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# Microbial pesticide removal in rapid sand filters for drinking water treatment – potential and kinetics

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## Abstract

Filter sand samples, taken from aerobic rapid sand filters used for treating groundwater at three Danish waterworks, were investigated for their pesticide removal potential and to assess the kinetics of the removal process. Microcosms were set up with filter sand, treated water, and the pesticides or metabolites mecoprop (MCP), bentazone, glyphosate and *p*-nitrophenol were applied in initial concentrations of 0.03-2.4 µg/L. In all the investigated waterworks the concentration of pesticides in the water decreased – MCP decreased to 42-85%, bentazone to 15-35%, glyphosate to 7-14% and *p*-nitrophenol 1-3% – from the initial concentration over a period of 6-13 days. Mineralisation of three out of four investigated pesticides was observed at Sjælsø waterworks Plant II – up to 43% of the initial glyphosate was mineralised within six days. At Sjælsø waterworks Plant II the removal kinetics of bentazone revealed that less than 30 minutes was needed to remove 50% of the bentazone at all the tested initial concentrations (0.1-2.4 µg/L). Increased oxygen availability led to greater and faster removal of bentazone in the microcosms. After one hour, bentazone removal (an initial bentazone concentration of 0.1 µg/L) increased from 0.21%/g filter sand to 0.75%/g filter sand, when oxygen availability was increased from 0.28 mg O<sub>2</sub>/g filter sand to 1.09 mg O<sub>2</sub>/g filter sand. Bentazone was initially cleaved in the removal process. A metabolite, which contained the carbonyl group, was removed rapidly from the water phase and slowly mineralised after 24 hours, while a metabolite which contained the benzene-ring was still present in the water phase. However, the microbial removal of this metabolite was initiated over seven days.

**Keywords:** pesticides; bentazone; removal; kinetics; rapid sand filter; drinking water; ground water

## 1. Introduction

In Europe, 70% of the drinking water supply is based on groundwater (Navarrete et al., 2008). Unfortunately much of the groundwater is affected by pesticides; for example, in 2010, pesticides and metabolites were detected in 25% of active waterworks wells and 44% of all monitoring wells in Denmark (GEUS, 2011). According to the European Union (EU) Water Framework Directive and Groundwater Directive, the concentration of pesticides in drinking water and groundwater should not exceed 0.1 µg/L for a single compound, or 0.5 µg/L for the sum of all pesticides (European Parliament and Council, 2000; European Parliament and Council, 2006). In 2010, these guideline values was exceeded in 4.5% of the active waterworks wells in Denmark, and during 1992–2010 the pesticides mecoprop (MCP), bentazone, glyphosate, and the degradation product *p*-nitrophenol were among the 10 most frequently detected pesticides (GEUS, 2011).

The herbicide bentazone is used legally in the EU, and as such it is still a potential polluter of groundwater resources (Boivin et al., 2004). In Denmark, bentazone is used extensively, evidence for which can be found in the fact that 39 tonnes of the substance were sold in 2010 (The Danish Ministry of the Environment, 2010). In aquifer materials bentazone has low adsorption distribution coefficients,  $K_d$  values (Clausen et al., 2001) and it is difficult to degrade (Albrechtsen et al., 2001; Broholm et al., 2001). Therefore, it can easily be transported in aquifers (Boivin et al., 2004) and into groundwater extraction wells. Moreover, bentazone was detected in 2.7% of active Danish drinking water abstraction wells from 1992-2010 and exceeded the guideline value of 0.1  $\mu\text{g/L}$  in 0.4% of the sampled wells (GEUS, 2011).

Accordingly, bentazone and other pesticides are prone to enter groundwater-based waterworks. Pesticides can be removed from groundwater through the drinking water treatment process, e.g. via granular activated carbon (GAC) (Heijman et al., 2002), advanced oxidation (Suty et al., 2004) and to some extent membrane biofilm reactors (Modin et al., 2008). In Denmark, drinking water supply is based primarily on the treatment of groundwater, which involves aeration followed by rapid sand filtration (Winter et al., 2003), and the policy is that water utilities close pesticide-contaminated extraction wells (GEUS, 2011). As a result, pesticide concentrations in the inlet water to waterworks do not exceed guideline values.

The use of biological rapid sand filtration is widespread in Europe (Zearley and Summers, 2012). Commonly, drinking water has a residence time in rapid sand filters of 7.5 to 12 minutes (Winter et al., 2003); however, this can vary according to the load of the filters. A few recent investigations have shown potential for the degradation of some pesticides in rapid sand filters utilised in groundwater-based waterworks (Corfitzen et al., 2009) and that biological filters used to treat surface water are able to remove pesticides after a six-month adaption period (Zearley and Summers, 2012). Other studies have shown that pesticide degradation is possible in biologically active treatment systems (De Wilde et al., 2008; Turner et al., 2010; Baghapour et al., 2013). However, in these systems differ from rapid sand filters in the larger amount of present organic matter and in most systems degradation dependent on long adaption periods (Baghapour et al. 2013). If pesticides could be removed from drinking water by optimising the microbial processes which take place in rapid sand filters, this innovation could generate substantial commercial interest because of the environmental sustainability and low costs of this treatment (Corfitzen et al., 2009).

Nevertheless, investigations into the potential and kinetics of microbial degradation and mineralisation of the compounds mecoprop (MCPP), bentazone, glyphosate and *p*-nitrophenol in different rapid sand filters for the treatment of groundwater are not available.

The overall aim of this study is to investigate whether substantial pesticide removal, with a special focus on the herbicide bentazone, is possible during the time

it takes water to pass through a rapid sand filter. In order to achieve this aim, the following issues were investigated:

- The general removal potential of the pesticides and metabolites MCP, bentazone, glyphosate and *p*-nitrophenol in different rapid sand filters
- The removal kinetics of pesticides during contact time with rapid sand filters
- Whether the removal of pesticides in rapid sand filters leads to complete mineralisation

## 2. Materials and methods

Three different experimental laboratory set-ups were used:

**Degradation potential of filter sand:** Filter sand from three Danish waterworks – Islevbro, Sjælsø Plant I and Sjælsø Plant II – was investigated for the removal potential of the pesticides mecoprop (MCP), bentazone, glyphosate, and the degradation product *p*-nitrophenol.

**Removal kinetics:** Bentazone removal at different initial concentrations was investigated with filter sand from Sjælsø waterworks Plant II. The removal was investigated intensively over one hour, which is the residence time of the water in the rapid sand filter, and the experiment lasted for seven days to investigate for mineralisation.

**Effect of oxygen:** Bentazone removal in the filter sand from Sjælsø waterworks Plant II was investigated under enhanced oxygen concentrations. The removal was investigated intensively in the initial phase of the experiment (the first few hours), and the experiment lasted for two days.

### 2.1 Waterworks

The investigations included filter sand from three different groundwater-based waterworks with the water treatment process consisting of the aeration of anaerobic groundwater followed by filtration in primary and then secondary rapid sand filters. After filtration the treated water is channelled to clean water tanks and subsequently distributed. Disinfection is not included in the treatment process. The water quality of the treated water complied fully with the (EU) drinking water guideline. Selected parameters for water quality can be seen in Table 1.

Islevbro waterworks, HOFOR, Rødovre, Denmark, has 163 wells and a technical production capacity of 1042 m<sup>3</sup>/h. The water quality of the groundwater is characterised by reduced conditions in the aquifer, expressed by low nitrate concentrations, for instance. Different pesticides, e.g. MCP and glyphosate, have been detected in the extraction wells (Table 1). Groundwater is aerated with

**Table 1. Water quality data based on information from the waterworks. The range is given for each parameters for the given time period for wells and the effluent water from the filters. The waterworks monitors for more than 20 pesticides and degradation compounds, but this table only includes detected pesticides.**

|                        |       | Islevbro         |                  | Sjælsø Plant I   |                | Sjælsø Plant II  |                |
|------------------------|-------|------------------|------------------|------------------|----------------|------------------|----------------|
|                        |       | Wells            | Effluent water   | Wells            | Effluent water | Wells            | Effluent water |
| <b>Dry filter sand</b> |       |                  |                  |                  |                |                  |                |
| TOC*                   | mg/g  | 2.71             |                  | 78.8             |                | 0.517            |                |
| <b>Water</b>           |       | <b>2010-2011</b> | <b>2011-2012</b> | <b>2011-2012</b> | <b>2012</b>    | <b>2011-2012</b> | <b>2012</b>    |
| Oxygen                 | mg/L  | 0.23-2.2         | 7.3              | 0.31-0.62        | -              | 0.25-0.44        | -              |
| Nitrate                | mg/L  | 0.018-3.7        | 2.57             | 0.043-0.378      | -              | <0.03-0.061      | -              |
| Nitrite                | mg/L  | 0.005-0.017      | 0.06             | <0.0016-0.012    | <0.0016-0.0079 | <0.0016          | <0.0016-0.0077 |
| Ammonium               | mg/L  | 0.251-0.97       | 0.10             | 0.38-0.77        | <0.004-0.01    | 0.92-1.26        | <0.004-0.016   |
| Manganese              | mg/L  | 0.028-0.1        | -                | 0.005-0.22       | <0.001-0.003   | 0.012-0.054      | <0.001         |
| Iron                   | mg/L  | 0.01-3.6         | 0.3              | 0.2-4.3          | <0.01-0.02     | 0.38-2.6         | <0.01-0.05     |
| Sulphate               | mg/L  | 67-160           | 33.1             | 9-58             | -              | <0.5-14          | -              |
| Hydrogen sulphide      | mg/L  | 0.012-0.02       | -                | 0.01-0.04        | -              | 0.03-1.19        | -              |
| Methane                | mg/L  | 0.01-0.13        | -                | 0.06-0.5         | -              | 1.13-9.2         | -              |
| BAM*                   | µg/L  | 0.014-0.076      | -                | <0.01-0.018      | -              | < 0.01           | -              |
| 4-CPP*                 | µg/L  | 0.016            | -                | <0.01-0.11       | -              | < 0.01           | -              |
| DCPP*                  | µg/L  | 0.02-0.20        | -                | <0.01-0.014      | -              | < 0.01           | -              |
| 2,6-DCPP*              | µg/L  | -                | -                | <0.01-0.025      | -              | <0.01            | -              |
| MCPP*                  | µg/L  | 0.04-0.13        | -                | -                | -              | -                | -              |
| Glyphosate             | µg/L  | 0.022            | -                | -                | -              | -                | -              |
| Phenol                 | mg/L  | -                | -                | -                | -              | < 0.05           | -              |
| NVOC*                  | mg/L  | 2.33             | 2.41             | 2.2-3.5          | 1.7-3.9        | 2.1-3.9          | 2.7-4.5        |
| Conductivity at 12°C   | mS/m  | -                | -                | 65-108           | -              | 66-82            | -              |
| Alkalinity             | meq/L | 5.12-7.18        | 5.4              | -                | -              | -                | -              |
| pH                     |       | 7-7.9            | -                | -                | -              | -                | -              |

- no data available

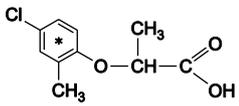
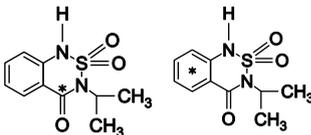
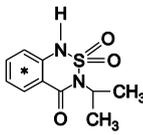
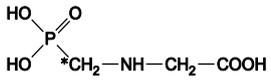
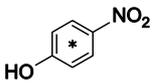
\* TOC = Total organic carbon; BAM = 2,6-Dichlorobenzamide; 4-CPP = (RS)-2-(4-chlorophenoxy)propionic acid; DCPP = (R)-2-(2,4-dichlorophenoxy)propionic acid; 2,6-DCPP = 2-(2,6-dichlorophenoxy)propionic acid; MCPP = (RS)-2-(4-Chloro-2-methylphenoxy)propanoic acid; NVOC = Non-volatile organic carbon

corrugated plate aerators, while the average residence time in the sand filter is 10.5 min. In these investigations 0.8–1.2 mm quartz sand from the afterfilter's top layer was used.

Sjælsø waterworks, Nordvand A/S, Hørsholm, Denmark, consists of two separate plants, each with a capacity of 400–1000 m<sup>3</sup>/h treating two different water sources. Anaerobic groundwater is extracted from 49 wells. Groundwater which is treated at Plant I has low concentrations of nitrate and high sulphate concentrations. In all, 2,6-Dichlorobenzamide (BAM) and three phenoxy acids have been detected at the extraction wells (Table 1). Groundwater is aerated with cascade aerators, and in our investigations 3.0–5.0 mm filter sand with anthracite coal from the prefilter's top layer was used. The inlet concentrations of methane and hydrogen sulphide in Plant II were high (Table 1), which indicates strongly reduced conditions in the aquifer. Therefore, the water was treated in an intensive tray aerator (INKA chamber). No pesticides were detected in the extraction wells. In the experiments 3.0–5.0 mm filter sand from the prefilter's top layer was used. Normal residence time in Plant I's prefilter is 89 min, while it is 56 min in Plant II.

## 2.2 Chemicals

In order to investigate the potential of filter sand to degrade pesticides, four <sup>14</sup>C-labelled pesticides (mecoprop, bentazone, glyphosate and *p*-nitrophenol), each of which was among the 10 most frequently detected pesticides during 1992-2010 (GEUS, 2011), were selected due to their properties (Table 2). [Carbonyl-<sup>14</sup>C-]bentazone was used in the experiments, and unless otherwise noted it is referred to as ‘bentazone’ throughout this research. In cases where stock solutions of the

| Table 2. Information on investigated pesticides and metabolites               |   |   |   |   |   |
|---|---|---|---|---|---|
|   | Mecoprop  | Bentazone   |   | Glyphosate  | <i>p</i> -Nitrophenol   |
| <b>Type and use of pesticide</b>  | The phenoxy acid is a herbicide used in agriculture, horticulture and for domestic purposes. Partially banned in Denmark in 1997. (The Danish Ministry of the Environment, 2011; Buss et al., 2006) | Herbicide used in cultivated areas, which is legally used in the European-Union. (EU pesticide database, 2013; Boivin et al., 2004) |   | The trade name is Roundup and it is the most sold herbicide for weed control in agriculture, silviculture, urban areas worldwide. (Woodburn, 2000; Borggaard and Gimsing, 2008) | Metabolite of the insecticide parathion, which is banned in the Europe Union (GEUS, 2011; Schilman et al., 2009; The Council of the European Communities, 1991; The Commission of the European Communities, 2001) |
| <b>Detection in active Danish drinking water wells 1992-2010 (GEUS, 2011)</b> | 2.5%  | 2.7%  |   | 1.7%  | 3.2%  |
| <b>≥0.1µg/L (GEUS, 2011)</b>  | 0.1%  | 0.4%  |   | 0.0%  | 0.0%  |
| <b>Sorption in aquifer sediment</b>   | Mobile (Agertved et al., 1992; Tuxen et al. 2000)   | Mobile (Clausen et al., 2001; Boivin et al., 2004)  |   | Low mobility (Vereecken, 2005)  | Mobile (Nielsen et al., 1996)   |
| <b>Volatility, K<sub>H</sub> (M/atm)</b>                                      | Non-volatile<br>4.65E+05<br>(EU Pesticide Database, 2013)   | Non-volatile<br>1.41E+06<br>(EU Pesticide Database, 2013)   |   | Non-volatile<br>4.83E+08<br>(EU Pesticide Database, 2013)   | Non-volatile<br>7.79E+04<br>(Trempe et al., 1993)   |
| <b>Degradability</b>  | Degraded weakly under anaerobic conditions (Janniche, 2010)   | Difficult to degrade in aquifers (Albrechtsen et al., 2001; Broholm et al., 2001)   |   | Degradable under aerobic and anaerobic conditions (Borggaard and Gimsing, 2008; Rueppel et al., 1977)   | Degraded in aerobic aquifers (Nielsen et al., 1996)   |
| <b>Radiochemicals</b>   |   |   |   |   |   |
| <b>Position of <sup>14</sup>C-label</b>                                       | Ring- <sup>14</sup> C   | Carbonyl- <sup>14</sup> C   | Benzene-ring-U- <sup>14</sup> C   | Phosphonomethyl- <sup>14</sup> C  | <sup>14</sup> C(U)  |
|   |    |    |  |   |    |
| <b>Radio-chemical purity (%)</b>  | > 95  | 97.96   | 99  | 99  | > 99  |
| <b>Specific activity (mCi/mM)</b>   | 23  | 44  | 20  | 50  | 77  |
| <b>Solvent of stock solution</b>  | Acetonitrile  | Methanol  | Methanol  | Sterile water   | Ethanol   |
| <b>Producer</b>   | Izotop, Institute of Isotopes Co., Ltd., Hungary  | Izotop, Institute of Isotopes Co., Ltd., Hungary  |   | ARC American Radiolabeled Chemicals, Inc., USA  | ARC American Radiolabeled Chemicals, Inc., USA  |

pesticides were prepared in an organic solvent, this was stripped off before application and the pesticides were dissolved in sterile MilliQ water. To investigate pesticide removal at concentrations close to water quality guidelines, pesticides were in general added to an initial concentration of 0.1 µg/L (Table 3).

**Table 3. Initial conditions in the microcosms in the different experiments. Added amount of filter sand and water appear as well as the initial concentration of the added pesticides.**

| Waterworks                                  |        | Potential of filter sand |                |                 | Removal kinetics | Effect of oxygen |
|---|--------|--------------------------|----------------|-----------------|------------------|------------------|
|   |        | Islevbro                 | Sjælsø Plant I | Sjælsø Plant II | Sjælsø Plant II  | Sjælsø Plant II  |
| <b>Filter sand</b>                          | (g)    | 250                      | 250            | 250             | 250              | 100              |
| <b>Water</b>                                | (mL)   | 100                      | 100            | 100             | 100              | 100              |
| <b>Initial concentration</b>                |        |                          |                |                 |                  |                  |
| Mecoprop                                    | (µg/L) | 0.38                     | 0.04           | 0.03            | -                | -                |
| Glyphosate                                  | (µg/L) | -                        | 0.05           | 0.05            | -                | -                |
| p-Nitrophenol                               | (µg/L) | -                        | 0.16           | 0.16            | -                | -                |
| [Carbonyl- <sup>14</sup> C]-Bentazone       | (µg/L) | 0.1                      | 0.1            | 0.1             | 0.1/0.5/2.4      | 0.6              |
| [Benzene-ring-U- <sup>14</sup> C]-Bentazone | (µg/L) | -                        | -              | -               | 0.16             | -                |

- no data

### 2.3 Collection of filter sand

Water was collected from the inlet connecting to the clean water tanks. Filter sand was collected from the top 20 cm of the filter bed with a specially designed aluminium bucket on an extendable shaft, which was disinfected with 1% hypochlorite. The filter sand was transported to the laboratory in an autoclaved plastic bag inside a clean bucket.

### 2.4 Preparation of microcosms, pH and oxygen concentration

Within two hours of collecting water and filter sand at the waterworks, 250 g wet filter material was transferred with a sterilized spoon to 300 ml serum bottles, which had been acid-washed and heated to 555°C for 12 hours. A total water volume of 100 ml was added, including volumes of dissolved chemicals. At Islevbro set-up with inlet water to filters was compared to set-up with outlet water from the filters, without any substantial difference in the removal of MCPP (Table 4), and outlet water from the filters was used in the following experiments.

Abiotic controls were set up with filter sand, which was either autoclaved three times (20 min, 1 bar and 121°C, the microcosms cooled for approx. 30 min – to less than 80°C – before autoclaving was repeated) or was mixed with sodium azide to a concentration of 2 g/L to inhibit all microorganisms. Microcosms were closed with Teflon caps and aluminium lids, and they were left at 10°C in darkness overnight before sampling. Incubation conditions were static.

The pH remained at 7 during the experiment and the oxygen concentration was measured before and after the experiment with an HACH HQ40d oxygen electrode.

## 2.5 Sampling

Sampling was frequent in the initial stages of the experiments, in order to investigate removal behaviour during a period approximately equivalent to the residence time in the filter, and lasted for 1–6 hours. In the second phase the removal potential of the filter sand was investigated, and sampling was less frequent and lasted for 2–13 days after the experiment started.

The microcosms were spiked with dissolved [ $^{14}\text{C}$ ]-pesticide to a concentration of 0.03–2.4  $\mu\text{g/L}$  (Table 3). When sampling, 3 ml atmospheric air was added to the microcosms and the 2–3 ml water samples were collected with a syringe through the cap of the microcosms. A 0.25  $\mu\text{m}$  hydrophilic PTFE-filter (Frisenette Aps, Advantec<sup>®</sup>, Dismic<sup>®</sup>-13<sub>HP</sub>, disposable syringe filter unit, diameter: 13 mm) was used to remove suspended matter from the water sample.

The analysis for  $^{14}\text{C}$  was based on a double vial system, whereby  $^{14}\text{CO}_2$  produced in the collected water sample was stripped off and captured by a base trap (1 ml 2M NaOH). Thus the produced  $^{14}\text{CO}_2$  and the  $^{14}\text{C}$ -activity of the pesticide in the water phase could be quantified. The base traps were set up as described by Janniche et al. (2010). The pesticide concentration at a given sampling time was calculated as a fraction of the initial concentration and corrected for the removed pesticide during sampling (given as  $^{14}\text{C}/^{14}\text{C}_0$  (%)). Mineralisation was calculated as the cumulated  $^{14}\text{CO}_2$  as a fraction of the initial pesticide concentration and corrected for the equilibrium to headspace (given as  $^{14}\text{CO}_2/^{14}\text{C}_0$  (%)).

Due to frequent sampling in the first 1–6 hours, experiments were processed at an ambient temperature (20°C). After this period the microcosms were incubated at 10°C in darkness.

## 2.6 Removal kinetics – deviations in experimental set-up

To obtain higher oxygen concentrations in the microcosms, they were purged over night with sterile filtered atmospheric air and closed afterwards. When sampling the microcosms, sterile pure oxygen was added instead of atmospheric air. To avoid clogging, the syringe filters were replaced by a 0.22  $\mu\text{m}$  nylon and GF filter (Frisenette Aps, Q-max<sup>®</sup> GPF Syringe Filters, diameter 25 mm).

## 2.7 Effect of oxygen – deviations in experimental set-up

In this experiment the aeration procedure from 'Removal kinetics' was used. Furthermore, water-air contact was enhanced by changing incubation conditions from static to gently swirling, by placing the microcosms in an orbital shaker during the experiment. Oxygen concentration was monitored during the experiment with Oxygen-Sensitive Minisensors in the filter sand and by applying a Fibox 3 – a fibre optic oxygen meter (Loligo Systems ApS).

Due to a high concentration of suspended material in the samples, extracted volumes were changed to 7 ml four times during the investigations, in order to assure

a substantial water sample for further analysis. Additionally, the last sample was pre-filtered through a 0.45 µm GF/F filter (Whatman syringe filter, GF/F Filter membrane with a polypropylene housing, diameter: 25mm).

### 2.8 Characterisation of the filter material

The water content of the filter material was quantified through weight loss after 24 hours at 105°C. The bulk density of the dry filter sand was found by weighing 40 ml, without compressing the filter sand. This method could underestimate the actual bulk density in the rapid sand filter, but repeated experiments showed variance below 1%.

The amount of total organic carbon (TOC) in the filter sands was measured for the sample. The TOC analysis was carried out by employing a total element carbon analyser (LECO Induction Furnace CS-200) after the removal of carbonates by adding 5% sulphurous acid (H<sub>2</sub>SO<sub>3</sub>).

## 3. Results and discussion

### 3.1 Degradation potential of filter sand

To investigate the potential of filter sand to degrade pesticides, filter sand was collected from three waterworks which received water of substantially different qualities (Table 1).

All of the investigated rapid sand filters removed the investigated pesticides partially (at Islevbro only MCPP and bentazone were investigated), either by abiotic or microbial processes (Table 4), and concentrations in the microcosms decreased during the experiment between six and 13 days. MCPP decreased to 42-85%, bentazone to 15-35%, glyphosate to 7-14% and *p*-nitrophenol to 1-3% of the initial concentration. Due to the position of the <sup>14</sup>C-label in glyphosate (Table 2) only a complete removal of the compound would be detected – partial degradation to the primary metabolite 2-amino-3-(3-hydroxy-5-methyl-isoxazol-4-yl)propanoic acid (AMPA) would not be detected. The mineralisation of pesticides in terms of <sup>14</sup>CO<sub>2</sub> production was observed only at Sjølsø Plant II. After six days, <sup>14</sup>CO<sub>2</sub> production from bentazone reached 8-14%, glyphosate 42-43% and *p*-nitrophenol 7-10% of the initially added pesticide (mineralisation of MCPP was not detected). Previous investigations on the removal of micro pollutants in biological drinking water filters for the treatment of surface water also found removal of pesticides at the same concentration range after an adaption period of six months. However, these investigations showed that nine out of 16 pesticides were recalcitrant to biodegradation (Zearley and Summers, 2012).

**Table 4. Fractionation of <sup>14</sup>C-bentazone after incubation with filter material from different filter sands. The fraction of <sup>14</sup>C (or <sup>14</sup>CO<sub>2</sub>) of the initial amount of <sup>14</sup>C<sub>0</sub> is shown at two selected times. Data are from microcosms (two replicates) and abiotic controls. The removal of MCPP at Islevbro was tested with both outlet water from filter (OW), and inlet water to filter (IW).**

|                        | Fraction of bentazone in water phase ( <sup>14</sup> C/ <sup>14</sup> C <sub>0</sub> ) |                 |            |                 | <sup>14</sup> CO <sub>2</sub> -production from degradation ( <sup>14</sup> CO <sub>2</sub> / <sup>14</sup> C <sub>0</sub> ) |                 |            |                 |
|------------------------|--|-----------------|------------|-----------------|---|-----------------|------------|-----------------|
|                        | Microcosms   | Abiotic control | Microcosms | Abiotic control | Microcosms  | Abiotic control | Microcosms | Abiotic control |
|                        | 4 hours  |                 | 13 days    |                 | 4 hours   |                 | 13 days    |                 |
| <b>Islevbro</b>        |  |                 |            |                 |   |                 |            |                 |
| MCPP OW                | 60-61%   | 64%             | 42-48%     | 57-61%          | -   | -               | -          | -               |
| MCPP IW                | 60%  | 73%             | 51-57%     | 73-75%          | -   | -               | -          | -               |
| Bentazone              | 72-74%   | 81%             | 26-33%     | 74-83%          | -   | -               | -          | -               |
| <b>Sjælsø Plant I</b>  |  |                 |            |                 |   |                 |            |                 |
|                        | 4 hours  |                 | 6 days     |                 | 4 hours   |                 | 6 days     |                 |
| MCPP                   | 103%   | 63%             | 67-74%     | 67%             | -   | -               | -          | -               |
| Bentazone              | 62-75%   | 60%             | 31-35%     | 62%             | -   | -               | -          | -               |
| Glyphosate             | 8-9%   | 9%              | 7-8%       | 4%              | -   | -               | -          | -               |
| 4-nitrophenol          | 29%  | 56%             | 1-3%       | 22%             | -   | -               | -          | -               |
| <b>Sjælsø Plant II</b> |  |                 |            |                 |   |                 |            |                 |
|                        | 4 hours  |                 | 6 days     |                 | 4 hours   |                 | 6 days     |                 |
| MCPP*                  | 103%   | 112%            | 70-85%     | 92%             | -   | -               | -          | -               |
| Bentazone              | 59-71%   | 101%            | 15-18%     | 103%            | -   | -               | 8-14%      | -               |
| Glyphosate             | 19-20%   | 17%             | 9-14%      | 8%              | 31-36%  | -               | 42-43%     | -               |
| 4-nitrophenol          | 28-33%   | 102%            | 3%         | 96%             | 4%  | -               | 7-10%      | -               |

\* low initial concentrations (0.033-0.036 µg/L) – uncertain results.

- no evident tendency in results

For Islevbro and Sjælsø waterworks Plant I, [<sup>14</sup>C]-pesticide was removed from the water phase in the abiotic controls, so a part of the pesticide was removed by abiotic processes, such as sorption. According to high Henry's law constants, >10<sup>4</sup> M/atm, volatilisation was not likely to remove the pesticides (Table 2) (EU pesticide database, 2013; Tremp et al, 1993; Liss and Slater, 1974). For Sjælsø Plant I the removal of MCPP and glyphosate was merely abiotic, since there was no difference between abiotic controls and microcosms. However, in all other cases, more pesticide was removed in the biologically active microcosms than in the abiotic controls. Microbiological removal did not result in immediate mineralisation (<sup>14</sup>CO<sub>2</sub> production), and removal must have been caused by a degradation to a metabolite, which was eliminated from the water phase by sorption or volatilisation, or the compound was taken up by the microorganism (Nowak et al., 2011). Consequently, pesticide removal in the filter sands from Islevbro waterworks and Sjælsø waterworks Plant I was caused partially by abiotic and partially by microbiological processes.

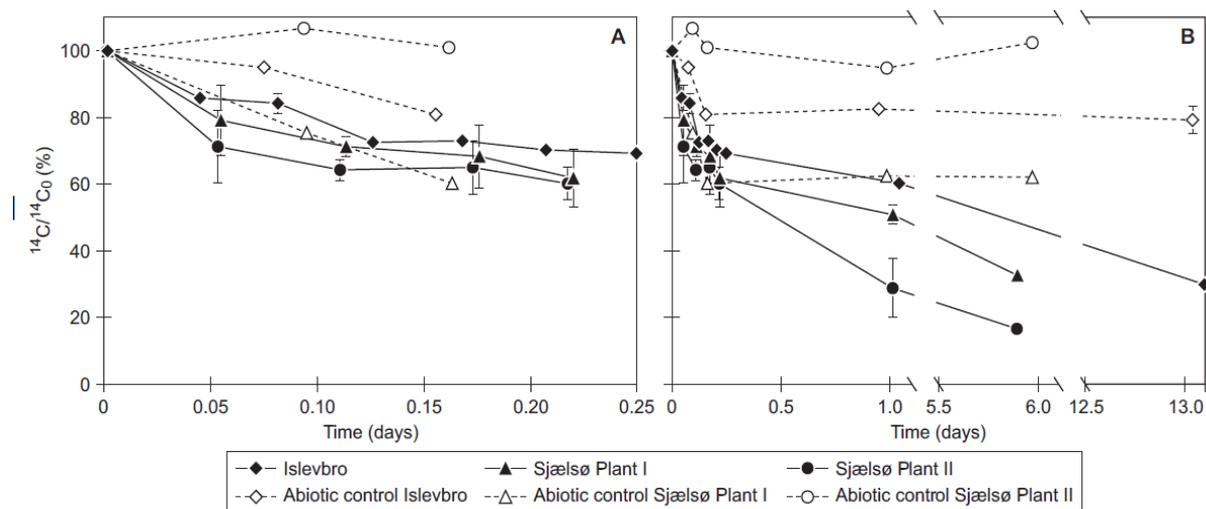
At Sjælsø waterworks Plant II, more than 90% of bentazone and *p*-nitrophenol was removed by microbial processes, due to the difference in microcosms and abiotic controls, and evident mineralisation was measured for bentazone, glyphosate and *p*-nitrophenol (Table 4). Microbiological removal was substantial in this filter, though abiotic processes also had an influence especially on the removal of glyphosate (Table 4).

Except for glyphosate, which adsorb to inorganic material (Borggaard and Gimsing, 2008; Vereecken, 2005), a high proportion (33–78% over six days) of the pesticides at Sjælsø waterworks Plant I was removed by abiotic processes. This was probably due to sorption onto the filter material, due to the very high content of TOC

(78.8%) (Table 1). However, a major part of the TOC in the filter was anthracite coal, which actually has low sorption capacity. At Islevbro, with 2.71% TOC in the filter, abiotic removal was lower but substantial (17-43% over 13 days), whereas sorption was much lower (0-8% over six days) at Sjælsø waterworks Plant II with a quite low content (0.5%) of TOC in the filter samples (Table 1). Thus, the abiotic removal of the pesticides was related to TOC content in the filter material, which causes sorption.

The removal potential of bentazone was substantial in all three rapid sand filters (Figure 1), and at the end of the experiments the remaining concentration of bentazone in the water was less than 33% of the initial concentration (after 13 days, filter sand from Islevbro waterworks). The elimination was greatest in microcosms with filter material from Sjælsø waterworks Plant II, where the concentration decreased to 15-18% after six days. This was evidently a microbial removal, since concentration in the abiotic controls stayed at approximately 100% throughout the experiment (Figure 1).

Since biological removal was more prevalent at Sjælsø waterworks Plant II, the removal kinetics and processes for bentazone were investigated further in this rapid sand filter.

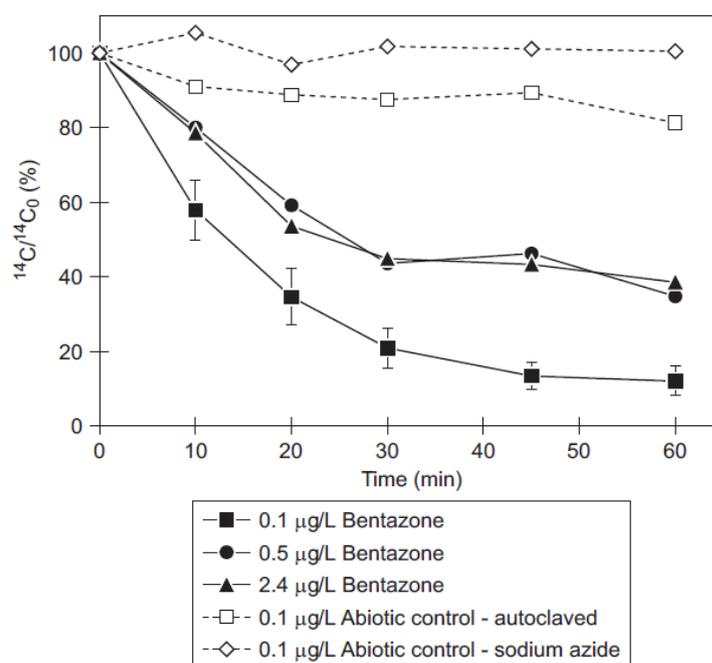


**Fig. 1.** Potential for degradation of bentazone with filter sand from three different waterworks, shown for the first six hours (A) and the entire experiments (B). Mean concentrations and standard deviation are given as a percentage of the initial concentration. Initial concentration was 0.1  $\mu\text{g}/\text{L}$  in microcosms (duplicates) and corresponding abiotic controls.

### 3.2 Removal kinetics

The removal of bentazone was investigated at different initial concentrations during the residence time in the sand filter, which was 56 minutes for Sjælsø waterworks Plant II.

Bentazone was removed rapidly in the microcosms, and the removal was microbial because abiotic removal was insignificant (Figure 2). For an initial concentration at 0.1 µg/L, mean concentration in the microcosms decreased to 35% after only 20 minutes, and after 60 minutes it had dropped further to 12% of the initial concentration. At higher initial concentrations bentazone decreased similarly but the relative removal rate was slightly slower (Figure 2). During the first hour of the experiment the remaining concentration in these microcosms decreased to 35% of the initial concentration of 0.5 µg/L and to 39% for an initial concentration of 2.4 µg/L. The time it took to remove 50% of the bentazone concentration from the water phase, i.e. the 50% dissipation time ( $DT_{50\%}$ ), was read off the curves (Figure 2) and was less than 30 minutes for all the initially tested concentrations (0.1-2.4 µg/L) (Table 5).

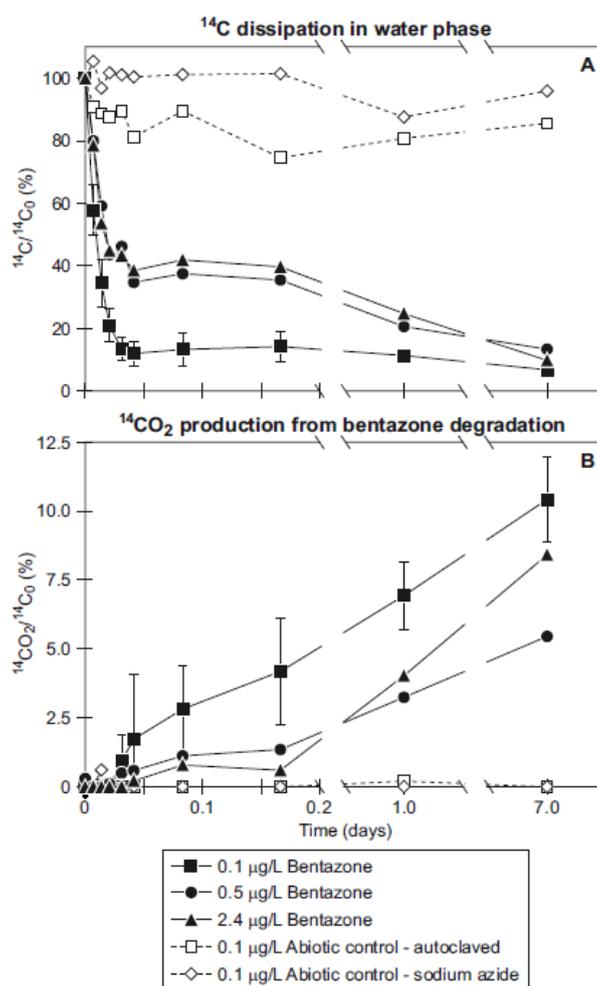


**Fig. 2.** Removal kinetics investigated at three different initial concentrations in a short-term investigation. Microcosms consisted of 250g filter sand and 100 ml water from Sjælsø waterworks Plant II. The mean concentrations and standard deviation are given as percentage of the initial concentration. Microcosms with an initial concentration of 0.1 µg/L (triplicate) are depicted along with two corresponding abiotic controls (initial concentration 0.1 µg/L, inhibited in two different ways) and two microcosms with initial concentrations of 0.5 µg/L and 2.4 µg/L.

**Table 5. The 50% dissipation time, DT<sub>50%</sub>, for bentazone was read off the curves in Figure 2 at different initial concentrations.**

| Initial concentration (µg/L) | DT <sub>50%</sub> (min) |
|------------------------------|-------------------------|
| 0.1                          | 13                      |
| 0.5                          | 26                      |
| 2.4                          | 24                      |

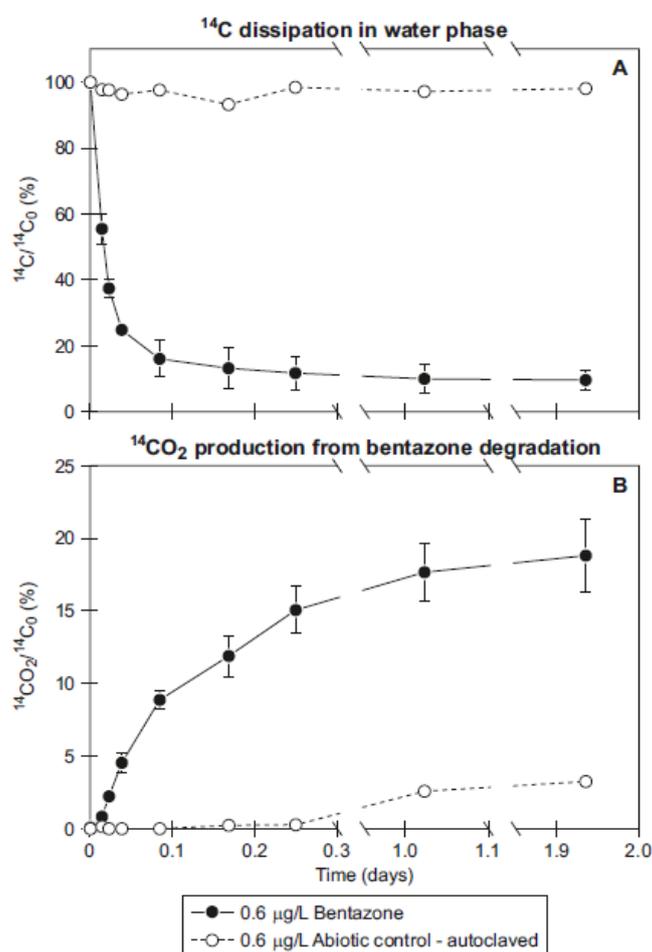
No <sup>14</sup>CO<sub>2</sub> production was observed in the abiotic controls, but it was substantial in all microcosms (Figure 3). The mean <sup>14</sup>CO<sub>2</sub> production in the microcosms (initial concentration of 0.1 µg/L) was 10.4% after seven days, which means that <sup>14</sup>C-labelled carbonyl group was completely mineralised.



**Fig. 3.** Removal kinetics – long-term investigation. Microcosms with 250g filter sand (Sjælsø waterworks Plant II), 100 ml water and an initial bentazone concentration of 0.1 µg/L (triplicates), 0.5 µg/L (one microcosm) and 2.4 µg/L (one microcosm) were investigated along with two different abiotic controls (initial concentration 0.1µg/L). Mean values and standard deviation are shown for A) concentration of bentazone in the water (<sup>14</sup>C/<sup>14</sup>C<sub>0</sub>), and B) <sup>14</sup>CO<sub>2</sub> production (<sup>14</sup>CO<sub>2</sub>/<sup>14</sup>C<sub>0</sub>) from the degradation of bentazone.

### 3.3 Effect of oxygen

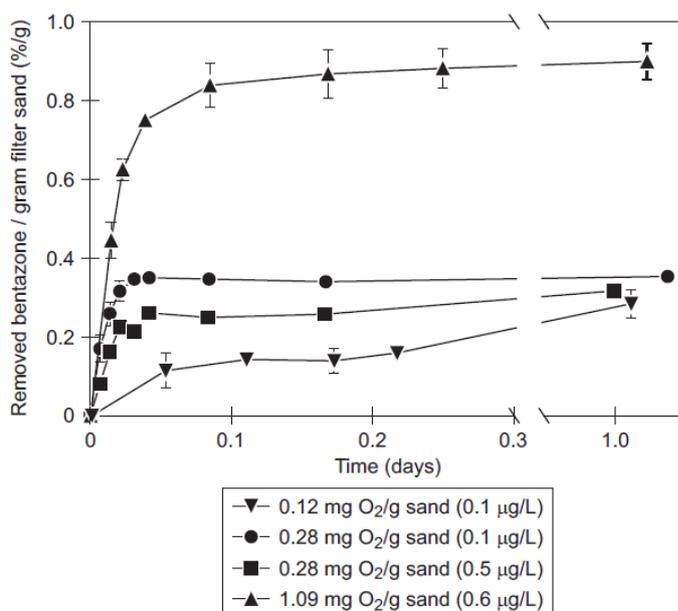
In the experiment 'Removal kinetics', oxygen availability was increased and the observed removal of bentazone was faster than in the 'Degradation potential of filter sand' investigation. Since the microbial metabolism and further fate of bentazone in soils depend very much on the presence of oxygen (Knauber et al., 2000), it was investigated whether differences found in the removal of bentazone between the experiments could be explained by the limited availability of oxygen. In rapid sand filters found in waterworks, oxygen is easily available to microorganisms. Pure oxygen was added, and oxygen availability was increased to 0.28 mg O<sub>2</sub>/g filter sand in 'Removal kinetics' compared to an oxygen availability of 0.12 mg O<sub>2</sub>/g filter sand



**Fig. 4.** Removal of bentazone under high oxygen concentrations. Microcosms with 100g filter sand (Sjælsø waterworks Plant II), 100 ml water and an initial bentazone concentration of 0.6 µg/L (triplicates) were investigated along with the one corresponding abiotic control (initial concentration 0.6 µg/L). Mean values and standard deviation are shown for A) concentration of bentazone in the water (<sup>14</sup>C/<sup>14</sup>C<sub>0</sub>), and B) <sup>14</sup>CO<sub>2</sub> production (<sup>14</sup>CO<sub>2</sub>/<sup>14</sup>C<sub>0</sub>) from the degradation of bentazone.

in 'Degradation potential of filter sand'. This increased the removal efficiency of the filter sand after one hour at a significance level of 99.95%. However, oxygen measurements during the investigations showed that concentrations decreased throughout both experiments. The experiment 'Effect of oxygen' was set up to validate the effect of oxygen on bentazone removal. In this experiment oxygen availability reached 1.09 mg O<sub>2</sub>/g filter sand (Figure 4).

Increased oxygen availability led to the greater and faster removal of bentazone in the microcosms (Figure 5). After one hour, bentazone removal (an initial bentazone concentration on 0.1 µg/L) increased from 0.21%/g filter sand to 0.75%/g filter sand when oxygen availability was increased from 0.28 mg O<sub>2</sub>/g filter sand to 1.09 mg O<sub>2</sub>/g filter sand. This increased the removal efficiency of the filter sand at a significance level of 99.95%. Increasing oxygen availability by a factor of 3.9 increased the removal efficiency of the filter sand by a factor 3.6.



**Fig. 5** Effect of oxygen on the removal of bentazone from the water phase. The available amount of oxygen per gram of filter sand was calculated in each experiment as the sum of oxygen in the water and the headspace at the start and the total added amount during the experiment. The amount of bentazone removed from the water phase (<sup>14</sup>C/<sup>14</sup>C<sub>0</sub> (%)) per gram of filter sand in the microcosms is shown for each of the experiments. The initial concentration of bentazone is given in brackets.

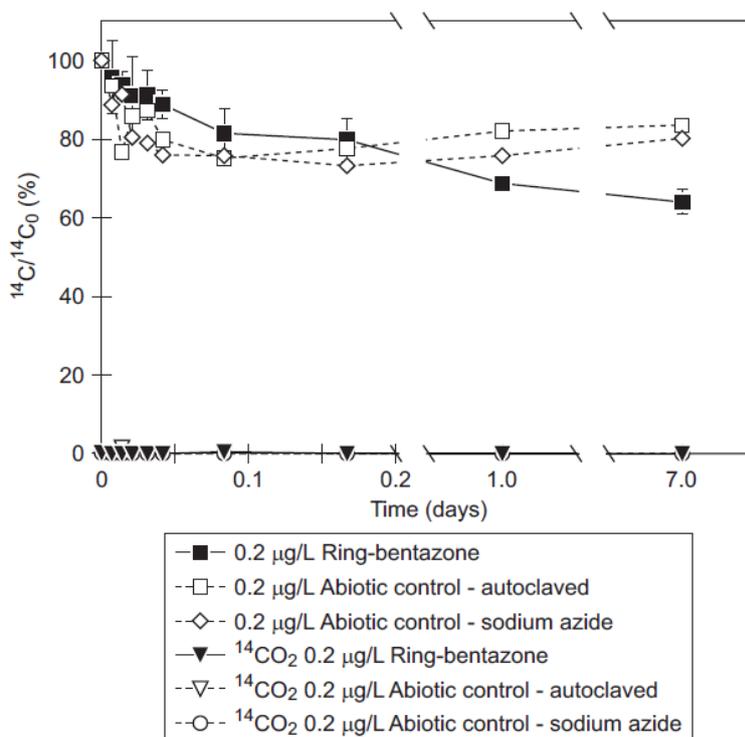
The experiment with oxygen availability of 1.09 mg O<sub>2</sub>/g filter sand was the only experiment where oxygen concentration was continuously above 8 mg O<sub>2</sub>/L. In the full-scale rapid sand filter, oxygen concentration was above 8 mg O<sub>2</sub>/L and the removal efficiency of the filter sand in the experiment with oxygen availability of

1.09 mg O<sub>2</sub>/g filter sand was therefore the best simulation for the full-scale rapid sand filter.

### 3.4 Complete degradation – investigations of ring-bentazone

The degradation potential for [benzene-ring-U-<sup>14</sup>C]bentazone (mentioned as ring-bentazone) was investigated, in order to examine whether the whole bentazone molecule would be mineralised during the removal process.

Very little ring-bentazone was removed during the first hours of the experiment, but after seven days the remaining concentration in the microcosms was 18% lower than in the abiotic controls (Figure 6), and the total concentration of ring-bentazone decreased to 64% of the initial concentration. <sup>14</sup>CO<sub>2</sub> production as a result of removing ring-bentazone could not be measured within the timeframe of the experiment (Figure 6). The microbial removal of ring-bentazone from the water phase therefore did not entail complete mineralisation.



**Fig. 6** Removal of ring-bentazone in the water. Microcosms consisting of 250g sand and 100 ml water from the rapid sand filter at Sjælsø waterworks Plant II, and an initial ring-bentazone concentration of 0.2 µg/L (triplicates) were investigated

When bentazone was added to the microcosms, the <sup>14</sup>C-labelled carbonyl group was immediately removed by a microbial process from the water phase (Figure 3 and 4), which means that either the whole bentazone molecule was removed from the water phase or it was broken down and only partially removed. Investigation where

the  $^{14}\text{C}$ -label was positioned in the benzene-ring showed that in the same experimental period the benzene-ring was present in the water phase for longer than the carbonyl group (Figure 6), which means that the immediate removal was a partial removal of bentazone. Hence, an interpretation of the removal is that the thiadiazine group in bentazone must have been cleaved initially by a microbial process. Afterwards, a metabolite, which contained the  $^{14}\text{C}$  from the carbonyl group, was removed rapidly from the water phase and later metabolised to  $^{14}\text{CO}_2$ , while microbial removal of a metabolite with the benzene-ring was slow or initiated later (seven days).

Removal of bentazone in filter sand has parallels with degradation in soil matrixes, in that they are both oxygen-dependent processes (Knauber et al., 2000) and removal is initiated by microbial degradation. In soil metabolism the degradation of bentazone is explained by hydroxylation of the benzene-ring to 6-OH-bentazone or 8-OH-bentazone, or by microbial degradation to anthranilic acid. This is followed by incorporating the reactive metabolites into the organic soil matrix (Huber and Otto, 1994). This does not correspond with degradation in filter sand – since the benzene-ring is detectable in the water phase for longer than the carbonyl group, the bentazone molecule must be broken down further before it can be incorporated into the filter sand matrix. Knauber et al. (2000) demonstrated that 12-15% of bentazone was immediately mineralised in soil, while 65-85% was hydroxylated by microbial activity and bound to the humic matrix. The bound residues were mineralised over a longer period (141 days) (Knauber et al., 2000). The sizes of these fractions are similar to the results for filter sand, where 8-19% was mineralised and 68-83% was removed from the water phase. Bound residues from pesticide degradation in soils have recently been found to be incorporated in living biomass (Nowak et al., 2011), which could also influence the removal of bentazone metabolites from the water phase.

#### 4. Perspectives

To our knowledge, there is hardly any existing literature on the degradation of pesticides in rapid sand filters used for drinking water treatment. In other technical systems biological removal of pesticides is possible, for instance in treatment of surface water, waste water and groundwater. However, the investigated systems needed long adaptation periods, from 25 days up to six months (Zearley and Summers, 2012; Baghapour et al., 2013; Hunter and Shaner, 2011). Previous studies of the degradation of bentazone in aquifers have likewise shown long adaptation time (Albrechtsen et al., 2001; Broholm et al., 2001). Hence, it is extraordinary that this study established the microbial removal of bentazone in a rapid sand filter, which did not depend on an adaptation phase for the microorganisms.

It was observed that regardless of the initial concentration of bentazone, the remaining concentration in the microcosms stalled at approximately 10%. Since it

was not possible to degrade the residual part, it could indicate that a more persistent metabolite was formed.

Investigations of ring-bentazone showed that large amounts of metabolites containing the benzene-ring were still present in the water phase after seven days. The structure of this metabolite was different from bentazone since the removal of carbonyl- $^{14}\text{C}$ -bentazone indicated a radical transformation of the molecule. It is important to clarify the properties of the metabolite, in order to assure safe drinking water for consumers. Additionally, the production of  $^{14}\text{CO}_2$  was delayed (six hours to seven days) compared to the removal of bentazone, thus indicating that the rapid removal of bentazone was only a partial decomposition and led to an accumulation of metabolites in the filter.

## 5. Conclusion

The investigations showed:

- A clear removal potential of the pesticides MCPP, bentazone, glyphosate, and *p*-nitrophenol in rapid sand filters at Danish waterworks. The largest microbial removal was observed with filter material taken from Sjælsø Plant II.
- At Sjælsø waterworks Plant II bentazone concentration in the water phase decreased as a result of microbial removal to less than 50% of the initial concentration within 30 minutes for all tested start concentrations (0.1–2.4  $\mu\text{g/L}$ ).
- Oxygen concentration was of substantial importance for removal kinetics and removal potential of bentazone. Hence, the efficiency of bentazone removal by filter sand increased when oxygen availability increased.
- The rapid removal of bentazone (less than 60 minutes) was due to a microbial transformation of the molecule seen in the removal of the  $^{14}\text{C}$ -labelled carbonyl group from the water phase. This transformation was followed by a slower mineralisation after 24 hours and complete microbial removal after seven days.

Overall, this study showed that substantial pesticide removal is possible within the contact time of rapid sand filters at Danish waterworks, and that rapid removal is followed by a slower mineralisation of the compound. Hence, there is a potential for microbial removal of pesticides from contaminated groundwater in Danish waterworks. This is of commercial interest due to substantial attention given to the maintenance of today's water treatments.

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