Science of the Total Environment 409 (2011) 1164–1171

Contents lists available at ScienceDirect

Science of the Total Environment

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

Impact of calcium and TOC on biological acidification assessment in Norwegian rivers

Susanne C. Schneider *

Norwegian Institute of Water Research, Gaustadalleen 21, 0349 Oslo, Norway

ARTICLE INFO

Article history:
Received 5 May 2010
Received in revised form 16 November 2010
Accepted 16 November 2010
Available online 31 December 2010

Keywords:
Phytobenthos
Benthic algae
Periphyton
pH
Norway
Water Framework Directive

ABSTRACT

Acidification continues to be a major impact in freshwaters of northern Europe, and the biotic response to chemical recovery from acidification is often not a straightforward process. The focus on biological recovery is relevant within the context of the EU Water Framework Directive, where a biological monitoring system is needed that detects differences in fauna and flora compared to undisturbed reference conditions. In order to verify true reference sites for biological analyses, expected river pH is modeled based on Ca and TOC, and 94% of variability in pH at reference sites is explained by Ca alone, while 98% is explained by a combination of Ca and TOC. Based on 59 samples from 28 reference sites, compared to 547 samples from 285 non-reference sites, the impact of calcium and total organic carbon (TOC) on benthic algae species composition, expressed as acidification index periphyton (AIP), is analyzed. Rivers with a high Ca concentration have a naturally higher AIP, and TOC affects reference AIP only at low Ca concentrations. Four biological river types are needed for assessment of river acidification in Norway based on benthic algae: very calcium-poor, humic rivers (Ca<1 mg/l and TOC>2 mg/l); very calcium-poor, clear rivers (Ca<1 mg/l and TOC<2 mg/l); calcium-poor rivers (Ca between 1 and 4 mg/l); moderately calcium rich rivers (Ca>4 mg/l). A biological assessment system for river acidification in Norway based on benthic algae is presented, following the demands of the Water Framework Directive.

1. Introduction

Acidification of rivers and lakes caused by acidic precipitation has lead to dramatic consequences for freshwaters in large areas of Europe and North America (Henriksen, 1979; Schindler, 1999). Emissions of acidifying gases in Europe peaked in the 1970s/1980s (Schöpp et al., 2003), and chemical data showed recovery of freshwaters since the early 1990s (Skjelkvåle et al., 1998; Stoddard et al., 1999; Skjelkvåle et al., 2005). While model simulations today predict that recovery will continue, they also predict that acid precipitation will continue to exceed the critical load of many surface waters, particularly in extremely sensitive areas such as southern Norway (Wright et al., 2005). Acidification can be a result of acid precipitation, but also of exposing minerals containing sulfide, which occasionally occur in Norway (Hindar, 2005), to air, thereby causing their oxidation. Freshwater acidification will therefore remain an issue in northern Europe for the coming decades.

Despite chemical recovery, evidence of widespread biological recovery is scarce (Kowalik et al., 2007; Schartau et al., 2008). Delayed biological compared to chemical recovery is a long known phenomenon and has recently been observed with respect to acidification by several authors (Kowalik et al., 2007; Schartau et al., 2008; Ormerod and Durance, 2009). The biotic response to chemical recovery involves a multitude of chemical, physical, and biological interactions leading to lagged or threshold responses and thus is not a straightforward consequence of changing water chemistry (Monteith et al., 2005). As acid deposition has declined, the importance of episodic acidification events has become more obvious (Teien et al., 2004; Larssen and Holme, 2006; Evans et al., 2008). Laudon (2008) found that drought and sea salt episodes are among the most important factors delaying recovery in Sweden by causing pulses of acidic water entering streams in areas with historically high levels of acid deposition. Summer droughts operate by lowering the water table of wetlands, thus causing re-oxidation of previously reduced compounds and leading to acidic, SO_4^{2-}-rich water entering streams during the following hydrologic event (Laudon, 2008 and literature cited therein). The deposition of sea salts contributes by displacing H^+-ions or aluminium from acidified soils (Hindar et al., 1995). Soils remain sensitive to such effects due to the persistence of base-cation depletion. Sensitive aquatic organisms do not tolerate these acidic pulses and consequently disappear. Recolonization usually is not a straightforward process and takes time (Yan et al., 2003), and thus benthic communities indicate acid conditions even when samples are taken months after an acid episode. The focus on biological recovery is relevant within the context of the EU Water Framework Directive, where a biological monitoring

---

* Tel.: +47 98294098.
E-mail address: susi.schneider@niva.no.

0048-9697/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.scitotenv.2010.11.019

system is needed that detects differences in fauna and flora compared to undisturbed reference conditions (EC, 2000).

Schneider and Lindstrøm (2009) developed an indicator system based on non-diatomaceous benthic algae to characterize mean annual river acidity in Norway. In addition to a dose-response relationship, as established by Schneider and Lindstrøm (2009) for periphytic algae composition and river pH, the Water Framework Directive (WFD) requires that the actual value at a sampling site is to be compared to the expected value that would be present if the site was unimpacted. The expected value can differ with river type, since both natural and anthropogenic impacts can influence river acidity and benthic algae species composition. Here we analyze the impact of calcium and total organic carbon (TOC) on acidification assessment and present a river type specific, WFD compliant system based on non-diatomaceous benthic algae which can be used for assessment of river acidification in Norway.

2. Materials and methods

In order to compare the acidification index periphyton (AIP) at reference sites and non-reference sites, 606 samples from 313 unlimed river sites throughout Norway with data on water chemistry and benthic algae species composition were used. All samples were collected in the context of numerous projects between 1976 and 2009 and the results are stored in the periphyton database of the Norwegian Institute of Water Research (NIVA). Water chemistry samples were taken at the sampling sites between 1 and 24 times per year and the results are stored in the NIVA database. Water chemistry was analyzed according to Norwegian standard procedures during all years. Site-specific, mean annual water chemistry data for the 1 year previous to the benthic algae sampling were used to characterize pH, color, Ca and TOC (total organic carbon) concentration. For the samples where only color has been measured TOC concentration was estimated from color by using a linear correlation established from 186 samples from 98 sites where data for both TOC and color exist (Pearson $r = 0.91$, $p < 0.001$).

Benthic algae, i.e., algae that live attached to the river bottom or in close contact on or within patches of attached aquatic plants, were surveyed once between July and November according to the established method in Norway (Lindstrøm et al., 2004) along an approximately 10 m length of river bottom using an aquascope. At each river site, visible benthic algae were collected and stored separately in vials. Microscopic algae were collected from 10 stones, with diameters ranging between 10 and 20 cm, taken from each sampling site. An area of about 8×8 cm from the upper side of each stone was brushed with a toothbrush to transfer the algae into a beaker containing approximately 1 l of river water and a subsample was taken. All samples were preserved with a few drops of formaldehyde. The preserved benthic algae samples were later examined under a microscope, and determined to species level, if possible. The AIP was calculated according to Schneider and Lindstrøm (2009).

For characterizing river type, total organic carbon concentration (TOC) and calcium concentration (Ca) were used, in accordance with System A for rivers in the Water Framework Directive (EC, 2000). Each variable was coded into three categories according to Table 1. For three reference samples water chemistry data from the year before the biological sampling did not exist, but instead from few years before or after the biological sampling. In these cases, the water chemical data were not used for correlation analyses, but they were used to categorize river type by using the categories given in Table 1. Where several samples from different years existed from the same site, average values per site were used.

Table 1
Categories used for river typology.

	1	2	3
TOC	<2 mg TOC/l	2-5 mg TOC/l	>5 mg TOC/l
Ca	<1 mg Ca/l	1-4 mg Ca/l	>4 mg Ca/l

A Kruskal-Wallis test was applied to detect significant differences in AIP between typology categories. For pairwise comparisons between groups, Mann–Whitney *U* tests were used, and to correct for multiple testing, a Bonferroni correction with the refinement of Holmes was applied (Stahel, 1995; Bärlocher, 1999). Pearson product–moment correlation was applied to test for correlations between TOC and color, and Spearman correlation analysis was used to test for correlations between AIP and the typology categories. All tests were performed with the program STATISTICA 9.1.

The correlation between pH and Ca concentration for reference sites was fitted to an exponential model of the form $\mathrm{pH} = a^*(b - \exp(c^*\mathrm{Ca}))$. A linear model of the type $\mathrm{pH} = a + b^*\mathrm{Ca} + c^*\mathrm{TOC} + d^*\mathrm{Ca}^*\mathrm{TOC}$ was applied to the reference sites where data for pH, Ca, and TOC exist. All modeling was performed with the program R 2.5.0.

3. Screening of reference sites

Assessment systems compliant with the demands of the WFD are required to compare the actual value at a sampling site to an expected value that would be present if the site was unimpacted. This expected value can either be derived theoretically or from reference sites. Reference sites therefore play a crucial role for the assessment system, and special attention was given to the selection of reference sites prior to the analyses of the biological data.

Possible reference sites in Norway were investigated by Schartau et al. (2007) and Schartau et al. (2009). These authors selected, based on data on critical load of acid deposition, water chemistry, and expert opinion, 249 river water bodies as possible references in Norway. Sixty-seven benthic algae samples from 35 river sites from the NIVA database belong to these possible reference water bodies. Since reference sites play such a crucial role in WFD compliant assessment systems, additional criteria were applied to these 35 sites in order to either verify that they represent “true reference sites” or reject questionable reference sites, when necessary. In order to ensure that the phytobenthic algae communities truly represent undisturbed communities, reference sites must not be impacted by any significant non-natural disturbance. The absence of obvious disturbances for the reference sites used in this study, such as mining, waste water treatment plants, factories, or intensive land use, was verified by Schartau et al. (2007, 2009). For the two most important impacts in Norway, eutrophication and acidification, the following additional criteria were applied.

3.1. Additional validation with respect to eutrophication

As an indicator of eutrophication, total phosphorus concentration was used. Sites with a mean annual TP concentration above 7 μg/l were excluded as reference sites. The threshold of 7 μg TP/l for clear water sites is in accordance with the classification of freshwater which has formerly been used in Norway (SFT, 1997). For sites with a mean TOC concentration above 5 mg/l a threshold of 10 μg/l TP was used, because TP content of humic waters is naturally higher (Meili, 1992). One sample was excluded from the list of reference sites after this eutrophication check.

3.2. Additional validation with respect to acidification

Finding reference sites which were not impacted by acidification was exceptionally difficult, since large parts of Norway were exposed to heavy acidification during many decades (Larssen et al., 2008). The only parameter for which enough data were available to allow for a validation of possible reference sites was pH. Mean annual pH, however, is not necessarily an indicator of acidification, since the