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An adaptable automatic trace metal monitoring system for on line measuring in natural waters

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ABSTRACT

An adaptable automatic trace metal monitoring system (ATMS) was assembled and embedded in a mobile monitoring station belonging to the French Water Agency Artois-Picardie (AEAP) and deployed in the field to measure the concentration of trace metals (electroactive and acid leachable fractions) in natural waters by anodic stripping voltammetry with a hanging mercury drop electrode. Cathodic stripping voltammetry procedures were included to estimate the concentration of dissolved oxygen and reduced sulphur species. The concept of the measuring system enables easy adaptation of methods and procedures to analytes of concern and gives the opportunity to undertake in real-time a routine analysis of the dynamic behaviour of trace metals in river, pond and seawater. The system was tested in two aquatic bodies: in a pond where eutrophication processes occur recurrently and in the Deûle River, where sediments are highly contaminated by several metals such as Pb and Zn and frequently resuspended because of the river traffic. Preliminary field studies demonstrated that trace metal concentrations can evolve quickly as a function of time, depending on the turbidity and luminescence, *i.e.* day–night cycles. The obtained results were compared with an Environmental Quality Standard (EQS), the Criteria Maximum Concentration (CMC) and the Criterion Continuous Concentration (CCC). The whole system is also prepared for the task of “early warning”.

1. Introduction

Now-a-days there is a well expressed need to measure trace metal concentrations in aquatic systems on a regular basis. When the measurements are carried out in the laboratory after a sampling campaign, numerous precautions must be taken to avoid artefacts bound to sample contamination, adsorption processes, and/or evolution of the sample before the analyses. In addition, if the obtained information concerns only a few discrete samples, and if the sampling frequency is not high enough, it is difficult to go further in the understanding of the dynamic behaviour of trace metals in the aquatic systems. It is already known from the literature that the concentrations of total dissolved metals and/or their labile fractions evolved quickly with time. It could be ascribed to the variation of phytoplanktonic activity or the temperature fluctuation at the scale of the day and in this case, daily cycles have been evidenced [1–4]. Local perturbations and particularly the resuspension of contaminated sediments (like barge traffic or dredging) could also have a transitional effect on the concentration and the speciation of trace elements [5–9] that could be of a great importance for the aquatic organisms when these phenomena occur recurrently. Some of such events could be the reason for “early warning” signalisation.

Up to now, only a few studies were dedicated to the “on line” measurements of trace metals in aquatic systems, probably because the implementation of a compact and automated system close to the river bank and in a protected area being supplied by electricity is not an easy task if the measurements last several days [1–4,7,10–12]. Although several techniques can be applied to the determination of trace metals in samples, only electrochemical techniques, to our best knowledge, can be really deployed in the field with a sufficient sensitivity.

Voltammetric techniques are widely used in laboratories to measure trace metal concentrations (*e.g.* [13]). They permit also to study metal speciation because electroactive species detected by voltammetry represent only the part of the total metal concentration, which mostly consists of free metal hydrated ions and labile metal complexes [14–16]. Addition of reagents into the

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voltammetric cell, treatment of the samples by UV radiations and titration experiments consisting of addition of either a ligand or an analyte, result in a better knowledge about the metal complexation processes in the dissolved phase [17,18].

In the last decades, a lot of effort has been put in developing solid mercury-free electrodes for trace metal analysis [19–22]. The progress is evident, but sensitivity and stability of the response with time are still prone to improvements. However, we preferred to use the knowledge and the experience that already exist with the mercury drop electrode regarding possible complications in analytics of trace metals in a complex natural matrix. So, an automatic voltammetric system containing mercury drop electrode was assembled with the idea of eventually replacing the electrode by a solid mercury-free one.

Through a scientific collaboration of the French Water Agency Artois-Picardie (AEAP) who built two mobile monitoring stations (MMS) for the continuous evaluation of water quality by measuring key physico-chemical and chemical parameters such as temperature, conductivity, pH, turbidity and oxygen concentrations, and the Laboratory Géosystèmes from the University Lille 1 where adaptable ATMS was assembled, the conditions for continuous on-site measurement of trace metals were achieved.

The aim of this paper is firstly to describe the conception and the optimisation of an adaptable ATMS to measure the concentration of electrochemically active and acid leachable fractions of trace metals present in a natural sample at about 1 h rate for several days. The second part of this paper is focused on applications in the field to display what kind of paramount information such an ATMS can provide in order to better understand the dynamic behaviour of trace metals in the aquatic environments. The first site was a pond located in the town of Le Quesnoy, where eutrophication processes occur recurrently [23] and the second site was the Deûle River impacted by metal smelting plants [24–26] with daily sediment resuspension due to barge traffic.

2. Monitoring sites, materials and methods

2.1. Sites description

Two study sites located in northern France were considered to test and validate the ATMS. The first one is a pond situated in the town Le Quesnoy. Its surface is around 13 ha with an average depth of 1.9 m and a water volume estimated to 240,000 m^3. Water supply represents on average over 1 year 70 $L\,s^{-1}$ and comes essentially from rainfalls and in a lesser extent from a small stream located in the south-east of the pond. The water residence time is about 39 days [23] and the outlet is situated in the north of the pond, close to the implementation of the MMS belonging to the AEAP. The pond is used for recreation activities including mainly fishing, and swimming. No industries are located in the vicinity of the pond, but agriculture and cattle breeding contribute to accelerate and enhance the pond eutrophication processes, as pointed out by high concentrations of nutrients and organic matter in the water [23]. The ATMS was embedded in the MMS from 3rd to 6th July 2010 in order to test it and carry out the first on line measurements.

The second site is located in the Deûle River, in the town of Auby, close to the city of Douai, France). It is a small water system included in the watershed of the Scheldt River. The Deûle River is about 60 km long, has a catchment area of around 1071 km^2 and an average flow of 8 $m^3\,s^{-1}$ (measured near Wambrechies city). As the river is intensively used for fluvial traffic, most of its riverbanks are channelled, especially between the cities of Douai and Lille. Along the water course of the Deûle River, several areas have been severely polluted by metallurgical activities, especially in the area where the ATMS was located. The system was implemented in a small cabin belonging to "Voies Navigables de France (VNF)" built just downstream the UMICORE and NYRSTAR factories that produce high quantity of Zn sold as standard zinc cathodes and high quality battery-grade cathodes. The ATMS was installed in the VNF cabin from 5th to 11th April 2011 and as the MMS was not available, analytical apparatus was also added in the cabin to routinely measure temperature, conductivity, pH and turbidity.

2.2. Chemicals and instrumentation

All the vessels and the tubing used were cleaned with 10% nitric acid (Fisher Scientific, *analytical grade*) and rinsed with ultra-pure water (Millipore, mQ system). Metal solutions used for calibration were prepared from standard 1 $g\,L^{-1}$ (Merck). Acidifications of samples were performed from concentrated HNO_3 (Fisher, *Optima*). 5 M sodium acetate prepared from $NaCH_3COO$ Ultrapure (Prolabo, *Normatom*) was used to buffer solution at pH 4 for zinc measurements. Saturated KCl used in the reference electrode is from suprapur KCl (Merck, *suprapur*). For UV digestion the sample was prepared with 5 μL of suprapur concentrated HNO_3 and 100 μL of H_2O_2 30% (Merck) for 10 mL of river solution. The sample was then irradiated for at least 24 h with 6 UV lamps (Philips, PL-L 55W TUV UV-C) [27].

All voltammetric measurements were carried out with voltammetric analyser μAutolab II (Metrohm, Switzerland) controlled by GPES 4.9.007 software (Eco Chemie) coupled with the three electrode system of 663VA Stand (Metrohm, Switzerland). The working electrode was a static mercury drop electrode (SMDE) (size 3, 0.52 mm^2 of area). Potentials were given versus Ag|AgCl (sat. KCl) reference electrode. A platinum wire was used as a counter electrode. Electrochemical experiments were done in a home made 3 ways (one input and two outputs) flow-through cell (see voltammetric cell in Fig. 1) designed to fit to the 663VA Stand (Metrohm, Switzerland) and having by its construction a fixed sample volume of 22 mL. The solution was stirred with a Teflon rotating stirrer at 1500 rpm (position 3 on the 663VA Stand). When needed, prior to analysis, dissolved oxygen was removed from the solution by purging with ultra-pure nitrogen, for at least 5 min. Two Burettes Dosimat 765 (Metrohm, Switzerland) or a home made system with three Cavro XE 1000 syringe pumps, (Tecan, Switzerland) controlled with a home made program were used to automate pH modification.

Three peristaltic pumps were used for sample circulation: MasterFlex I/P Model 77600-62, Cole-Parmer; MasterFlex, Model 77800-50, Cole-Parmer; and Gilson, Minipuls2 or Watson-Marlow, 503S. The two pumps used to fill and empty the cell were connected to a home made box containing relays in order to control their power ON/OFF via μAutolab PIO2 Port C by the GPES software.

In the small cabin belonging to VNF, turbidity, oxygen, temperature, conductivity and pH were measured with the turbidimeter Hach Lange, TSS portable; with its LXG321.99.00001 probe, the multimeter WTW, 197i with its TA 197 OXI probe for oxygen and temperature, the multimeter WTW multi 350i with its Tetracon 325 probe for conductivity and with its Crison 52-21 pH electrode.

In the pond Le Quesnoy, the MMS was already equipped with several apparatus allowing measurements every 10 min of several physico-chemical and chemical parameters: conductivity, pH, temperature and dissolved oxygen were measured with probes provided by the company Yokogawa, whereas turbidity was recorded with a Metrawatt multimeter.

Ca and Mg for hardness calculations were measured by Flame Atomic Absorption Spectroscopy with a Varian SpectrAA-10 and 1 $g\,L^{-1}$ standard solutions (Merck) were used for calibration.

2.3. Sampling and measuring protocols

In order to minimise sample modification before analysis, the adaptable online monitoring voltammetric platform was

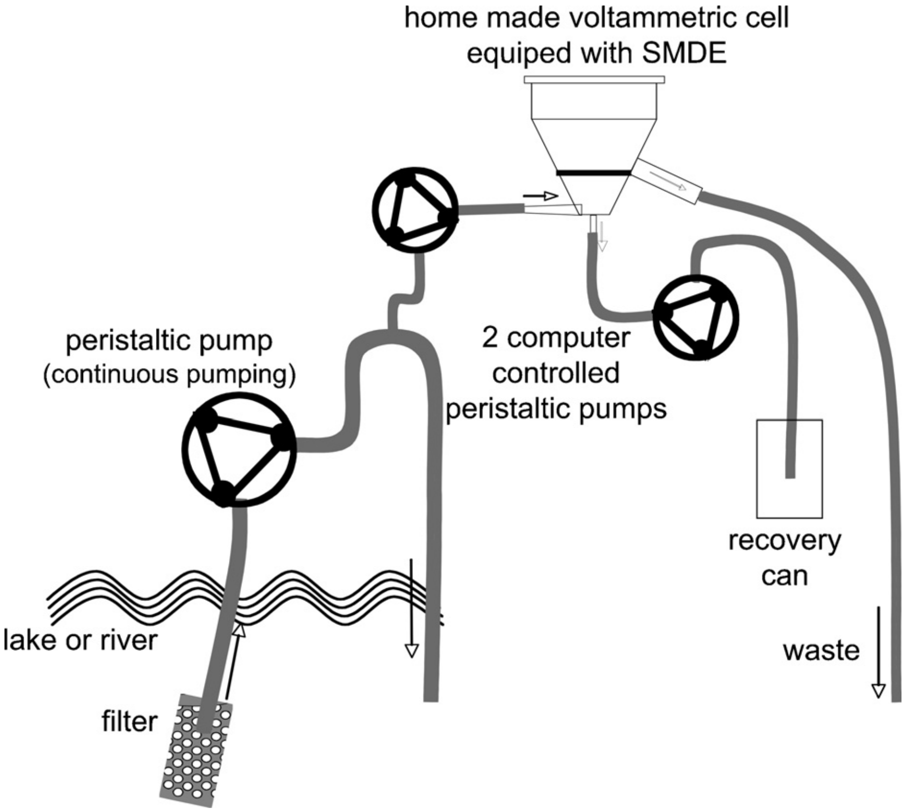

Fig. 1. On line pumping scheme of the ATMS.

positioned as close as possible to the studied water body (Fig. 1). A PTFE tube with a metal free filtering extension (1 mm pore diameter) was placed in the river in order to avoid entering of bigger particles into the voltammetric cell. The tube was fixed at about 1 m depth during all the monitoring experiments.

A first peristaltic pump working continuously was used to make a water circulation from the river, passing by the monitoring platform and going back to the river with a flow of 3.5 L min^{-1}. A second computer-controlled peristaltic pump was used to take the sample from the by-passing flow to rinse and fill the voltammetric cell, using a flow rate of 0.1 L min^{-1}. The output tube placed at the middle height of the cell wall served as an overflow and as regulation of the sample volume at 22 mL. A third peristaltic pump, also computer-controlled, was used to empty the cell through the output at its bottom. At the same time the knocked off mercury drops from preceding measurements were removed, so any adsorption of the new sample on old mercury drops was avoided, which is particularly essential for reduced sulphur species measurements [28]. Before each sample analysis, the electrochemical cell was rinsed three times with the river/lake water using alternatively the second and the third peristaltic pump.

For the purpose of automatic monitoring a program was written in the Project mode of the GPES software, where six different measurement methods were applied consecutively, each one in triplicate. The two pumps and the two burettes were addressed from the same Project. Each curve was stored in a separate file with auto-incrementing numbers. According to these operating conditions, the duration of one cycle was about one hour and a half. If not stated otherwise, the measurement parameters were the following: Differential Pulse Anodic Stripping Voltammetry (DPASV) or Differential Pulse Cathodic Stripping Voltammetry (DPCSV) (or DPCV when no deposition step was applied) pulse amplitude = 25 mV; potential step increment = 2 mV; time between pulses = 0.1 s; pulse duration = 0.05 s; equilibration time = 5 s.

The first measuring method was a cathodic scan (DPCV) adjusted for oxygen measurement. After degassing, DPCSV was used as second method to evaluate reduced sulphur species. The third method used to determine metal concentrations at natural pH was the DPASV. By the fourth method after acidification to pH 2, acid leachable fractions of metals were determined applying DPASV. After adjusting the pH to 4, the fifth method, also DPASV, was used to measure acid leachable Zn. The sixth method, again DPCSV at pH 4, was applied to check the evolution of the sample during the cycle. A representative curve for each method is shown in Fig. 2.

The six chosen methods could of course be changed in any of their parameters and be adapted to the content of the monitored water system. More burettes with specific reagents could be envisaged in order to detect and determine another specific analyte. Literature acknowledges a lot of possibilities. For example, Al, As, Co, Fe, Mo, Ni, Pt, Sb, Se, Sn, Ti, U or V can be detected by AdCSV if the proper ligand is added [29], as well as nitrates [30], low concentrations of fulvic acid [31] and specific organic molecules like pesticides (for instance, see [32]). Also, a quick pseudopolarography, as an appropriate method that needs no addition of any analyte, could be included as well, to give information about speciation/complexation of particular metal at natural or acidified pH [33–35].

2.4. Data treatment and calibration

By continuous measurement during several days, numerous voltammetric curves are produced and registered. The commercial software for peak height determination is not appropriated for automatic determination of many signals, while manual treatment of each curve would require a lot of time. To overcome it, a home written program was adapted to treat the whole set of curves at a time [36]. This specific software offers visualisation of the whole set of curves in 2D and 3D,

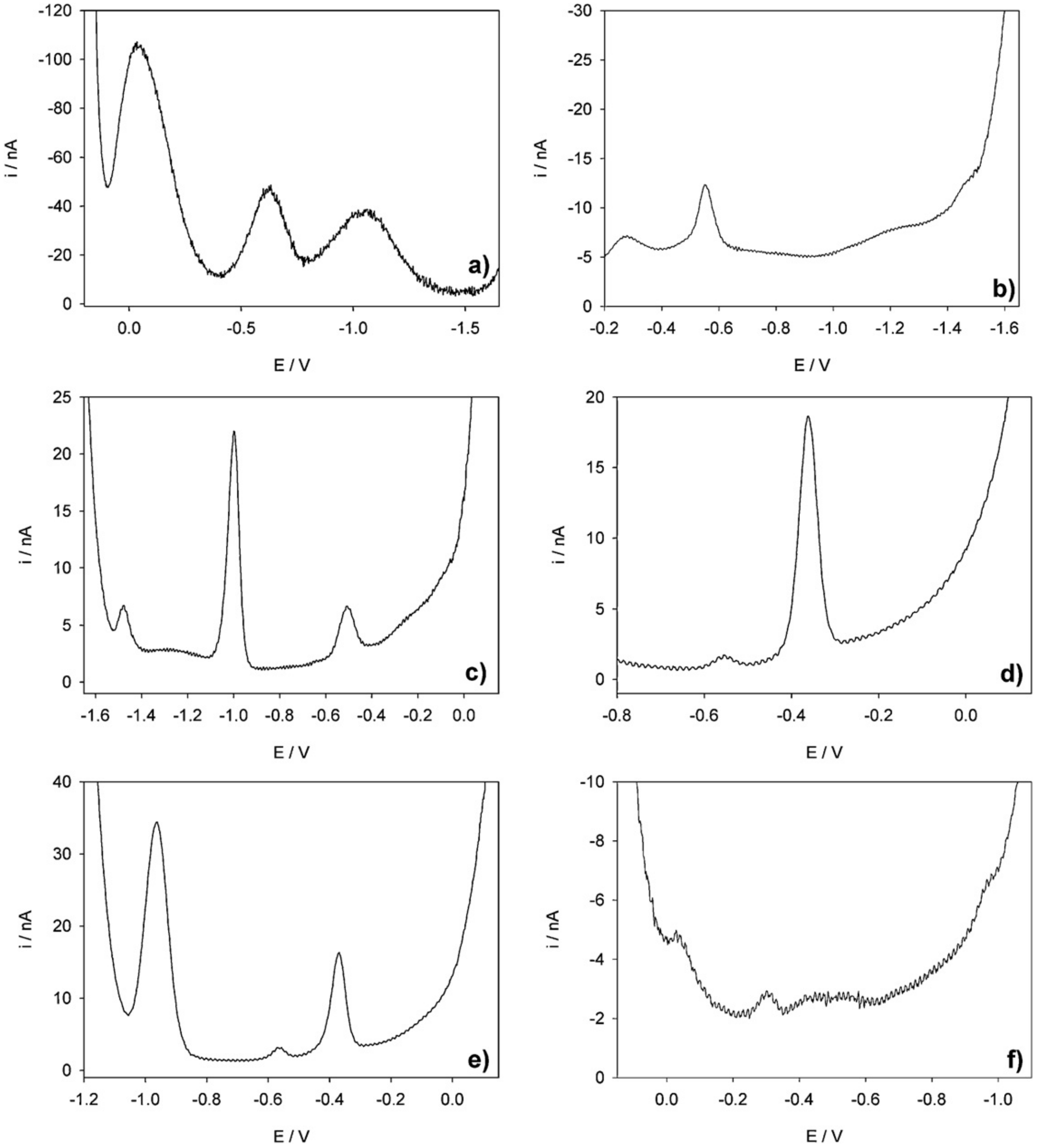

Fig. 2. Examples of signals obtained for the 6 voltammetric procedures. Methods: DPCV (a), DPCSV (b and f), DPASV (c, d and e); potential step increment = 2 mV, pulse amplitude = 25 mV; deposition time: 0 s (a and f), 120 s (b), 300 s (c, d and e); pH natural (a, b and c), pH 2 (d), pH 4 (e and f).

selection of different curve smoothing options, ranges selection of each peak positions, application of linear tangent fit baseline subtraction before peak height or peak surface determination (the updated version of the software (ECDSOFT) can be found on http://www.irb.hr/en/str/zimo/laboratoriji/lfkt/djelatnici/Dario Omanovic/Software/).

Calibration curves for Mn, Zn, Cd and Pb at natural pH were obtained in the laboratory, using the samples taken at the monitoring sites. To properly calibrate the voltammetric signals, two main approaches can be proposed: (i) a sample treatment by UV radiations to destroy natural organic matter (NOM) present in the sample. Namely, NOM contains surface active substances which could strongly influence voltammetric signal, while in addition, active complexing sites of NOM (ligands) could bind added metal producing curvature calibration response. After such UV treatment, standard addition method permits to obtain a linear calibration curve with a slope value (also called sensitivity) characteristic of the electroactive species without organic surfactant interferences [37]; and (ii) a titration curve where the slope is determined from the part where the NOM complexing ligands have been saturated by the addition of the titrating metal into the solution. In some cases linear part of the calibration line is hardly assessed because saturation of the electrode can coincide with saturation of the organic ligands. For that reason, we decided to calibrate our apparatus after UV radiations of the samples. However, to diminish as much as possible adsorption of OM onto the mercury drop electrode during the monitoring experiments, the accumulation step of 3 s duration at −1.65 V was introduced in the measuring as well as in the calibration procedure [34]. Note further that these calibration procedures must be considered as semi-quantitative since a fraction of metal bound to NOM is electrolabile but has undoubtedly a mass transfer and a charge transfer kinetic quite different than the free hydrated metallic cation added.

The other fractions of the sample were acidified to pHs 2 and 4. Before measurement samples were left 20 min for equilibration. At least four standard additions of metal ions were added, each

Table 1
Sensitivities in A M^{-1} and their 95% confidence interval at natural pH, pH 2 and pH 4 obtained from the calibration experiment for the measured metals in corresponding matrices.

		Sensitivities (A M^{-1})	
		Le Quesnoy	Deûle
Natural pH	Mn	0.020 ± 0.002	0.022 ± 0.002
	Zn	–	0.44 ± 0.05
	Pb	–	1.21 ± 0.04
pH 2	Cd	–	0.343 ± 0.004
	Pb	0.70 ± 0.04	0.54 ± 0.01
pH 4	Zn	0.281 ± 0.007	0.237 ± 0.006

concentration measured three times. The obtained calibration line slopes, *i.e.* sensitivities, were used to estimate the concentrations of the measured analytes (Table 1).

The effect of the temperature variation of 4 °C (that is the maximal variation observed during our monitoring experiments) has been tested on voltammetric response for Zn, Cd and Pb because diffusion coefficient of the species and the dynamic viscosity of the solvent depend on the temperature and play a paramount role during the deposition process. A maximal variation of 5% on the voltammetric signal was measured. As the calibration of the curves was carried out at about 25 °C in July and 18 °C in April and these temperatures were close enough with those during the field experiments, no temperature correcting factor was applied to recalculate metal concentrations. However, to compare data recorded during the summer and the winter times, a temperature correction must be undertaken.

3. Results and discussion

3.1. Measuring protocols

Immediately after filling the cell with a new sample, DPCV technique was applied with a scan from 0.2 V to −1.65 V in order to detect two oxygen reduction waves at 0 V and −1 V, corresponding respectively to the reduction of O_2 to H_2O_2 and of H_2O_2 to H_2O [38]. As the first peak measured at 0 V was higher than the peak at −1 V and also with a smaller background noise, it was mainly used for O_2 monitoring (Fig. 2a). A third peak with similar variations (not identified) has been detected at a potential of −0.64 V. Oxygen calibration was carried out by adding or removing oxygen from the Deûle River solution by purging it with O_2 or N_2 respectively. The WTW oxygen probe results were used as reference. Linearity was found in the range from 2.61 to 25 mg L^{-1} of O_2 with a R^2 of 0.996 and a sensitivity of 11.3 ± 0.2 nA mg^{-1} L.

After the O_2 measurement, it was necessary to remove it from the solution to enable reduced sulphur and metal species measurement. A purge with N_2 during 300 s was applied and DPCSV with a deposition time of 120 s at −0.2 V was performed, followed by a stripping step from −0.2 V to −1.65 V (Fig. 2b). Deposition at −0.2 V was chosen as the most positive potential before which thiols start to deposit as well [28]. Separated measurements of these sulphur species after acidifying, purging and returning to natural pH showed that they were not completely volatile sulphides. However, their response to variation of deposition potential appeared to be similar to the one of HS^-. Further investigation should be done to determine the exact nature of those analytes if the study requires it.

As indicated by the peak at −0.25 V, iodide measurements and calibration could as well be included with this scan by depositing and stripping from around −0.15 V [39].

To analyse electrochemically active manganese, zinc, cadmium, lead and copper at natural pH, the DPASV technique was applied as the next protocol (Fig. 2C). A deposition potential of −1.65 V and a scan from −1.65 V to 0.15 V were chosen in order to span all the present metals in the potential window of the method, available at the natural pH. Deposition time of 300 s was chosen. The applied deposition potential was suitable for avoiding surface-active substances interferences that could arise during the deposition step in untreated natural samples [34]. Calibration was conducted in UV-digested water in separate samples for each metal. Obtained sensitivities for Mn, Zn and Pb are given in Table 1.

In order to monitor the acid leachable metal concentration, a pre-programmed automatic addition of 400 μL of 10% nitric acid was carried out with equilibration time lag of 300 s. As the acidification to pH 2 causes the foot of the hydrogen reduction wave to appear more positively, only total cadmium, lead and copper could be analysed. The previously presented DPASV conditions were used but applying a deposition and an initial stripping potential of −0.8 V (Fig. 2d). Calibration curves were obtained with non UV-digested acidified samples. Sensitivities of 0.343 ± 0.004 and 0.54 ± 0.01 A M^{-1}, for Cd and Pb respectively were calculated.

To determine the acid leachable zinc concentration, a pre-programmed automatic addition of 400 μL of 5 M sodium acetate was carried out in order to increase the pH from 2 to 4. DPASV procedure using deposition and initial stripping potential of −1.2 V was applied (Fig. 2e). Sensitivity of Zn in a non UV-digested sample at pH 4 was found to be 0.237 ± 0.006 A M^{-1}.

For the last measurement step of the same sample in the cell, another cathodic scan was performed, in order to check the behaviour of the sample after pH adjustments to 2 and 4. In case of our monitoring stations, cathodic scans from 0.15 V to −1.1 V gave the signals with some peaks (Fig. 2f). In case of expressed interest, especially for non volatile reduced sulphur species, characterization, identification and calibration of the analytes detected by this procedure could be performed.

3.2. On-line continuous measurement applications

3.2.1. Le Quesnoy

At the location Le Quesnoy, the ATMS was put into the mobile monitoring station of the Water Agency. Together with voltammetric measurements there were continuous measurements of temperature, conductivity, pH, turbidity and oxygen. The results for the period of three days measurements are shown in Fig. 3. From the measurements the signals for oxygen, reduced sulphur species, labile Mn, total Zn and total Pb were sorted out and identified. Their peak heights (average of three measurements) are shown versus time. At natural pH, the voltammetric signals of Pb were generally not detectable (DL_{Pb} = 1 nM) and those of Zn were often too close to the detection limit (DL_{Zn} = 3 nM) to calculate concentration values (data not shown). Signals of oxygen match well with the results of oxygen probe and together with temperature, conductivity and pH clearly show daily variations. These variations could be explained by biological activity cycles induced by light and temperature as seen in Bourg and Bertin [40]. However, variations of acid leachable Zn and Pb species and at natural pH electroactive Mn and sulphur species, which are periodic as well but not so clearly, seem to be linked to the turbidity. All of these parameters are indeed showing an increase during the day especially on 5th July and a relative decrease at night. A substantial augmentation on 6th July around 05:00 is also recorded for all variables. This could be interpreted by bioturbation and resuspension of the sediments especially since Mn and sulphur species are markers of this resuspension from anoxic sediments [6]. Additionally, since Mn(II) species are generally more stable than reduced sulphur species in oxic conditions, the concentration peaks related to manganese are more scattered in time than those related to sulphides (Fig. 3) This observation was also clearly noticed in the Deûle River. Sensitivities for Mn, Zn and Pb, obtained

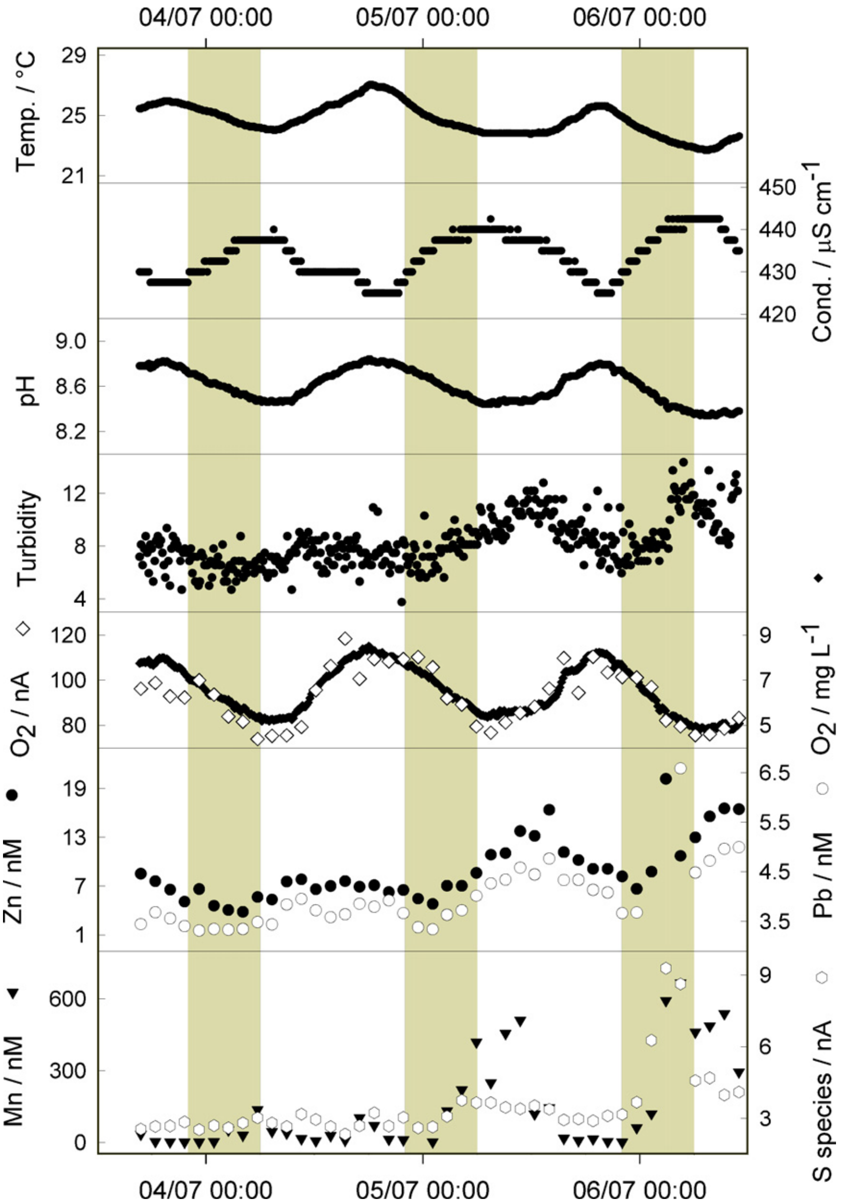

Fig. 3. Variation of different parameters measured from 03/07/2010 to 06/07/2010 at Le Quesnoy. Temperature, conductivity, pH, oxygen and turbidity taken over from the Water Agency; voltammetric measurements of oxygen, Zn and Pb (pH 2), Mn and sulphur species (natural pH) – for parameters of measurements see the text.

from calibration lines are given in Table 1 and the corresponding variations of Mn, Zn and Pb in those three days were estimated to be from 0.71 to 709.9 nM, from 3.03 to 22.3 nM and from 3.15 to 11.3 nM, respectively.

3.2.2. The Deûle River

At the location Auby on the Deûle River six days continuous on-site measurements were performed. The same parameters were measured as in Le Quesnoy, except that oxygen was measured only by voltammetry. Voltammetric results were shown as average from three consecutive measurements (Fig. 4). Comparing to the first location, day–night periodicity was less expressed except for temperature, probably because that at this period, the phytoplanktonic development is more limited with mainly diatoms development. However, certain day–night regularity does exist. Two other differences between the two locations are also pointed out through the turbidity (from 10.4 to 64.7 instead of 3.75–14.4 in Le Quesnoy) due to intensive boat traffic and through the temperature (from 13.4 to 16.6 instead of 22.7–27.1 °C in Le Quesnoy). Thus it seems that in the Deûle River at this period, resuspension of sediments is playing a greater, and biological activity a lesser role in most parameters variations, explaining more apparent randomized variations.

According to calibration and obtained sensitivity (shown in Table 1), the variations of Mn, Zn and Pb at natural pH, of Pb at pH 2 and of Zn at pH 4 in those six days were estimated to be from 64.0 to 230 nM, from 82.8 to 223 nM, from 2.21 to 5.57 nM, from 27.4 to 109 nM and from 227 to 934 nM, respectively. Furthermore, we calculated that the electrolabile fractions of Pb and Zn measured at natural pH (data not shown) compared to the acid leachable fractions ranged between 4 and 15% and between 16 and 49% respectively.

If we compare these results with the results obtained in Le Quesnoy we must point out that the measurements at the first location were done in summer, while the second were done in spring. The temperature was quite stable in summer, with only day–night variation, while in spring, there was a clear rising of the temperature during the six days of the experiment, superimposed to daily variations. Conductivity and pH variations were less regular in the

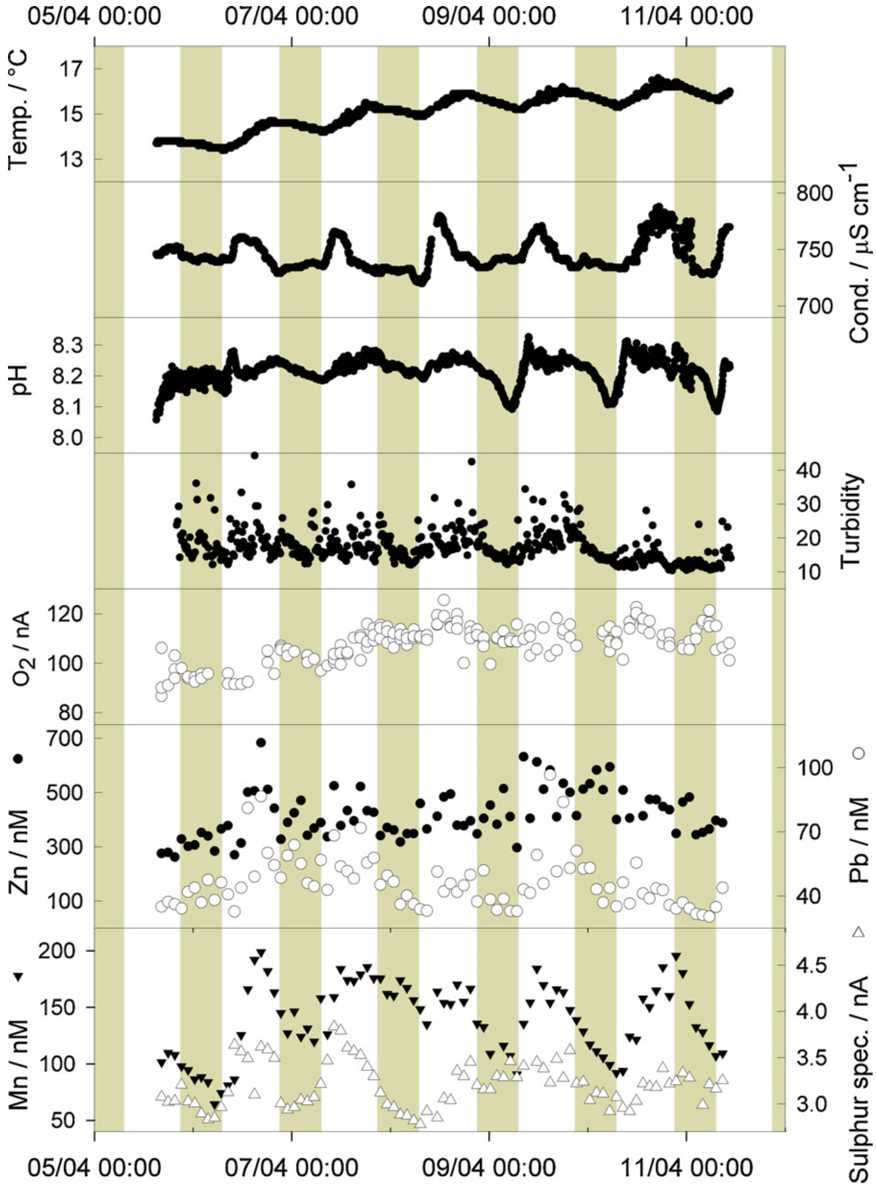

Fig. 4. Variation of different parameters measured from 05/04/2011 to 11/04/2011 in the Deûle River. Temperature, conductivity, pH and turbidity measured with corresponding probes; voltammetric measurements of oxygen, Zn and Pb (pH 2), Mn and sulphur species (natural pH) – for parameters of measurements see the text.

Deûle River, showing a more complex system with more overlapping influences at a time. Results for oxygen were also less periodic in the Deûle River, however, showing day–night oscillations and a certain rising trend over the days of the experiment. The values for turbidity were also higher in average because of the boat traffic in the Deûle River. For the metals, we see that in Le Quesnoy, manganese concentrations varied in a larger range with a background concentration approximately 50–100 times lower than in the Deûle River. As shown previously, the relative stability of Mn(II) in oxic conditions coupled with the frequent anoxic sediment resuspension events in the Deûle River contribute to the high background dissolved concentration of manganese. As for lead and zinc, the total concentrations were 10–50 times higher in the river than in the pond due to the presence of Pb and Zn smelting plants in the Deûle River banks.

3.2.3. Environmental quality estimation

In order to evaluate the water quality of the two sites, the measured concentrations were compared with Environmental Quality Standard on the Annual Average (EQS-AA) of dissolved metals from the European Union Water Framework Directives [41] and with the Criteria Maximum Concentration (CMC) and the Criterion Continuous Concentration (CCC) calculated according to the United States Environmental Protection Agency [42] (Table 2). The CMC is an estimate of the highest concentration of a material in a surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect; the EQN-AM and the CCC are an estimate of the highest concentration of a material in a surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect. The CMC and CCC are a function of the metal of interest and of water hardness. These three parameters are defined for the concentration of total metal in 0.45-µm-filtered water. For this study, it does not correspond to any of the two measured unfiltered fractions of metals, but could serve for orientation. The acid-leachable concentrations of zinc and lead have then been used for the comparison, thus overestimating the toxicity (Table 2). No acute toxicity has been detected for Pb and Zn on both sites. For Le Quesnoy, Zn presents no chronic toxicity and no conclusions can be drawn for Pb. The Deûle River seems to exhibit chronic toxicity for Pb while Zn is ambivalent.

Table 2
Environmental Quality Standard for Annual Average (EQS-AA) of dissolved metal concentrations and Criteria Maximum Concentrations (CMCs) and Criterion Continuous Concentrations (CCCs) of dissolved Zn and dissolved Pb for Le Quesnoy and the Deûle River. EQNs were found in European Union Water Framework Directives (WFDs) and CMCs and CCCs were calculated from water hardness as recommended in USEPA [42]. For Pb, $\text{CMC} = \exp[1.273 \times \ln(\text{hardness}) - 1.460] \times [1.46203 - 0.145712 \times \ln(\text{hardness})]$ and $\text{CCC} = \exp[1.273 \times \ln(\text{hardness}) - 4.705] \times [1.46203 - 0.145712 \times \ln(\text{hardness})]$. For Zn, $\text{CMC} = \exp[0.8473 \times \ln(\text{hardness}) - 0.884] \times 0.978$ and $\text{CCC} = \exp[0.8473 \times \ln(\text{hardness}) - 0.884] \times 0.986$. Quality of the two studied sites according to the different norms: NT – non toxic (acid-leachable < norm) or T – toxic (norm < acid-leachable).

Site – hardness (mg L^{-1} of $CaCO_3$ equivalent)	Metal	EQS-AA (nM)	CMC (nM)	CCC (nM)
Le Quesnoy – 79	Pb	34.75 NT	161 T	2.59 NT
	Zn	119.2 NT	1278 NT	1288 NT
Deûle – 127	Pb	34.75 T	271 T	4.35 NT
	Zn	119.2 T	1916 NT	1931 NT

4. Conclusion

An adaptable automatic trace metal monitoring system for on-line measurement, based on voltammetric methods, has been assembled with commercially available and rather inexpensive parts. Static mercury drop electrode was deployed as a working electrode for its still best stability, sensitivity and reproducibility. Mn, Zn, Cd, Pb, oxygen and reduced sulphur species were successfully monitored up to 16 times per day in two different water systems: Le Quesnoy pond and the Deûle River at Auby city in northern France. Two main controlling factors were distinguished for both places. First was turbidity with irregular but with cyclic variations, some large and sudden peaks being detected mostly during the day. Second was luminosity and temperature. All other parameters were then evolving with at least one of these two factors [40]. Biological activity was supposed and was deducible from the measured parameters. For orientation, the obtained results were compared with an Environmental Quality Standard, the Criteria Maximum Concentration and the Criterion Continuous Concentration. Calculated for filtered water fractions, they were compared with non-filtered metal fraction, overestimating a potential hazard. Biological tests will now be needed to study the pertinence of the non-filtered water fractions toward toxicity, especially since these are the fractions the living organisms are exposed to.

In the future, the challenge would be to follow more in detail and more quantitatively the effects of biological uptake and chemical speciation of dissolved metals. Also, in the future, a system such as the one described in the present work, could be easily adapted to new demands, depending on the water system that should be monitored, on a possible particular analyte that should be measured, on the improvement of mercury-free sensors that are expected and on the application of “early warning” protocols, which are important for the sustainable environmental management of the water bodies.

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