A CHEMICAL SURVEY OF STANDING WATERS IN SOUTH-EAST ENGLAND, WITH REFERENCE TO ACIDIFICATION AND EUTROPHICATION

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Introduction

The worldwide occurrence of nutrient enrichment and surface water acidification and their consequences for aquatic systems have been well documented, including many examples from the UK (e.g. Battarbee et al. 1988; Tailing & Heaney 1988; Sutcliffe & Jones 1992; Carvalho & Moss 1995). However, most limnological and palaeolimnological studies have been undertaken on natural lakes in the UK. Very little is known about the distribution and magnitude of lake acidification and eutrophication in south-east England where there are no natural lakes but a large number (ca. 2000) of shallow, artificial ponds.

The potential for human influences on water quality is considerable in this region, as population densities are the highest in the UK (Department of Environment 1990), and acid deposition is also high. For example, mean deposition ranges calculated for the south-east over the period 1989 to 1992 (sum of wet+dry+cloud, corrected for altitude enhancement) were: non-marine sulphur 0.58 to 1.58, oxidised nitrogen 0.39 to 0.88, and reduced nitrogen 0.25 to 1.08 kiloequivalents H^+ per hectare per year (Critical Loads Advisory Group 1996). Hydrogen ion concentrations of precipitation are among the highest measured in the UK, with recorded depositions of 0.02 to 0.04 g H^+ per m^2 per year (Beebee et al. 1990).

The south-east region of England is a lowland area, less than 300 m above sea-level, and has gentle relief, developed wholly on sedimentary rocks. The region covers a range of geology, from the base-rich Eocene London Clay, Upper Jurassic Oxford Clay, and Upper Cretaceous Chalk, to the base-poor

Lower Cretaceous sandstones and clays of the Hastings Beds, the Upper and Lower Greensands, and the Eocene Barton, Bracklesham and Lower Bagshot Beds. Soils in the region are essentially loamy, clayey brown earths, brown calcareous earths, stagnogleys and rendzinas, which are fertile and thus support a range of agricultural land-uses, such as dairying, mixed farming, horticulture and arable. Most standing waters have a high percentage of urban and/or agricultural activity in their catchments, causing enrichment via agricultural runoff, domestic sewage effluent, industrial waste, road salting and construction runoff.

There is also the potential for acidified waters in this region, as the base-poor bedrocks have been classified as having medium susceptibility to acidification (Edmunds & Kinniburgh 1986). However, freshwater sensitivity maps (Hornung et al. 1990, 1995) that combine solid geology, soils and land-use data, indicate that agricultural practices and the presence of base-rich soils types may over-ride the influence of geology upon surface water chemistry in most of this region. Exceptions are the strongly acidified ponds, formerly supporting populations of the natterjack toad *Bufo calamita,* which are found in areas of Hampshire where base-poor sandy, podsolic soils occur (Beebee et al. 1990).

There are few water chemistry data on a regional scale for standing waters in south-east England, although site data do exist for reservoirs and a small number of ponds. These document the existence of highly nutrient-rich aquatic systems in the region, especially London drinking-water reservoirs (e.g. Flint 1949; Mackenzie 1956). In a survey of eutrophication in Britain, Collingwood (1977) reported concentrations of soluble reactive phosphorus (SRP) ranging from 45 to 700 µg per litre in the Thames Water Authority region, compared with values of less than $25\mu g$ SRP per litre for the English Lake District (Cumbria).

Most of the standing waters in south-east England are small (<30 ha), shallow (<10 m), isothermal, artificial waters, generally considered to be ponds rather than lakes (the large, deep, stratified waters) typical of upland Britain. The origins of the sites in this study include decoy ponds, ornamental ponds, boating lakes, reservoirs, mill ponds, disused gravel-pits and castle moats. Many of these are highly valued for their recreation, aesthetic and conservation roles (e.g. Sites of Special Scientific Interest and water-sports centres). However, county pond surveys report a decline in pond numbers over the last century; e.g. Hertfordshire has lost more than half its ponds in the last 10 years (Hertfordshire County Council 1987), and a survey conducted by Bedfordshire County Council Planning Department showed that 75 to 80% of the ponds marked on the Ordnance Survey maps of 1902 had disappeared by 1978 (Probert 1989). Many of those remaining are under threat of destruction and dereliction from pollution, dumping and infilling, drainage, development and inadequate land management.
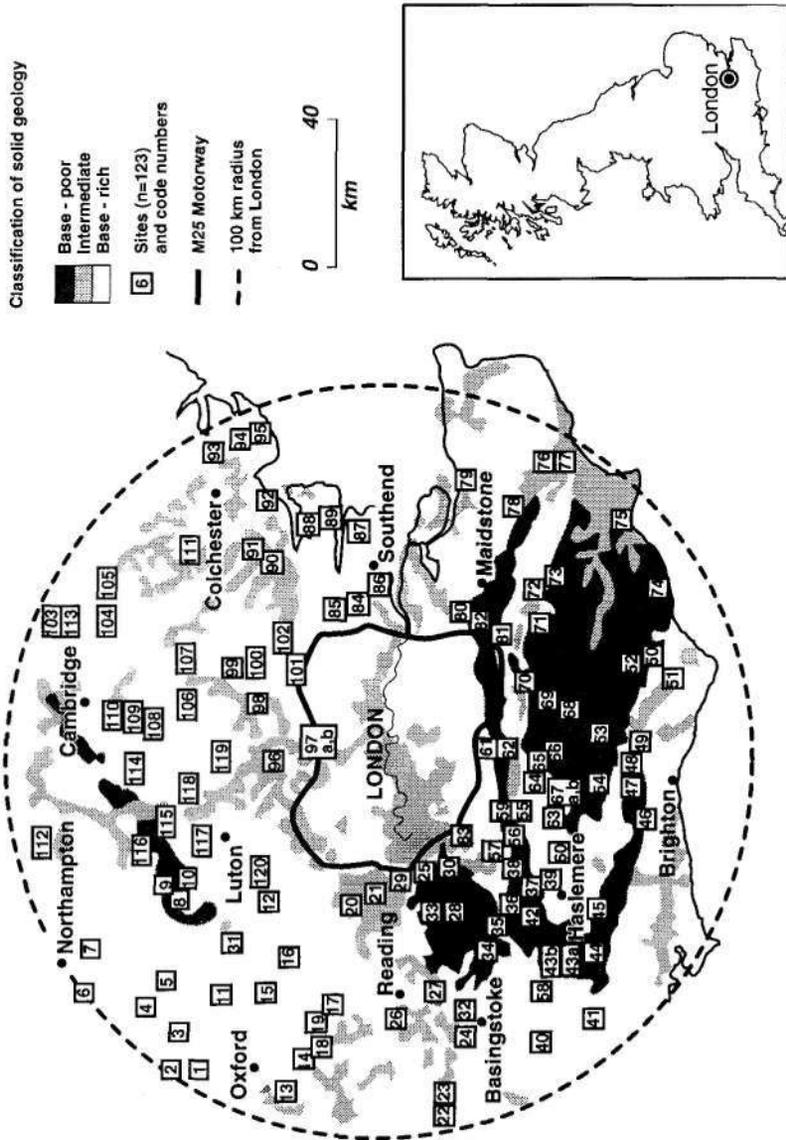
FIG. 1. Location map of the study region in south-east England and sampling sites, including major types of bedrock.
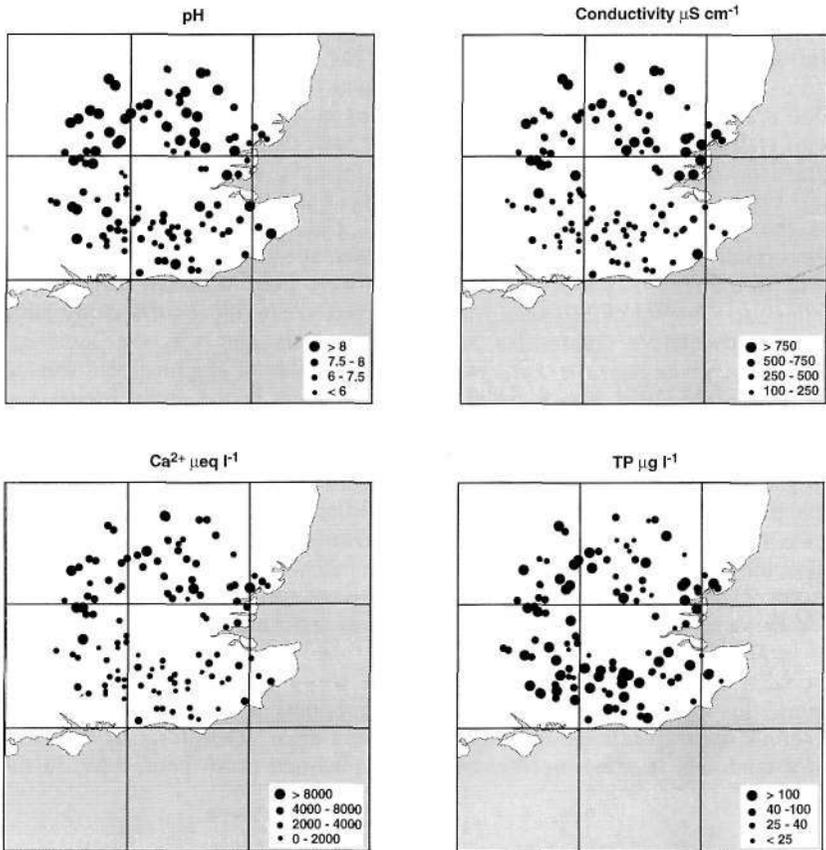
FIG. 2. Geographical distribution of four selected chemical variables: pH, conductivity, calcium and total phosphorus ($n = 123$).

It is important to establish the current water quality status of the ponds that remain, to assist with future management and conservation programmes. Consequently, a water chemistry survey was undertaken on 120 randomly-selected ponds, to develop a comprehensive, baseline dataset of the small, standing waters typical of this region. A more detailed further study of a subset of 31 sites describing seasonal patterns in chemistry is to be published elsewhere (Bennion & Smith 1997) and the diatom communities of these waterbodies are discussed by Bennion (1994, 1995).

Study area and site selection

The study area (Figs 1 and 2) is defined as the region lying within a 100 km radius of Central London. It excludes the area within the M25 motorway, as high urban densities cause potential problems in terms of finding waterbodies with well-defined catchments. Owing to the lack of published regional water chemistry data, the water quality status of artificial surface waters in south-east England is largely unknown. As both acid and nutrient-rich waters exist in the study area, a random-sampling strategy was considered most appropriate in order to maximise the representation of both types of water-body in the survey. Random-number tables were used to obtain random grid references. A total of 120 sites was considered to provide a sufficiently large and representative dataset for statistical analysis and was the logistical maximum, given the time constraints and the number of chemical variables to be measured. There are ca. 1500 ponds and pools in the study region and therefore the dataset represents ca. 8% of the total.

The sites are widely and evenly distributed throughout the study region and all geological types are represented (Figs 1 and 2). All sites are at altitudes of less than 200 m (above sea-level), and most are below 100 m; lake surface areas range from 0.1 to 30 ha. Little is known about the hydrology of these sites, although most are fed by small surface inflows and have outflows, which in many cases are dammed. A number of sites are spring-fed, and some water-bodies receive water from direct precipitation and runoff only. The influence of groundwater is likely to be minor. The land-use in the site catchments includes arable farming, dairy farming, sheep grazing, deciduous and coniferous woodland, lowland heath and scrub, parkland and orchards, nature reserves, rural dwellings and urban residential areas. Therefore, by selecting sites randomly, a good representation was obtained of all pond types in the region.

Analysis of chemical variables

All water samples were collected in acid-washed polyethylene bottles and, where possible, were taken from the area adjacent to the outflow. For reasons of time and distance, the 120 sites were visited on one occasion between mid-January and the end of February 1990. However, a subsequent monthly survey of a subset of 31 of these waters indicated that the spot-samples provided representative data (Bennion 1993). In practice, a total of 123 samples were collected (because three land-owners requested analysis of a second pond on their property).

Twelve chemical variables (see Table 1) were measured in the laboratory using standard techniques (Harriman et al. 1990); total phosphorus was analysed on unfiltered samples following the method of Murphy & Riley (1962).

Table 1. Summary statistics of the water chemistry dataset of 123 surveyed surface waters.
Mean = arithmetic mean; SD = standard division; Abs 250 nm = absorbance at 250 nm;
TP = total phosphorus.

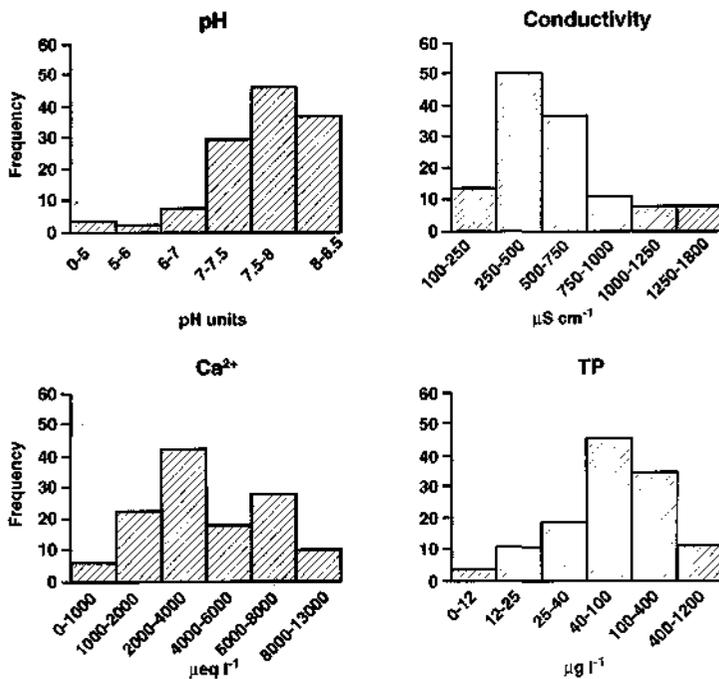| Determinand	Units	Min	Max	Mean	SD
pH		3.2	8.4	7.6	0.74
Alkalinity	(meq/l)	0.01	9.84	3.30	2.09
Conductivity	(µS/cm)	109	1696	563	317
Na^+	(µeq/l)	298	88950	1798	7987
K^+	(µeq/l)	20	3310	223	413
Ca^{2+}	(µeq/l)	100	12525	4138	2518
Mg^{2+}	(µeq/l)	91	20710	767	1918
Cl^-	(µeq/l)	278	114236	2116	10241
SO_4^{2-}	(µeq/l)	158	11055	1795	1871
NO_3^-	(µeq/l)	0	4763	392	· 570
Abs 250nm	(abs units)	0.02	0.73	0.18	0.11
TP	(µg/l)	6.8	1123	135	199

FIG. 3. Frequency histograms with six class boundaries for four selected chemical variables: pH,
conductivity, calcium and total phosphorus ($n = 122$; Site 92 omitted).

Ranges and statistical distribution of chemical variables

The summary statistics for twelve chemical variables are shown in Table 1, illustrating the broad ranges of values found for each variable and reflecting the variation in water quality within the dataset. The ranges of values and frequency distributions, divided into six classes, for four selected chemical variables (excluding Site 92, which had extremely high ionic concentrations) are illustrated by histograms in Fig. 3. The pH values have a skewed distribution, with a high negative momental skewness of -3.0, indicating that most of the values are greater than the mean of 7.6. pH values for the full dataset range from 3.2 to 8.4, although the majority of sites have pH values in the range 7.0 to 8.5; only five sites have a pH of less than 6.0. Conductivity values range from 109 to 1696 with a mean of 563 microsiemens per cm (at 25˚C); only 14 sites have values greater than $1000\mu S$ per cm. Alkalinity concentrations are likewise generally high, with a mean of 3.30 milliequivalents per litre. The five low pH sites expectedly have low alkalinities and are the only sites with values below 0.1 meq per litre. Five sites have high alkalinities, greater than 7 meq per litre.

There is great variation in the concentrations of all ions. Calcium values display a normal distribution, with most values in the range 2000 to 6000 microequivalents per litre. Similarly, concentrations of sodium, potassium, magnesium, chloride, sulphate and nitrate have normal distributions. The order of abundance of major cations in this dataset (in µeq/1) is: $Ca^{2+} > Na+ > Mg^{2+} > K^+$. The order of abundance of major anions (in ueq/1), assuming that alkalinity is principally bicarbonate, is: $HCO_3- > Cl- > SO_4^{2-} > NO_3-$ Total phosphorus (TP) concentrations range widely from 7 to 1123 micrograms per litre, with a mean of 135 µg per litre. Only one site has TP below 8.0 µg per litre and three sites lie in the range 8 to 12 µg per litre. The majority of sites have TP concentrations in the range 25 to 200 µg per litre, although ten sites have concentrations above 400 µug per litre.

Principal components analysis

A standard Principal Components Analysis (CA) was performed to detect the major gradients in the dataset and identify outliers with extreme or unusual chemistry, using CANOCO (ter Braak 1987) version 3.10 (ter Braak 1990) and data standardised (Jongman et al. 1987) and log_{10}- transformed as indicated in Table 2. PCA is a form of indirect gradient analysis which assumes a linear relationship between variables and is thus suited to chemistry datasets. It is an extension of fitting straight lines and planes by least-squares regression in order to best explain the data. This is done by choosing the best values for the sites, known as site or sample scores (Jongman et al. 1987). The slope of the line fitted for the chemical data against the PCA axis is the

Table 2. Product-moment correlation coefficients for twelve chemical variables at 122 sites (excluding Site 92). Alk = alkalinity; Cond = conductivity; Abs = absorbance at 250 nm; TP = total phosphorus. All data are $\log_{10}$– transformed (except pH and Abs). Only significant ($P \leq 0.005$) correlations are shown.

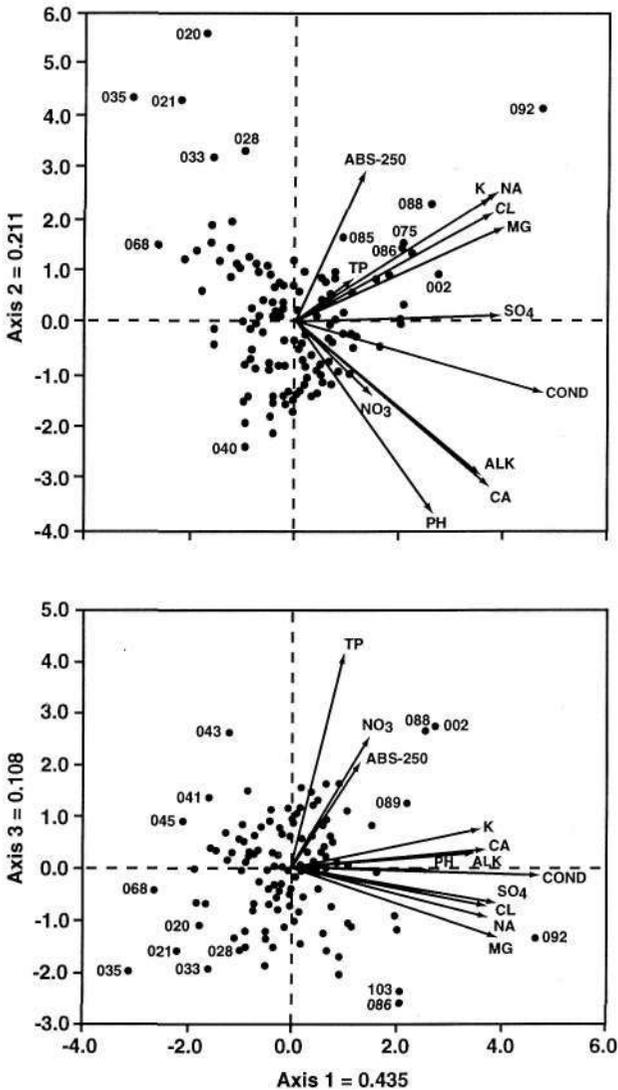|	pH	Alk	Cond	Na+	K+	Ca²⁺	Mg²⁺	Cl-	SO₄²⁻	NO₃-	Abs	TP
pH	–											
Alk	0.93	–										
Cond	0.35	0.46	–									
Na+	–	–	–	–								
K+	–	–	0.56	0.70	–							
Ca²⁺	0.57	0.56	0.57	–	–	–						
Mg²⁺	–	–	0.79	0.77	0.68	0.29	–					
Cl-	–	0.29	0.67	0.80	0.59	–	0.61	–				
SO₄²⁻	–	–	0.51	0.46	0.48	0.45	0.67	0.51	–			
NO₃-	0.43	0.43	0.67	–	–	0.37	–	–	–	–		
Abs	–	–	0.30	0.29	0.51	–	0.29	0.33	–	–	–	
TP	–	–	–	–	0.37	–	–	–	–	–	0.29	–

FIG. 4. PCA biplot of axes 1 and 2 (above), and axes 1 and 3 (below), for 117 sites and 12 chemical variables (six outliers, Sites 20, 21, 28, 33, 35 and 92, were made passive). Sites are represented by rilled circles and those mentioned in the text are labelled; chemical variables are shown as solid arrows.

environmental loading. Thus, a positive loading means that the value of the variable increases along the axis, and a negative loading means that the value decreases along the axis. The site scores and environmental loadings obtained from a PCA can be used to prepare a biplot, in which the variables are represented by arrows, the direction indicating the direction in which the value of the environmental variable increases most, and the length of the arrow equalling the rate of change in that direction. Variables that are highly correlated have small angles between their arrows (ter Braak 1990).

PCA, with all 123 sites and twelve chemical variables treated as active samples, identified six significant outliers (more than 5 standard deviations from the mean). Coastal Site 92 has extremely high ion concentrations, particularly sodium and chloride (e.g. $Na+ = 88,950$; $Ca^{2+} = 10,150$; $Mg^{2+} = 20,710$; $Cl- = 114,236$; $SO_4^{2-} = 11,055$; all in µeq/l). Sites 20, 21, 28, 33 and 35 are outliers as they are the only acid sites (pH <6.0) in the dataset. PCA was then repeated with the outliers treated passively (given negligible weightings). The percentage of the variance explained by the first four axes is high (83.2%), indicating that the twelve measured chemical variables account for most of the variance in the data. A biplot of axis 1 against axis 2 (upper Fig. 4) shows that axis 1, the most important axis accounting for 44% of the variance, is correlated with the major cations sodium, potassium and magnesium, the anions chloride and sulphate, and conductivity. The small angles between the biplot arrows for these variables indicate that they are highly positively correlated, and the length of the arrows indicates that they have a high variance. Axis 2, accounting for 21% of the variance, is correlated with pH, alkalinity, calcium and nitrate, and these variables also have a high variance. A biplot of axis 1 against axis 3 (lower Fig. 4) shows that axis 3, accounting for 11% of the variance, is correlated with total phosphorus, absorbance at 250 nm and nitrate. Total phosphorus has a high axis 3 loading; the uppermost sites on the biplot are characterised by very high concentrations (e.g. Sites 2, 43, 88).

Geographical distribution of pH

There is a clear geographical pattern in the distribution of pH values, related to bedrock geology (Figs 1 and 2). The five low pH sites lie on base-poor rocks in the west of the study region, with predominantly heathland catchments. Of these, two sites (20 and 21) are on the Reading Beds near Beaconsfield, one site (35) is on the Lower Greensands near Guildford, and two sites (28 and 33) are on the Bagshot Beds near Woking. There is a tendency for the highest pH sites (pH >8.0) to occur on the chalks and clays in the north and north-west of the study region, and sites with pHs in the range 6.0 to 8.0 tend to occur in the south and south-west of the region, which is

largely comprised of base-poor bedrocks. This is particularly true of the Hastings Beds and the Greensands, where pH values are generally lower than in the remainder of the study region.

On the basis of the Edmunds & Kinniburgh (1986) classification system of surface waters and their susceptibility to acid deposition, one would expect to find a greater number of acid surface waters in the dataset. Approximately 25% of the sampled sites lie on rock types classed as having medium acid susceptibility (Fig. 1), but only five sites (4%) have pH values below 6.0. These are on base-poor bedrocks but all five sites have high conductivities and ionic concentrations, suggesting that external sources of acid anions in addition to geology and/or atmospheric loading are responsible for the low pH values. The chemical composition of the five sites seems to be atypical for the study region and they are clear outliers in the principal components analysis. All other sites in the dataset which lie on medium acid susceptibility bedrock have high pH values, high alkalinities and high conductivities, and display no signs of acidification at present. The effect of acid deposition therefore may be to increase base cation leaching and not to lower pH. These observations are supported by the maps of sensitivity to acidification that include soils and land-use data as well as geology (Hornung et al. 1990, 1995). Land-use, in particular, strongly influences water quality. Consequently, further research into the impact of acid deposition on standing waters in south-east England needs to focus on the most susceptible areas, especially the heathlands where land-use, particularly the influence of agriculture and urbanisation, is less intense.

Geographical distribution and sources of conductivity

The distribution of conductivity values largely follows the pattern of pH, with lower conductivity sites occurring in the south and south-west of the study region (Fig. 2). Conductivity values range from 109 to 1696 uS per cm, compared with values generally below 500 μS per cm in lowland areas of Northern Ireland (Gibson 1986). High values in the study area might be explained by base-rich bedrocks and soils, and land-use. Proximity to the coast also influences these variables, as sites with very high values are found in coastal locations.

Geographical distribution and sources of calcium, sodium, magnesium, potassium and chloride

Calcium concentrations have a marked geographical distribution (Fig. 2). Sites with relatively high concentrations (>4000 μeq/l) are located in the north and north-west of the region on the chalks and clays, whereas sites with low concentrations (<4000 μeq/l) are generally located in the southern part of the

region, dominated by base-poor rocks. Sodium, magnesium, potassium and chloride followed similar though less marked geographical patterns.

Most of the waterbodies have relatively high calcium concentrations as expected, given the large proportion of sites lying on base-rich clays and chalks. For example the dataset mean is 4138 µeq per litre, compared with values of less than 100 µeq per litre for some upland lakes on base-poor geology (Battarbee et al. 1988). The marked north/south distribution in the study region suggests that calcium concentrations are largely controlled by local geology, although liming and agricultural practices are probably also influential. This pattern is generally true for all the major ions, although proximity to the coast is also important, particularly for sodium and chloride concentrations. Significant correlations between sodium, chloride, magnesium and potassium (Table 2) suggest that these ions originate largely from the same source or sources. However, calcium is not significantly correlated with sodium, nor is it strongly correlated with the other ions, implying that it is largely derived from a different source. In addition, calcium has the strongest correlation with conductivity, alkalinity and pH, suggesting that the calcium content of the bedrock has a major influence on water chemistry, as expected. A similar pattern was observed in a limnological survey of lakes on Rathlin Island, County Antrim (Flower 1982), where sodium was significantly, positively correlated with magnesium and potassium, and calcium was not significantly correlated with the other ions.

Some inland sites have relatively high concentrations of sodium and chloride (e.g. concentrations of Na^+ and Cl^- respectively, in µeq/l are: Site 1, 4390 and 3623; Site 28, 2332 and 2263; Site 103, 6695 and 1233), which might be explained by road salting (Sutcliffe & Carrick 1983a,b; Beebee 1987; Gibson 1989) or the inflow of sewage effluent (Sutcliffe & Carrick 1983b; Harper & Stewart 1987).

Geographical distribution and sources of sulphate and nitrate

High concentrations of sulphate were found at many sites. The usual range in global surface waters is 100 to 625 µeq per litre (Wetzel 1983) but many sites in our dataset exceed 1000 µeq per litre. Possible sources are: bedrock geology, as drainage from calcareous areas tends to contain higher than average sulphate concentrations (Nriagu & Hem 1978); sulphate derived from sea-spray, as values are usually high at coastal sites; fertilisers containing sulphate, given the extent of arable farming in the region; atmospheric sources, given the proximity of sites to industrial activity and the high regional sulphur deposition, which would result in high concentrations even in alkaline waters with high buffering capacity. Very high concentrations of sulphate have also been observed in borehole water from southern England (Sutcliffe & Carrick 1983a).

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Nitrate concentrations are generally high. In unpolluted fresh waters, average concentrations range from undetectable levels to ca. 160 μeq per litre (Wetzel 1983), whereas in our dataset a number of sites exceed values of 500 μeq per litre. The lack of a clear geographical distribution, and the relatively low correlation between nitrate and the other ions (Table 2), suggest that nitrate concentrations may be largely influenced by land-use (e.g. inputs from household sewage, industrial waste, agricultural runoff and nitrogen-based fertilisers) rather than by geological or atmospheric sources. In some areas of the UK, a significant amount of nitrate is derived from atmospheric sources, for example in upland areas where surface water concentrations exceeding 200 μeq nitrate per litre have been recorded, related to industrial activity in the Pennines region (Battarbee et al. 1992). However, in south-east England, where agriculture is intensive, atmospheric sources are probably minor in comparison with terrestrial inputs.

Geographical distribution and sources of total phosphorus

Total phosphorus (TP) was measured to provide an indication of the potential productivity of the waterbodies (Fig. 2). Phosphorus concentrations fluctuate markedly and are subject to greater seasonal variation than the major ions (e.g. Bennion & Smith 1997). However, our samples were taken in winter, which is generally the period of lowest phytoplankton activity and maximum epilimnetic phosphorus content, and therefore the concentrations should provide representative estimates of overall TP levels in various waterbodies. Of these, only Site 108 with TP below 8.0 μg per litre, may be classed as oligotrophic, following the modified OECD lake trophic classification system (OECD 1982). Three sites (103, 110 and 114) in the range 8 to 12 μg TP per litre may be classed as oligotrophic-mesotrophic. Ten sites (21, 28, 74, 76, 79, 85, 86, 102, 105 and 111) are in the mesotrophic category (12 to 25 μg TP per litre), and nineteen sites (1, 4, 5, 25, 30, 33, 38, 49, 56, 63, 71, 73, 82, 83, 93, 100, 101, 110 and 119) may be classed as mesotrophic-eutrophic (25 to 40 μg TP per litre). All other sites have very high TP concentrations and may be classed as eutrophic (40 to 100 μg TP per litre) through to hypertrophic (>100 μg TP per litre).

The major sources of phosphorus in south-east England are agricultural (including effluent, phosphate-based fertilisers and animal waste), domestic (e.g. effluent from local sewage works, and septic tanks associated with rural houses), and to a lesser extent industrial waste. Therefore both point and diffuse sources are important in this region. Regional densities of population and agricultural activity are high, and so the relatively high concentrations of TP in our dataset are not unexpected. Collingwood's (1977) survey of eutrophication in Britain found that the most affected areas were the most heavily populated, including the south, south-east and midlands. Similar TP ranges and high concentrations have been observed in lakes in the agricultural

lowland areas of Northern Ireland (Gibson 1986, 1989). TP concentrations as high as 1000 µg per litre have also been noted in the shallow, productive Norfolk Broads affected both by agricultural drainage and sewage effluent (Osborne & Phillips, 1978), and in a recent survey of the Cheshire and Shropshire meres in lowland north-west England, annual mean TP values ranged from 73 to 1170 µg per litre (Bennion et al. 1996).

The absence of a relationship between TP concentrations and bedrock geology suggests that land-use in the individual site catchments largely controls surface water phosphorus concentrations. TP is only significantly correlated with potassium (Table 2), indicating that fertilisers may be the major source of nutrients to some sites. TP and nitrate are not significantly correlated. A number of studies have shown that this often occurs because as one plant nutrient increases another becomes limiting (e.g. Gibson 1986, 1989). Individual investigations would be required to identify the particular nutrient sources at each site. A palaeolimnological investigation, including the application of a diatom-TP transfer function to a sediment core from Marsworfh Reservoir in Hertfordshire, indicates that TP concentrations in this lake have increased over the last century, with more marked increases over the last few decades due largely to sewage effluent and agricultural runoff (Bennion 1994). Current TP concentrations in many standing waters in south-east England may be considerably higher than those present at the turn of the 19th and 20th centuries, although palaeolimnological studies would be required on a range of lakes to determine whether nutrient enrichment is a regional phenomenon. Lake trophic status, here represented by the nutrients TP and-nitrate, is important in explaining the overall variance in the water chemistry data, as indicated by the results of the PCA. Thus the "long" nutrient gradients (see PCA, pp. 36-37) and even distribution of sites over a large range of values, suggest that the random survey provides a good representation of the range of concentrations found in standing waters in the study region.

Conclusions

The majority of the sampled waters have high pH values, are rich in base cations with consequently high alkalinities and conductivities, and have high concentrations of plant nutrients. The low number of acid sites suggests that surface water acidity is not a widespread regional problem in south-east England. However, the survey shows that a large number of standing waters in the region have high total phosphorus and nitrate concentrations, and 89% may be considered moderately to strongly eutrophic (>25 µg TP per litre). The data indicate that a large number of surface waters in this lowland region are likely to experience problems associated with eutrophication, such as algal blooms, low oxygen content and low light transparency, and there is clearly a need for investigations into the ecological impacts of such phenomena. The

implementation of eutrophication management schemes is desirable at many sites in south-east England.

Acknowledgements

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