Improved removal of pesticides in biological granular activated carbon filters by pre-oxidation of natural organic matter

L. T. J. van der Aa, R. J. Kolpa, L. C. Rietveld and J. C. van Dijk

ABSTRACT

Two drinking water pilot plants were in operation for up to 600 days to assess the influence of pre-oxidation on the removal of natural organic matter (NOM), easily assimilable organic carbon (AOC) and pesticides during (biological) granular activated carbon ((B)GAC) filtration. Pre-oxidation resulted in an increase in AOC concentrations. BGAC filters following the pre-oxidation removed up to 70% of the produced AOC. However, in none of the BGAC filters were AOC concentrations reduced to the concentrations before pre-oxidation. The increased biodegradation of NOM was confirmed by the increased removal of dissolved organic carbon (DOC) in the steady-state situation. The increased biodegradation of NOM was assumed to be one of the main reasons that BGAC filters were more effective in DOC removal than the GAC filters. For seven pesticides it was demonstrated that, at a desired mixed effluent water quality of $0.1 \times 10^{-3}\,\mathrm{g\,m^{-3}}$, the maximum throughput of the BGAC filter was 1.5–3.2 times larger than the maximum throughput of the GAC filter. It was assumed that pre-oxidation reduced NOM adsorption, pore blocking and pre-loading, resulting in more effective pesticide removal.

Key words | adsorption, atrazine, biodegradation, breakthrough curve, NOM, ozone

L. T. J. van der Aa (corresponding author)
Waternet,
P.O. Box 94370,
1090 GJ Amsterdam,
The Netherlands
E-mail: rene.van.der.aa@waternet.nl

L. T. J. van der Aa
L. C. Rietveld
J. C. van Dijk
Delft University of Technology,
Faculty of Civil Engineering and Geosciences,
Department of Water Management,
P.O. Box 5048,
2600 GA Delft,
The Netherlands

R. J. Kolpa
Oasen,
P.O. Box 122,
2800 AC Gouda,
The Netherlands

INTRODUCTION

In drinking water treatment, activated carbon (AC) is used to remove different kinds of organic compounds, including natural organic matter (NOM), disinfection by-products, organic micro-pollutants and substances causing color, taste and odor. In granular activated carbon (GAC) filtration, the water flows through a filter bed filled with AC grains. During this filtration, organic substances adsorb onto the GAC, gradually the GAC becomes saturated with organic substances and finally breakthrough occurs. GAC is regularly replaced by fresh or by reactivated GAC to restore its adsorption capacity. During the normal operation of drinking water treatment plants (DWTPs) bacteria occur in GAC filters, resulting in biodegradation of a part of the NOM. Oxidation, especially ozonation, prior to GAC filtration enhances these biological processes. Therefore, GAC filtration downstream of a pre-oxidation step is

called biological GAC (BGAC) filtration, also known as biological AC filtration (Jekel 1979; Sontheimer et al. 1988; Graveland 1994). In GAC and BGAC filters, adsorption and biodegradation occur simultaneously. BGAC filtration is more effective than GAC filtration for the removal of NOM (Sontheimer et al. 1988; Graveland 1994), atrazine (Orlandini 1999), mycrocystines (Wang et al. 2007) and other organic micro-pollutants. Excessive ozone dosing can lead to undesired bromate formation (Von Gunten & Hoigne 1994; Van der Helm et al. 2009).

Usually DWTPs, especially those treating surface water, have different treatment processes in a series. Each water treatment step may have different objectives. For example, pre-oxidation may target stimulation of biodegradation in BGAC filters, disinfection, oxidation of micro-pollutants and the improvement of color, taste and odor (Kruithof &

Maschelein 1999). The processes are influenced by raw water quality and operations of pre-treatment steps. In turn, the effluent water quality of a treatment step influences the performance of subsequent steps. The staging of different techniques, some of them even with multiple targets, makes the operation of DWTPs complex. In addition, in some cases, the specific purposes of the design of drinking water treatment processes are outdated and the operational goals are changed (Bosklopper *et al.* 2004; van der Helm 2007; van der Helm *et al.* 2008). Nowadays in the Netherlands, the removal of micro-pollutants, for example pesticides, and the substances causing color, taste and odor are the main goals for (B)GAC filtration (Graveland 1994; Kruithof & Maschelein 1999). When (B)GAC filtration is included in a DWTP, the water is usually pre-treated. Common pre-treatment techniques are coagulation-sedimentation, rapid sand filtration and pre-oxidation. The actual removal of NOM and micro-pollutants depends greatly on the water quality, pre-oxidation dosage, type of AC, empty bed contact time (EBCT) and filter run time. After installing (B)GAC filtration, the possibilities for influencing the type of AC, EBCT and influent water quality are limited. The most important operational parameters are the pre-oxidation dosage and the reactivation frequency. During a filter run the AC becomes saturated with adsorbed organic substances and the removal by adsorption ceases. Pre-oxidation partly removes organic micro-pollutants (Kruithof & Maschelein 1999). Pre-oxidation also reduces the adsorbability of NOM and improves the biodegradability of NOM (Sontheimer *et al.* 1988; de Laat *et al.* 1991; Lambert & Graham 1995) and therefore its removal by (B)GAC filtration. Because NOM significantly hinders the adsorption of other compounds due to pore blocking, competition and pre-loading (Summers *et al.* 1989; Carter *et al.* 1992; Knappe *et al.* 1997), pre-oxidation of NOM also affects the removal of organic micro-pollutants by (B)GAC filtration. Pre-oxidation of NOM by ozone induces the formation of assimilable organic carbon (AOC) (van der Kooij *et al.* 1989; Siddiqui *et al.* 1997; Yavich *et al.* 2004; Hammes *et al.* 2006; van der Aa *et al.* 2011). In case the AOC is not sufficiently removed in subsequent treatment steps, this will have a negative impact on the biostability of the treated water. In the Netherlands drinking water is often distributed without any residual disinfectant. Therefore, much attention is given to biofilm formation and regrowth in the distribution system (van der Kooij 1992; Escobar *et al.* 2001; Servais *et al.* 2004).

The objective of this study was to assess the influence of pre-oxidation on AOC formation during pre-oxidation and on the removal of NOM, AOC and pesticides in (B)GAC, as experienced in full scale utilities. Adsorption and biodegradation occur simultaneously and both processes vary during the filter run time. This makes it difficult to judge (B)GAC filtration from only laboratory experiments. Therefore, the removal of the target compounds was studied in pilot plants during complete filter run times up to 600 days. At Weesperkarspel DWTP, one GAC and three BGAC pilot filters were operated to treat surface water. Because the NOM concentration at Weesperkarspel is high, biostability is an important issue. Therefore, the focus was on the removal of dissolved organic carbon (DOC) and AOC. At Tull en 't Waal DWTP, one GAC and one BGAC pilot filter were operated to treat river bank filtrate. Because micro-pollutants, including pesticides, remain a concern to drinking water (Schwarzenbach *et al.* 2006), here the focus was on pesticide removal. AOC formation during pre-oxidation and removal of DOC and AOC during (B)GAC filtration were also examined.

MATERIALS AND METHODS

Weesperkarspel pilot plant: surface water

At Loenen – Weesperkarspel DWTP of Waternet, the water cycle company of Amsterdam and surrounding areas, the raw water from the Bethunepolder was pre-treated in the full-scale plant with coagulation, sedimentation, a reservoir and rapid sand filtration. This pre-treatment reduced the DOC concentrations from 8 to 10 $g\,C\,m^{-3}$ to 5 to 7 $g\,C\,m^{-3}$. The water temperature varied between 3 and 21 $°C$. The pre-treated water was used to feed a pilot plant, which was operated for 600 days. The pilot plant consisted of three ozonation systems, followed by four identical gravity (B)GAC filters. The cylindrical filters had diameters of 0.25 m and were all filled with Norit GAC 830P, a commercially available coal-based AC, to bed heights of 2.10 m. They were operated in down flow mode. All flows

were kept constant at 0.155 m^3 h^{-1}, resulting in surface loading rates of 3.2 m h^{-1} and EBCTs of 40 min. The influent waters of filters W-GAC8, W-BGAC5, W-BGAC6 and W-BGAC7 received ozone dosages of 0, 0.5, 1.5 and 2.5 g O$_3$ m^{-3}, respectively. In none of the filters, also not in filter W-GAC8, were bacterial growth prevention actions taken. Figure 1 and Table 1 provide an overview of the pilot plant and the water quality parameters of the filter influents. During operation all (B)GAC filters were backwashed with air and water every 4–20 days, depending on filter bed resistance. The variation in backwash intervals was due to seasonal algae blooms, especially diatom blooms. The filters were monitored on influent and effluent, once or twice per month. The measured parameters were DOC, UV-extinction at a wavelength of 254 nm, AOC, pH and temperature.

Tull en 't Waal pilot plant: riverbank filtrate

At Tull en 't Waal DWTP of Vitens (formerly Hydron MN), the largest drinking water company in the Netherlands, a pilot plant was operated for 516 days. In the pilot plant, riverbank filtrate from the River Rhine was pre-treated with aeration, rapid sand filtration, pellet softening and rapid sand filtration. This pre-treatment reduced the DOC concentration to 1.3–2.0 g C m^{-3}. The water temperature was constant at about 12 °C. Half of the pre-treated water was oxidized with peroxide and ozone. The set point for peroxide varied between 0 and 12 g H$_2$O$_2$ m^{-3}, see Table 2. Ozone was dosed at a fixed ozone/DOC ratio of 0.7 g O$_3$ g C^{-1}. A cocktail of seven pesticides and growth regulators was spiked to both oxidized and non-oxidized waters. The major selection criteria for the cocktail were frequency
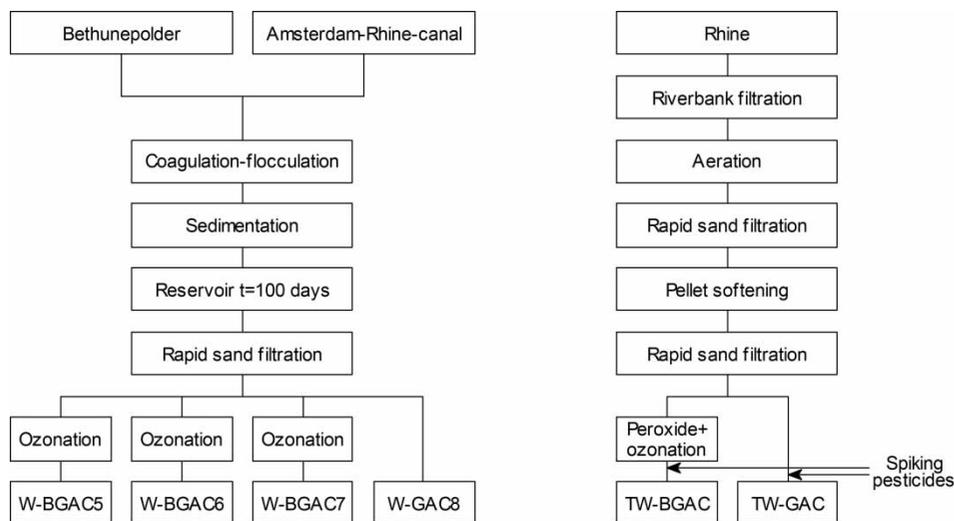

Figure 1 | Flow schemes at Weesperkarspel pilot plant (left) and Tull en 't Waal pilot plant (right).

Table 1 | Influent water qualities Weesperkarpsel pilot plant (Run 1)

Parameter	W-BGAC5	W-BGAC6	W-BGAC7	W-GAC8
Ozone dosage [g O$_3$ m^{-3}]	0.5	1.5	2.5	–
Temp [°C]	12.2 (3.6–20.6)	11.6 (3.8–20.6)	11.6 (3.8–20.6)	12.8 (3.0–20.6)
pH [–]	7.7 (7.3–7.8)	7.7 (7.1–7.8)	7.7 (7.6–7.8)	7.7 (7.3–7.9)
DOC [g C m^{-3}]	6.0 (5.2–7.6)	5.9 (4.9–7.5)	5.8 (4.9–6.7)	6.0 (5.0–6.9)
UV254 [m^{-1}]	13.5 (11.6–16.9)	10.8 (5.4–14.4)	8.5 (6.4–10.4)	14.4 (11.7–17.8)
AOC [10^{-3} g Acetate-C m^{-3}]	35.0 (16–99)	85.0 (40–199)	114 (42–265)	11.5 (5.7–32)

Notes about water quality parameters: Table values are average concentrations, values between parentheses are minimum and maximum concentrations.

Table 2 | Influent water qualities Tull en 't Waal pilot plant (Run 2)

Parameter	TW-GAC	TW-BGAC
Peroxide dosage day 0–236 [g H_2O_2 m^{-3}]	–	3.3 (1.4–4.6)
Peroxide dosage ay 237–257 [g H_2O_2 m^{-3}]	–	11.6 (7.7–16.9)
Peroxide dosage day 258–516 [g H_2O_2 m^{-3}]	–	–
Ozone dosage [g O_3 m^{-3}]	–	1.1 (0.1–1.3)
Atrazine dosage [10^{-3} g m^{-3}]	1.78 (1.34–2.28)	1.85 (0–2.30)
Metribuzin dosage [10^{-3} g m^{-3}]	1.92 (1.62–2.40)	1.97 (0–2.52)
Chloridazon dosage [10^{-3} g m^{-3}]	2.05 (1.69–2.69)	2.07 (0–2.49)
Bentazon dosage [10^{-3} g m^{-3}]	1.98 (0.98–3.00)	2.06 (0–3.20)
Metolachlor dosage [10^{-3} g m^{-3}]	1.93 (1.60–2.56)	1.96 (0–2.48)
Propoxur dosage [10^{-3} g m^{-3}]	0.22 (0–1.15)	0.23 (0–1.53)
Metalaxyl dosage [10^{-3} g m^{-3}]	1.82 (1.42–2.24)	1.86 (0–2.29)
Temp [°C]	12	12
pH [–]	8.4 (8.1–8.6)	8.4 (8.1–8.6)
DOC [g C m^{-3}]	1.6 (1.3–2.0)	1.6 (1.3–1.8)
UV254 [m^{-1}]	3.7 (2.7–4.0)	2.8 (2.4–3.5)
AOC [10^{-3} g Acetate–C m^{-3}]	13.4 (2.8–42)	53 (50–56)

Notes about water quality parameters: Table values are average concentrations, values between parentheses are minimum and maximum concentrations.

and concentration of occurrence of the compounds in the raw water and analytical possibilities. The cocktail included atrazine, bentazon, chloridazon, metalaxyl, metolachlor, metribuzin and propoxur. The pesticides were dosed after pre-oxidation. It was assumed that from the dosing point onwards the concentration of residual ozone would be negligible and that the pesticides would not oxidize. The average influent concentrations of atrazine, metribuzin, chloridazon, bentazon, metolachlor and metalaxyl were approximately equal to the target set point of 2×10^{-3} g m^{-3} (see Table 2). The influent concentration of propoxur varied greatly and the average concentration was only 12% of the other components. The non-oxidized water was led into TW-GAC and the pre-oxidized water was led into TW-BGAC. In none of the filters, also not in filter TW-GAC, were bacterial growth prevention actions taken. Both filters were pressurized (B)GAC filters operated in down flow mode. The cylindrical filters had diameters of 0.59 m and both were filled with Norit GAC 1020, a commercially available coal-based AC, to bed heights of 2.0 m. The flows were kept constant at 1.63 m^3 h^{-1}, resulting in surface loading rates of 6.0 m h^{-1} and EBCTs of 20 min. Figure 1 and Table 2 provide an overview of the pilot plant and the water quality parameters of the filter influents. At days 105, 244 and 340, both filters were backwashed with water. Both filters were monitored on influent, effluent and over the bed height, twice a month. Measured parameters were DOC, UV-extinction at a wavelength of 254 nm, pH, temperature and pesticides. AOC was measured incidentally.

Analytical methods

At both locations ozone was analyzed according to the DPD method (Gilbert 1981). AOC was measured in duplicate, applying the simultaneous incubation of strains P17 and NOX (van der Kooij *et al.* 1982), with a detection limit of 1×10^{-3} g acetate-C m^{-3}. Bentazon was analyzed by solid phase extraction using octadecyl modified silica C18. After elution with ethylacetate, the extract was methylized with diazomethane. The extract was concentrated, led through gas chromatography and mass spectometric detection (quadrupool). The detection limit was 10×10^{-6} g m^{-3}. Atrazine, chloridazon, metalaxyl, metolachlor, metribuzin and propoxur were analyzed by gas chromatography and phosphate and nitrogen sensitive thermo-ionic specific

detection. The detection limit for these compounds was 15×10^{-6} g m^{-3}. Other water quality parameters were determined according to standard procedures (Standard Methods 2005). The detection limit for DOC was 0.2 g C m^{-3}.

RESULTS AND DISCUSSION

Dissolved organic carbon removal

Figure 2(a) shows the DOC concentrations in the influents and effluents of the (B)GAC filters at Weesperkarspel pilot plant (Run 1). At the highest pre-ozonation dosage of 2.5 g O$_3$ m^{-3}, corresponding with an average ozone/DOC ratio of 0.43 g O$_3$ g C^{-1}, the average DOC removal during pre-ozonation was 0.17 g C m^{-3} (3%), as seen in Table 1. This corresponds with other reported NOM removal at similar ozone/DOC ratios (Sontheimer *et al.* 1988). In all four (B)GAC filters, initial DOC removal was 4.5–4.8 g C m^{-3} (92–96%); thus, 0.2–0.4 g C m^{-3} (4–8%) was not removed. Because it takes time to develop biodegradation in BGAC filters (Sontheimer *et al.* 1988; Servais *et al.* 1994; Velten 2008), it is assumed that no biomass was present at the

start of the filter runs. After 40 days of operation, the DOC concentration in the effluent of each filter increased rapidly according to a typical S-shaped adsorption breakthrough curve. Complete breakthrough was never reached. Instead, from day 200 onwards, the average DOC removals were 1.23 g C m^{-3} (20%) for W-GAC8 (no pre-ozonation), 1.27 g C m^{-3} (20%) for W-BGAC5 (pre-ozonation dosage 0.5 g O$_3$ m^{-3}), 1.52 g C m^{-3} (25%) for W-BGAC6 (pre-ozonation dosage 1.5 g O$_3$ m^{-3}) and 1.76 g C m^{-3} (30%) for W-BGAC7 (pre-ozonation dosage 2.5 g O$_3$ m^{-3}). Because the DOC removal continued until the end of the run, it is assumed that this part of the NOM was biodegraded as a result of biomass development in the filters (Sontheimer *et al.* 1988; Servais *et al.* 1994; Velten 2008). The biodegradation of NOM in BGAC filters from day 200 onwards, including the observed oxygen consumption and carbon dioxide production, was discussed elsewhere (van der Aa *et al.* 2011). During the entire run, DOC removal in the (B)GAC filters was more efficient with increasing pre-ozonation dosage.

Although not enforced by law, the utility's treatment objective is a DOC concentration less than 3 g C m^{-3}. In the full scale utility, the BGAC filters are followed by slow sand filters. These slow sand filters remove about 0.25 g C m^{-3} of DOC. Therefore, the self-set treatment objective after BGAC filtration is a DOC concentration less than 3.25 g C m^{-3}. The cumulative average DOC concentration as a function of throughput, represented as the number of bed volumes (BVs) that passed through the filter, was calculated as a measure for the mixed effluent water quality of a large number of filters. At a certain throughput, renewal or reactivation of the AC is necessary to fulfil the treatment objective. The throughput at the end of the filter run time is called the maximum throughput. It can be converted into the amount of AC to be used per m^3 of produced water. The maximum throughput was determined for all the (B)GAC filters at Weesperkarspel for different hypothetical treatment objectives (see Figure 3). It increased with increasing ozone dosages. For example, at the self-set treatment objective of a DOC concentration less than 3.25 g C m^{-3}, the maximum throughput varied between 9,448 BV for W-GAC8 (no pre-ozonation) and 15,691 BV for W-BGAC7 (pre-ozonation dosage 2.5 g O$_3$ m^{-3}). In other words, with increasing ozone dosages a lower AC renewal
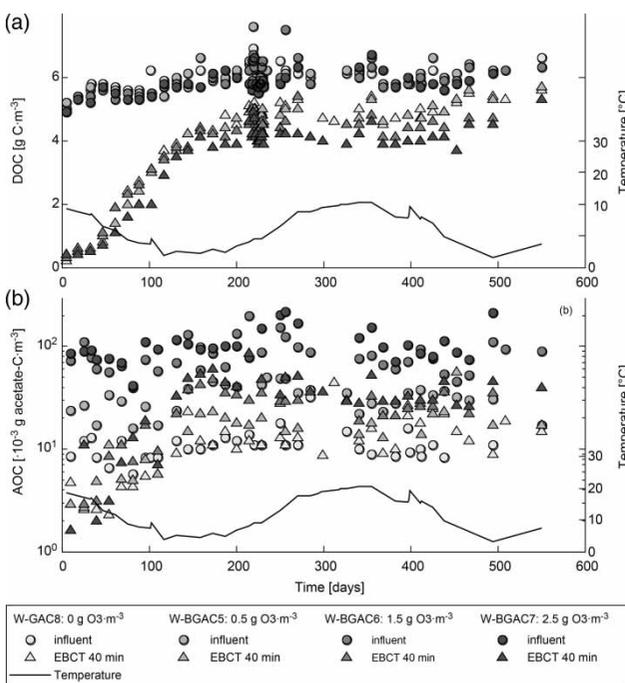

Figure 2 | DOC (a) and AOC (b) in Weesperkarspel pilot (B)GAC filters (Run 1).
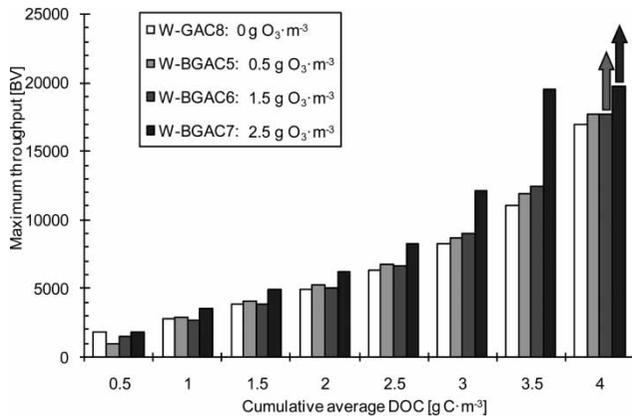
Figure 3 | Maximum throughput Weesperkarspel pilot (B)GAC filters calculated from DOC breakthrough curves (Run 1). Note: when the cumulative average DOC criterion was not reached during the filter run, the throughput at the end of the filter run is presented; the arrow indicates that the maximum throughput is larger than the presented throughput.

or reactivation frequency is needed to meet the treatment objective.

Figure 4(a) shows the DOC concentrations in the influents and effluents of the (B)GAC filters at Tull en 't Waal pilot plant (Run 2). Average DOC removal by pre-oxidation was limited to $0.02\,\mathrm{g\,C\,m^{-3}}$ (2%). Initial DOC removal was $1.2-1.3\,\mathrm{g\,C\,m^{-3}}$ (77–81%) for both (B)GAC filters; leaving

$0.3-0.4\,\mathrm{g\,C\,m^{-3}}$ (19–23%) that was not adsorbed at all. DOC removal in TW-BGAC was more efficient than in TW-GAC. The 'steady-state' DOC removals from day 200 onwards were on average $0.21\,\mathrm{g\,C\,m^{-3}}$ (13%) of the influent concentrations for TW-GAC and $0.38\,\mathrm{g\,C\,m^{-3}}$ (25%) of the influent concentrations for TW-BGAC. Again, biodegradation was assumed to have caused this removal.

As the DOC concentrations are already very low, there is no treatment objective for DOC at Tull en 't Waal. The maximum throughput for the (B)GAC filters at different, hypothetical, desired DOC concentrations in the mixed effluent was derived from the cumulative average DOC concentration curves, as shown in Figure 5. The maximum throughput for TW-BGAC was always larger than for TW-GAC. The maximum throughput increased as a function of EBCT for both filters. Two different mechanisms may be the reason for that. First, the adsorption capacity is used more effectively at long EBCTs because the mass transfer zone is relatively shorter than at short EBCTs (Sontheimer *et al.* 1988). Secondly, at longer EBCTs, more NOM can be biodegraded, resulting in lower effluent concentrations (Sontheimer *et al.* 1988; Uhl 2000; Velten 2008). Both mechanisms may occur simultaneously.

Regarding DOC, for both Weesperkarspel plant and Tull en 't Waal pilot plant, the ratio of BGAC and GAC maximum throughput varied from 1 to infinite. Other

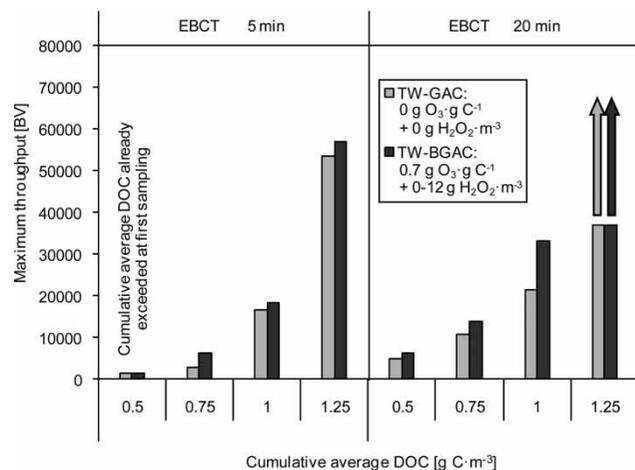**Figure 4** | DOC (a) and atrazine (b) in Tull en 't Waal pilot (B)GAC filters (Run 2).

Figure 5 | Maximum throughput Tull en 't Waal pilot (B)GAC filters calculated from DOC breakthrough curves (Run 2). Note: when the cumulative average DOC criterion was not reached during the filter run the throughput at the end of the filter run is presented; the arrow indicates that the maximum throughput is larger than the presented throughput.

researchers reported ratios between 3 and 10 (Jekel 1979; Sontheimer 1979; Schalekamp 1990; Graveland 1994). The ratio mainly depends on the concentration of non-biodegradable DOC and the desired mixed effluent DOC concentration.

Assimilable organic carbon formation and removal

Figure 2(b) shows the AOC concentrations in the influents and effluents of the (B)GAC filters at Weesperkarspel pilot plant (Run 1). Pre-ozonation resulted in the formation of AOC. The average AOC influent concentrations were: 12×10^{-3} g acetate-C m^{-3} in W-GAC8 (no pre-ozonation), 35×10^{-3} g acetate-C m^{-3} in W-BGAC5 (pre-ozonation dosage 0.5 g O$_3$ m^{-3}), 85×10^{-3} g acetate-C m^{-3} in W-BGAC6 (pre-ozonation dosage 1.5 g O$_3$ m^{-3}) and 114×10^{-3} g acetate-C m^{-3} in W-BGAC 7 (pre-ozonation dosage 2.5 g O$_3$ m^{-3}). At the start of the filter runs, all (B)GAC filters removed 90–100% of the AOC. However, at filter run times longer than 50–80 days, the AOC removal in the filters with pre-ozonation was not sufficient to remove the AOC produced during pre-ozonation. From 200 days onwards, the AOC removal reached a steady-state in all filters. In the (B)GAC filters, the AOC removal increased with increasing pre-ozonation dosage. During the steady-state, W-GAC8 on average removed no AOC. For the other filters, the average steady-state AOC removals were: 13×10^{-3} g acetate-C m^{-3} (36%) for W-BGAC5, 63×10^{-3} g acetate-C m^{-3} (69%) for W-BGAC6 and 96×10^{-3} g acetate-C m^{-3} (71%) for W-BGAC7. AOC production during pre-oxidation increased with increasing ozone dosages to a greater extent than AOC removal in the (B)GAC filters. Thus, the AOC concentrations in the (B)GAC effluents increased with increasing ozone dosages.

From the cumulative average AOC concentrations, the maximum throughput was determined for different desired AOC concentrations in the mixed effluent (see Figure 6). The maximum throughput decreased with increasing ozone dosages. The maximum throughputs for a desired mixed effluent AOC concentration of 11.53×10^{-3} g acetate-C m^{-3}, which is equal to the AOC concentration in the water before pre-oxidation, were 4,875 BV for W-BGAC7, 5,247 BV for W-BGAC6, 6,302 BV for W-BGAC5 and 13,833 BV for W-GAC8. When the throughput is less than
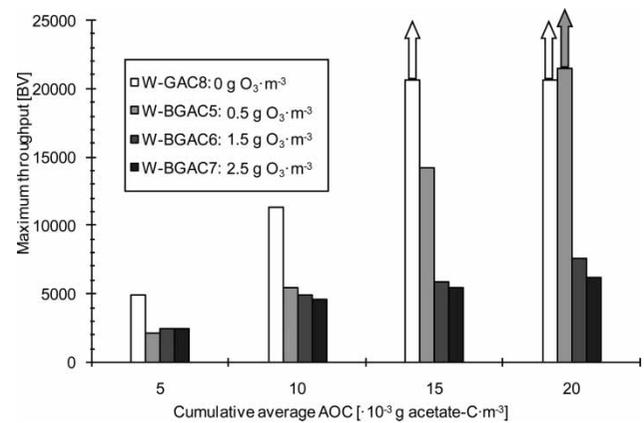

Figure 6 | Maximum throughput Weesperkarspel pilot (B)GAC filters calculated from AOC breakthrough curves (Run 1). Note: when the cumulative average AOC criterion was not reached during the filter run, the throughput at the end of the filter run is presented; the arrow indicates that the maximum throughput is larger than the presented throughput.

these maxima, pre-oxidation followed by BGAC filtration is expected to have a positive effect on biostability. Otherwise, when the throughput exceeds these maxima, pre-oxidation followed by BGAC filtration is expected to have a negative effect on biostability. Non-chlorinated water with an AOC concentration less than 10×10^{-3} g acetate-C m^{-3} is considered as biologically stable (van der Kooij 1992). In the Netherlands, there is no legislation for AOC concentrations in drinking water. In the full scale utility the BGAC filters are followed by slow sand filters. These slow sand filters remove about 5×10^{-3} g acetate-C m^{-3} of AOC. Therefore, the self-set treatment objective after BGAC filtration would be AOC concentration less than 15×10^{-3} g acetate-C m^{-3}. The corresponding maximum throughputs vary from 5,411 BV for W-BGAC7 to infinite for W-GAC8.

At Tull en 't Waal pilot plant, AOC concentrations were only incidentally measured. The influent of TW-GAC, which is equal to the influent of the pre-oxidation, contained an AOC concentration of 4×10^{-3} g acetate-C m^{-3} (one outlier excluded), on average. In TW-GAC, the AOC concentration remained constant. On average, the pre-oxidation increased the AOC concentration to 53×10^{-3} g acetate-C m^{-3}. TW-BAC typically removed the formed AOC to 14×10^{-3} g acetate-C m^{-3} (data not shown). This average removal of 74% corresponds to the observations at Weesperkarspel pilot plant.

Pesticide removal

Figure 4(b) shows the breakthrough curves of atrazine for both (B)GAC filters at EBCTs of 5, 10 and 20 min at Tull en 't Waal pilot plant (Run 2). At all EBCTs, TW-BGAC removed atrazine more effectively than TW-GAC. In both filters breakthrough was not complete at the end of the experiment, not even at an EBCT of 5 min. From the break-through curves of DOC (Figure 4(a)), it can be concluded that after 100 days of operation the AC was (almost) satu-rated with NOM at an EBCT of 5 min. At this EBCT even after 500 days of operation, both the GAC and the BGAC filter still adsorbed atrazine. Similar observations were reported by other researchers (Knappe et al. 1997; van der Hoek et al. 1999; Cromphout & Rogge 2002). Either the atra-zine adsorbed on sites within the AC which were not suitable for the NOM molecules, or the atrazine replaced adsorbed NOM.

All dosed pesticides showed the start of breakthrough at EBCTs of 5 and 10 min. However, not all pesticides showed breakthrough at an EBCT of 20 min. Cumulative average concentrations at the end of the filter run for influ-ents and at different EBCTs are presented in Figure 7 for all dosed pesticides. For each pesticide, the maximum throughput was calculated from the breakthrough curves at EBCTs of 5 and 10 s, for a cumulative average concen-tration for individual pesticides of 0.1×10^{-3} g m^{-3}, which

is the current Dutch drinking water standard (see Table 3). The ranking of the pesticides, from small to large maximum throughput, is bentazon, metalaxyl, meto-lachlor, atrazine, metribuzin, chloridazon. Propoxur was excluded from this ranking because of the failed dosing. The ranking is the same for TW-GAC and TW-BGAC, both at EBCTs of 5 and 10 min.

Except for one observation (metribuzin at EBCT 5 min: 99%), the maximum throughput was always larger for TW-BGAC than for the TW-GAC (155–316%). Other research-ers reported ratios between 3 and 10 (Sontheimer et al. 1988; Schalekamp 1990; Graveland 1994). The pesticides were dosed after pre-oxidation. It was assumed that from the dosing point onwards the concentration of residual ozone was negligible and that the pesticides were not oxi-dized. At high concentrations, biodegradation of organic micro-pollutants is possible. For example, atrazine can be biodegraded to 20×10^{-3} g m^{-3} (Huang & Banks 1996). It was assumed that at a concentration of 2×10^{-3} g m^{-3}, pes-ticides were not biodegraded. The authors suggest that pre-oxidation reduced NOM adsorption by biodegradation and/or by an increase in polarity of NOM molecules, which decreases adsorption affinity (Sontheimer et al. 1988; de Laat et al. 1991; Lambert & Graham 1995). Because of the reduced NOM adsorption, more adsorption sites remained available for pesticides and pore blocking and pre-loading diminished, resulting in an improved pesticide
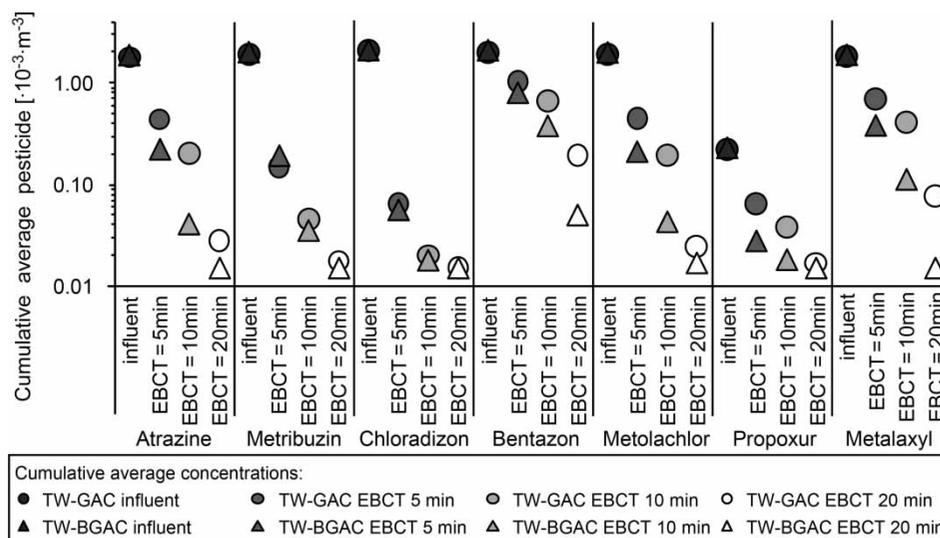

Figure 7 | Cumulative average pesticide concentrations Tull en 't Waal pilot (B)GAC filters (Run 2) at day 516.

Table 3 | Maximum throughputs TW-GAC and TW-BGAC calculated from pesticide breakthrough curves (Run 2) plus comparisons between maximum throughputs of different filters and at different EBCTs

	TW-GAC EBCT 5 min MaxTP (BV)	TW-GAC EBCT 10 min MaxTP (BV)	TW-BGAC EBCT 5 min MaxTP (BV)	TW-BGAC EBCT 10 min MaxTP (BV)	MaxTP EBCT 10 min MaxTP EBCT 5 min (%) TW-GAC	TW-BGAC	MaxTP TW-BGAC MaxTP TW-GAC (%) EBCT 5 min	EBCT 10 min
Atrazine	57,825	56,033	89,603	>73,717	97	>82	155	>132
Metribuzin	93,597	>74,035	92,572	>73,717	>79	>80	99	n.d.
Chloradizon	>148,070	>74,035	>147,434	>73,717	n.d.	n.d.	n.d.	n.d.
Bentazon	13,095	10,178	22,318	32,206	78	144	170	316
Metolachlor	28,700	54,843	82,212	>73,717	191	>90	286	>134
Propoxur	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Metalaxyl	23,842	34,477	57,865	70,391	145	122	243	>204

Notes: n.d. = not determined; propoxur n.d. because of failed dosing; MaxTP = maximum throughput.

adsorption (Huang & Banks 1996) and a larger maximum throughput.

Not all breakthrough curves reached cumulative average concentrations of 0.1×10^{-3} g m^{-3} at EBCTs of 10 min. Therefore, the comparison between maximum throughputs at EBCTs of 5 and 10 min only gave relevant results for six data-pairs (see Table 3). In two cases the maximum throughput at an EBCT of 10 min was smaller than at an EBCT of 5 min (TW-GAC atrazine and bentazon). This may be caused by preloading of the AC with NOM at larger EBCTs. In four cases the maximum throughput at an EBCT of 10 min was larger than at an EBCT of 5 min (TW-GAC metolachlor and metalaxyl, TW-BGAC bentazon and metalaxyl). This may be caused by reduced pre-loading of the AC with NOM at larger EBCTs, due to increased NOM biodegradation. No general conclusion about the influence of EBCT on the maximum throughput could be made.

CONCLUSIONS

In this study, the influence of pre-oxidation on the removal of DOC, AOC and pesticides during (B)GAC filtration was assessed in pilot plant installations at two different DWTPs.

It was concluded that, at both Weesperkarspel and Tull en 't Waal BGAC filtration removed DOC more effectively than GAC filtration did. The maximum throughput increased with increasing pre-oxidation dosage. In all filters, after approximately 200 days, DOC removal more or less reached a steady-state situation, which is typical for biodegradation. During this steady-state situation, the GAC filters on average removed 13–20% and the BGAC filters typically removed 25–30% of the DOC. Both in TW-GAC and in TW-BGAC, DOC removal was more efficient with increasing EBCTs.

Pre-oxidation resulted in an increase in AOC concentrations at both Weesperkarspel and Tull en 't Waal. The BGAC filters following the pre-oxidation removed up to 70% of the produced AOC. However, in none of the BGAC filters were AOC concentrations reduced to the concentrations before pre-oxidation. Therefore, pre-oxidation followed by BGAC filtration is expected to have a negative effect on biostability.

At Tull en 't Waal, BGAC filtration removed bentazon, metalaxyl, metolachlor, atrazine, metribuzin, chloridazon and propoxur more effectively than GAC filtration. At a desired mixed effluent water quality of 0.1×10^{-3} g m^{-3} for each (individual) pesticide, which is the Dutch drinking water standard, the maximum throughput of the BGAC filter was 1.5–3.2 times larger than the maximum throughput of the GAC filter. The ranking of the pesticides, from small to large maximum throughput, is bentazon, metalaxyl, metolachlor, atrazine, metribuzin, chloridazon. The maximum throughput of propoxur could not be compared to the maximum throughput of the other pesticides because of

dosing problems. A comparison between the maximum throughputs at EBCTs of 5 and 10 min showed mixed results. No optimal EBCT could be determined.

To determine the optimal operational conditions for (B)GAC filters, it is necessary to: (1) consider the different water quality parameters in an integrated way, for example pesticides, NOM and biostability, and (2) predict the future performance of the (B)GAC filters, depending on the actual status of the filters and future influent water quality.

ACKNOWLEDGEMENTS

REFERENCES

van der Aa, L. T. J., Rietveld, L. C. & van Dijk, J. C. 2011 Effects of ozonation and temperature on the biodegradation of natural organic matter in biological granular activated carbon filters. Drink. Water Eng. Sci. 4 (1), 25–35.

Bosklopper, T. G. J., Rietveld, L. C., Babuska, R., Smaal, B. & Timmer, J. 2004 Integrated operation of drinking water treatment plant at Amsterdam water supply. Water Sci. Technol. Water Supply 4 (5–6), 263–270.

Carter, M. C., Weber Jr., W. J. & Olmstead, K. P. 1992 Effects of background dissolved organic matter on TCE adsorption by GAC. J. Am. Water Works Assoc. 84 (8), 81–91.

Cromphout, J. & Rogge, W. 2002 Cost-effective water treatment of polluted surface water by using direct filtration and granular activated carbon filtration. Water Sci. Technol. Water Supply 2, 233–240.

Escobar, I. C., Randall, A. A. & Taylor, J. S. 2001 Bacterial growth in distribution systems: effect of assimilable organic carbon and biodegradable dissolved organic carbon. Environ. Sci. Technol. 35 (17), 3442–3447.

Gilbert, E. 1981 Photometrische Bestimmung niedriger Ozonkonzentrationen in Wasser mit Hilfe von Diaëthyl-p-phenylendiamin (DPD) (Photometric determination of low ozone concentrations in water using Diethyl-p-phenylenediamine (DPD)). GWF Wasser Abwasser 122 (9), 410–416.

Graveland, A. 1994 Application of biological activated carbon filtration at Amsterdam water supply. Water Supply 14, 233–241.

Hammes, F., Salhi, E., Köster, O., Kaiser, H.-P., Egli, T. & von Gunten, U. 2006 Mechanistic and kinetic evaluation of organic disinfection by-product and assimilable organic carbon (AOC) formation during the ozonation of drinking water. Water Res. 40 (12), 2275–2286.

van der Helm, A. W. C. 2007 Integrated Modeling of Ozonation for Optimization of Drinking Water Treatment. Ph.D. Thesis, Water Management Academic Press, Delft, The Netherlands.

van der Helm, A. W. C., Rietveld, L. C., Bosklopper, T. G. J., Kappelhof, J. W. N. M. & van Dijk, J. C. 2008 Objectives for optimization and consequences for operation, design and concept of drinking water treatment plants. Water Sci. Technol. Water Supply 8 (3), 297–304.

van der Hoek, J. P., Hofman, J. A. M. H. & Graveland, A. 1999 The use of biological activated carbon filtration for the removal of natural organic matter and organic micropollutants from water. Water Sci. Technol. 40 (9), 257–264.

Huang, C. M. & Banks, M. K. 1996 Effect of ozonation on the biodegradability of atrazine in GAC columns. J. Environ. Sci. Heal. B 31 (6), 1253–1266.

Jekel, M. 1979 Experience with biological activated carbon filters. In: Oxidation Techniques in Drinking Water (W. Kuhn & H. Sontheimer, eds). U.S. Environmental Protection Agency EPA-570/9-79-020, pp. 715–726.

Knappe, D. R. U., Snoeyink, V. L., Roche, P., Prados, M. J. & Bourbigot, M.-M. 1997 The effect of preloading on rapid small-scale column test predictions of atrazine removal by GAC adsorbers. Water Res. 31 (11), 2899–2909.

van der Kooiji, D. 1992 Assimilable organica carbon as indicator of bacterial regrowth. J. Am. Water Works Assoc. 84 (2), 57–65.

van der Kooiji, D., Visser, A. & Hijnen, W. A. M. 1982 Determining the concentration of easily assimilable organic carbon in drinking water. J. Am. Water Works Assoc. 74 (10), 540–545.

van der Kooiji, D., Hijnen, W. A. M. & Kruithof, J. C. 1989 The effects of ozonation, biological filtration and distribution on the concentration of easily assimilable organic carbon (AOC) in drinking water. Ozone Sci. Eng. 11, 297–311.

Kruithof, J. C. & Maschelein, W. J. 1999 State-of-the-art of the application of ozonation in Benelux drinking water treatment. Ozone Sci. Eng. 21, 139–152.

de Laat, J., Dore, M. & Mallevialle, J. 1991 Effects of preozonation on the adsorbability and the biodegradability of aquatic humic substances and on the performance of granular activated carbon filters. Water Res. 25 (2), 151–164.

Lambert, S. D. & Graham, N. J. D. 1995 Removal of non-specific dissolved organic matter from upland potable water supplies – II. Ozonation and adsorption. Water Res. 29 (10), 2427–2433.

Orlandini, E. 1999 Pesticide Removal By Combined Ozonation and Granular Activated Carbon Filtration. Ph.D. thesis, Wageningen University and International Institute for Infrastructure, Hydraulic and Environmental Engineering, Delft, The Netherlands.

Schalekamp, M. 1990 Development of ozone in Zurich, Switzerland. *Water Supply* **8** (3–4), 377–386.

Schwarzenbach, R. P., Escher, B. I., Fenner, K., Hofstetter, T. B., Johnson, C. A., von Gunten, U. & Wehrli, B. 2006 The challenge of micropollutants in aquatic systems. *Science* **313** (5790), 1072–1077.

Servais, P., Billen, G. & Bouillot, P. 1994 Biological colonization of granular activated carbon filters in drinking-water treatment. *J. Environ. Eng.* **120** (4), 888–899.

Servais, P., Anzil, A., Gatel, D. & Cavard, J. 2004 Biofilm in the Parisian suburbs drinking water system. *J. Water Supply Res. Technol. AQUA* **53** (5), 313–323.

Siddiqui, M. S., Amy, G. L. & Murphy, B. D. 1997 Ozone enhanced removal of natural organic matter from drinking water sources. *Water Res.* **31** (12), 3098–3106.

Sontheimer, H. 1979 Process engineering aspects in the combination of chemical and biological oxidation. In: *Oxidation Techniques in Drinking Water* (W. Kuhn & H. Sontheimer, eds). U.S. Environmental Protection Agency EPA-570/9-79-020, pp. 702–714.

Sontheimer, H., Crittenden, J. C. & Summers, R. S. 1988 *Activated Carbon for Water Treatment*, 2nd edition. AWWA – DVGW Forschungssstelle Engler Bunte Institut, Karlsruhe, Germany.

Standard Methods 2005 *Standard Methods for the Examination of Water & Wastewater 2005*, 21st edition. American Public Health Association/American Water Works Association/Water Environment Federation, Baltimore, USA.

Summers, R. S., Haist, B., Koehler, J., Ritz, J., Zimmer, G. & Sontheimer, H. 1989 The influence of background organic matter on GAC adsorption. *J. Am. Water Works Assoc.* **81** (5), 66–74.

Uhl, W. 2000 *Einfluss von Schüttungsmaterial und Prozessparmetern auf die Leistung von Bioreaktoren bei der Trinkwasseraufbereitung (Influence of filter material and process parameters on the performance of bioreactors in the drinking water treatment)*. Ph.D. Thesis, IWW Rheinisch-Westfällisches Institut für Wasserforschung gemeinnützige GmbH, Institut an der Gerhard-Mercator-Universität Duisburg, Mülheim an der Ruhr, Germany.

Van der Helm, A. W. C., Grefte, A., Baars, E. T., Rietveld, L. C., Van Dijk, J. C. & Amy, G. L. 2009 Effects of natural organic matter (NOM) character and removal on ozonation for maximizing disinfection with minimum bromate and AOC formation. *J. Water Supply Res. Technol. AQUA* **58** (6), 373–385.

Velten, S. 2008 *Adsorption Capacity and Biological Activity of Biological Activated Carbon Filters in Drinking Water Treatment*. Ph.D. Thesis, Swiss Federal Institute of Technology Zurich, Zurich, Switzerland.

Von Gunten, U. & Hoigne, J. 1994 Bromate formation during ozonation of bromide-containing waters: interaction of ozone and hydroxyl radical reactions. *Environ. Sci. Technol.* **28** (7), 1234–1242.

Wang, H., Ho, L., Lewis, D. M., Brookes, J. D. & Newcombe, G. 2007 Discriminating and assessing adsorption and biodegradation removal mechanisms during granular activated carbon filtration of microcystin toxins. *Water Res.* **41** (18), 4262–4270.

Yavich, A. A., Lee, K.-H., Chen, K.-C., Pape, L. & Masten, S. J. 2004 Evaluation of biodegradability of NOM after ozonation. *Water Res.* **38** (12), 2839–2846.