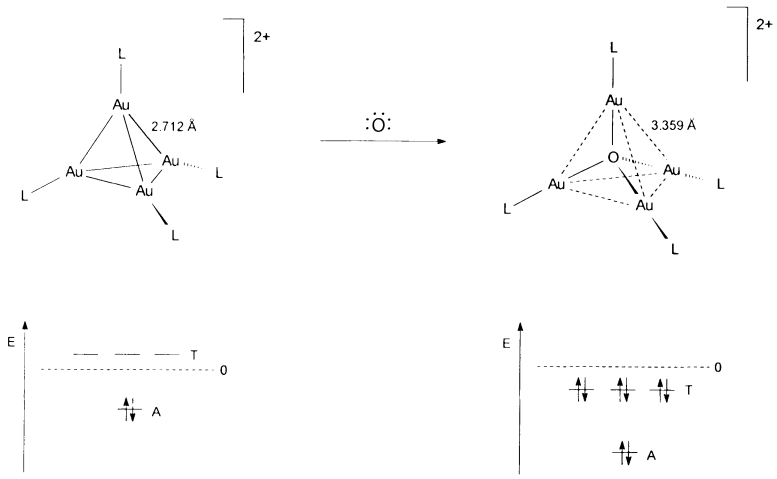


FIG. 2 Top, the gold cluster dication $[(LAu)_4]^{2+}$ (L is PAr_3, Ar is aryl) with and without an interstitial oxygen atom. Bottom, schematic drawing of the bonding molecular orbitals of the $[Au_4]^{2+}$ and $[Au_4O]^{2+}$ cores, respectively. (A and T represent fully symmetrical singly and triply degenerate orbitals.)

$\{^1H\}^{31}P$-NMR spectrum, and one set of *o*-tolyl or phenyl resonances in the ^1H- and ^{13}C-NMR spectra, respectively. This indicates the full equivalence of all four ligands and of their aryl groups. Any starting material $[(L)Au]_3O^+ BF_4^-$ remaining in solution is detected by separate resonances with distinctly different sets of NMR data[5]. These data are also clearly distinguished from the lines of the isoelectronic tetra(gold)ammonium salts $\{[(o\text{-tol})_3P]Au\}_4N^+ BF_4^-$ (**3a**) and $[(Ph_3P)Au]_4N^+ BF_4^-$ (**3b**) (ref. 4).

At very low temperature (−90 °C) the ^{31}P-NMR singlet lines of **2a** and **3a**, but not of **2b** and **3b**, are split reversibly into a closely spread set of signals. This splitting arises from the different relative orientation of the four individual tri(*o*-tolyl)phosphine propellers in each dication, which are not able to change rapidly their sign or rotation by concerted *o*-tolyl rotation (left- to right-handed) on the NMR timescale. Note that there is a set of isomers for **2a** and **3a**, which differ only in their individual combination of propeller directionality, but have non-equivalent phosphorus atoms. This is also the origin of the disorder in the cubic crystal (as discussed above). The hindrance of phenyl rotation in the Ph_3P groups of **2b**, **3b** is much less, and therefore no splitting is observed even at −90 °C.

Tetrahedral metallo-complexes of the oxide ion O^{2-} in an environment other than an oxide lattice are extremely rare, and the few examples reported in the literature are molecular (not dicationic) species stabilized by anionic ligand clamps or metal–metal bonds[13]. In the title compound the Au–Au distances (the edges of the Au_4O tetrahedron) are 3.3590 (4) Å long, which is still much shorter than the sum of the van der Waals radii of Au(I). It is therefore justified to ascribe the unprecedented stability of the $(LAu)_4O^{2+}$ unit to significant bonding between the closed-shell centres Au^+ ($[Xe]5d^{10}$, 'auriophilicity')[14].

Note that the 'empty' tetrahedral dicationic $[(LAu)_4]^{2+}$ cluster has recently also been described[15], and that it has much shorter Au–Au edges of only 2.712 Å (average), even though L represents the bulky *t*-Bu_3P ligand in this case. On insertion of an oxygen atom into this tetrahedron (Fig. 2), the six valence electrons of oxygen fill the three degenerate bonding orbitals obtained in point group T_d (or T) symmetry,[16] which are vacant in the metal cluster Au_4^{2+}.

This model system is clearly important as gold metal does not form any stable binary oxide phase, but 'sub-surface oxides' are assumed to play an important role in heterogeneous catalysis at coinage-metal surfaces[17]. Silver metal in particular is widely used in the catalysis of oxidation processes, and convincing evidence has been accumulated that oxygen atoms thereby are not just absorbed at the metal surface, but are actually entering lattice interstices between the first and second layers of silver atoms. These interstitial oxygen atoms are activating the surface silver atoms, the oxidation state of which is changed from zero in bulk metal to +1 at the surface. The bonding situation of an oxygen atom in the new $[Au_4O]^{2+}$ units resembles that of a sub-surface oxygen atom in a tetrahedral void of a cubic close-packed lattice (typical of coinage metals). Attempts to isolate the silver analogue have not yet been successful. □

Received 6 June; accepted 1 September 1995.

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ACKNOWLEDGEMENTS. We thank J. Riede for establishing the X-ray data set. This work was supported by Deutsche Forschungsgemeinschaft and by Fonds der Chemischen Industrie.

Controlled reversal of lake acidification by treatment with phosphate fertilizer

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LAKES that have become acidified by airborne pollutants typically have low biological productivity and support an impoverished flora and fauna[1]. In their natural state, these lakes were poorly buffered, and had a pre-industrial pH on the acid side of neutral[2]. Although they can be neutralized by adding base, the resulting calcium-rich water supports plant and animal communities that are unlike those found in natural softwater lakes[1]. It is known, however, that the long-term buffering of soft waters can be appreciably influenced by their biological productivity[3–5]. Here we report field-study results that show that by adding phosphate fertilizer to stimulate primary productivity, it is possible to generate sufficient base by

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TABLE 1 Measured characteristics of Seathwaite tarn

Variable	Units	Minimum	Mean	Maximum	Method
Max. depth	m	22.5	24.6	26	Lead line
Volume	m^3	2,399,910	2,906,996	3,256,571	Staff gauge
Area	m^2	207,503	250,402	262,309	Hypsographic curve
Rainfall	mm		2,486		Raingauge
Res. time	months		3		Calculation
pH*		5.01	5.16	5.32	Glass electrode
Alkalinity	$\mu eq\ dm^{-3}$	−30	−10.7	10	Gran titration
Total CO_2*	$\mu eq\ dm^{-3}$	11	17	28	GLC
Al	μM	3.6	6.5	9.3	Pyrocatechol violet
Ca	μM	23	28	33	AAS
Mg	μM	23	33	37	AAS
Na	μM	158	193	224	AAS
K	μM	7	9	13	AAS
SO_4	μM	36	42	50	Ion chromatography
Cl	μM	191	228	269	Ion chromatography
NO_3	μM	23	36	52	Ion chromatography
DOC*	$mg\ dm^{-3}$	0.3	1.2	2.9	Carla Erba
Chl *a*	$\mu g\ dm^{-3}$	0.3	1.2	1.9	Methanol/665 nm
DRP	$\mu g\ dm^{-3}$	<0.6			Molybdenum blue

The characteristics are shown along with mean and range values of determinands in all the integrated surface 5-m lakewater samples collected during 1991. (Abbreviations used: AAS atomic absorption spectroscopy, DOC dissolved organic carbon, Chl *a* chlorophyll *a*, GLC gas–liquid chromatography, DRP dissolved reactive phosphorus).

* Measured on single dip sample collected in sealed glass bottles.

the assimilation of nitrate to raise the pH of acid lake waters without drastically altering their community structure. Owing to the high efficiency of base production, only modest additions of phosphate are required, phytoplankton growth is not excessive and there is a marked increase in biological productivity at all trophic levels. In the longer term, additional quantities of base should be generated by the anoxic decomposition of organic material accumulating on the lake bed.

Previous studies[6] concerned primarily with eutrophication have shown that base is generated when productivity is further stimulated by simultaneously adding phosphate and nitrate. When nitrate is assimilated it generates base (consumes acid) according to equation (1).

$$106CO_2 + 138H_2O + 16NO_3^- \rightarrow (CH_2O)_{106}(NH_3)_{16} + 16OH^- + 138O_2 \quad (1)$$

Base is also generated through the oxidative decomposition of organic material. If oxygen is the electron acceptor, there is no net generation of base, but if other inorganic oxidants such as nitrate, sulphate or iron oxhydroxides are involved, their dissimilative reduction associated with the decomposition of organic matter generates base. The generated base is expressed as an alkalinity. It must not be confused with the temporary rise in pH associated with CO_2 consumption which affects neither alkalinity nor acidity. There is no advantage in adding nitrate rather than lime because 1 mol of nitrate is required to generate 1 mol of base. But providing nitrate is already present in the water, adding 1 mol of phosphate generates 16 mol of base through assimilation alone, making it remarkably efficient at base generation. As there are increasingly high concentrations of nitrate in many acid waters[7], including most of those in Europe, adding modest amounts of phosphate may generate sufficient base to combat acidity without inducing excessive productivity. Here we describe a large-scale experiment which for the first time has been specifically designed to test the effect on acidity of adding phosphorus. Phosphorus is added to a lake to stimulate primary productivity and the natural base-producing mechanisms, including assimilation of nitrate, that are potentially almost self-sustaining.

The quantity of base generated by assimilative and dissimilative processes depends on many factors, including the flushing rate of the basin, the rate of incorporation into the sediment and gaseous transfers to the atmosphere[5]. In the initial stages of fertilization the only process of any significance is likely to be assimilative uptake of nitrate, but dissimilative processes will become increasingly important as the deep sediments become more anoxic.

We describe here the results of a fertilization experiment conducted in Seathwaite tarn, an upland reservoir in the English Lake District (54° 23′ N; 3° 09′ W). The results cover the first critical period of assimilative base generation when the quantity of base generated can be predicted from mass-balance calculations and the known additions of phosphate. Seathwaite tarn (Table 1) was chosen as the study site because it had a moderate acidity (pH 5), one main inflow (Tarn Head beck) and a gauged outflow. The experiment was conducted over a three year period; a pretreatment year followed by two years of fertilization. Dosing with phosphate commenced in March 1992 with the addition of a concentrated solution of sodium phosphate ($50\ g\ dm^{-3}$ of P) from a fast-moving boat. Approximately $75\ dm^3$ was added every fortnight in 1992 and the dosing rate increased by ~50% in the summer of 1993. This treatment was estimated to have produced an average concentration of phosphate of $20\ \mu g\ dm^{-3}$ in 1992 and $28\ \mu g\ dm^{-3}$ in 1993. Water samples were collected at fortnightly intervals from the main inflow, the lake and the outflow. The inflow and outflow samples were collected using a flow-sensitive sampler which provides a reasonable approximation to flow-weighted mean concentration[8]. Throughout the experiment, the measured change in pH was compared with the pH predicted from a mass balance[9] of the acidic species entering via the inflow (Fig. 1).

Figure 1*a* shows that most of the phosphorus added to the lake is rapidly assimilated by growing phytoplankton. The average concentration ($\mu g\ l^{-1}$) of phytoplankton chlorophyll in 1991 was 1.2, but this increased to 3.9 in 1992 and 12.7 in 1993. Most of this increase was due to the rapid growth of small species that are commonly referred to as 'nanoplankton'. These species are consumed in large numbers by filter-feeding crustacea which greatly accelerate the rate at which the fixed carbon is deposited in the deep sediment. Figure 1*b* shows the effect that the additions of phosphorus had on the assimilative uptake of nitrate in the lake. In 1991, the measured concentration of nitrate was very similar to that predicted by a mass balance of the nitrate entering the lake from the inflows and direct precipitation. In the growing seasons of 1992 and 1993, the measured concentration of nitrate was lower than that predicted by the mass-balance model, but was very similar to the concentration predicted by the assimilative-uptake model. Figure 1*c* shows the effect that this assimilative uptake of nitrate had on the pH of the lake. Before

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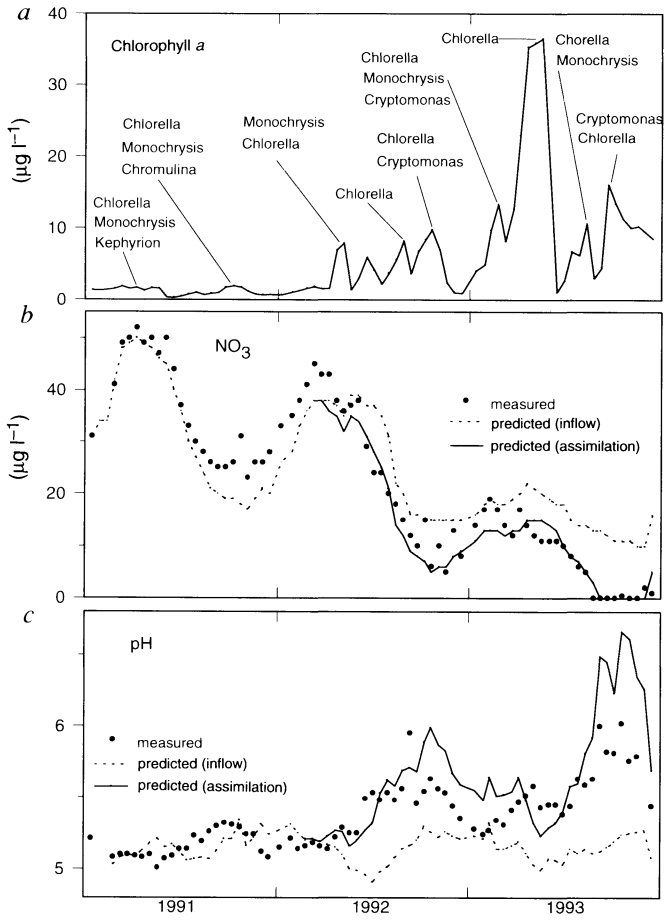


FIG. 1 The effect of adding phosphate phosphorus to Seathwaite tarn in 1992 and 1993. *a*, The changes in the concentration of chlorophyll *a* with the dominant phytoplankton genera indicated. *b*, The change in the concentration of nitrate nitrogen. *c*, The change in pH. Two predicted plots for nitrate and pH have been included in *b* and *c*.
METHODS. The 'inflow' predictions use fortnightly measurements of concentrations in the inflow and rain in mass-balance calculations which assume a one-box model[9] for the lake water. Outflows were calculated from the measured inflow adjusted by volume changes estimated from the measured lake level. Concentrations in the outflow were assumed to be the same as those measured in the surface 5 m of the lake. The inflow concentrations in the main stream accounting for 64% of the total inflow were assumed to be representative. Direct precipitation inputs onto the lake surface were almost negligible, but included. The 'assimilation' predictions further assume that nitrate is assimilated according to the Redfield ratio, that is 16 mol of N to each mole of P added. To predict pH an acidity function, AF(μeq dm^{-3}), was used in the mass-balance calculations. The carbonate and Al species were calculated from the measured p_{CO_2} and inorganic Al in the stream. Temperature, pH and DOC are the other necessary input parameters. $AF = [H^+] + (Al(OH)^{2+}] + 2[Al^{3+}] + [Al(OH)_3] - [Al(OH)_4^-] - [HCO_3^-] - 2[CO_3^{2-}] - [OH^-] + 3[DOC]$. E. Tipping (unpublished results) has observed that the acidity associated with DOC in acidic Lake District waters can be approximately represented in μeq dm^{-3} by 3[DOC] where [DOC] is in mg dm^{-3}. The resulting predicted value for AF in the lake was used, along with the measured concentrations of Al and p_{CO_2} to calculate the lake pH. The 'assimilation' predictions further assume that nitrogen is assimilated as nitrate in a 16:1 ratio to phosphorus, and that during this assimilation acid is consumed according to equation (1).

fertilization, the measured pH was similar to that predicted from the mass balance of inflow concentrations. After fertilization, the measured pH was consistently higher than that predicted by the simple mass balance. By assuming that base was generated during nitrate assimilation according to equation (1), a further model prediction of pH could be made. This 'assimilation' prediction is close to the measured pH in the early part of each year, but tends to be higher later in the year.

This work has demonstrated that addition of phosphate to an acidic unproductive lake can generate sufficient base through assimilation of nitrate to increase appreciably the pH. Moreover, the phytoplankton growth required to bring about this change was modest and did not give rise to any unacceptable changes in the qualitative composition of the community. Previous studies[6,10] have used higher dose rates of fertilizer, resulting in eutrophic conditions inappropriate for treating acidity.

This preliminary work has only considered the generation of base by assimilation. It assumes that none of the organic material undergoes oxidative decomposition, a process which results in no net generation of base. For this first two years of treatment, most of the organic material is likely to be flushed from the lake or reside in the sediment, but some oxidative decomposition may contribute to the measured pH in the lake being slightly lower than predicted (Fig. 1*c*). In the longer term, a greater proportion of organic material is likely to decompose within the lake. However, if this occurs anoxically, further base will be generated by dissimilative reduction processes[5]. Such base generation has been shown to occur at the sediment–water interface of lakes with well oxygenated water columns[3]. If all the added phosphorus ultimately led to dissimilative reduction, ~100 mol of base could be generated from each mol of phosphorus added[11]. Previous studies[11,12] suggest that 32% of the assimilated organic material undergoes aerobic respiration, 25% is washed out of the lake, 25% is buried in the sediments, 13% is consumed by reduction of nitrate to nitrogen and 5% goes to FeS production and burial. According to the above assumption, 21 mol of base will be generated for each mol of phosphorus added to the lake. In Seathwaite tarn the mean pH would change from 5.16 to 5.85. As a progressively greater proportion of the photosynthesized organic material decomposes within the lake, more of the phosphorus will be released and be available to stimulate further phytoplankton growth. With time this recycling of phosphorus within the lake will increase the efficiency of the added phosphorus, ultimately providing sufficient positive feedback to approach a self-sustaining increase in productivity and pH.

This treatment will work best for lakes with a residence time in excess of a year. The poor enhancement of pH in Seathwaite tarn during high-flow winter months (Fig. 1*c*) is to be expected because its mean residence team is only 3 months (Table 1). Other attributes required for success are a modest initial acidity and a sustained loading of nitrate from the atmosphere or catchment. Because ammonia is preferentially assimilated in catchments it is rarely present in acid lakes. If ammonia was present, its assimilation would generate acid rather than base[13], precluding treatment by adding phosphate.

Inducing such modest pH changes as the 0.5 pH observed here can be worthwhile. Solubility and adsorptive control of heavy-metal concentrations is particularly marked in the pH range 5–6, and so small pH increases may markedly reduce the metal content of polluted waters[14]. The poor productivity of most acid waters is associated with poor supplies of phosphorus. Fertilization of Seathwaite tarn has dramatically increased zooplankton and micro-benthic populations. Although it is too early to assess fully the effects on the scant brown-trout population, there are already signs of an improved growth rate.

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It is operationally difficult to dissolve calcium carbonate whereas phosphate can be provided in a concentrated solution and easily added. For the treatment described here, a total of 5.9 m^3 of phosphate fertilizer solution has been used. To bring about the same effect, 34 tonnes of calcium carbonate would have had to be added. Clearly the phosphate option can be cost-effective, especially if there is ultimately appreciable recycling of phosphorus. Most importantly, adding phosphate does not result in an unnatural chemistry and the pH is restored to pre-acidification levels rather than artificially high values.

Treating an acid lake with phosphate has the dual benefits of increasing the pH and productivity. Generally algal production is an important factor in controlling the long-term acidity of lakes. This study shows that phosphate can have beneficial effects within the environment, and that its complete elimination may enhance problems of low productivity and acidity. □

Received 7 April; accepted 8 September 1995.

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ACKNOWLEDGEMENTS. We thank E. Tipping, C. Reynolds, D. Hewitt, B. Simon, B. James, F.-C. Tsang and others for their contributions. This work was funded by the UK Natural Environment Research Council, the Department of the Environment, the Joint Environmental Programme of National Power and PowerGen, the National Rivers Authority and Albright and Wilson (UK) Ltd.

Vertical mixing and coral death in the Red Sea following the eruption of Mount Pinatubo

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THE eruption of Mount Pinatubo in the Philippines led to a cold air-temperature anomaly throughout the Middle East during the winter of 1992[1]. Here we report that the vertical mixing in the Gulf of Eilat (Aqaba) that winter was unusually deep—extending to >850 m—resulting in increased supply of nutrients to surface waters, which fuelled extraordinarily large algal and phytoplankton blooms. By spring, a thick mat of filamentous algae covered broad sections of the underlying reef causing extensive coral death. Branching colonies and solitary mushroom corals were most severely affected. This sequence of events, in which a short-term atmospheric cooling leads to a remarkable ecological response, is made possible by the unusually weak water-column stratification of the Gulf of Eilat. The depth of local vertical mixing during winter is determined by the net heat loss across the sea–air interface, so that anomalously cold winters drive the deeper mixing that can lead to increased phytoplankton blooms. Records of such events in fossil reefs may provide useful indicators of past variations in regional air temperatures.

The seasonal variability of air and sea-surface temperature in the Gulf of Eilat—a desert-bordered, 1,820-m-deep basin, 180 km long and 6–25 km wide—is shown in Fig. 1. As salinity varies little (40.3–40.8‰), vertical variations in water density are determined mainly by temperature[2]. Evaporation in the Gulf (~350 cm yr^{-1}) greatly exceeds precipitation (~3 cm yr^{-1})[2]. The compensatory influx of water to the Gulf, from the Red Sea, is confined by shallow sills to the upper warm layer[3]. Consequently, the temperature at depth is unusually high (for example, 20.6 °C at 1,200 m) and vertical stratification is weak[2,4,5].

The annual cycle of mixed-layer depth, seasonally driven by surface-water temperature changes, is shown in Fig. 2. As in oceanic regions, the deep vertical mixing is convectively driven by sea-surface cooling (that is, net upward heat flux), as opposed to mechanical wind mixing which usually maintains a shallow (< 50 m) summer mixed layer. Interannual variations in the maximum depth of mixing (Fig. 3) are therefore directly linked to variations in the net heat flux during winter (November–March), with variations in the latter parameter accounting for nearly 88% of the variance in mixing depth (Table 1). That local sea-surface cooling controls the vertical mixing in the northern Gulf of Eilat, is further corroborated by a one-dimensional mixed-layer model, which successfully simulates the temporal variability and maximum depth of mixing (Fig. 3, Table 1). As the interannual variations in heat flux during winter are determined mostly by variations in latent- and sensible-heat losses (Fig. 3), and because these two sources of heat loss are strongly dependent on the air–sea temperature difference[6], the latter parameter is highly correlated with the maximum depth of winter mixing (Table 1); variations in air temperature alone explain 81% of the variation in mixing. Winter averages of other parameters that could have potentially affected interannual variations in net heat flux, including solar radiation, relative humidity, wind speed and cloud cover, were not significantly ($P > 0.3$) correlated with either the net heat flux or the maximum mixing depth.

Seasonal changes in the biomass of phytoplankton (Fig. 1) and benthic algae[7] follow the above mixing-stratification pattern. During summer, the stratified photic layer is depleted of nutrients and therefore supports low phytoplankton and algal biomass. As mixing reaches below the photic depth in late autumn (Fig. 2), nutrients are transported to the photic layer, enhancing phytoplankton and algal growth. The deep mixing during winter, however, although reaching nutrient-rich layers, does not allow further increase in phytoplankton density because of the transport of living cells to aphotic depths, where they respire but do not photosynthesize[8]. Spring blooms start when stratification starts, in mid-March (Fig. 1). As concentrations of nutrients increase with depth[2], more nutrients are transported to the photic zone during winters with deeper mixing. Thus, the correlation between the average surface chlorophyll concentration during the spring bloom (15 March–15 May) and the

TABLE 1 Correlation coefficients between variables

	Q_t	Air–sea temp. diff.	Mixing: Observed	Mixing: Model	Chlorophyll
Q_t					
Air–sea temp. diff.	−0.88*	—			
Mixing (observed)	0.94*	−0.93*	—		
Mixing (model)	0.98†	−0.85‡	0.95*	—	
Chlorophyll	0.96†	−0.86‡	0.91*	0.97†	—

Pearson correlation coefficients between winter averages ($n = 7$ yr, 1988–95) of heat flux (Q_t), air–sea temperature difference, the maximum depth of observed and simulated mixing, and the spring-bloom average of surface chlorophyll *a* concentration (see Fig. 3 legend for details). The conventional sign of heat flux is positive upwards (sea surface cooling). Note that the 'observed' mixing depth for the winters 1988/89 and 1992/93 were underestimated because our profiles of salinity and temperature in these two winters did not reach the bottom of the mixed layer. Replacing the observed by simulated depths for those two years increases the correlation coefficients between the 'observed' values and chlorophyll concentration, air–sea temperature difference and heat flux by ~0.03 and improves the significance level for the latter two parameters to $P < 0.001$.
* $P < 0.01$, † $P < 0.001$, ‡ $P < 0.05$.

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