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Dissolved organic carbon reconstructions from diatom assemblages in PIRLA project lakes, North America

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[Microfiche in pocket]

Diatom-based palaeolimnological reconstructions of dissolved organic carbon (DOC) are presented for four regional data sets of the North American 'Paleoecological Investigation of Recent Lake Acidification (PIRLA)' project, and for a combined, three-region set. Species optima and tolerances along the DOC gradient were estimated by using maximum likelihood and weighted-averaging regression. Weighted-averaging regression appears to be the most robust and tractable technique for estimating optima, and the apparent error (mean standard error of the relation) was as good for weighted-averaging calibration as for maximum likelihood calibration. Calculated species optima are not entirely consistent among regions and the best 'indicators' for DOC in the PIRLA data-sets are not in good agreement with those found in the literature. Example reconstructions demonstrate that DOC changes are often less than 100 μmol l^{-1}, and that the DOC declines in some recently acidified lakes parallel reconstructed pH declines.

Introduction

Surface-water organic acids (OA) have not received the attention they deserve in recent studies on lake acidification. This is because characterization of this complex of organic compounds is difficult and not standardized; the dynamic interactions between terrestrial and lake pools are poorly known; earlier studies on OA are generally not from 'acidification-sensitive' ecosystems; and long-term records of OA change are rare and anecdotal. Interest in 'natural acidity' has developed recently from various directions: soil scientists and limnologists; laboratory and field researchers; ecosystem manipulators and modellers; and believers and nonbelievers in the effects of SO_4^{2-} deposition on lake-water chemistry.

It is essential to study the limnological gradient of organic matter (OM) from a palaeolimnological perspective, particularly because of the recent debate about the role of 'natural' versus 'anthropogenic' acidification (see, for example, Gorham *et al.* (1986); Kerekes *et al.* (1986); Krug & Frink (1983); Brakke *et al.* (1987)). In water, OM exists as a chemically and physically diverse assemblage, and it may be represented as dissolved organic carbon concentration (DOC), total organic carbon concentration (TOC), 'true colour', 'apparent colour', and noncarbonate alkalinity (Cook *et al.* 1987). Here we consider DOC as a surrogate for OA; OM can also be viewed as a combination of strong and weak acids (average pK values between 3.5 and 4.0 according to Kramer *et al.* (1989)). Between pH values of 4.5–7.0, high amounts of these organic acids (DOC = 750 μmol l^{-1}) can lower pH by up to 2 units, compared with lake-water buffered only by the bicarbonate system (Cook & Jager 1990). Many of the difficulties in understanding OM dynamics stem from the complex assemblage of chemicals being studied. The lack of a standard methodology makes various research approaches difficult to compare. There has been general concern that acidification models are too simple (Marmorek *et al.* 1988; Kramer *et al.* 1989), largely because they have not treated OA as temporally dynamic. Reconstruction of lake-water OA changes is therefore also important for validating acidification models.

The many uncertainties in knowledge of OA in surface waters have been an obvious part of the lake acidification debate. Rosenqvist (1978) proposed that OA from soils, not mineral acid deposition, are the major cause of lake-water acidity, but palaeolimnological studies have not supported this hypothesis (see, for example, Jones *et al.* 1986). Krug & Frink (1983) argued that strong-acid deposition decreased DOC with relatively little effect on lake-water pH. In another example of a debated mechanism, Rosenqvist (1978) and Kramer *et al.* (1989) suggested that surface waters might become acidified as a result of cation exchange during forest growth, but budgets of forest soil chemistry did not support major effects on surface-water acidity (Nilsson *et al.* 1982).

Reconstruction of lakewater OA (as various operational indicators) has been attempted previously by using multiple regression of diatom abundances in cluster analysis groups with respect to total organic carbon (Davis *et al.* 1985) and by using multiple regression of diatom and Cladocera abundances in colour categories versus colour measurements (Huttunen *et al.* 1988). There have been several suggestions in ecological data-sets that indicators of OA may have a major effect on diatom and chrysophyte abundances (Davis *et al.* 1985, Anderson *et al.*1986, Walker & Paterson 1986, Scruton *et al.* 1987, Taylor *et al.* 1988, Kingston *et al.* 1990). By reconstructing several chemical parameters in PIRLA II, we can provide data for testing hypotheses about chemical interactions during acidification.

Data-sets

The research project 'Paleoecological Investigation of Recent Lake Acidification (PIRLA)' was a multi-university, multi-disciplinary investigation (Charles & Whitehead 1986*a*); all methods were coordinated among regions (Charles & Whitehead 1986*b*); quality assurance (QA) within and among study regions was maintained at a high standard, both for chemical and biological data (Kreis 1990). Diatom methods, including sampling, slide preparation, taxonomy, and QA procedures (Charles & Whitehead 1986*b*, Camburn *et al.* 1984–1986), were coordinated so that the four regions could be directly compared, and that reconstructions could potentially be based on combined data from several regions. Chemical parameters are arithmetic means of several discrete (1 m depth), ice-free water samples. The pH parameter in this paper is measured in samples equilibrated to atmospheric CO_2 (pH_{aer}). It is important to note that PIRLA was designed to study primarily pH and total alkalinity (TAlk), and to avoid high DOC levels that might confound interpretations of lake acidity.

The initial PIRLA study is now designated as 'PIRLA I', whereas the current research (PIRLA II) concentrates on the Adirondack region of New York (Charles & Smol 1990). There are four PIRLA I study regions: Adirondack Park (ADIR), northern New England (NENG), northern Great Lakes states (NGLS), and northern Florida (NFLA). PIRLA II includes a subproject on reconstruction of parameters besides pH, especially DOC.

Regional and three-regions-combined DOC and pH data are summarized in table 1. The northern Florida lakes had very different environmental characteristics and diatom floras, whereas the other three regions were quite similar in terms of environmental gradients and

Table 1. Summary of DOC and pH data for the individual PIRLA regions and for the combined northern data set. DOC is a combination of measured and calculated values in ADIR and NENG. The pH measure used here is the arithmetic mean of samples equilibrated with atmospheric CO_2

(See text for details and abbreviations; med., median; s.d., standard deviation; min., minimum; max., maximum.)

			DOC						pH_{aer}					
region	no. of lakes	no. of taxa	no. of lakes	mean	med.	s.d.	min.	max.	no. of lakes	mean	med.	s.d.	min.	max.
ADIR	47	151	47	315.2	276.0	148.2	197.0	1039.0	47	6.18	6.54	1.09	4.34	7.77
NENG	63	203	63	283.2	271.0	168.6	21.0	833.0	60	6.11	6.46	0.96	4.48	8.14
NGLS	36	134	36	304.6	229.0	173.7	62.0	899.0	36	6.21	6.56	0.83	4.41	7.32
NFLA	32	125	32	956.4	687.0	810.5	125.0	3497.0	32	5.37	5.01	0.94	4.24	7.79
3REG	146	117	146	298.8	269.0	164.3	21.0	1039.0	143	6.16	6.26	0.98	4.34	8.14

diatom floras. Therefore, we compare the DOC predictive powers of the individual PIRLA I regions and use the combined data from the three northern regions (ADIR + NENG + NGLS = 3REG; 146 of 178 lakes) to investigate whether a larger data set is superior for DOC reconstruction.

In 37 out of 47 PIRLA I ADIR lakes, true colour was measured and DOC was not. This was also the case for three NENG lakes. To use DOC as a surrogate for OA, and because it is significantly more interesting to chemists than colour, we calculated 'DOCNEW' values for the lakes that did not have measured values. This was done by using linear models of colour and DOC for Eastern Lake Survey lakes from the same regions (D. J. Blick, U.S.E.P.A. Corvallis, personal communication).

For 3REG reconstructions, we selected all taxa that occurred at 1 % or more in three lakes, and that were also present in at least 13 of the surface sediment samples; this gave us 117 taxa. In each regional reconstruction, we used all taxa that occurred at 1 % or more in one lake.

The two lakes used for example reconstructions are known to have recently acidified. Big Moose Lake (ADIR; 43° 49′ 02″ N, 74° 51′ 23″W) is a drainage lake with reconstructed declines in pH and TAlk and modelled increases in aluminium (Charles 1984; Charles *et al.* 1988) that correspond well with known fisheries decline. Brown Lake (NGLS; 45° 46′ 50″ N, 89° 29′ 30″ W) is a seepage lake that has reconstructed pH declines similar to historical water chemistry records (Kingston *et al.* 1990; Eilers *et al.* 1989).

Numerical methods and results

Weighted-averaging regression (ter Braak & Looman 1987) was used to estimate DOC weighted averages (abundance weighted means) and weighted standard deviations ('tolerances') for the diatom taxa in each individual region data-set and for the combined 3REG data-set (table 2, on microfiche in pocket). Optima and tolerances for all taxa in the 3REG data were estimated by fitting a Gaussian logit model (GLM) by using logit regression, as implemented by GLIM (Baker & Nelder 1978). A Gaussian logit model is a special case of the generalized linear model with logit link function and binormal error distribution and is a quasi-likelihood model when used with proportional data (ter Braak & van Dam 1989). For each taxon the GLM was tested at $\alpha = 0.05$ by using deviance and one-sided t-tests against the simpler linear logit model (LLM) to ascertain if the optimum or the GLM, or both, were significant. If they were not significant, the LLM was tested against the null model of the taxon having no relationship with DOC ($\alpha = 0.05$). The simplest significant model was evaluated for each taxon (ter Braak & van Dam 1989).

Several taxa have no significant unimodal (GLM) or sigmoidal (LLM) relationship with DOC (table 3); others have fitted curves with a minimum rather than a maximum, and some have poorly defined optima with estimates beyond the sampled range of DOC (21–1039 μmol l^{-1}). The latter problem arises inevitably in any modern data set because some taxa occur at or near the edge of their ecological ranges (ter Braak & Prentice 1988). In these cases, taxa that have a significant fit to an LLM and have a decreasing linear logit curve are assumed to have an optimum of < 21 μmol l^{-1}, whereas those with increasing linear logit curves are assigned an optimum of > 1039 μmol l^{-1}. In these cases the tolerances are undefined. Tables 2 and 3 show that 54 taxa have no significant modelled relationship with DOC, and only 35 show a significant Gaussian unimodal relationship.

TABLE 3. RESULTS OF FITTING GAUSSIAN LOGIT, LINEAR LOGIT AND NULL MODELS TO THE THREE-REGION DATA IN RELATION TO DOC

characteristic shown by taxon	number of taxa
Gaussian unimodal curves with maxima	67
unimodal curves with minima	14
a significant fit to Gaussian logit model	35
a significant fit to a decreasing linear logit model	26
a significant fit to an increasing linear logit model	2
no significant fit to a Gaussian or linear logit model	54
total number of taxa	117

Weighted-averaging calibration (ter Braak 1987) with (WA(tol)) and without (WA) weighting taxa inversely by their squared tolerance, was used to infer DOC both for the modern data and for the fossil samples in the individual regions and for the 3REG data. A simple inverse linear rescaling was used to de-shrink the initial weighted-average estimates (ter Braak & van Dam 1989). Maximum-likelihood (ML) calibration using the GLM parameters was also used for the 3REG data (ter Braak & van Dam 1989). The standard error (SE) of (observed DOC-inferred DOC) for the modern training sets was used as a mean squared error (MSE) to compare the predictive performance of the different methods (table 4).

TABLE 4. STANDARD ERROR (OBSERVED DOC–INFERRED DOC) FOR RECONSTRUCTION METHODS WITH AN INVERSE REGRESSION DE-SHRINKING

data-set	number of lakes	number of taxa	WA	WA (tol)	ML
ADIR	47	151	98.4	88.2	—
NENG	63	203	123.3	123.6	—
NGLS	36	134	80.1	92.9	—
NFLA	32	125	448.8	360.9	—
3REG	146	117	146.1	146.3	157.9
3REG	146	63[a]	145.3	145.7	145.3

[a] All taxa with a significant fit to a Gaussian or linear logit model (see tables 2 and 3).

Although WA(tol) produces slightly lower MSE than WA (table 4), it produces consistently larger MSE when bootstrapping or cross-validation are used to derive more reliable and more robust SE (Birks *et al.*, this symposium; H. J. B. Birks unpublished results). Maximum-likelihood calibration and logit regression are both extremely demanding computationally, and yet produce results (table 4) slightly inferior to WA; this is so for pH in SWAP (Birks *et al.*, this symposium). Moreover, problems arise in ML calibration because the numerical optimization procedure that was used fails to converge for 33 (22%) modern samples containing 117 taxa and for 42 (29%) modern samples containing 63 taxa. Of the 545 fossil samples, 132 (24%) similarly fail to converge, probably because their diatom assemblages contain taxa of markedly contrasting DOC optima.

ter Braak & van Dam (1989) and Birks *et al.* (this symposium) have shown that, for pH inference, simple WA regression and calibration not only provide a good approximation to ML, but also are often superior to ML; WA is a reliable, robust, and rapid pH-inference procedure. For DOC inference, WA appears to have similar advantages over ML. We only present DOC inferences derived by WA regression and calibration.

Regression and calibration by WA, but with classical linear regression for de-shrinking the initial estimates, were used with the same data-sets to infer pH. This methodology follows exactly Birks *et al.* (this symposium).

All computations (except logit regression) were implemented by the FORTRAN 77 program WACALIB 2.1 (Birks *et al.*, this symposium).

Discussion of DOC optima

Regional optima for the same common taxon (table 2) can be broadly similar (e.g. *Cymbella perpusilla* + sp. 1 + sp. 2, *Navicula tenuicephala*) or quite different (e.g. *Asterionella ralfsii* var. *americana* < 45 μm). All taxonomic authorities are given in table 2. Constrained canonical correspondence analysis (CCA) ordinations were used to evaluate 'indicator organisms'. By using diagnostics within CANOCO version 3 (C. J. F. ter Braak, unpublished results), the cumulative fit per taxon as a fraction of the taxon's total variance reveals a few organisms that are very consistent in terms of their explanation of the DOC gradient from region to region. The ten taxa with the strongest DOC response in the 3REG data set are: *Melosira distans* var. *tenella*, *Fragilaria construens* var. *binodis*, *Navicula mediocris*, *Frustulia* cf. *magaliesmontana*, *Pinnularia biceps* var. 1, *Navicula subatomoides*, *Neidium bisulcatum*, *Neidium affine*, *Cymbella perpusilla* + sp. 1 + sp. 2, and *Achnanthes linearis*. Examination of the size of the first axis contrained to DOC and the first unconstrained axis shows that DOC explains a small but significant amount of taxon variance in NGLS, ADIR, and NFLA, but the signal is much weaker in the NENG and 3REG data; CCA of the NENG data reveals that DOCNEW contributes very little to the first two axes.

Several taxa have been proposed as 'indicators' for various humic acid surrogates in studies from Norway and Canada, including *Frustulia rhomboides* var. *saxonica*, *Anomoeneis serians* var. *brachysira*, *Navicula subtilissima*, *Navicula heimansii*, *Frustulia rhomboides*, *Achnanthes marginulata*, *Achnanthes austriaca* var. *helvetica*. *Navicula krasskei*, *Achnanthes levanderi*, *Melosira ambigua*, *Tabellaria flocculosa* strain 3p, *Asterionella ralfsii* var. *americana*, *Cyclotella stelligera*, and *Cyclotella kuetzingiana* (Davis *et al.* 1985, Anderson *et al.* 1986; Taylor *et al.* 1988). The PIRLA data do not consistently support these findings, and we caution that indicators from one region may show different and conflicting relationships elsewhere. For example, *A. serians* var. *brachysira* and

F. rhomboides var. *saxonica* have optima near the measured DOC means for the PIRLA data, but more importantly, they do not have high fits to DOC in terms of taxon variance explained.

Furthermore, good 'indicators' of DOC are not consistent from region to region within PIRLA. Therefore, individual regional DOC weighted-average means and reconstructions are probably the most reliable for the PIRLA data, subject to further research on error estimation.

Reconstructions

Example reconstructions of DOC are presented in figure 1, along with reconstructions of pH, TAlk, and total Al (J. C. Kingston & H. J. B. Birks, unpublished data). The magnitude of DOC change is small relative to the MSE of the relation in each region (table 4), but in each case DOC declines coincidentally with lakewater pH. In Big Moose Lake, total Al increases dramatically as pH, TAlk, and DOC decline from the 1940s. In Brown Lake, total Al has an opposite trend to DOC until the topmost sediment interval, where they increase together.

In the ADIR PIRLA I cores, two lakes have DOC increases greater than the MSE for the relation, five lakes have decreases less than the MSE, and five lakes show no change. In the

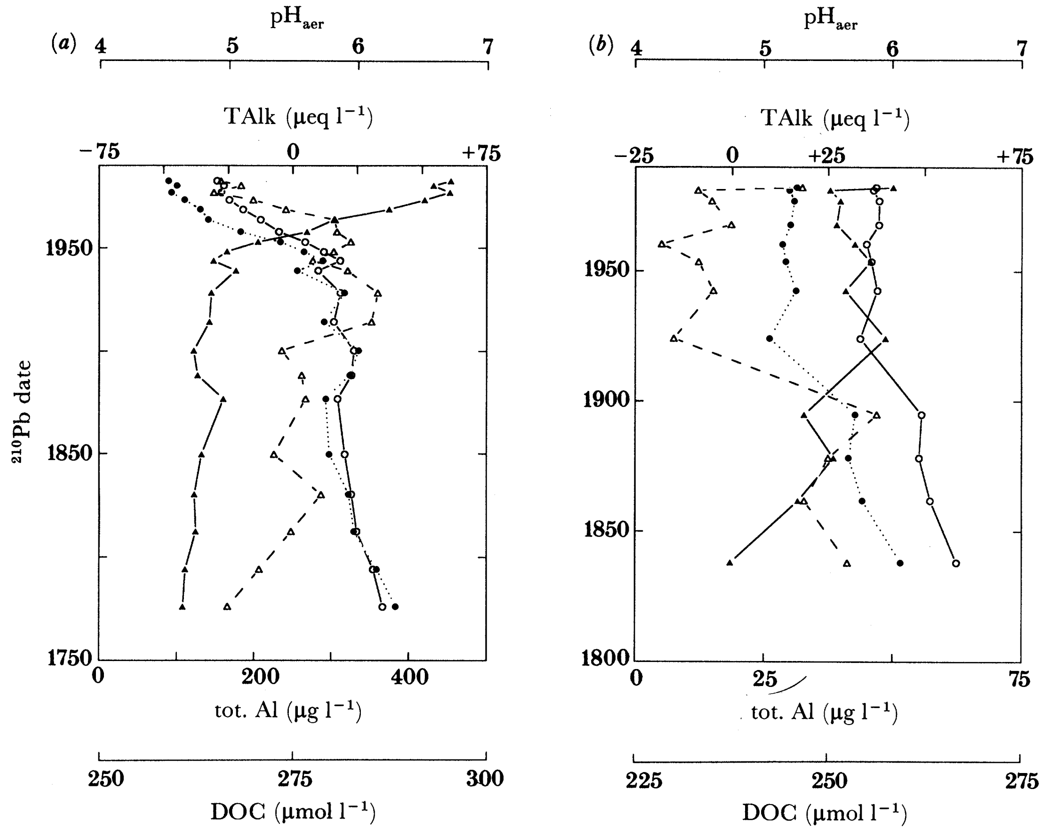

FIGURE 1. Example weighted-averaging (WA) reconstructions of four parameters in two PIRLA I sediment cores, based on data from individual regions. DOC methods are explained in the text, whereas reconstructions of pH_{aer}, total alkalinity, and total aluminium are included to provide a more complete picture of limnological changes during lake acidification (J. C. Kingston & H. J. B. Birks, unpublished data). Mean standard errors of the DOC relationships are given in table 4; (*a*) Big Moose Lake, New York, core 2 (ADIR); (*b*) Brown Lake, Wisconsin, core 2*a* (NGLS); (○——○), pH_{aer}; (●······●), TAlk; (▲——▲), total aluminium; (△——△), DOC.

NGLS PIRLA I cores, one lake has an increase greater than the MSE of the relation, one lake has an increase less than the MSE, one lake has a decrease greater than the MSE, two lakes have decreases less than the MSE, three lakes show essentially no change, and one lake has large fluctuations.

Discussion of reconstructions

Our reconstructions of pH and TAlk for Big Moose Lake match those previously published (Charles 1984; Charles *et al.* 1988; Charles & Smol 1988) and correspond well with measured water chemistry. The DOC reconstruction indicates a lower magnitude of decline than might be expected from hypotheses on the effects of mineral acid deposition (T. J. Sullivan, personal communication) but the direction of the trend meets expectations of recent loss of DOC. The reconstructed total Al increase is similar to previous modelling efforts (Charles 1984), but the reconstructed concentration overestimates the measured concentration and the modelled 1982 concentration by a factor of two. This is caused by a 'no analogue' situation at the top of the core, with high abundances of species such as *Fragilaria acidobiontica* and *Navicula tenuicephala*.

Brown Lake is part of the 50-year water-chemistry comparison between the Birge and Juday surveys of the late 1920s and EPA surveys of the late 1970s and early 1980s (Eilers *et al.* 1989; detailed data in the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa K1A 0S2). The historical and recent values of pH (6.47, 5.94), alkalinity (56.5, 10.7 μeq l^{-1}) and apparent colour (25, 12) each match our reconstructions very well.

The three PIRLA I lakes with large reconstructed increases in DOC are each naturally acidic; Barnes Lake and Little Echo Pond (ADIR) have also acidified recently (Charles *et al.* 1990; D. F. Charles, personal communication), whereas Otto Mielke Lake (NGLS) has become slightly less acidic (Kingston *et al.* 1990). Processes leading to these DOC increases are unknown, but may relate to land clearance, forest regrowth, or wetland expansion.

Conclusions

Diatom response to environmental gradients in the PIRLA regional calibrations shows that pH consistently explains more of the species variance than DOC, that pH and DOC are generally unrelated to each other, and that DOC can usually be reconstructed to show the timing, magnitude and direction of trends. We suspect that improved DOC reconstructions could result from a more even sampling of the natural DOC gradient in lakes, which, as we mentioned earlier, was not a priority in PIRLA I. Some PIRLA reconstructions support hypotheses that surface-water DOC declines are caused by deposition of mineral acids (figure 1). In general, DOC declines coincidentally with lakewater pH in recently-acidified PIRLA study lakes. Although the magnitude of these DOC declines seems small, the acid–base character of the DOC (charge density and dissociation constants) might also be changing.

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Discussion

R. A. Skeffington (*National Power Technology and Environmental Centre, Leatherhead, Surrey, KT22 7SE, U.K.*) Is there any evidence from controlled experimental studies that diatoms respond to DOC, alkalinity or Al *per se*? In particular a response to alkalinity seems unlikely as it is a measurement that essentially records the results of a titration, and humans are the only organisms that perform titrations. Diatoms must be responding to something that correlates with alkalinity, such as pH. How confident can Dr Kingston be that the apparent statistical relation between diatom abundance and DOC, alkalinity and Al are not simply reflections of the correlation of these variables with pH?

J. C. Kingston. There is an algal physiology literature of potential mechanisms of carbon species influence over phytoplankton, with implications for acidification effects (see, for example, Williams & Turpin (1987)). There is a larger literature on toxic metal effects on phytoplankton, mainly from point-source effects of factories or mine drainage. Some detailed physiological research (A. Smith, personal communication), as well as controlled enclosure experiments (Pillsbury & Kingston 1990) does show toxic effects of Al on the very phytoplankton species that are known to decline in recently acidified lakes.

The program CANOCO provides excellent diagnostic tools for determining colinearity of measured environmental parameters, and we avoid reconstructions by WACALIB of highly colinear variables. Each data set must be critically examined, but we are usually able to reconstruct the four parameters. Each of these parameters can be shown to explain new, significant amounts of variance in the total species data.

To say that only humans can perform titration misses the point. Although we do not know the exact physiological mechanisms of action in most cases, we can evaluate with great confidence whether measured environmental variables do explain variance in the species data, and we can prevent misleading interpretation of colinear variables.

R. B. Davis (*Department of Botany and Plant Pathology, University of Maine, U.S.A.*). Could some of the regional differences in diatom response to DOC be the result of different sources of the DOC?

J. C. Kingston. Yes, it is suspected, but not investigated very thoroughly at present, that the acid-base characteristics of DOC from different sources can be very different. Therefore, a certain concentration of DOC from upland soils may be quite different from the same concentration of DOC from a sedge fen, or from a *Sphagnum* bog. Regional differences in vegetation and soils exist across eastern North America, and an operational environmental parameter such as DOC does not account for this. We are most interested in acid–base characteristics, which are rarely measured (Wright *et al.* 1988).

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