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Testing the pesticide adsorption capacity of BWT drinking water filter

Testing adsorption of the pesticide desphenyl-chloridazon (DPC) by the AC100 filter

Report 120045

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Created for

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1. Description of the assignment and background knowledge

Description

This report has been created for BWT Denmark A/S. The report presents the results obtained during a long-term laboratory adsorption test on the pesticide desphenyl-chloridazon (DPC) by the active carbon filter AC100, sold by BWT Denmark A/S mainly to private households.

This report is a continuation of a previous experiment, where AC100 filters were tested for 3 months with DPC alongside another compound. Results of the initial experiment may be found in report No. 996743. Therefore, the results presented in this report start with week 12.

Background knowledge

DPC

Pesticides are synthetic substances used to control pests. Pesticides that control undesired weed growth are called herbicides. The herbicide *Chloridazon* was used in Denmark for agricultural purposes from the 1960's to 1996. After that, the purchase and application of Chloridazon was prohibited. The herbicide Chloridazon was, among others, used as a selective pesticide for weed control for production of, e.g., beets and onions.

The known degradation products of Chloridazon are DPC and Methyl-desphenyl-chloridazon (MDCP). The chemical structure of DPC is shown in Figure 1.

Figure 1 Chemical structure of DPC[1]

[1] Miljøstyrelsen, December 2020: MUDP rapport – Fjernelse af pesticider og chlorerede opløsningsmidler i vand.

Unfortunately, both DPC and MDCP can still be found in Danish groundwater, with a higher prevalence of the first mentioned. Therefore, DPC was incorporated in the Danish Groundwater Monitoring (GRUMO), a part of the National Monitoring and Assessment Program for the Aquatic and Terrestrial Environment (NOVANA). The DPC pesticide-residue became a part of the groundwater monitoring after a round of groundwater screening in 2017 by the Danish Environmental Protection Agency (EPA), as part of the GRUMO activities. In the mentioned groundwater screening, the DPC pesticide-residue was detected surprisingly in approx. 30 % of the investigated groundwater wells, where approx. 17 % of wells contained DPC concentrations exceeding the permissible criteria for the maximal pesticide occurrence in drinking water (0.1 µg/L)[2] . In the most recent groundwater campaign (2020), DPC was the most frequently found pesticide-residue in groundwater monitoring wells and second most frequently detected pesticide in water supply wells.

This clearly shows the importance that DPC is considered as a widespread problem in the Danish groundwater[3]. The map of Denmark (Figure 2) shows all the places where DPC has been detected above 0.1 µg/L in 2020.

[2] GEUS, 2021: appendix to groundwater report 2020. (Link: Grundvandsovervågning_omslag, 2016 copy (geus.dk))
[3] GEUS, 2021: groundwater report 2020. (Link: Grundvand 1989-2020 (geus.dk))

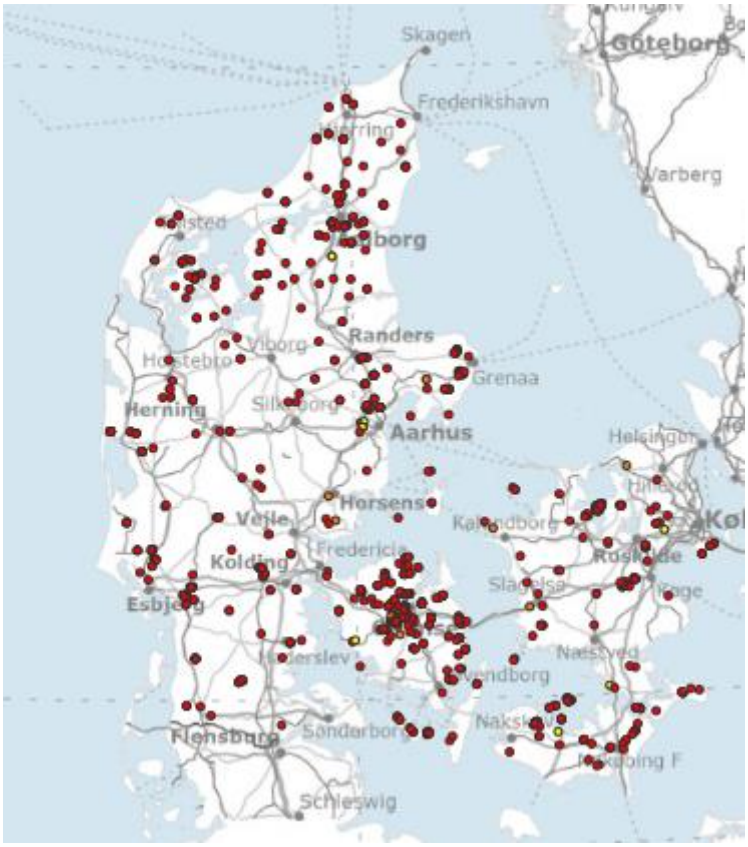


Figure 2 Map showing wells with DPC >0.1 µg/L from 2020[4]

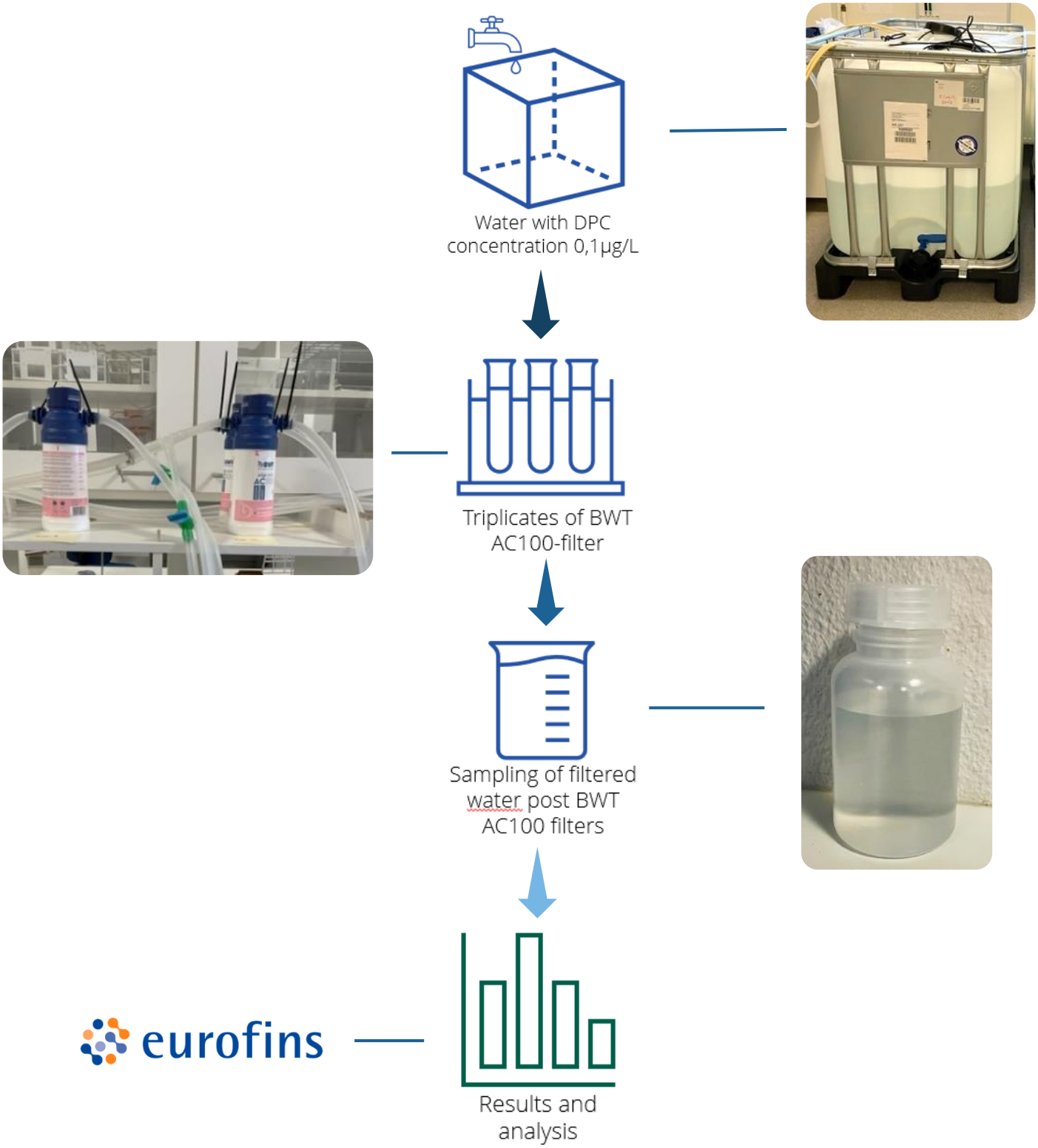
The nature of DPC molecule makes it possible to effectively remove DPC from drinking water by a range of activated carbons, UV-treatment and UV combined with hydrogen peroxide (H_2O_2), where the latter could produce unwanted biproducts. The application of an effective activated carbon directly adsorbs DPC from the water phase.

[4] GEUS – National boringsdatabase (Jupiter)

2. Methods

Flowchart

The flowchart demonstrates the experimental setup in the laboratory. A more detailed description of the individual parameters in the experimental design are given in the following sections.



Experimental setup

AC100 filters

BWT AC100 filters were setup in triplicates to ensure accuracy of the obtained results, detect any possible deviations in performance among investigated filters and ensure a reliable data interpretation. The investigated filters (Figure 3, left) were connected to the container containing tap water spiked with DPC to a concentration of 0.1 ug/l (Figure 3, right).

Water with DPC

To ensure a reliable amount of DPC, which the consumers can experience in real life, pure DPC (Sigma Aldrich) was added to drinking water in a container at a final concentration of 0.1 ug/L. The container volume was 600 L of tap water (Figure 3, right). Water and DPC was continuously added to the container as the water was pumped through the filters to obtain the desired DPC concentration (0.1 ug/L).

A desired DPC concentration of 0.1 ug/L was chosen to realistically insinuate the maximal DPC abundance in tap water, which the consumers can be exposed to. The drinking water regulations in Denmark indicate that the concentration of pesticides in drinking water, delivered to consumers and private households, must not exceed 0.1 ug/L. The threshold of 0.1 µg/L for a single pesticide-residue in drinking water is determined by the Danish Environmental Protection Agency (EPA). It is important to mention that both higher and lower concentrations of DPC can be detected in the Danish groundwater (the map shown in Figure 2 clearly illustrates the sites with a concentration of DPC above 0.1 µg/L in groundwater used for drinking water production).

Pumping water through the filters

To mimic the average consumption of drinking water in the kitchen of private households, an annual consumption of 5-6 m^3 was found to be realistic. This was set to 16,8 L per day to reach the 5-6 m^3/year.

The applied conditions in the laboratory tests aim to simulate “real life usage” of the filters in a best possible way. Therefore, a dose of 840 mL of the DPC-spiked tap water was run through each of the three filters, and dosing was performed 20 times a day using a pre-set automatic peristatic pump. The pump is shown in Figure 3. The duration of the experiment was 3 months.

Figure 3 Experimental setup. The container with water containing DPC is shown on the right, and the three filters (triplicates) (purple circle) and the pump (red circle) are displayed on the left. For close-up of the experiment, see "flowchart".

The outlet water from the filters was filtered once more through a large filter with activated carbon before the sewer system, to ensure full removal of all potential DPC residues.

Sampling

The buffer-capacity of AC100 filters is estimated to be approx. 450-500 mL. The peristatic pump pumped the water through the filters 20 times per day, with still periods of 58 min. between each active pumping, where the approx. 450-500 mL of water was retained in the filters, thereby having a long contact time with the filter.

To ensure that the water with a long contact period within a filter was not among the sampled water, 4 L of water from the container with DPC-spiked water was run through the filter before each sample collection. In this way, we ensured that the sampled water had a short contact time (approximately 20-30 seconds) with the activated carbon in the AC100 filters. By using water samples with a very short contact period within the filter, the experiment is expected to mimic "real life"-usage in private households.

The sampling procedure was as follows:

For each investigated filter upon a sampling point, 3 samples of 100 mL were taken with at least an hour in between. The obtained samples from a single filter were then pooled together, and a representative sample was sent to analyses to ensure an average measurement for these triplicate samples for each of the tested filters.

During the experimental period of 3 months, samples were collected 4 times, as indicated in the table below (Table 1).

Table 1 shows the weeks of the experiment where samples were collected.

Week of the experiment for sample collection
12
16
20
24

In addition to water samples after AC100 filter, the influent water (DPC spiked water from the container) was also sampled and sent to analysis for each sampling point. This was to reveal the exact DPC concentration in the water before the AC100 filters, and thus allowing to calculate the DPC reduction. These results were applied below when calculating the removal of DPC of the filters.

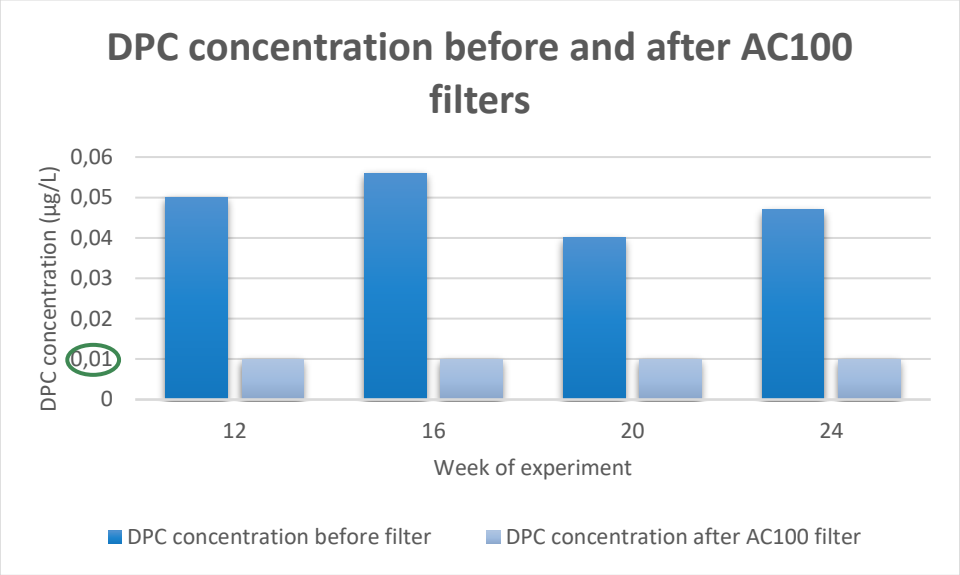
3. Results

All samples were sent to Eurofins for DPC analyses. Eurofins and other similar companies have a detection limit for most of the pesticides at 0.01 µg/L. Therefore, all samples with a concentration below 0.01 µg/L will be detected as <0.01 µg/L.

The results obtained from outlet water samples collected after AC 100 filters over a period of 3 months, show that the DCP concentrations in all outlet water samples were always below the detection limit of 0.01 µg/L. The detection limit is marked with a green circle in Table 2. Identical results were observed during the first 3 months of the experiment with the same AC100 filters, where all measurable DCP was removed from the inlet water (report No. 996743).

The influent water samples revealed that the average DPC concentration in this DPC spiked water from the container ranged from 0.04 ug/L to 0.056 ug/L (average: 0.048 µg DPC/ L).

Table 2 DPC concentration in the inlet and filtered water. Y-axis displays the DPC concentration (ug/L). X-axis displays the week of the experiment. The deep blue column is the DPC concentration in the inlet water before the filters. The light blue column is the DPC concentration in the water after filtering through AC100 filters. All samples after filtering were at the lowest possible measuring concentration (<0.1 ug/L).



The total amount of water (L) and DPC (ug) run though the filter

16.8 L of water was pumped daily through each of the tested filters, which on a weekly basis is equal to 117.6 L per filter. The amount of water run through each of the tested filters at each sampling time is displayed in Table 3 below. It is important to notice that the presented volumes include the volume of DPC-containing water run through the respective filters during the first 3 months of the experiment.

Table 3 shows the amount of water filtered through each AC100 filter for each 4 weeks of the experiment, when samples were collected.

Week of experiment	DPC-spiked water through the filters (L) of the respective week
12	1411.2
16	1881.6
20	2352
24	2822.4

Alongside the estimate of the total water volume run through a filter, the total load of DPC through the filters was estimated as well and is shown in Table 4 below. The total load of DPC per tested filter was calculated using a) the measured concentration of DPC in the influent water and b) the water volume run through the individual filter.

Table 4 shows the amount of DPC filtered through each AC100 filter for each 4 weeks of the experiment, when samples were collected.

Week of experiment	The amount of DPC (µg) filtered through the filters of the respective week
12	66.3
16	88.4
20	110.5
24	132.7

4. Summary

AC100 filters were tested for the adsorption of the pesticide DPC from drinking water. DPC concentration in inlet water was adjusted to the maximum concentration of drinking water the consumers can be exposed to according to drinking water regulative (<0.1 ug/L). Three AC100 filters were run in the laboratory for additional 3 months, after a previous and similar experiment testing the adsorption of DPC and other compounds. The amount of water run through each filter was 16.8 L/day for a total of 6 months, corresponding to an annual water consumption in the kitchen for up to 6 m^3/year and the expected lifetime of a filter.

The current and the previous test unanimously confirmed that under the test conditions described above, all tested AC100 filters (triplicates) were able to remove all measurable DPC from the inlet DPC-containing drinking water.

5. Appendix

This table shows the influent and outlet concentration before and after the application of AC100 filters. Standard deviation has been calculated.

Week	Influent concentration (µg/L)	Average outlet concentration from the filters (µg/L)	Standard deviation
12	0.05	<0.01*	0
16	0.056	<0.01*	0
20	0.04	<0.01*	0
24	0.047	<0.01*	0

*Concentrations below 0.01 µg/L cannot be measured.