

Water contamination with metabolites of the herbicide chloridazon and the possibility of their elimination in the technological process of water treatment

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ABSTRACT

Chloridazon was an herbicide used on sugar beet crops. Its use has been banned, but its metabolites chloridazon-desphenyl and chloridazon-methyl-desphenyl are still present in the environment. As they pose a threat to human health, the best method to remove them from the water must be found. The pilot research installation for the removal of chloridazon metabolites from water consisted of an ozone producing PROTEC 145 OZ UV lamp working at a dose of 400 to 4,000 J/m² and biological activated carbon filters (BACF). The content of metabolites during the removal process was determined by high-performance liquid chromatography coupled with tandem mass spectrometry. Based on the results of the research conducted for water contaminated with chloridazon metabolites, the possibility of reducing the concentration of chloridazon-desphenyl down to the limit of detection was confirmed. The results show that the UV lamp and BACF can be effective in removing organic pollutants from the water, but their efficiency depends on the type and concentration of the contaminants.

Keywords: Herbicides; Chloridazon; Chloridazon-desphenyl; Chloridazon-methyl-desphenyl; Metabolites; Water treatment; Water contamination

1. Introduction

In the modern world, the use of pesticides in agriculture is very common because it brings many benefits in terms of significantly improving the quality and quantity of crops produced. Pesticides are compounds that allow the control of weeds and pests that damage agricultural crops [1,2]. Worldwide, an average of 2 million tonnes of pesticides are used per year. The classification of pesticides is based on the target species and includes groups such as herbicides, insecticides, and fungicides. The most widely used pesticide groups are herbicides, whose use accounts for up to 47.5% of total pesticide consumption [3].

Pesticides used in agriculture can be very mobile in the environment and therefore can easily migrate to water, soil, or air. It is also important that pesticides decompose in the environment, and the resulting products of this decomposition can be dangerous and lead to contamination of, for example, surface waters and groundwater [1,4,5]. The pesticide contamination of aquatic environments is mainly caused by the runoff from agricultural fields and the inflow of industrial wastewater [3]. In the aquatic environment, pesticides can also appear due to the discharge of rainwater, as well as the return flow from irrigated fields. During precipitation, soluble pesticides can be carried away by water particles, which can cause their rapid transport to the soil

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zone, from where they eventually reach groundwater and then surface waters [1].

Drinking water contaminated with pesticides can adversely affect human health and cause cancer or neurological and reproductive disorders [6,7]. The previous Water Directive on the quality of water intended for human consumption 98/83/EC specified a maximum water concentration of each pesticide and its breakdown products of 0.1 µg/L for a single pesticide and 0.5 µg/L for the sum of all pesticides present in the sample [8]. In the new EU Directive 2020/2184 on the quality of water intended for human consumption, it is recommended to identify and monitor pesticides that may be present in the environment [9]. Pesticides are considered problematic in all countries of the European Union, as there is ample evidence that many water resources are contaminated with organic pesticides. Concern about the deterioration of water quality due to the presence of pesticides has resulted in the development of monitoring programs that cover these pollutants.

Chloridazon was registered for use before and after emergence to control weeds in sugar beet, beet, and feed crops. This herbicide was also registered for commercial use in ornamental plants, including bulbs and roses. Chloridazon (CHL) has known environmental transformation products that include chloridazon-desphenyl (CHLD) and chloridazon-methyl-desphenyl (CHLMD) as depicted in Fig. 1.

As a result of the potential risk, the monitoring of the presence of CHL and its metabolites CHLD and CHLMD in natural waters is carried out in many countries. Chloridazon and its metabolites have the potential to occur in surface and groundwater systems because of their persistence and solubility in water. The mobility and fate of these compounds in water can depend on various factors such as soil type, pH, temperature, and microbial activity. Controlling the occurrence of this herbicide has been carried out for some time, for example, in Italy, The Netherlands, Spain, or Germany [10–14].

Recently, the presence of one of the herbicides in groundwater and surface waters has attracted considerable interest among scientists. Chloridazon, an herbicide that inhibits the photosynthesis process of annual broad-leaved weeds [15–19] was used for the preemergence or early postemergence control of weeds in sugar beet crops [20]. Until 2020 chloridazon has been widely used because it was considered relatively harmless at the time. As mentioned above, chloridazon is degraded to form its two metabolites, CHLD and CHLMD. The exact proportions of these metabolites can depend on various factors, such as the conditions of

decomposition, the presence of the microbial population, and the pH of the environment. These metabolites are classified as mobile compounds because of their polarity and solubility; therefore, they can pollute surface and groundwater. The decomposition of chloridazon can occur through various mechanisms, such as photolysis, hydrolysis, and microbial degradation. Photolysis occurs when chloridazon is exposed to sunlight, and it breaks down into its constituent parts through a chemical reaction. Hydrolysis occurs when chloridazon is exposed to water and breaks down into its metabolites. Microbial degradation occurs when bacteria or fungi in the environment break down chloridazon into its metabolites. The rate and extent of decomposition can depend on various environmental factors, such as temperature, pH, soil type, and microbial activity. For example, higher temperatures and acid soils can increase the rate of decomposition, while low temperatures and alkaline soils can slow the decomposition process. Until 2020 CHL used in agriculture has decomposed and accumulated with its decomposition products in surface and groundwater, whose concentration cannot be ignored at the moment. It should be noted that the concentration of CHL in water in some parts of Europe reached 3.5 µg/L, significantly exceeding the allowed values. Furthermore, the main metabolite, CHLD, was present in natural water at a concentration of as high as 24.0 µg/L, while the other metabolite, CHLMD, was present at a concentration of 6.1 µg/L [16]. Due to persistence and mobility, pesticide metabolites in groundwater tend to occur more frequently and at higher concentrations than their parent pesticides. In recent years, pesticide degradation products have become a significant problem for water supplies, especially in countries with low regulatory limits. Pesticide metabolites, due to their higher polarity and lower volatility and biodegradability than their parent compounds, contribute to increased groundwater contamination [20]. The concentrations of chloridazon and its metabolites in water vary depending on several factors, such as the location and time of sampling and the type of water (e.g., surface water or groundwater).

In the Netherlands, the problem of pesticides in natural waters was already observed in the late 1990s. In 1998, trace concentrations of polar pesticides were determined in surface waters, among which chloridazon was also identified. 4.3 ng/L chloridazon was detected in the Amsterdam-Rhine canal in March 1998 and 70 ng/L chloridazon was detected in the Scheldt in July 1998 [10,11].

An analysis of the presence of chloridazon in water was also carried out in South America. Barra et al. [12] published a paper on forecasting the influx of chloridazon to surface

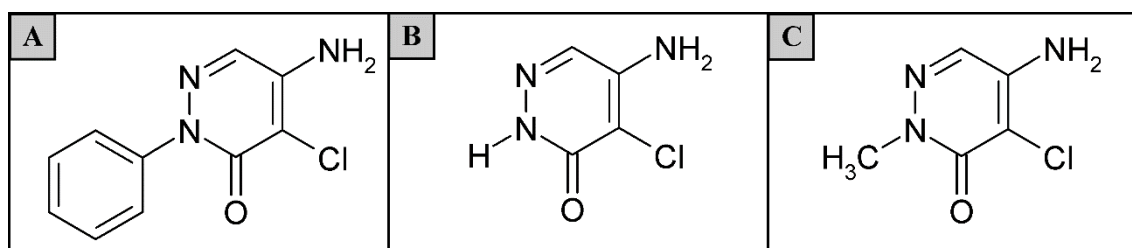


Fig. 1. Chemical structure of (A) chloridazon, (B) chloridazon-desphenyl and (C) chloridazon-methyl-desphenyl.

waters from an agricultural catchment in Chile. The area analyzed in the publication was the Tijeral River basin catchment area, located in the Biobio basin. Surface water samples were taken from the entire area at the outlet from the catchment. As a result of the investigation, the chloridazon concentration at the outlet of the analysed basin ranged from 430 to 1,380 ng/L.

In Italy in 2007, Carafa et al. [13] analyzed seasonal fluctuations of selected herbicides and their metabolites in water. Five seasonal sampling campaigns were conducted between May 2004 and May 2005. As a result of the investigation, one of the pesticides detected was chloridazon. Its concentration in Sacca di Goro in the coastal lagoon was determined on average at 15.3 ± 28.1 ng/L (maximum 101.5 ng/L), while in water samples from the Adriatic Sea, the chloridazon concentration was determined on average at 9.6 ± 16.2 ng/L (maximum 40.6 ng/L).

Research by Loos et al. [15] showed the first European survey of the occurrence of polar organic substances in groundwater, including chloridazon metabolites. 164 groundwater samples were tested from 23 European countries. Chloridazon-desphenyl was detected in 26 water samples above the European groundwater quality standard, and chloridazon-methyl-desphenyl was detected in 6 samples.

The La Rioja region in northern Spain is a region characterized by intensive agricultural activity, with areas mainly occupied by cereals, vineyards, olives, and fruit trees. In 2011, it was the sixth Spanish region in terms of pesticide use per hectare, at 14 kg/ha. Herrero-Hernández et al. [14] in their publication conducted a study on the analysis of the presence of 22 commonly used herbicides, 8 of their main degradation products, and 8 insecticides in La Rioja vineyard areas. This monitoring covered 12 surface waters and 78 groundwaters, covering the three subareas into which this vineyard region is divided: Rioja Alavesa (ALV), Rioja Alta (ALT), and Rioja Baja (BAJ). Water samples were collected in four campaigns: September 2010, March 2011, June 2011 and September 2011. In the area of La Rioja Alavesa, chloridazon was detected only during the June 2011 campaign, at an average concentration of 0.026 µg/L. In the La Rioja Alta subarea, chloridazon was detected in two campaigns. In the June 2011 campaign, its concentration reached an average of 0.033 µg/L, while in the September 2011 campaign, the average chloridazon concentration in the samples was 0.020 µg/L. In the area of La Rioja Baja, during the June 2011 campaign, chloridazon reached an average concentration of 0.034 µg/L, the highest of all the cases analyzed. In contrast, in the September 2011 campaign, chloridazon reached an average concentration of all 40 samples of only 0.007 µg/L.

Hintze et al. [20] investigated the effect of interactions between groundwater and surface water on the distribution of pesticide metabolites in groundwater. Research focused on CHL and its two metabolites, CHLD and CHLMD. The research was carried out in 2017–2019 in Switzerland, where the alluvial plain was equipped with 20 monitoring wells to characterize the spatial distribution of CHL and its metabolites in the aquifer. For groundwater, each sampling campaign consisted of 11 to 23 groundwater sampling points. The concentration detected in the case of groundwater ranged from 0.0060 to 0.2 µg/L. The concentration of CHL

above the allowed value occurred mainly in the canal and in monitoring wells along the canal. CHLD and CHLMD were detected in 90% and 95% of groundwater samples. The CHLD concentration was up to 2.3 µg/L and the CHLMD concentration was lower, reaching the value of 0.85 µg/L. The research carried out allowed the conclusion that the introduction of metabolites through interactions of surface water with groundwater can affect not only the spatial distribution of metabolites in groundwater but also the long-term dynamics of the spread of metabolites in groundwater and pumping wells, after discontinuing the use of parent pesticides. However, surface waters can also reduce metabolite concentrations through interactions with, for example, rivers of mountain area catchments [20].

Chloridazon metabolites are not considered active herbicides as they do not have significant herbicidal activity. Instead, they are products of chloridazon degradation that result from chemical and biological processes in the environment. Their presence in water bodies can serve as an indicator of chloridazon use and degradation and can be used to assess the overall environmental impact of the herbicide. Therefore, chloridazon metabolites are typically included in pesticide monitoring programmes in water, which are established by regulatory authorities to ensure that water quality standards are met and to protect human health and the environment from potential adverse effects of pesticide contamination. Although CHL metabolites are not active as herbicides, they should be monitored and the best way to remove them from drinking water should be found, as their accumulation and prolonged persistence in water can pose a potential risk to human health. In Table 1 the chosen technological processes that allow the removal of chloridazon and its metabolites from water, along with their effectiveness, are presented.

Despite the fact that there are technological processes that enable the removal of chloridazon and its metabolites from water, unfortunately, they cannot always be used at the water treatment plant. Therefore, it is necessary to develop a technology to remove CHL and its metabolites from water intended for human consumption, which will be characterized by high efficiency and relatively low operating cost.

The purpose of the research discussed in this article was to check the possibility of removing organic compounds from water, in particular the metabolites of the herbicide CHL, using UV radiation and biologically active carbon filters.

2. Methods

The research was carried out on a pilot scale. The research installation consisted of two processes of water treatment. The first device of the research installation was the PROBIKO-AQUA UV PROTEC 145 OZ lamp capable of operating in the dose range of 400 to 4,000 J/m², while the second device consisted of an activated carbon filter column. The entire UV lamp system consists of a UV reactor and a control cabinet. The UV reactor, made of stainless steel, had two mounting options: horizontal and vertical. During the research, the UV lamp in the research installation was mounted in a horizontal position. The UV reactor

Table 1
Chosen processes that have been reported to allow the removal of chloridazon and its metabolites from water

Process	Description	Reported effectiveness	Source
Adsorption on graphene oxide	Adsorption of contaminants onto surfaces	Chloridazon 42.5%–44.9%; Chloridazon-methyl-desphenyl 23.6%–26.1%; Chloridazon-desphenyl 16.7%–19.2%.	[16]
Adsorption on natural and ammonium kerolite	Adsorption of contaminants onto surfaces	Adsorption capacity at natural kerolite at 25°C – 11×10^{-2} mol/kg; Adsorption capacity at ammonium kerolite at 25°C – 13×10^{-2} mol/kg Fenton oxidation – chloridazon; at 10, 20 and 20 mg/L > 99% at 60 min; at 60 mg/L 64% at 60 min;	[17]
Advanced oxidation processes	Removal by Fenton and photo-Fenton oxidation	Photo-Fenton oxidation – chloridazon; at 20 mg/L > 99% at 5 min; at 40 mg/L 81% at 5 min; at 60 mg/L 57% at 5 min.	[21]
Advanced oxidation processes	Removal by oxidation in a UV/H ₂ O ₂ system. Generation of free, highly reactive hydroxyl radicals	Chloridazon – 100%	[22]
Photodegradation	Removal of contaminants by exposure to UV radiation	Chloridazon – below 100%	[22]
Biodegradation	Removal of contaminants by microorganisms	Chloridazon – 100%; Chloridazon-desphenyl (formed in the degradation process) – resistant to biodegradation.	[10]

is equipped with one low pressure radiator with a power of 45 W and a life of 12,000 h. The required temperature of the medium flowing through the UV reactor should be in the range of 0.5°C–40°C. The PROTEC 145 OZ lamp by PROBIKO-AQUA is a specific lamp as it is capable of producing ozone and removing organic compounds from water. The water that flowed through the UV reactor was fed to the biological activated carbon filters (BACF) pilot installation of a biological activated carbon filter consisting of a column of activated carbon filter WG-12. This filter was biologically active; it had been used continuously since 2015 [23,24]. The internal diameter of the BACF column was 100 mm. The adsorbent was placed on a 22 cm gravel support layer and its total height in the filter was 2.0 m. The filter medium was granular activated carbon (GAC) – WG-12 (Gryfskand Ltd., Poland) made from low-ash coal, connected by a binder and activated by water vapor (iodine quantity: 1,100 mg/g, methylene blue adsorption: 0.30 g/g, specific surface area (BET): 1,100 m²/g, particle size: 0.75–1.5 mm). The supporting layer was made of gravel quartz. The 140-mm diameter tube was the water jacket of the BACF column. The task of the water jacket is to maintain a constant temperature throughout the height of the bed, through the continuous flow of water from the bottom up, at the same temperature as the filtered water temperature. There are five nozzles to take water samples along the entire height of the column and five nozzles to collect samples from the bed elsewhere. The test stand was covered throughout the research period with black geotextile to prevent the development of algae in the filter bed. The water samples were taken at a depth

of 35, 75, 115, 155, and 195 cm. Fig. 2 shows a diagram of the pilot installation used in the investigation on the possibility of removing the herbicide metabolites of CHL from the water. The test installation includes seven sampling points: in front of the UV lamp, behind the UV lamp, and five connectors at different depths of the filter column. During the study, three waters intended for human consumption were used – one uncontaminated without chloridazon metabolites (Poznan tap water), and two waters in which the presence of chloridazon metabolites was detected (waters A and B).

In all of these waters, basic quality parameters were tested, such as pH, temperature, oxygen content, redox potential, alkalinity, chemical oxygen demand (COD), and total organic carbon (TOC). The results are given in Tables 2–4. These waters were also analyzed for the presence of CHL, CHLD, and CHLMD. None of these compounds was found in tap water. Water A contained only CHLD at 0.119 ± 0.042 µg/L. Water B contained CHLD at 0.768 ± 0.269 µg/L and CHLMD at 0.104 ± 0.042 µg/L.

The following physical and chemical analyzes of water quality were performed in the collected water samples: pH, temperature, dissolved oxygen, redox potential, total alkalinity of the water, COD (KMnO₄), TOC, determination of CHL and its metabolites. The temperature, pH, dissolved oxygen, and redox potential were determined using the Elmetron CX-401 multifunction meter. The total alkalinity of the water was determined by a titration method in accordance with PN-EN ISO 9963-1: 2001. COD (KMnO₄) was determined by the titration method according to the PN-EN ISO 8467:

LEGENDA:

- 1 - Collection point before UV lamp
- 2 - Collection point after UV lamp
- 3 - Collection point BAF 1 (35 cm)
- 4 - Collection point BAF 2 (75 cm)
- 5 - Collection point 3 (115 cm)
- 6 - Collection point 4 (155 cm)
- 7 - Collection point BAF 5 (195 cm)
- 8 - A rotameter that measures the flow rate of incoming water
- 9 - A rotameter that measures the flow rate of water through a BAC

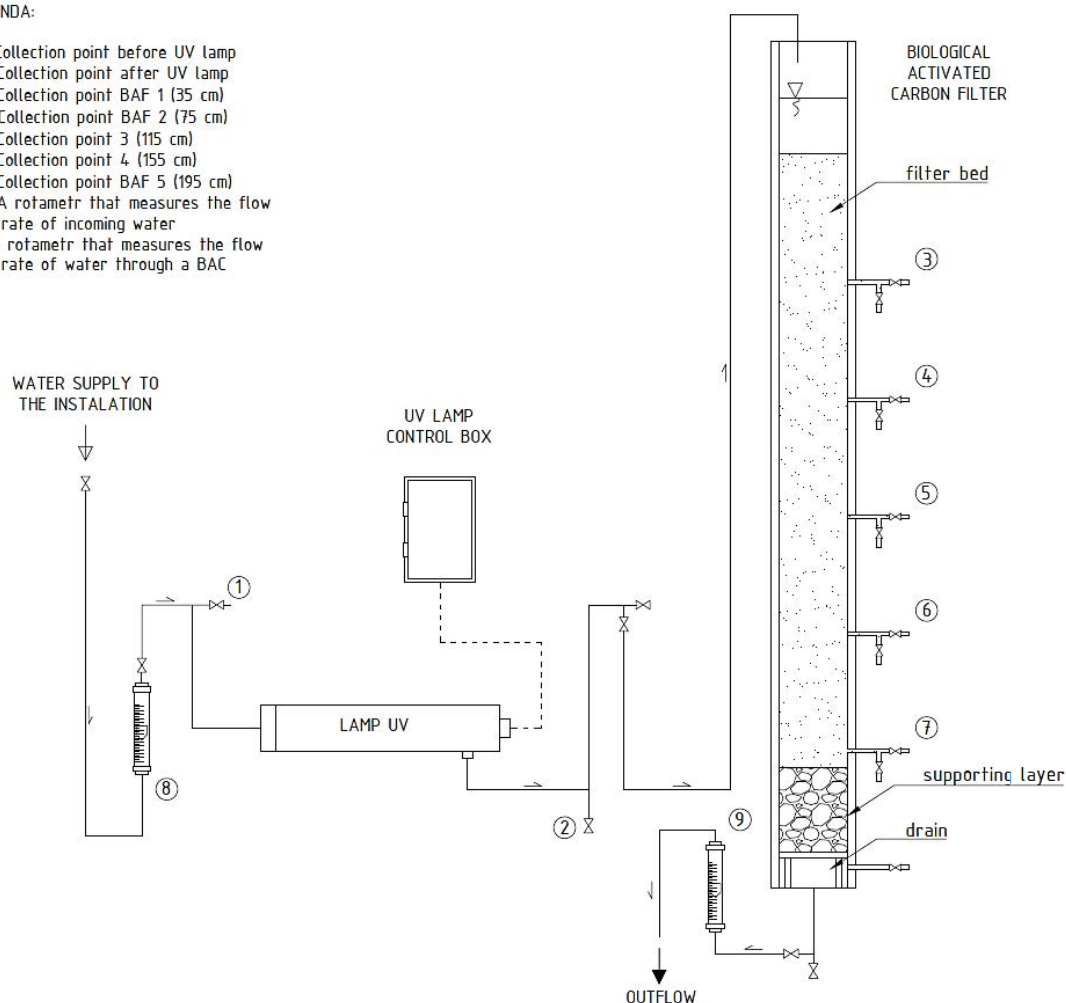


Fig. 2. Diagram of a research installation to remove chloridazon metabolites from water.

Table 2
Quality of tap water not contaminated with chloridazon metabolites

Parameter	Minimum value	Maximum value	Average value	Standard deviation
pH	7.4	7.66	7.52	0.099
Temperature, °C	11.0	18.9	15.7	3.3
Oxygen, mg-O ₂ /L	6.54	8.27	7.20	0.678
Redox potential, mV	224.6	359.3	258.8	59.8
Alkalinity, mval/L	3.4	3.55	3.46	0.045
COD (KMnO ₄), mg-O ₂ /L	2.81	4.02	3.58	0.385
TOC, mg-C/L	5.65	7.91	6.44	0.908
CHL, µg/L	nd	nd	nd	nd
CHLD, µg/L	nd	nd	nd	nd
CHLMD, µg/L	nd	nd	nd	nd

nd – not detected

2001 standard. TOC was determined using the Analytik Jena Multi N/C carbon analyzer. The purge method was used for the determination in the non-purgeable organic

carbon (NPOC) analysis that detects TOC in the sample. A 40 mL sample of water was acidified with 200 µL of 2 M HCl (pH = 2) outside the analyzer. CHL and its metabolites

Table 3
Quality of water A contaminated with chloridazon metabolites

Parameter	Minimum value	Maximum value	Average value	Standard deviation
pH	7.51	7.97	7.81	0.263
Temperature, °C	10.0	20.0	15.5	5.1
Oxygen, mg·O ₂ /L	6.43	7.16	6.84	0.374
Redox potential, mV	298.2	348.4	320.7	25.5
Alkalinity, mval/L	5.03	5.05	5.04	0.012
COD (KMnO ₄), mg·O ₂ /L	1.14	1.28	1.21	0.068
TOC, mg·C/L	1.78	3.58	2.52	0.941
CHL, µg/L	nd	nd	nd	nd
CHLD, µg/L	0.119	0.193	0.119	0.042
CHLMD, µg/L	<0.050	<0.050	<0.050	<0.050

nd – not detected

Table 4
Quality of water B contaminated with chloridazon metabolites

Parameter	Minimum value	Maximum value	Average value	Standard deviation
pH	7.30	7.68	7.48	0.191
Temperature, °C	10.0	19.6	15.3	4.9
Oxygen, mg·O ₂ /L	6.36	7.27	6.86	0.463
Redox potential, mV	293.7	355.5	321.6	31.3
Alkalinity, mval/L	6.05	6.13	6.09	0.038
COD (KMnO ₄), mg·O ₂ /L	1.19	1.35	1.27	0.080
TOC, mg·C/L	0.90	2.43	1.72	0.773
CHL, µg/L	nd	nd	nd	nd
CHLD, µg/L	0.714	1.260	0.768	0.269
CHLMD, µg/L	0.104	0.138	0.104	0.042

nd – not detected

CHLD and CHLMD were determined using the UltiMate 3000 HPLC high-performance liquid chromatograph from Dionex (Sunnyvale, CA, USA) coupled with a 4000 QTRAP mass spectrometer from ABSciex (Foster City, CA, USA). For determination, a Kinetex Evo C18 column (150 mm × 2.1 mm, 2.6 µm) from Phenomenex (Torrance, CA, USA) was used that was thermostated at 35°C. The water samples before injection (25 µL) were diluted 9:1 v/v with acetonitrile. A gradient analysis of the mobile phases of A (0.1% formic acid) and B (acetonitrile) was used with a constant flow of 0.3 mL/min. The amount of component B in the phase mixture was changed as follows: 0 min. 10% B, 1 min. 10% B, 1.5 min. 100% B, 4.1 min. 100% B. The eluate from the column was directed to the mass spectrometer source. The electrospray source operating in positive ion generation mode was used. Nitrogen was supplied to the source and spectrometer at a pressure of 10 psi (as the curtain gas), 40 psi (as the nebulizer gas), 45 psi (as the auxiliary gas). The source was operated at a temperature of 450°C and a voltage of 4,500 V. CHL was determined at declustering potential (DP) 140 V and collision energy (CE) 32 eV using the 222 to 104 m/z transition. CHLD was determined at DP 100 V and CE 30 eV using the 146 to 117 m/z transition. CHLMD was determined at DP 125 V and CE 42 eV using the 160 to 88 m/z transition.

3. Results and discussion

Figs. 3 and 4 show changes in TOC content during tap water flow and water contaminated with CHL metabolites through a UV lamp.

Based on the analysis of changes in the concentration of TOC in tap water irradiated with a UV lamp, it can be concluded that the lamp used in the research installation works correctly because a decrease in the concentration of TOC was found in each analyzed case (Fig. 3). The maximum reduction in TOC was observed on the 9th day of the installation operation for a flow of 300 L/h, which was identical to the maximum radiation dose of 4,000 J/m². At that time, the efficiency of TOC reduction was 32%, which in this case was a reduction in TOC by more than 2.5 mg/L. According to the lamp manufacturer, the maximum radiation dose can be achieved with a flow of 635 L/h or less. However, at a flow of 250 L/h, which was maintained from day 15 to day 43, poorer effects of TOC removal from the water were observed. For this flow, the efficiency was in the range of 9.5%–13%.

In the case of water contaminated with CHL metabolites, a decrease in TOC concentration was also observed after the use of a UV lamp (Fig. 4). In water A, CHL metabolites

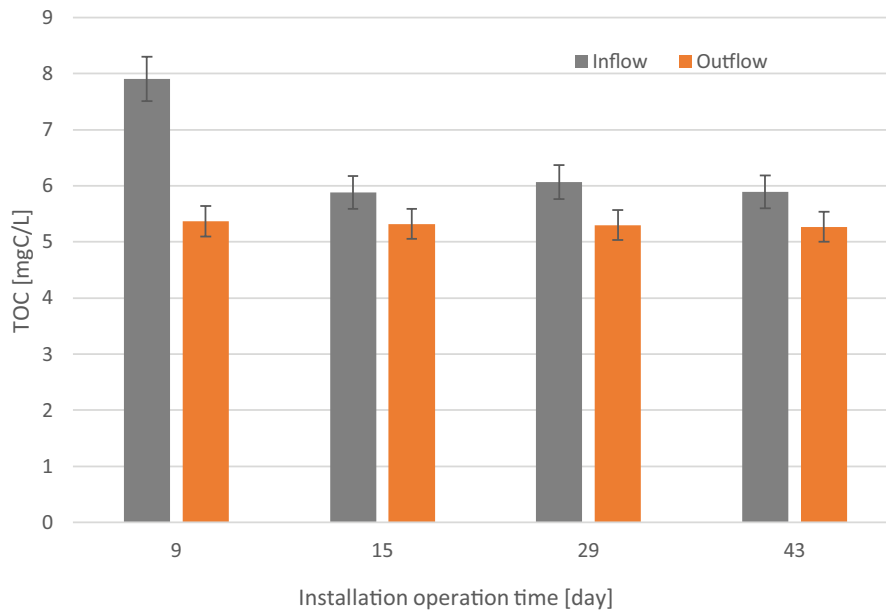


Fig. 3. Changes in total organic carbon after running tap water not contaminated with chloridazon metabolites through UV radiation ($Q = 300$ L/h for the ninth day; $Q = 250$ L/h for the remaining days; $D = 4,000$ J/m²).

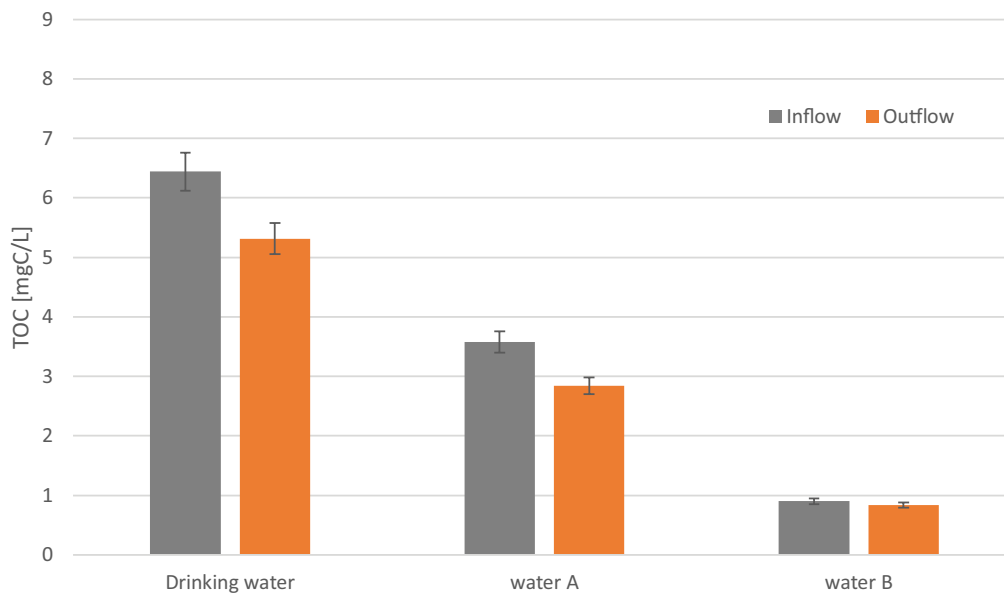


Fig. 4. Changes in total organic carbon concentration after the flow of tap water and waters contaminated with chloridazon metabolites through UV radiation ($Q = 400$ L/h; $D = 4,000$ J/m²).

represented approximately 5% of TOC. After exposure to a radiation dose of 4,000 J/m², an average reduction of approximately 21% of the TOC concentration was observed, that is, 0.74 mg·C/L. Unfortunately, because of the very low concentration of CHL metabolites in water, it is not possible to determine which part of the removed TOC was due to their removal. The obtained results confirm that the lamp works to remove organic pollutants from the water.

In the case of water B, the concentration of the determined metabolites was higher than that in water A, while the TOC was significantly lower. The CHLD concentration

was approximately 44% TOC, while the CHLMD concentration was approximately 6% TOC. Undoubtedly, the decrease in TOC was related to the removal of the CHLD metabolite from the water, because at its high concentration in water B, it was possible to demonstrate its reduction to the limit of its quantification. Studies have shown a significantly lower effectiveness of TOC concentration reduction (Fig. 4), which was undoubtedly related to a different type of organic matter. For the radiation dose of 4,000 J/m², approximately 7% of organic matter was removed, that is, 0.065 mg·C/L, from the water.

Figs. 5 and 6 show changes in TOC content in the cross-section of biologically active carbon filters for tap water and water contaminated with CHL metabolites, respectively.

A decrease in the concentration of TOC was found in the outflow of the biologically active carbon filter (Fig. 5). The best TOC removal effect was observed at a depth of 35 cm of the BACF bed.

In the case of water contaminated with CHL metabolites subjected to UV radiation (Fig. 6) for water A, the concentration of TOC at a depth of 35 cm of the filter slightly increases compared to the inflow. However, a downward trend was observed during the flow of this water into the BACF. For a depth of 155 cm, the TOC concentration is

reduced by 1.7 mg/L, indicating the removal of organic compounds through the carbon filter.

For water B, the value of TOC concentration increases deeper into the filter bed. The value obtained at a depth of 195 cm compared to the tributary increased by approximately 39%. In a case of water B, the lack of efficiency in reducing TOC was observed during filtration through the filter bed. Due to suspicion that the A and B metabolites of CHL present in water could cause partial inactivation of BACF bacteria, the Eberhardt, Madsen and Sontheimer index (EMS) was calculated, which informs about the process taking place in biologically active carbon filters. The index value is calculated based on the ratio of COD and dissolved oxygen losses [25]. The indicator allows for the evaluation

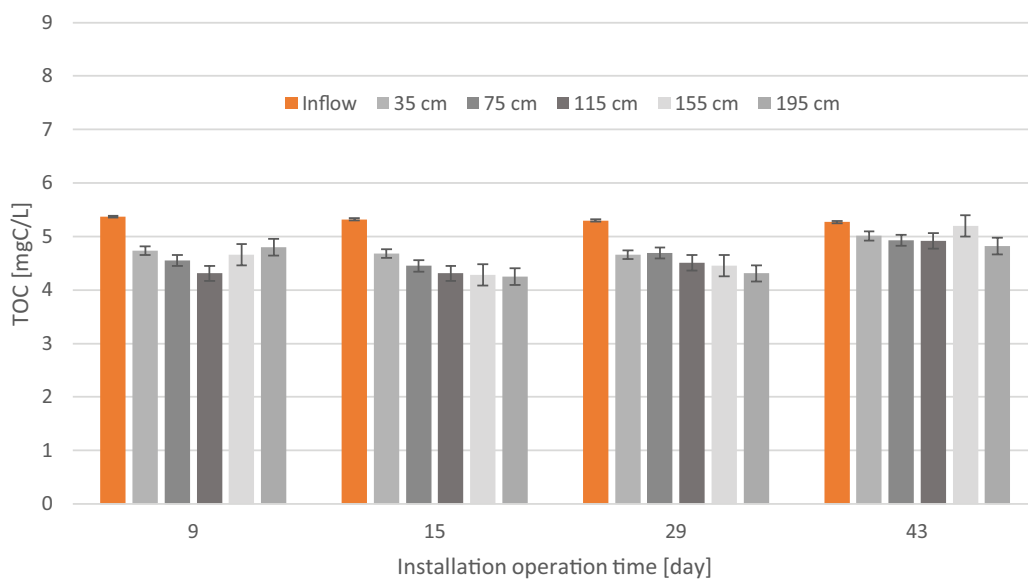


Fig. 5. Changes in total organic carbon in the BACF cross-section after the flow of tap water exposed to UV radiation ($Q = 400$ L/h; $D = 4,000$ J/m²).

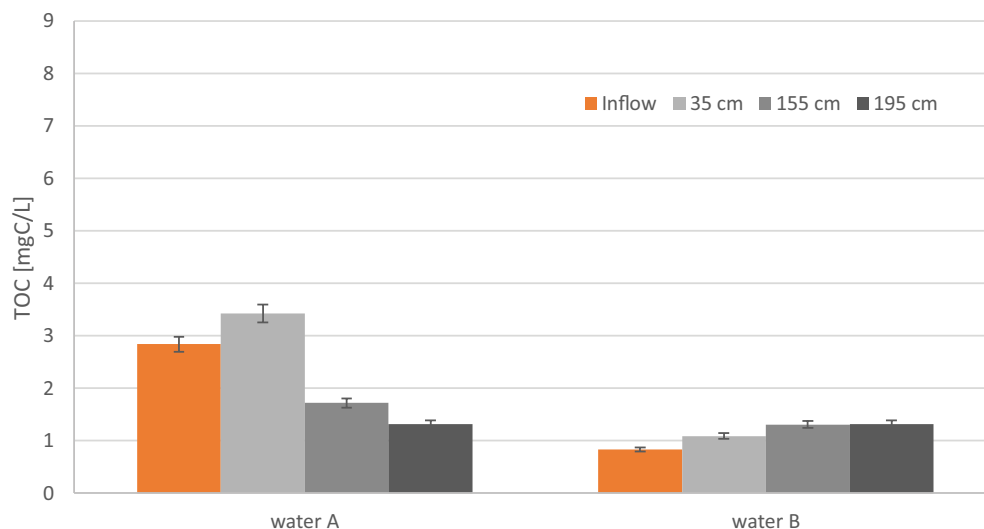


Fig. 6. Changes in total organic carbon in the BACF cross-section after the flow of water contaminated with chloridazon metabolites exposed to UV radiation ($Q = 400$ L/h; $D = 4,000$ J/m²).

of the development of microbiological activity in filters and the evaluation which of the sorption or biodegradation processes is dominant. It is calculated from the formula:

$$EMS = \frac{\Delta COD}{\Delta O_2} [-]$$

where ΔCOD – change in COD in samples taken at the input and exit of the filter ($mg \cdot O_2/L$); ΔO_2 – change in the concentration of the concentration of the concentration of dissolved oxygen in samples taken at the input and exit of the filter ($mg \cdot O_2/L$).

Due to the value of the indicator obtained, the following can be distinguished:

- EMS = 1 – the same intensity of sorption and biodegradation;
- EMS < 1 – the biodegradation process predominates;
- EMS > 1 – the sorption process predominates;
- EMS = 0 – neither sorption nor biodegradation occurs.

The EMS index values obtained for tap water and water contaminated with CHL metabolites are presented in Figs. 7 and 8.

When analyzing the EMS coefficients obtained for tap water exposed to the UV radiation, it was observed that the biodegradation process took place throughout the installation operation (EMS < 1). Therefore, the organic compounds contained in this water were decomposed by

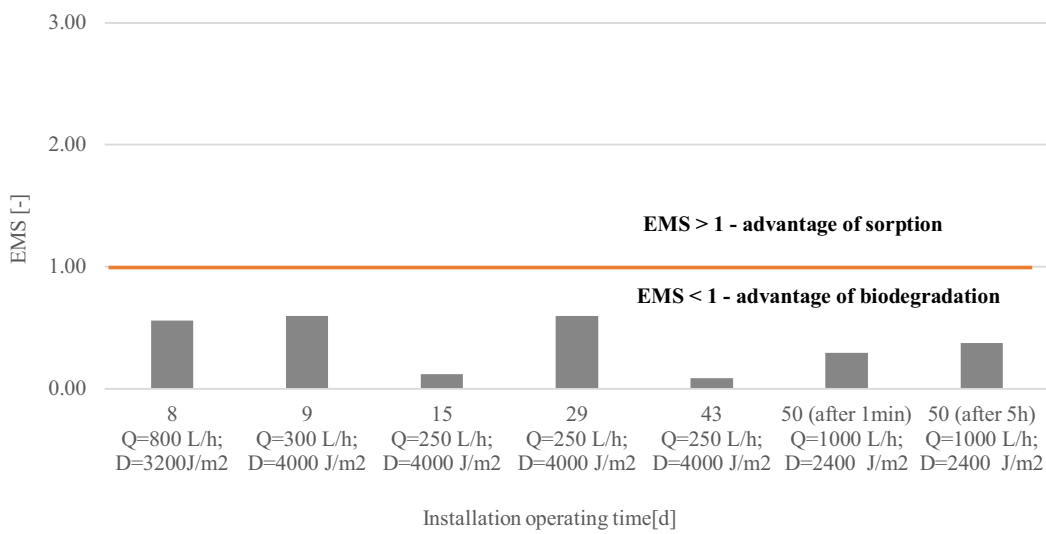


Fig. 7. EMS index for tap water treated with a UV lamp ($Q = 400 \text{ L/h}$; $D = 4,000 \text{ J/m}^2$).

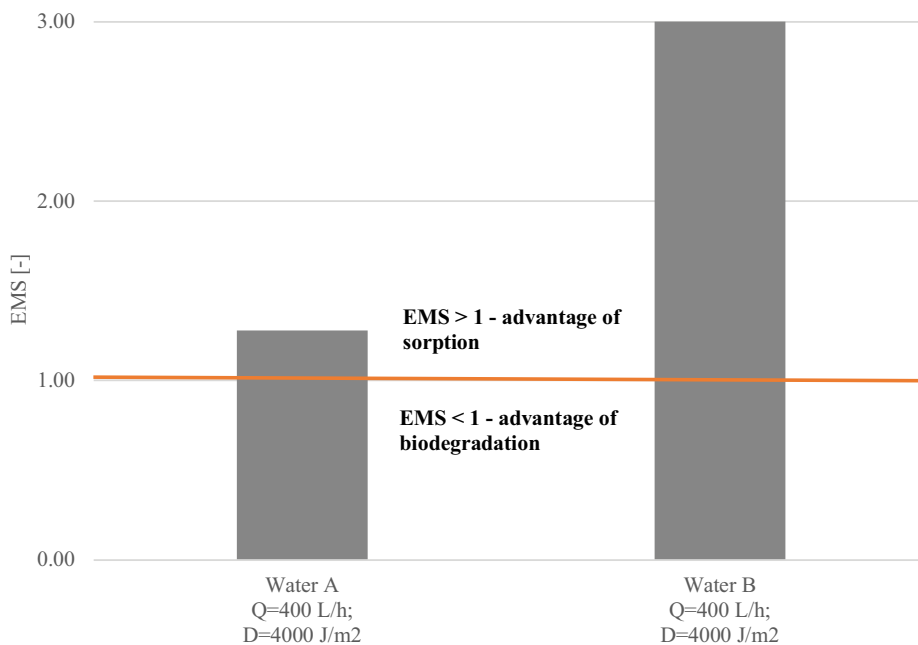


Fig. 8. EMS index for water contaminated with chloridazon metabolites exposed to a UV lamp ($Q = 400 \text{ L/h}$; $D = 4,000 \text{ J/m}^2$).

microorganisms that create a biofilm in the carbon filter bed. Biologically active carbon filters are an effective technology for the removal of organic compounds from water. BACF consist of activated carbon beds that support the growth of microorganisms. These microorganisms break down organic compounds through biodegradation, whereas adsorption by activated carbon enhances the removal of organic compounds from the water. Biodegradation in BACF occurs due to the presence of various types of microorganisms, including bacteria, fungi, and protozoa. The specific types of microorganisms present depend on the type of organic compounds in the water, the nature of the activated carbon and the environmental conditions within the filter. For example, the presence of certain nutrients, such as nitrogen and phosphorus, can promote the growth of bacteria that degrade specific types of organic compounds. The effectiveness of biodegradation in BACF can be influenced by various disruptors, including changes in temperature, pH, and dissolved oxygen levels. The presence of toxic compounds or other inhibitory substances can also reduce the effectiveness of biodegradation [25–28].

Adsorption is another mechanism by which organic compounds are removed from BACF. Activated carbon has a high surface area and porosity, which allows it to adsorb a wide range of organic compounds from water. Adsorption is influenced by the type of activated carbon used, its surface area, and the pore size distribution. Furthermore, the presence of microorganisms in the filter can enhance adsorption by forming biofilms on the activated carbon surface [25–28].

In the case of waters A and B contaminated with CHL metabolites exposed to a UV lamp, the sorption process prevailed in the carbon filter bed ($EMS > 1$). In the case of water A, as shown above (Fig. 6), there was a reduction in TOC, probably indicating the adsorption of organic compounds present in the water by a biologically active carbon filter.

In the case of water B, the EMS coefficient is approximately 2.5 times higher. For water B, an increase in both TOC and COD ($KMnO_4$) was observed. The increase in TOC indicates that the content of organic compounds increased with the flow through the filter. This could be due to the death of microorganisms in the BACF bed and the detachment of the biological membrane due to the deleterious effects of the herbicide and its metabolites.

In Table 5, the average concentrations of CHL and its metabolites determined in the samples of water flowing through the research installation are presented.

In the case of both analyzed waters (A and B) contaminated with CHL metabolites, the values obtained are mostly below the quantification limits (Table 6) and no CHL and metabolites were detected in tap water. The limit of quantification and the detection limit for the equipment used in the laboratory have been determined. The results of samples A and B of the water were compared with those obtained in a certified laboratory, which were made available by the company from which the contaminated waters come from.

Water A was analyzed in our laboratory for the presence of CHL, CHLD and CHLMD, but none of these substances were determined (Table 5). The reliability of these results

was confirmed by the fact that they are consistent with those obtained in a certified laboratory, where CHL and CHLMD were also not reported and for CHLD a concentration of $0.119 \pm 0.042 \mu\text{g/L}$ was determined that is below the detection limit of our method. Additionally, for all samples analyzed taken at different points of installation for water A, the quantification limit was not exceeded at any point for CHL or its metabolites.

The results obtained in our laboratory for water B showed CHLD and CHLMD below their quantification limits (i.e., $<0.21 \mu\text{g/L}$ and $<0.13 \mu\text{g/L}$) while CHLD was determined at $0.604 \pm 0.067 \mu\text{g/L}$. These results were similar to those reported by the certified laboratory, where CHLD was found at $0.768 \pm 0.269 \mu\text{g/L}$ and CHLMD at $0.104 \pm 0.042 \mu\text{g/L}$, while CHL was below the reporting limit (Table 5). Furthermore, for all analyzed samples of water B taken at different points of the installation, the limit of quantification was not exceeded at any point for these compounds.

Table 5

Average concentrations of chloridazon and its metabolites in water samples as they flow through the test facility (CHL – chloridazon, CHLD – chloridazon-desphenyl, CHLMD – chloridazon-methyl-desphenyl, SD – standard deviation)

Sample	CHL \pm SD	CHLD \pm SD	CHLMD \pm SD
Water A			
Water inlet ^a	<0.05	0.119 ± 0.042	<0.05
Water inlet ^b	<0.21	<0.59	<0.04
AFTER UV (400 L/h)	<0.21	<0.59	<0.04
AFTER BACF 35 cm	<0.21	<0.59	<0.13
AFTER BACF 155 cm	<0.21	<0.59	<0.04
AFTER BACF 195 cm	<0.21	<0.59	<0.04
Water B			
Water inlet ^a	<0.05	0.768 ± 0.269	0.104 ± 0.042
Water inlet ^b	<0.21	0.604 ± 0.067	<0.13
AFTER UV (400 L/h)	<0.21	<0.59	<0.13
AFTER BACF 35 cm	<0.21	<0.59	<0.13
AFTER BACF 155 cm	<0.21	<0.59	<0.13
AFTER BACF 195 cm	<0.21	<0.59	<0.04

^acertified laboratory; ^blocal laboratory.

Table 6

Comparison of reporting limits for the analytical methods used in the certified^a and local^b laboratories (CHL – chloridazon, CHLD – chloridazon-desphenyl, CHLMD – chloridazon-methyl-desphenyl)

Analyte	Reporting limit ($\mu\text{g/L}$) ^a	Limit of quantification ($\mu\text{g/L}$) ^b	Limit of detection ($\mu\text{g/L}$) ^c
CHL	0.05	0.21	0.06
CHLD	0.05	0.59	0.18
CHLMD	0.05	0.13	0.04

The lack of analytical possibilities to determine very low concentrations of chloridazon and its metabolites in water after the use of UV radiation and carbon filters does not allow one to determine the effectiveness of the technological processes used. Studies have shown that among the water analyzed, the highest concentration of CHL metabolites appeared in water B, indicating the possible cause of the inactivation of microorganisms in the column of BACF and resulting in the increase in TOC observed in Fig. 6.

4. Conclusions

- The results show that the UV lamp and BACF can be effective in removing organic pollutants from water, but their efficiency depends on the type and concentration of the contaminants.
- The PROTEC 145 OZ lamp is a lamp capable of removing organic compounds from water and works well with a properly selected dose of radiation. This fact is confirmed by the results obtained for the determination of total organic carbon in the water samples analyzed taken upstream and downstream of the UV lamp. In the case of tap water, a decrease in TOC concentration was observed after using a UV lamp, with a maximum reduction of 32% for a flow of 300 L/h and radiation dose of 4,000 J/m².
- For water contaminated with CHL metabolites, the average reduction in TOC concentration was 21% for water A and 7% for water B. The efficiency of TOC removal was better in the outflow of the BACF, with the best effect observed at a depth of 35 cm. However, for water B, the TOC concentration increased deeper into the filter bed, indicating the partial inactivation of BACF bacteria by CHL metabolites. The EMS index value indicated that the sorption process dominated in this case.
- In the case of tap water treated with the PROTEC 145 OZ UV lamp, flowing through BACF, the biodegradation process prevailed for all analyzed samples, which was confirmed by the calculated EMS < 1. Therefore, the organic compounds contained in this water were decomposed by microorganisms that create a biofilm in the carbon filter bed. In the case of waters A and B, the EMS coefficient was greater than 1, proving the advantage of the sorption processes over the biodegradation processes in the bed. The herbicide metabolites present in the water flowing to BACF could probably disturb or even deactivate the work of microorganisms inhabiting the biologically active carbon bed.

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