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Publication date:
2017

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):

Lee, C. O., Musovic, S., Hedegaard, M. J., Tatari, K., Laugesen, H., & Albrechtsen, H-J. (2017). *Pesticide degradation potential of pesticides in biological rapid sand filters at 10 different waterworks*. Abstract from Water Quality Technology Conference (WQTC) 2017, Portland, United States.

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2017

Portland,
Oregon, USA

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NOVEMBER 12-16, 2017

Pesticide degradation potential of pesticides in biological rapid sand filters at 10 different waterworks

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Abstract

Denmark gets 100% of its drinking water from groundwater, and as such, source water protection is a priority. Despite this, pesticides and their metabolites were detected in 36-38% of monitoring wells and 25-27% of drinking water wells in Denmark in the period 2013-2015. Denmark treats its water with biological rapid sand filters, which previous studies have shown to have some pesticide degradation potential. The aim of this research was to determine the pesticide degradation potential of five relevant pesticides or metabolites at a wide range of water works across Denmark.

The selected waterworks had at least one of the examined pesticides in the raw water feeding the filters. Inlet water quality varied greatly across the examined water works with varying inlet concentrations of iron, manganese, ammonium, methane, and hardness. The degradation potential of MCP, glyphosate, BAM (degradation product of dichlorbenil), atrazine, and bentazone were determined using microcosms. The microcosms consisted of sand and effluent water from the examined waterworks, and were spiked with ¹⁴C labeled pesticides at concentrations between 0.6-2.5 µg/L. Samples were collected at the start of the experiments and after 1 hour, 1 day, and 5 days.

Preliminary results showed that 90% of the examined filter material from the water works had between 90-98% removal of MCP with one of the water works achieving 66% mineralization and 5 of the water works achieving mineralization of >20%. Glyphosate removal was also high in all of the examined water works, with removal efficiencies between 80-98%. However, high glyphosate removal in most of the autoclaved controls suggested that glyphosate was initially sorbed to the filter media, while biological degradation subsequently lead to mineralization of >20% in 70% of the examined water works. Smaller degradation capacities were observed for BAM, atrazine, and bentazone. Between 10-20% removal of BAM and atrazine was observed in five waterworks with approximately 6% mineralization of both compounds observed at one of the waterworks. Bentazone removal was between 10-18% in six of the waterworks, with 8 % mineralization observed at the same waterworks where mineralization of BAM and atrazine occurred. The results show the potential for enhanced removal of pesticides in biological rapid sand filters. This could offer an alternative to more expensive or energy consuming treatment processes, and be used to maintain water production from contaminated wells.



Introduction

Pesticides are used worldwide and are beneficial in increasing crop yield and preventing unwanted organisms (Helbling et al., 2014). Unfortunately though, their extensive use has led to polluted source waters for drinking water (Fenner et al., 2013). The quality standards for pesticides in the European Union has a limit of 0.1 µg/L for individual pesticides and their relevant metabolites, with 0.5 µg/L total (European parliament council directive 2006/118/EC). Denmark gets 100% of its drinking water from groundwater, and as such, source water protection is a priority. Despite this, pesticides and their metabolites were detected in 36-38% of monitoring wells and 25-27% of drinking water wells in Denmark between 2013-2015. Denmark also has stricter regulations on a few other individual pesticides and metabolites. For example, In 2015, 2,6-Dichlorobenzamide (BAM), a degradation product of the pesticide dichlobenil, was detected in 20% of monitoring points, with 2.2% being greater than 0.1 µg/L (Thorling et al., 2017). Although BAM has been banned in Denmark since 1997 (Sørensen et al., 2007), and it is still the most frequently detected pesticide-related product in Danish groundwater.

The range and scope of BAM pollution in Danish groundwater, despite the fact that the parent compound has been banned for two decades, shows how persistent pesticides and their metabolites can be in groundwater. Drinking water treatment processes such as advanced oxidation (Suty et al., 2004), filtration with granular activated carbon (GAC), and reverse osmosis (Snyder et al., 2007), have all been shown to remove pesticides, although each of these treatment techniques have their own limitations and drawbacks. Ozonation has been found to remove many organic compounds of concern although pesticides were found to be the most persistent (Broséus et al., 2009). GAC has been shown to be effective, although breakthrough of compounds and the costs associated with new GAC or regeneration are potential drawbacks. Reverse osmosis has also been shown to be highly effective, but could be deemed unrealistic in many applications due to the high cost and energy consumption (Lee et al., 2012) as well as issues related to disposing of the concentrated waste stream.

Recent research has shown the potential for biological rapid sand filters to biodegrade pesticides (Hedegaard et al., 2014; Hedegaard and Albrechtsen, 2014). Biological degradation of pesticides in these filters could be a substantial, sustainable, and environmentally friendly treatment technology. The aim of this research was to evaluate a wide range of biological rapid sand filters in Denmark, to determine the pesticide degradation potential of several relevant pesticides/metabolites.

Material and Methods

Water works selection

To get a wide scope of the pesticide degradation potential in biological rapid sand filters, 10 different water works were examined. The waterworks varied in geographical location, inlet water quality (hardness, pH, inlet NH₄ and CH₄ concentrations), filter design (including filter material), and operating parameters (flowrates and backwashing procedures). Nine out of the 10 examined waterworks, had a history of having at least one of the selected pesticides present in the raw water (Table 1). The one filter that was not fed with water containing pesticides, had previously been shown to have a relatively high pesticide degradation potential for some pesticides (Hedegaard and Albrechtsen, 2014).



Table 1: Inlet concentrations of the pesticides examined ($\mu\text{g/L}$) at the selected water works investigated for pesticide degradation potential

WATEWORKS	MCP	GLYPHOSATE	BAM	ATRAZINE	BENTAZONE
WW 1	-	-	<0.01 - 0.016	-	-
WW 2	-	-	<0.01 - 0.014	-	-
WW 3	-	-	<0.01 - 0.028	-	-
WW 4	-	-	0.011-0.02	-	<0.01- 0.92
WW 5	<0.01 - 0.05	-	-	-	-
WW 6	<0.01 - 0.02	-	<0.01 - 0.04	-	<0.01 - 0.01
WW 7	-	-	<0.01 - 0.017	<0.01 - 0.025	-
WW 8					
WW 9	-	-	0.04- 0.21	-	-
WW 10	-	-	-	-	<0.01 - 0.056

Selected pesticides

The examined pesticides for this research were selected based on their relevance for both Danish drinking water and worldwide (Table 2). Four pesticides (MCP, glyphosate, atrazine, and bentazone) and one metabolite (BAM) were selected. Although BAM is a metabolite of the now banned pesticide dichlorbenil, it is the most frequently occurring pesticide/metabolite at Danish waterworks. Bentazone was also selected because of its high occurrence at Danish water works. Although atrazine was only the 15th most detected pesticide/metabolite at Danish water works, it has six different metabolites that are also among the top 20 most detected pesticides/metabolites. MCP was selected because it has been previously been shown to have a large biodegradation potential in a biological rapid sand filter (Hedegaard et al., 2014) and glyphosate was selected due to its overwhelming large use worldwide.



Table 2: Pesticide information and relevance for the selected pesticides examined

PESTICIDE	COMPOUND INFORMATION	RELEVANCE
MCCP	Phenoxy acid. Simulates plant growth hormones, many different genes known to degrade these compounds (<i>tdfA</i> ; <i>rdpA</i> ; <i>sdpA</i>)	Use is regulated. 10th most frequently detected in Danish waterworks (1.2%)
GLYPHOSATE	Primary degraded to AMPA. Many degradation pathways (Hove-Jensen et al., 2014)	Legally used. World's most applied herbicide. 18th most frequently detected in Danish waterworks (0.5%)
BAM	Degradation compound of Dichlorobenil. Gene encoding for degradation: <i>bbdA</i> located on the IncP-1 β plasmid pBAM1 (T'Syen et al., 2015)	Use is forbidden. Primarily a concern in Denmark. Most frequently detected in Danish waterworks (19.9%)
ATRAZINE	Metabolites: DEIA, Deisopropyl-atrazin, Deethyl-atrazin, Didealk.-dydr. atrazine, Hydroxy-atrazin and the 'sister compound' Simazin – all on the top most detected in Danish water works. Genes known be involved in degradation are <i>atzABC</i> and <i>trzD</i>	Use is forbidden. 15th most frequently detected in Danish waterworks (0.7%)
BENTAZONE	First transformation to 6OH-, 8OH-bentazone and AIBA. Currently there are no known genes associated with the biodegradation of bentazone	Use is regulated. 3rd most frequently detected in Danish waterworks (3.0%)

Measuring pesticide degradation potential

Sand was collected from the secondary filters (if possible) of the selected water works along with treated effluent water. All filters were backwashed prior to collecting the sand. Sand was collected from the top 20 cm of the filter and kept cool until starting the microcosms. All experiments were started within two days of collecting the sand.

Microcosms were used to determine the pesticide degradation potential at the selected waterworks. Each microcosm consisted of 100 grams of drained wet weight sand from the selected waterworks, along with 100 mL of effluent water. For each pesticide, microcosms were prepared in duplicates along with an abiotic control giving a total of 15 microcosms for each waterworks examined. For the abiotic control, sand was added to the bottles and autoclaved three times before adding the effluent water. At time 0, ^{14}C labeled pesticides were added and shaken for 1 minute before sampling. Samples were then collected at 1 hour, 1 day, and 5 days. A shaker table was used to ensure the microcosms were properly mixed in between sampling events.

All microcosms started with an initial ^{14}C activity of 400 DPM/mL corresponding to influent pesticide concentrations between 0.6-2.5 $\mu\text{g/L}$. A double vial, acid-base trap was used to quantify the ^{14}C activity in the water and quantify the $^{14}\text{CO}_2$ produced. For each sample, 2 mL of water was collected into a 20 mL vial, after being filtered through a 0.2 μm PTFE filter. A 6 mL vial containing 1 mL of 2M NaOH was placed into the 20 mL vial with the sample, which was then acidified by adding 0.1 mL of 37% HCl.

Results

Preliminary results showed MCP and Glyphosate removal was rapid and substantial in the investigated filter sand. After 5 days, the filter sand had removed 90-98% of the MCP at nine of the examined waterworks, while >20% mineralization was achieved in six cases with one waterworks showing 66% mineralization. Glyphosate removal was between 80-98% in the filter sand from all examined waterworks after 5 days, although much of the initial removal is likely due to sorption, as seen with the high removal observed in the autoclaved control (Fig. 1A). However, at many of the waterworks, the $^{14}\text{CO}_2$ production steadily increased in the duplicate batches over 5 days, while no removal was observed in the abiotic control (Fig. 1B). This suggests that the sorbed glyphosate is being steadily degraded over time.

BAM, atrazine, and bentazone saw much lower removal at all examined waterworks after 5 days, compared with MCP and glyphosate. BAM and atrazine removal was only between 10-20% at five of the 10 examined waterworks with the rest having little to no observed removal. The largest mineralization potential for BAM and atrazine was approximately 6% and was only observed at one waterworks. Bentazone removal was between 10-18% at six of the waterworks, with 8 % mineralization observed at the same waterworks where mineralization of BAM and atrazine occurred. Although the removal and mineralization potential for BAM, atrazine, and bentazone are much lower and occur much less frequently than for MCP and glyphosate, some potential was still observed. This suggests that there are naturally occurring microorganisms that can biodegrade these compounds under the right conditions. Future research is needed in this area to determine if these microorganisms can be incorporated into engineered water treatment systems to provide a safe, reliable, and sustainable process for removing these unwanted compounds.

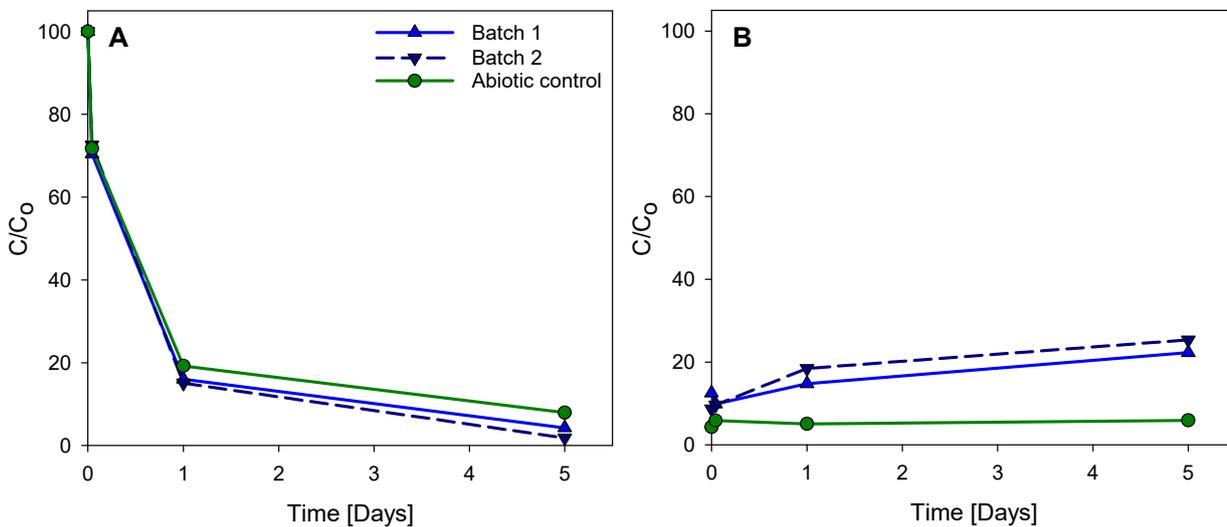


Figure 1: Removal of glyphosate in the water phase (A) and $^{14}\text{CO}_2$ production (B) at one of the selected waterworks. Batch 1 and 2 are duplicates while the third batch is the autoclaved, abiotic control.



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Conclusions

Preliminary results from the microcosms showed that:

- Pesticide degradation was widely observed at the 10 selected waterworks
- All pesticides showed some degradation
 - MCPP and Glyphosate were readily degraded at almost all waterworks, with high mineralization also observed at many of the waterworks
- Observed biodegradation of BAM, Atrazine, and Bentazone was also observed
 - Much less pronounced with little mineralization

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