Impact of filtration material on nitrification in biological filters used in drinking water production

A. Kihn, A. Andersson, P. Laurent, P. Servais and M. Prévost

ABSTRACT

The presence of ammonia during drinking water production can be the source of several water quality problems during distribution and during disinfection when chlorine is used. It is therefore important to optimize the ammonia removal before disinfection. The purpose of this work was to compare nitrification on an opened superstructure (Picabiol) and two closed superstructure (Picacarb and Calgon F400) granular activated carbon (GAC) during colonization of new filters and after longer operating times in pilot and full-scale filters. Fixed nitrifying biomass levels, ammonia removal and oxygen consumption were monitored at high and low temperatures and at two different ammonia loadings. In first stage pilot filters supplied by an ammonia concentration higher than 0.4 mg l^{-1} $N\text{-}NH_4$ and at temperatures higher than 20°C, nitrification capacity was higher on Picabiol than on Picacarb. At low temperature, no ammonia removal occurred on both materials. Calgon and Picabiol provided equal nitrification performances. In full-scale second stage filters fed with ammonia concentrations ranging from 0.02 to 0.16 mg l^{-1} $N\text{-}NH_4$, nitrification performances were similar on Picabiol and on Calgon. In cold water, none of these filtration materials provided a proper nitrification; nitrifying biomass, however, did not disappear on the GAC filters during winter.

Key words | ammonia, biological filtration, drinking water production, fixed nitrifying biomass, granular activated carbon, nitrification

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INTRODUCTION

In drinking water production, reducing ammonia concentration has become a general concern to improve the quality of the distributed water. The presence of ammonia in drinking water can be the source of several water quality problems during distribution, such as bacterial regrowth, production of taste and odour (Bouwer and Crowe 1988; Rittmann and Huck 1989) and production of nitrites by incomplete oxidation of ammonia. In drinking water production, both physico-chemical and biological processes can be applied to remove ammonia. In the first group of processes, ion exchange and chemical oxidation are of primary concern. The most common method used is chlorination until break point. During this step, ammonia consumes high chlorine doses (theoretical consumption of 7.6 mg Cl_2 per mg $N\text{-}NH_4$). In addition, the level of chlorination required to reach break point usually induces, by reaction between organic matter and chlorine, the formation of undesirable disinfection by-products such as trihalomethanes (THM) (Doré 1989) which are now known to be potentially carcinogenic (Cantor *et al.* 1990). This shows the importance of optimizing the elimination of ammonia before disinfection.

At present, biological processes, like biological filtration, seem to be the most promising techniques to remove ammonia. In this process, simultaneous removal of biodegradable dissolved organic matter and ammonia can take place (Bouwer and Crowe 1988). Biological nitrification is a two step process in which sequential oxidation of ammonia into nitrite and nitrite into nitrate occurs. Until recently, it was admitted that *Nitrosomonas* and *Nitrobacter* were the most common genera of autotrophic bacteria, known respectively as ammonia oxidizers and

nitrite oxidizers (Watson *et al*. 1989). New detection techniques of nitrifying bacteria showed, however, that nitrification in natural environments and in biofilms is complex and that it is difficult to identify all the autotrophic bacterial species capable of nitrification in such environments (Mobarry *et al*. 1996; Hovanec and DeLong 1996; Hovanec *et al*. 1998). In addition, even though several species of heterotrophic bacteria are able to produce nitrates and nitrites (Verstraete and Alexander 1973; Focht and Verstraete 1977), their contribution to total nitrification seems to be insignificant in comparison to autotrophic processes.

Up to now, the factors controlling nitrification efficiency in biological filters used during drinking water production were mostly investigated by indirect measurement using the monitoring of the ammonia concentration in the inflow, interstitial and outflow waters of filters (Bablon *et al*. 1988; Chien *et al*. 1997; Niquette *et al*. 1999). These studies showed that the choice of a suitable filtration medium could influence the biological elimination in filters used during drinking water production. Filters filled with granular activated carbon (GAC) provided a better nitrification than sand or anthracite filters especially when external conditions were unfavourable (low ammonia concentration, low temperature). Bouillot *et al*. (1992) found that, on a volumetric basis, granular activated carbon appears to be three times more effective than sand.

Indeed, several studies on heterotrophic bacterial fixation showed that a GAC filter has a higher fixation capacity than sand or anthracite (Bouwer and Crowe 1988; Billen *et al*. 1992; Urfer *et al*. 1997). In addition, an opened superstructure GAC supports a higher heterotrophic biomass than a closed superstructure GAC. Indeed, the structure of the medium has a direct impact on the number of attachment sites available to bacteria and the level of shear stress to which the bacteria are exposed during filtration and counter-flow backwashing (Rittmann 1982; Niquette *et al*. 1998).

When biological filters are starting, a long period of colonization is required before constant ammonia removal is reached; nitrifying bacteria are known for their slow growth and their poor growth yield (Rittmann and Snoeyink 1984). During this period, ammonia breakthrough and nitrite formation can alter the quality of the water produced. The start-up time depends on temperature, ammonia loading and pH (Bourdon *et al*. 1988; Hasley and Leclerc 1993; Chien *et al*. 1997).

The direct impact on fixed autotrophic bacterial biomass of factors such as filtration material, ammonia loading and temperature has not yet been clearly established because of a lack of an appropriate methodology to quantify the fixed nitrifying biomass. This additional information, along with the ammonia removal, could help water producers to achieve better management of biological nitrification and to avoid degradation of the quality of the distributed water especially during the transition period before reaching a steady state biological activity in new filters. Furthermore, the estimation of nitrifying biomass could be useful to improve modelling of biological filter functioning.

The purpose of this work was to compare the impact of an opened superstructure and two closed superstructure activated carbons on nitrification in biological filters. In this study, the periods required to begin efficient nitrification and to achieve maximal nitrifying biomass on three GAC filter materials were determined. A recently developed method to estimate nitrifying biomass fixed on the filtration material (Kihn *et al*. 2000) was used in this study to test the impact of temperature and ammonia concentration during colonization and on the long-term fixed nitrifying biomass. Experiments were conducted both on pilot-scale first stage filters and on full-scale second stage filters.

MATERIALS AND METHODS

St Rose treatment plant

The present study was conducted at the St Rose water treatment plant in Laval (Quebec, Canada). The raw water, drawn from the Mille-Iles river, has the following characteristics: high organic load (dissolved organic carbon (DOC) between 4 and 10 mg l^{-1} C), low alkalinity (between 20 and 50 mg l^{-1} $CaCO_3$) and low ammonia content (20–160 μg l^{-1} $N\text{-}NH_4$). The water is subject to important seasonal fluctuations in concentrations of

Table 1 | Characteristics of the different tested GAC (data provided by the GAC manufacturers)

	Picabiol	Calgon F400	Picacarb
Origin	Wood	Bituminous coal	Bituminous coal
Type of activation	Chemical	Physical	Physical
Effective size (mm)	0.97	0.55–0.75	0.95
Coefficient of uniformity	< 1.7	1.6–2.1	1.9
Dry bulk density (g cm^{-3})	0.35	0.42	0.48
Specific surface (m^2 g^{-1})	1050	900–1100	1100
Size of pores (μm)	10–100	$\ll 0.1$	$\ll 0.1$

ammonia, DOC and in temperature (1 to 28°C). The St Rose water treatment plant has a nominal capacity of 110,000 m^3 day^{-1} (with an average annual flow of 50,000 m^3 day^{-1}). The present treatment line includes dynamic settling ($Alum + SiO_2$), rapid sand/anthracite filtration, ozonation, biological activated carbon (BAC) filtration, pH adjustment and disinfection with ClO_2.

First stage pilot filters

The pilot plant consisted of filtration columns (10.16 cm-diameter PVC cylinders) filled with 30 cm of GAC and equipped with sampling ports to collect the filtration media. The pilot downflow filters were fed with settled water from the treatment plant at a hydraulic loading of 5 m h^{-1} to provide an initial empty bed contact time (EBCT) of 3.6 minutes. The filtration rate was kept constant to avoid the interference of a change in hydraulic forces on the nitrifying biomass. The ammonia concentration in the settled water ranged from 20 to 160 μg l^{-1} $N\text{-}NH_4$. The highest concentrations were observed in the beginning of winter (day 170–210), whereas the lowest levels were observed in summer (around day 50 in this study). This water was continuously enriched with 0.4 or 1.2 mg l^{-1} $N\text{-}NH_4$ added under the form of a $(NH_4)_2SO_4$ solution. All the pilot filters were backwashed once a week by applying an air scour at 70 m h^{-1} for 2 to 3 minutes and then rinsing the filtration bed with counter-flow settled water for 20–25 minutes at 25 m h^{-1}. Sample collections were performed one day after backwashing.

Three types of granular activated carbon were tested during two different periods: an opened superstructure GAC containing tubular pores (Picabiol; Pica Company, France) and two closed superstructure activated carbon with a smooth surface (Picacarb; Pica Company, France and Calgon F400; Calgon Carbon, USA). Characteristics of the three filter media are presented in Table 1. The impact of the filtration material was monitored by measuring the nitrifying biomass (expressed in terms of potential nitrifying activity) in the surface layer of the pilot filters, the ammonia removal and the oxygen consumption in the filtration columns. Ammonia removal and oxygen consumption values were determined as the difference between concentrations in the inlet and outlet water. In addition, the effect of high (20 ± 3°C) and low (<7°C) *in situ* temperature, as well as ammonia loading on the colonization by nitrifying biomass were investigated. In order to keep the temperature at 20°C throughout the study, a heating system for the inlet water was installed. The pilot study was divided in two parts. The different operating conditions for the filtration columns are presented in Table 2. Measurements in all pilots were performed from the start of the feeding of the columns (day 0).

Table 2 | Operating conditions of the pilot columns during the two phases of the study

Phase of the study	Temperature (°C)	Filling material	Ammonia enrichment (mg l^{-1} N)
1	20	Picabiol	0.4
(286 days)	(± 3, 187, 16–25)*		after day 146
			1.2
		Picabiol	1.2
		Picacarb	0.4
		Picacarb	1.2
	< 7	Picabiol	1.2
		Picacarb	1.2
	20	Picabiol	0.4
(339 days)	(± 3, 39, 15–24)*	Calgon F400	0.4

*Standard deviation, no. of sampling campaigns, minimum–maximum values.

Full-scale second stage BAC filters

Nitrification in full-scale BAC-filters of the St Rose plant was studied in two filters, a filter filled with an opened superstructure GAC (Picabiol) and a filter filled with a closed superstructure GAC (Calgon F400) (see Table 1). These filters were in service for more than 7 years without regeneration of the GAC. Each filter had a surface of 80 m^2, a hydraulic loading of 3.9 to 5 m h^{-1} and an EBCT of 20 to 30 minutes. The ammonia concentrations entering the second stage filters were 20–160 μg l^{-1} N-NH_4. Backwashing frequency varied during the year depending on temperature and water demand (from 96 hours in summer to 336 hours in winter). During the backwash procedure, the water level was drained to the GAC surface, followed by an air scour (3 minutes). The filters were then rinsed for 15 minutes at 16 m h^{-1}. Sample collections were performed in the middle of a filtration cycle. Solid medium samples were collected from the filters at different depths using a core sampler to estimate the average nitrifying biomass fixed on the GAC. Filters were sampled four times during the high temperature (>15°C) period and four times during the low temperature (<5°C) period.

Analytical monitoring

Ammonia

NH_4 was measured using the indophenol colorimetric method (AFNOR 1990) on duplicate samples. This method is fairly precise (± 3 μg l^{-1} N-NH_4 method standard deviation) even at low ammonia concentrations (detection limit 5 μg l^{-1} N-NH_4) (Andersson *et al.* 2000).

Oxygen measurement

Dissolved oxygen was measured by the Winkler method (Rodier *et al.* 1996) in the inlet and outlet water of the pilot filters.

Density of the nitrifying bacterial biomass

The applied method consisted of estimating the potential nitrifying activity (PNA), which is proportional to the

nitrifying biomass. The PNA was determined by measuring the production rate of oxidized nitrogen (NO_2 and NO_3) when a sample of solid support with fixed bacteria was incubated in nitrifier media containing a saturating ammonia concentration under optimal conditions (Kihn *et al.* 2000). In practice, 2 cm^3 samples of colonized GAC were collected from the surface of the GAC in the case of pilot filters and from surface and different depths in the case of full-scale filters. Each 2 cm^3 GAC sample was then washed with an ammonia free solution, followed by an aerated incubation at 32°C with 5 ml of a nitrifier medium containing 10 mg l^{-1} N ammonia solution. After 0, 15 and 30 minutes, sub-samples were filtered through 0.2 μm to stop the biological reaction. Nitrate and nitrite concentrations were then measured by colorimetry (Jones 1984) and plotted against time. The potential nitrifying activity was expressed in μg h^{-1} cm^{-3} N. The precision of the method was estimated to 16% (Kihn *et al.* 2000).

Adsorbed metals

A 5 g sample of dried GAC was burnt at 650°C. Ashes were dissolved in concentrated HCl. The acid solution was then diluted in 100 ml of demineralized water. The amount of metals was measured by atomic adsorption. Precision of the method was estimated to ± 2%.

RESULTS

Comparison between Picabiol and Picacarb

Data gained on pilot filters during the first phase of the study showed that for all the filtration columns fed with heated water (20°C) a period of 14 days was necessary before significant nitrification occurred (Figures 1a and 2a). After this, a rapid increase of the ammonia removal was observed. The maximum ammonia removal was reached after 40 days of operating for the pilot columns containing Picabiol for both feeding concentrations. In the columns containing Picacarb, the ammonia removal increased for about 170 days in the column enriched with 1.2 mg l^{-1} $N\text{-}NH_4$ and up to the end of the study in the column enriched with 0.4 mg l^{-1} $N\text{-}NH_4$.

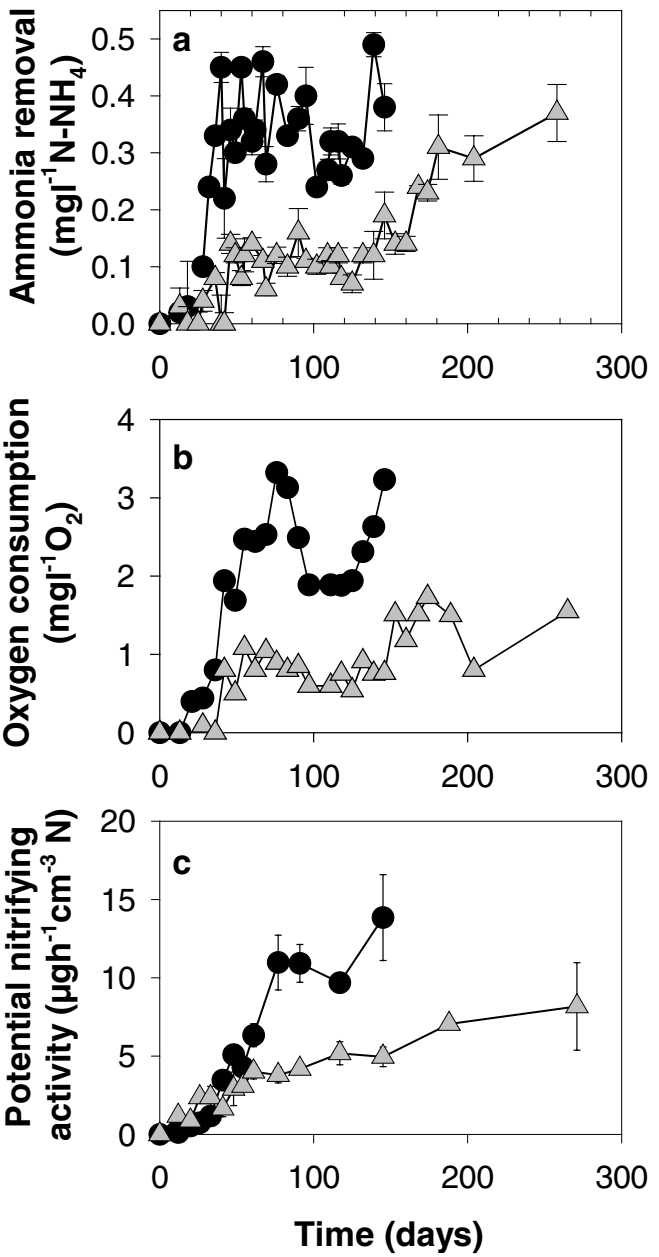

Figure 1 | Comparison of the ammonia removal (a), the oxygen consumption (b) and the potential nitrifying activity (PNA) in the surface layer (c) in the pilot filtration columns filled with Picabiol (•) and Picacarb (△). These filtration columns were fed with settled water enriched with 0.4 mg l^{-1} $N\text{-}NH_4$ at 20°C. The EBCT in the pilots decreased during the course of the study due to GAC sampling for PNA measurements.

The maximum ammonia removal value reached during this study in the columns containing Picabiol was equal to 0.49 mg l^{-1} $N\text{-}NH_4$ (88% of the ammonia feeding

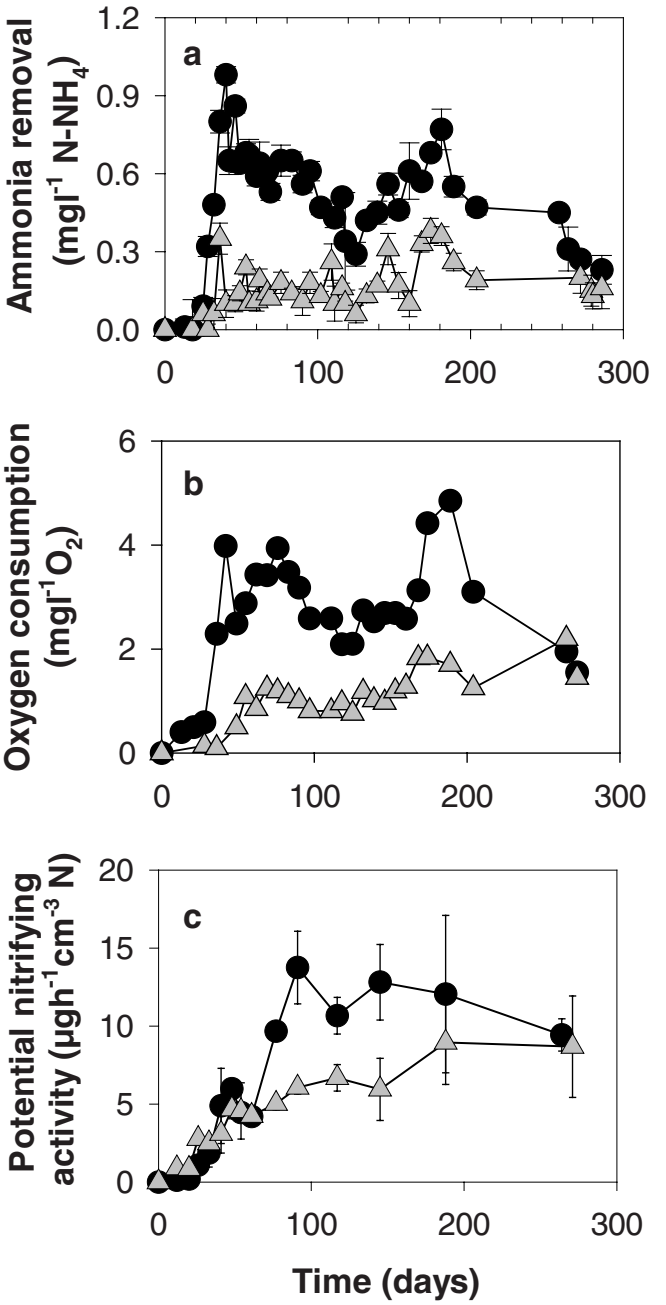

Figure 2 | Comparison of the ammonia removal (a), the oxygen consumption (b) and the potential nitrifying activity (PNA) in the surface layer (c) in the pilot filtration columns filled with Picabiol (•) and Picacarb (△). These filtration columns were fed with settled water enriched with 1.2 mg l^{-1} N-NH_4 at 20°C. The EBCT in the pilots decreased during the course of the study due to GAC sampling for PNA measurements; this decrease was higher for the Picabiol column than for the Picacarb column.

the filter) and 0.98 mg l^{-1} N-NH_4 (75%) for the columns fed with settled water enriched with 0.4 mg l^{-1} N-NH_4 and 1.2 mg l^{-1} N-NH_4, respectively. For the columns containing Picacarb, a maximum ammonia removal at the end of the study of 0.37 mg l^{-1} N-NH_4 (71%) and 0.38 mg l^{-1} N-NH_4 (35%) was measured for ammonia enrichments of 0.4 and 1.2 mg l^{-1} N-NH_4, respectively. It was difficult to determine a steady-state value as the EBCT decreased in all the columns throughout the study. Indeed, to measure fixed nitrifying biomass, a certain amount of media (approximately 20 cm^3 per sampling campaign) was removed from the filtration columns. This decrease of the contact time due to media loss, and thus a decrease in the total fixed nitrifying biomass, was, however, more important for the column containing Picabiol and enriched with 1.2 mg l^{-1} N-NH_4 because of a higher number of PNA measurements. For the columns fed with settled water enriched with 1.2 mg l^{-1} N-NH_4, the final contact time after 286 days of functioning was 1.5 and 2.7 minutes for the Picabiol and the Picacarb filter, respectively. This explains the decrease in ammonia removal in the column containing Picabiol after colonization (Figure 2a). From day 50 until the end of the study, the contact time in the Picabiol filter was shorter than in the Picacarb column while the ammonia removal in the Picabiol column was similar or higher. This indicates that Picabiol is a more efficient material to support nitrification.

The ammonia enrichment was tripled in the column containing Picabiol and initially enriched with 0.4 mg l^{-1} N-NH_4 to test the response of the nitrifying biomass to an ammonia increase. Table 3 shows the average values of the ammonia removal before and after modification of the ammonia concentration. The average ammonia removal was twice as high 12 days after the ammonia concentration was tripled.

Ammonia removal was also measured in the pilot filters fed with settled *in situ* water enriched with 1.2 mg l^{-1} N-NH_4 during the winter period (Figure 3a). When temperatures varied from 3.2 to 6.7°C, the ammonia removal stayed below 1% for both filtration columns filled with either Picabiol or Picacarb. The study was stopped after 68 days as the *in situ* temperature rose above 7°C.

Dissolved oxygen was determined in the inlet and outlet water of the filtration columns. The oxygen

Table 3 | Effect of an increase in the ammonia feeding concentration (from 0.4 to 1.2 mg l^{-1} N-NH_4) on the potential nitrifying activity (PNA) in the surface layer and on the ammonia removal in the pilot filtration column filled with Picabiol

Ammonia enrichment		Ammonia removal (mg l^{-1} N)	Potential nitrifying activity (μg h^{-1} cm^{-3} N)
0.4 mg l^{-1} N-NH_4	Average values	0.33	11.5
		($\pm$ 0.08, $n = 10$)*	($\pm$ 2.1, $n = 3$)*
	Minimum and maximum values	0.24–0.54	9.7–13.8
1.2 mg l^{-1} N-NH_4	Average values	0.67	11.5
		($\pm$ 0.14, $n = 18$)*	($\pm$ 2.9, $n = 11$)*
	Minimum and maximum values	0.51–1.00	8.1–14.1

*Standard deviation, no. of sampling campaigns.

consumption estimated for the different columns is shown in Figures 1b and 2b. Oxygen consumption correlated well with ammonia removal ($r^2 = 0.85$, $n = 79$) under our experimental conditions for both filtration materials tested. The slope of the linear regression was equal to 4.9 ± 0.3 mg O_2 per mg N. The oxygen consumption to achieve complete nitrification is between 4.3 and 4.5 mg O_2 per mg N-NH_4 (Bouwer and Crowe 1988; Hasley and Leclerc 1993). The difference from the value observed in our study, 0.4–0.6 mg l^{-1} O_2, was probably due to oxygen consumption by fixed heterotrophic bacteria, which oxidize a part of the biodegradable dissolved organic matter in the columns. Some dissolved organic carbon (DOC) measurements showed an average DOC removal of 0.14 mg l^{-1} C in the pilot filters. To achieve such a removal, approximately 0.4 mg l^{-1} O_2 is needed considering a molar ratio of 1 between the carbon oxidized and the oxygen consumed.

During the study at low temperature, no oxygen consumption was observed (data not shown) and no significant nitrification occurred.

Vertical profiles of potential nitrifying activity showed that the biomass in the surface layer was significantly correlated to the total biomass, expressed in terms of PNA, contained in the pilot columns containing either Picabiol or Picacarb ($n = 17$, $\alpha = 0.05$). We considered, therefore, the PNA in the surface layer as an index of the total biomass in the columns. Samples for the correlation of the PNA of the total biomass and the PNA measured in the surface layer of the columns were collected preferentially in the column containing Picabiol enriched with a concentration of 1.2 mg l^{-1} N of ammonia. Vertical profiles for the correlation were obtained by measuring PNA at three different depths, using approximately 3% of the filtration material. The high number of profiles and sampling campaigns on the surface explains the high loss of filtration material in this column and thus the decrease of the EBCT.

Potential activity of the nitrifying biomass fixed in the surface layer on Picabiol and Picacarb in the first stage pilot filters is presented in Figures 1c and 2c. At 20°C, the nitrifying biomass fixed on both materials was rather similar from day 0 to day 50, whatever the ammonia enrichment of the feeding water. After this period, the fixed biomass increased more rapidly on Picabiol than on Picacarb.

For the Picabiol column enriched with 1.2 mg l^{-1} N-NH_4, the biomass fixed in the surface layer reached a maximum value of 14 ± 2 μg h^{-1} cm^{-3} N after 91 days and then the fixed biomass level decreased to reach a PNA of 9 ± 1 μg h^{-1} cm^{-3} N. For the column filled with Picabiol and enriched with 0.4 mg l^{-1} N-NH_4, the

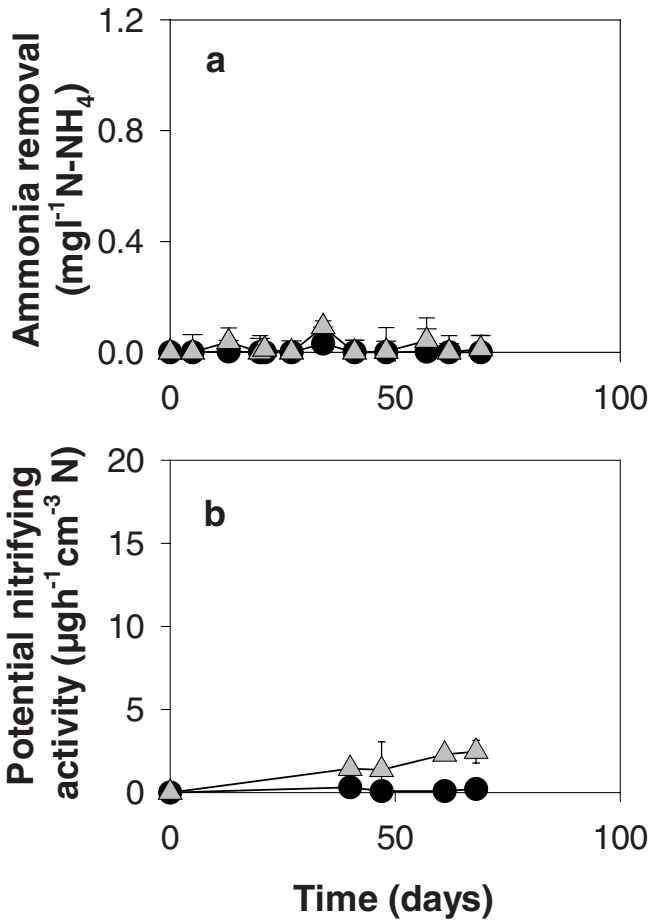

Figure 3 | Comparison of the ammonia removal (a) and the potential nitrifying activity (PNA) in the surface layer (b) in the pilot filtration columns filled with Picabiol (•) and Picacarb (△). These filtration columns were fed with settled water enriched with 1.2 mg l^{-1} $N\text{-}NH_4$ at low temperatures (<7°C). The EBCT in the pilots decreased during the course of the study due to GAC sampling for PNA measurements.

nitrifying biomass reached a maximum value of 14 ± 3 µg h^{-1} cm^{-3} N at day 146. After this day, the ammonia enrichment was tripled for this column to test the nitrifying biomass response to a sudden increase of the substrate concentration. The monitoring of the biomass (Table 3) showed no further increase of fixed biomass in the surface layer. At 20°C, the ammonia concentration in the inlet water seemed to have no effect, in the range tested here, on the maximum level of fixed biomass in the surface layer.

The biomass fixed in both columns containing a closed superstructure GAC continued to increase much more slowly after the first 50 days for another seven months before reaching, at the end of the study, a value of 8 ± 3 µg h^{-1} cm^{-3} N and 9 ± 3 µg h^{-1} cm^{-3} N for an ammonia enrichment of 0.4 and 1.2 mg l^{-1} $N\text{-}NH_4$, respectively.

At low temperatures, nitrifying biomass accumulation was higher on the Picacarb support (Figure 3b). After 68 days of functioning, the potential nitrifying activity on the Picabiol (0.21 ± 0.05 µg h^{-1} cm^{-3} N) was far lower than the value obtained on the Picacarb (2.5 ± 0.6 µg h^{-1} cm^{-3} N). The biomass level in the column containing the Picacarb was twice as high at 20°C than at 7°C after 68 days of colonization.

Comparison between Picabiol and Calgon F400

Data from the second phase of the pilot study showed that after a start-up period of two weeks, the ammonia removal increased rapidly (Figure 4a). During the first 3 months of operating, the ammonia removal was slightly higher on the Picabiol columns than on the Calgon F400 columns. Then nitrification performances became similar on both filtration media. The maximum ammonia removal was reached after 178 days for both columns and was 0.52 mg l^{-1} $N\text{-}NH_4$ on Calgon F400 and 0.54 mg l^{-1} $N\text{-}NH_4$ on Picabiol. Until the end of the study, nitrification on the closed superstructure medium was roughly similar to that on the opened superstructure GAC. As for the ammonia removal, fixed nitrifying biomass in the surface layer on Calgon F400 was lower than on the Picabiol at the beginning of the study (Figure 4b). The colonization of the Picabiol continued throughout the study and reached a maximum PNA of 9 ± 1 µg h^{-1} cm^{-3} N. Unfortunately, the PNA measurements in the Calgon column were not evaluated after day 175 due to technical problems.

The average ammonia removal percentage was determined for two ranges of temperature (temperatures lower than 5°C and temperatures higher than 15°C) in two second stage full-scale filters, one containing Picabiol, the other Calgon F400. Nitrification performances were equal on Calgon F400 and on Picabiol for an EBCT of 20–30 minutes (Table 4). At high temperature, the average ammonia removal in both filters was almost complete. When the temperature was below 5°C, the ammonia

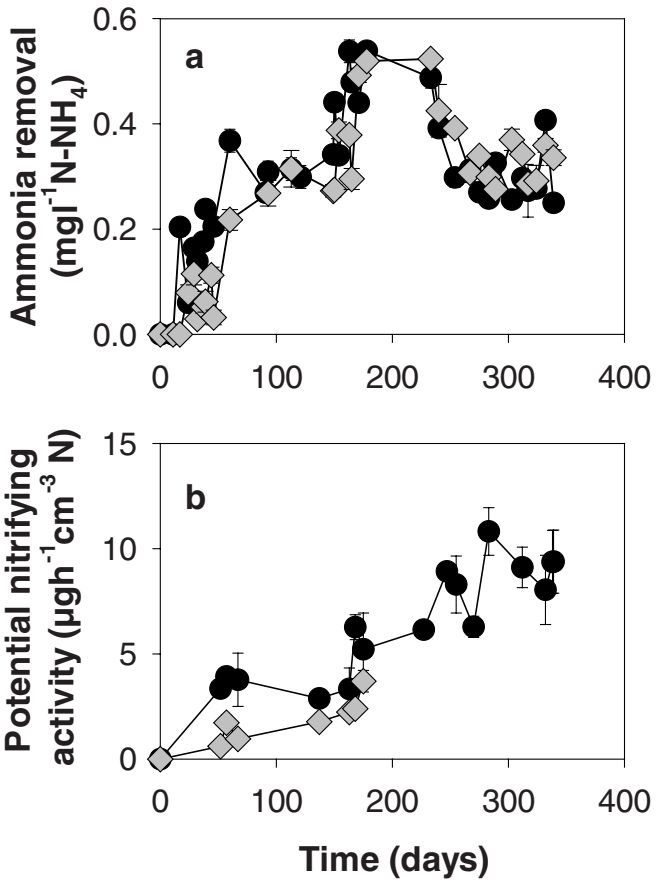

Figure 4 | Comparison of the ammonia removal (a) and the potential nitrifying activity (PNA) in the surface layer (b) in the pilot filtration columns filled with Picabiol (•) and Calgon F400 (◇). These filtration columns were fed with settled water enriched with 0.4 mg l^{-1} $N\text{-}NH_4$ at 20°C.

removal became insignificant. A hypothesis test on the average values ($\alpha = 0.05$) showed that the biomass levels were not significantly different on both materials for both temperature ranges. A significant biomass was measured at low temperature even at the end of the five month winter with temperatures close to 1°C.

DISCUSSION

Our monitoring of the colonization of first stage GAC filters at 20°C showed that nitrification occurred two weeks after the filters were in service. This start-up time was comparable to the time mentioned in literature for sand filters (Bourdon *et al.* 1988; Hasley and Leclerc 1993). The monitoring of the colonization by nitrifying biomass at 20°C showed that when new first stage filters were started, Picabiol provided a better material than Picacarb or Calgon F400 for at least 3 months. Indeed, Bouwer and Crowe (1988) discussed that nitrification is theoretically favoured by a medium with a large specific surface and a highly porous structure. After longer operating times the difference became smaller and finally performances became equal on Picabiol and Calgon. For a lower ammonia concentration in the full-scale tests, there was no difference in average ammonia removal and nitrifying

Table 4 | Average potential nitrifying activity (PNA) and ammonia removal measured in the full-scale filters during two periods characterized by different temperature ranges

	Picabiol			Calgon		
Temperature (°C)	Ammonia removal (%)	Volume specific removal (µg h^{-1} cm^{-3})	Potential nitrifying activity (µg h^{-1} cm^{-3})	Ammonia removal | (%)	Volume specific removal (µg h^{-1} cm^{-3})	Potential nitrifying activity (µg h^{-1} cm^{-3})
>15	96	1.06	2.3	94	1.03	2.0
	(± 5, $n=3$)*	(± 0.49, $n=3$)*	(± 0.5, $n=3$)*	(± 4, $n=4$)*	(± 0.28, $n=4$)*	(± 0.5, $n=4$)*
<5	4	0.01	1.1	2	0.01	1.3
	(± 7, $n=4$)*	(± 0.02, $n=4$)*	(± 0.3, $n=4$)*	(± 3, $n=4$)*	(± 0.01, $n=4$)*	(± 0.7, $n=4$)*

*Standard deviation, no. of sampling campaigns.

biomass between Picabiol and Calgon after more than 7 years of operating. The ammonia concentration in the inflow water within the tested range has little impact on the time required for the colonization of the columns containing either Picabiol or Picacarb. The maximum biomass measured in the surface layer of the columns filled with Picabiol was 14 $\mu g\ h^{-1}\ cm^{-3}$ N whatever the ammonia enrichment. The fact that the biomass level was quite similar at both feeding concentrations and that an increase in ammonia in the inlet water of the Picabiol column did not result in an increase of biomass in the surface layer seemed to indicate that the maximum nitrifying biomass fixation capacity was reached for Picabiol.

At steady state, a maximum ammonia removal on Picabiol of 0.54 mg l^{-1} $N\text{-}NH_4$ was observed in this study for an EBCT of 3.2 minutes and an ammonia enrichment of 0.4 mg l^{-1} $N\text{-}NH_4$. After increasing the ammonia enrichment to 1.2 mg l^{-1} in this column, a maximum removal value of 1.0 mg l^{-1} $N\text{-}NH_4$ was measured 33 days after the modification. In the column enriched with 1.2 mg l^{-1} $N\text{-}NH_4$ from the beginning of the study, the maximum ammonia removal was 0.98 mg l^{-1} $N\text{-}NH_4$. This showed that, for a high ammonia concentration, the contact time in the pilot plants was too short to completely remove the ammonia. In former studies, the importance of the contact time in biological filters has been demonstrated for dissolved organic carbon removal (Servais *et al*. 1991, 1992).

In the second part of the study, Picabiol was colonized far slower than in the first part. In fact, the filtration material used during the second part had been in service in full-scale filters for about 7 years before being tested in the pilot filters. An accumulation of biomass was still observed after several months of operating, whereas the same maximum nitrifying biomass level was reached, in the first part of the study, after 80 days. This could be due to the fact that with the age of operating, the quantity of heavy metals and calcium adsorbed on the carbon grain surface increases and has a negative effect on nitrification performances or obstructs the pores of the grain. Indeed, measurement of adsorbed metals on the carbon grains showed that iron, aluminium and manganese were far higher in the second part of the study (data not shown); this could explain the delay in colonization during the second phase of the pilot study.

At temperatures lower than 7°C, neither the Picabiol pilot nor the Picacarb pilot provided a proper ammonia removal. In these pilots, fixation of nitrifying biomass occurred at low temperature; it was more pronounced on the Picacarb than on Picabiol. In the full-scale filters, a significant nitrifying biomass was measured on both GAC filters during winter while ammonia removal was extremely low. The fact that nitrifying biomass did not disappear on either of the media throughout the winter time and that colonization occurred at low temperature, cannot be explained by a growth of nitrifying bacteria as no significant ammonia removal was observed. This suggests that biomass adsorption and/or fixation took place continuously on GAC.

CONCLUSIONS

In first stage filters filled with GAC and supplied by an ammonia concentration higher than 0.4 mg l^{-1} $N\text{-}NH_4$, we found that a period of 2 weeks was necessary before a significant ammonia removal and nitrifying biomass fixation occurred at 20°C in all the filters tested. An opened superstructure GAC provided a better colonization material than a closed superstructure GAC for the first months. After longer operating times, nitrification performances tended to become similar on Picabiol and on Calgon. On Picacarb, the ammonia removal stayed lower for an equivalent EBCT during the course of the study. At low temperature, none of the filling materials provided a sufficient nitrification. However, some nitrifying biomass fixation occurred on Picacarb.

In the second stage full-scale filters with high EBCT (20–30 min), supplied with a low ammonia concentration, the ammonia removal and the level of fixed nitrifying biomass were equal on Picabiol and on Calgon F400 at temperatures higher than 15°C. At low temperature (<5°C), nitrification performances were poor in both filters. The fixed nitrifying biomass did not disappear from the support media, even after 5 months of operating in cold water. Thus, a temperature rise in spring allows a rapid recovery of nitrification performance.

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