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Should a water colour parameter be included in lake total phosphorus prediction models used for the Water Framework Directive?

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A R T I C L E I N F O

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A B S T R A C T

Under the Water Framework Directive (WFD) lakes are classified according to a variety of criteria. This classification facilitates state of the environment assessments and helps identify work needed to achieve the objectives of the WFD, which are broadly to maintain and/or restore water quality and ecological status at a level recognised as good or high. To achieve high or good status, lakes must meet a criterion for total phosphorus (TP) that is linked to a predicted reference condition value that is derived by various models. Lakes which fail to meet good status may require expensive remedial actions to be undertaken, thus accurate identification of the reference condition TP concentration is vital for effective environmental management. However, the models currently employed could be improved for some regions, particularly those with carbon rich soils. By examining 19 reference condition lakes (i.e. lakes essentially non-impacted by humans) in peaty areas of Scotland, we found that a simple parameter linked to water colour and humic substances was a better predictor of TP than the currently employed models (R^2 0.585 vs $R^2 < 0.01$). Therefore, for Scotland and elsewhere, in regions with carbon rich soils and lakes with humic waters the TP predictive models could be improved by development and incorporation of a parameter related to water colour and humic components.

1. Introduction

Under the European Union's Water Framework Directive (WFD) (EC, 2000) lakes are classified for environmental status using a range of ecological and chemical water quality parameters. In many member states (i.e. EU member countries) part of the classification process involves assessing total phosphorus (TP) concentration against quality thresholds (corresponding to high, good, moderate, poor or bad status) that are determined according to a site specific or lake type specific TP reference condition. The TP reference condition is intended to reflect undisturbed or minimally impacted conditions (Stoddard et al., 2006). Lakes that do not meet the set criteria for TP cannot be classified as having good ecological status, which is one of the goals set for waterbodies under the WFD, thus failures may lead to environment improvement actions having to be undertaken. Under the WFD, TP reference conditions are commonly determined according to models developed by Cardoso et al. (2007) from a large dataset of >500 European reference lakes (lakes considered to have no or only very limited anthropogenic input of phosphorus) that were gathered together via the European Commission (EC) FP6 Project REBECCA (EC, 2005). The models attempt to take account of catchment geographical variables (geology, elevation, region) as well as lake characteristics (i.e. water depth, water chemistry and lake size/area). Differing models were derived for the various Geographical Intercalibration Groups (GIGs; i.e. regions established for the purposes of the WFD intercalibration exercise, see Van de Bund et al., 2004; Carvalho et al., 2008) and model subtypes for humic and non-humic water conditions were derived in an attempt to address the recognised (though poorly understood) potential influence of humic substances on nutrient levels and planktonic primary production (Cardoso et al., 2007; Nürnberg and Shaw, 1998). However, the dataset upon which the models were based did not include high elevation lakes (>800 m aod) and only a very limited number of lakes from peat-rich (or C rich) zones. Also, lakes with annual mean TP concentrations above 35 μg/L were excluded from the dataset even if they were otherwise identified as meeting reference condition criteria. Valid reasons were presented for this exclusion (Cardoso et al., 2007), but the consequence was that

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lakes with naturally high TP were under represented or absent in model development.

Assessment of the derived models against measured concentrations revealed that they were able to account for ~51% of the variance in TP concentrations for the lakes in the reference lake dataset, demonstrating that whilst they were more (or at least no less) powerful predictors than previous models based on diatom and chironomid data (Bradshaw and John Anderson, 2001; Brooks et al., 2001) they did have a degree of remaining uncertainty (Cardoso et al., 2007). This left the model developers to conclude that further validation and testing of the models was needed, perhaps using independent test sets of lakes at reference condition.

The Northern and Atlantic TP predictor models are used in Scotland and the non-humic model (Eq. (1)), employing elevation (altitude) and morphoedaphic index as independent predictors, is currently applied for the derivation of reference TP conditions for lakes in Scotland (which are generally referred to as 'lochs') under WFD where sufficient data allow (Scottish Government, 2009). Morphoedaphic index is the ratio between total dissolved solids (edaphic factor) in lake water (as measured by alkalinity, m equivalents/L) to the lake mean depth in metres (morphometric factor) (Cardoso et al., 2007). The humic version of the model (Eq. (2)) is not currently used for WFD purposes in Scotland (Scottish Government, 2009), but with a better understanding of how humic substances influence TP levels in natural settings it may be possible to derive an improved model that successfully incorporates a humic related parameter. One additional impediment to such improvements is the lack of standardisation in humic water definitions and thus identification of exactly where a humic model should apply (see Table 1).

$$\text{Non humic model}: \text{Log}\,(\text{TP}) = 1.36(0.03) - 0.09(0.02)\,\text{Log}\,(\text{alt}) + 0.24(0.06)\,\text{Log}\,(\text{MEI}_{\text{alk}}) \quad (1)$$

$$\text{Humic model}: \text{Log}\,(\text{TP}) = 1.62(0.12) - 0.09(0.02)\,\text{Log}\,(\text{alt}) + 0.24(0.06)\,\text{Log}\,(\text{MEI}_{\text{alk}}) \quad (2)$$

where TP = total phosphorus, μg/L; alt = altitude or elevation, m; MEI_{alk} = Morphoedaphic index.

Models are valuable for environmental regulation of waterbodies because they are simple to implement and are generally based on comprehensive supporting data, such as the large (>500 EU lakes) dataset. However, whilst useful, the existing TP models could be improved (i.e. in terms of predictive strength) for some EU member states because of local or regional factors. For example, in Scotland there are many upland regions and areas with highly C rich soils and peat that may influence the natural levels of phosphorus present in lochs. According to the WFD 2010 loch classifications (SEPA, 2012) 62 Scottish lochs failed to meet the TP standard for good status, which in each case could potentially necessitate development and implementation of remedial action (i.e. environment improvement actions). Therefore, if TP reference conditions are underestimated by the predictor models the failing lochs may have their status incorrectly downgraded and, if so, any corrective action undertaken may not be truly warranted or even desirable (i.e. in terms of natural ecology of a site).

Table 1
Humic water classification systems as defined by different regimes.

	GIG inter-calibration lake type[a]	Scottish directions 2009[b]
Units	Hazen (Hz), mg Pt/L	Annual mean dissolved organic carbon (DOC), mg/L
Non-humic	<30	<5
Humic	>30	≥5

[a] Van de Bund et al. (2004).
[b] Scottish Government (2009).

In this study we examined the utility of the currently employed clear model and the humic alternative for predicting TP reference conditions in Scottish lochs by first investigating the predicted vs measured TP concentrations in 19 lochs that are at reference condition (i.e. close to pristine). We then assessed the possible utility of an additional model parameter linked to humic substance concentration: water colour and/or UV–vis light absorbance and/or dissolved organic carbon, DOC, the relationships between which have been demonstrated in freshwater lakes (e.g. Nürnberg and Shaw, 1998) and have been successfully exploited in other fields (e.g. Farmer et al., 2002; Graham et al., 2006; Jackson et al., 2005; Oliver et al., 2008). Finally, based on loch water characteristics, we assessed how applicable an expanded model may be for all WFD-classified lochs in Scotland. Given the widespread and increasing use of predicted reference nutrient conditions within environmental assessment programmes, e.g. within the EU (EC, 2000; Phillips et al., 2008), USA (USEPA, 2000) and recently China (Huo et al., 2011), wide applicability of our results is anticipated.

2. Methods

2.1. Reference condition lochs and current model evaluation

A set of 19 reference condition lochs (Fig. 1 and Table 2) from peat or C rich soil areas was identified from the network of lochs monitored by the Scottish Environment Protection Agency (SEPA). Because of the monthly monitoring programme, sufficient measured TP and associated data were available for each loch to satisfy the original data requirements used in the compilation of the larger European reference lake dataset (Cardoso et al., 2007). TP data for the 19 reference lochs, primarily within the years 2007–2009, were extracted from the water monitoring archive and evaluated against the TP reference conditions predicted by the models (Eqs. (1) and (2)). To maintain consistency with the original data specifications employed in derivation of the prediction models (Cardoso et al., 2007), data from the April–September time period was used to calculate average values for the lochs. The analytical method used to determine TP followed standard methods (GB-SCA, 1992) and was supported by full laboratory QA/QC measures and United Kingdom Accreditation Service (UKAS) accreditation. All reagents used were of analytical grade.

2.2. Hazen and UV–vis absorbance unit inter-conversion

For sites to be categorised according to the GIG-IC lake typologies (Table 1) and thus allow assigning to humic categories to facilitate assessment of the TP predictor models, an equation was derived for inter-converting colour in Hazen units (now largely historical) with UV–vis absorbance units at 254 and 400 nm wavelengths (i.e. the SEPA national colour determination method, following GB-SCA, 1984). The Hazen standard unit is defined as the colour produced by 1 mg/L platinum (Pt) in the form of chloroplatinic acid (H_2PtCl_6) in the presence of 2 mg/L cobaltous chloride hexahydrate ($[CoCl_2(H_2O)_4]\cdot 2H_2O$) (GB-SCA, 1984). A 100 Hazen standard (5.12×10^{-4} M Pt) in a 50 mm cell has an absorbance at 400 nm of 0.4515 a.u., which can be used to determine the molar absorptivity using the Beer–Lambert Law: $A = \varepsilon \cdot c \cdot l$ (where A = absorbance, ε = molar absorptivity in L/mol/cm, c = molar concentration and l = light path length in cm). This yields a molar absorptivity of