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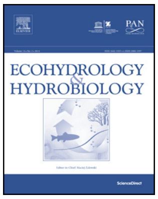

Original Research Article

Nitrates monitoring by UV–vis spectral analysis

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ABSTRACT

The monitoring of nitrates using the second derivative of UV–vis spectra has been tested for a large set of samples (≈900) covering a large range of freshwater environments in the Moselle River drainage basin (headwater streams in the Vosges Mountains; tributaries, including the Madon River and Vologne River; and waters of various origins exposed to anthropogenic activities in villages). Satisfactory linear correlations (coefficient of determination > 0.74) were obtained between nitrate concentrations (measured by ion chromatography with a conductivity detector) and the maxima of the second derivative in the UV range for sets of mesotrophic and eutrophic samples. The meaningfulness of the linear regressions was verified by applying a Fisher-Snedecor test using a level of confidence of 0.05. The quality of the correlation decreased when the samples came from oligotrophic environments due to the limited sensitivity of the ion chromatography technique. UV–vis spectroscopy combined with the second derivative method appears to be a good alternative for monitoring nitrate-related eutrophication in the laboratory as well as in situ using submersible spectrophotometers.

1. Introduction

Nitrates are of particular interest in aquatic ecosystems because they are linked, together with phosphates, to eutrophication. The atmospheric deposition of NH_3 and NOx, which are emitted by agriculture (fertilizers) and by the combustion of fossil fuels, contributes to the eutrophication of freshwater ecosystems (Hruška et al., 2012; Akelsson et al., 2013). Direct run-off of fertilizers from crop fields during intense rain events is another route by which nitrates are introduced into aquatic systems (Garnier et al., 2014; Pacheco and Sanches Fernandes, 2016; Rather et al., 2016; Lawniczach et al., 2016). Effluent from municipal wastewater treatment plants discharged into water bodies also contributes to nutrient loads (Aissa-Grouz et al., 2015; Teklehaimanot et al., 2015). Exploring the fate of carbon and nutrients at the watershed level is a necessary step toward understanding the carbon and nutrient cycles at a global scale under varying climate and hydrological conditions.

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Nitrates are also an issue in the provision of safe drinking water to populations as high concentrations of nitrates are susceptible to induce methaemoglobinaemia in children (WHO, 2011). The ecohydrological perspective of this on field monitoring is to allow a reliable and easy-to-maintain high frequency recording of the spatial and temporal variations of nitrate concentration in running waters, this at the watershed scale. The characterization of this spatial dynamics participates in the evaluation of the pressures but also to the natural processing capacities when comparing the values of concentrations with the land uses and their natural buffering capacities. This is the first step of the ecohydrology implementation strategy (Zalewski, 2015).

Colorimetric techniques have been available for years to quantify nitrogen species in the lab (Pappenhagen, 1958; Lambert and Zitomer, 1960), and automated systems operating in monitoring stations located on river banks have been proposed. There are issues related to the reaction time (which prevents high rate monitoring), the measurement range, the interference of water color and turbidity (Blaen et al., 2016) as well as to the management of reagents and waste. Ion-selective electrodes have been proposed for nitrates (Le Goff et al., 2003; Capella et al., 2013) and nitrites (Wang et al., 2016) in river samples, but concerns associated with drifting and biofouling are still high (Blaen et al., 2016) and may require regular replacement of sensors.

In parallel, optical techniques (UV–vis spectroscopy, fluorescence spectroscopy, etc.) are widely suggested for the monitoring of aquatic systems (Hou et al., 2015; Baker et al., 2015; Bridgeman et al., 2015; Murphy et al., 2015). These techniques allow scientists to rapidly obtain information on water quality, mostly related to dissolved organic matter, without the use of potentially toxic reagents. However, in the case of UV–vis spectra, inorganic ions such as nitrate (NO_3^-), nitrite (NO_2^-), bisulfide (HS^-), bromide (Br^-) or iodide (I^-) absorb in the UV range (below 300 nm) (Guenther et al., 2001). On-line monitoring of hydrogen sulfide in sewers has been proposed based on a submersible spectrophotometer (Gutierrez et al., 2010). In the case of nitrates, different wavelengths have been indicated in the literature for peak absorbance (Huebsch et al., 2015). Direct correlation between absorbance and nitrate concentration is possible but is often hindered by the presence of inorganic ions and organic substances that absorb in the UV range (Kröckel et al., 2011). The global NOx (i.e., nitrates + nitrites) concentration is sometimes preferred (Drolc and Vrtovšek, 2010) to avoid the difficulties of discriminating between these ion species. Turbidity might also be an issue for in situ applications when filtration cannot be applied prior to measurements (Zielinski et al., 2011). To circumvent these difficulties, multivariate calibration has been proposed that is based on different chemometric techniques. Partial least squares regression has allowed workers to estimate nitrates, as well as non-purgeable organic carbon, in groundwater (Dahlén et al., 2000). Principal component analysis (PCA) of UV–vis spectra has been proposed for detecting water quality anomalies due to the presence of organic contaminants in water distribution systems (Hou et al., 2015). PCA was also used to estimate nitrite concentrations in source-separated nitrified urine in the presence of large nitrate concentrations ($\approx 1\ g\ L^{-1}$) (Mašić et al., 2015).

Ferree and Shannon (2001) have evaluated the use of the second derivative of UV–vis spectra to estimate nitrate concentrations in constructed wetlands and wastewater samples. The method was initially proposed by Simal et al. (1985), but the addition of sulfamic acid to remove interference from nitrites prevented the on-line use of the method. Suzuki and Kuroda (1987) demonstrated that the method could be used without sulfamic acid, but the testing of real samples (rainwater) was limited. A larger set of 20 freshwater samples from lakes and rivers was later tested successfully by Wollin (1987). Since then, this method, which should be easily implemented using the computerized spectrophotometers that are available currently, does not seem to have received much interest. However, its application to on-line spectra collected by a submersible spectrophotometer in a periurban aquatic system has shown good agreement with dual-wavelength nitrate sensors (Namour et al., 2016).

Our purpose has been to test the second derivative method on a much wider range of freshwater and groundwater samples ($\approx$900) covering a wide range of statuses (from oligotrophic to eutrophic) and concentrations ($0–60\ mg\ NO_3\ L^{-1}$) in the presence of possibly interfering substances (ions, organic matter) to better evaluate its potential for high rate monitoring of rivers.

2. Materials and methods

2.1. Sampling

All the samples were collected from the Moselle River drainage basin (Fig. 1). The Moselle River is a tributary of the Rhine River having its source near the Bussang Pass in the Vosges Mountains.

Since 2011, 16 headstreams, flowing over granite and sandstone bedrock, have been sampled monthly. Upstream of the sampling points, the land is occupied by forests

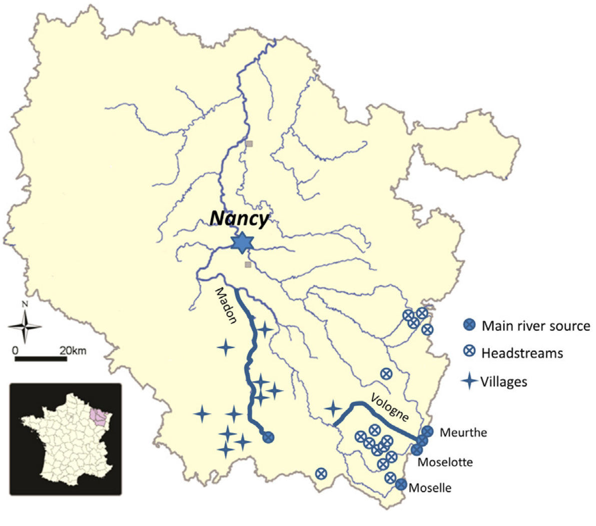

Fig. 1. Sampling sites.

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