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S. Papias, M. Masson, S. Pelletant, Stéphanie Prost-Boucle, Catherine Boutin. In situ continuous monitoring of nitrogen with ion-selective electrodes in a constructed wetland receiving treated wastewater: An operating protocol to obtain reliable data. Water Science and Technology, 2018, 77 (6), pp.1706-1713. 10.2166/wst.2018.052 . hal-01884674

HAL Id: hal-01884674

https://hal.science/hal-01884674v1

Submitted on 1 Oct 2018

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Author-produced version of the article published in Water Science and Technology, 2018; 77 (6):1706-1713
The original publication is available at http://wst.iwaponline.com/content/ppiwawst/early/2018/02/12/wst.2018.889.full.pdf
doi : 10.2166/wst.2018.052

In situ continuous monitoring of nitrogen with ion-selective electrodes in a constructed wetland receiving treated wastewater: an operating protocol to obtain reliable data

Sandrine Papias, Matthieu Masson*, Sébastien Pelletant, Stéphanie Prost-Boucle and Catherine Boutin

Irstea, UR MALY Milieux aquatiques, écologie et pollutions, centre de Lyon-Villeurbanne, 5 rue de la Doua, BP 32108, 69616 Villeurbanne Cedex, France.

**corresponding author: matthieu.masson@irstea.fr*

Abstract

Constructed Wetlands receiving treated wastewater (CWtw) are placed between Wastewater Treatment Plants and receiving water bodies, under the perception that they increase water quality. A better understanding of the CWtw functioning is required to evaluate their real performance. To achieve this, *in situ* continuous monitoring of nitrate and ammonium concentrations with Ion-Selective Electrodes (ISEs) can provide valuable information. However, this measurement needs precautions to produce good data quality, especially in areas with high effluent quality requirements. In order to study the functioning of a CWtw instrumented with 6 ISEs probes, we have developed an appropriate methodology for probe management and data processing. It is based on an evaluation of performance in the laboratory and an adapted field protocol for calibration, data treatment and validation. The result is an operating protocol concerning an acceptable cleaning frequency of two weeks, a complementary calibration using CWtw water, a drift evaluation and the determination of limits of quantification (1 mgN/L for ammonium and 0.5 mgN/L for nitrate). An example of a 9-month validated dataset confirms that it is fundamental to include the technical limitations of the measuring equipment and set appropriate maintenance and calibration methodologies in order to ensure an accurate interpretation of data.

Keywords: ammonium, electrochemical sensor, free-water surface constructed wetland, long-term monitoring, nitrate

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INTRODUCTION

The quality of surface waters with respect to eutrophication and nutrients concentrations is an objective of the Water Framework Directive which asks to achieve a good chemical and ecological status of all water bodies across the European Union by 2021. Moreover, the classification of a territory as a nutrient-sensitive area often implies more binding emission limit values for nitrogen and phosphorus for the Wastewater Treatment Plants (WWTPs). In this context, the use of Constructed Wetlands receiving treated wastewater (CWtw) has recently become attractive in France under the perception that they increase water quality. Placed between the WWTP and the receiving water body, the CWtw is not included in the WWTP. Therefore, more than 500 CWtws are in operation in France, most of them have been built in the last 5 years (Prost-Boucle & Boutin 2013). It also highlights that they have a multitude of configurations (meadows, ponds, ditches and "miscellaneous", i.e. specific design using filling material) and intended outcomes, but no clear link between them. In these systems, the fate of conventional pollutants, such as nitrogen, depends on processes occurring in the different compartments of CWtws: free water, soil, plants. In order to monitor nitrogen concentrations along the CWtw and to assess CW performances, *in situ* and continuous measurement can be considered as a method of choice compared to classic method needing field sampling then laboratory measurement (Olsson et al. 2014). Ion-Selective Electrodes (ISEs), electrochemical sensors based on potentiometric methods (Cammann 1979), are more and more installed in WWTPs as they allow *in situ* and continuous measurement of ions such as nitrate and ammonium (Åmand et al., 2013). However, ISEs need carefully precautions and specific protocols must be deployed (installation, calibration, maintenance, data validation) to guarantee reliable data (Guigues et al., 2002; Thomann et al. 2002). In the case of sensitive areas with low outlet water concentrations for nitrogen (typically <2 mgN/L for ammonium), management of ISE probes and data processing must be considered as a challenge because the limits of the sensors may be met (Kaelin et al. 2008).

In this context, we propose a reliable methodology to increase the quality of data from ISE probes installed in a CWtw characterized by low ranges of nitrate (NO_3-N) and ammonium (NH_4-N) concentrations. This methodology is based on an evaluation of probe performance in the laboratory and an adapted field protocol for calibration, data treatment and validation. An example of treated and validated data shows the potential and limits of these probes for the long-term monitoring (9 months) of the nitrogen dynamic in the CWtw.

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METHODS

Site description and instrumentation

The studied CWtw is located in the city of Marguerittes (Southern France) and is operated since summer 2013. The CWtw is similar to a free water surface CW and consists of two ponds in series, P1 and P2 (Figure 1), of 3575 m² and 6370 m² respectively. The pond P1 receives between 1000 and 3000 m^3/d of treated wastewater from the 15000 population equivalent WWTP. Then, the water flows into the pond P2 composed of five different areas before discharging into the Canabou River. The measured average hydraulic residence time (hydraulic tracing with uranine/fluorescein; recovery rates between 69 and 90%) along the CWtw is approximately 3 days.

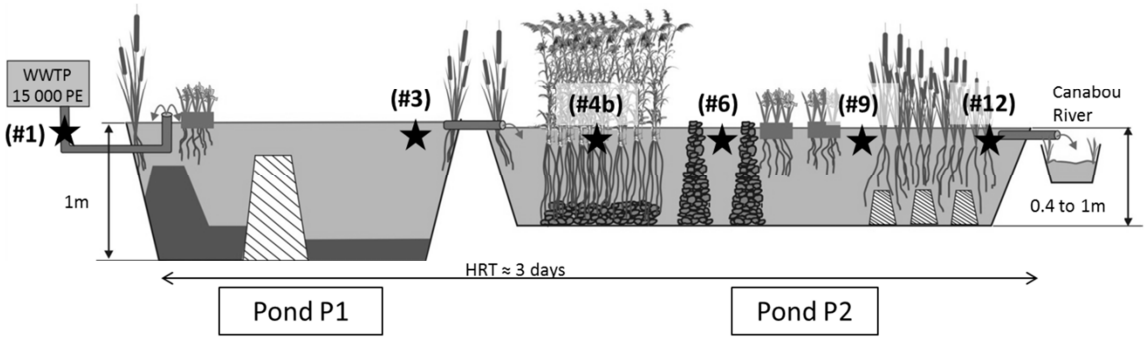

Figure 1 Schematic representation of the CWtw constituted by two main ponds (P1 and P2) and location of the 6 ISE probes (#1), (#3), (#4b), (#6), (#9) and (#12) (black stars).

The CWtw has been instrumented with 6 ISE probes (specific sensors VARION AN/A WTW-Secomam) measuring NO_3-N and NH_4-N concentrations with a 5-min step recording. This study presents a 9-month dataset running from August 2015 to April 2016. A focus is made on probe #1, located at the outlet of the WWTP, which represents the influent of the CWtw (Figure 1). According to manufacturer instructions, the measurement ranges of NO_3-N and NH_4-N concentrations are 0.1-100 mg/L with a response time of 3 min in both surface water and wastewater. During the installation of new sensors (typically every 6-9 months), a calibration with manufacturer solutions (from 5 to 60 mgN/L) was systematically performed. It was followed by a matrix adjustment using water from the CWtw spiked with sodium nitrate and ammonium sulfate (AnalaR NORMAPUR quality) to reach NO_3-N and NH_4-N concentrations around 5 mgN/L.

Measurement of reference NO_3-N and NH_4-N concentrations

Ionic chromatography was used as reference method for the determination of NO_3-N and NH_4-N concentrations in the solutions used for laboratory tests and in the grab samples collected in the CWtw. The NF EN ISO 10304-1 (2009) and NF EN ISO 14911 (1999) standards were applied,

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respectively, for NO_3-N and NH_4-N measurements. Limits of Quantification (LoQ) for NO_3-N and NH_4-N are 0.45 mgN/L and 0.02 mgN/L respectively, and precision was better than 6% for NO_3-N and 8% for NH_4-N.

Laboratory tests

The performance of ISE probes was evaluated in laboratory based on the ISO 15839 (2003) standard (Rieger et al. 2002). The applied protocol needed the preparation of several solutions spiked with well-defined NO_3-N and NH_4-N concentrations (ammonium sulfate and sodium nitrate, AnalaR NORMAPUR quality). French bottled mineral water (Saint Antonin) was used for its composition without nitrogen (NO_3-N and NH_4-N concentrations were below 0.45 mg/L and 0.02 mg/L, respectively). Because the measurement is influenced by the ionic strength and the matrix of the measuring water (Rieger et al. 2002), the solution used for the experimentations (S_{exp}) was prepared by diluting 3-times the mineral water with ultra-pure water to fit the ionic strength of the CWtw. NO_3-N and NH_4-N concentrations of the different solutions prepared by spiking S_{exp} were systematically controlled using the reference methods. The following key parameters have been evaluated:

- The response times of the sensors to sudden increasing and decreasing changes of NO_3-N and NH_4-N concentrations were estimated by successively immersing the probe in S_{exp} spiked with NO_3-N and NH_4-N concentrations of 5.0 and 80 mgN/L (i.e. 5% and 80% of the concentration range).
- The linearity between measured concentrations and theoretical concentrations was evaluated by measuring NO_3-N and NH_4-N concentrations in S_{exp} adjusted to 0.5, 1.0, 2.0, 5.0, 10, 25, 40, 60, 80 and 95 mgN/L. This experiment was repeated 6-times in intermediate precision conditions. The check of the linearity was performed by comparing the mean bias for each concentration with maximum permissible deviation values determined on the basis of the laboratory expertise.
- Based on NF T 90-210 (2009) standard, assumed LoQs of 0.5 and 1.0 mgN/L for NO_3-N, and 1.0 and 2.0 mgN/L for NH_4-N have been analyzed.
- The interferences were quantified in a solution containing NO_3-N and NH_4-N concentrations of 5.0 mgN/L in which successive adds of chloride potassium were completed (maximum concentration for chloride : 700 mg/L; for potassium : 800 mg/L) as chloride and potassium ions represent the main interferences for NO_3-N and NH_4-N measurements, respectively (Winkler et al. 2004).

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Field procedures

The maintenance frequency has been set at two weeks. Sensors were cleaned with CWtw water then tap water if necessary. If biofouling was observed, a soft tissue could be used. To evaluate the impact of the cleaning frequency on measurements, NO_3-N and NH_4-N concentrations measured by the probes before and after cleaning procedure were systematically recorded.

ISE probes are subject to drift over time (Winkler et al. 2004) and a protocol was developed to evaluate this potential drift. After cleaning procedure, the probes were systematically immerged in a drift control solution (Sol_{DC}) for NO_3-N and NH_4-N measurement. The Sol_{DC} consists on filtered water (<0.45 µm) collected in the CWtw and spiked with ammonium sulfate and sodium nitrate (AnalaR NORMAPUR quality) to reach NO_3-N and NH_4-N concentrations of 5 mgN/L. The Sol_{DC} was stored at 4°C in the dark. Every two weeks, the NO_3-N and NH_4-N concentrations of the Sol_{DC} were measured using reference methods to control the stability of NO_3-N and NH_4-N concentrations, and then 1L of Sol_{DC} was brought to the field for drift control.

Despite the initial manufacturer calibration and matrix adjustment, additional local calibration has been performed. Every two weeks, water was systematically sampled close to each probe just before the cleaning maintenance. The NO_3-N and NH_4-N concentrations given by the probes during the sampling were associated with the corresponding concentrations measured in the grab samples by reference methods in laboratory. The resulting dataset was split in two parts: 50% were used for local calibration and the other 50% were used for data validation. In order to cover a broader range of concentrations, 3 additional couples of points were produced by using water from the CWtw adjusted to 10, 15 and 20 mgN/L for NO_3-N and 5.0, 10 and 15 mgN/L for NH_4-N.

RESULTS AND DISCUSSION

ISE performance evaluation in laboratory

The response times for increasing concentration changes were evaluated to about 2 min for the two sensors. The response times for decreasing concentration changes were found to be close to 15 s (Table 1). These results are consistent with response times given by the manufacturer (< 3min). The estimated response times seem to be sufficiently low to observe the variation of NO_3-N and NH_4-N concentrations along the CWtw. Moreover, this result confirms that an acquisition frequency of 5 min is well adapted.

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Table 1 Results of the performance evaluation for the ISE probe obtained in laboratory. LoQs were analyzed with maximum permissible deviation (MPD) values of 30% and 60%.

		NO_3-N sensor	**NH_4-N sensor**
Response time (s)	to increasing concentrations	130	125
	to decreasing concenrations	14	13
LoQ (mgN/L)	with 30% MPD value	0.5	1.0
	with 60% MPD value	1.0	2.0
Interference ratio	Chloride	negligeable	-
	Potassium	-	1:25

160

For each sensor, two LoQs have been verified depending on the maximum permissible deviation values (high value: 60%; intermediate value: 30%; Table 1) which are chosen by the laboratory based on its own expertise. Given that NO_3-N and NH_4-N concentrations measured along the CWtw are generally low and inferior to 2 mgN/L, the lowest LoQs is chosen, i.e. 0.5 mgN/L for
165 NO_3-N and 1.0 mgN/L for NH_4-N, to allow the quantification of a maximum of data. In return, we assume a lower quality of data close to the LoQ concentrations.

According to manufacturer, chloride and potassium may be considered as the main interfering ions for NO_3-N and NH_4-N measurement, respectively. During the interference tests, the NO_3-N concentrations remain rather constant with increasing chloride concentrations (Table 1). This
170 suggests that the chloride interferences on NO_3-N measurement may be considered as negligible despite chloride concentration variations observed along the CWtw (160-230 mg/L; data not shown). The NH_4-N concentrations linearly increase with increasing potassium concentrations. The interference is evaluated to be 1 mgN/L NH_4-N for a potassium concentration increase of 25 mg/L (Table 1). The potassium concentrations measured along the CWtw varied from 15 to 25 mg/L (data
175 not shown). This suggests that NH_4-N concentrations are potentially interfered by +/- 0.2 mgN/L in the case of the studied CWtw and may be neglected. For both sensors, the estimated interferences are lower than those announced by the manufacturer (3% for chloride and 10% for potassium) and are consistent with the cross-sentivities values given by Winkler et al. (2004) with 1:300 for chloride and between 1:15 and 1:30 for potassium.

180 The verification of the linearity in the range of 0.5-100 mgN/L was performed by comparing, for each concentration, the mean bias (n=6) with maximum permissible deviation values defined by the laboratory (Table 2). For NO_3-N concentrations superior to 2.5 mgN/L and NH_4-N concentrations superior to 5 mgN/L, the mean bias were inferior to 20%. For lowest concentrations the mean biases increased and ranged between 25% and 65% (Table 2). Increase of bias for low concentrations is
185 consistent with electrochemical theory that suggests non-Nernstian response (i.e. nonlinear response) for low concentrations around few mgN/L (e.g. Winkler et al. 2004). However, taking into

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account maximum permissible deviation values of 60% for concentrations lower than 5×LoQ concentrations and of 20% for higher concentrations, these results suggest that the linearity of the sensors may be verified from 0.5 to 100 mg/L for NO_3-N and from 1 to 100 mg/L for NH_4-N. The estimated bias may be also used to compare concentrations measured by two different probes.

The repeatability, calculated as the standard deviation of the measurements of each concentration level, was generally better than 10% for both sensors and for the whole concentration range (Table 2). This low value may be used to evaluate significance of NO_3-N and NH_4-N concentration variations measured by a given probe.

Table 2 Mean relative bias (n=6) and repeatability (calculated as standard deviation, n=6) for each tested concentration. The maximum permissible deviation (MPD) values were defined by the laboratory at 60% for concentrations inferior to 5×LoQ and at 20% for higher concentrations.

	NO_3-N sensor		**NH_4-N sensor**	
Concentration (mgN/L)	LoQ - 5×LoQ 0.5 – 2.5	> 5×LoQ 2.5 - 100	LoQ - 5×LoQ 1.0 – 5.0	> 5×LoQ 5.0 - 100
Relative mean bias	25% - 46%	-2% - 20%	32- 64%	-3 - 20%
MPD values	60%	20%	60%	20%
Repeatability	7% - 12%	2% - 7%	4% - 7%	3%

Cleaning frequency

No strong difference (generally <20%) is observed between NO_3-N and NH_4-N concentrations measured before and after cleaning procedure (Figure 2), excepted for one probe for which stronger deviations are observed for the NO_3-N sensor. Moreover, no difference has been observed between summer (maximum potential of biofouling development) and winter. Therefore, these results suggest that the biofouling impact may be considered as negligible for an exposure time of two weeks without any maintenance in this CWtw.

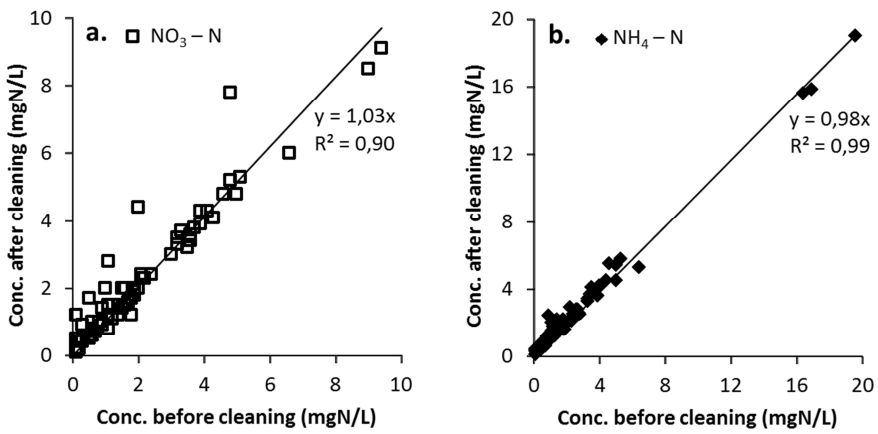

Figure 2 NO_3-N (a) and NH_4-N (b) concentrations measured just before and after cleaning procedure by the 6 probes installed on the CWtw.

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Evolution of the drift over time and correction

This part is focused on the probe #1 installed at the entry of the CWtw. The drift control procedure started 5 months after the installation of the probe and covered the 4 last months of the sensor life. The NO_3-N concentrations measured in the drift control solutions stayed rather constant during the 4 last months (Figure 3a). Therefore, no correction is considered for the NO_3-N signal.

Concerning NH_4-N sensor, a drift is observed after 30 days of monitoring (Figure 3a). Assuming a linear drift over time, we estimate that NH_4-N concentrations increased by 0.1 mgN/L every day. However, an offset daily correction of 0.1 mgN/L applied on the raw signal leads to negative values which suggests that the drift experimentally determined is overestimated. Another way to estimate the drift is possible thanks to the grab samples with concentrations below 0.10 mgN/L assuming that their corresponding probe concentrations should remain steady over time and form a baseline. Despite the low number of grab samples concentrations (n=4), this baseline seems to increase linearly with time (Figure 3b). The slope of the relationship, i.e. 0.03 mgN/L/d, was used to estimate a more appropriate drift. The raw NH_4-N signal was corrected by subtracting 0.03 mgN/L/day from November 2015.

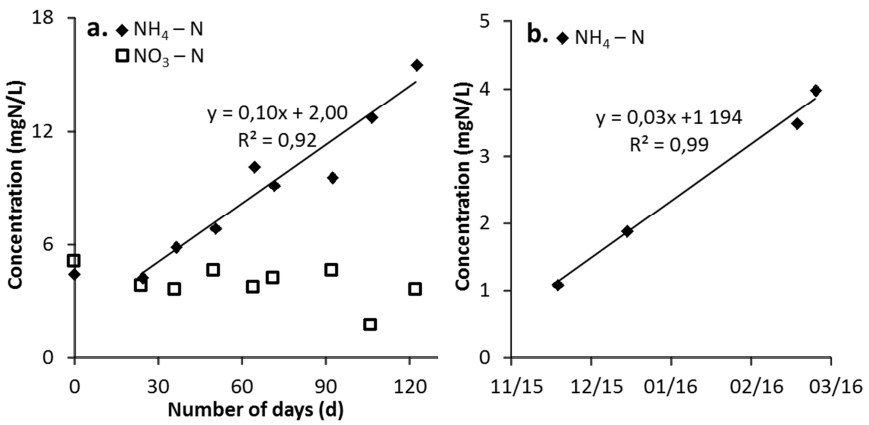

Figure 3 a) Evolution of the NO_3-N (open squares) and NH_4-N (black diamonds) concentrations measured by the probe (1) in the Sol_{DC} during the 4 last month of the sensor life. b) Evaluation of the NH_4-N drift based on the increase in time of the NH_4-N concentrations measured by the probe for the period where concentrations measured in the grab samples were low (<0.10 mgN/L).

Local calibration and data validation

After the drift correction, local calibration is completed using i) 50% of available couples of probe-grab sample points and ii) the 3 additional couples of adjusted concentration points (Figure 4a, 4b). Each slope of linear regression is used to correct the data measured by the probe. For the studied probe #1, a correction by a factor 1.24 is applied on NO_3-N concentrations (Figure 4a). The local calibration of NH_4-N concentrations is more complex as all NH_4-N concentrations measured into

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grab samples are always below 1 mgN/L (i.e. below the LoQ determined for the NH_4-N sensor). In consequence, only the 3 additional couples of adjusted concentration (5, 10 and 15 mgN/L) points are used to build the calibration curve (Figure 4b). For the probe #1, a correction factor of 0.60 is applied to the NH_4-N signal already corrected from the drift.

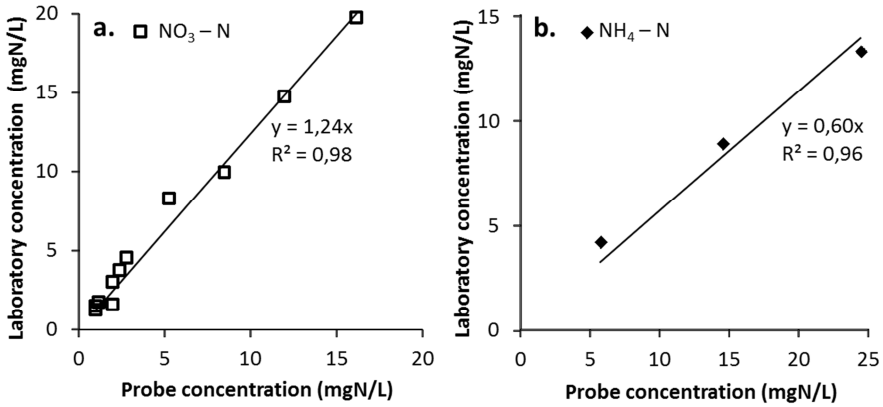

Figure 4 NO_3-N (a) and NH_4-N (b) local calibrations performed for the probe #1.

The other part of available couples of probe-grab sample points is used for data validation. Relative errors are calculated as the difference of the concentrations measured by the probe and measured in the grab sample and divided by the concentration measured in the grab sample. For NO_3-N concentrations between LoQ and 5×LoQ (i.e. 0.5-2.5 mgN/L), the relative errors are negative and close to -30% (Table 3). For NO_3-N concentrations superior to 5×LoQ (i.e. 2.5 mg/L), the relative errors slightly decrease and varied between -2% to 20% (Table 3). These results suggest that measurement by the ISE probe is of good quality for NO_3-N monitoring in the CWtw. For NH_4-N, data for validation is not available as the whole dataset have been used for the local calibration. To remedy this situation, additional samples could be prepared using CWtw water spiked with NH_4-N to cover the concentration range measured by the probe (until 40 mgN/L). Half of these samples could be used for local calibration and the other half could be used for validation. Moreover, for the next dataset produced by new sensors, cross-validation will be considered to improve the local calibration and validation procedure.

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Table 3 Sample set used for validation of NO_3-N measurement: raw probe concentrations, corrected probe concentrations (from local calibration) and reference laboratory concentrations. Relative errors between corrected and reference concentrations.

	Raw conc. (mgN/L)	Corrected conc. (mgN/L)	Reference conc. (mgN/L)	Relative error
< 5×LoQ	0.8	1.0	1.4	-27%
	1.2	1.5	2.0	-26%
> 5×LoQ	3.3	4.1	4.1	-1%
	3.8	4.7	3.9	20%
	4.8	6.0	5.1	16%
	5.2	6.5	6.6	-2%

Example of data processing

Figure 5 shows the raw NO_3-N and NH_4-N concentrations measured by the probe (#1) and the corrected concentrations. Drift correction has only been performed for NH_4-N signal, while local calibration correction has been applied for NO_3-N and NH_4-N signals. During the 9-month studied period, the NO_3-N concentrations monitored at the entry of the CWtw are clearly variable and ranged between the LoQ value (0.5 mgN/L) and ~13 mgN/L (Figure 5a). Only few values are below the LoQ (<10% of data). Daily variations are observed with maximum concentrations generally measured around midnight (Figure 5a). The amplitude of theses variations are far greater than the measurement repeatability evaluated in the laboratory (<10%), confirming the significance of the NO_3-N daily peaks. Only *in situ* and continuous measurement allows the observation of NO_3-N concentration dynamic at this temporal scale over long period.

Contrary to NO_3-N, data treatment has strongly modified the NH_4-N concentrations (Figure 5b) and corrected NH_4-N concentrations are ~2-fold lower than the raw concentrations. Several NH_4-N peaks are observed with maximum NH_4-N concentrations reaching 15 mgN/L. These peaks are not easily observable with traditional monitoring (i.e. weekly sampling and analysis in laboratory). Unfortunately, the validation of NH_4-N data is less effective than for NO_3-N due to very low concentrations in the grab samples. About 50% of data are below the LoQ (i.e. 1 mgN/L).

The performance evaluation of sensors in laboratory coupled with the quality procedure on the field help to improve the quality of data exploitation. The knowledge of the probe limitations (e.g. LoQ, response time, repeatability…) avoids misinterpretations of temporal NO_3-N and NH_4-N recordings. For example, we recommend to not discuss concentrations inferior to 0.5 mgN/L for NO_3-N, inferior to 1 mgN/L for NH_4-N. In case of nitrogen flux estimation along the CWtw, the values inferior to the LoQ may be replaced by LoQ/2 values. Furthermore, an apparent NH_4-N increase can be the result of the signal drift and not the degradation of water quality entering into the CWtw (for example the global increase observed since November 2015 on the raw signal, Figure 5b). Differences of NO_3-N and NH_4-N concentrations measured by a probe at different times or by several

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doi : 10.2166/wst.2018.052

probes in different locations may be now discussed in regards of the evaluated bias, relative errors and repeatability.

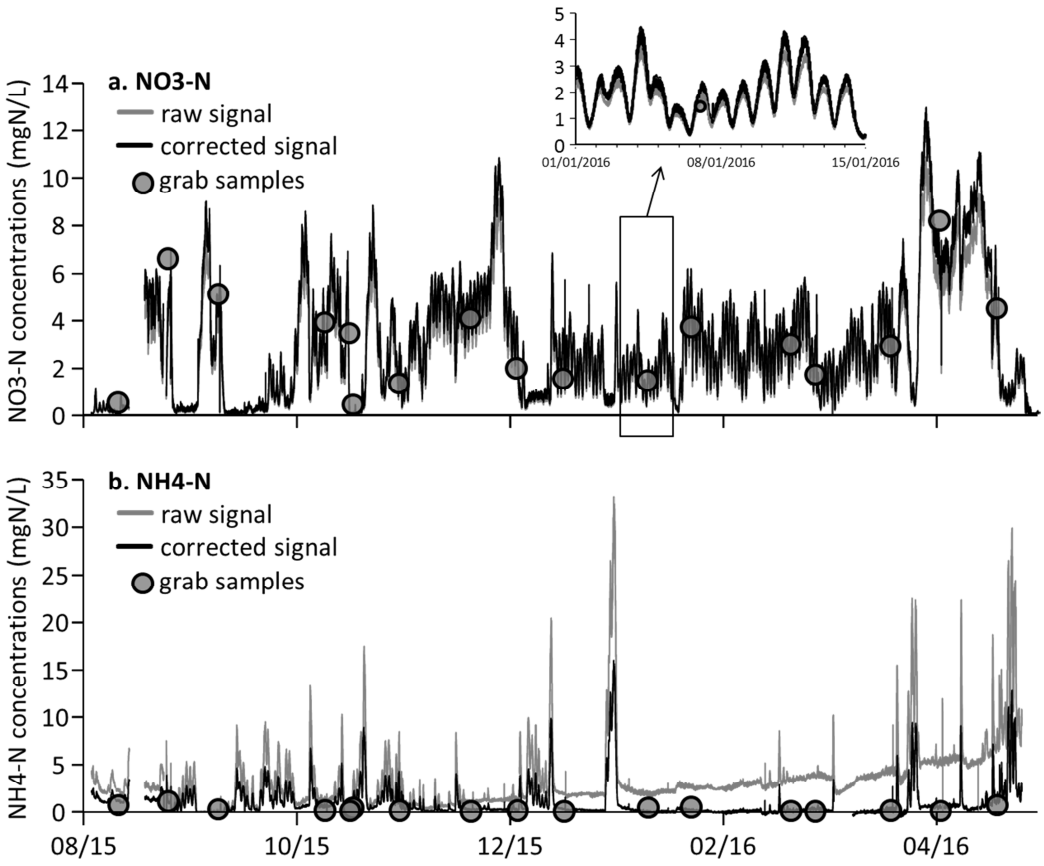

Figure 5 Raw signals (black lines) recorded by the probes #1 for NO_3-N (a) and NH_4-N (b) during August 2015 to March 2016 and signals after correction procedures. The black circles represent the grab samples and the dashed lines represent the LoQ estimated for the probe.

CONCLUSIONS

The methodology implemented for the monitoring of low NO_3-N and NH_4-N concentrations in a CWtw has allowed an efficiency correction of produced data. This methodology is firstly based on an evaluation in the laboratory of the sensor performances (mainly LoQs and repeatability of the measurements). Specific procedures have been implemented to correct data. The evaluation of the potential impact of the biofouling shows that a 2-week maintenance frequency is sufficient. The monitoring of signal drift show no drift for the NO_3-N signal whereas NH_4-N signal drift can been corrected using grab samples. Despite initial calibration and matrix adjustment, a local calibration with grab samples is necessary. Observing these procedures for data correction, a good agreement exists between corrected probe concentrations and reference concentrations measured in the laboratory. The consolidated data made it possible a reliable quantification of NO_3-N and NH_4-N concentrations along the CWtw and a better interpretation of the temporal recordings of low

concentrations, taking into account the technical limitations of the probes (mainly LoQ and repeatability). The presented methodology still needs to be improved by i) the production of NH_4-N concentrated samples for validation, ii) the use of cross validation, or iii) data comparison of two probes installed at the same location.

Acknowledgments

The authors thank the AFB (the French National Agency for Biodiversity) for providing financial support to this work (ZRV program http://zrv.irstea.fr). We gratefully acknowledge the following Irstea colleagues for field campaigns and chemical analysis: Myriam Arhror, Jérémie Aubert, Vincent Bourgeois, Corinne Brosse, Clément Crétollier, Olivier Garcia and Loïc Richard.

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Author-produced version of the article published in Water Science and Technology, 2018; 77 (6):1706-1713
The original publication is available at http://wst.iwaponline.com/content/ppiwawst/early/2018/02/12/wst.2018.889.full.pdf
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