Towards a new drinking water resource classification approach at a river basin scale
S. Piel, E. Baurès, S. Masclet, J. Perot and O. Thomas

ABSTRACT
This study proposes a new approach for improving resource quality management, monitoring and treatment plant management, whatever the environmental and climatic stressors. First trend analysis of water quality at a river basin scale, based on historical water quality data and multivariate exploitation (principal component analysis, PCA), led to a classification of the monitoring stations with regard to the main pressures (land use, urbanization and hydroclimatic impacts). This method was applied to the Vilaine’s watershed, the largest river basin in Brittany, western France, and one which is under agricultural and urban pressure. A complementary research using a UV index was proposed for the evaluation of spatial and temporal variations of water quality. This approach may be considered as a useful and relevant tool to quickly assess the variation of water quality and the main explanatory factors. It also points out monitoring stations under specific stressors considered as outliers regarding UV parameters. Finally, PCA and UV index give complementary results. PCA allows factors influencing drinking water resource to be highlighted and the UV index allows global water quality under specific times and impacts to be reflected.

Key words | risk situation, river basin, UV index, water quality, water resource

INTRODUCTION
Regulations on water quality in Europe have been strengthened since the end of the 1990s with the adoption by the European Commission (EC) of the Drinking Water Directive (Directive 98/83/EC) and the Water Framework Directive (Directive 2000/60/EC). These two directives established a framework to ensure safety for water intended for human consumption and to launch a policy of resource management and protection at a European level. In addition, a new kind of preventive approach for risk management has recently been initiated by WHO with the implementation of water safety plans (Bartram et al. 2009). This approach aims to introduce the concept of risk assessment and management throughout the cycle of water production.

In this way, a tool for water quality assessment was developed in France jointly by the Ministry of Ecology and six French Water Agencies, corresponding to the six metropolitan hydrographic watersheds, considering knowledge and regulation evolutions. The System for Evaluation of the Quality of Water (SEQ-Eau in French) is based on both the notion of indicators, groups of similar parameters, such as ‘organic matter’ (OM) or ‘nitrate’, and the requirements of the various uses, whether drinking water supply, irrigation, recreational, etc. (Oudin et al. 1999). The system is flexible and enables water quality to be evaluated according to the most relevant criteria for a given use. For instance, concerning drinking water production, the SEQ is divided into 14 indicators. For each one, according to a grid of concentration limits (consistent with European directives) defining five classes, colors are given for the considered sampling point: from blue for very good quality to red for very bad quality. It aims to assess the adapted type of treatment to be implemented: respectively disinfection, simple, classical and complex...
treatments. The last class, red, is considered as unsuitable for drinking water production.

Unfortunately this system is often used to make a yearly water quality assessment and only consider a mean value of monthly data. This method has the effect of smoothing data, and therefore specific events, like hydroclimatic ones, could be missed while the water quality could be degraded at these specific times (Delpla et al. 2009) when it needed an adaptation of treatments. Moreover, with regard to the micropollutants list, metabolites are not considered whereas they could be present at higher concentrations than parent compounds and in some cases be more toxic (Belfroid et al. 1998), or even be unknown. On the other hand, water treatment companies must comply with stringent legislation on water quality and also face emerging problems related to the continuous development of new chemicals in water, including pharmaceuticals and endocrine disruptors, the environmental and health effects of which are still poorly understood.

All these issues were once again highlighted on 22 February 2011, when the EC pronounced its conclusions about the need for a revision of the Drinking Water Directive (Directive 98/83/EC), concluding that no legislative revision of the Directive under the ordinary legislative procedure was required (DG Env 2011). Nevertheless a guide is being drafted to conduct risk assessment for small water supplies. Data exchange and reporting have to be reviewed, particularly in order to reduce the administrative burden. Moreover, improvement in quality compliance for drinking water especially from small suppliers is required, as well as a risk-based approach for more effective environmental and sanitary quality controls. Our study contributes to the reduction of the amount of water quality data by proposing a UV index approach and goes further by assessing the impact of specific events, especially hydroclimatic ones, on resource quality.

The main purpose of our study is to propose a new classification approach at a river basin scale according to global water quality and water quality variation factors, including hydroclimatic and pollutant discharge factors. The final goal is to improve resource quality management and monitoring, as well as treatment plant management, whatever the environmental and climatic stressors.

**METHODS**

**Methodology**

Two data exploitations have been carried out: (i) on historical results extracted from water quality databases (OSUR Web) and (ii) on experimental data gathered during two recent monitoring campaigns at a river basin scale, during dry and rainfall periods (Figure 1).

Statistical analyses, trend analysis and relations between parameters are conducted on historical data in order to classify stations regarding water quality variation factors, hydroclimatic conditions and pollutants discharge. 

Experimental data exploitation consists of *in-situ* measurements, basic physicochemical parameters and UV-visible spectra analysis (examination of spectra shapes and characteristic regions between 200 and 350 nm) in order to classify sampling stations according to their global water quality as studied with UV index during both campaigns.

The overall outcomes allow us to determine which factors are the main ones responsible for water quality variations in the watershed and what kind of impact they could generate on the UV index. Thus ‘At Risk Conditions’ (ARC), defined by quality parameter overruns or by risk to
consumer, could be assessed on each station and recommendations on water treatment could be drawn.

In the long-term, this study aims at knowing directly the global water quality of specific stations using a simpler method including UV indexes, and which then allows appropriate actions to be undertaken especially in drinking water treatment in order to protect the population.

Study site

Brittany is the primary agricultural region of France, especially in terms of animal farming for milk and meat, corn cultivation and vegetables crops. Thus its main industrial activity is the food industry, which represents 80% of French production (Institut d’Aménagement de la Vilaine 2003). Surface water accounts for 80% of the drinking water resource available in the watershed (Observatoire Eau Bretagne 2009). Brittany’s biggest watershed is the Vilaine basin, which covers two thirds of the region (10,500 km²). The main river is about 220 km in length from its source to its mouth, and crosses Rennes, a city of approximately 300,000 inhabitants. Furthermore, at the extreme downstream of the basin, the largest drinking water treatment plant (DWTP) of the region is located, with a nominal production capacity of 90,000 m³ per day.

Data acquisitions

Historical

Data are provided from the OSUR Web (Water Agency ‘Loire-Bretagne’) database for water quality, and from the Banque Hydro (Ministry of Ecology) database for river flows (Q), measured at the same nine limnimetric stations (Figure 2). The data acquisition covers the period 1971–2010. These nine stations were chosen because of their proximity to experimental ones (Figure 2), as well as their strategic localization on the main Vilaine basin and on the two main sub watersheds, the Meu and Oust rivers. Among the nine stations, three are located in the upstream part of the Vilaine basin (V1, V4 and V5), four in the downstream part (M12, V18, O19 and V25) and two downstream wastewater treatment plants.

Figure 2 | Sampling stations location.
(WWTP) (V2 and V8). The main WWTP is for 360,000 inhabitant equivalents (Rennes).

Before examining the main outcomes of this work, it has to be underlined that using a water quality database provided by a Water Agency monitoring program may lead to heterogeneous series because sampling frequency is variable depending on the monitoring station, and may be low for some of them.

Experimental

Thirty one sampling points, presented in Figure 2, were identified according to a preliminary study of land use: agricultural, industrial and urban activities were distinguished. Amongst them, in the upstream part of the basin, nine are located on the Vilaine (V1 to V17) and eight on tributaries: Cantache (C3), Ille (I6), Flume (F9), Meu (M10 to M12) and Seiche (S14 and S15). Then in the downstream part, six are located on the Vilaine (V18 to V30) and seven on tributaries: Oust (O19 to O24), Aff (Af20), Arz (Ar22) and Isac (Is26).

Complementary to the 39 years of water quality data exploitation, two sampling campaigns were carried out recently during a dry period (CDP), on 29 and 30 March 2011 and during a rainfall period (CRP), on 7 and 8 September 2010. Daily rainfalls were between 10 and 20 mm during CRP.

Parameters

During the two campaigns (CDP and CRP), some parameters were measured in-situ: pH, water and air temperatures (Tw, Ta), redox potential (RedOx), conductivity (Cond), dissolved oxygen (O2D), oxygen saturation rate (O2S) and turbidity (Turbi). After sampling, several basic physicochemical parameters were analyzed in the laboratory: dissolved organic carbon (DOC), total organic carbon (TOC), nitrate (NO3), nitrite (NO2), Kjeldhal nitrogen (KN), ammonia (NH4), total suspended solids (TSS), orthophosphate (PO4), total phosphorus (Pt) and chlorophyll A (ChlA). Associated flow rates (Q) were collected from the Banque Hydro database. All parameters are common with historical data and were measured with respect to standardized methods (AFNOR).

Moreover, a complementary laboratory measurement was realized on each sample: UV-visible spectra acquisition between 200 and 700 nm with a UV-visible spectrometer Perkin Elmer Lambda 35 (10 nm optical path length quartz cell, acquisition step: 1 nm, Scan speed: 1,920 nm/min). UV spectrophotometry is a simple analytical method for monitoring natural waters and effluents. It provides both quantitative and qualitative information on water quality of an aquatic system (Thomas & Burgess 2007).

The acquisition of UV-visible spectra was realized with an appropriate corrective dilution factor to avoid absorbance saturation. Thus, absorbance values were corrected by this factor before exploitation.

RESULTS AND DISCUSSION

Historical data

Trend analysis

Figures 3(a), (b) and (c) show the evolution of nitrate, phosphate and DOC, since 1971 to 2010 for the station...
downstream of the Rennes WWTP (V8). For nitrate (Figure 3(a)), the first observation is the increase of its concentration between 1971 and 1990 followed by a decrease corresponding to the implementation of European Nitrate Directive in 1991 (Directive 91/676/EEC). In more detail the annual variation is very high with a strong concentration peak in winter corresponding to organic fertilizer spreading (cattle manure and pig slurry, according to local animal waste management practices) (Delpla et al. 2011), and to the rainy period.

For phosphate concentration (Figure 3(b)), the annual variation is also distinctly observable and a sudden decrease appears at the end of the year 1996. The average concentration of PO₄ was 2.12 mg/L between 1971 and 1996 and then decreased to 0.47 mg/L for the period 1996-2010. This corresponds to the commissioning of the new WWTP downstream of Rennes, including a better treatment scheme with a dephosphatation step. In the same way, this improvement could be noticed at the extreme downstream of the basin for PO₄ but also for KN, NH₄ and Pt. For instance, at station V25 (Figure 2), the average concentration of PO₄ was 0.47 mg/L between 1986 and 1996 and then dropped to 0.18 mg/L for the period 1996-2006. For NH₄, the average concentration decreased from 0.32 to 0.18 mg/L between both periods.

Concerning organic carbon, only oxidability (OxA) data are available between 1971 and 1992; after this period, DOC was measured (Figure 3(c)). The average concentrations were 7.76 mg/L for OxA between 1971 and 1992, 9.72 mg/L between 1992 and 1996 and 7.41 mg/L after 1996 for DOC. This decrease is also due to the improvement of the WWTP.

Relation between parameters

A principal component analysis (PCA) was performed using R 2.11.0 software for each of the nine stations in the historical data base presented in Figure 2. PCA is a powerful pattern recognition technique that attempts to explain the variance of a large dataset of intercorrelated variables (water quality parameters in this study) with a smaller set of independent variables or principal components (Hopke 1985). It helps to extract and identify the factors/sources responsible for variations of river water quality at the different sampling sites. Among the nine stations, only results for three of them are shown here (Figures 4(a), (b) and (c)). Results are presented in variable factor maps (VFMs) form. The contribution of all parameters is used for the construction of each dimension of the PCA. This construction

![Figure 4](https://iwaponline.com/ws/article-pdf/12/6/727/416972/727.pdf)  
**Figure 4** | Variable factor maps and associated eigenvalues graphs: (a) V1 (upstream), (b) V8 (downstream Rennes), (c) V25 (downstream).
allows the detection of which amongst them are extreme and the most responsible for the water quality variations (Lê et al. 2008).

For each VFM, only two dimensions have been considered in the interpretation because of their relative weight in variance explanation. Indeed, on eigenvalue graphs (Figure 4), a clear break in the slope appears after the second component showing that other dimensions have a lower importance in variance explanation.

The V1 VFM (Figure 4(a)) shows two first axes representing 48% of the total variance. Dimension 1 (Dim 1), with a variance of 25% is mainly linked to Tw, Ta, Cond, NO3 and Q and represents hydroclimatic influence. Dimension 2 (Dim 2), with TSS, Pt and Turbi, represents rain and streaming impacts. These same two characteristic dimensions are found for V4 and V5, the two other upstream stations.

Rain and streaming impacts are especially important near the source, with Dim 2 representing 23% of the total variance at station V1 and only 15% at V4 and V5. Moreover, another statistical analysis, based on Spearman correlation, underlined that the correlation coefficients between the sum of the daily rainfalls of the sampling date and of the three days before and the physicochemical parameters strengthen the impact of rain and streaming. This is particularly observable for KN, DOC, TSS, Pt and Turbi for which correlation coefficients range from 0.38 to 0.52.

The V8 VFM (Figure 4(b)) shows two first axes representing 41% of the total variance. Dim 1 (25%) is mainly related to nutrients and organic load, NH4, Pt, PO4 and KN, which represent a pollution gradient. For Dim 2 (16%), variables representing the hydroclimatic influence are found: Ta, Tw, Q and NO3. This map is representative of station V8 located downstream of the Rennes WWTP. For station V2 located downstream of the Vitré WWTP, which is of smaller capacity with 34,500 inhabitant equivalents, the VFM is close to that of V1. Finally, the V8 VFM is representative of a treated wastewater discharge.

The V25 VFM (Figure 4(c)) shows two first axes representing 36% of the total variance. Parameters accounting for climate and hydrology impacts define Dim 1 (19%) like the V1 VFM, Ta, Tw, Cond, NO3 and Q, while Dim 2 (17%), mainly linked to DOC, KN, NH4, Pt and PO4, represents a pollution gradient. These same characteristic dimensions are found for the three other downstream stations, M12, V18 and O19.

Finally, three groups are highlighted by PCA: the ‘upstream’ group rather dominated by circumstantial effects like rainfall events, the ‘downstream’ group, dominated by chronic effects with continuous discharge, and the ‘discharge’ group.

Figure 5 summarizes all PCA results for water quality parameters on the main Vilaine (V) watershed, and on the two main sub watersheds, Meu (M) and Oust (O). The three groups, ‘upstream’, ‘discharge’ and ‘downstream’, are represented respectively by triangle, square and circle. For each group the dimension signification and associated parameters are described.

This statistical analysis allows us to conclude that the resource pumping for drinking water production seems to be more troublesome upstream than downstream in terms of water quality variations. Hydroclimatic factors appear in all groups of the PCA and could involve difficulties for
resource quality monitoring and treatment plant management especially for small water supplies, of between 50 and 5,000 inhabitants (Bessonneau et al. 2011). In France, small suppliers represent more than 90% of the 26,000 suppliers, and provide approximately 10% of the population (DGS 2008). Bessonneau et al. (2011) underline that 80% of non-compliant results come from distribution units providing less than 500 inhabitants and especially in rural areas. The causes of these non-compliances could be linked to incidents at treatment plant or distribution system operations or to other causes of environmental origin. In addition, identification of hazards that may occur for a resource highlighted that weather events, weather patterns and seasonal variations are the first cause of danger (Bartram et al. 2009). Adjustments, decisions and actions should be taken and realized in time to meet this challenge and to protect the population.

Towards new indexes

UV-visible spectra exploitation procedure

The UV-visible spectra exploitation procedure was developed in both campaigns in order to classify all sampling stations of the Vilaine basin according to their global water quality and to introduce the development of new water quality indexes.

UV spectra exploitation was based on two regions: 205–220 nm and 250–350 nm. The first is related to the presence of nitrate, contained in the majority of natural water and which is the most stable form of nitrogen in water. According to the concentration levels of nitrate, a characteristic shoulder appears between 205 and 220 nm (Pouet et al. 2007). The second is related to the presence of OM, including humic substances and humic-like substances, and of suspended solids. The presence of OM is characterized by a shoulder at around 260–270 nm (Pouet et al. 2007). The absorption level and the general mean slope of the spectrum in the 250–350 nm region could vary depending on the nature of suspended solids and the presence of high colloid concentrations (Vaillant et al. 2002). From these two characteristic regions, a classification of the 31 sampling stations was proposed. To carry out this classification, the sum of absorbances between 250 and 350 nm ($\Sigma A_{250-350}$) was first calculated for every sampling point and on the CDP and CRP campaigns (Figures 6(a) and (b)). Second, the absorbance at 215 nm ($A_{215}$) was extracted (Figures 6(a) and (b)). Points of the same class were grouped together with circles while unclassifiable points were left isolated. Then, for each group, associated UV-visible spectra were represented.

Station classification

From the CDP campaign, UV spectra exploitation (Figure 6(a)) allows three groups of stations to be highlighted. The first is composed of two upstream points on the Vilaine (V4 and V5), two small upstream tributaries, the Flume and Cantache (F9 and C3) and the two main tributaries, the Meu and Oust (M10, 11, 12 and O19, 21, 23, 24). Sampling points close to the two main cities of the basin, Rennes (V8, 13, 16 and 16) and Vitré (V2), represent another group. The third group concerned especially all downstream sampling points of the Vilaine (V18, 25, 27, 28, 29 and 30).

Each group could be characterized by a range of $\Sigma A_{250-350}$, representing the presence of OM and suspended solids, and a range of $A_{215}$, representing the presence of nitrate.

The first sampling point group is essentially related to agricultural pressure and $\Sigma A_{250-350}$ ranges from 9.5 to 12.6 and $A_{215}$ from 2.7 to 4. The second is essentially linked to urban pressure and $\Sigma A_{250-350}$ ranging from 12.4 to 14.1 and $A_{215}$ from 2.2 to 2.9. The third group is characterized by $\Sigma A_{250-350}$ ranging from 14.3 to 17.5 and $A_{215}$ from 2.6 to 3.7, and seems to be the sum of both types of pressure with intermediate $A_{215}$ and high $\Sigma A_{250-350}$.

From upstream to downstream, the water quality of the Vilaine appears to be degraded by all these influences in terms of OM and suspended solids, $\Sigma A_{250-350}$ increases, while the presence of nitrate is relatively homogeneous over all stations of the basin ($A_{215}$ relatively equal on all stations).

Moreover, outliers could be distinguished by their $\Sigma A_{250-350}$ and $A_{215}$ values (Figure 6(a)) and some explanations also arise from in-situ measurements. Is26 has the lowest level of pH, 6.7, and the lowest O2D and O2S values, 5.8 mg/L and 56%, respectively. V31, sampled in the chlorination tank of the DWTP, presents the lowest
Figure 6 | UV spectra groups: (a) CDP and (b) CRP.
ΨA250–350 (2.2), i.e. an abatement of 84% compared to raw water (V30, ΨA250–350 = 13.77), and its A215 is close to the other sampling points, which could be explained by the absence of denitrification, ion exchange or membrane processes in the DWTP.

Figure 6(b) presents results for the CRP campaign. All points are scattered on both axes and could not be classified as the CDP campaign was. Before examining the main outcomes of this figure, it has to be underlined that: (i) rainfall could not be homogeneous over the whole of the basin because of its size (15,000 km²) and (ii) there are a large number of sampling points, they were collected over 2 days, the first day for upstream stations, V1 to V16, and the second for those downstream, V17 to V31.

Interesting observations could be drawn on the evolution of the global quality between CDP and CRP campaigns. For the three groups found for CDP, A215 is lower during CRP than during CDP. This could be due to a dilution phenomenon (Delpla et al. 2009). It is also observable in the UV-visible spectra shape between 205 and 220 nm which has a majority of concave slopes (Figure 6(b)).

Moreover on the PCA results (Figure 5), the impact of hydroclimatic factors, which are linked to dimension 1 or 2 for all groups, are confirmed on the UV-visible spectra interpretation (Figure 6). All groups are impacted, at different levels, by the rainfall event during the CRP campaign with variations of nitrate, OM and suspended solids concentrations.

CONCLUSION

The first PCA analysis brings out three groups of stations comparing water quality parameter variations. The ‘upstream group’ influenced by circumstantial effects (rainfall events), the ‘downstream’ one dominated by chronic effects (e.g. continuous discharge) and, finally, the ‘discharge group’ characterized by the presence of a WWTP upstream of the station.

Secondly, UV-visible spectra exploitation gives a classification of the 31 sampling points during CDP comparing indexes, ΨA250–350 and A215, representing respectively the presence of OM, suspended solids and nitrate. This allows three water quality groups to be identified and recognizes a degradation of the water quality between upstream and downstream parts of the basin. Moreover, it also reflects water quality variations due to a rainfall event during the second sampling campaign according to the different areas of the basin. The general tendency is a reduction of nitrate (A215) and an increase of OM and suspended solids (ΨA250–350).

In conclusion, sampling sites could be influenced by the same effects but could have characteristic spectra completely different. Indeed, these two analyses give complementary results. Indexes should be a good tool to reflect global water quality at a river basin scale at a specific time and to describe the impact of urbanization, land use and hydroclimatic factors. The proposed methodology based on UV monitoring allows water quality variation to be assessed easily and quickly, and gives a new approach for improving resource quality management, monitoring...
and the management of treatment plants, taking into account environmental and climatic stressors.

REFERENCES


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