Limnological characteristics of 25 lakes of the French Massif Central

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Keywords : water chemistry, French Massif Central, crater lake, PCA, hierarchical clustering.

Concentrations of a wide range of chemical variables were determined in 206 water samples taken between May 1996 and May 1998 from a set of 25 natural lakes in the French Massif Central. From each lake 6 to 9 samples were collected. Mean and standard deviation of total alkalinity, conductivity, pH, concentrations in K^+ , Mg^{2+} , Ca^{2+} , Na^+ , Cl^- , SO_4^{2-} , total phosphorus, nitrate-nitrogen, dissolved silica, chlorophyll *a*, and water colour were calculated for each lake. These results are briefly compared with those obtained in an earlier study in which chemical analyses were carried out on a reduced set of lakes from the same region. In most lakes and for most elements, concentrations observed in the present study were similar to those observed previously. The seasonal variations of the elements which are most strongly influenced by biological processes were also investigated. Using hierarchical cluster analysis three main lake groups were distinguished : i) alkaline lakes, ii) deep lakes with low alkalinity and iii) shallow lakes with low alkalinity. The major patterns of variation in the data set were also investigated using principal components analysis (PCA), which confirms that total alkalinity and maximum water depth are the main environmental gradients in this set of lakes. In conclusion, the potential of this data-set for building diatom-based transfer functions to reconstruct past limnological conditions is discussed.

Caractéristiques limnologiques de 25 lacs du Massif Central français

Mots-clés : chimie des eaux, Massif Central, lac de cratère, ACP, classification hiérarchique.

Les concentrations en éléments majeurs des eaux de 25 lacs naturels du Massif Central ont été déterminées à partir de l'analyse chimique de 206 échantillons prélevés entre mai 1996 et mai 1998. Pour chaque lac, 6 à 9 échantillons ont été analysés. Les valeurs moyennes et les écart-types sont calculés pour les variables chimiques telles que l'alcalinité totale, la conductivité, le pH, les concentrations en K^+ , Mg^{2+} , Ca^{2+} , Na^+ , Cl^- , SO_4^{2-} , phosphore total, $N-NO_3$, silice dissoute, chlorophylle *a*, et la couleur de l'eau. Ces résultats sont comparés brièvement avec ceux obtenus lors d'analyses chimiques antérieures effectuées sur un nombre réduit de lacs de la même région. Il apparaît que dans la plupart des lacs étudiés les concentrations en éléments majeurs sont restés stables. Les variations saisonnières des éléments fortement influencés par les processus biologiques sont aussi discutées. La classification hiérarchique permet de distinguer trois groupes principaux de lacs : i) lacs caractérisés par leurs eaux alcalines, ii) lacs profonds d'eau peu alcaline et iii) lacs peu profonds d'eau peu alcaline. L'analyse en composantes principales (ACP) confirme que l'alcalinité totale et la profondeur d'eau maximale représentent les gradients environnementaux majeurs pour l'ensemble de ces lacs. En conclusion, le potentiel de ce jeu de données pour établir des fonctions de transferts entre les peuplements de diatomées et la chimie des eaux en vue de reconstruire les conditions limnologiques passées est discuté.

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1. Introduction

The French Massif Central is a region of considerable interest for palaeoclimate and palaeoenvironmental studies. Pollen analysis especially has been used in many sites in the region, usually palaeolakes, and has revealed changes in climate and vegetation over the past 400,000 years BP (Beaulieu & Reille 1995). Among the techniques that can be used to complete and refine the palynological reconstruction of past environments and climates, diatom analysis is particularly powerful (Stoermer & Smol 1999). Sedimentary archives with good, long-term diatom record exist in the region and a few have been investigated (Pailles 1989, Rioual et al. 2001). Their contribution to the debate on long-term past environment and climate changes, however, have been limited as their interpretation as, so far, remained mainly qualitative.

To improve on these interpretations with quantitative inferences of the past limnological conditions, diatom-based inference models, also known as transfer functions, are required. A transfer function is based on a calibration data set, which consists of species data and contemporary environmental data. In recent years many regional calibration data-sets have been built in northern Europe (Birks et al. 1990, Bennion et al. 1996, Korsman & Birks 1996, Weckström et al. 1997), in the Alps (Lotter et al. 1997, 1998, Wunsam & Schmidt 1994), in North America (Fritz et al. 1993, Pienitz et al. 1995, Dixit et al. 2001, Reavie & Smol 2001) and in some semi-arid regions of the World (Gasse et al. 1995, Reed 1998). Despite this abundance of data there is still need, however, for the derivation of transfer functions from additional geographic regions to improve the accuracy of diatom-based reconstructions of limnological parameters.

In the French Massif Central, or even in France, no such diatom calibration data-set have been developed yet. With this in mind, a monitoring programme for 25 natural lakes in the French Massif Central was carried out. This monitoring aimed to characterise the limnology of these lakes and to identify seasonal variations in water chemistry throughout the year. Another purpose was to assess the feasibility of developing diatom-based predictive models from these lakes in order to reconstruct past limnological conditions from the numerous sedimentary records of the region.

This paper presents the results of this lake water chemistry monitoring, firstly, in terms of water chemistry gradients across the lakes studied and secondly, in terms of seasonal variations by taking examples from a few lakes. The sampling strategy is also discussed

with regard to providing reliable estimates of mean annual water chemistry, for their use in diatom-based transfer functions. The diatom data-set will be the subject of a further work.

2. Study region : the French Massif Central

The Massif Central is the largest mountainous area of France covering 85,000 km² ranging from 46° to 43°N and 2° to 6°E. The average altitude is ~700 m.a.s.l. The bedrock is dominantly of crystalline nature (granite, gneiss and schist) but volcanic rocks (basalt, trachyte, labradorite) are also well represented and most of the relief over 1000 m a.s.l. has a volcanic origin. The climate of the Massif Central is predominantly Atlantic but the more elevated areas to the east and south are drier, with strong winds, low mean annual temperatures, numerous frost days and a short growing season (Reille et al. 1992).

The 25 lakes selected for this project are not evenly distributed throughout the study area. Nineteen are located within a radius of 25 km around the small town of Besse-en-Chandesse. This small area constitutes a «lake district» unique in France (Devaux et al. 1995). One lake (Gour de Tazenat) lies about 100 km away from Besse-en-Chandesse at the far north of the volcanic range «Chaîne des Puys». Five more lakes, are located more than 200 km to the south-east of Besse-en-Chandesse, around the town of Le Puy-en-Velay (Fig. 1). The 25 selected lakes show a large heterogeneity in terms of morphological characteristics (Table 1) and can be grouped in three major categories according to the origin of their formation.

2.1. Crater lakes

Crater lakes, also called maars, are formed after a phreatomagmatic explosion resulting from the interaction between magma and subsurface aquifers or rivers. As discussed by Juvigné et al. (1993) phreatomagmatism is typical of the Tertiary and Quaternary volcanism in the French Massif Central. Most of these craters are presently occupied by peat mires or meadows (for example the sites of Ribains and Estivadoux). Only eight craters in the region still hold a lake. The «typical» maar lake is circular, deep, has a narrow littoral rim and a profile sloping steeply from less than 50 m away from the shore, extending to a flat-bottomed, sub-circular, central area (Truze & Kelts 1993). Because of quite a large initial depth (often around 100 m) combined with a rather small area, crater lakes present large aspect ratio values (maximum depth divided by

Lakes of glacial origin represent a very heterogeneous group of lakes in terms of morphological characteristics. During the last glacial period, and especially the glacial maximum, the highest parts of the Massif Central were partly covered by ice. Glaciers were better developed on the western side and, therefore, lakes of glacial origin are quite numerous in the Artense region that forms a cirque located between the

Table 1. List of the 25 lakes studied, with their geographical location and main morphological characteristics. The lakes are grouped according to their origin (volcanic maar or dam, glacial, mixed).

Tableau 1. Liste des 25 lacs étudiés avec leur position géographique et leurs principales caractéristiques morphologiques. Les lacs ont été regroupés selon leur origine (maar ou barrage volcanique, glaciaire, mixte).

Name	Latitude	Longitude	Origin	Substratum	Altitude (m.a.s.l.)	Max. relief (m)	Lake area A0 (ha)	Catchment area Ad (ha)	Ad/A0	Max. depth Zmax (m)	Aspect ratio $Z_{max}/\sqrt{A0}$
Lac du Bouchet	44°54'36"	3°47'29"	volcanic, maar	basalt	1205	96	43.8	97.9	2.2	28	0.042
Lac Chauvêt	45°27'39"	2°50'00"	volcanic, maar	basalt, diorites	1166	129	50.9	111.6	2.2	66	0.093
Lac de la Godivelle d'en Haut	45°23'19"	2°55'08"	volcanic, maar	basalt	1239	53	13.8	13.4	1.0	44	0.118
Lac d'Issarlès	44°49'04"	4°04'19"	volcanic, maar	granite, basaltic scoriae	997	268	88.3	123.3	1.4	109	0.116
Lac Pavin	45°29'48"	2°53'17"	volcanic, maar	granite, basalt, metamorphic rocks	1197	210	45.2	36.7	0.8	92	0.137
Lac de Saint Front	44°58'57"	4°10'15"	volcanic, maar	basalt	1235	109	29.8	124.5	4.2	6	0.011
Lac de Servière	45°28'48"	2°51'36"	volcanic, maar	basalt	1200	180	16.2	50.8	3.1	29	0.072
Gour de Tazenat	45°58'52"	5°59'36"	volcanic, maar	porphyritic tuff, microgranite	630	210	32.9	417.6	12.7	66	0.115
Lac Estivadox	45°29'35"	2°54'09"	volcanic, maar	gneiss, basalt	1245	57	2.2	35.3	16.0	1	0.007
Ribains, Les Narces	44°50'09"	3°49'16"	volcanic, maar	basalt	1075	146	0.5	1183	2366.0	1	0.014
Lac d'Aydat	45°40'00"	2°59'21"	volcanic, dam	basalt	825	505	60.3	3000	49.8	15	0.019
Lac de la Cassière	45°41'18"	3°00'49"	volcanic, dam	basalt	861	183	12.4	204.6	16.6	7	0.020
Lac Chambon	45°34'16"	2°55'21"	volcanic, dam	basalt	880	858	50.6	3604.6	71.3	4	0.006
Lac de Montcineyre	45°27'36"	2°53'53"	volcanic, dam or maar?	basalt	1174	146	39.7	135.7	3.4	18	0.029
Lac de Coindé	45°22'15"	2°39'32"	glacial	granite	790	96	2.5	34.6	13.7	5	0.031
Lac de la Cousteix	45°23'24"	2°39'52"	glacial	granite	857	27	0.9	41.4	45.3	5	0.052
Lac de la Crégut	45°24'28"	2°40'47"	glacial	granite	900	84	35.5	172.6	4.9	26	0.044
Lac de l'Esclauze	45°23'37"	2°46'37"	glacial	basalt	1033	37	28.3	132.3	4.7	4	0.008
Lac Ferrand	44°44'37"	4°09'53"	glacial	granite	1247	73	1.4	20.4	14.6	5	0.042
Lac de la Godivelle d'en Bas	45°23'06"	2°55'39"	glacial	basalt	1200	226	12.1	435.3	36.0	3	0.009
Lac de la Landie	45°25'24"	2°46'03"	glacial	basalt	1000	134	23.9	255.1	10.7	21	0.043
Lac de Laspialades	45°25'07"	2°41'47"	glacial	granite	950	25	2.4	34.7	14.5	5	0.032
Lac des Bordes	45°25'29"	2°58'28"	artificial ?	basalt	1186	87	12.1	33.9	2.8	1	0.003
Lac de Bourdouze	45°28'13"	2°55'40"	glacial or dam?	basalt	1168	86	22.9	209.9	9.2	4	0.008
Lac de Guéry	45°36'58"	2°49'24"	glacial and volcanic, dam	basalt	1246	279	26.8	652.2	24.3	20	0.039

Monts-Dores, Cézallier and Cantal (Lacassagne 1995). Many glacial lakes included in this training set were formed by ice erosion of the rock surface.

3. Methods

3.1. Sample collection and preservation

Water samples were collected on nine occasions, every three months between May 1996 and May 1998. For the purpose of building an extensive data set in a limited period of time (5 days in the field for each of the 9 campaigns) water samples were taken using a sampler of simple design at approximately 50 cm depth at a distance of 10 m from the shore. Sampling stations were the same on each visit and in very shallow water, care was taken not to contaminate the water sample with disturbed mud. Unfiltered water was poured into a 100 ml acid washed polyethylene bottle for total phosphorus analysis and Gran titration; no preservative was added. The bottle, which was rinsed beforehand thoroughly with lake-water, was completely filled to ensure that as little air as possible was left in the bottle before capping. Water for filtrable reactive phosphorus (FRP), anions, cations and colour analyses, was filtered under vacuum on a glass fibre filter paper using a simple filter apparatus and a hand pump. The type of filter used was in most cases Whatman® GF/F. GF/C filters were used only when dealing with water showing high concentration of suspended matter as in these instances GF/F filters clogged too rapidly. The filter was pre-washed by allowing 100 ml of lake-water to pass through before filtration of the sample itself. The glass fibre filter paper on which a known volume of water had been filtered (usually 500 ml) was kept cool and in the dark until acetone extraction for pigment analysis. The 100 ml sample of filtered water with no added preservative was used for filtrable reactive phosphorus (FRP) and colour analyses. Samples for anion and cation analyses were kept in two separate 20 ml containers (type Bibby Sterilin® tubes). The sample for cation analyses was acidified with approximately 1 % by volume of concentrated nitric acid (type AristarR) in order to retain the metal ions in solution. Both samples for ion analyses were frozen on return to the laboratory. For analysis of dissolved silica, 20 ml of water was filtered on a nitrate-cellulose-filter paper (0.5 µm pore size) and kept in a Sterilin tube. After sampling all bottles were kept in a cold box in the dark at around 4°C and analyses were carried out within a week.

3.2. Field measurements

Conductivity measurements were taken directly by placing a probe (Fox Instruments®) in the lake. Water pH was measured using a pH meter (Hanna Instruments®) that was calibrated using two standard solutions (pH = 4 and pH = 7) at the beginning of each day in the field. For the less buffered lakes a low ionic electrode was used instead of a general-purpose combination electrode. A likely source of error arises from high temperature and high photosynthesis rates resulting in carbon dioxide depletion causing brief periods of very high pH lake-water (usually in mid-afternoons). Because of this, measurements were carried out in the laboratory in addition to the field pH measurement. The two readings were averaged after calculating the concentrations of hydrogen ions [H⁺]. Surface water temperatures were also measured in the field.

3.3. Laboratory methods for water chemistry

Alkalinity was measured by Gran titration (Gran 1952), considered as the most accurate procedure (Marchetto et al. 1997). Filtrable reactive phosphorus (FRP) was measured following a standard method in which the absorbance of the water sample and the added reagent is measured by spectrophotometry (Hach® DR/4000U) at a wavelength of 885 nm (Murphy & Riley 1962 in Wetzel & Likens 1991). Ortho-phosphate concentration can then be determined from a regression equation of the absorbances of standard solutions against their known concentrations. Determinations of total phosphorus (TP) concentration were made using the method described by Johnes & Heathwaite (1992), originally developed to perform a simultaneous digestion of organic nitrogen and organic phosphorus. The principle of the method is to use the breakdown products of the alkaline nitrogen oxidation to form an acid environment for phosphorus oxidation. Both these reactions require heat and pressure and are thus performed in a microwave digester (model CEM® MDS-2000). This method did not produce reliable results for total nitrogen. However, the solution became acid enough for phosphorus oxidation. Following oxidation the ortho-phosphate concentrations can be determined as above against a calibration curve of digested standards. Dissolved silica concentration was measured using a spectrophotometer at 700 nm according to the standard method described in Wetzel & Likens (1991). Concentrations of ammonium ions (NH₄⁺) were determined using a membrane electrode (ABB Kent-Taylor®, model 8002) following the method developed by Beckett & Wilson (1974). The determination of chlorophyll *a* content of phytoplankton

was performed following the method developed by Talling & Driver (1961). The method described by Bennett & Drikas (1993) was used to objectively evaluate the colour in water samples, expressed in Hazen units. The turbidity of filtered water samples was first measured using a Hanna® turbidity meter (model HI93703). Then, absorbances at 456 nm of the filtered water samples were measured.

Anion analyses were performed using a Dionex® 2000I ion chromatograph. Measurements for nitrate, sulphate and chloride concentrations were produced. Some samples presenting high chloride concentrations had to be diluted. Samples from Lac d'Aydat, Lac de l'Esclauze and Gour de Tazenat were diluted two times, those from Ribains five times and those from Lac de la Cassière six times. Values obtained for nitrate concentrations were later converted to nitrate-nitrogen ($\text{NO}_3\text{-N}$). Cation concentrations of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Mn , Zn^{2+} , Al^{3+} , Fe^{3+} were measured using ICP-AES (inductively coupled plasma - atomic emission spectrometry) on a Perkin-Elmer Optima® 3300RL.

3.4. Cation/anion balance

Ionic balances were calculated for all samples following the procedure adopted for the AL:PE project (European Commission, 1995). The variables considered in the ionic balance are the cations Ca^{2+} , Mg^{2+} , Na^+ , K^+ and H^+ and the anions Cl^- , SO_4^{2-} , NO_3^- and total alkalinity. The following formula was used to calculate the imbalance between cations and anions : $100 \times (\Sigma^+ - \Sigma^-) / \Sigma^+$.

3.5. The data set

The data-set corresponds to 16 chemistry variables averaged for each of the 25 lakes investigated (6 to 9 samples per lake) and 8 catchment and lake morphometry variables. Variables for which values were often below the detection limits (such as NH_4^+ and FRP) were not included in the analyses. For TP, the median was taken instead of the mean value in order to alleviate the problem caused by a few extremely high measured values. The nature of the bedrock geology was included in the analyses as 3 qualitative classes (basalt, mixed basalt-granite, granite). A binary system was used for coding these dummy variables. Data transformations were performed to ensure that frequency distributions of these parameters were normal (which is required to obtain better fit of the values in the regression models of the statistical analyses) : square-root transformation for alkalinity (Alk), SO_4 , SiO_2 , Fe, Mn, altitude (Alt), lake area (Area), Zmax,

aspect ratio (Asp) ; $\log_{10}$ -transformation for conductivity (Cond), Cl, TP ; $\log_{10}(x+1)$ -transformation for K, Mg, Ca, Na, NO_3 , Colour, Ad/A0 ; and $\log_{10}(x+2)$ -transformation for Chlorophyll α (Chla). Variables such as pH, Al and Zn were left unchanged as no transformation significantly improved their distribution.

3.6. Data analyses

Following Zar (1996), analysis of variance (ANOVA) was used to test hypotheses regarding seasonal variations of the ionic balance and to compare the results presented here with those from previous studies.

Relationships among the variables of the data set were examined using Pearson productmoment correlations. The statistical significance of these correlation coefficients were assessed using Student's *t* test.

After standardizing the data by subtracting the mean and dividing by the standard deviation, hierarchical cluster analysis was performed from a set of dissimilarities calculated for the 25 objects (lakes). Each object is assigned to its own cluster and then the algorithm proceeds by iteration, at each stage joining the two most similar clusters, continuing until there is just a single cluster. At each stage distances between clusters are recomputed by the Lance-Williams dissimilarity update formula according to the Ward's minimum variance method which aims at finding compact, spherical clusters. Hierarchical cluster analysis was performed using R, a free software available on the World Wide Web (at <http://www.r-project.org>), which was initially written by Ihaka & Gentleman (1996).

PCA is a method of indirect gradient analysis, where the response variables are explored exclusively and any variation in the response data is based on its inherent structure (ter Braak 1988). PCA relates to a linear response model and is often used to summarise the major patterns of variation in chemistry data. In the PCA diagram, variables with high positive correlation have small angles between their biplot arrows. Variables with long arrows have high variance and their proximity to the axes summarises the relative weight of each variable in determining each axis (ter Braak, 1987). The direction of each arrow indicates ascending values for each environmental variable. PCA was implemented by means of the computer program CANOCO (version 4.0, ter Braak & Smilauer 1997). As environmental variables are expressed in different units the options for centring and standardisation by species were selected. The ordination diagram was plotted using the computer program CALIBRATE (version 0.81, Juggins & ter Braak 1997).

4. Results and discussion

4.1. Cation/anion balance

The ionic balance control is shown graphically in Figure 2 where the sum of anions and cations are plotted against each other. For a perfect balance all results should lie along the diagonal. Of the 206 balances determined for the whole training set, 133 exhibited a deviation $> 10\%$. Mean ionic balance was -20% (SD = 38.8). The majority (78 %) of these impaired balances had an excess of anions possibly indicating a systematic methodological interference. Similarly, an excess of anions was reported by Toetz (1995) in a study of alpine wetlands. This author attributed it to an overestimation of alkalinity. Examination of the total sums of anions and cations reveals a systematic overestimation of the sum of anions for the very poorly buffered lakes such as Lac Servire, Lac de la Godivelle-d'en-Haut and Lac Estivadoux. These lake-waters are very weakly mineralised (for example in Lac Estivadoux Σ^- ranges from 55 to 150 $\mu\text{eq/l}$) thus one is dealing with very low quantities and high relative errors of determination considering a constant absolute error in the method of analysis. The analysis of correlation between imbalance and the different chemical species however, shows that the situation is different for the more buffered lake-systems and varies from lake to lake. In many cases, ionic balances are more significantly related to variations in concentrations of cations, either Mg^{2+} , Ca^{2+} , Na^{2+} or K^{+} (*i.e.* Cassire, Chauvet, Esclauze, Godivelle-d'en-Haut, Gury, Issarls, Montcineyre, Tazenat). In some cases (Pavin, Bordes, Bouchet, Laspialades), the imbalances were more closely related to sulphate and chloride concentrations. In fact in only a

few cases was a strong correlation observed between alkalinity and ionic imbalances (Aydat, Bordes and Bourdouze). Concentrations in nitrates were significantly correlated with the imbalance in a few lakes (Chambon, Esclauze, Pavin). In other lakes, no relationships were observed linking the imbalances to a particular chemical species and it should be assumed that these are due to methodological variations. Seasonality appears also to affect the ionic balance. Average balances for the 4 different sampling months (May, August, November and February) were significantly different (see Table 2 with results of an ANOVA single factor). February and November show the largest excess in anions. One can suggest that this is due to the higher concentration of ammonia ions (NH_4^+) usually observed in lake-water during the winter period and not accounted for in the ionic balance formula. For example in eutrophic Lac d'Aydat up to 4 mg/l of $\text{NH}_4^+\text{-N}$ was measured by Lafforgue et al. (1995). This represents $\sim 220 \mu\text{eq/l}$ to be added to the sum of cations and could largely compensate for the excess in anions observed in the lake-water especially in May 1996, February 1997 and February 1998. More negative imbalances could be corrected by adding Al^{3+} , Fe^{2+} , Zn^{2+} and Mn^{2+} in the calculation of the ionic balances though the contributions of these elements to Σ^+ is quite small (on average 4 %). Anionic contribution of humic substances (*e.g.* fulvic acid) was not considered in the balance and that might partly explain the excess of cations observed in 14 % of the samples (De Haan & Voerman 1988).

4.2. Summary data

In Table 3 are summarised, in terms of mean and standard deviation values or in terms of median and

Fig. 2. Ionic balance control for the 206 water samples analysed.

Fig. 2. Contrle des quilibres ioniques pour les 206 chantillons analyss.

Table 2. Results of the analysis of variance (ANOVA single factor) on the mean ionic imbalances for the four periods of sampling (May, August, November and February).

Tableau 2. Résultats des analyses de variance (ANOVA, un seul facteur) sur les moyennes des déséquilibres ioniques pour les quatre périodes d'échantillonnage (mai, août, novembre et février).

a) Summary statistics

<i>Groups</i>	<i>n</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
May	66	-338.8	-5.1	416.3
August	46	-836.2	-18.2	2006.1
November	42	-958.2	-22.8	1411.0
February	50	-1988.8	-39.8	1940.5

b) Results of the ANOVA single-factor

<i>Source of Variation</i>	<i>Sum of Squares</i>	<i>Degree of freedom</i>	<i>Mean Squared deviation from the mean</i>	<i>F</i>	<i>P-value</i>	<i>F critical</i>
Between Groups	34618.9	3	11539.6	8.53	2.31E-05	2.65
Within Groups	270268.7	200	1351.3			
Total	304887.6	203				

$F > F$ critical, the null hypothesis «the mean ionic imbalances are the same for all months» is rejected.

range values, the chemical data for the 25 lakes investigated.

There is a very wide range for total alkalinity (Table 3). Among lakes presenting very weakly buffered waters ($< 100 \mu\text{eq/l}$) are crater lakes such as Lac de Servièrre, Lac de la Godivelle-d'en-Haut and Lac du Bouchet. Lakes characterised by a small catchment area and the absence of an inlet such as Lac Estivadoux, Lac de Laspialades and Lac Ferrand are also weakly buffered. The last two lakes also lie on a granite bedrock. At the opposite end of the gradient are lakes such as Cassière, Aydat, Ribains and Gour de Tazenat. Aydat and Ribains have very large catchments on basaltic substratum and Gour de Tazenat is a crater-lake with an inlet from a well buffered catchment.

For the major cations (K, Mg, Ca, Na), the standard deviations were generally low (Table 3). The majority of these water samples showed the following sequence of dominant cations: $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$. In some lakes (Bordes, Bouchet, Esclauze, Godivelle-d'en-Haut, Ribains) water samples were magnesium dominated and characterised by the following sequence: $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Na}^+ > \text{K}^+$. Lac Pavin showed a sequence dominated by sodium ($\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+}$

$> \text{K}^+$) and Lac Estivadoux was potassium dominated ($\text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+$). The distribution of the major cations, expressed as microequivalent proportion (%) of total cations, is illustrated in Fig. 3. Na^+ and K^+ were treated as a single variable. The ternary diagram for the major anions (Fig. 4) shows that the large majority of the water samples analysed are carbonate-dominated. The relative dominance sequence of anions for 20 of these lakes is Total alkalinity $> \text{Cl}^- > \text{SO}_4^{2-}$. In some oligotrophic lakes (Bouchet, Ferrand, Godivelle-d'en-Haut, Issarlès) the dominant anions are Total alkalinity $> \text{SO}_4^{2-} > \text{Cl}^-$. In Lac de Servièrre these series are $\text{SO}_4^{2-} > \text{Cl}^- \geq \text{Total alkalinity}$.

Chloride is a common ion that has little biological significance in fresh waters, but is of interest because it behaves conservatively in lakes, neither undergoing precipitation nor redox reactions. Artificial sources of chloride include sewage and road salt, used as a de-icing agent to improve winter driving conditions (Brock 1985). Chloride tends to accumulate as waste in lake-water (Úlehlová & Pribil 1978). This might be the case in Lac de la Cassière which has a particularly high concentration of chloride (Table 3). This lake, which is partly surrounded by housing and roads and

Table 3. Summary of chemical data for the 25 lakes investigated during the period 1996-98. $\bar{x}$ = mean, S = standard deviation.* The means for pH were calculated from the concentrations of hydrogen ions $[H^+]$.

** For total phosphorus (TP) and filtrable reactive phosphorus (FRP), the median and range are given instead of the mean and standard deviation (see text).

*** For each lake, only two samples (February and May 1998) were analysed for colour.

Tableau 3. Résumé des données chimiques pour les 25 lacs étudiés durant la période 1996-98. $\bar{x}$ = moyenne, S = écart type.* Les moyennes pour le pH ont été calculées à partir des concentrations en ions hydrogène $[H^+]$.

** Pour le phosphore total (TP) et le phosphore réactif filtrable (FRP), la médiane et les valeurs limites sont données au lieu des moyennes et écart-types (voir le texte).

*** Pour chaque lac, seulement deux échantillons (février et mai 1998) ont été analysés pour déterminer leur couleur.

Lake name	Alkalinity ($\mu\text{eq/l}$)	Conductivity ($\mu\text{S/cm}$)	pH *	K ⁺ (mg/l)	Mg ²⁺ (mg/l)	Ca ²⁺ (mg/l)	Na ⁺ (mg/l)	Cl ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)	Al (mg/l)	Fe (mg/l)	Mn (mg/l)	Zn (mg/l)	TP ($\mu\text{g/l}$) **	FRP ($\mu\text{g/l}$) **	NO ₃ -N ($\mu\text{g/l}$)	SiO ₂ (mg/l)	Chl <i>a</i> ($\mu\text{g/l}$)	Colour (HU) ***	<i>n</i>
1. Lac d'Aydat	$\bar{x}$ 1005 S 182	112 27	7.7	3.06 0.41	4.38 0.30	10.74 0.56	5.54 0.47	6.97 0.62	2.49 0.25	0.05 0.03	0.05 0.05	0.01 0.01	0.06 0.04	35 19-80	5 0-47	398 306	13.3 3.3	12 12	11.8	9
2. Lac des Bordes	$\bar{x}$ 225 S 65	34 8	6.2	1.27 0.28	1.40 0.20	1.94 0.33	1.26 0.22	3.32 0.27	0.60 0.20	0.06 0.04	0.23 0.22	0.01 0.00	0.09 0.03	51 44-128	2 0-11	43 67	1.4 0.9	18 11	17.1	7
3. Lac du Bouchet	$\bar{x}$ 166 S 29	27 7	6.1	0.19 0.15	1.51 0.02	2.13 0.12	0.26 0.15	1.44 0.27	3.45 0.44	0.03 0.02	0.00 0.00	0.00 0.01	0.08 0.03	11 1-177	0 0-6	24 18	0.3 0.4	1 1	2.1	9
4. Lac de Bourdouze	$\bar{x}$ 400 S 107	40 11	6.9	0.80 0.28	1.74 0.15	3.26 0.56	2.59 0.89	1.91 0.91	0.54 0.23	0.04 0.02	0.10 0.08	0.01 0.00	0.09 0.04	35 18-51	2 0-11	31 37	5.3 0.9	6 5	14.1	8
5. Lac de la Cassière	$\bar{x}$ 1123 S 121	194 32	7.3	2.30 0.41	6.40 0.97	14.73 2.33	14.74 2.14	27.62 2.73	7.76 0.77	0.05 0.04	0.04 0.04	0.00 0.01	0.06 0.04	48 23-100	2 0-13	50 45	3.7 2.4	25 15	7.2	9
6. Lac Chambon	$\bar{x}$ 577 S 118	67 15	6.6	1.44 0.27	2.04 0.28	5.33 0.69	3.36 0.49	2.61 0.62	2.23 0.34	0.06 0.03	0.20 0.15	0.04 0.03	0.07 0.04	41 9-70	5 0-17	111 129	21.6 2.4	6 3	9.4	9
7. Lac Chauvet	$\bar{x}$ 189 S 28	24 7	6.4	0.32 0.13	0.95 0.11	1.82 0.23	0.72 0.23	1.35 0.27	1.28 0.11	0.03 0.01	0.00 0.00	0.00 0.00	0.06 0.04	8 0-390	1 0-29	28 26	4.5 0.4	1 0	3.3	9
8. Lac de Coindé	$\bar{x}$ 303 S 77	41 13	6.9	0.21 0.15	0.93 0.09	5.31 0.37	1.26 0.23	2.46 0.68	2.59 1.52	0.04 0.01	0.01 0.02	0.00 0.00	0.06 0.04	10 0-41	0 0-6	80 114	6.1 0.9	1 0	15.6	7
9. Lac de la Cousteix	$\bar{x}$ 282 S 85	43 11	6.6	0.76 0.27	1.24 0.26	3.86 0.79	1.44 0.42	3.72 0.47	1.84 0.95	0.08 0.02	0.20 0.14	0.01 0.00	0.07 0.03	21.5 5-44	1 0-16	153 140	5.2 1.4	4 2	39.2	8
10. Lac de la Crégut	$\bar{x}$ 357 S 92	39 10	6.5	0.92 0.30	1.54 0.27	3.29 0.56	1.56 0.37	2.09 0.46	1.18 0.25	0.05 0.01	0.19 0.14	0.02 0.02	0.07 0.03	12 0-24	2 0-12	183 102	10.6 1.2	0 0	9.9	9
11. Lac de l'Esclauze	$\bar{x}$ 307 S 53	54 13	6.9	1.25 0.29	2.27 0.45	3.58 0.86	2.21 0.72	6.54 0.29	0.56 0.39	0.05 0.02	0.34 0.22	0.01 0.00	0.07 0.03	27 5-74	2 0-18	109 122	1.9 1.1	7 3	30.1	8
12. Lac Estivadou	$\bar{x}$ 53 S 25	18 8	4.7	1.17 0.50	0.25 0.11	0.48 0.25	0.37 0.49	1.32 0.54	0.26 0.27	0.06 0.02	0.06 0.07	0.03 0.02	0.12 0.02	61 39-369	2 0-18	15 29	0.8 0.5	7 4	38.6	6
13. Lac Ferrand	$\bar{x}$ 138 S 37	25 11	6.1	0.18 0.11	0.62 0.06	2.19 1.48	0.90 0.32	1.36 0.40	2.05 0.32	0.04 0.01	0.04 0.09	0.01 0.00	0.08 0.02	10 0-22	0 0-6	133 129	2.6 1.5	5 6	4.9	9
14. Lac de la Godivelle d'en Bas	$\bar{x}$ 579 S 144	56 19	6.6	1.20 0.43	2.10 0.64	4.94 1.57	2.36 0.81	1.81 0.53	0.73 0.54	0.05 0.01	0.34 0.38	0.01 0.00	0.07 0.02	29 1-50	4 0-20	69 79	11.3 2.2	5 3	24.4	8
15. Lac de la Godivelle d'en Haut	$\bar{x}$ 79 S 16	18 4	5.5	0.53 0.14	0.68 0.04	0.98 0.23	0.29 0.42	1.33 0.26	2.12 0.23	0.05 0.02	0.01 0.01	0.00 0.00	0.06 0.03	4 0-15	0 0-4	53 50	0.3 0.3	0 0	0.8	8
16. Lac de Guéry	$\bar{x}$ 242 S 75	33 8	6.9	0.50 0.15	0.87 0.16	2.97 0.49	1.52 0.42	1.76 0.30	0.79 0.52	0.05 0.03	0.15 0.26	0.01 0.01	0.09 0.10	12 10-32	1 0-12	196 402	8.6 1.7	2 1	9.8	9
17. Lac d'Issarlès	$\bar{x}$ 221 S 36	33 7	6.2	0.56 0.33	1.12 0.14	3.03 0.44	1.54 0.45	1.79 0.59	2.34 0.76	0.06 0.04	0.04 0.08	0.00 0.00	0.12 0.16	8 0-48	1 0-9	279 190	7.2 0.5	1 1	7.4	9
18. Lac de la Landie	$\bar{x}$ 354 S 65	52 12	6.5	1.43 0.25	2.08 0.26	3.91 0.67	1.97 0.37	3.58 1.12	1.61 0.52	0.04 0.03	0.11 0.13	0.01 0.02	0.07 0.06	10 0-26	1 0-14	229 169	5.6 0.8	1 0	20.1	9
19. Lac de Laspialades	$\bar{x}$ 106 S 26	24 8	6.2	0.10 0.11	0.84 0.10	1.58 0.20	0.75 0.16	1.76 0.28	1.22 0.61	0.07 0.02	0.20 0.14	0.02 0.02	0.09 0.04	11 0-16	1 0-12	67 76	3.7 0.7	3 3	36.5	8
20. Lac de Montcineyre	$\bar{x}$ 207 S 24	25 7	6.4	0.75 0.19	0.81 0.06	1.61 0.15	1.31 0.29	1.29 0.17	0.49 0.15	0.03 0.01	0.00 0.00	0.00 0.00	0.06 0.02	6 0-18	1 0-8	32 28	5.5 0.7	1 1	3.1	8
21. Lac Pavin	$\bar{x}$ 487 S 72	52 10	6.5	2.96 0.24	1.50 0.09	2.46 0.12	4.02 0.26	2.20 1.50	2.70 2.38	0.04 0.04	0.00 0.00	0.00 0.00	0.07 0.04	10 0-297	1 0-24	40 77	14.9 1.0	2 1	1.1	9
22. Ribains (Les Narces)	$\bar{x}$ 1323 S 427	127 47	6.9	1.30 0.90	8.31 2.16	9.01 2.78	5.03 1.69	5.21 3.69	2.40 1.52	0.08 0.03	3.34 2.10	0.09 0.04	0.09 0.02	155 48-312	21 16-116	334 632	13.4 5.2	34 28	152.5	7
23. Lac de Saint Front	$\bar{x}$ 617 S 138	61 11	7.0	0.50 0.21	2.69 0.28	6.01 0.66	2.28 0.40	1.55 0.30	1.46 0.44	0.03 0.02	0.17 0.49	0.01 0.01	0.11 0.14	62 31-74	1 0-3	20 34	3.6 2.9	26 12	4.9	8
24. Lac de Servièrre	$\bar{x}$ 35 S 14	21 13	5.7	0.36 0.19	0.32 0.07	0.66 0.11	0.17 0.29	1.36 0.47	2.12 0.40	0.03 0.01	0.01 0.03	0.00 0.00	0.06 0.04	8 0-25	0 0-7	65 37	0.3 0.3	1 1	2.7	9
25. Gour de Tazenat	$\bar{x}$ 1110 S 94	131 24	7.0	2.37 0.36	5.18 0.70	12.13 1.57	6.07 0.99	6.30 0.84	8.63 2.77	0.05 0.04	0.03 0.07	0.00 0.00	0.07 0.04	12 0-168	1 0-15	81 84	1.7 1.1	2 1	3.9	9

Fig. 3. Ternary diagram showing the distribution of the major cations in the 25 lakes of the data-set. The cations are expressed as microequivalent proportions (%) of total cations. See Table 3 for site numbers.

Fig. 3. Diagramme triangulaire montrant la répartition des cations majeurs dans les 25 lacs du jeu de données. Les cations sont exprimés en microéquivalents comme pourcentages des cations totaux. Voir Tableau 3 pour les numéros des lacs.

does not have an above ground outlet, may also be hydrologically closed to a much greater extent than any other sites of the training-set, leading to greater evapo-concentration of Cl^- .

Iron is most abundant in shallow lakes invaded by macrophytes such as Ribains, Godivelle-d'en-Bas, Escalauze, Bordes and by contrast in low quantities in deep crater lakes such as Chauvet, Pavin, Bouchet, Godivelle-d'en-Haut, Servièrès, Tazenat and Issarlès (Table 3). Manganese concentrations were below the detection limit in most samples and showed a fairly similar distribution across the range of lakes to the one observed for iron (Table 3). Mean concentrations of zinc varied little between lakes and between samples from the same lake. Of the lakes that show wider variations are Lac de Guéry and Lac d'Issarlès (Table 3) that are both subject to large level fluctuations, due to their use as reservoirs for the hydroelectricity industry, and therefore increased shore erosion. For aluminium, most of the samples recorded concentrations below the

detection limit. The lakes showing the highest concentrations of aluminium were Cousteix, Ribains, Laspialades, Bordes and Estivadoux, which are all characterised by brown-coloured water (Table 3). It has been shown that presence of dissolved humic matter can increase the availability of trace metals in the water (Stewart & Wetzel 1982).

In most lakes, very low levels of FRP were recorded throughout the sampling campaigns (Table 3). The TP records were characterised in several deep crater-lakes (e.g. Pavin, Tazenat, Chauvet, Issarlès) by high concentration episodes (as shown by the wide ranges but low median values in Table 3). These events, which all occurred in periods of overturn of the lake water column (November or February), are probably associated with mixing of phosphorus-rich water from the hypolimnion. Analytical errors were discounted as replicate measurements showed similar readings.

Concentrations of ammonium were measured on only one occasion in November 1996. Apart from Lac

Fig. 4. Ternary diagram showing the distribution of the major anions in the 25 lakes of the data-set. The anions are expressed as microequivalent proportions (%) of total anions. See Table 3 for site numbers.

Fig. 4. Diagramme triangulaire montrant la répartition des anions majeurs dans les 25 lacs du jeu de données. Les anions sont exprimés en microéquivalents comme pourcentages des anions totaux. Voir Tableau 3 pour les numéros des lacs.

d'Aydat (1130 $\mu\text{g/l}$ of NH_4^+), all lakes showed concentrations of ammonium below the detection limit.

Typically, standard deviations are high for chlorophyll *a* (Table 3). On average, the chlorophyll *a* concentration was found to be about 20 % of the total phosphorus. This relationship compares well with the OECD findings (Janus & Vollenweider 1981).

In most of the lakes studied, silica is not depleted (Table 3). However, in three crater lakes, Lac de la Godivelle-d'en-Haut, Lac du Bouchet and Lac de Servièrre, concentrations of dissolved silica were often below detection limits. In lakes characterised by large catchment and river inputs such as Chambon and Aydat, a high concentration of silica is maintained throughout the year. In Lac Pavin also, despite the small size of its catchment, high concentrations of silica remained constant throughout the sampling campaign (mean : 14.9, SD $\pm$ 1.0 mg/l). Sub-lacustrine springs rich in dissolved silica are thought to be partly res-

ponsible for this sustained high level (Michard et al. 1994).

Water colour was measured on two occasions only (February and May 1998). The limited data permit no detailed interpretation especially in terms of seasonal variations. However, this parameter clearly distinguishes brown-coloured lakes, which includes the shallow ponds such as Ribains, Estivadoux, L'Esclauze and the lakes where *Sphagnum* spp. are extensive such as Cousteix, Laspialades, Godivelle-d'En-Bas, from the deep crater-lakes with clear water (e.g. Godivelle-d'en-Haut, Pavin, Bouchet, Servièrre, Chauvet, Tazenat). These groups do not reflect the nutrient status of the lakes as eutrophic lakes such as Cassière and Saint-Front have little coloured water whereas Laspialades (average TP $\sim$ 10 $\mu\text{g/l}$) is highly coloured (Table 3).

Meybeck et al. (1975) analysed water samples, taken between April 1969 and February 1974, from 14 lakes out of the 25 studied here. The comparison between

the results from the present study with those from Meybeck et al. (1975) shows that little change has occurred in the water chemistry of these lakes. This is especially true for mean concentrations in $[\text{HCO}_3^-]$, $[\text{K}^+]$, $[\text{Mg}^{2+}]$, $[\text{Ca}^{2+}]$, $[\text{Na}^+]$ and $[\text{SiO}_2]$ which are very similar in both data-sets as indicated by an analysis of variance (results not shown). Concentrations of $[\text{Cl}^-]$ and, to a lesser extent, of $[\text{SO}_4^{2-}]$ have not remained as constant. In most lakes, $[\text{Cl}^-]$ has increased markedly since Meybeck et al. (1975), carried out their analyses while $[\text{SO}_4^{2-}]$ decreased.

4.3. Data analysis

— Correlation matrix

Geogenic variables (Mg, Ca, K, Na and alkalinity) were highly correlated to each other and with variables such as conductivity, pH, and chloride (Table 4). Correlations between geogenic variables and sulphate, TP, dissolved silica and chlorophyll *a* concentrations were also highly significant. The correlation between concentrations of iron [Fe] and Manganese [Mn] was high. Total phosphorus concentrations showed high correlation with Chlorophyll *a*. Alkalinity and inter-correlated variables expressing the ionic strength of the water were positively correlated with Ad/A0 and negatively with altitude. Similar relationships between chemistry and altitude were observed in Great Britain

(Kernan 1998) and in Switzerland (Müller et al. 1998). A likely explanation is that weathering rates and erosion increase at lower altitude.

— Lake classification using hierarchical cluster analysis

Three main groups of lakes were identified by hierarchical cluster analysis (Fig. 5). Group I consists of the sites with high conductivity, high alkalinity and pH and high concentrations of geogenic variables. Group I is further divided into two sub-groups. Group Ia consisting only of the site of Ribains, which cluster separately from the other high conductivity sites because of its high concentrations in TP and Chlorophyll *a*, highly coloured water and large Ad/A0. Group II contains deep lakes and can be divided into two sub-groups. Group IIa, includes low alkalinity deep sites, whilst Group IIb includes deep sites with higher alkalinity. Group III consists of shallow sites and is further divided into three sub-groups. Group IIIa contains the shallow sites with low trophic status whilst Group IIIc contains shallow sites of comparatively higher trophic status. Group IIIb consists only of the dystrophic site Estivadoux.

— Principal component analysis

The percentage of variance in the data explained by the first four axes was high (78 %). The first axis ($\lambda = 0.373$) (Fig. 6) contrasts lakes of group I with high

Table 4. Pearson product moment of correlation coefficient between environmental variables (following transformations) measured in the 25 lakes investigated. * and ** indicate significant correlations at $\alpha = 0.005$ and $\alpha = 0.001$ respectively, based on Student's *t* test.

Tableau 4. Coefficients de corrélation entre les variables environnementales (après transformations) mesurées dans les 25 lacs étudiés. * et ** indiquent respectivement les corrélations significatives aux seuils $\alpha = 0.005$ et $\alpha = 0.001$ d'un test de Student *t*.

	Alk	Cond	pH	K	Mg	Ca	Na	Cl	SO4	TP	NO3	SiO2	Chla	Al	Fe	Zn	Mn	Col	Alti.	Area	Ad/A0	Zmax	Asp.
Alk	1.00																						
Cond	0.97**	1.00																					
pH	0.79**	0.79**	1.00																				
K	0.69**	0.72**	0.41	1.00																			
Mg	0.96**	0.95**	0.73**	0.63**	1.00																		
Ca	0.94**	0.96**	0.86**	0.55*	0.90**	1.00																	
Na	0.92**	0.95**	0.75**	0.76**	0.86**	0.88**	1.00																
Cl	0.73**	0.85**	0.63**	0.67**	0.79**	0.78**	0.84**	1.00															
SO4	0.53*	0.60**	0.35	0.33	0.55*	0.61**	0.55*	0.56*	1.00														
TP	0.56*	0.55*	0.28	0.40	0.58*	0.46	0.49	0.45	-0.07	1.00													
NO3	0.34	0.37	0.41	0.21	0.33	0.42	0.28	0.35	0.16	0.01	1.00												
SiO2	0.54*	0.46	0.52*	0.41	0.36	0.47	0.50	0.17	-0.03	0.26	0.50	1.00											
Chla	0.56*	0.57*	0.37	0.36	0.61*	0.49	0.55*	0.53*	0.03	0.91**	0.02	0.16	1.00										
Al	0.19	0.21	-0.04	0.13	0.22	0.17	0.18	0.29	0.01	0.39	0.43	0.26	0.29	1.00									
Fe	0.43	0.38	0.19	0.15	0.50	0.31	0.27	0.30	-0.12	0.62**	0.48	0.36	0.52*	0.68**	1.00								
Zn	-0.11	-0.16	-0.27	-0.15	-0.09	-0.15	-0.15	-0.25	-0.31	0.40	-0.08	-0.06	0.33	0.29	0.18	1.00							
Mn	0.25	0.20	0.04	0.11	0.27	0.14	0.12	0.08	-0.36	0.70**	0.34	0.41	0.54*	0.61**	0.80**	0.38	1.00						
Col	0.24	0.25	0.13	0.08	0.28	0.23	0.16	0.30	-0.31	0.65**	0.37	0.26	0.50	0.70**	0.78**	0.32	0.77**	1.00					
Alti.	-0.52*	-0.60**	-0.51*	-0.37	-0.49	-0.66**	-0.52*	-0.63**	-0.60**	-0.04	-0.44	-0.26	-0.01	-0.32	-0.07	-0.29	-0.02	-0.20	-1.00				
Area	-0.12	-0.09	-0.24	-0.25	-0.09	-0.10	-0.14	-0.05	-0.10	-0.28	-0.05	-0.25	-0.29	-0.45	-0.42	-0.02	-0.39	-0.54*	-0.06	-1.00			
Ad/A0	0.57*	0.53*	0.35	0.23	0.54*	0.52*	0.42	0.38	0.09	0.64**	0.50	0.48	0.54*	0.61**	0.81**	0.06	0.76**	0.73**	-0.29	-0.45	-1.00		
Zmax	-0.09	-0.12	-0.07	0.07	-0.12	-0.11	-0.06	-0.18	0.36	-0.66**	0.05	-0.01	-0.62**	-0.29	-0.46	-0.12	-0.64**	-0.67**	-0.06	0.66**	-0.55*	-1.00	
Asp.	-0.19	-0.20	-0.18	-0.08	-0.21	-0.18	-0.16	-0.20	0.43	-0.75**	0.09	-0.14	-0.67**	-0.14	-0.40	-0.24	-0.62**	-0.60**	-0.09	0.30	-0.45	0.90**	-1.00

Fig. 5. Dendrogram showing the classification obtained by hierarchical cluster analysis of the 25 lakes in the data-set. Below the dendrogram, a table summarises for each group the average values of some key environmental variables (alkalinity in $\mu\text{eq/l}$, conductivity in $\mu\text{S/cm}$, Zmax in m, TP, Chla and $\text{NO}_3\text{-N}$ in $\mu\text{g/l}$, SiO_2 in mg/l).

Fig. 5. Dendrogramme montrant la classification obtenue par l'analyse hiérarchique des 25 lacs du jeu de données. En-dessous du dendrogramme un tableau résume pour chaque groupe les valeurs moyennes de quelques variables environnementales (alcalinité en $\mu\text{eq/l}$, conductivité en $\mu\text{S/cm}$, Zmax en m, TP, Chla et $\text{NO}_3\text{-N}$ en $\mu\text{g/l}$, SiO_2 en mg/l).

alkalinity on the right-hand side of the PCA biplot, with those of group II positioned on the left-hand side. The second axis ($\lambda = 0.209$) contrasts shallow lakes of Group III, with deep lakes from Group II and Group I (Gour de Tazenat). As with hierarchical cluster analysis, the sites of Ribains (#22), very shallow, highly coloured and alkaline, and Estivadoux (#12), shallow and very acid are clearly isolated.

4.4. Seasonal variations

Because a lake is a dynamic entity, it can never be said to have a fixed chemical composition. Some elements are relatively conservative and vary little, whereas others are strongly influenced by sediment-water interactions and by biological processes. In the present data-set, however, the mean values obtained from all

samples and the seasonal means (corresponding to the means for 2 or 3 samples taken in February, May, August and November respectively) were for many parameters not significantly different as indicated by an analysis of variance on the 25 lakes (results not shown). Concentrations in $\text{NO}_3\text{-N}$, was the exception, as seasonal means were significantly different from each others across the lakes of the data-set. This is illustrated in Fig. 7, which shows that in many lakes investigated a «typical» nitrate cycle depletion as described by Brock (1985), *i.e.* high winter declining through spring and summer, can be observed. In a few lakes seasonal patterns of variation were observed for chemical parameters such SO_4 , TP, SiO_2 and chlorophyll *a*, but these trends were absent in most lakes of the data-set.

Fig. 6. Principal components analysis (PCA) ordination diagram showing the relationship between the 25 lakes and 26 environmental variables in the data-set.

Fig. 6. Diagramme de l'analyse en composantes principales (ACP) montrant la relation entre les 25 lacs et les 26 variables environnementales du jeu de données.

Algal biomass, as represented by chlorophyll *a* concentration, appeared not to be linearly related to water temperature (Fig. 8). Two peaks, one occurring in winter (temperature $\sim 5^{\circ}\text{C}$) and the other occurring in summer ($\sim 25^{\circ}\text{C}$), can be distinguished. The winter peak could be related to diatom blooms while the summer peak could be related to blooms of green or blue-green algae. This hypothesis could only be verified however, by carrying out an analysis of the complete phytoplankton flora contained in the samples.

5. Conclusion

This study contributes valuable data to our knowledge of the regional limnology of the French Massif Central since many of the lakes included in this data-set are not well-known. For the lakes that are more routinely

studied, such as Lac Pavin and Lac d'Aydat, our results compared well with the literature available.

As shown by cluster analysis and PCA, at least three main groups of lakes could be identified. The main environmental gradients revealed by numerical analysis are on the one hand, the lake water alkalinity and its correlated variables, and on the other hand the lake morphology (water depth, area, aspect ratio) which is also negatively correlated with the nutrient status (TP, Chlorophyll *a*). These two gradients have a dominant role in explaining the distribution of diatom species in the lakes investigated (Rioual 2000) and this will be the subject of a following paper.

To be used in the calibration data set of a diatom-based transfer function the chemical data has to be summarised as a single estimate for each variable and for

Fig. 7. Stacked columns showing the seasonal variations in concentrations of nitrate-nitrogen ($\text{NO}_3\text{-N}$) in 14 lakes of the French Massif Central.
Fig. 7. Variations saisonnières des concentrations en azote du nitrate ($\text{NO}_3\text{-N}$) cumulées pour 14 lacs du Massif Central.

Fig. 8. Relationship between chlorophyll *a* concentration and surface water temperature (206 water samples).
Fig. 8. Relation entre la concentration en chlorophylle *a* et la température des eaux de surface (206 échantillons).

each lake. The frequency of sampling, thus, has to be appropriate to allow reliable estimate of the contemporary water chemistry to be made (Bennion & Smith 2000). From the present data it appears that the choice of this single estimate should be made according to the chemical parameters and the types of lakes considered.

For the chemical variables with low seasonal and inter-annual variability (*e.g.* alkalinity, geogenic variables) the annual mean calculated from four seasonal samples is adequate. For variables with a clear seasonal variations (*e.g.* $\text{NO}_3\text{-N}$ and in some lakes SiO_2), the seasonal mean corresponding to the period when diatom populations bloom is more appropriate than the

annual mean. Sampling could in this case be concentrated in a short period. The choice of the most representative season however is not straightforward and would vary according to the type of lake. While in most deep lakes the main bloom of planktonic diatoms occurs during spring overturn, some dimictic lakes show also a significant second bloom in autumn. In shallow lakes, dominated by benthic algae, summer is often the key period for diatom growth. For variables with high standard deviation (*e.g.* TP), the median values appear to be more representative than the annual mean. For many lakes investigated in this study, which are too shallow to stratify for long periods of time,

sampling the surface waters is perfectly appropriate. By contrast, it is worth considering sampling the hypolimnetic water in deep lakes.

In contrast with Nordic and arctic regions (Duff et al. 1999, Blom et al. 2000) or alpine regions (Müller et al. 1998) where deglaciation left behind very dense arrays of lakes, the Massif Central as most of France, is relatively poor regarding the number of lakes (Meybeck 1995). The 25 lakes investigated, which represents almost the entire number of lakes that can be sampled in the region, are moreover very variable in terms of origins, morphology and water chemistry. Alkalinity and water depth are the only environmental gradients well represented by this set of lakes. Designing a large training set of lakes across another limnological gradient of interest (e.g. TP) cannot therefore be envisaged in this region. To alleviate the problem of having too few and diverse lakes for the purpose of developing robust transfer functions for several limnological parameters, the data of this training set will have to be merged with other data from the European Diatom Database Initiative (EU project EDDI available on the World Wide Web at <http://craticula.ncl.ac.uk:8000/Eddi>).

If, however, this diversity represents a problem in designing transfer function, it has the advantage to offer potential modern analogues for the very different lake conditions which are recorded in the palaeolakes of the region during the last climatic cycles. This dataset can therefore be used as a source for analogue matching, a promising technique for palaeolimnological reconstructions (Flower et al. 1997).

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