Science of the Total Environment xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

A Water Framework Directive-compatible metric for assessing acidification in UK and Irish rivers using diatoms

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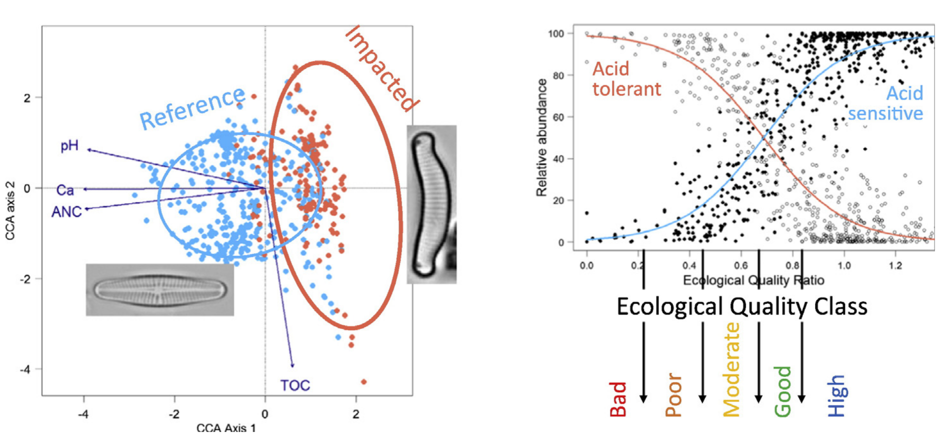
HIGHLIGHTS

- A new diatom metric for assessing the acidification status of rivers is proposed.
- Metric calibrated using reference sites and EU Water Framework Directive-compliant.
- Validated at sites with long-term biological and chemical data
- Good agreement between diatom ecological status class and long-term data

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 17 December 2015
Received in revised form 23 February 2016
Accepted 23 February 2016
Available online xxxx

Keywords:
Diatoms
Ecological status
Water Framework Directive
Acidification
Rivers
Monitoring

ABSTRACT

Freshwater acidification continues to be a major problem affecting large areas of Europe, and while there is evidence for chemical recovery, similar evidence for biological recovery of freshwaters is sparse. The need for a methodology to identify waterbodies impacted acidification and to assess the extent of biological recovery is relevant to the EU Water Framework Directive, which requires methods to quantify differences in biology between impacted and unimpacted or reference sites. This study presents a new WFD-compliant metric based on diatoms (Diatom Acidification Metric: DAM) for assessing the acidification status of rivers. A database of 558 benthic diatom samples and associated water chemistry data was assembled. Diatom taxa were assigned to one of 5 indicator classes on the basis of their pH optimum, assessed using Gaussian logistic regression, and these indicator values used to calculate a DAM score for each site using weighted averaging. Reference sites were selected on the basis of their acid neutralising capacity (ANC) and calcium concentration, and a regression model developed to predict expected DAM for each site using pH and total organic carbon (TOC) concentration. Site-specific DAM scores were used to calculate ecological quality ratios ranging from ≥1, where the diatom assemblage showed no impact, to (theoretically) 0, when the diatom assemblage was indicative of major anthropogenic activities. The

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http://dx.doi.org/10.1016/j.scitotenv.2016.02.163

boundary between 'high' and 'good' status was defined as the 25th percentile of Ecological Quality Ratios (EQRs) of all reference sites. The boundary between 'good' and 'moderate' status was set at the point at which nutrient-sensitive and nutrient-tolerant taxa were present in equal relative abundance. The methodology was evaluated using long-term data from 11 sites from the UK Uplands Waters Monitoring Network and is shown to perform well in discriminating naturally acid from acidified sites.

1. Introduction

There is a long history of research into the response of diatoms to pH, from pioneering studies of Hustedt (1937–39) to palaeoecological studies on the causes of lake acidification (Flower and Battarbee, 1983; Renberg and Hellberg, 1982), recovery, and the effects of remediation strategies (Allott et al., 1992; Battarbee et al., 2014b; Guhrén et al., 2006). The focus of this research has been primarily on lakes, where the relationship between diatom assemblages and pH can be modelled with a precision of approximately ± 0.3 pH units (Birks et al., 1990). This work was important in highlighting the role of acid deposition in the acidification of surface waters in large areas of both Europe and North America (Battarbee et al., 2010a) and, ultimately, in shaping government policy (Derwent and Wilson, 1992). Treaties aimed at limiting transboundary air pollution have led to large reductions in the emission and deposition of pollutants and chemical data show recovery of freshwaters since the 1990s (Stoddard et al., 1999). However, the evidence for biological recovery is scarce, with many areas still impacted by episodic (Feeley et al., 2013; Kowalik et al., 2007) or chronic acidification (Ormerod and Durance, 2009). Consequently, there is a continuing need to identify and monitor affected freshwaters and quantify their recovery towards a target state.

Acidification was one of a number of impacts that demonstrated the deleterious effects of human activities on the ecology and ecological services of aquatic environments, and which provided the impetus for the Water Framework Directive (WFD: European Union, 2000). A core concept of the WFD is that ecological status (defined as "… an expression of the structure and functioning of aquatic ecosystems", WFD Article 2) is determined by reference to the condition of an ecosystem that would prevail in the absence of significant human disturbances. The magnitude of any disturbance or impact is then expressed as an Ecological Quality Ratio (EQR) calculated as the ratio of metrics defining observed and expected states. Defining the "expected" state has been a major challenge for the past decade (Pardo et al., 2012). In principle, palaeoecological studies provide a powerful means for doing this albeit in standing waters only (Bennion et al., 2010). Such an approach can be used to identify lakes whose pH has changed little in recent times (Battarbee et al., 2010b). These can then serve as "reference sites" (sensu Wallin et al., 2003) from which properties of biological quality elements in their near-pristine state can be measured for use as "expected" values for EQR calculations.

Although various metrics for assessing pH in running waters using diatoms have been developed (Andrén and Jarlman, 2008; Coring, 1996; Kwandrans, 2007; Van Dam and Mertens, 1995) none is suitable as a WFD acidification assessment system for two reasons: they do not address the issue of "expected" values of metrics under conditions of "no, or only very minor, anthropogenic alterations" (European Union, 2000), and they do not provide an ecological basis for setting quality status boundaries. The former is particularly significant as it is important that ecological status assessments can distinguish those water bodies which have been acidified by human causes from those which are naturally acidic. An ecological rationale for setting boundaries is also important as the WFD provides, in Annex V (European Union, 2000), ecological criteria by which ecological status should be assessed, and expects member states to take action to improve water quality in those water bodies that achieve moderate status or less.

In this paper we describe a new diatom-based metric for assessing the acidification status of rivers. Our metric is calibrated against a database of reference sites in the UK and Ireland enabling an EQR and ecological status class to be calculated for any new diatom sample. Thus, our method is compliant with the requirements of the WFD and will form part of the suite of tools for the holistic assessment of the quality element "macrophytes and phytobenthos" in the UK and Ireland.

2. Methods

2.1. Dataset

The dataset used to derive the diatom metric comprised 558 samples from 435 sites with data on diatom species composition and associated water chemistry, and was assembled from a number of previous projects: UK Uplands Water Monitoring Network (UKUWMN, Formerly the UK Acid Waters Monitoring Network: Patrick et al., 1996: N = 32), the Welsh Acids Waters Survey (Reynolds et al., 1999: N = 203) the Critical Loads of Acidity and Metals project (Kernan and Curtis, 2000: N = 78) and the FORWATER project (Kelly-Quinn et al., 2008: N = 245). These studies focussed on those areas of the UK and Ireland associated with slow-weathering geology, low alkalinity and, therefore, susceptibility to acidification. Sampling areas were principally in upland regions of south-west England, the Pennines, Wales, the Lake District, Scotland, and Ireland, along with lowland samples from the New Forest (Hampshire) and Ashdown Forest (Sussex). Sampling and analytical methodologies follow those of Kelly et al. (2008) and are compliant with European standards (CEN, 2003, 2004). Samples were collected by brushing the upper surface of cobble-sized stones using a toothbrush and storing the resulting suspension in a plastic bottle for transport to the laboratory where they were digested using hydrogen peroxide (Battarbee, 1986) and permanent slides prepared using Naphrax high resolution mountant (Brunel Microscopes Ltd, UK). At least 300 valves were identified using 1000× magnification oil immersion objectives. Taxonomy followed Krammer and Lange-Bertalot (1986-1991) and Hartley et al. (1996). All nomenclature was adjusted to that used by Whitton et al. (1998) which follows conventions in Round et al. (1990) and Fourtanier and Kociolek (1999-2003). Water chemistry samples were collected at the diatom sampling sites between 4 and 12 times per year and analysed using methods described in Monteith et al. (2014) for pH, acid neutralising capacity (ANC), calcium, and total organic carbon (TOC), and expressed as annual mean values. Species-environment relationships in the data were explored using canonical correspondence analysis (ter Braak, 1986) and the relative importance of pH and TOC in accounting for variation in diatom species composition was assessed using CCA-based variance partitioning (Borcard et al., 1992). All numerical analyses were performed using R software (R Core Team, 2015) with the vegan package (Oksanen et al., 2015).

2.2. Definition of reference conditions

A pre-requisite for reference (i.e. non-acidified) waters is that concentrations of base cations are in balance, or exceed, concentrations of strong acid anions, i.e. ANC is positive. In contrast, waters with negative ANC, i.e. where the surfeit of acid anions relative to base cations, tend to be balanced by elevated concentrations of acid cations (H^+ and Al^{3+}) and can almost invariably be considered to be acidified. The use of a critical ANC value (ANC_{crit}) to determine the threshold above which damage from acidification is unlikely to occur forms the basis of the