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Modelling the fate of nitrite in an urbanized river using experimentally obtained nitrifier growth parameters

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Abstract

Maintaining low nitrite concentrations in aquatic systems is a major issue for stakeholders due to nitrite's high toxicity for living species. This study reports on a cost-effective and realistic approach to study nitrite dynamics and improve its modelling in human-impacted river systems. The implementation of different nitrifying biomasses to model riverine communities and waste water treatment plant (WWTP)-related communities enabled us to assess the impact of a major WWTP effluent on in-river nitrification dynamics. The optimal kinetic parameters and biomasses of the different nitrifying communities were determined and validated by coupling laboratory experiments and modelling. This approach was carried out in the Seine River, as an example of a large human-impacted river with high nitrite concentrations. The simulation of nitrite fate was performed at a high spatial and temporal resolution ($\Delta t = 10$ min, $\overline{dx} = 500$ m) including water and sediment layers along a 220 km stretch of the Seine River for a 6-year period (2007-2012). The model outputs were in good agreement with the peak of nitrite downstream the WWTP as well as its slow decrease towards the estuary. Nitrite persistence between the WWTP and the estuary was mostly explained by similar production and consumption rates of nitrite in both water and sediment layers. The sediment layer constituted a significant source of nitrite, especially during high river discharges ($0.1-0.4$ mgN $h^{-1}m^{-2}$). This points out how essential it is to represent the benthic layer in river water quality models, since it can constitute a source of nitrite to the water-column. As a consequence of anthropogenic emissions and in-river processes, nitrite fluxes to the estuary were significant and varied from 4.1 to 5.5 TN d^{-1} in low and high water discharge conditions, respectively, over the 2007-2012 period. This study provides a methodology that can be applied to any anthropized river to realistically parametrize autochthonous and WWTP-related nitrifier communities and simulate

32 nitrite dynamics. Based on simulation analysis, it is shown that high spatio-temporal resolution
33 hydro-ecological models are efficient to 1) estimate water quality criteria and 2) forecast the
34 effect of future management strategies. Process-based simulations constitute essential tools to
35 complete our understanding of nutrient cycling, and to decrease monitoring costs in the context
36 of water quality and eutrophication management in river ecosystems.
37 *Keywords:* Nitrite, Modelling, Nitrification, WWTP, River, Water quality

38 1. Introduction

39 Along with the on-going improvement of nitrogen removal efficiency in Waste Water Treat-
40 ment Plants (WWTPs), total nitrogen concentrations in WWTP effluents have been reduced
41 ([García-Barcina et al., 2006](#); [Carey and Migliaccio, 2009](#); [Rocher et al., 2011](#)). Even though
42 the total nitrogen load has decreased, nitrite concentrations can still exceed the European stan-
43 dard of good environmental status of 0.09 mgN L^{-1} in urbanized river systems ([Helder and](#)
44 [De Vries, 1983](#); [Morris et al., 1985](#); [von der Wiese and Wetzel, 1998](#); [Garnier et al., 2006](#);
45 [Rocher et al., 2011](#)), as well as in agricultural ecosystems ([Corriveau et al., 2010](#)). In these
46 anthropogenic systems, concentrations are well above 0.01 mgN L^{-1} found in pristine streams
47 ([Meybeck, 1982](#)). Compared to nitrate, nitrite is toxic at low concentrations. A well-known
48 consequence of nitrite toxicity is the blue baby syndrome due to direct ingestion of nitrite or
49 to conversion of ingested nitrate to nitrite ([Knobeloch et al., 2000](#)). Maintaining low nitrite
50 concentrations is thus a major environmental issue. However, nitrite in rivers is rarely studied
51 independently from nitrate, due to its much lower concentration.

52 The presence of nitrite in aquatic systems results from its production and persistence. Nitrite
53 is an intermediate compound produced by nitrification, denitrification and/or dissimilatory
54 nitrate reduction to ammonium pathways in water and sediment ([Wilderer et al., 1987](#); [Kelso](#)
55 [et al., 1997](#); [Philips et al., 2002](#); [Park and Bae, 2009](#)). Nitrification is a two-step process
56 involving two distinct microbial communities. Ammonia oxidizers (AO) transform ammonia
57 to nitrite, and nitrite oxidizers (NO) use nitrite and generate nitrate. Ammonia oxidation is
58 generally considered to be the limiting step ([Kowalchuk and Stephen, 2001](#)) avoiding nitrite
59 accumulation. However nitrite has been shown to persist in oxic river waters due to low water
60 residence time, low nitrification rates, as well as similar ammonia and nitrite oxidation rates,
61 or non steady-state nitrification ([Brion et al., 2000](#); [Philips et al., 2002](#)). In oxic waters of

62 large rivers, benthic exchanges of nitrogen at the sediment-water interface are expected to be
63 low due to low surface-to-volume ratios (Pinay et al., 2002). Based on this general knowledge,
64 nitrification in the water column is supposed to be the main process affecting nitrite production
65 and consumption in large oxic rivers, especially in high river discharge conditions. Anyhow,
66 nitrite can be produced in river bed sediments and transferred to the water column by diffusion
67 (Morris et al., 1985; Kelso et al., 1997). It is important to quantify the impact of this benthic
68 nitrite production on nitrogen cycling and export to estuaries in the case of large human
69 impacted river systems.

70 WWTPs constitute a potential source of nutrients *e.g.* nitrite as well as microorganisms
71 (nitrifiers included) to riverine waters, depending on the processing of the influent (Servais et al.,
72 1999a; Brion et al., 2000; Cébron et al., 2003). Species and activity of microorganisms (nitrifiers
73 included) present in WWTP effluents can differ from those found in the river upstream the
74 effluent and alter the river ecological functioning (Goñi Urriza et al., 2000; Féray and Montuelle,
75 2002; Cébron et al., 2003). Consequently WWTP effluents potentially modify the nitrifying
76 community structure and biomass, and sometimes lead to an increase in nutrient concentrations
77 *e.g.* ammonium in river systems, even though treatment processes were significantly improved
78 during the last decades. As a potential consequence, nitrifying kinetics and nitrite dynamics
79 within the aquatic system are impacted.

80 Models constitute efficient integrative tools to study spatio-temporal variations of nitrogen
81 dynamics in rivers and improve our understanding of in-river biogeochemical cycling. Many
82 hydro-ecological models of different complexity are available (Rauch et al., 1998; Reichert,
83 2001; Arheimer and Olsson, 2003; Cox, 2003; Kannel et al., 2011; Sharma and Kansal, 2013).
84 They tend to simulate a large range of biogeochemical processes, requiring a large number of
85 parameters. However, not all models represent nitrite as an intermediate between the 2-step
86 nitrifying process, and even less models consider explicitly the involved nitrifier biomasses.
87 These models can be used to simulate average nitrite profiles at a pluri-annual time scale
88 (Garnier et al., 2007), or to simulate nitrite dynamics at a high resolution along small river
89 stretches and for a short period of time (Reichert, 2001). To our knowledge, no former study
90 focused on nitrite dynamics at a high spatio-temporal resolution, and at large spatio-temporal
91 scales.

92 The aim of our study is to propose a cost-effective and realistic approach to study nitrifica-
93 tion dynamics and improve the modelling of nitrogen species (and especially nitrite) in human-
94 impacted river systems. The Seine River is a pertinent study case for this purpose, as this river
95 receives effluents from the biggest European WWTP (called SAV for “Seine AVal”), and is
96 characterized by high nitrite concentrations, exceeding the good EU WFD criteria downstream
97 this WWTP (Rocher et al., 2011). Nitrogen removal in the SAV WWTP has significantly
98 increased since the addition of nitrification and denitrification units in 2007 and 2011, and
99 changed the nitrogen dynamics in the Seine River (Rocher et al., 2011). These modifications
100 most likely changed kinetic parameters of nitrifying communities in the SAV effluent, as well
101 as the subsequent nitrite dynamics within the Seine River downstream SAV.

102 The originality of this study is the distinction between natural river and WWTP nitrifying
103 communities. The biomass and kinetic parameters of each river and WWTP-related nitrify-
104 ing community were characterized using a cost-effective approach. (1) Potential ammonia and
105 nitrite oxidation activity in river and WWTP waters were studied separately using batch in-
106 cubations with inhibitors for the two processes. The evolution of nitrite concentrations with a
107 lumped model representing the 2-step nitrification process were then fitted in order to deter-
108 mine optimal values of biomass and kinetic parameters (maximal growth rate, half-saturation
109 constant) of ammonia and nitrite oxidizers. (2) Experimentally deduced biomass and kinetic
110 parameters defined for riverine and WWTP-related nitrifying communities were validated in a
111 hydro-ecological model of the Seine River including water and sediment layers along a 220 km
112 stretch for a 6-year period (2007-2012). This allowed the assessment of WWTP impact on
113 the fate of nitrite and nitrifiers along a human-impacted river. Nitrogen mass balances were
114 assessed up- and downstream the WWTP for different hydrological conditions. The model was
115 used to quantify the effect of benthic and pelagic processes on nitrite fluxes exported to the
116 estuary, and to forecast the effect of new management strategy impacts on river water quality.

117 **2. Methods**

118 *2.1. Study site*

119 The Seine River is the second longest French river (776 km long), which flows north-west
120 towards the English Channel. The climate is temperate, with oceanic and semi-continental
121 influences. The mean annual discharge is $210 \text{ m}^3 \text{ s}^{-1}$ in Paris for the period 1978-2011. Over

122 this time period, the first discharge decile is $90 \text{ m}^3 \text{ s}^{-1}$ (discharge lower than this value 10
123 % of the time), while the last one is $670 \text{ m}^3 \text{ s}^{-1}$. The summer river discharge is artificially
124 maintained at its value in Paris from upstream water release reservoirs. Two major tributaries
125 are the Marne and Oise Rivers, with an average discharge of 95 and $100 \text{ m}^3 \text{ s}^{-1}$, respectively.
126 Water temperatures range from $5 \text{ }^\circ\text{C}$ in winter to $25 \text{ }^\circ\text{C}$ in summer. The Seine River is a highly
127 anthropized system dominated by agriculture, urbanization and industry. Downstream Paris,
128 the Seine River is strongly impacted by urbanization with a population of 12 million inhabitants
129 concentrated over an area of about $12,000 \text{ km}^2$ (Fig. 1). The biggest Parisian and European
130 WWTP (SAV) is located downstream of Paris and treats waste water from more than 5 million
131 population equivalent (treatment capacity of $1.7 \cdot 10^6 \text{ m}^3 \text{ d}^{-1}$) (Rocher et al., 2011). In 2007, a
132 tertiary biological treatment composed of a nitrification/denitrification unit was implemented
133 in the SAV WWTP for 70 % nitrogen removal.

134 2.2. Sampling design

135 River water samples (10-20 L) were collected in November 2012 upstream SAV (at Asnières),
136 and in the SAV effluent (Fig. 1). Samples were brought back to the laboratory after sampling
137 and stored at $4 \text{ }^\circ\text{C}$ in the dark. Aliquots were immediately filtered over $0.2 \text{ }\mu\text{m}$ PVDF filters
138 and analyzed for nitrite concentrations.

139 2.3. Laboratory incubations and analyses

140 Unfiltered water samples (200-250 mL) were incubated in Erlenmeyers of 500 mL in the dark
141 at $20 \text{ }^\circ\text{C}$ under constant agitation (120 rpm) for 14 days. According to Cébron and Garnier
142 (2005), two selective inhibitors, *i.e.* allylthiourea (0.1 mM) and sodium chlorate (10 mM), were
143 used to study separately NH_4^+ and NO_2^- oxidation reactions. Aliquots were sampled daily
144 to measure NO_2^- concentrations. Additional water samples were incubated in the presence of
145 the two inhibitors to verify the complete nitrification inhibition. Samples from both sites were
146 also amended with NH_4^+ (14 mgN L^{-1}) and incubated to observe NO_2^- dynamics with active
147 (non-inhibited) ammonia and nitrite oxidizers. The concentrations of NO_2^- were determined
148 using the colorimetric method of Rodier (1984).

149 2.4. Nitrification model (C-RIVE)

150 The nitrification processes in the incubated water samples were simulated with the C-RIVE
 151 model (Vilmin et al., 2012), the stand-alone version of the biogeochemical module of the PROSE
 152 hydro-ecological model (see section 2.6). C-RIVE is an adaptation of the RIVE model (Billen
 153 et al., 1994; Garnier et al., 1995), which mimics carbon, nitrogen, phosphorus and oxygen
 154 cycling in river systems. Living species involved in these biogeochemical cycles, as nitrifiers,
 155 are explicitly represented. The nitrification process has recently been detailed in RIVE and
 156 C-RIVE models, including the appearance of nitrite and nitrous oxide intermediates (Cébron
 157 et al., 2005; Garnier et al., 2007; Polus et al., 2011; Vilmin et al., 2012).

158 A brief description of the formulation used to describe the nitrification processes is given
 159 here. Description, unit and fixed value for parameters and variables are given in Table 1.
 160 The evolution of nitrifier biomass $[BN]_{i,j}$ is determined by nitrifier growth and mortality, and
 161 depends on temperature, NH_4^+ or NO_2^- , and O_2 concentrations (Eq. 1, as described by Polus
 162 et al. (2011)).

$$\frac{d[BN]_{i,j}}{dt} = \left(\mu_{i,j} - mort_i - \frac{V_{sed,i}}{h} \right) [BN]_{i,j} \quad (1)$$

163 i is the index referring to the nitrifying community, *i.e.* ammonia oxidizers (*AO*) or nitrite
 164 oxidizers (*NO*). j is the index referring to the sample location (river water or SAV effluent).
 165 Note that the sedimentation velocity $V_{sed,i}$ is set to zero for the simulations of the incubated
 166 water samples, as these samples are agitated during the experiment.

167 Growth rates of ammonia and nitrite oxidizers ($\mu_{i,j}$) are calculated according to the following
 168 equations 2 and 3 (Garnier et al., 2007):

$$\mu_{AO,j} = \mu_{\max,AO,j} f(T) \left(\frac{[NH_4^+]}{[NH_4^+] + K_{NH_4^+,j}} \right) \left(\frac{[O_2]}{[O_2] + K_{O_2,AO}} \right) \quad (2)$$

$$\mu_{NO,j} = \mu_{\max,NO,j} f(T) \left(\frac{[NO_2^-]}{[NO_2^-] + K_{NO_2^-,j}} \right) \left(\frac{[O_2]}{[O_2] + K_{O_2,NO}} \right) \quad (3)$$

169 with a temperature dependance described by the following equation (Polus et al., 2011):

$$f(T) = f(T_{\text{opt}}) e^{-\frac{(T-T_{\text{opt},i})^2}{\sigma_i^2}} \quad (4)$$

170 The quantity of consumed ammonium, nitrite and oxygen depends on growth rates $\mu_{i,j}$,
 171 nitrification yields Y_i and nitrifier biomass $[BN]_{i,j}$ according to the following equations (Eqs.
 172 5, 6 and 7).

$$\frac{d[DIN_{\text{cons}}]}{dt} = - \sum_j \frac{\mu_{i,j}}{Y_i} [BN]_{i,j} \quad (5)$$

$$\frac{d[DIN_{\text{prod}}]}{dt} = + \sum_j \frac{\mu_{i,j}}{Y_i} [BN]_{i,j} \quad (6)$$

$$\frac{d[O_2]}{dt} = - \sum_j r_{O_2,i} \frac{\mu_{i,j}}{Y_i} [BN]_{i,j} \quad (7)$$

173 where DIN_{cons} and DIN_{prod} are NH_4^+ and NO_2^- for ammonia oxidizers, and NO_2^- and NO_3^-
 174 for nitrite oxidizers.

175 2.5. Fitting procedure

176 Optimal values of initial $[BN]_{i,j}$, $\mu_{\text{max},i,j}$, $K_{NH_4^+,j}$ and $K_{NO_2^-,j}$ were obtained by fitting nitrite
 177 concentrations in non-inhibited and/or inhibited incubations. The fitting was achieved with a
 178 screening of the model response to a large number of parameter sets. The minimization of the
 179 root mean square error (RMSE) between experimental and modelled values was used as the
 180 objective function to determine the optimal values. Table 1 displays the ranges and the optimal
 181 values of parameters $[BN]_{i,j}$, $\mu_{\text{max},i,j}$, $K_{NH_4^+,j}$ and $K_{NO_2^-,j}$. Mortality rates, nitrification yields
 182 and the temperature dependency function ($T_{\text{opt},i}$ and σ_i) were previously determined (Brion
 183 and Billen, 1998; Garnier et al., 2007), and were therefore kept constant in the current fitting
 184 procedure.

185 A flow chart explains the different steps to obtain optimal parameters (Fig. 2). Non-
 186 inhibited water samples were incubated for 2 weeks. The observed NO_2^- time-series were
 187 analysed to determine if a second batch incubation was necessary to determine nitrifier growth
 188 kinetic parameters and biomass. Two cases were considered :

- 189 • NH_4^+ and NO_2^- oxidation did not occur simultaneously in the non-inhibited water sample.
190 In this case, the whole initial amount of NH_4^+ was converted to nitrite during the first
191 days of the incubation. NO_2^- concentration reached the maximum possible value of 14
192 $mgN L^{-1}$ (corresponding to the initial concentration of NH_4^+) before it started to decrease
193 due to NO_2^- oxidation (see Seine River water sample, Fig. 3a).
- 194 • NH_4^+ and NO_2^- oxidation occurred simultaneously. NO_2^- concentration therefore did not
195 reach the maximal value of 14 $mgN L^{-1}$ (see SAV water sample, Fig. 3b).

196 In the first case, one single incubation was needed. Growth parameters and biomass of
197 ammonia oxidizers were first fitted from the beginning of the batch experiment to the 14 mgN
198 L^{-1} NO_2^- concentration peak (first 8 days, see Seine River water sample, Fig. 3a). Nitrite
199 oxidation was then fitted until the end of the batch experiment (days 9 to 15).

200 In the second case, the non-inhibited incubation did not allow identifying ammonia and
201 nitrite oxidizer parameters separately. An additional incubation, inhibiting nitrite oxidation,
202 was used to determine biomass and kinetic parameters of ammonia oxidizers. Using the values
203 obtained for ammonia oxidizers, biomass and kinetic parameters of nitrite oxidizers were then
204 determined in the non-inhibited batch. During this calibration of nitrite oxidation, a dimen-
205 sionless acceleration factor (r_{AO}) of maximal growth rates was used for ammonia oxidizers. This
206 factor was used and justified by the fact that nitrite production was slightly lower in inhibited
207 compared to non-inhibited batches (see SAV water sample, Fig. 3b), most likely due to higher
208 mortality rates of ammonia oxidizers or to lower maximal growth rates in the presence of the
209 inhibitor. A similar factor was used to account for increased degradation efficiencies of organic
210 carbon under oxic *versus* anoxic conditions (Canavan et al., 2006).

211 2.6. Hydro-ecological model (PROSE)

212 The nitrifying growth parameters and biomasses obtained with the procedure described
213 above were implemented and validated in the PROSE hydro-ecological model to simulate nitrifi-
214 cation dynamics along a 220 km stretch of the Seine River for a 6-year period (2007-2012).
215 The domain started 10 km upstream Paris down to Poses at the entrance of the Seine Estuary
216 (Fig. 1), including 25 km of the Marne River. Four major tributaries were taken into account
217 as boundary conditions. Anthropogenic pressures (WWTP effluents, combined sewer overflows

218 and dry weather effluents) constituted point sources in the model (Even et al., 1998, 2004,
219 2007b).

220 The PROSE model simulates the hydro-ecological response of a river system to point sources
221 or diffuse pollutions, in steady or transient states (Even et al., 1998, 2007b; Flipo et al., 2004).
222 It is composed of three modules, which compute hydrodynamic, transport and biogeochemical
223 processes, in the column water and the benthic sediment. The ProSe model has been applied
224 successfully to several case studies in the Seine River basin (Even et al., 1998, 2004, 2007b; Flipo
225 et al., 2004, 2007; Polus et al., 2010, 2011; Vilmin et al., in press) and in the Seine Estuary
226 (Even et al., 2007c). The role of benthic sediments has been recently improved by recalibration
227 of the sediment erosion processes in the PROSE model (Vilmin et al., 2015).

228 In addition to nitrification (described in section 2.4), the model simulates the fate of am-
229 monium *via* heterotrophic mineralization of organic matter and phytoplankton uptake. Nitrate
230 concentrations are affected by phytoplankton uptake and by denitrification. In the model, ni-
231 trite is considered as the intermediate variable in the nitrification process, whereas incomplete
232 denitrification is not considered in the present study.

233 Simulated time series of NH_4^+ , NO_2^- and NO_3^- concentrations were validated at four weekly
234 monitoring stations (from upstream to downstream: Asnières, Sartrouville, Poissy, Poses) man-
235 aged by the public sewage company of Paris (Syndicat Interdépartemental pour l'Assainissement
236 de l'Agglomération Parisienne, SIAAP). Note that the biggest WWTP (SAV) is located be-
237 tween Sartrouville and Poissy. The longitudinal profiles of the simulated concentration quantiles
238 (10%, 50% and 90%) were compared to weekly observations at ten stations managed by the
239 SIAAP and eight stations of the national river monthly monitoring network (Réseau de Contrôle
240 et de Surveillance, referred to as RCS) along the studied stretch. The longitudinal profiles of
241 the biomasses of ammonia and nitrite oxidizers from the Seine River and the SAV effluent were
242 compared at low and high water discharge conditions, following the approach developed to an-
243 alyze in-river sediment (Vilmin et al., 2015) and phosphorus (Vilmin et al., in press) dynamics.
244 The distinction between low and high discharge conditions was based on the daily discharge
245 measured at the Paris gauging station (Fig 1). Discharge rates lower and higher than $205 \text{ m}^3\text{s}^{-1}$
246 (median discharge rate for the 2007-2012 period) were defined as low and high river discharge
247 conditions, respectively.

248 Finally, nitrogen budgets were derived from model outputs for low and high water discharge
 249 conditions over the simulated 6-year period. Nitrogen stocks were calculated in two compart-
 250 ments (water column and sediment layer) in two river domains (upstream and downstream the
 251 SAV WWTP). Nitrogen fluxes linked to the different simulated biogeochemical processes and
 252 exchanges at the sediment-water interface were calculated as model outputs and integrated over
 253 the two river domains (upstream and downstream the SAV WWTP). Averaged daily fluxes for
 254 the simulated 6-year period were calculated in each domain for low and high water discharge
 255 condition, respectively.

256 3. Results

257 3.1. Optimal sets of biomasses and kinetic parameters of natural nitrifying communities in 258 in-river waters and WWTP effluents

259 The best statistical adjustments of nitrite concentrations over 15 days in batch incubations
 260 are shown for ammonia and nitrite oxidizers in river water and SAV effluent (Fig. 3). Modelled
 261 nitrite outputs were in good agreement with measured nitrite concentrations, when using the
 262 optimal parameter sets for Seine water (correlation = 0.93 and RMSE = 2.32 mgN L⁻¹ — 0.44
 263 mgN L⁻¹ without the point at day 8) and for SAV effluent non-inhibited batches (correlation >
 264 0.99 and RMSE = 0.01 mgN L⁻¹). The optimal values of nitrifier biomass $[BN]_{i,j}$ (0.001-0.02
 265 mgC L⁻¹), maximal growth rate $\mu_{max,i,j}$ (0.04-0.07 h⁻¹) and half-saturation constant $K_{NH_4^+,j}$
 266 (1.5-2 mgN L⁻¹) and $K_{NO_2^-,j}$ (0.3-10 mgN L⁻¹) are summarized in Table 1. Our values observed
 267 for natural communities under reconstructed *in situ* conditions were in the range of values
 268 determined for pure cultures under optimal conditions *i.e.* $[BN] \in [0.00004-0.07]$ mgC L⁻¹,
 269 $\mu_{max} \in [0.008-0.1]$ h⁻¹, $K_{NH_4^+} \in [0.002-74]$ mgN L⁻¹ and $K_{NO_2^-} \in [0.00003-28]$ mgN L⁻¹ (Tables
 270 2 and 3). The estimated ammonia oxidizer biomass ($[BN_{AO}]$) was higher than nitrite oxidizer
 271 biomass ($[BN]_{NO}$) in both WWTP and river samples. The SAV WWTP effluent contained one
 272 to two orders of magnitude more nitrifying biomass (0.027 and 0.008 mgC L⁻¹ for ammonia and
 273 nitrite oxidizers, respectively), as deduced from the experiments, than the Seine River water
 274 (0.0075 and 0.001 mgC L⁻¹ for ammonia and nitrite oxidizers, respectively). The maximal
 275 growth rate (μ_{max}) was in the same order of magnitude for ammonia oxidizers and nitrite
 276 oxidizers in river and WWTP samples (0.04-0.07 h⁻¹). As found in the literature, $K_{NH_4^+}$ and
 277 especially $K_{NO_2^-}$ were more variable than μ_{max} values. $K_{NH_4^+}$ values were similar in river and

278 SAV samples (2 and 1.5 mgN L⁻¹, respectively), while $K_{NO_2^-}$ values were 30 times higher in
279 river waters than in SAV effluent (10 and 0.3 mgN L⁻¹, respectively).

280 *3.2. Validation of the optimal sets of parameters in an hydro-ecological model along a 220 km* 281 *stretch for a 6-year period*

282 The optimal parameter sets determined for ammonia and nitrite oxidizing communities in
283 river water and SAV effluent were then used to parametrize the PROSE model. The 6-year
284 outputs of NO_2^- concentrations are presented for 4 stations from upstream to downstream the
285 SAV WWTP and compared with weekly data collected at SIAAP stations (Fig. 4). Good
286 adjustments of NO_2^- concentration time-series were observed upstream the SAV WWTP ef-
287 fluent (Asnières, Sartrouville) for the whole 6-year simulated period, at low river discharge
288 (RMSE < 0.034 mgN L⁻¹) and high discharge conditions (RMSE < 0.015 mgN L⁻¹; Table 4).
289 Representing two distinct nitrifying communities (river and WWTP) led to an accurate simu-
290 lation of concentrations downstream the SAV WWTP (Poissy, Poses), especially during high
291 river discharge periods (RMSE < 0.057 mgN L⁻¹; Table 4). A slight overestimation of NO_2^-
292 concentrations was sometimes observed at Poses, due to less well constrained river morphology
293 upstream this station, which involves uncertainties in the location of benthic river sediments.
294 [Vilmin et al. \(2015\)](#) validated sediment transport downstream the WWTP, but not so far in
295 the downstream area of the river system, due to the lack of geomorphological data. Uncer-
296 tainties in the location of benthic river sediments may induce uncertainty in nitrification rates
297 within fluid sediments at this station. However, all the stations upstream this location show
298 good adjustments (similar to those observed at Poissy). Simulated NH_4^+ and NO_3^- were also
299 validated along the 220 km stretch (see Appendix Figs. [A.1](#) and [A.2](#)).

300 *3.3. Assessment of in-river water-quality*

301 Longitudinal profiles of 10 %, 50 % and 90 % concentration quantiles for the 2007-2012
302 period were calculated with the PROSE model for NH_4^+ , NO_2^- , and NO_3^- (Fig. 5). The spatial
303 variability of these quantiles was high around point source effluent output. Regarding nitrite
304 concentrations, the water quality status moved from moderate to bad status just downstream
305 the SAV WWTP, and before the confluence with the Oise River. Nitrite concentrations in-
306 creased slightly along the first 100 km after the Oise River, before decreasing towards the
307 estuary.

308 Using distinct variables for river and WWTP nitrifiers in the hydro-ecological PROSE model
309 also allowed simulating the fate of the biomass of each nitrifying community issued from the
310 two main sources (*i.e.* upper drainage basin, WWTP effluent) in the Seine hydrological system
311 (Fig. 6). Nitrifiers from the SAV WWTP contributed to 16-76 % of the nitrifying biomass
312 present in the river downstream the SAV effluent, especially in low river discharge conditions
313 (50-76 %).

314 3.4. Effect of sampling frequency on river environmental assessment

315 Although simulated times series were validated with weekly monitoring data (Fig. 4),
316 NH_4^+ , NO_2^- , and NO_3^- concentrations calculated by the model were compared to the values
317 measured at a monthly time step at the RCS sampling station located at Meulan (longitudinal
318 abscisse = 100 km, Fig. A.3). The model provided accurate estimates of in-river NH_4^+ ,
319 NO_2^- , and NO_3^- concentrations of monthly sampled waters. NH_4^+ concentrations showed high-
320 frequency variability which was not accounted for by monthly sampling. Low NO_2^- variations
321 were observed upstream the SAV WWTP, but its variability increased downstream. The model
322 reproduced well the observed concentrations at the sampling dates (with correlation coefficients
323 at Meulan of 0.88 and 0.71 for NH_4^+ and NO_2^- concentrations, respectively). Nevertheless the
324 monthly measurement captured only few peaks during the study period, which had an effect
325 on the deduced statistical criteria. The 90 % quantiles for NH_4^+ and NO_2^- concentrations
326 estimated with the PROSE model ($dt = 10$ min) were therefore greater than those estimated
327 with the monthly sampling data. Nitrate showed very low short-term variability.

328 3.5. Testing the effect of new treatment strategy

329 A simulation with no nitrifying biomass in the SAV effluent was performed to mimic the
330 implementation of effluent micro-filtration (Fig. 4). Without nitrifiers in the SAV effluent,
331 nitrite concentrations would reach values corresponding to a bad ecological status according to
332 the European WFD along almost the whole stretch from SAV to the estuary. According to the
333 model results, mean nitrite concentrations at the estuary would increase by over 60 % without
334 the input of nitrifying biomass from the WWTP.

335 4. Discussion

336 4.1. Fitting nitrifying parameters to model the fate of nitrite in human-impacted rivers

337 Our approach combines deduction of kinetic parameters using laboratory experiments and
338 stand-alone modelling, and validation of these parameters in hydro-ecological modelling in order
339 to upscale our results from laboratory to river scale. This approach is consequently based on
340 identical nitrification model frames in stand-alone and river-scale models.

341 Our results highlight the importance of determining biomasses and kinetic parameters of
342 natural nitrifying communities in rivers and in point source effluents carrying active nitrifiers,
343 *i.e.* in WWTPs. The higher nitrifying biomass in WWTP effluents compared to river water
344 (this study) is explained by tertiary biological treatments removing nitrogen in urban effluents
345 and the presence of nitrifying biomass in the WWTP. These higher biomasses are in agreement
346 with previous results found when WWTP was only subjected to secondary treatments (Servais
347 [et al., 1999b](#); [Brion and Billen, 1998](#); [Cébron et al., 2003](#)). This suggests that the release of
348 nitrifying biomasses related to WWTP effluents must be considered, when microfiltration, chlo-
349 rine or ultraviolet radiation is not performed at the outlet. This biomass must be characterized
350 depending on the treatment applied in WWTPs.

351 In addition to biomass estimation, our method enables the determination of kinetic parame-
352 ters and can be applied to any riverine ecosystem. These parameters are necessary to calculate
353 the nitrifying activity, which appears to be more important than the nitrifying biomass it-
354 self ([Röling, 2007](#)). The low variability of the maximal growth rate (0.04-0.07 h⁻¹), which is
355 consistent with the literature, suggests a robust parametrization of this parameter and a low
356 variability of growth rates depending on nitrifying communities (ammonia or nitrite oxidizers)
357 and on their origin (river or WWTP). Considering a constant mortality, the range of maximal
358 growth parameters can easily be transferred to any system, and tuned if necessary. The differ-
359 ence in affinity ($K_{NO_2^-}$) between river and WWTP (10 and 0.3 mgN L⁻¹, respectively) is most
360 likely related to variations in nitrifying community structure, and environmental conditions.
361 The low $K_{NO_2^-}$ in tertiary advanced WWTP effluent might be explained by the dominance of
362 *Nitrobacter* species, as already observed in the SAV WWTP effluents prior to 2007 ([Cébron and](#)
363 [Garnier, 2005](#)), and in 2012 (T. Cazier, pers. comm.). *Nitrobacter sp.* has already been shown
364 to exhibit low $K_{NO_2^-}$ in activated sludge reactors ([Jiménez et al., 2011](#)) and in 1000 mgN L⁻¹

365 enriched synthetic waste water (Blackburne et al., 2007). The similarity of $K_{NO_2^-}$ obtained in
366 WWTP-type chemostat (Cébron et al., 2005) and in SAV WWTP effluent (our study) suggests
367 that nitrifying communities in tertiary advanced WWTP effluents might be characterized by
368 low $K_{NO_2^-}$. The high $K_{NO_2^-}$ in river waters, in the range of values found in the literature (Table
369 3), might rather be explained by other reasons *e.g.* species competition, or limitations other
370 than nitrite.

371 Our results bring complementary information on the difference between river and WWTP-
372 related nitrifying communities, leading to improvements in the modelling of nitrite dynamics
373 and nitrogen cycling in the river. Our approach is based on several initial assumptions from
374 previous experimental and modelling studies in the Seine River (Brion and Billen, 1998; Cébron
375 et al., 2005; Garnier et al., 2007): a constant mortality rate of 0.01 h^{-1} , a yield of 0.09 and 0.026
376 mgC mgN^{-1} for ammonia and nitrite oxidizers, respectively, and a temperature function (see
377 Eq. 4) with T_{opt} of $23 \text{ }^\circ\text{C}$ and σ of $12 \text{ }^\circ\text{C}$. The fixed mortality rate (*i.e.* first-order mortality
378 constant) strongly controls the growth rate value, but it does not impact the net growth rate of
379 nitrifiers (*i.e.* growth - mortality). More experimental studies should be undertaken to precise
380 the spatio-temporal variations of yields and temperature functions suggested in other studies
381 (detailed here after), which could potentially affect nitrite dynamics in the river. First, even if
382 protein synthesis is essential to maintain optimal nitrifying activity (Tappe et al., 1999), yields
383 have been shown to vary with temperature and oxygen, suggesting the potential uncoupling
384 between nitrifier growth and activity (Andersson et al., 2006). Second, optimal temperatures
385 for growth generally range between 20 and $35 \text{ }^\circ\text{C}$ depending on species, and can vary with
386 the seasonal nitrifier community composition. To date, no dataset exists to constrain the
387 variability of yields and temperature functions with environmental parameters and community
388 composition. However, the good adjustment of nitrogen species in our study suggests that
389 spatio-temporal variations of yields and temperature functions might have been low or might
390 be well represented by generic and constant parameters. The use of generic parameter values
391 is thus validated which is in adequation with the deterministic approach generally used in river
392 modelling.

393 As modelling is based on initial assumptions, it is essential to use identical initial assump-
394 tions in stand-alone models and fully coupled hydro-ecological models to achieve a good param-

395 eterization of ecosystem models. In our case, we used the same initial assumptions of constant
396 mortality rates, yields and temperature function parameters during the fitting procedure in the
397 batch model (C-RIVE) and during the 6-year simulation performed with the hydro-ecological
398 model (PROSE-C-RIVE).

399 Our approach could be applied to any river system, using an hydro-ecological model which
400 takes into account point sources e.g. WWTP effluents. The minimum required is to consider
401 both natural and WWTP-related communities of ammonia and nitrite oxidizing communities
402 and use our kinetic parameters for each nitrifying community to parameterize the model. The
403 best approach is to (1) sample the river water upstream of the main WWTP and the WWTP
404 effluent, and (2) apply our methodology to evaluate biomasses and kinetic parameters of the
405 nitrifying communities present in the specific system. Applying our approach, and not only
406 our parameters, is especially necessary in systems receiving effluents from WWTPs with other
407 technologies used for nitrogen removal.

408 *4.2. Nitrogen cycling in human impacted river systems: example of the Seine River*

409 The strength of distributed process-based modelling tools is to represent the fate of variables
410 and fluxes linked to the various simulated biogeochemical processes, which are difficult to
411 quantify through direct methods (*e.g.* in situ ammonia and nitrite oxidation rates, nitrifying
412 biomasses). The PROSE model was used here to assess nitrifier biomasses along a 220 km
413 stretch and to quantify the fluxes linked to the biogeochemical transformations of NH_4^+ , NO_2^- ,
414 and NO_3^- at a pluri-annual time scale.

415 *4.2.1. Effect of WWTP effluents on in-river nitrifying biomasses*

416 Our results confirm that effluents of advanced WWTP constitute a significant source of
417 nitrifier biomass to river ecosystems (16-76 %, this study). Our approach allows the study of
418 biomass evolution for the two distinct nitrifying communities (river and WWTP) along the
419 river. For the 2007-2012 period, the nitrifying biomass (whatever its origin and specificity) was
420 stable during its transit towards the estuary at high water conditions (Fig. 6a), indicating that
421 nitrifying biomass was mostly transported downstream, without noteworthy net growth. At
422 low water conditions, the biomass of nitrifiers flowing from the WWTP increased (Fig. 6b),
423 as already observed before 2007 when ammonium concentrations promoted nitrifier growth
424 (Servais et al., 1999b; Brion and Billen, 1998; Cébron et al., 2003). The amplitude of ammonia

425 oxidizer growth downstream the WWTP was however lower than before 2007 due to the lower
426 in-stream ammonia concentrations since the addition of nitrification-denitrification units in
427 SAV WWTP in 2007. These results highlight the feedback of the decrease of ammonia release
428 by WWTPs on nitrifying communities/biomass in river systems.

429 Our results also show differences in biomass evolution along the river stretch between
430 WWTP and river nitrifiers. While WWTP nitrifier biomass increased at low water condi-
431 tions, the biomass of river nitrifiers tended to decrease. This is related to the higher affinity of
432 WWTP nitrifiers for nitrite compared to nitrifiers initially present in the river. This indicates
433 that studying nitrifier kinetics in river waters and WWTP effluents, and the survival of the
434 different communities in the system (Féray and Montuelle, 2002), is needed to understand the
435 evolution of nitrite in river systems. The evolution of nitrifier biomass along the river depends
436 thus on point sources (*i.e.* WWTP), ecosystem hydrology (*i.e.* high or low river discharge), en-
437 vironmental conditions (*e.g.* ammonia and nitrite concentrations), and nitrifier activity (related
438 to biomass and kinetics).

439 The explicit representation of nitrifying biomass for autochthonous and WWTP communities
440 allows the simulation of the growth of both communities and their relative impact on river water
441 quality.

442 4.2.2. Persistence of nitrite in the water column downstream WWTP effluents

443 The longitudinal profile of nitrite concentrations shows strong spatial variations, especially
444 downstream main singularities (tributaries and effluents, see Fig. 5). The dilution of nitrite
445 by the Oise River (70 km downstream of Paris) significantly reduces NO_2^- concentrations in
446 the system. This shows that accounting for the main tributaries is essential for a good repre-
447 sentation of river biogeochemistry. The longitudinal profile also displays that nitrite is mostly
448 produced just downstream the WWTP effluent, before it is slowly consumed by increasing ni-
449 trite oxidizers towards the estuary. WWTP-related nitrite oxidizing communities, which are
450 efficient in the presence of riverine nitrite concentrations, take part in this consumption. How-
451 ever, the nitrite brought by the SAV effluent and produced downstream the WWTP is not
452 totally consumed before the entrance of the estuary. NO_2^- concentrations still reach values cor-
453 responding to a poor ecological status as defined by the European Water Framework Directive
454 (Fig. 5).

455 The quantification of daily averaged biogeochemical fluxes (for the whole 2007-2012 period)
456 in the water column, in the unconsolidated sediments, and at the sediment-water interface
457 enables us to explain the longitudinal evolution of in-river concentrations up- and downstream
458 the SAV WWTP, for low and higher river discharge conditions (Fig. 7). The persistence of
459 nitrite downstream the WWTP is mostly explained by the net production of nitrite in the
460 water column which is 80 % higher downstream than upstream the WWTP during low river
461 discharge, and more than 7 times higher during high river discharge. This high net production
462 downstream the WWTP is notably due to the high NH_4^+ levels in the water column. Nitrite
463 consumption rates are also higher downstream the WWTP, so that nitrification processes are
464 closer to equilibrium (same NH_4^+ and NO_2^- oxidation rates) than upstream SAV WWTP. The
465 ratio of NO_2^- oxidation rate per NH_4^+ oxidation rate is in fact much lower downstream SAV
466 WWTP (1.2 and 2.8 for low and high river discharge, respectively) than upstream SAV WWTP
467 (over 17 for both low and high discharge conditions). This is due to the fact that WWTP
468 nitrifiers were more abundant and efficient for nitrite oxidation (*i.e.* low $K_{NO_2^-}$) compared to
469 the autochthonous ones. These results highlight the importance of nitrifiers released by WWTP
470 effluents in nitrite production and consumption in the water column downstream WWTPs.

471 4.2.3. Importance of benthic processes in nitrogen cycling and nitrite export to estuaries

472 Nitrogen cycling is directly controlled by biotic processes (mineralization, denitrification, ni-
473 trification, and uptake by phytoplankton), and indirectly by hydro-sedimentary processes. Ac-
474 cumulation of particles (notably organic matter, heterotrophic and nitrifying micro-organisms)
475 on the river bed, and their re-suspension, determine the intensity of benthic processes and
476 of exchanges at the sediment-water interface. Hydro-sedimentary processes were calibrated
477 and validated by [Vilmin et al. \(2015\)](#), which allows an estimation of sediment accumulation
478 in the river bed and of the intensity of benthic biogeochemical processes and sediment-water
479 exchanges.

480 Inorganic nitrogen in the water column is largely dominated by NO_3^- (88-97 %) (Fig. 7).
481 Nitrate concentrations are mainly driven by the fluxes flowing from the upper agricultural
482 drainage basin to the river system ([Garnier et al., 2006](#); [Polus et al., 2011](#)) and, to a lesser
483 extent, by anthropogenic effluents. Given the large amount of NO_3^- in the water column, the
484 fluxes linked to in-river biogeochemical processes have very little effect on the NO_3^- fluxes

485 exported at the estuary. In fact, these in-river processes (in the water column and in the
486 sediment layer) contribute to less than 1 % of the increase of NO_3^- fluxes between the Paris
487 urban area and the estuary.

488 NH_4^+ concentrations are not only affected by nitrification processes, but also by the miner-
489 alization of organic matter and uptake by phytoplankton. At high discharge conditions, NH_4^+
490 is produced in the river system both up- and downstream the SAV WWTP (Fig. 7). At low
491 discharge conditions downstream SAV, the river system constitutes a significant sink of ammo-
492 nium, and therefore contributes to the Seine River self-purification. 7.5 tons of N of NH_4^+ are
493 consumed per day, while 2.0 tons are produced by mineralization of organic matter, along this
494 142 km stretch. 25 % of this total consumption (7.5 tons of N) is due to NH_4^+ consumption in
495 the benthic layer.

496 The Seine River usually constitutes a source of nitrite, with a higher nitrite production
497 than consumption (Fig. 7). Part of this nitrite is produced in river bed sediments (0.025-0.244
498 TN d^{-1}) and transferred to the water column by diffusion (Morris et al., 1985; Kelso et al.,
499 1997), except downstream the WWTP at low river discharge conditions (-0.01 TN d^{-1}), when
500 more NO_2^- is consumed than produced in the benthic layer. At low river discharge conditions
501 upstream the WWTP, a large part of the NO_2^- produced in the water column (up to 30%,
502 this study) originates from the benthic nitrifying activity. The impact of benthic sediments is
503 also significant during high discharge conditions, when one fifth of the NO_2^- produced in the
504 water column originates from the unconsolidated sediment layer. Even though the contact time
505 between the water and the sediment layer is smaller in high discharge conditions, the sediment
506 layer has a significant effect on nitrite fluxes. This is explained by the imbalance between nitrite
507 production and consumption in the sediment layer during high discharge conditons. As a result
508 of point sources and in-stream biogeochemical processes, the river is a source of nitrite to the
509 estuary (means of 4.1 and 5.6 TN d^{-1} in low and high river discharge, respectively).

510 Our results point out the importance of taking biological activity in benthic sediments into
511 account. In fact, a large proportion of in-river nitrification takes place in this sediment layer; the
512 produced nitrite is then transferred to the water column by diffusion and transport (erosion,
513 bioturbation/bioirrigation). Even if sediments are known to have less impact on nitrogen
514 cycling *i.e.* nitrate dynamics in large river systems with low surface-to-volume ratios (Pinay

515 [et al., 2002](#)), their effect on nitrite export at estuaries is definitely significant. Considering the
516 importance of benthic sediments in nitrite dynamics (this study), the role of benthic anaerobic
517 nitrate reduction (denitrification, DNRA), and their coupling with nitrification, in riverine
518 nitrite dynamics must be evaluated through an approach similar to the one developed for
519 nitrifiers in this study.

520 *4.3. Assessment and management of nitrite in rivers*

521 Accounting for distinct biomasses and kinetic parameters of nitrifying communities in the
522 river and in point source effluents (*i.e.* WWTP) allowed a proper modelling of concentrations
523 and dynamics of nitrite in the Seine River. The quantification of biomass and kinetic param-
524 eters of ammonia and nitrite oxidizers is thus essential to parameterize nitrifying communities
525 in hydro-ecological models in anthropized rivers. Once the model provides reliable results
526 compared to monitoring data, it can be used to complete our understanding of the ecological
527 functioning of the system or to support monitoring and management strategies ([Poulin et al.,](#)
528 [1998](#); [Rode et al., 2010](#); [Bende-Michl et al., 2011](#)).

529 Compared to local sampling, models allow the simulation of the water quality of river
530 systems at extremely small spatio-temporal resolution, over a large spatio-temporal extent and
531 for a large number of variables and fluxes. One model output is the annual 90 % quantile of
532 NH_4^+ , NO_2^- , and NO_3^- concentrations which is, according to the European Water Framework
533 Directive, the statistical criterion used to assess the water quality status accounting for transient
534 nutrient concentration peaks. The model allows to access the high spatial variability of water
535 quality criteria, which is not always captured by local sampling ([Polus et al., 2010](#)).

536 As monitoring is an expensive task in water quality assessment, sampling strategies need
537 to be optimized ([Nadeo et al., 2013](#)). Model outputs are efficient to determine the minimum
538 sampling time step necessary to estimate water quality levels. Our results suggest that monthly
539 sampling is enough for the assessment of nitrate dynamics, and the assessment of the water
540 quality level regarding nitrate concentrations. The variability of nitrate is mostly explained by
541 diffusive fluxes due to agricultural practices. On the contrary, monthly sampling is not sufficient
542 to capture ammonia and nitrite concentration peaks, and leads to the over- or underestimation
543 of the annual 90 % ammonia and nitrite concentration quantiles compared to averaged high-
544 frequency model outputs. Weekly sampling at least is required to calculate accurate quality

545 criteria accounting for the high variability of ammonia (along the whole river) and nitrite
546 (after WWTP effluent). The optimal sampling frequency depends on sampling location (hydro-
547 morphological characteristics, presence of anthropogenic loads), and indicator variability in the
548 receiving environment (Lázsló et al., 2007). Hydro-ecological models validated at fine spatio-
549 temporal scales, as the PROSE model, can be usefully coupled with monitoring surveys in order
550 to avoid expensive high frequency sampling and improve the assessment of water quality levels
551 regarding highly variable substances as NH_4^+ and NO_2^- . As river ecosystems are submitted to
552 variable natural and most often anthropogenic forcings, adaptability of monitoring frequency
553 is required if changes in nutrient variability are generated by modified loads.

554 The validated model can also be employed to assess the impact of future management strate-
555 gies or the implementation of new waste water treatment technologies (Even et al., 2007a; Kan-
556 nel et al., 2007; Richter et al., 2013). For instance, we evaluated the effect of the implementation
557 of micro-filtration, chlorine or ultraviolet radiation at the outlet of nitrification/denitrification
558 units, *i.e.* suppression of microorganisms, on nitrite dynamics in the river. The results show
559 that the implementation of such a filtration system in the WWTP would lead to an increase of
560 nitrite concentrations downstream the WWTP towards the estuary. This result underlines the
561 importance of maintaining in the effluent ammonia and nitrite oxidizer communities, which in-
562 creases the nitrifying activity and eliminates part of the ammonium and nitrite discharged and
563 produced in the river system. The method proposed in this paper can be applied to investigate
564 the effect of diverse human perturbations on nitrogen cycling in any river system.

565 5. Conclusions

566 A cost efficient method is proposed here to study the nitrogen cycling (including nitrite
567 dynamics) in anthropogenic rivers subject to nitrite contamination. Accounting for distinct
568 communities of ammonia oxidizers and nitrite oxidizers in river water and WWTP effluents in
569 the river, and quantifying their biomasses and kinetics, leads to an accurate simulation of nitrite
570 concentrations downstream WWTP effluents and allows the assessment of each community
571 distribution along the river. The representation of benthic processes is essential for an correct
572 simulation of nitrite dynamics and fluxes in large urbanized rivers. In the case of the Seine River
573 downstream the Paris urban area, benthic nitrite production constitutes for example one fifth
574 of the total nitrite flux exported to the estuary at high flow conditions. Our results point out

575 how essential the coupling of monitoring and modelling tools is to improve our understanding of
576 in-river biogeochemical cycles, to improve the assessment of the quality of aquatic systems, and
577 to decrease water quality management costs. Besides the additional information that models
578 can provide to *in situ* measurements on ecosystem functioning, models can be used to forecast
579 the impact of possible future management strategies.

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782 Tables

Table 1: Variables and parameters used in C-RIVE. Fixed values, screened ranges and optimal values of parameters for river and WWTP samples are given.

		Unit	Fixed values or screened ranges	Optimal values	
				River	WWTP
<i>Variables</i>					
NH_4^+	Ammonium concentration	[mgN L ⁻¹]			
NO_2^-	Nitrite concentration	[mgN L ⁻¹]			
NO_3^-	Nitrate concentration	[mgN L ⁻¹]			
O_2	Dissolved oxygen concentration	[mgO ₂ L ⁻¹]			
BN_{AO}	Ammonia oxidizer biomass	[mgC L ⁻¹]	[0.0001-0.03]	0.0075	0.027
BN_{NO}	Nitrite oxidizer biomass	[mgC L ⁻¹]	[0.0005-0.03]	0.001	0.008
<i>Ammonia oxidizer parameters</i>					
$T_{opt,AO}$	Optimal temperature	[°C]	23		
σ_{AO}	Standard-deviation of the temperature function	[°C]	12		
$mort_{AO}$	Mortality rate	[h ⁻¹]	0.01		
Y_{AO}	Nitrification yield	molC(molN) ⁻¹	0.09		
$K_{O_2,AO}$	Half-saturation constant for oxygen	[mgO ₂ L ⁻¹]	0.5		
$r_{O_2,AO}$	Mol of O_2 consumed for 1 mol of NH_4^+ oxidized	[]	1.5		
$V_{sed,AO}$	Sedimentation rate	[m h ⁻¹]	0.1		
h	Water depth	[m]			
$\mu_{max,AO}^*$	Maximal growth rate	[h ⁻¹]	[0.01-0.2]	0.04	0.05
$K_{NH_4^+}$	Half-saturation constant for ammonium	[mgN L ⁻¹]	[0.1-20]	2	1.5
<i>Nitrite oxidizer parameters</i>					
$T_{opt,NO}$	Optimal temperature	[°C]	23		
σ_{NO}	Standard-deviation of the temperature function	[°C]	12		
$mort_{NO}$	Mortality rate	[h ⁻¹]	0.01		
Y_{NO}	Nitrification yield	[molC(molN) ⁻¹]	0.026		
$K_{O_2,NO}$	Half-saturation constant for oxygen	[mgO ₂ L ⁻¹]	1.1		
$r_{O_2,NO}$	Mol of O_2 consumed for 1 mol of NO_2^- oxidized	[]	0.5		
$V_{sed,NO}$	Sedimentation rate	[m h ⁻¹]	0.1		
$\mu_{max,NO}^*$	Maximal growth rate	[h ⁻¹]	[0.01-0.2]	0.07	0.04
$K_{NO_2^-}$	Half-saturation constant for nitrite	[mgN L ⁻¹]	[0.1-20]	10	0.3

Table 2: Synthesis of kinetic parameters and biomasses of ammonia oxidizers in environmental waters and bacterial cultures.

μ_{\max} [h^{-1}]	K_M [$mgN L^{-1}$]	[BN] [$mgC L^{-1}$]	Y_{nit} [$mgC mgN^{-1}$]	Reference
Environmental microbial communities				
0.008-0.09	0.2-8	0.00026-0.068		Knowles et al. (1965)
0.028-0.05	0.8-1.5		0.05-0.077	Cébron et al. (2005)
<i>Nitrosomonas</i> cultures				
0.003				Schmidt et al. (2003)
0.014-0.065				Blackburne et al. (2007)
0.032-0.05	0.84-2.38		0.07-0.13	Brion and Billen (1998)
0.032	0.028		0.147	Wiesmann (1994)
0.036	0.78-1.30			Helder and De Vries (1983)
	0.76			Drtil et al. (1993)
	1.96-56			Belser (1979)
	11.1-74.2			Park and Bae (2009)
	0.98-9.8			Henriksen and Kemp (1988)
	0.002			Martens-Habbena et al. (2009)

Table 3: Synthesis of kinetic parameters and biomasses of nitrite oxidizers in environmental waters and bacterial cultures.

μ_{\max} [h^{-1}]	K_M [$mgN L^{-1}$]	[BN] [$mgC L^{-1}$]	Y_{nit} [$mgC mgN^{-1}$]	Reference
Environmental microbial communities				
0.02-0.1	0.18-8	0.00004-0.06		Knowles et al. (1965)
0.051-0.064	0.001-0.028		0.01-0.02	Cébron et al. (2005)
<i>Nitrobacter</i> cultures				
0.04				Schmidt et al. (2003)
0.058(28°C)				Gould and Lees (1960)
0.051-0.064	0.001-0.028		0.014-0.024	Brion and Billen (1998)
0.045	0.000032		0.042	Wiesmann (1994)
0.005-0.6	1.2-1.3			Blackburne et al. (2007)
0.058(32°C)	22.4			Boon and Laudelout (1962)
0.04	0.5-19.2			Both et al. (1992)
0.064	1.6-3.7			Helder and De Vries (1983)
	0.05-3			Jiménez et al. (2011)
	1.54-28			Park and Bae (2009)
	4.9-8.4			Henriksen and Kemp (1988)
<i>Nitrospira</i> cultures				
	0.9-1.1			Blackburne et al. (2007)

Table 4: Statistical criteria (RMSE in $mgN L^{-1}$) for 6-year NO_2^- time-series at the four monitoring stations shown in Fig.4. LW = low water conditions, HW = high water conditions.

Station	LW	HW	2007-2012
Asnières	0.019	0.015	0.017
Sartrouville	0.034	0.012	0.025
Poissy	0.089	0.035	0.067
Poses	0.184	0.057	0.141

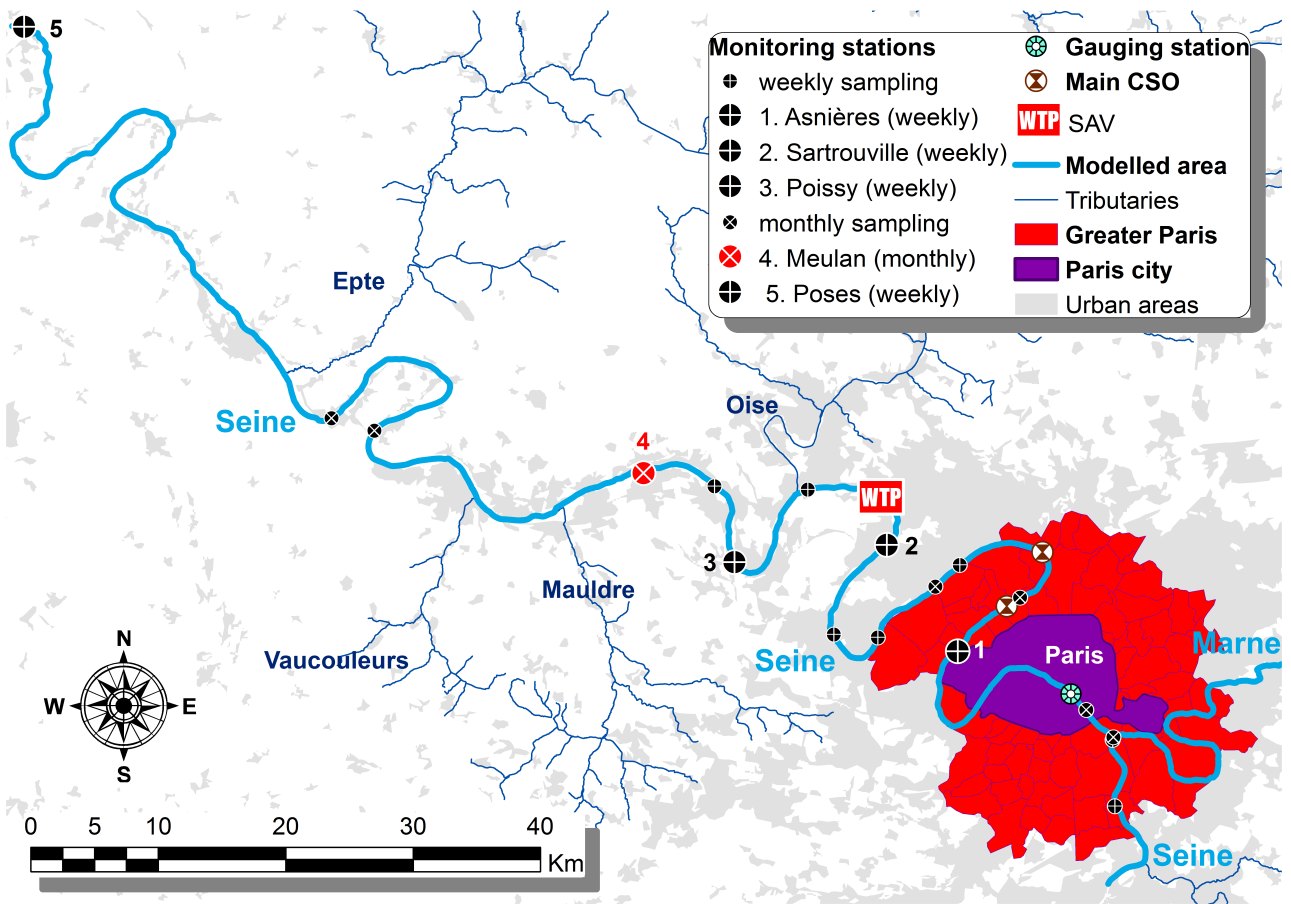


Figure 1: Study site and sampling stations.

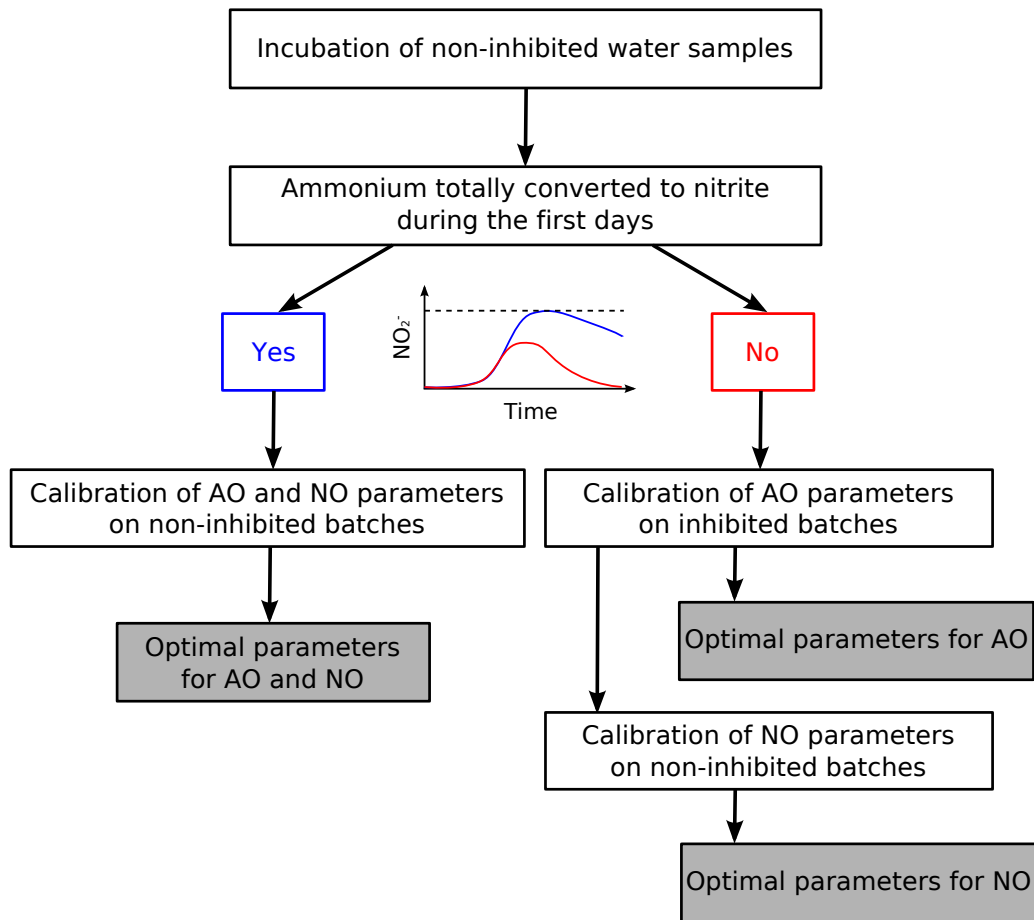


Figure 2: Procedure to find optimal kinetic parameters (growth rate, half-saturation constant) and initial biomasses of AO and NO.

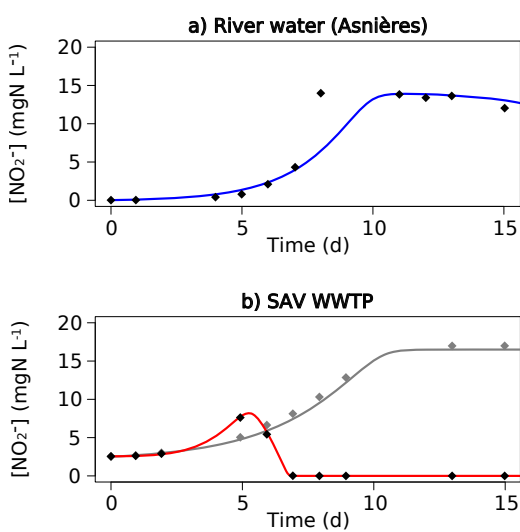


Figure 3: Best adjustment of nitrite concentrations-time curves during nitrification incubations (a) at Asnières, and (b) in the SAV WWTP effluent in November 2012. Points and curves represent data and model best adjustment results, respectively. The blue and red lines are the best adjustment on non-inhibited batch, and the grey line is the best adjustment on batch inhibited for nitrite oxidation.

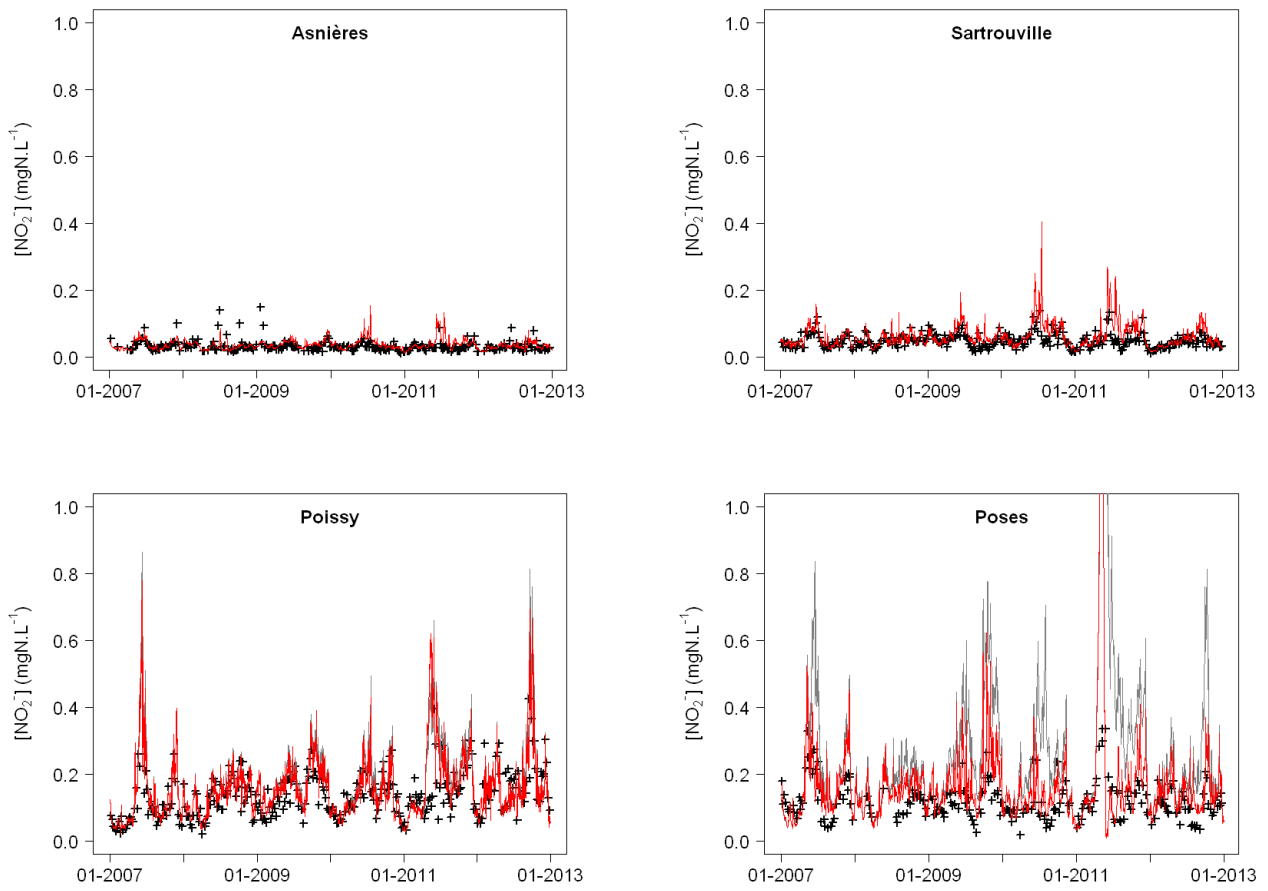


Figure 4: 6-year time-series of NO_2^- concentrations at 4 stations from Paris to 200 km downstream. Red lines = simulated concentrations with Seine river and WWTP nitrifier communities, gray lines = simulated with micro-filtration of the WWTP effluent.

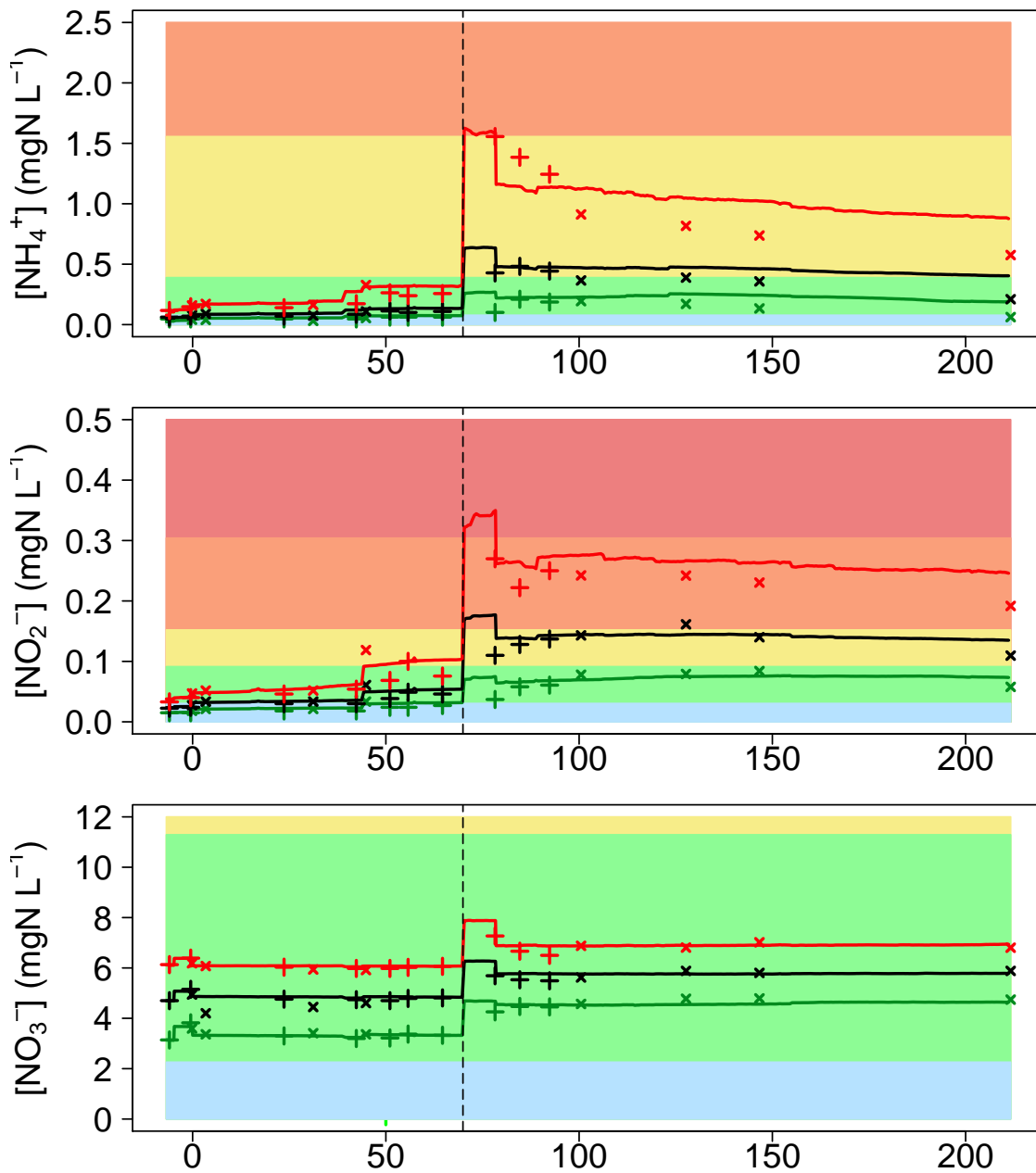


Figure 5: Longitudinal profiles of median and 10% and 90% quantiles of 6-year NO_2^- concentrations (black, green and red points and lines). \times = RCS data; $+$ = SIAAP data; lines = model outputs. Each color band refers to water quality level according to the EU WFD. Blue and red are the extreme very good and bad status.

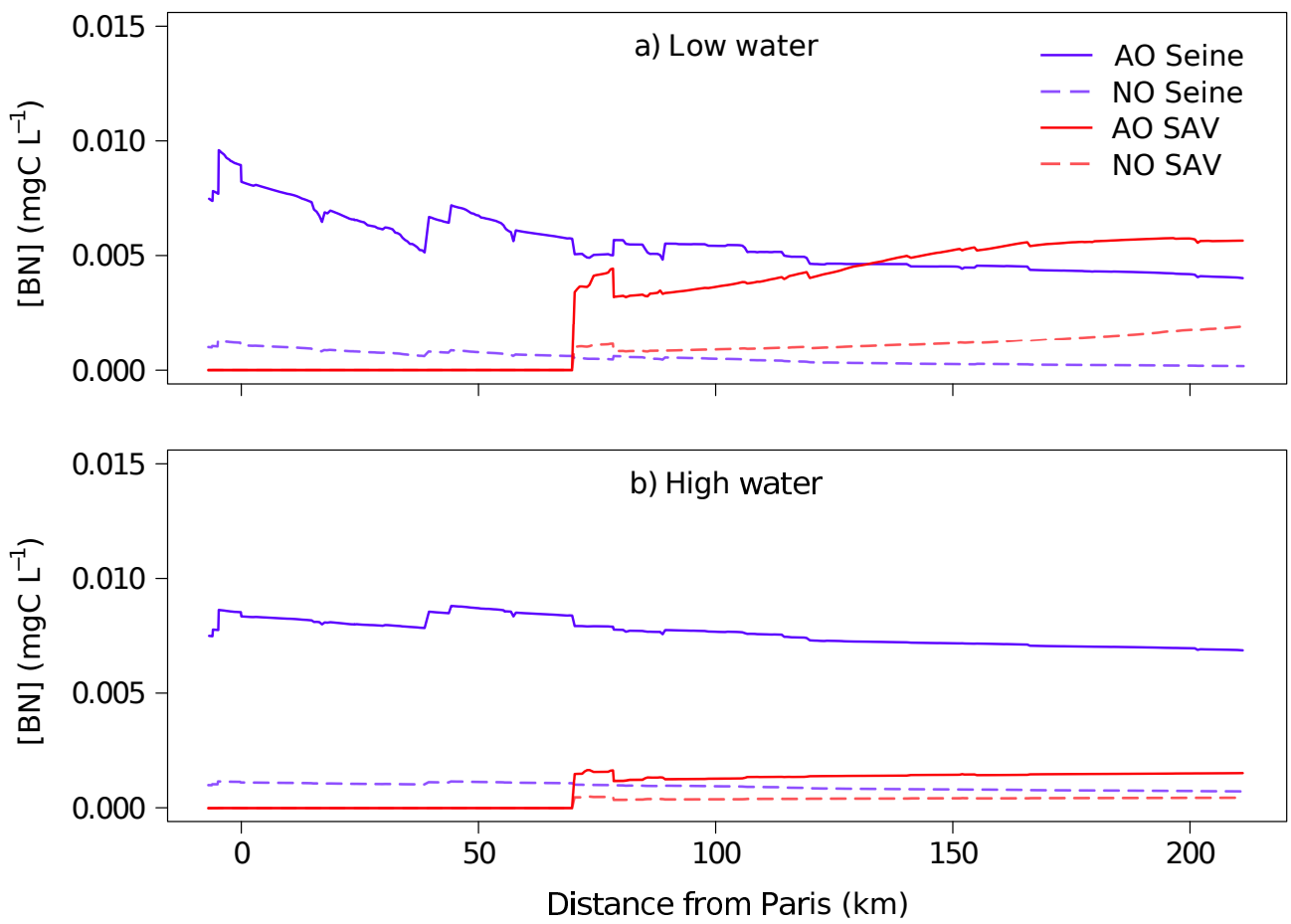
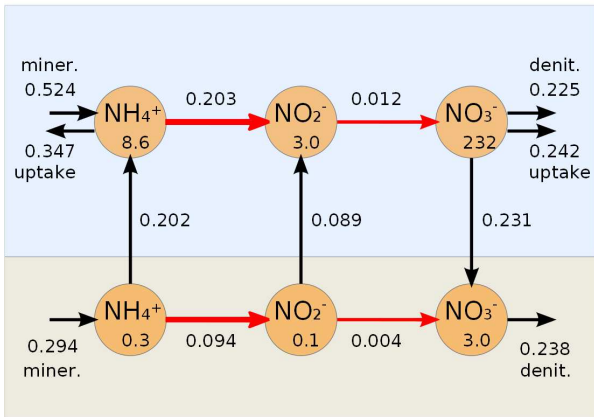
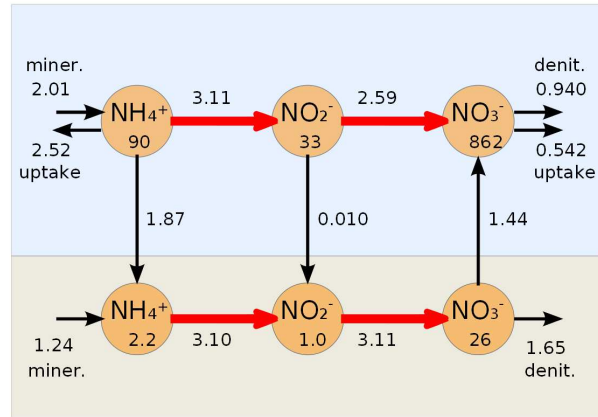


Figure 6: Biomass of active ammonia and nitrite oxidizing communities (a) in low water and (b) high water conditions.

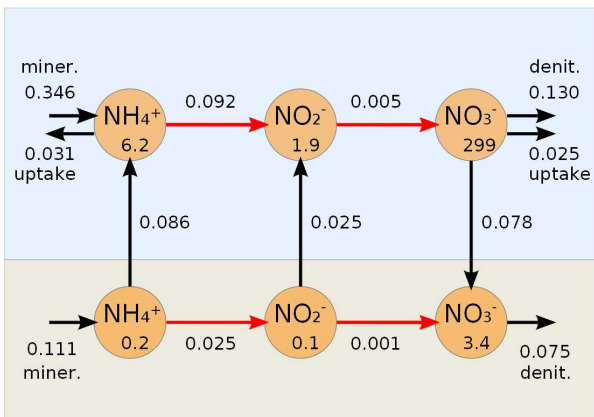
Low water conditions - upstream SAV (~77 km)



Low water conditions - downstream SAV (~142 km)



High water conditions - upstream SAV



High water conditions - downstream SAV

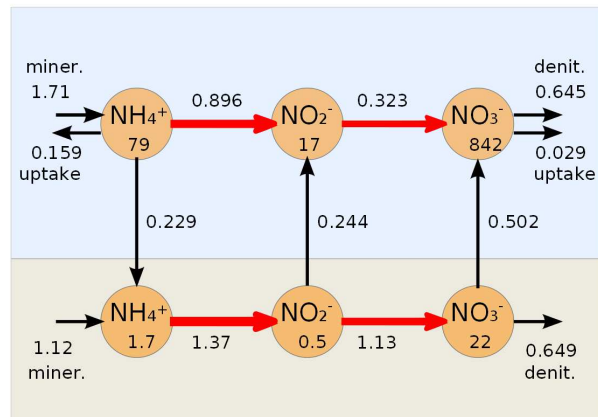


Figure 7: Nitrogen budget in the Seine River, upstream and downstream the SAV WWTP, in low and high water conditions. Stocks are in TN and fluxes are in TN d⁻¹. Ammonia and nitrite oxidation fluxes are in red. Mineralization (miner.), phytoplankton uptake (uptake), denitrification (denit.) and benthic fluxes (arrows between water and sediment compartments) are in black.

Appendix

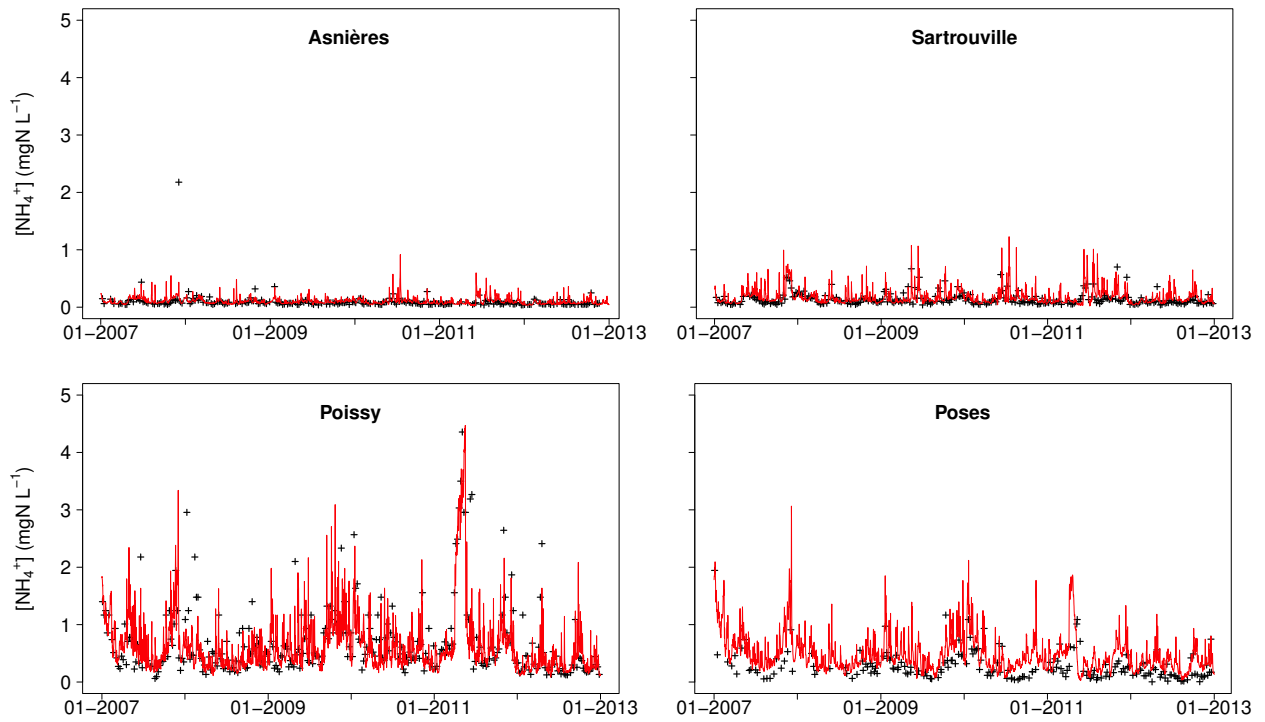


Figure A.1: 6-year time-series of NH_4^+ concentrations at 4 stations from Paris to 200 km downstream.

784

Table A.1: Statistical criteria (RMSE in $mgN L^{-1}$) for 6-year NH_4^+ time-series at the four monitoring stations shown in Fig. A.1. LW = low water conditions, HW = high water conditions.

Station	LW	HW	2007-2012
Asnières	0.060	0.164	0.123
Sartrouville	0.115	0.072	0.096
Poissy	0.404	0.404	0.404
Poses	0.328	0.306	0.318

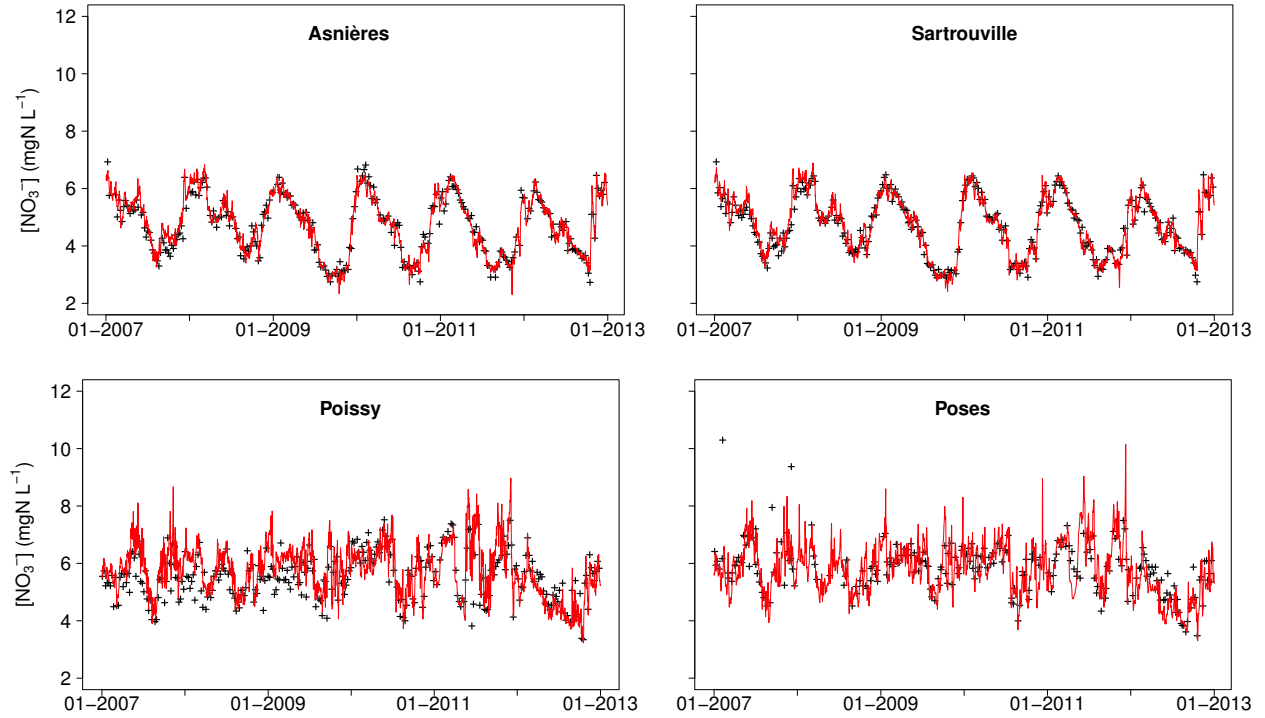


Figure A.2: 6-year time-series of NO_3^- concentrations at 4 stations from Paris to 200 km downstream.

Table A.2: Statistical criteria (RMSE in mgN L^{-1}) for 6-year NO_3^- time-series at the four monitoring stations shown in Fig. A.2. LW = low water conditions, HW = high water conditions.

Station	LW	HW	2007-2012
Asnières	0.233	0.277	0.256
Sartrouville	0.218	0.213	0.215
Poissy	0.587	0.485	0.537
Poses	0.629	0.702	0.663

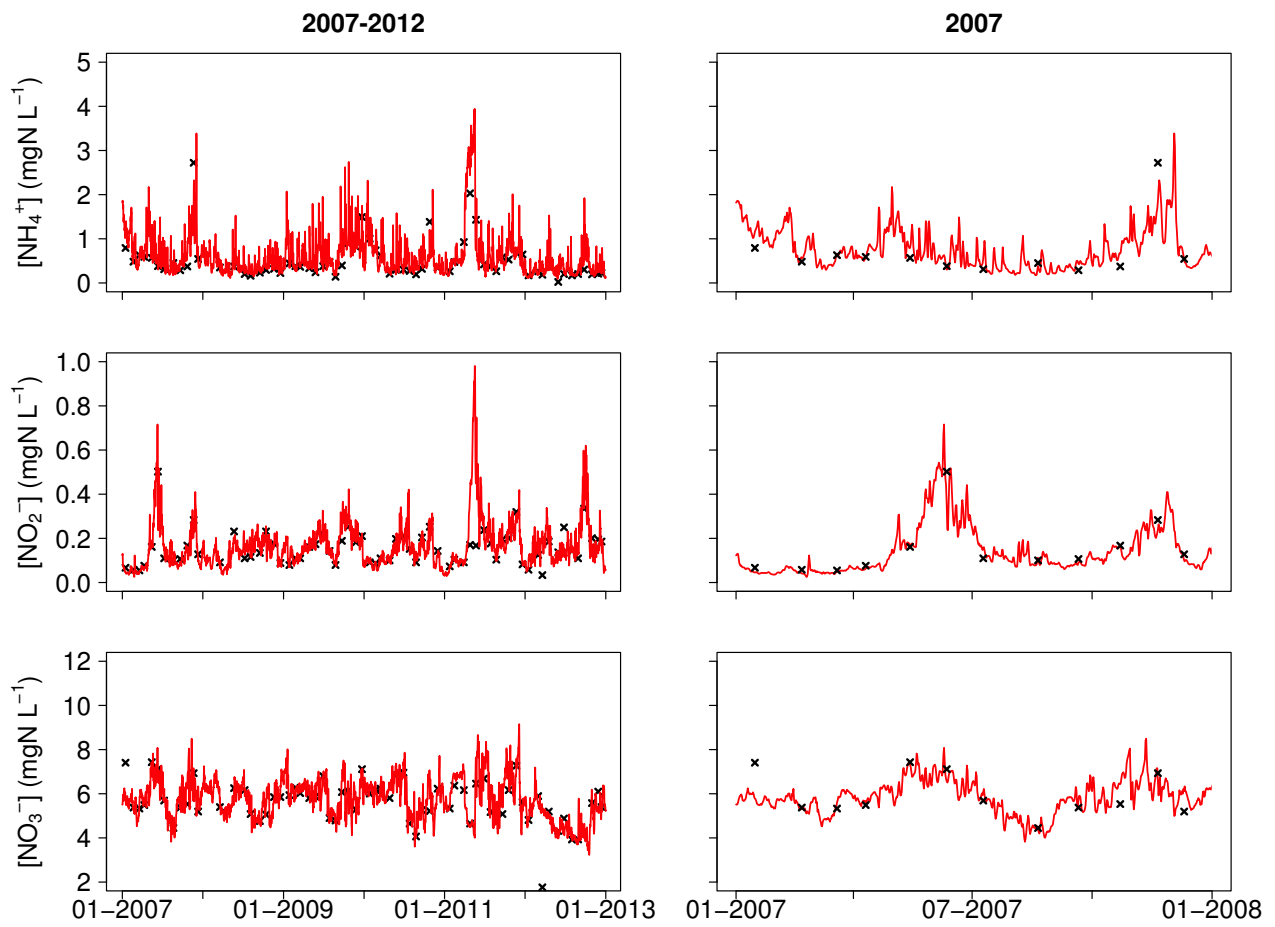


Figure A.3: 6-years and 1-year time-series of NH_4^+ , NO_2^- and NO_3^- concentrations at Meulan. Crosses are data from the RSC monthly monitoring program.