there is an obligation and strong political pressure for greatly increased emphasis on the control of pollution levels. It is along these lines that the recently agreed EC Water Framework Directive (European Parliament, 2000) requires all inland

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water to reach "good ecological status" by 2015. The development of predictive capabilities for the management of streams implies taking spatial and temporal scales into account (Minshall, 1988). Lotic ecosystems have developed in response to dynamic patterns and processes occurring along four dimensions; the fourth (time) imposes a temporal hierarchy on the three spatial dimensions of the river basin (Ward, 1989). Over the past two decades, interest in environmental temporal changes has resulted in numerous studies designed to monitor the physicochemical responses of a catchment. Hence, acidification, and the major cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) and anions (HCO_3^-, NO_3^-, SO_4^{2-} and Cl^-) determining the ionic strength of surface water have been studied by many authors (Kopacek et al., 2001; Harriman et al., 2001; Moldan et al., 2001; Bhangu and Whitfield, 1997; Hutchins et al., 1999). In addition, most hydrochemical studies seeking to identify stream water chemistry have been based on the headwater catchment scale (Smart et al., 1998; Evans and Monteith, 2001). There are relatively few studies dealing with major river systems.

The requirements for large data resources, such as staff and time, are clear reasons explaining why studies that have attempted to look at spatial and temporal variability for abiotic and biotic features of whole systems are apparently absent (Cellot et al., 1994). Working on a large scale provides a tool to study ecosystem response and to evaluate any physicochemical trends. Many underlying questions dominate the study of water quality on a large temporal scale: is the water quality changing over time? If changes are occurring, is the water quality improving or deteriorating? Quality monitoring of ecosystems is vital to determine whether variations in the water physicochemistry are leading to the desired improvements in the water quality of damaged systems. It is also necessary to develop a scientific understanding and predictive models to support decision making on future pollution reduction.

The present study reports the results of an investigation of the trends in long-term (decade time-series) changes in the water physicochemistry in south-west France. In contrast with the numerous studies dealing with events on scales of days, seasons and years (Minshall, 1988), the present study examines 30 years of water quality (19 physicochemical variables) at 45 sites within the Adour–Garonne basin, a major basin in France. The originality of the study is to gather a large temporal and spatial scale in the same data set. The main objectives were therefore (1) to determine the long-term directional changes in water chemistry, (2) to identify the major variables concerned and (3) to discuss any potential recovery that may be expected.

2. Materials and methods

2.1. *Study area*

The Adour–Garonne hydrographical network covers the Atlantic region of south-west France. It extends over 116,000 km^2 from Charentes and Massif Central to the Pyrenees, gathering 120,000 km of watercourses including 68,000 km permanent rivers flowing into the Atlantic. The Garonne is the main channel, running over 580 km from the central Pyrenees in Spain to the Gironde estuary on the Atlantic coast. Its major tributaries come from the Massif Central plateau (Aveyron, Lot, Tarn) and minor ones from the Pyrenees range (The Gaves). The Adour–Garonne watershed covers a broad range of altitudes (high mountains to plains and coastal areas) and geological substrates: calcareous, sedimentary, sandstone, crystalline and volcanic (Tison et al., 2004). From south to north-west, topography and climate determine three great landscape types: the Pyrenees Mountains with a pronounced relief, a vast green hilly zone of piedmont and the valley of the Garonne River with flooding zones and alluvial terraces. The oceanic influence predominates over the whole basin, but lessens to the south-east with its Mediterranean influence, dry winds and lower rainfall (Mastrorillo et al., 1998).

The geographical features, involving climate, geology and relief are summarised in the concept of hydroecoregion. This typology of aquatic ecosystems results from the implementation of the Water Framework Directive (Wasson et al., 2001). The basin covers 6 hydroecoregions (HER), from south to north: Pyrenees (headwaters of the left bank tributaries of the Garonne), Côteaux aquitains (main floodplain) and limestone Causses; to the east: Grands Causses and Massif Central (headwaters of the right bank tributaries to the Garonne); and at the west: with the coastal streams Les Landes.

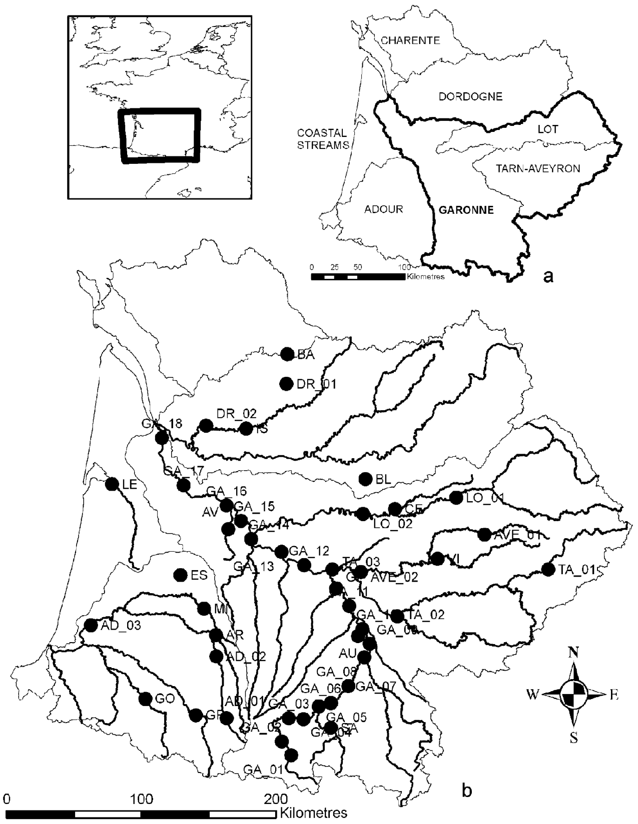

Fig. 1 – Location of main sub-basins (a) and the Adour–Garonne basin network with location of sampling sites (b) (for abbreviations, see Table 1).

The catchment is vital as a regional water resource for drinking water, industry, irrigation and agriculture (35,000 irrigated farms) supplying over 6.5 million consumers. Thirty per cent of the population lives in rural areas, 28% in 35 towns of over 20,000 inhabitants. Etchanchu and Probst (1988) considered that the Garonne basin is one of the least impacted by flow regulation in Europe and one of the least polluted. It has suffered from intensive damming and industrial impact during the second half of the 20th century (Steiger et al., 1998) and the quantity of fertiliser applied has dramatically increased in the past few years (Semhi et al., 2000).

2.2. Sampling sites

The data used in this study come from national water quality monitoring programmes (Réseau National de Bassin). The French hydrographic network is divided into 6 main basins and the south-western part is monitored by the Adour–Garonne Basin Water Agency (Agence de l'Eau Adour–Garonne). Thus, long-term monitoring of run-off chemistry over the last three decades in the Adour–Garonne basin, recorded by the Water Agency, provides a huge database for analysis of physicochemical trends. We focused our survey on 45 sites, including 18 along the longitudinal gradient of the River Garonne, gathering the longest and most complete temporal data set collected since 1975. The temporal scale covers the last three decades, from 1975 until 2004. The sampling sites are distributed over the 7 main sub-basins: Adour, Charente, Dordogne, Garonne, Lot, Tarn-Aveyron and coastal streams (Table 1, Fig. 1a, b). Due to missing values in the series for some variables, the annual mean values of each variable were calculated. We then decided to concentrate on three decades: the first from 1975 to 1984, the second from 1985 to 1994 and the third from 1995 to 2004. Mean values per decade were also calculated.

The 19 major physicochemical variables taken into account are: cations (NH_4^+, Ca^{2+}, K^+, Na^+), anions (HCO_3^-, Cl^-, NO_3^-, NO_2^-, PO_4^{2-}, SO_4^{2-}), NH_3, pH, conductivity, biological oxygen demand (BOD5), suspended matter, dissolved oxygen ($mg\,l^{-1}$), oxygen saturation, and air and water temperature.

2.3. Data analysis

We used the method of self-organising maps (SOMs), which is an unsupervised algorithm of an artificial neural network model (Kohonen, 1982). SOM is an efficient method for analysing systems ruled by complex non-linear relationships and provides an alternative to traditional statistical methods for classifying complex data (Lek and Guegan, 2000; Park et al., 2003a). Successful results in aquatic ecology using such models have been well documented (Chon et al., 1996; Park et al., 2003b; Gevrey et al., 2004). SOM is used to classify the samples such that similar sites with close chemical values are organised as neighbours on a map. The SOM neural network consists of two layers of neurons: the input layer and the output layer. The output layer is represented by a map or a rectangular grid with l by m neurons (or cells), laid out in a hexagonal lattice. The principle is to classify the sample vectors (SVs), described by a set of descriptors on the map according to the similarities between the descriptors. Two SVs that are similar (from a descriptor point of view) are classified in the same cell of the map or in neighbouring cells, while two different SVs are classified in separate cells that could be distant from each other.

The sequential SOM algorithm used in this study can be summarised as follows (see Kohonen, 1995; Giraudel and Lek, 2001 for more details):

- The virtual vectors (VV_j, $1 \leqslant j \leqslant c$) are initialised with a random sample drawn from the input dataset.
- The VVs are updated in an iterative way.
  - A sample vector (SV_k) is randomly chosen as an input vector.
  - The Euclidean distance between this SV_k and each VV (each cell) is computed.
  - The VV closest to the SV_k is selected and called the "best matching unit" (BMU).
  - The BMU and its neighbours are moved slightly towards the SV_k using the rule

    $$VV_j(t+1) = VV_j(t) + \eta(t)N(t,r)(SV_k(t) - VV_j(t)),$$

    where t is the number of iterations, $SV_k(t)$ is a sample vector, in other words, $SV_k(t)$ is a vector of the values of the input neurons at iteration t, $VV_j(t)$ is a virtual vector that represents the weights between a neuron j of the output layer and all the neurons of the input layer at iteration t, $\eta(t)$ is the learning rate that is a decreasing function of iteration t and $N(t, r)$ is the neighbourhood function wich r representing the distance in the map between the winning neuron and its neighbouring neurons. This function defines the size of the neighbourhood of the winning neuron (BMU) to be updated during the learning process. The learning process is continued until a stopping criterion is met, usually when weight vectors stabilise or when a number of iterations are completed. At the end of the learning process, the BMU is determined for each site and each site is associated with the corresponding cell of the map.

In this study, the SVs are represented by the sites for each decade (3 per site) described by the chemical variables. The input layer then comprised 19 neurons connected to 135 samples (i.e. 135 SVs). The output layer comprised 70 neurons organised in an array with 10 rows and 7 columns. This number of neurons was defined according to a compromise between the formula $c = 5\sqrt{n}$ proposed by the Laboratory of Computer and Information Science (CIS), Helsinki University of Technology (2000), where c is the number of cells and n is the number of training samples (sample vectors), and the computation of the topographic and quantisation errors, two evaluation criteria to quantify the resolution and topology preservation. The software package for the SOM method is available and freely downloadable from the website: http://www.cis.hut.fi/projects/somtoolbox/.

Additionally, in order to define boundaries between possible subsets existing in the map (regrouping cells similar enough to be in the same cluster), a hierarchical cluster analysis with the Ward linkage method is applied. In this way the cluster

Table 1 – Location and characteristics of sampling sites (HER-1 = Hydrocoregion level 1)

Code	River	Site	Altitude	Code HER-1	HER-1	Relief	Geology	Climate
GA_01	Garonne	Pont du Roi	580	1	Pyrénées	High mountains	Metamorphic granite	Moist mountain
GA_02	Garonne	Chaum	479	1	Pyrénées	High mountains	Metamorphic granite	Moist mountain
GA_03	Garonne	Valentine	364	1	Pyrénées	High mountains	Metamorphic granite	Moist mountain
GA_04	Garonne	Labarthe Inard	321	1	Pyrénées	High mountains	Metamorphic granite	Moist mountain
GA_05	Garonne	Boussens	260	14	Coteaux aquitains	Mild relief	Detritus	Meridional oceanic
GA_06	Garonne	Cazères D7	233	14	Coteaux aquitains	Mild relief	Detritus	Meridional oceanic
GA_07	Garonne	Marquefave	191	14	Coteaux aquitains	Mild relief	Detritus	Meridional oceanic
GA_08	Garonne	Pinsaguel	150	14	Coteaux aquitains	Mild relief	Detritus	Meridional oceanic
GA_09	Garonne	St-Pierre	131	14	Coteaux aquitains	Mild relief	Detritus	Meridional oceanic
GA_10	Garonne	Gagnac	119	14	Coteaux aquitains	Mild relief	Detritus	Meridional oceanic
GA_11	Garonne	Verdun	96	14	Coteaux aquitains	Mild relief	Detritus	Meridional oceanic
GA_12	Garonne	Lamagistère	52	14	Coteaux aquitains	Mild relief	Detritus	Meridional oceanic
GA_13	Garonne	Aqueduc	40	14	Coteaux aquitains	Mild relief	Detritus	Meridional oceanic
GA_14	Garonne	St.-Léger	37	14	Coteaux aquitains	Mild relief	Detritus	Meridional oceanic
GA_15	Garonne	Mas d'Agenais	17	14	Coteaux aquitains	Mild relief	Detritus	Meridional oceanic
GA_16	Garonne	Couthures	16	14	Coteaux aquitains	Mild relief	Detritus	Meridional oceanic
GA_17	Garonne	Cadillac	6	14	Coteaux aquitains	Mild relief	Detritus	Meridional oceanic
GA_18	Garonne	Bordeaux	4	14	Coteaux aquitains	Mild relief	Detritus	Meridional oceanic
AD_01	ADOUR	Pouzac	505	1	Pyrénées	High mountains	Metamorphic granite	Moist mountain
AD_02	ADOUR	Estirac	164	14	Coteaux aquitains	Mild relief	Detritus	Meridional oceanic
AD_03	ADOUR	Dax	5	14	Coteaux aquitains	Mild relief	Detritus	Meridional oceanic
AR	ARROS	Tasque	120	14	Coteaux aquitains	Mild relief	Detritus	Meridional oceanic
AU	AUSSONNELLE	Cornebarieu	140	14	Coteaux aquitains	Mild relief	Detritus	Meridional oceanic
AV	AVANCE	Plantey	48	14	Coteaux aquitains	Mild relief	Detritus	Meridional oceanic
AVE_01	AVEYRON	Ampiac	490	3	Massif central Sud	Mountains	Metamorphic granite	Moist mountain
AVE_02	AVEYRON	Loubéjac	75	14	Coteaux aquitains	Mild relief	Detritus	Meridional oceanic
BA	BANDIAT	Villejaleix	141	9	Tables calcaires	Plains	Sedimentary limestone	Temperate oceanic
BL	BLEOU	Gourdon	170	11	Causses aquitains	Mild relief	Sedimentary limestone	Meridional oceanic
CE	CELE	Cabrerets	165	11	Causses aquitains	Mild relief	Sedimentary limestone	Meridional oceanic
DR_01	DRONNE	Valeuil	99	11	Causses aquitains	Mild relief	Sedimentary limestone	Meridional oceanic
DR_02	DRONNE	Coutras	4	14	Coteaux aquitains	Mild relief	Detritus	Meridional oceanic
ES	ESTAMPON	Roquefort N132	62	13	Landes	Plains	Detritus	Meridional oceanic
GO	GAVE OLORON	Oloron	211	14	Coteaux aquitains	Mild relief	Detritus	Meridional oceanic
GP	GAVE PAU	Rieulhes	342	14	Coteaux aquitains	Mild relief	Detritus	Meridional oceanic
GI	GIMONE	Lafitte	84	14	Coteaux aquitains	Mild relief	Detritus	Meridional oceanic
IS	ISLE	Bénevent	35	14	Coteaux aquitains	Mild relief	Detritus	Meridional oceanic
LE	LEYRE	Facture	6	13	Landes	Plains	Detritus	Meridional oceanic
LO_01	LOT	Livinhac	194	3	Massif central Sud	Mountains	Metamorphic granite	Moist mountain
LO_02	LOT	Douelle	112	11	Causses aquitains	Mild relief	Sedimentary limestone	Meridional oceanic
MI	MIDOUZE	Laujuzan	79	14	Coteaux aquitains	Mild relief	Detritus	Meridional oceanic
SA	SALAT	Caumont	358	1	Pyrénées	High mountains	Metamorphic granite	Moist mountain
TA_01	TARN	Millau	360	19	Grands causses	Mountains	Sedimentary limestone	Sub-mediterranean
TA_02	TARN	Rabastens	101	14	Coteaux aquitains	Mild relief	Detritus	Meridional oceanic
TA_03	TARN	Moissac	65	14	Coteaux aquitains	Mild relief	Detritus	Meridional oceanic
VI	VIAUR	La Garde	195	3	Massif central Sud	Mountains	Metamorphic granite	Moist mountain

boundaries are defined in the units of the SOM map according to the similarities of the VV of the output neurons.

To analyse the contribution of each descriptor (chemical variables) to structure the trained SOM, each descriptor and the associated connection weight calculated for each virtual vector during the training process can be visualised in grey shading on the SOM map. A map can then be visualised separately for each descriptor.

3. Results

Trends were modelled on the data set at 45 sampling sites distributed all over the Adour–Garonne basin over the 1975–2004 period split into 3 subsets: 1975–1984, 1985–1994 and 1995–2004. The mean value of each of the 19 physico-chemical variables was used for each decade. Sampling sites for each decade were classified through the learning process of the SOM according to the chemical variables, and a SOM map was established for each variable.

3.1. *Spatial trends*

The sampling sites were first classified on the SOM map according to their similarity by physicochemical characteristics (Fig. 2). Different map sizes were tested and we chose the optimum map size of [10 × 7] based on the minimum values of quantisation (0.383) and topographic errors (0.06). The distribution of the sites on the map appears to be heterogeneous with concentrated zones located in the top left and right corners, in the left centre and in the bottom left corner.

Based on similarity between SOM cells (i.e. virtual units), 5 clusters of samples were identified (Fig. 2). These distribution patterns showed the characteristics of longitudinal key conditions of water systems, from the head of the basin at the top of the SOM map (cluster 1) to the downstream area at the bottom (cluster 2). Cluster 1a is mainly from the head of the Adour–Garonne basin at high altitudes. Cluster 1b1 is mostly from the head of Lot and Tarn, in the lower-altitude mountains in the Massif-Central and the piedmont zone of the Adour–Garonne. Cluster 1b2 is characterised by sites

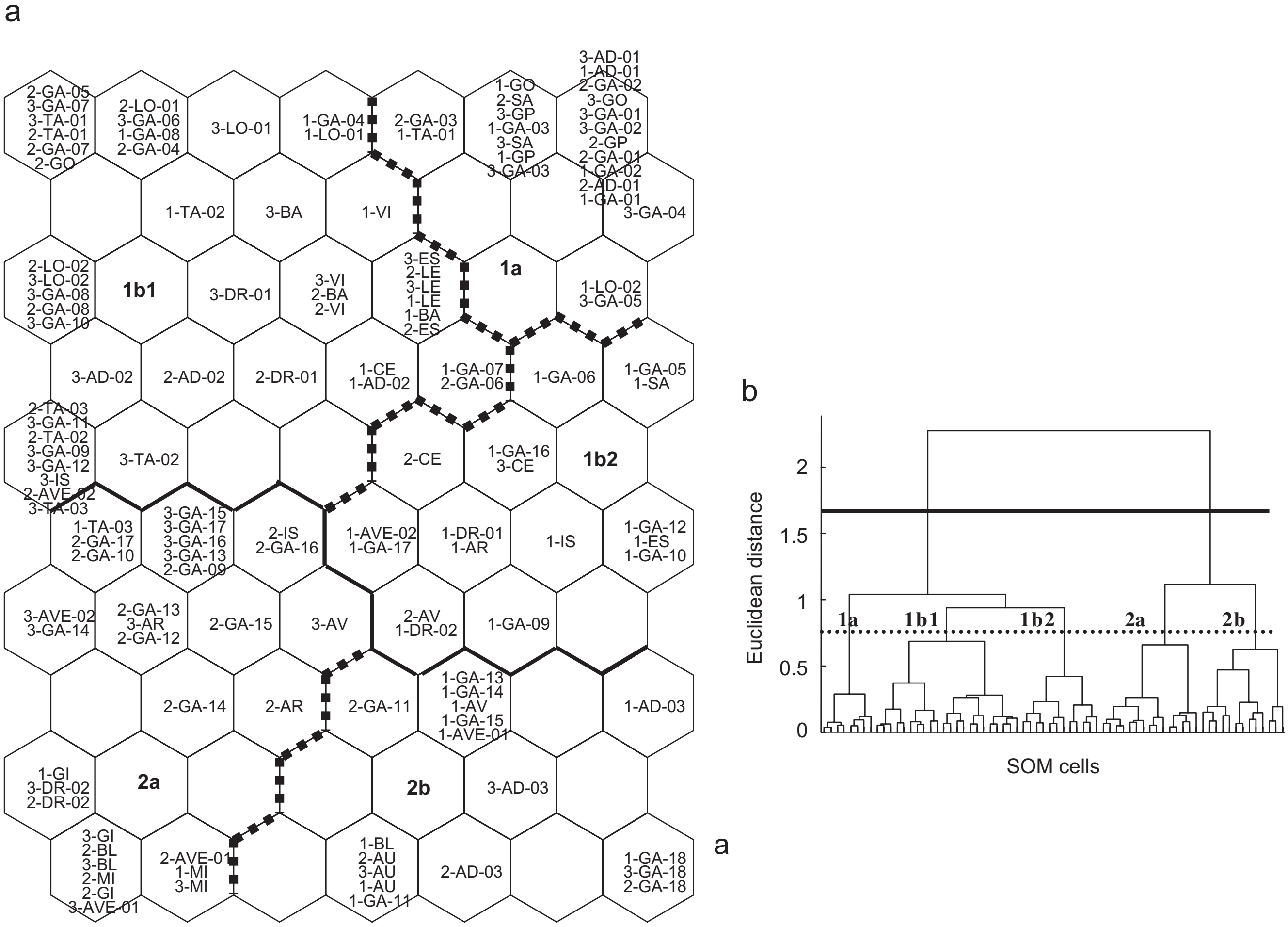

Fig. 2 – Classification of sampling sites based on similarities from a physicochemical point of view on the SOM output layer. (a) The acronyms in the hexagonal units represent the different sites, and are shown in Table 1. Numbers before acronyms (1–3) mean first, second and third decades. There are 5 clusters in total: two main clusters 1 and 2 with subclusters (1a, 1b1, 1b2, 2a and 2b). (b) Hierarchical cluster analysis according to the similarity between SOM cells after model training defining the 5 clusters.

represented solely by the first decade. Cluster 2 is from downstream areas, affected more or less strongly by eutrophication. Cluster 2b sites are located in brackish zones.

A map was drawn for each physicochemical variable to define their contribution to building the site map (Fig. 3). Except for pH, each physicochemical variable displays a high gradient distribution. Dark areas represent high contributions of the variables to the construction of the map, and light ones exhibit low values. According to the contribution of the input variables, the SOM map proposes 5 major gradients corresponding to the main clusters in Fig. 2: (1) oxygen concentration (O_2 mg l^{-1}) is characteristic for cluster 1a, in which the values vary from the bottom to the left or right top corner (a gradient of oxygenation); (2) cluster 1b1 is mainly determined by high values of oxygen saturation, air temperature and pH; (3) cluster 1b2 is determined by high BOD5; (4) in cluster 2a water temperature, bicarbonates, calcium and nitrates are the major determinants; (5) cluster 2b is characterised by reduced nitrogen, chlorine, suspended matter, sodium and sulphate. Conductivity and potassium are specific parameters of clusters 2a and 2b.

For each site, the Euclidean distance between the SOM cell where the site corresponding to the first decade has been plotted and the SOM cell where the site corresponding to the last decade has been plotted was computed. All the distances calculated for each site were represented graphically. In Fig. 4a with the River Garonne sites and Fig. 4b for all the sites except the Garonne continuum, where sites are in abscissa and Euclidean distance in ordinates, the higher the bar plots are, the more the sites are concerned by important physicochemical changes. In order to obtain a better spatial understanding of the extent of the change, we transposed Figs. 4a and b onto a geographic map representation (Fig. 5), where bar plots are converted into dots. We defined a 5-class colour gradient from white to black, in which the more important the Euclidean distance is, the darker the dot is. These changes show different scales of magnitude leading to patterns of spatial distribution within the basin. Sites with minor changes (Euclidean distance <0.24) represent almost half the study sites (21/45). These sites are broadly distributed throughout the basin, although some trends are apparent. The sites seem to be mainly located upstream in the Pyrenean headwaters, in the coastal zones and in the estuary zones. Seven sites are strongly affected by chemical changes (Euclidean distance >0.5), 4 of them located in the middle part of the Garonne continuum in the Toulouse suburb, and the 3 others in the northern part of the basin. Two sites (LO_02 and BL) are in the “Causses aquitains” and 1 site (IS) in the north of “Coteaux aquitains”. A group gathering 17 sites affected by moderate changes (Euclidean distance between 0.25 and 0.5) is spread all over the basin without any evident pattern of distribution.

3.2. *Temporal changes*

In addition to physicochemical changes leading to a spatial distribution pattern, temporal stages are also visible. By

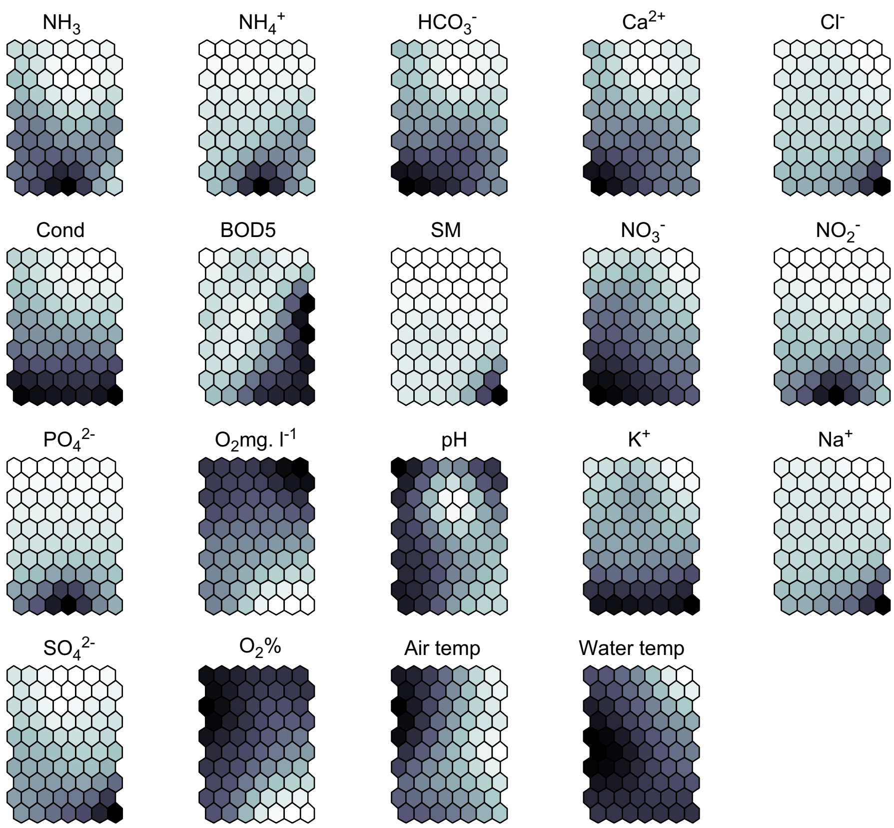

Fig. 3 – Map of each descriptor displaying the contribution of the 19 environmental variables at the sampling sites. Dark areas represent high values of each input variable, while light areas are for low values.

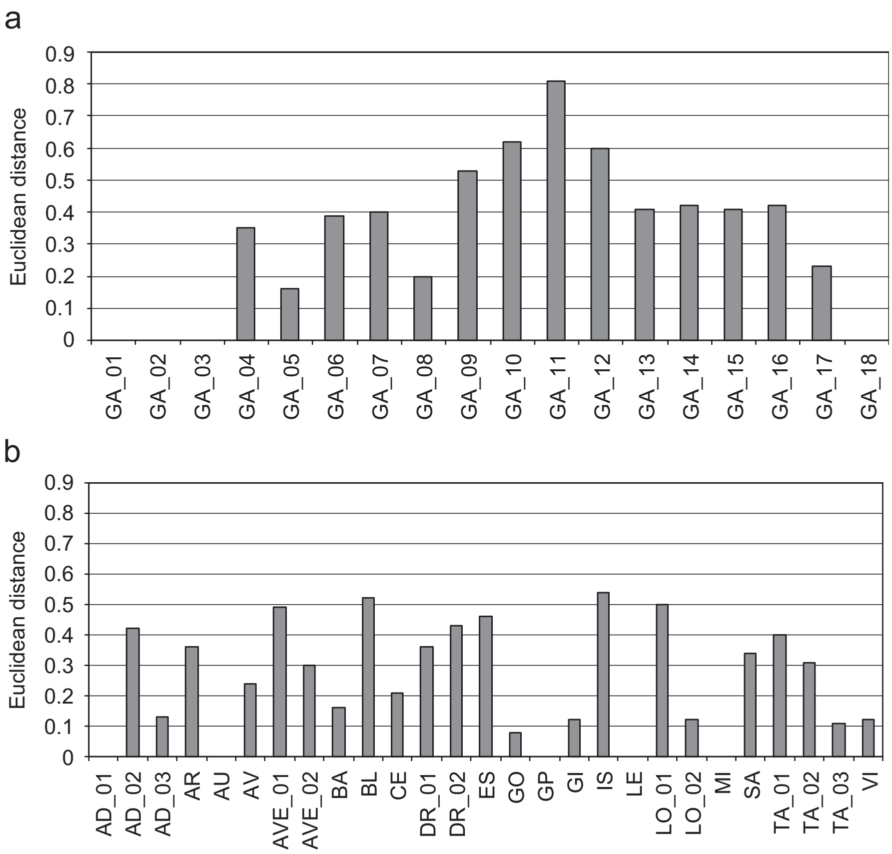

Fig. 4 – Bar plot of Euclidean distance between SOM cells for the Garonne continuum sites (a) and for the sites except the River Garonne (b).

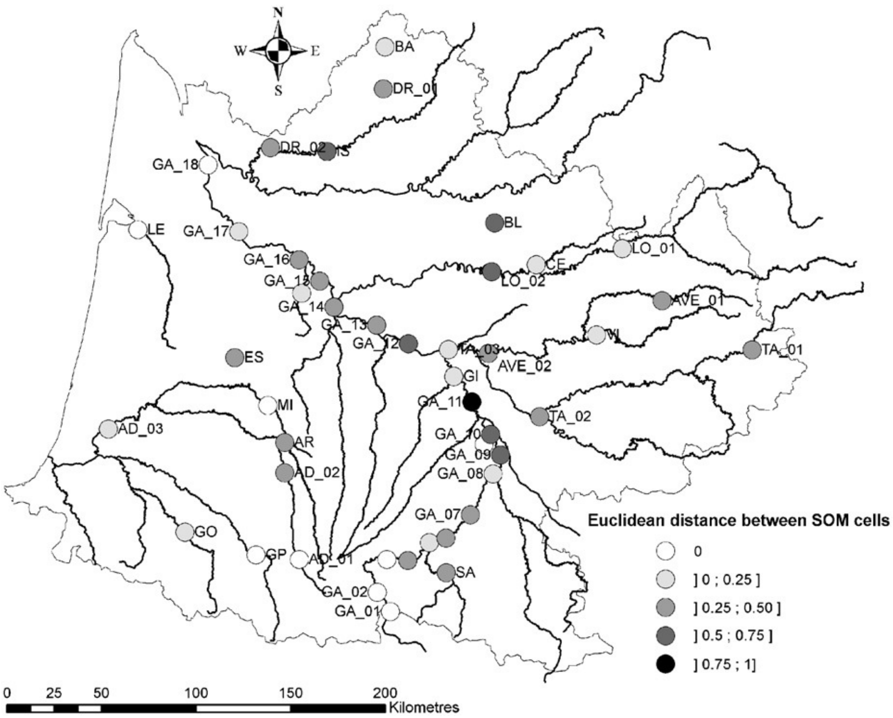

Fig. 5 – Geographic representation of the temporal trends of the water chemistry based on the Euclidean distance between the SOM cells.

superimposing the sampling sites and physicochemical parameters on the SOM map, general trends of physicochemical parameters can be revealed during the last 3 decades for the Garonne continuum (Fig. 6a) and its tributaries (Fig. 6b).

Depending on these temporal shifts of the sites on the SOM map, the chemical trends are presented in 2 ways:

- First, during the last 3 decades, numerous sites moved in one major direction, except for sites GA_05 and GO. Of the 45 sites, 25 are affected by a shift mainly in direction of the left side of the map (11/18 sites for the Garonne river), corresponding to the global air and water temperature gradient. In this first group, gathering more than half the sites, we can separate 3 sub-groups (below are given a few examples): (i) a group of sites shifting from the right to the left centre: GA_09, GA_12, GA_15, AD_02 or IS; (ii) some sites moving from the right to the left top corner: GA_06, GA_07, GA_10 or TA_01; and (iii) sites evolving from the right bottom to the left bottom corner: DR_02, AVE_01 or BL. Respectively, these directions correspond to increasing water temperature, oxygenation and eutrophication gradients. We have to note that only one site (GA_04) presents an original pattern sliding to the right side.
- Second, a group of 20 sites that did not show any significant shift: GA_01, GA_02, GA_18, BA, GI or LE.

The aspects noted above describe an overall view of the chemical trends over 3 decades. Nevertheless, it is necessary to point out how these events occurred in time. The diagram of temporal representations of the sampling sites' shifting in the SOM map stresses the importance of the first arrow representing the evolution between the first and second decades. In fact, 21 sites present a major shift from the first to the second decade, and then transition to the third decade is slowed down or stopped (circular arrow). This is the case for sites GA_07_09_10_12, ES or LO_02, for example. A group of 3 sites (GA_04, GA_06 and GA_11) shows major changes during the transition between the second and third decades. Only one site (IS) is characterised by a "linear" change between decades, with both arrows exhibiting more or less the same amplitude range.

When chemical changes occurred over time, they were not linear. Most of the sites affected by changes were so during the transition between the first decade (1975–1984) and the second decade (1985–1994). During the last 10 years of the studied database (third decade 1995–2004), the

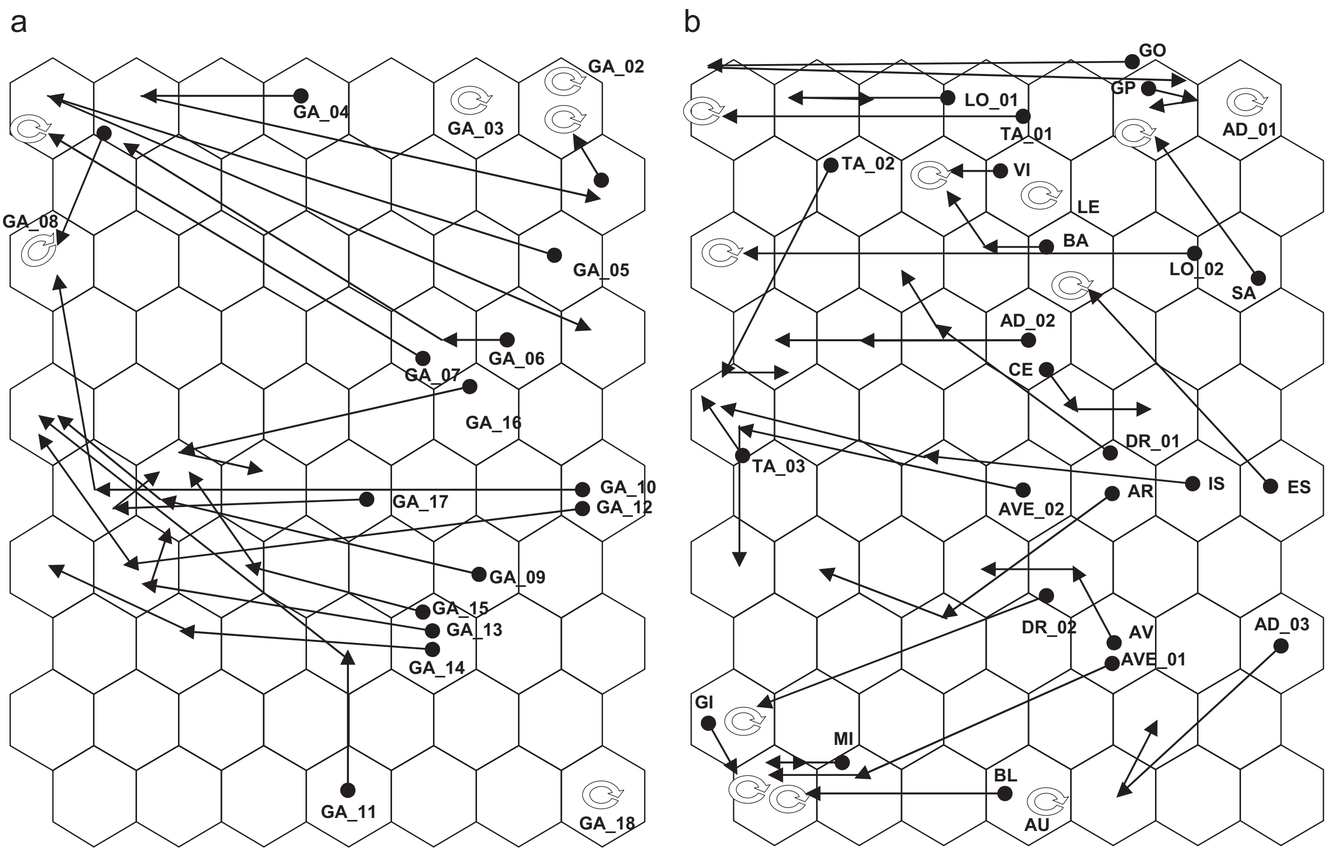

Fig. 6 – Temporal representation of the sampling site shift in the SOM map during the last three decades for (a) sampling sites along the Garonne continuum and (b) the other sites located over the Adour–Garonne basin. The point positions the first decade, the first arrowhead the second decade and the second arrowhead the last decade. Thus, each arrow represents the shifts occurring in a site during one decade. The circular arrow means that there is no change of site within the cell. For acronyms, see Table 1.

physicochemical changes appear to have slowed down or stopped. This suggests that the river systems will head towards a new balance of physicochemical status in the near future.

4. Discussion

Along the River Garonne continuum, 3 distinct homogeneous sections with transitional stages are defined according to the chemical changes occurring. Changes in many sites located on the Garonne tributaries can also be gathered under these different headings.

(i) Sites located upstream in the Pyrenees Mountains show a great chemical stability over time, thus without any kind of trend. The physicochemistry remains mainly characterised by a high level of dissolved oxygen and low temperature. Sites of the headwater of the Adour River present the same chemical pattern with a general absence of trend.

(ii) The second section, and the major one, extends from the piedmont to sites not under tidal influence. All these sites are affected by marked chemical changes and hence two sub-groups are apparent: (1) sites from piedmont to plain, characterised by a high level of dissolved oxygen, show an increase of this parameter since 20 years ago. In some of them, an increase in both oxygen saturation and in air temperature occurred; (2) 8 sites from the Toulouse suburb to the tidal zone are affected by major chemical changes over the last two decades. It appears that the trends are mainly towards an increase in air and water temperature and also towards a decrease of phosphorus and nitrogen load. Moreover, many sites located on the Garonne tributaries are undergoing changes in water temperature. Nevertheless, these sites, on the Garonne continuum, did not show any evident improvement of eutrophic status;

(iii) Sites located in tidal zones have conserved chemical stability during the last decades, this being the case for the Garonne and Adour estuaries. We observe that the site at the transition between brackish water and freshwater shows moderate changes relating to an increase of water temperature.

In parallel with these general tendencies described above along the Garonne continuum, some complements of changes in water physicochemistry have been identified in different local environmental contexts (geology, land-cover) without any kind of spatial distribution. These events are described below:

- Sites with a high level of pollutant compounds did not show any major changes in their water chemistry over the last 20 years, nor in temperature. These sites are located in city suburbs or agricultural areas.
- Some sites located in or draining calcareous areas presented similar patterns and seem to be affected by a strong decrease of phosphorus load.

It clearly appears that the predominant parameter controlling the evolution of the environmental conditions and showing major adjustments over time is the temperature. The majority of the sites were affected in this way. Thirty years of extensive physicochemistry data show that coherent warming occurred in Adour–Garonne Rivers and streams, reflecting global changes. There are currently numerous climate scenarios produced by various global climate models (Allen et al., 2000), but most model predictions for northern Europe do imply significant increases in air temperatures over the next 50–100 years (Benestad, 2002). In recent years, climate change has been identified as an important source of aquatic disturbance and can be considered as thermal pollution on a large to global scale (Mohseni and Stefan, 2001; Stefan et al., 2001). Nevertheless, few long-term data sets are available to enable the study of the implications of this climate change (Caissie, 2006) and could lead to contradictions. Webb and Nobilis (1997) carried out a long-term study, in which they analysed 90 years of water temperature data from north-central Austria. No specific trends were reported in water temperatures in this long-term study. In contrast, in 1994 the same authors (Webb and Nobilis, 1994) reported a significant increase of 0.8 °C over a similar time period in the River Danube and attributed the increase mostly to human activities. Increases in water temperature over a 30-year period were also observed in Scotland. Hari et al. (2006) concluded in their study on Alpine rivers and streams of Switzerland, that during the last quarter of the 20th century substantial stream warming occurred, most of which can be attributed to an abrupt increase in temperature. In the analysis of the water temperature of the Loire for the period 1976–2003, Moatar and Gailhard (2006) showed a change in the energy regime with very significant rises in spring and summer (from 1.5 to 2 °C).

Parallel to this, during the last two decades there has been a substantial tendency for the reduction of pollutant loading and the simultaneous amelioration of the trophic condition. In the present study, the statistical analysis of the chemical data set indicates that nutrient enrichment exhibits a noticeable decrease. This tendency is corroborated by the assessments and the survey carried out by the Adour–Garonne water agency. The river quality improved at 35% of the survey sites, 61% remained stable and only 4% showed significant degradation. Indeed, the depollution effort has been increasing since the 1980s. Between 1971 and 1997, for all pollutant compounds (organic matter, suspended matter) water quality improved in spite of increased industrial activity. In the 1980s, only 30–36% of mineral and organic toxic pollutants in effluents from built-up areas and industry were treated. The clean-up rate of the Adour–Garonne basin built-up areas went from 35% at the end of 1991 to 46.5% in 1997. It should, however, be noted that this progression, started well in 1992–1994, has tended to slow down since 1995. In 2004, 57% of urban pollution was eliminated from the basin (Agence de l'Eau Adour-Garonne, 1984, 1996, 1999, 2006). This trend has been taking place in other large French rivers. Lair (2001) showed a decrease of the phosphate fluxes in the Middle Loire, which suggests that catchment area treatments performed by water agency authorities were successful.

In contrast, Wright et al. (2001), in a study of nitrogen deposition in streams across Europe, concluded that few of the sites exhibit significant long-term trends in nitrate concentration. Stoddard et al. (1999) and Skjelkvåle et al. (2001, 2005) demonstrated significant trends in nitrate concentration, consisting of a universal increase largely restricted to the 1980s, followed by reversal of NO_3^- trends in the 1990s, especially in North/Central Europe and North America. Jackson et al. (2001) concluded that freshwater eutrophication and pollution has decreased in many waterways.

The global nitrogen cycle has been altered by human activity, and increased nitrogen input has altered the chemistry of the aquatic ecosystem and contributes to eutrophication. In 1994, Vitousek concluded in a study dealing with ecology and global change, that the global nitrogen cycle altered by human activity probably currently presents the most important component of global change and will do so for some decades to come. In the present study, as well as in recent studies dealing with global change, it has been shown that nitrogen enrichment and increase of eutrophication in hydrosystems could be a reversible process over a short time-scale of 1 decade.

5. Conclusion

The distinctive feature of this study is that it concerns physicochemical data covering a large spatial and time-scale, contrasting with previous analyses dealing with shorter scales. The results show clear and widespread evidence of changes affecting the chemistry of watercourses in the Adour–Garonne basin. Over half of the sites studied were found to be undergoing change. Trends are generally clearest in the Garonne River continuum, but many of the same trends can also be identified in tributaries.

The overall pattern of change involves in particular the onset of an increase in water temperature, which has been occurring for the last 20 years, and the recovery from eutrophication during the last decade. As would be expected, the strongest trend affects hydrosystems in their temperature regime: the warming seems to be more effective during the second decade of the study (1984–1994). Additionally, at many sites nitrogen and phosphorus loads were lower between 1995 and 2004, confirming a downward trend in eutrophication status. This is the result of depuration efforts in sewage treatment works despite the constant increase of anthropogenic pressure. Sites that did not present any such trends are at the extremes, located at either end of the river gradient: headwater and tidal zones. Other sites unaffected by changes are those strongly disturbed by human activities showing a high level of eutrophication. Here, any minor changes would not be perceptible.

We are in the midst of one of the largest experiments in the history of Earth, where human effects on climate, biogeochemical cycles and land use are having important consequences on the ecosystem (Chapin et al., 2000). Whereas eutrophication of aquatic systems seems to be a reversible process on a short time scale, global warming represents the most important, complex and underestimated component of global change. Scheffer et al. (2001) mentioned that all ecosystems exposed to gradual changes assume a response in a smooth way, but which can be interrupted by sudden drastic switches preceded by a loss of resilience. In a river continuum, this unidirectional change in water temperature should lead to the homogenisation of the hydrosystem regime and lessen the river gradient. The headwaters, within natural or near-natural conditions without any perceptible change, constitute suitable sensors of change and should be considered as milestones to survey and assess any adjustments occurring in freshwaters. It is along these lines that the European Water Framework directive (European Parliament, 2000) encourages the assessment, maintenance and restoration of good ecological status. Hence, distinguishing natural ecological conditions paves the way for implementing the directive. Taking temperature as a predominant parameter in ecology investigation could be determinant in terms of policy to regulate and assess reversibility of ecological status. The next step will be to gather long-term biological series to evaluate the effects of physicochemical changes on the community structure of different trophic web components.

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REFERENCES

Agence de l'Eau Adour-Garonne, 1984. Statistical memento on water and its use in the Adour-Garonne basin (Memento statistique sur l'Eau et son utilisation dans le bassin Adour-Garonne), pp. 1–40.

Agence de l'Eau Adour-Garonne, 1996. Journal of Water Agency (Revue de l'Agence de l'Eau) 66 (Spring), 1–32.

Agence de l'Eau Adour-Garonne, 1999. Journal of Water Agency (Revue de l'Agence de l'Eau) 76 (Summer), 1–48.

Agence de l'Eau Adour-Garonne, 2006. Journal of Water Agency (Revue de l'Agence de l'Eau) 94 (June), 1–32.

Allen, M.R., Scott, P.A., Mitchell, J.F.B., Schnur, R., Delworth, T.L., 2000. Quantifying the uncertainty in forecasts of anthropogenic climate change. Nature 407, 617–620.

Benestad, R.E., 2002. Empirically downscaled temperature scenarios for northern Europe based on a multi-model ensemble. Climate Res. 21, 105–125.

Bhangu, I., Whitfield, P.H., 1997. Seasonal and long-term variations in water quality of the Skeena river at USK, British Columbia. Water Res. 31 (9), 2187–2194.

Caissie, D., 2006. The thermal regime of rivers: a review. Freshwater Biol. 51 (8), 1389–1406.

Carpenter, S.R., Caraco, N.F., Corell, D.L., Howarth, R.W., Sharpley, A.N., Smith, V.H., 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecol. Appl. 8 (3), 559–568.

Cellot, B., Dolec Olivier, M.J., Bornette, G., Pautou, G., 1994. Temporal and spatial environmental variability in the Upper Rhône River and its floodplain. Freshwater Biol. 31, 311–325.

Chapin III, F.S., Zavaleta, E.S., Eviners, V.T., Naylor, R.L., Vitousek, P.M., Reynolds, H.L., Hooper, D.U., Lavorel, S., Sala, O.E., Hobbie, S.E., Mack, M.C., Díaz, S., 2000. Consequences of changing biodiversity. Nature 405, 234–242.

Chon, T.S., Park, Y.S., Moon, K.H., Cha, E.Y., 1996. Patternizing communities by using an artificial neural network. Ecol. Model. 90, 69–78.

Etchanchu, D., Probst, J.L., 1988. Evolution of the chemical composition of the Garonne river during the period 1971–1984. Hydrol. Sci. J. 33, 243–256.

European Parliament, 2000. Directive 2000/60/EC of the European Parliament and of the Council Establishing a Framework for Community Action in the Field of Water Policy. Off. L327, 72.

Evans, C.D., Monteith, D.T., 2001. Chemical trends at lakes and stream in the UK Acid Waters Monitoring Network, 1988–2000. Hydrol. Earth Syst. Sci. 5 (3), 351–366.

Gevrey, M., Rimet, F., Park, Y.S., Giraudel, J.L., Ector, L., Lek, S., 2004. Water quality assessment using diatom assemblages and advanced modelling techniques. Freshwater Biol. 49, 208–220.

Giraudel, J.L., Lek, S., 2001. A comparison of self-organizing map algorithm and some conventional statistical methods for ecological community ordination. Ecol. Model. 146, 329–339.

Hari, R.E., Livingstone, D.M., Siber, R., Burkhardt-Holm, P., Güttinger, H., 2006. Consequences of climatic change for water temperature and brown trout populations in Alpine rivers and streams. Global Change Biol. 12, 10–26.

Harriman, R., Watt, A.W., Christie, A.E.G., Collen, P., Moore, D.W., McCartney, A.G., Taylor, E.M., Watson, J., 2001. Interpretation of trends in acidic deposition and surface water chemistry in Scotland during the past three decades. Hydrol. Earth Syst. Sci. 5 (3), 407–420.

Hutchins, M.G., Smith, B., Rawlins, B.G., Lister, T.R., 1999. Temporal and spatial variability of stream waters in Wales, the Welsh borders and part of the west Midlands, UK—1. Major ion concentrations. Water Res. 33 (16), 3479–3491.

Kohonen, T., 1982. Self-organized formation of topologically correct feature maps. Biol. Cybernet. 43, 59–69.

Kohonen, T., 1995. Self-Organizing Maps. Springer, Heidelberg.

Kopacek, J., Vesely, J., Stuchlik, E., 2001. Sulphur and nitrogen fluxes and budgets in the Bohemian Forest and Tatra Mountains during the Industrial Revolution (1850–2000). Hydrol. Earth Syst. Sci. 5 (3), 391–405.

Jackson, R.B., Carpenter, S.R., Dahm, C.N., McKnight, D.M., Naiman, R.J., Postel, S.L., Running, S.W., 2001. Water in a changing world. Ecol. Appl. 11 (4), 1027–1045.

Jenkins, A., Ferrier, R.C., Helliwell, R.C., 2001. Modelling nitrogen dynamics at Lochnagar, N.E. Scotland. Hydrol. Earth Syst. Sci. 5 (3), 519–527.

Lair, N., 2001. Cross overlook on the Middle Loire river status: potamoplankton and water quality, which lessons to draw from twenty years studies? (Regards croisés sur l'état de la Loire moyenne : potamoplancton et qualité de l'eau, quel enseignement tirer de 20 années d'études?). Hydroécol. Appl. 13 (2), 3–41.

Lek, S., Guegan, J.-F., 2000. Artificial Neuronal Networks, Application to Ecology and Evolution. Springer, Heidelberg.

Mastrorillo, S., Dauba, F., Oberdorff, T., Guégan, J.F., Lek, S., 1998. Predicting local fish species richness in the Garonne River basin. C.R. Acad. Sci. 321, 423–428.

Minshall, G.W., 1988. Stream ecosystem theory: a global perspective. J. North Am. Benthol. Soc. 7 (4), 263–288.

Moatar, F., Gailhard, J., 2006. Water temperature behavior in the River Loire since 1976 and 1881. C.R. Geosci. 338, 319–328.

Mohseni, O., Stefan, H.G., 2001. Water budgets of two watersheds in different climatic zones under projected climate warming. Climate Change 59, 389–409.

Moldan, F., Wright, R.F., Löfgren, S., Forsius, M., Ruoho-airola, T., Skjelkvale, B.L., 2001. Long-term changes in acidification and recovery at nine calibrated catchments in Norway; Sweden and Finland. Hydrol. Earth Syst. Sci. 5 (3), 339–349.

Park, Y.S., Cereghino, R., Compin, A., Lek, S., 2003a. Applications of artificial neural networks for patterning and predicting aquatic insect species richness in running waters. Ecol. Model. 160, 265–280.

Park, Y.S., Chang, J.B., Lek, S., Cao, W.X., Brosse, S., 2003b. Conservation strategies for endemic fish species threatened by the Three Gorges Dam. Conserv. Biol. 17, 1748–1758.

Scheffer, M., Carpenter, S., Foley, J.A., Folke, C., Walker, B., 2001. Catastrophic shifts in ecosystems. Nature 413, 591–596.

Semhi, K., Suchet, P.A., Clauer, N., Probst, J.-L., 2000. Impact of nitrogen fertilizers on the natural weathering-erosion processes and fluvial transport in the Garonne basin. Appl. Geochem. 15, 865–878.

Skjelkvåle, B.L., Mannio, J., Wilander, A., Andersen, T., 2001. Recovery from acidification of lakes in Finland; Norway and Sweden 1990–1999. Hydrol. Earth Syst. Sci. 5 (3), 327–337.

Skjelkvåle, B.L., Stoddard, J.L., Jeffries, D.S., Tørseth, K., Høgåsen, T., Bowman, J., Mannio, J., Monteith, D.T., Mosello, R., Rogora, M., Rzychon, D., Vesely, J., Wieting, J., Wilander, A., Worsztynowicz, A., 2005. Regional scale evidence for improvements in surface water chemistry 1990–2001. Environ. Pollut. 137, 165–176.

Smart, R.P., Soulsby, C., Neal, C., Wade, A., Cresser, M.S., Billett, M.F., Langan, S.J., Edwards, A.C., Jarvie, H.P., Owen, R., 1998. Factors regulating the spatial and temporal distribution of solute concentrations in a major river system in NE Scotland. Sci. Total Environ. 221, 93–110.

Stefan, H.G., Fang, X., Eaton, J.G., 2001. Simulated fish habitat changes in North American lakes in response to projected climate warming. Trans. Am. Fish. Soc. 130, 459–477.

Steiger, J., James, M., Gazelle, F., 1998. Chennalization and consequences on floodplain system functioning on the Garonne River, SW France. Regul. Rivers: Res. Manage. 14, 13–23.

Stoddard, J.L., Jeffries, D.S., Lükewille, A., Clair, T.A., Dillon, P.J., Driscoll, C.T., Forsius, M., Johannessen, M., Kahl, J.S., Kellogg, J.H., Kemp, A., Mannio, J., Monteith, D.T., Murdoch, P.S., Patrick, S., Rebsdorf, A., Skjelkvåle, B.L., Stainton, M.P., Traaen, T., Van dam, H., Webster, K.E., Wieting, J., wilander, A., 1999. Regional trends in aquatic recovery from acidification in North America and Europe. Nature 401, 575–578.

Tison, J., Giraudel, J.L., Coste, M., Delmas, F., Park, Y.-S., 2004. Use of the unsupervised neural network for ecoregional zoning of hydrosystems through diatom communities: case study of Adour–Garonne watershed (France). Arch. Hydrobiol. 159, 409–422.

Vitousek, P.M., 1994. Beyond global warming: ecology and global change. Ecology 75 (7), 1861–1876.

Ward, J.V., 1989. The four-dimensional nature of lotic ecosystems. J. North Am. Benthol. Soc. 8 (1), 2–8.

Wasson, J.-G., Chandesris, A., Pella, H., Souchon, Y., 2001. Definition of the French hydroecoregions. Methodology for determining reference conditions according to the Framework Directive for water management (Définition des hydroécorégions françaises. Méthodologie de détermination des conditions de référence au sens de la Directive cadre pour la gestion des eaux). Rapport de phase 1. Ministère de l'Aménagement du Territoire et de l'Environnement-Cemagref, 68pp.

Webb, B.W., Nobilis, F., 1994. Water temperature behavior in the River Danube during the twentieth century. Hydrobiologia 291, 105–113.

Webb, B.W., Nobilis, F., 1997. A long-term perspective on the nature of the air–water temperature relationship: a case study. Hydrol. Processes 11, 137–147.

Wright, R.F., Alewell, C., Cullen, J.M., Evans, C.D., Marchetto, A., Moldan, F., Prechtel, A., Rogora, M., 2001. Trends in nitrogen deposition and leaching in acid-sensitive streams in Europe. Hydrol. Earth Syst. Sci. 5 (3), 299–310.