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Stability of spatial patterns in water chemistry across temperate ecoregions

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Abstract

Human activity has polluted freshwater ecosystems across the planet, harming biodiversity, human health, and the economy. Improving water quality depends on identifying pollutant sources in river networks, but pollutant concentrations fluctuate in time. Continuous monitoring of many points in river networks is expensive, impeding progress in developing countries where water quality is degrading fastest. In this study, we analyzed 4523 water chemistry time series of ten parameters (NO_3^-, PO_4^{3-}, TP, DOC, SO_4^{2-}, Cl^-, Na^+, Ca^{2+}, Mg^{2+}, K^+) across four temperate ecoregions in France (ca. 560 000 km^2). We quantified the spatial stability of water chemistry across the monitoring stations using rank correlations between instantaneous concentrations and water quality metrics derived from 6-year time series (2010–2015). The strength of this rank correlation represents how well a water quality evaluation metric can be characterized with a single sampling for a given water quality parameter. Results show that a single sampling captured a mean of 88% of the spatial variability of these parameters, across ecoregions with different climate and land-use conditions. The spatial stability resulted both from high spatial variability among sites and high temporal synchrony among time series. These findings demonstrate that infrequent but spatially dense water sampling can achieve two of the major goals of water quality monitoring: identify pollutant sources and inform ideal locations for conservation and restoration interventions.

1. Introduction

Water pollution kills approximately 1.8 million people every year (Landrigan *et al* 2018) and degrades ecosystem functioning at a global scale (Foley *et al* 2011, Steffen *et al* 2015). In addition to pollutants that directly harm human health such as waterborne pathogens and toxins, excess nutrients from agriculture and urbanization can trigger cyanobacterial blooms and dead zones in freshwater and marine environments (Heathwaite 2010, Vorosmarty *et al* 2010, Elser and Bennett 2011, Sutton *et al* 2011, Van Meter and Basu 2017, Xie and Ringler 2017). These symptoms of over-fertilization, collectively known as eutrophication, affect two-thirds of freshwater and estuarine water bodies globally (Diaz and Rosenberg 2008, Conley *et al* 2009, Le Moal *et al* 2019).

In response to these water quality crises, national and international agencies invest billions of dollars annually in water quality monitoring (Hering *et al* 2010). These monitoring efforts are often designed to identify pollution sources and assess compliance with environmental legislation (Heathwaite 2010, Hering *et al* 2010, Skeffington *et al* 2015). Because water chemistry varies widely on event, seasonal, and inter-annual timescales (Kirchner and Neal 2013, Isaak *et al* 2014, Dupas *et al* 2018, Abbott *et al* 2018b), most monitoring frameworks sample locations repeatedly, in some cases nearly continuously (Jordan *et al* 2007, Skeffington *et al* 2015, Rode *et al* 2016, Bieroza *et al* 2018, Fovet *et al* 2018). While these high-frequency datasets can reveal important ecological dynamics (e.g. catchment and in-stream biogeochemical processing),

they are also expensive, precluding widespread deployment especially in developing countries, where water quality is degrading fastest (Crocker and Bartram 2014) and where poor water quality has the most direct consequences for public health (Landrigan *et al* 2018). In this context, it is a global priority to quantify water quality status as efficiently as possible (Crocker and Bartram 2014, Skeffington *et al* 2015).

We addressed this monitoring conundrum with an analysis of water chemistry time series from 4523 monitoring stations in France. We quantified the spatial stability of water chemistry across the monitoring stations using Spearman's rank correlations between instantaneous concentrations and water quality metrics derived from 6-year time series at each station. The strength of this rank correlation represents how well a water quality evaluation metric can be characterized with a single sampling for a given water quality parameter (Abbott *et al* 2018a). We analyzed 10 publicly available parameters, including nutrients associated with anthropogenic activity (NO_3^-, PO_4^{3-}, total phosphorus, and dissolved organic carbon), weathering products and atmospherically deposited solutes (SO_4^{2-}, Cl^-, Na^+, Ca^{2+}, Mg^{2+}, and K^+) (Moatar *et al* 2017). We compared concentrations of the ten parameters with three commonly used water quality metrics extracted from the time series: median concentration, 90th percentile concentration, and discharge-weighted concentration (Skeffington *et al* 2015). The objective of our study was to test whether a single sampling at multiple locations could capture the spatial variability of water chemistry at large scales, evaluating how well temporally sparse but spatially extensive water sampling could identify pollutant sources in a cost-effective manner.

2. Data and methods

2.1. Data extraction

We selected 4523 water quality stations, among the 16 852 present in the French public database (http://naiades.eaufrance.fr/) based on the two criteria:

(1) They had at least 4 years of data from 2010 to 2015.

(2) They had at least 30 sampling dates for the water quality parameters NO_3^-, PO_4^{3-}, total phosphorus (TP), dissolved organic carbon (DOC), SO_4^{2-}, Cl^-, Na^+, Ca^{2+}, Mg^{2+}, and K^+.

These 4523 water quality stations were distributed within four temperate ecoregions: Atlantic (2509), Continental (1608), Mediterranean (279), Alpine (125). 702 water quality stations were located near a discharge station (figure 1), 94% of which included sampling dates in all ten deciles of discharge (i.e. they captured more than 90% of the observed range in water flow). Sampling frequency was typically monthly, though some stations were sampled every two weeks. Catchment sizes ranged from $<10\,km^2$ to $>10\,000\,km^2$ (figure S1 is available online at stacks.iop.org/ERL/14/074015/mmedia) and the 702 catchments with discharge measurement were generally larger than the entire sample of 4523 catchments (median = 387 km^2 and 235 km^2, respectively).

2.2. Data analysis

We computed median and 90th percentile concentrations, both of which are used to assess the water quality status of water bodies as part of the European Water Framework Directive (table S1). We also calculated the discharge weighted concentration, which is a common metric of solute flux (Johnes 2007, Cassidy and Jordan 2011).

$$DWC = \frac{\sum_i Ci * Qi}{\sum_i Qi},$$

where Ci and Qi represent the concentration and discharge at the time of sampling.

Spatial stability describes the persistence of spatial patterns of water chemistry through time (Abbott *et al* 2018a). It is the product of spatial differences in concentration among sites and temporal variation of concentration of each individual site (figure 2), providing insight into basic ecosystem functioning and the hydrochemical footprint of human disturbance (Temnerud and Bishop 2005, Abbott *et al* 2018a). We quantified stability by comparing the ranks of individual sampling dates with the ranks of the three metrics using Sperman's correlations. A rank correlation of 1 indicates that it is possible to identify the relative water quality of all the stations from 2010–2015 time series, based on data from any individual sampling date (figure 2). Because sampling dates differed among water quality stations, we compared data sampled during the same month. When several samples were collected for one month, we selected one date randomly. All statistical analyses were performed with the R statistical software (R Development Core Team 2008).

Because the database included nested catchments, the monitoring stations are not spatially independent (Isaak *et al* 2014). We tested the influence of this spatial dependence by computing the rank correlations for three classes of independent catchments: $<100\,km^2$, 100–1000 km^2 and 1000–10 000 km^2.

We explored two hypotheses to explain high spatial stability (figure 2). First, temporal synchrony among catchments could preserve the relative ranking of solute concentration among stations through time (i.e. the time series of concentration cross less when they move up and down together; Erlandsson *et al* 2008, Abbott *et al* 2018a). To test this hypothesis, we quantified the temporal synchrony with Pearson correlations between 10 000 pairs of catchments among 4523^2

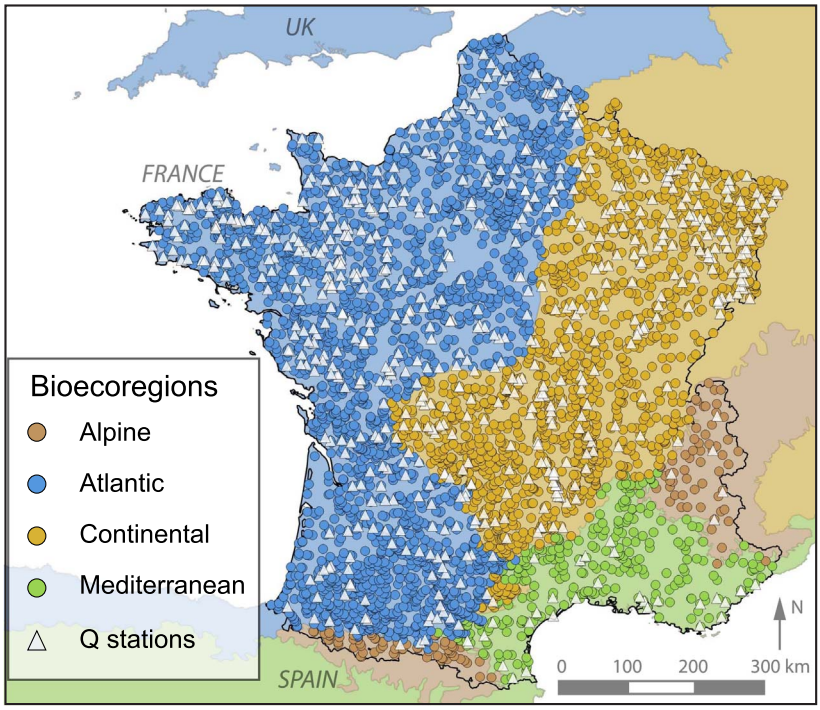

Figure 1. Location of 4523 water quality stations in France in four ecoregions. The triangles indicate where river discharge measurements (*Q*) were available.

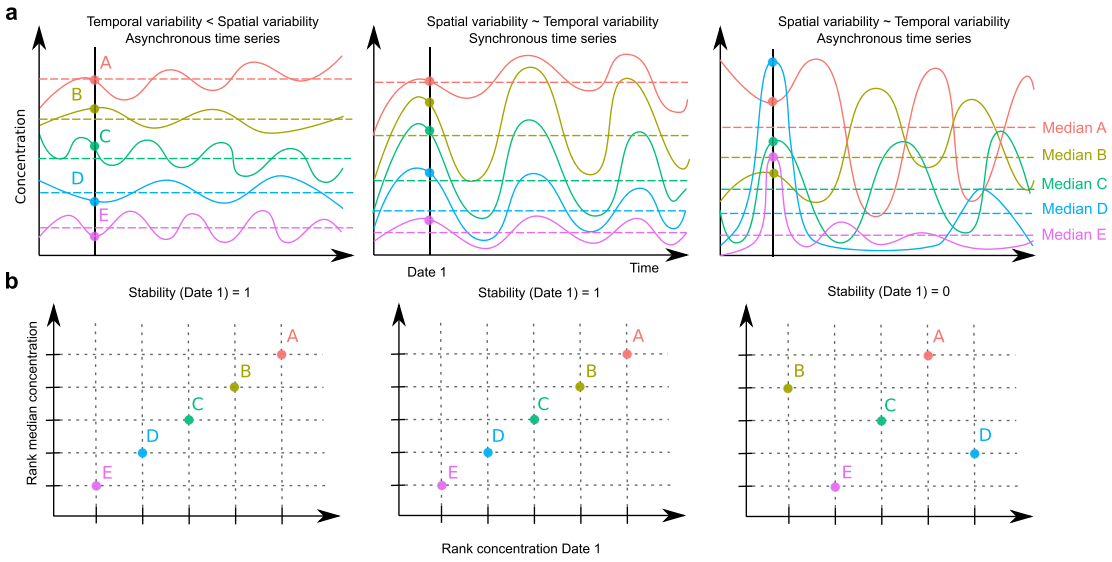

Figure 2. Conceptual figure of how spatial stability in water chemistry can result from high spatial variability or high temporal synchrony. (a) Three concentration time series for five simulated catchments (A–E). The vertical line represents the sampling date and horizontal lines represent median concentration for each catchment across the time series. (b) Spatial stability (Spearman's rank correlation between instantaneous and long-term median) for the three depicted scenarios.

possible pairs. Second, if there is higher spatial variability on concentrations than temporal variability, time-series cross less and the ranking of concentration among stations is preserved. We tested this hypothesis by quantifying spatial and temporal variability using the coefficient of variation (CV). We plotted median CV and an error bars representing 10th–90th percentiles.

3. Results and discussion

3.1. Spatially stable water chemistry across ecoregions

For all parameters and across all stations, average stability coefficients ranged from 0.83–0.97 for median concentrations, 0.80–0.96 for 90th percentiles, and

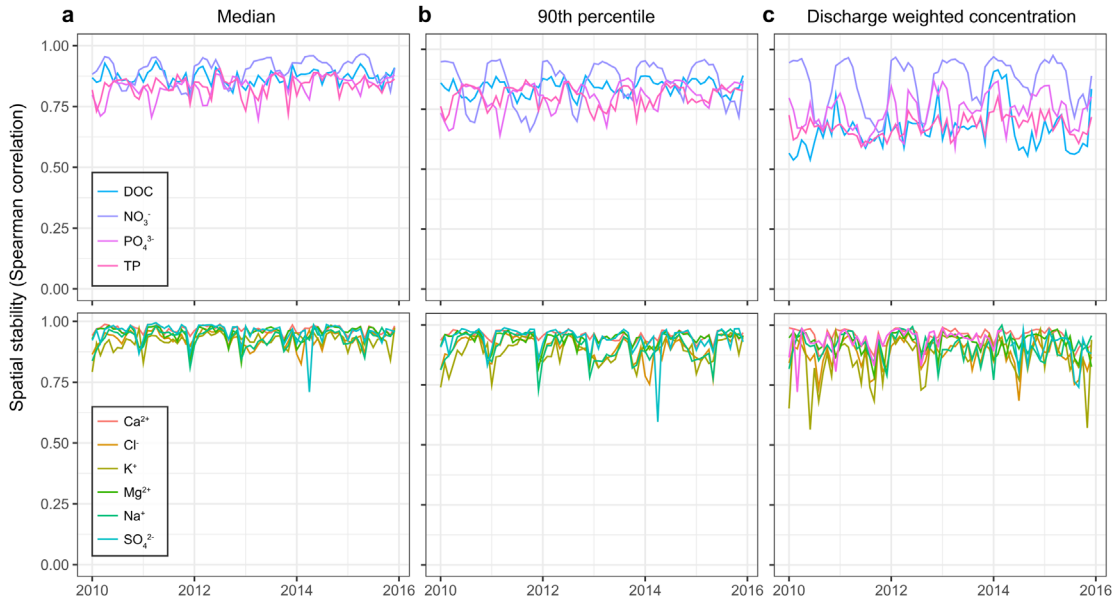

Figure 3. Spatial stability of three water quality metrics for ten water quality parameters. (a) median, (b) percentile 90th and (c) discharge weighted concentration.

0.68–0.95 for discharge weighted concentrations (figure 3). These high spatial correlations demonstrate that a single sampling can assess both the central tendency and extreme behavior of multi-annual water quality. For nitrate (NO_3^-), which alone causes 0.2–2.3 trillion USD of ecosystem damage annually (Sutton 2013, Bodirsky *et al* 2014), average stability coefficients were 0.90 for all of France and ranged from 0.85–0.92 for the four ecoregions (figure S2). While stability coefficients showed limited temporal variation for most parameters, they varied seasonally for NO_3^- and to a lesser extent phosphate (PO_4^{3-}), meaning that certain times of the year were more representative of the water quality metrics of interest for these parameters. The most representative period was similar among ecoregions (figure S2) but differed by water quality parameters and metrics (figures 3 and S2). For example, winter months were more representative of median NO_3^- while summer months were more representative of PO_4^{3-} 90th percentile (figure 3).

3.2. What causes spatial stability in water quality?

Two non-exclusive factors could contribute to spatial stability of water quality (figure 2). First, if spatial variability among multiple stations is much greater than the temporal variability of those stations (Hammond and Kolasa 2014, McGuire *et al* 2014), relative concentration rank would be stable. Second, if temporal changes are synchronous among stations (Dupas *et al* 2017, 2018, Abbott *et al* 2018a), coincident increases and decreases would preserve spatial patterns despite temporal variability. To test these hypotheses, we quantified the temporal synchrony among stations for each parameter with Pearson correlations between time series from pairs of monitoring stations—a proxy of temporal covariance (Abbott *et al* 2018a), and we compared the spatial and temporal variability with coefficients of variation. We found that both temporal synchrony (figure 4(a)) and high spatial variation (figure 4(b)) contributed to the observed spatial stability. While many parameters showed high temporal variability (median coefficients of variation ranged from 16% for Ca^{2+} to 62% for TP, figure 4(b)), spatial coefficients of variation were higher than temporal coefficients of variation across all water quality parameters (figure 4(b)). Temporal correlations (i.e. synchronies) were positive in 70% of catchment pairs (figure 4(a)).

Spatial stability of different water chemistry parameters was negatively correlated with temporal variability, but stability was not correlated with synchrony (figure S3). The mean synchrony coefficients estimated in the present study were lower than those observed at catchment scales for the same parameters (0.2–0.8 in Abbott *et al* 2018a versus 0.1–0.3 in this study). The reasons for this lower synchrony were likely the different sampling dates during the same month, and the large spatiotemporal variability in rainfall and catchments' responses to rainfall. We conclude that the influence of synchrony on spatial stability was weak at a national scale, compared to the high spatial variability. The effect of spatial nesting of upstream stations did not appear to influence estimates of spatial stability, which were similar for the catchment classes $<100\ km^2$, 100–1000 km^2 and 1000–10 000 km^2 (figure 5). The fact that spatial stability of discharge weighted concentration was notably lower for the catchment classes $<100\ km^2$ and 1000–10 000 km^2 can be explained by the low number of stations (figure S4(a)) and their relatively low spatial variability (figure S4(b)).

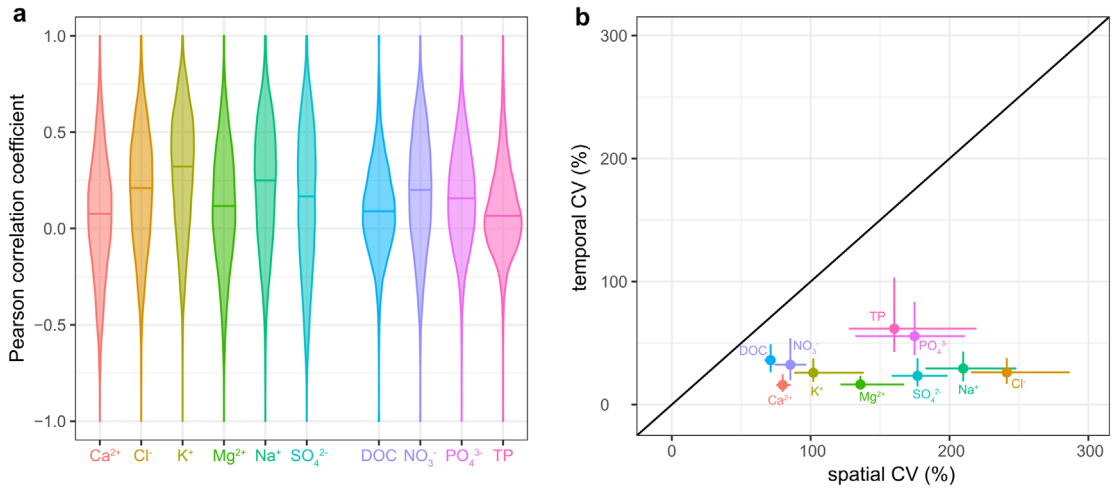

Figure 4. Spatial stability can be attributed to synchronous catchment dynamics and high spatial variability. (a) Temporal synchrony (Pearson correlation) of 10 000 pairs of monitoring stations in France. (b) Comparison of the temporal coefficients of correlation (CV) with the spatial CV calculated for each month from 2010 to 2015 (median and 10th–90th percentile).

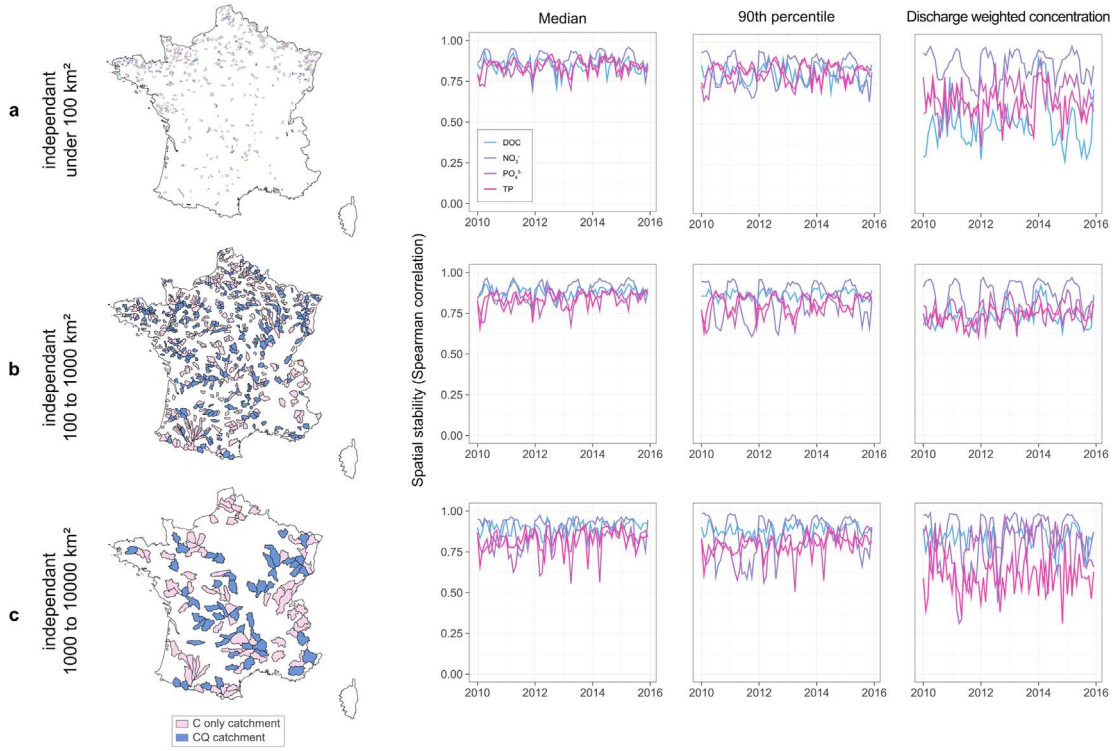

Figure 5. Spatial stability of three water quality metrics for three classes of independent catchments: (a) <100 km^2, (b) 100–1000 km^2 and (c) 1000–10 000 km^2.

3.3. Graduating from monitoring to managing global water quality crises

These finding are of ecological and practical importance because they demonstrate that that water quality can still be efficiently assessed with spatially extensive sampling throughout river networks even when distinct socio-ecohydrological dynamics are at play in different locations and scales. The diverse land-use and climatic conditions across the ecoregions did not decrease spatial stability, potentially because these same conditions increase absolute magnitude of spatial variation (Thomas *et al* 2016, Abbott *et al* 2018a). If spatial stability of water chemistry is a general phenomenon in freshwater landscapes of the Anthropocene, our findings have different applications for developed and developing countries. Water quality is generally improving in the developed world (Grizzetti *et al* 2012, Jarvie *et al* 2013, Dupas *et al* 2018, Abbott *et al* 2018b), while it is projected to

substantially degrade in developing countries (Seitzinger *et al* 2010, Crocker and Bartram 2014). In developed countries, reducing the routine monitoring frequency would allow an increase in the spatial extent and density of sampling or allow for a broader range of chemical analyses, including emerging pollutants, microbiological parameters, and more integrative ecological assessment (Landrigan *et al* 2018). In the developing world, infrequent but extensive synoptic screening could locate priority catchments which are either highly degraded and therefore candidates for restoration, or still pristine and therefore candidates for conservation (Abbott *et al* 2018a). It could also identify catchments that are resilient to anthropogenic nutrient loading, potentially allowing increased agricultural productivity without degrading water quality. In all socioeconomic contexts, these findings suggest ways that environmental agencies could reallocate resources for pollution monitoring and mitigation, if they decide to adopt a robust qualitative assessment instead of the current uncertain quantitative assessment.

We point out that the stability concept does not resolve the perennial issue of the large uncertainties encountered in quantitative water quality assessments when using medium-frequency monitoring (Skeffington *et al* 2015). However, because spatial stability, temporal variability, and temporal synchrony are easy to calculate with existing data, they can be quantified for many parameters of interest across a broad range of socioecological conditions. It would be particularly interesting to test the stability concept with compounds such as micro-pollutants, which are potentially more chemodynamic than the parameters included in this study, as figure S3 shows decreasing stability for increasing temporal CV. The increasing number of high-frequency monitoring datasets worldwide will also soon allow testing the stability concept with sub-hourly data. When spatial stability of water chemistry is detected, it could provide a shortcut to identifying compromised river reaches and pollutant sources, enabling efficient action on three of society's most urgent issues in the 21st century: loss of clean water for human use, degradation of aquatic habitat, and alteration of biogeochemical fluxes (Vorosmarty *et al* 2010, Elser and Bennett 2011, Sutton *et al* 2011, Landrigan *et al* 2018).

Data

Water quality data for France is publicly available at http://naiades.eaufrance.fr/.

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