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Surrogate measures for providing high frequency estimates of total phosphorus concentrations in urban watersheds

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ABSTRACT

Until robust *in situ* sensors for total phosphorus (TP) are developed, continuous water quality measurements have the potential to be used as surrogates for generating high frequency estimates. Their use has widespread implications for water quality monitoring programmes considering that TP, in particular, is generally recognised as the limiting factor in the process of eutrophication. Surrogate measures for TP concentration, such as turbidity, have proved useful within natural and agricultural contexts, but their predictive capability for urban watersheds is considered more difficult, due to the different sources of TP, though a strict relationship with turbidity/suspended matter has been clearly described even for these environments. In this context, we investigated this still unresolved problem for high frequency estimation of TP concentration in urban environments by monitoring a medium-sized (71 km^2) urban watershed (Lambro River watershed, north Italy) in which we detected 60 active combined sewer overflows, and an its natural sub-basin for comparison. We found two different relationships between turbidity and TP concentration in the investigated urban watershed that differently describe the prevalence of TP from point sources (domestic wastewaters) or diffuse origin (surface runoff). In this regard, we first characterise the prevailing sources of TP by using a marker for detecting domestic wastewater contamination (caffeine), then we describe the mutual relationships amongst the continuously monitored variables (in our case the occurrence of the First Flush and the clockwise turbidity/discharge hysteresis). Afterwards we discriminate, by observing variables that are continuously monitored (in our case, the discharge and the turbidity), amongst the continuous surrogate records according to their sources. In conclusion, we are able to apply the relevant turbidity/TP regression equations to each turbidity record and, thus, estimate the respective TP concentrations with high frequency. If traditional grab sampling techniques had been employed, the contributions of point sources (up to 34% across 237 monitored days) to the total estimated loads would not have been correctly evaluated, whilst the high frequency monitoring is able to catch the dynamics that occur over time scales of a few hours. We conclude that the reasonable uncertainty obtained in this study can be achieved in other urban watersheds, but further studies are required for watersheds of differing sizes and degrees of urbanisation.

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1. Introduction

Phosphorus is generally recognised as the limiting factor in the process of eutrophication and, therefore, is widely used as an indicator of the trophic conditions of lakes (OECD, 1982; Schindler et al., 2008). Restoration efforts that aim to control inputs from sources of phosphorus into watersheds (Goldman et al., 1993; Elser et al., 2007; Carraro et al., 2012a) are considered to be important strategies for decreasing the risk of cyanobacterial blooms in lakes (Carraro et al., 2012a,b).

Determinations of nutrient loads are typically based on the collection and analysis of grab samples in combination with instantaneous estimates of discharge, but the frequency and regularity of traditional sampling methods may not provide a good representation of the variations in constituent loading of P. This is particularly relevant in small watershed and in systems with flashy hydrology (Scholefield et al., 2005; Jones et al., 2012). For most water quality monitoring programmes, the frequency of grab sampling is determined by the balance between the resolution necessary to estimate accurate loads and the resource costs of sampling (e.g., Jones et al., 2012). Several Authors recommend high frequency, continuous monitoring to reduce the uncertainties in load calculations that result from infrequent sampling efforts and biased estimation methods (Quilbe et al., 2006; Johnes, 2007; Jones et al., 2012). A large proportion of annual phosphorus loads may be exported during short periods of high flows (Grayson et al., 1996; Demars et al., 2005). Moreover, whilst these research and monitoring efforts are episodically intensive, they generally have been too limited in their temporal and spatial scales to adequately address the factors that influence the development of detrimental events such as harmful algal blooms, oxygen depletion and fish kills (Glasgow et al., 2004).

In many situations, turbidity (TURB) has been used as a surrogate measure for the concentration of suspended solids as well as constituents such as total phosphorus (TP) that may be associated with suspended matter. The justification for the choice of this proxy is that: (i) the attenuation of light by a sample of water should be related to the amount of fine suspended material in the water, and (ii) most of the TP transported in streams is in a particulate form and attached to fine suspended material (Grayson et al., 1996; Stubblefield et al., 2007). However, these surrogate relationships are site-specific (Grayson et al., 1996; Tomlinson and De Carlo, 2003) and depend greatly on the source of sediment. Grayson et al. (1996), Kronvang et al. (1997), Stubblefield et al. (2007) and Jones et al. (2011) reported significant and high TURB/TP correlations both in natural and agricultural watersheds. Rasmussen et al. (2008) observed that non-urban sites present the highest correlations, whilst Miguntanna et al. (2010) highlighted a direct TURB/TP correlation for an urban watershed. Grayson et al. (1996) suggested that some of the outliers in the TURB/TP relationship could be attributed to "First Flush" events of urban stormwater. According to these studies, the TURB/TP relationship for an urban watershed seems more complex because it is influenced by additive factors (mainly organic matter of anthropogenic origin) than for a natural watershed (mainly mineral particles as clay, amorphous oxides as iron oxo-hydroxide, etc.), as described by Oliver et al. (1999). In summary, whilst in literature TURB has been found to be a suitable proxy for TP concentration in some natural and agricultural watersheds, its adequacy for urban environments still requires further insights. Furthermore, considering that nearly all European rivers drain populated areas, the need to understand the contributions from both diffuse and point source pollution has long been recognised (e.g., Demars et al., 2005).

The objective of this study is to develop a method for estimating TP concentrations with a high frequency in urbanized watersheds. A completely forested watershed and one urbanized have been continuously monitored with the same experimental design to evaluate potential discrepancies in the behaviour of surrogate measures in the estimation of TP concentration between these two environments. The suitability of potential explanatory variables that have been continuously monitored as surrogate measures for TP concentration in the Lambro River, Northern Italy is evaluated. We first evaluate the effectiveness of surrogate relationships for TP concentrations. Then, we investigate the different sources of particulate matter (using Principal Component Analysis) and attempt to classify samples according to their source (using Quadratic Discriminant Analysis and the Support Vector Machines). We conclude by discussing the applicability of this surrogate method to urban systems and suggesting potential improvements to our approach.

2. Material and Methods

2.1. Site description

The Lambrone watershed (71 km^2) is situated on the southern edge of the Alps (northern Italy) between the two branches of Lake Como (Lombardy Region) (Fig. 1). The main watercourse is the Lambro River, which is also the main tributary of Pusiano Lake. This is a medium-sized subalpine lake (Buraschi et al., 2005). The lake TP concentration increased until the mid-1980s (0.2 mg P/L at the 1984 winter overturn) and has progressively decreased towards the mesotrophic conditions (TP concentration 0.039 mg P/L at the 2013 winter overturn) since the construction of a wastewater treatment plant (WWTP) in 1985. Despite the improvement in the lake's trophic conditions, several cyanobacterial blooms have caused ecological problems, particularly those of the filamentous cyanobacterium *Planktothrix rubescens* (Carraro et al., 2012a,b).

The precipitation in this area is concentrated in spring and autumn and tends to increase progressively, from 1500 mm/yr to 2000 mm/yr, from south to north along the altitudinal gradient of the watershed (Salerno and Tartari, 2009). The soils of the Pusiano watershed belong to the following 4 groups in accordance with the WRB1998 classification system (FAO, ISRIC, ISSS, 1998): Leptosols, Regosols, Cambisols and Phaeozems (Salerno et al., 2014a,b). The elevation ranges from 282 to 1450 m a.s.l. (above sea level), with a mean slope of 24.2°. The basin's corrivation time, indicating the susceptibility of the basin on a temporal scale to a flash flood response (i.e., the hydrological response), is 4 h. The mean discharge calculated over the last 10 years is 1.6 m^3/s (Salerno and Tartari, 2009).