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Review

# Real-time monitoring of nutrients and dissolved organic matter in rivers: Capturing event dynamics, technological opportunities and future directions

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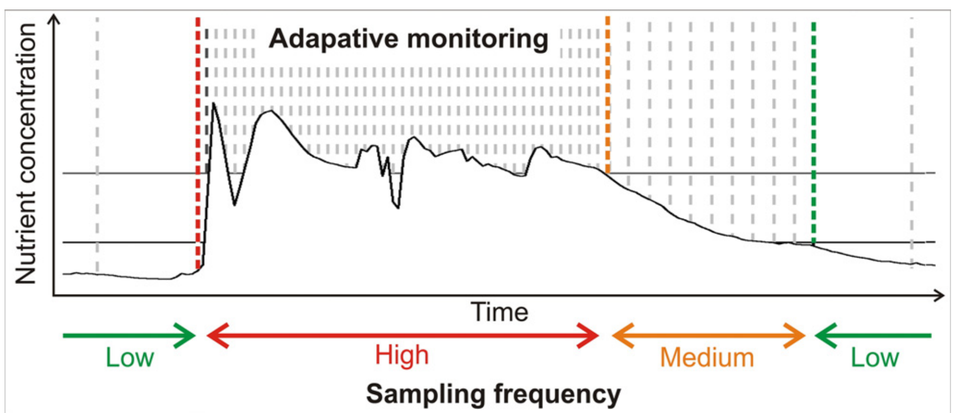
## HIGHLIGHTS

- In-situ river nutrient monitoring offers new insights into catchment processes.
- Real-time adaptive sampling provides data during biogeochemically active periods.
- This approach captures hot moments in nutrient dynamics and reduces data redundancy.
- New technologies may increase the coverage of nutrient sensors in river catchments.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Excessive riverine nutrient concentrations threaten aquatic ecosystem structure and functioning and can pose substantial risks to human health. Robust monitoring strategies are therefore required to generate reliable estimates of river nutrient loads and to improve understanding of the catchment processes that drive nutrient fluxes. Furthermore, these data are vital for prediction of future trends under changing environmental conditions and thus the development of appropriate mitigation measures. In recent years, technological developments have led to an increase in the use of in-situ nutrient analysers, which enable measurements at far higher temporal resolutions than can be achieved with discrete sampling and subsequent laboratory analysis. In this paper, we review the principles underlying the key techniques used for in-situ nutrient monitoring and highlight both the advantages, opportunities and challenges associated with high-resolution sampling programs. We then suggest how adaptive monitoring strategies, comprising several different temporal sample frequencies, controlled by one or more 'trigger variables' (e.g. river stage, turbidity, or nutrient concentration), can advance our understanding of catchment nutrient dynamics while simultaneously overcoming many of the practical and economic challenges encountered in typical in-situ river nutrient monitoring applications. We present examples of short-

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DOM
Sensor

term variability in river nutrient dynamics, driven by complex catchment behaviour, which support our case for the development of monitoring systems that can adapt in real-time to rapid changes in environmental conditions. Finally, we suggest future research directions based on emerging technologies in this field.


**Contents**



## 1. Introduction

Rivers transport and transform nutrients between terrestrial, aquatic, marine and atmospheric systems, thereby playing a key role in global biogeochemical cycling (Ensign and Doyle, 2006; Battin et al., 2008; Hood et al., 2015). Any increase in river nutrient concentrations, whether as a consequence of farming practices or urbanisation, may have substantial implications for aquatic ecosystem structure and functioning (Smith and Schindler, 2009). Eutrophication can result in algal blooms that decrease dissolved oxygen levels, change pH balances, and increase water turbidity. Such changes will impact river habitat and biodiversity, particularly the abundance of sensitive aquatic species (Camargo et al., 2005; Friberg et al., 2010). High river nutrient concentrations may also affect human health and well-being by threatening aquatic ecosystem services, such as freshwater provision for drinking and irrigation, maintenance of fisheries for food, recreational opportunities and aesthetic qualities such as taste, colour or odour (MEA, 2005; Bennett et al., 2009). Nitrate concentrations >50 mg $L^{-1}$ in drinking water can cause methemoglobinemia in humans, particularly infants, and may be associated with other adverse health effects including cancer and diabetes (Ward et al., 2005). Consequently, drinking-water treatment plants incur higher costs to reduce excessive nutrient levels to within quality standards, with some organic carbon fractions reacting to form potentially mutagenic and carcinogenic disinfectant by-products during the treatment process (Carpenter et al., 2013).

The environmental impacts of excessive nutrient concentrations highlight the need to understand spatial and temporal variability in river nutrient dynamics. Effective nutrient monitoring strategies can support catchment management by detecting the impact of natural phenomena (e.g. drought) or anthropogenic activities (e.g. land-management practices or point discharges) on river water quality. The resulting information may also help in determining ecological flows and detecting suitable locations or times for water abstraction (Bartram and Rees, 1999; Palmer and Bernhardt, 2006). Long-term continuous datasets of river nutrient concentrations enable the assessment of patterns, trends, and shifts in system behaviour (Burt et al., 2010) and also improve our understanding of the relationships with catchment processes that drive such variability (Bowes et al., 2009). For example, nitrate concentrations measured in both UK and US rivers since the 1930s exhibit marked increases through the post-war period and coincide with increasing applications of inorganic nitrogen fertiliser to arable farmland (McIsaac and Libra, 2003; Burt et al., 2010). More recently, monitoring data have been used to investigate links between river nutrient fluxes and upstream watershed management, demonstrating the potential for land management practices to both elevate and alleviate river nutrient loading (Valiela and Bowen, 2002; Lassaletta et al., 2009). This information helps any assessment of the effectiveness of mitigation measures to counteract nutrient loading and support future decisions relating to land and river management (Bowes et al., 2009), particularly in the context of predicted future changes in climate that are expected to drive shifts in river nutrient loads (Whitehead et al., 2009). The importance of this is reflected in national legislation and multilateral agreements (e.g. European Union Water Framework Directive or WFD, 2000/60/EC) relating to monitoring, and in some cases also improving, the status of freshwater environments.

River nutrient monitoring has evolved over time from sporadic, adhoc, sampling of local rivers (e.g. Casey and Clarke, 1979) to the establishment of national river water quality data systems with standardised sampling protocols, such as the UK Harmonised Monitoring Scheme that commenced in the mid-1970s (Simpson, 1980) and the General Quality Assessment Scheme that operated from 1990 to 2009 (Environment Agency, 2016) to the implementation of multi-lateral agreements that standardise water quality assessment procedures across member states and, in some cases, across multi-national drainage basins (e.g. European Union WFD; Hering et al., 2010). Traditionally, the frequency and coverage of river water sampling has been constrained by practical issues related to the costs of field personnel and laboratory analysis. Autosamplers enable short-term increases in sampling frequency but have limited volumes and samples may degrade if not preserved or processed quickly (Bende-Michl and Hairsine, 2010). Consequently, the spatial and temporal resolutions of many river