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Studies of effectiveness of odour removal from water during treatment processes

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ABSTRACT

One of the most difficult problems to solve in preparing water for human consumption is removal of its odour. Numerous studies showed that a permanent problem with odours and inappropriate water taste are encountered by nearly 3% of water enterprises. In some water supply systems this phenomenon has an incidental nature while in nearly 10% of them this problem persists for over 150 d in a year [1]. Substances responsible for the odour are permanent and difficult to remove using standard treatment technologies. This paper presents the results of works undertaken to identify a source of odour in water as well as selection and evaluation of the effectiveness of its removal in technological processes. The studies were conducted on a pilot scale, in different configurations including several processes, such as pre-ozonation and post-ozonation, coagulation on rapid filters, sorption on activated carbon and final disinfection. The conducted studies allowed for confirmation of high effectiveness of reduction of an increased threshold odour number on activated carbon.

Keywords: Odour; Geosmin; Natural organic matter (NOM); Coagulation; Ozonation; Activated carbon

1. Introduction

Water odour and taste under the European and national legislation [2–4] must be acceptable by consumers and without abnormal changes. Consumers, in order to evaluate whether water is safe for their health, can rely on their own interpretation on the basis of colour, taste and odour of water. With the use of the sense of sight, taste and smell, receiving external stimuli characterising water, they perform a subjective evaluation which does not always reflect the actual risk of consumer's health threats. Therefore, establishment of the consumer's opinion on the quality of provided water deliveries only on the basis of its disagreeable odour and taste negatively impacts the image of water companies which, in turn, results in the increase of client dissatisfaction, whereas, except for organoleptic properties of water with increased odour, they do not constitute a threat to health of an average consumer. Drinking water can contain a range of substances, minor organisms which in the aspect of public health do not constitute a threat, but are undesirable due to their negative impact on water taste and odour [5]. Odour in water is mainly caused by volatile substances, mainly gases. These substances can appear in water in the process of decomposition of both organic and non-organic substances. Such decomposition is caused by microorganisms. Whereas the source of specific odour (chemical) is human anthropogenic activity. Then, odour of water delivered to consumers becomes an increasing problem on a global scale.

The appearance of odour is often identified as presence of natural organic matter (NOM) in water. Compounds from the group of bicyclic aliphatic alcohols (BCA), such as geosmin

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(GSM), derivative of decalin and 2-methylisoborneol (MIB) – compound from group of terpenes. Pyrazine derivative (IPMP) as well as volatile carbonyl compounds are slightly less important [6]. Other compounds due to high threshold of perception, especially rarely achieved in natural conditions, are important as ingredients of dissolved organic matter (DOM). A major characteristic of these substances is high odour activity (they are perceptible for a human in nanogram concentrations). These substances are permanent and difficult to be removed with standard water treatment technologies. During such typical processes, odour substances are not decomposed and remain in treated water.

Odour substances in natural waters are created as secondary metabolites of bacteria, cyanobacteria (e.g., A*nabaena, Cylindrospermopsis, Oscillatoria, Phormidium, Aphanizomenon, Microcoleus, Schizothrix, Symploca, Lyngbya*) and actinobacteria (e.g. *Streptomyces, Microbispora, Micromonospora, Nocardia*) [7]. However, there is research showing that GSM can be produced not only by cyanobacteria responsible for water blooms, but also by settled microbenthos organisms that develop in the river bottoms and shallower parts of reservoirs. It can be produced by a much broader spectre of microorganisms capable of secreting BCA [8].

These substances, volatile by nature, are perceptible in very low concentrations below 50 ng/L [9]. Depending on conditions in which water quality analyses are conducted for GSM, an odour detection threshold is determined at the level from 1 to 15 ng/L and, for 2-MIB, at the level of 9–40 ng/L [10]. A threshold of a pyrazine derivative (IPMP) is even lower, that is, 0.5 ng/L, giving water the odour of decomposing plant matter [6]. Carbonyl compounds (β-ionone, nonadienal) and dimethyl trisulfide have detection thresholds at the level of 10–20 ng/L, and the frequency of their detection is much lower [11]. It is assumed that an odour detection threshold for GSM in case of an average water consumer is ca. 4 ng/L and MIB ca. 9 ng/L [12].

NOM concentration in drinking water is usually between 2 and 10 mg/L. These substances can also react with disinfectants, resulting in creation of disinfection by-products (DBP) [8,13–15]. Standard treatment processes, such as coagulation, sedimentation and filtration, as a rule, cannot reduce the concentration of odorants below the detection threshold, especially in case of increased quantity of such substances [15,16]. Quite good results can be achieved with a combination of a few stages, for example, oxidation combined with adsorption of primary ingredients of DOM and secondary products [16–20].

There are premises of the possibility of pre-ozonation and post-ozonation, or their combination, to remove micropollutants from water, also this resulting in odour. In case of stale odour, it is possible to remove it completely in the pre-ozonation process with a dose of 2 mg/L. An ozone dose of 0.5 mg/L in the post-ozonation process is sufficient for removal of stale odour [21,22]. In turn, for the purpose of removal of odour and taste periodically appearing in raw water, powdered activated carbon can be used [18,23,24]. The advantage of such a solution is the ability to apply it only in the period when the specific odour appears in water. The main goal of the research was to identify the causes of odour in the raw water taken at Maczki Water Treatment Plant (WTP). Furthermore, the studies were conducted to evaluate a processing effectiveness of ozonation and sorption on activated carbon in removal of specific odour from water obtained for consumption. It was assumed that these processes produced negligible oxidation by-products. The obtained results were used to develop an optimal modernization plan for water treatment system in Maczki WTP.

2. Material and methods

2.1. Maczki WTP

The studies were conducted in Maczki WTP located in the southern Poland where at the beginning of 2016 a problem of unacceptable odour of water for consumer consumption appeared. The nature of this odour was specified as stale, sludgy and earthy. Maczki WTP obtains water from the surface resources of the Central Canal Piaskowania (CCP). The CCP is located in forested area, thus has no direct contact with sanitary and industrial sewage from urbanised regions. Reed beds growing on the CCP's banks are a biological shield for the Maczki WTP intake, reducing the risk of cyanobacterial blooms. Reed beds also protect water resources from surface drainage. Additionally, this flora makes a natural barrier that slows down a flow of exogenous odorants to the intake in case of their appearance.

In years 2015 and 2016 the quality of water in the CCP in the profile of the intake was included in Category A2 (Table 1) due to exceeding the permissible values for manganese and, periodically, colour. However, the microbiological quality of water was good (Table 1) [25,26].

The water treatment process in Maczki WTP is adjusted to the quality of obtained water. Raw water is fed to settling tanks where initial removal of easily settling contamination takes place. Next, water flows to the filter building. Here are located 16 two-layer anthracite-sand rapid filters where water is subject to coagulation process with poly-aluminium chloride (PAC 16). PAC is dosed in the average dose of 1.64 mgAl/L (variability in years 2014–2017 starting with 0.98–2.87 mgAl/L) to the raw water pipeline before the filtration beds. Potassium permanganate is also added to water in the amount from 0.2 to 0.55 mg/L (average dose 0.4 mg/L) for the purpose of transformation of manganese from a dissolved form to a solid form facilitating its removal on filters. Water outflowing from the filtration system is subject to disinfection with sodium hypochlorite. In years 2014–2016 an average disinfectant dose was 0.93 mg/L (variability range from 0.8 to 1.15 mg/L) and increased by 23% in 2017 (variability range from 1.0 to 1.4 mg/L) as a result of microbiological deterioration of water quality in the CCP (Fig. 1). Treated water is stored in two pure water tanks from where it is directed to the water distribution system of the Silesian agglomeration.

At the beginning of 2016 odour started to appear both in the raw water and treated water (Fig. 2), and the nature of which was described as stale, sludgy and earthy. At first it was identified with GSM. Odour persisting in water was the cause of commencement of the studies aiming to identify the source of odour and modify the technological system in the manner guaranteeing its elimination in the specific treatment processes.

2.2. Organic contaminants in raw and treated water at Maczki WTP

The attempts aiming to find the source of odour were carried out in two stages. At the first stage (April 2016) the trial of identification of compounds at the concentration

Table 1
Variability of selected quality parameters of raw water in the CCP in years 2015–2016 [25,26]

	Colour (mg/L)			Manganese (mg/L)			Coliform bacteria (CFU/100 mL)			Odour (TON)		
	Minimum	Average	Maximum	Minimum	Average	Maximum	Minimum	Average	Maximum	Minimum	Average	Maximum
Year 2015	17	26	30	0.082	0.152	0.246	9	351	1,553	1	2	4
Year 2016	15	24	30	0.048	0.166	0.330	43	930	2,420	4	8	16
MPV[a] for A1	20 (10)			0.05			50 (50)			3 (3)		
MPV[a] for A2	100 (50)			0.1			5,000 (–)			10 (10)		

CFU, Colony forming unit.
[a]MPV, maximal permissible value, for specific categories according to the Regulation of the Polish Ministry of Environment [27]; sizes included in brackets are recommended values.

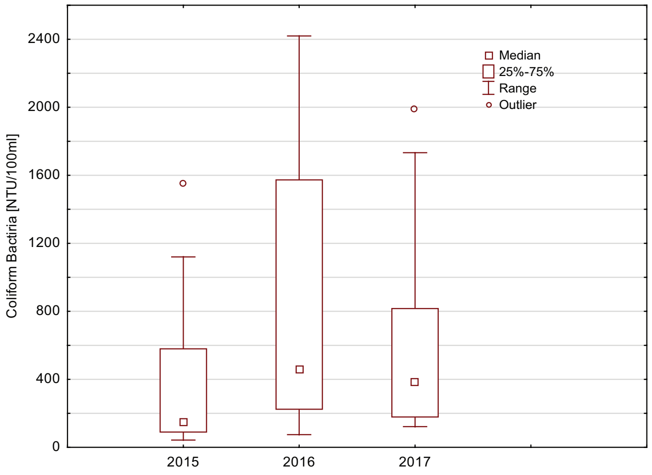


Fig. 1. Coliform bacteria in raw water in the Central Canal Piaskownia in years 2015–2017.

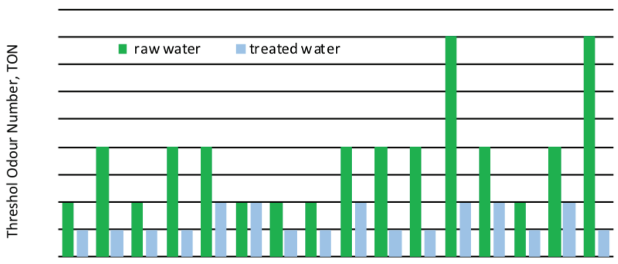


Fig. 2. The variability of odour in raw and treated water in Maczki WTP in 2016.

level of 0.05–1.0 mg/L was performed with the application of gas chromatography techniques (Agilent Technologies 7890B coupled with Agilent Technologies 5977A mass spectrometer). A series of studies included five samples collected in four points of the CCP and at the intake of Maczki WTP. GSM and 2-MIB were not observed in any samples in quantities detectable with the applied method. The second stage of works, the purpose of which was identification of compounds whose concentrations were at the level of 1 ng/L and below it, consisted of two research series conducted on 28 September and 6 October both in raw and treated water (Table 2). The techniques of preparation of samples for the analysis with the capillary gas chromatography in combination with mass spectrometry (GC-MS QP2010 – Shimadzu) were applied, that is, headspace (HS) analysis; solvent extraction; periodical gas extraction combined with adsorption of analytes on an adsorbent (Purge and trap); solid phase microextraction Sigma Aldrich solid-phase microextraction system.

The conducted studies showed a small number of organic compounds which in observed concentrations cannot result in the increased threshold odour number (TON) in treated water at the level of 4 TON. In addition, compounds characteristic for surface waters, products of organic matter decomposition and substances being the products of reaction of chlorine and organic matter were identified in treated water.

The presence of brominated and iodine derivatives was also observed, which is a sign of occurrence of bromides and iodides in water.

2.3. Research methodology

The conducted studies were performed in the pilot station with the use of various sequences of specific processes including ozonation and sorption on activated carbon. Studies were conducted in the period from 12.08.2016 to 30.09.2016. During the first 4 d the start-up of the processing system was performed as well as optimum technological parameters for water treatment were selected. The pilot station normally operated in the capacity of 1 m^3/h. In order to determine a risk of formation of ozonation by-products (bromates), a study for reduced capacity to 0.5 m^3/h was also conducted. The pilot research station included pre-ozonation in the aeration process with the use of ionised air, contact coagulation on the beds of anthracite sand filters, post-ozonation with the use of sectional ozone columns, sorption on activated carbon beds and disinfections with sodium hypochlorite (Figs. 3–5). The pilot station included the following processing modules (Table 3):

- Aeration column with diameter 300 mm equipped with the system of distribution of ionised air containing residual ozone from ozone columns with regulated time of water flow from 3 to 10 min,
- F1 gravel filter with diameter 400 mm and bed height 1 m,

Table 2
The characteristics of organic compounds in samples of raw and treated water collected in the autumn 2016 in Maczki WTP

Organic compounds (preparation technique of samples)	Raw water (μg/L)		Treated water (μg/L)		LOD (ng/L)
	28.09.2016	06.10.2016	28.09.2016	06.10.2016	
Trichloromethane (HS)[a]	0.2	0.01	14.4	16	50
Carbon tetrachloride (HS)	<0.05	0.05	0.05	0.03	50
Bromodichloromethane (HS)	<0.05	<0.05	13.1	13.4	50
Dibromochloromethane (HS)	<0.05	<0.05	8	8	50
Trichloroethylene (HS)	0.05	0.05	0.05	0.01	50
Tribromomethane (HS)	<0.1	<0.1	1	0.3	1000
Benzene (HS)	Traces <0.02	Traces <0.02	Traces <0.05	Traces <0.05	20
Toluene (HS)	Traces <0.02	Traces <0.02	Traces <0.05	Traces <0.05	20
2-Isopropyl-3-methoxypyrazine (SPME)[b]	<0.001	<0.001	<0.001	<0.001	1
2-isobutyl-3-methoxypyrazine (SPME)	<0.001	<0.001	<0.001	<0.001	1
2-Methylisoborneol (SPME)	<0.001	<0.001	<0.001	<0.001	1
Geosmin (SPME)	0.0051	0.0061	0.0028	0.0028	1

[a] HS, Headspace analysis.
[b] SPME, Solid-phase microextraction.

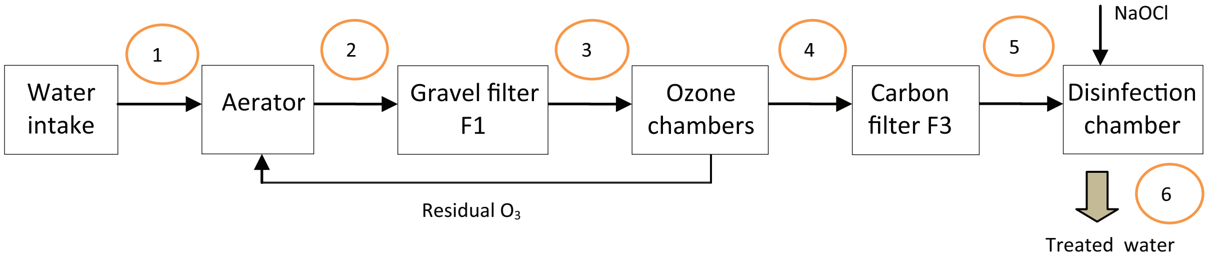


Fig. 3. Technological system for water treatment for study Variant I.

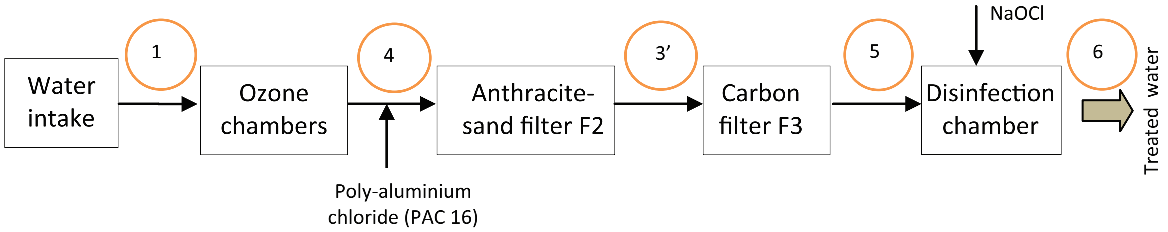


Fig. 4. Technological system for water treatment for study Variant II and III.

- Ozonation system equipped with two coupled chambers (KR1 lifting oxygenation chamber and KR2 retention chamber) with diameter 400 mm and height 415 mm, ozonator with capacity from 8 to 14 g/h and injector static mixer,
- F2 anthracite sand filter with diameter 400 mm and bed height 1.2 m,
- F3 activated carbon filter with diameter 250 mm and bed height 1 m,
- disinfectant (sodium hypochlorite) was added to the water sample collected in laboratory conditions.

In the pilot station, analysed water was collected in 6 points:

- Raw water from water intake Maczki WTP supplying the research system,
- Pre-oxidized water in outflow from the aerator,
- Water filtered through filter F1 (sampling point 3 – Fig. 3) and through filter F2 (sampling point 3 – Fig. 4),
- ozonated water,
- water after sorption on activated carbon beds F3 and
- chlorinated water.

During the studies, water samples were also collected from the actual technological system in Maczki WTP (Fig. 6):

- water flowing into the system of rapid filters,
- water flowing out from the system of rapid filters and
- treated water pumped into the pipe network.

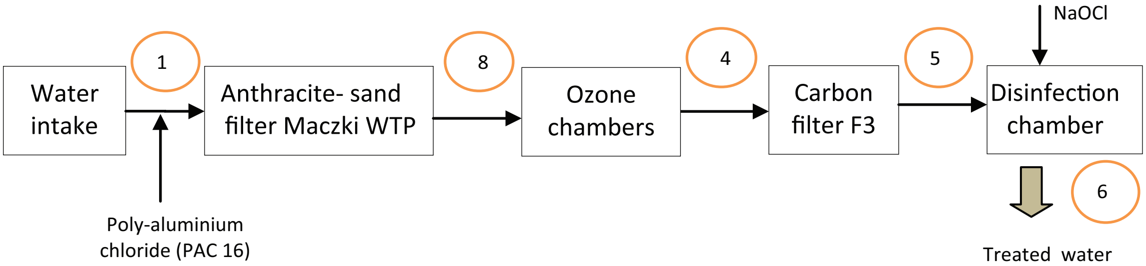


Fig. 5. Technological system for water treatment for study Variant IV.

Table 3
Unit water treatment processes used in the pilot station for four study variants

Unit process	Operating parameters	Study variants				
		Variant I	Variant II	Variant III	Variant IV	Maczki WTP
Water flow	Q (m^3/h)	1.0 and 0.5	1.0	1.0	1.0	400
Pre-ozonation	T_C (min)	–	0.5–1.0	0.5–1.0	–	–
	D (mg/L)	–	10.0	10.0	–	–
Aeration	T_C (min)	5.0	–	–	–	–
Contact coagulation in	D (mg/L)	–	–	2.95	1.51	1.51
filtration beds	v (m/h)	–	–	6.2	1.8	1.8
Filtration	v (m/h)	4.0	6.2	–	–	–
Post-ozonation	T_C (min)	6.6	–	–	13.0	–
	D (mg/L)	2.5–3.9	–	–	1.0–3.4	–
Sorption on activated	v (m/h)	10.2	10.2	10.2	10.2	–
carbon	T_C (min)	8.8	8.8	8.8	8.8	–
Disinfection	D (mg/L)	1.1	1.04	1.04	1.06	1.06

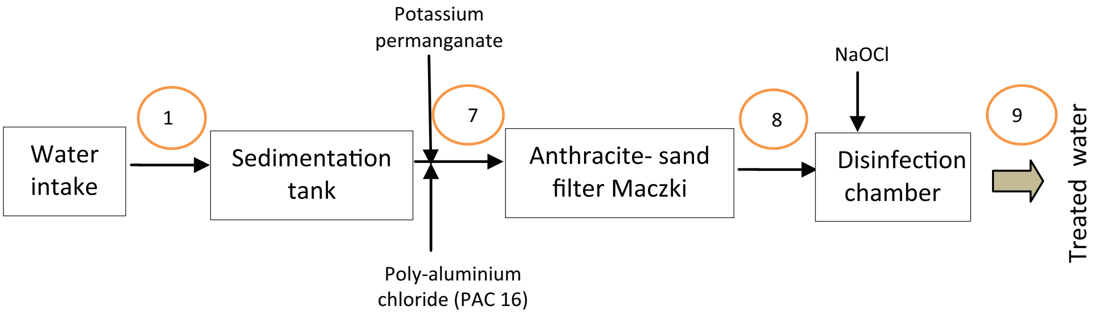


Fig. 6. Technological system for Maczki WTP.

Water quality parameters were marked in collected water samples according to the procedures specified in Table 4.

The pilot studies were conducted in four variants allowing for the evaluation of effectiveness of removal of odour from water in different configurations of unit processes.

2.3.1. Variant I

The studies were conducted from 16.08.2016 to 30.08.2016 (in conditions of normal flow 1 m^3/h) and from 31.08.2016 to 02.09.2016 (in conditions of decreased flow 0.5 m^3/h) (Fig. 3). They were performed in the system of initial aeration in the aerator, rapid filtration, post-ozonation, sorption on activated carbon beds and disinfection with sodium hypochlorite. Air ionised with residual ozone drawn from ozone chambers was fed to the aerator. Time of water contact with ionised air was 5 min. During the performance of studies, the speed of rapid filtration (filter F1) was constant and equal to 4.0 m/h. In the post-ozonation process, the ozone dose was variable and had values in the range from 2.5 to 3.9 mgO$_3$/L, which allowed for achievement of concentration of residual ozone in water in the range from 0.15 mgO$_3$/L to 0.25 mgO$_3$/L. Times of water contact with ozone in the KR1 lifting reaction chamber and KR2 retention chamber were the same and amounted to 6.6 min. The speed of water flow in the sorption system through the F3 activated carbon column was 10.2 m/h which allowed for achievement of time of contact with bed at the level of 8.8 min. Next, water was subject to disinfection process with sodium hypochlorite in a dose of 1.1 mg/L.

2.3.2. Variant II

The studies were conducted from 06.09.2016 to 09.09.2016 (Fig. 4). The process was performed in the system: pre-ozonation, rapid filtration on F2 two-layer anthracite-sand beds, sorption on F3-activated carbon and disinfection with sodium hypochlorite. The ozone dose in the ozonation process was variable and depended on the quality of raw water (0.5–1.0 mgO$_3$/L) and the contact time was equal to ca. 10 min. Such conditions of pre-ozonation allowed for achievement of concentration of residual ozone in the stream of water flowing into the filtration system at the level of 0.05 mgO$_3$/L. Beds of F2 rapid filters constituted full representation of actual filters used in Maczki WTP. F2 column was filled with a sand layer with height 0.8 m and granulation 0.71–1.25 and 40 cm layer of anthracite with granulation 1.4–2.5 mm. The filtration system operated with average speed of water flow through the F2 column at the level of 6.2 m/h. The sorption system on activated carbon beds operated with the same flow parameters as in Variant I, whereas an average dose of sodium hypochlorite in the disinfection process was 1.04 mg/L.

2.3.3. Variant III

Studies were conducted from 13.09.2016 to 19.09.2016 (Fig. 4). The process was performed in the system compliant with Variant II expanded by the process of contact coagulation PAC 16 (average dose 2.95 mgAl/L) performed in F2 filtration beds operating with speed of 6.2 m/h. The dose of sodium hypochlorite in the disinfection was 1.06 mg/L.

2.3.4. Variant IV

Studies were conducted from 24 to 30 September (Fig. 5). The studies were performed in the sequence of specific processes: contract coagulation with aluminium sulphate in filtration beds, post-ozonation, sorption on activated carbon beds and disinfection with sodium hypochlorite. The pilot station in the period from 16.08 to 19.09 did not fully reflect the actual conditions of coagulation performed in Maczki WTP. The reason for this was capacity of WTP limited to the level of 400 m^3/h (as a result of increased water odour) at which average filtration speed was barely 1.47 m/h and was more than four times lower from filtration in the pilot system. In such circumstances, the coagulation process for this variant was performed in the actual technological system in Maczki WTP with the use of an average coagulant (PAC 16) dose of 1.51 mgAl/L from where water was fed to the pilot station directly to the post-ozonation chambers. An average ozone dose was 1.9 mgO$_3$/L (variability range from 1.0 to 3.4 mgO$_3$/L) and was determined by the concentration of residual ozone maintained at the level 0.05 mgO$_3$/L. The time of water contact

Table 4
Scope of water physicochemical studies

Parameter	Standard	Analytical devices
Temperature (°C)	PN-77/C-04584	Digital thermometer with a probe on the duct
Odour (TON)	PN-EN 1622:2006	Sensory method simplified, even, non-selective
Turbidity (NTU)	PN-EN ISO 7027-1:2016-09	DrLange NEPHLA 3 Laboratory Turbidimeter
Colour (mg Pt/L)	PN-EN ISO 7887:2012	Visual method – Nessler cylinders 100 mL narrow type
pH reaction (–)	PN-EN ISO 10523:2012	Elmetron CX-721 Multi-Function Measuring Instrument
Absorption in 254 nm	PN-84/C-04572	Perkin Elmer Lambda 25 UV/VIS Spectrometer
Absorption in 272 nm		
TOC (mgC/L)	PN-EN 1484:1999	Thermo Electron HyPer TOC
DOC (mgC/L)		
Residual ozone (mg/L)	PB/43 ed. 1-22.02.2010	Hach TM II Pocket Colorimeter, chlorine meter
Free chlorine (mg/L)	PN-EN ISO 7393-2:2011	
Bromates (μg/L)	PN-EN ISO 15061:2003	DIONEX ICS-3000 Ion Chromatography System
Total THM (μg/L)	PN-EN ISO 10301:2002	Agilent Technologies 6850 Network HS/GC/ECD Gas Chromatograph

with ozone was ca. 13 min and the speed of filtration through F3 activated carbon was 10.2 m/h. Next, water was subject to the process of disinfection with sodium hypochlorite with an average dose of 1.06 mg/L which allowed for achievement of concentration of free chlorine at the level of 0.28 mg/L.

For the purpose of identification of the level of risk of generation of oxygenation by-products (OBP) in water, the increased concentration of residual ozone was maintained at the level of 0.2 mgO$_3$/L from 26.09.2016 to 29.09.2016. In this period, the pilot station operated with capacity of 1 m^3/h.

3. Results and discussion

Chemical parameters of water quality achieved in the cycle of conducted studies for particular variants are presented in Tables 5 and 6.

During the study, raw water was of a high quality (Tables 5 and 6). In the entire research period, the average water colour was 19 mgPt/L and reached the highest value (26 mgPt/L) on days from 30.08 to 1.09 (Variant I, Table 5). The observed colour was accompanied by increased turbidity (variability of turbidity in this period ranges from 4.44 to 6.36 NTU). Additionally, intensive odour of 8 TON was noted during this period which persisted in water from 22.08 to 1.09 and was accompanied by the highest content of organic substances in the study cycle expressed in total organic carbon (TOC) at the level of 3.58 mgC/L on 30.08 (average 2.17 mgC/L, variability range 1.46–3.58 mgC/L) with dominant 91% share of dissolved organic carbon (DOC 3.26 mgC/L). On 30.08 the effectiveness of the technological process in Maczki WTP allowed to achieve water quality with odour of 2 TON (reduction level 75%), colour 3 mgPt/L (reduction level 88%), turbidity 0.1 NTU (reduction level 98%) and TOC 3.28 mgC/L (reduction level 8%) and DOC 2.94 mgC/L (reduction level 10%) at the outflow, at the point supplying the water pipe network.

Raw water was characterised of average temperature 15.5°C (variability range 11.0°C–17.9°C). Turbidity of raw water supplying the pilot station (Fig. 7) was low and varied from 1.49 to 6.36 NTU (average 2.82 NTU). For research systems without coagulation process (Variant I and II), the average reduction of turbidity was achieved barely at the level of 70.5% which increased by 19.7% in systems where the coagulation process was applied (Variant III and IV, range of variability 70%–98%). Nevertheless, it allowed only to obtain average turbidity at the level of 0.22 NTU (Variant III 0.29 NTU, Variant IV 0.10 NTU) in the stream of treated water which was three times higher from the average turbidity of water treated in Maczki WTP (0.08 NTU). The effectiveness of turbidity removal in Maczki WTP during conducted studies varied in the range 93%–99% achieving the average value of 97%.

For four study variants, the applied water treatment processes allowed for removal of natural organic substances (NOM) from water (Table 6) and reduction of TON to the level of 1 TON, whereas, in the technological system in Maczki WTP, treated water was characterised with TON of 2 TON.

The conducted studies showed low-processing effectiveness of NOM removal from water in the systems without the coagulation (Variant I and II, Fig. 8). The lowest operation effectiveness in the discussed systems was observed on 08.09 (Variant II) where the pre-ozonation process resulted in barely 1.2% reduction of TOC (down to 2.42 mgC/L) and 1.7% reduction of DOC (down to 2.31 mgC/L). The effectiveness of removal of organic substances from water improved insignificantly in the full water treatment process, that is, considering the (initial and intermediate) oxygenation processes and sorption on activated carbon. On this date, in the subsequent systems of intermediate filtration (F2) and sorption on activated carbon beds (F3), the reduction level (Point 6) was 4.5% for TOC (Fig. 8) and 9.7% for DOC Fig. 8), whereas the processing effectiveness of the actual water treatment line in Maczki WTP allowed for reduction of TOC by 26.5% and DOC by 27.7% in treated water.

Legend to Figs. 8–13 is TOC vs 6, DOC vs 6 and UV 254 vs – efficiency of removal of TOC, DOC and UV 254 at Point 6, respectively, for Variant I and II (wc, without coagulation), Variant III and Variant IV.

Ultraviolet absorption (UV$_{254}$) allows for designation of DOC fraction and aromatic compounds which are precursors of OBP or DBP. Because nitrates, iron, bromides or non-reactive organic ingredients with coupled double bonds *are also capable of absorption* of a wave long 254 nm, the measurement of UV$_{272}$ absorbance was also a reliable factor in the cycle of studies. Reduction of absorbance in 254 nm on a day with lowest level of reduction of TOC and DOC, that is, 8 September, was also the lowest as it was 3.1% (Point 4) in ozonated water and increased 15 times to the level of 44.3% in comparison with treated water (Point 6, Fig. 8). Average reduction of absorbance in processing lines for Variant I and II (Point 6) was 51.9% for UV$_{254}$ (variability from 44.3% to 84.7%) and 41% for UV$_{272}$ (variability 30.9% to 52.1%), whereas it was higher in case of water treated in Maczki WTP and was equal to 65.6% (UV$_{254}$ variability 57.5% to 71.6%) and 52.9% (variability UV$_{272}$ 40.5% to 68.8%), respectively.

In case of application of systems including both coagulation and ozonation (Variant III and IV), the increased effectiveness of removal of natural organic mass was observed (Figs. 9 and 10). The highest level of removal of NOM was observed for Variant IV (reduction of TOC by 31%, DOC by 33.7% and UV$_{254}$ by 94%). The application of post-ozonation and sorption on activated carbon enabled the achievement of the highest effectiveness of removal of NOM (Figs. 11–13) in relation to actual processing system in Maczki WTP (Table 5). As the consequence of the NOM removal was an increased reduction of odour (odour decreased to 1 TON in the pilot station), whereas at Maczki WTP the odour lever was not decreased to an acceptable level (1–2 TON, Table 6).

In a raw water specific ultraviolet absorbance (SUVA) was on average 4.1 m^3/gC m, which is a sign of high hydrophobic and aromatic contents and high molecular weight fractions of DOC. With this nature of NOM, the effectiveness of coagulation in removal of these compounds should be at the level of 80% [28–31]. For this reason, in case of Variant III and IV, ozone was dosed in the amount allowing only for activation of organic matter particles and intensification of creation of aggregates in the coagulation process. This was confirmed by experimental results which were tested for correlation between removal effectiveness of NOM (defined by TON, DOC and UV 254) and odour removal. It turned out that the correlation was very high with correlation coefficient $r = 0.837$ between UV 245 and effectiveness of odour removal (for combined data set from Variant III and IV). Correlation

Table 5
The basic statistics for selected parameters of water quality in particular study variants

Intake point	Temperature (°C)			Turbidity (NTU)			Colour (mg Pt/L)			pH (–)		
	Minimum	Maximum	Average	Minimum	Maximum	Average	Minimum	Maximum	Average	Minimum	Maximum	Average
Variant 1												
RW	17.0	17.9	17.4	1.49	6.36	2.79	15	26	20.3	7.5	7.7	7.6
Point 4	18.0	23.5	19.4	0.29	1.69	0.96	3	8	5.5	7.9	8.3	8.1
Point 6	17.7	19.0	18.2	0.28	1.09	0.76	2	6	4.4	7.9	8.2	8.0
TW	15.6	20.4	17.6	0.04	0.12	0.08	2	4	2.6	7.3	7.7	7.5
Variant II												
RW	16.4	17.6	17.0	2.58	3.95	3.12	15	22	19.3	7.5	7.7	7.6
Point 4	17.8	22.7	20.3	2.84	4.45	3.50	18	22	19.5	8.0	8.2	8.1
Point 6	18.0	22.8	20.4	0.33	5.28	1.54	3	5	4.3	8.0	8.1	8.1
TW	17.0	18.1	17.5	0.06	0.2	0.09	2	3	2.2	7.3	7.6	7.4
Variant III												
RW	16.2	16.6	16.4	2.58	3.14	2.80	17	24	20.1	7.5	7.6	7.5
Point 4	17.0	17.6	17.3	2.76	3.61	3.14	17	24	21.1	7.8	8.0	7.9
Point 6	17.1	17.4	17.3	0.05	0.83	0.30	2	6	3.4	7.6	7.9	7.8
TW	15.0	19.0	16.5	0.05	0.12	0.08	2	3	2.1	7.3	7.5	7.4
Variant IV												
RW	11.0	12.3	11.7	2.52	2.70	2.60	15	20	17	7.5	7.6	7.6
Point 4	12.0	12.6	12.4	0.06	0.21	0.11	1	3	2.2	7.6	7.7	7.7
Point 6	12.6	12.8	12.7	0.05	0.14	0.10	1	2	1.4	7.6	7.8	7.7
TW	11.7	14.4	12.7	0.04	0.09	0.06	1	3	1,7	7.3	7.4	7.4

RW, Raw water.
TW, Treated water, at Maczki WTP.

Table 6
The content of organic substances in water for four variants of study

Parameter unit	Intake point	Study variant								
		Research system without coagulation – Variant I and II			Variant III			Variant IV		
		Minimum	Average	Maximum	Minimum	Average	Maximum	Minimum	Average	Maximum
TOC (mgC/L)	RW	2.39	2.71	3.58	1.75	1.81	1.86	1.50	1.74	1.94
	Point 4	1,65	2.63	3.48	1.68	1.88	2.14	1.15	1.46	1.80
	Point 6	1.44	2.36	3.28	1.50	1.61	1.73	1.13	1.40	1.22
	TW	1.14	1.32	1.51	1.31	1.45	1.65	1.40	1.51	1.81
DOC (mgC/L)	RW	2.23	2.58	3.26	1.49	1.63	1.76	1.28	1.51	1.66
	Point 4	1.56	2.41	3.17	1.56	1.66	1.81	0.89	1.18	1.70
	Point 6	1.18	1.90	2.94	1.11	1.24	1.40	0.9	1.16	1.44
	TW	1.41	1.86	2.26	1.23	1.35	1.42	0.9	1.20	1.45
UV in 254 nm ($d = 50$ mm) (10^{-3}/cm)	RW	0.215	0.403	0.578	0.251	0.341	0.383	0.271	0.322	0.354
	Point 4	0.080	0.19	0.37	0.210	0.300	0.360	0.020	0.140	0.360
	Point 6	0.060	0.15	0.250	0.08	0.150	0.320	0.02	0.080	0.110
	TW	0.100	0.150	0.230	0.090	0.110	0.120	0.040	0.100	0.120
SUVA (m^3/gC·m)	RW	3.22	3.33	3.60	3.92	4.25	4.72	3.72	4.45	5.33
Threshold odour number (TON)	RW	4	6	8	4	4	4	8	8	8
	Point 4	1	1	2	2	2	2	1	2	2
	Point 6	1	1	1	1	1	1	1	1	1
	TW	2	2	2	2	2	4	2	2	2

RW, Raw water.
TW, Treated water, at Maczki WTP.

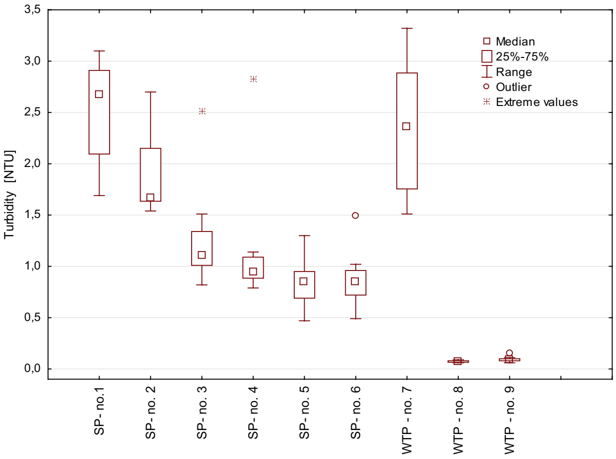


Fig. 7. Variability of turbidity in selected sampling points in the pilot station and processing line in Maczki WTP; SP – sampling point, WTP – water treatment plants.

including DOC was lower by 17% ($r = 0.699$) while correlation including TOC was lower by 18% ($r = 0.689$).While for Variant I and II (water treatment without coagulation) there was no or no significant correlation observed for all UV 245, TOC, DOC. No correlation was also observed for Maczki WTP.

Application of ozone, for removal of odour from water, increases the risk of exceeding the acceptable value of bromates in tap water, which is 10 μg/L. For this reason, contents of ozonation by-products were analysed in selected study

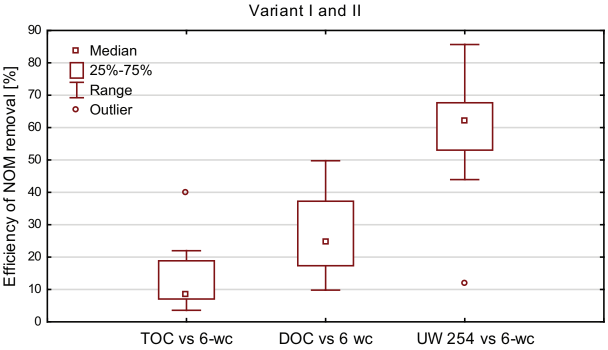


Fig. 8. Efficiency of NOM removal for Variant I and II.

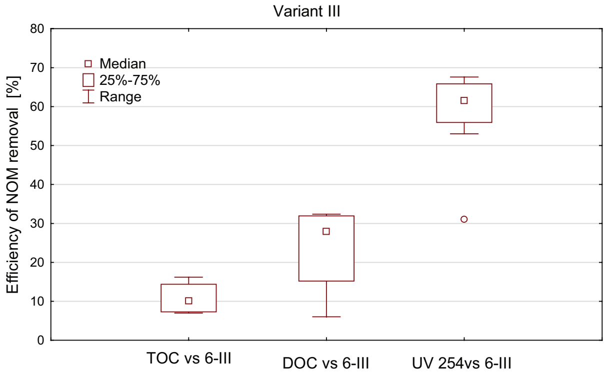


Fig. 9. Efficiency of NOM removal for Variant III.

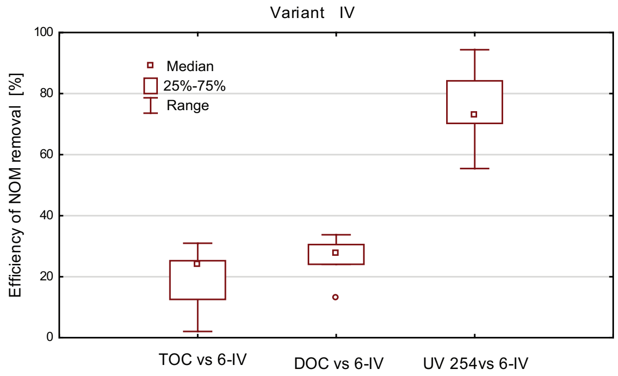


Fig. 10. Efficiency of NOM removal for Variant IV.

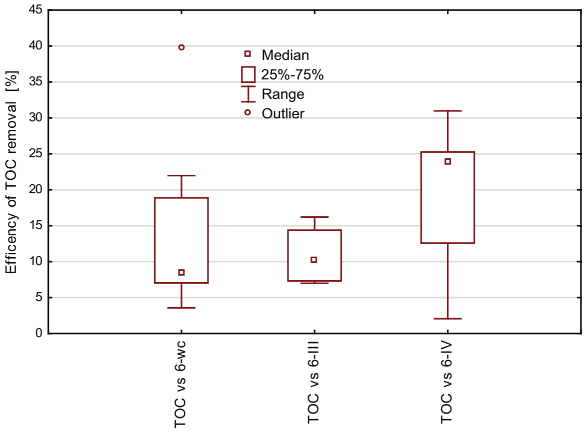


Fig. 11. Comparison of TON removal during study.

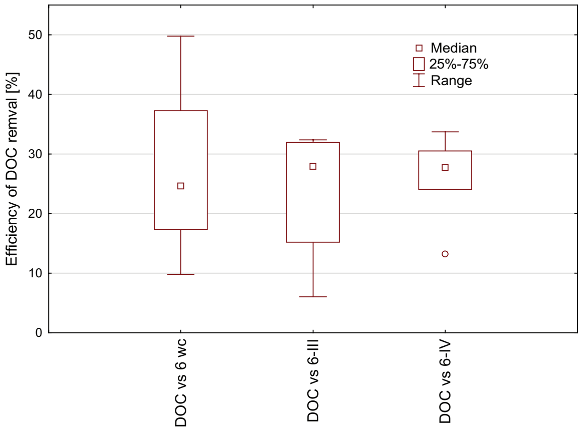


Fig. 12. Comparison of DOC removal during study.

points during the research. The highest bromates concentration was observed in Variant I (Fig. 14(a)) on 31.08. During this day the water flow was decreased by 50% to the value of 0.5 m^3/h. This resulted in the increase of bromate concentration up to 24 μg/L at Point 4 and up to 20 μg/L in treated water (Point 6). The highest bromate concentration 9.3 μg/L, for flow of 1 m^3/h with concentration of residual ozone 0.25 mgO$_3$/L, was observed on 25.08 in treated water at Point 6. For Variant III, where concentration of residual ozone in water was 0.05 mgO$_3$/L, the average bromate concentration was 0.2 μg/L (variability 0.1–0.3 μg/L).

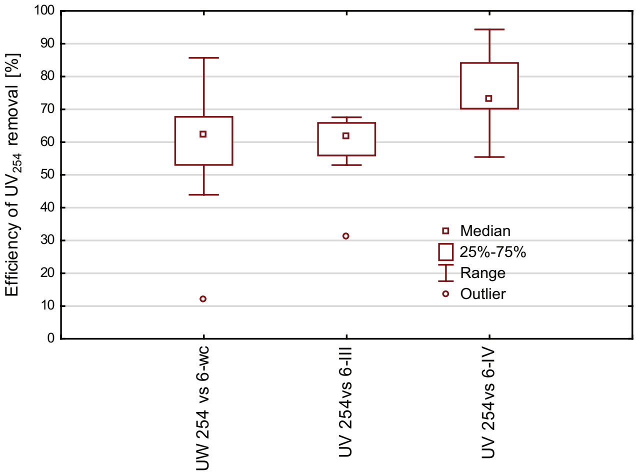
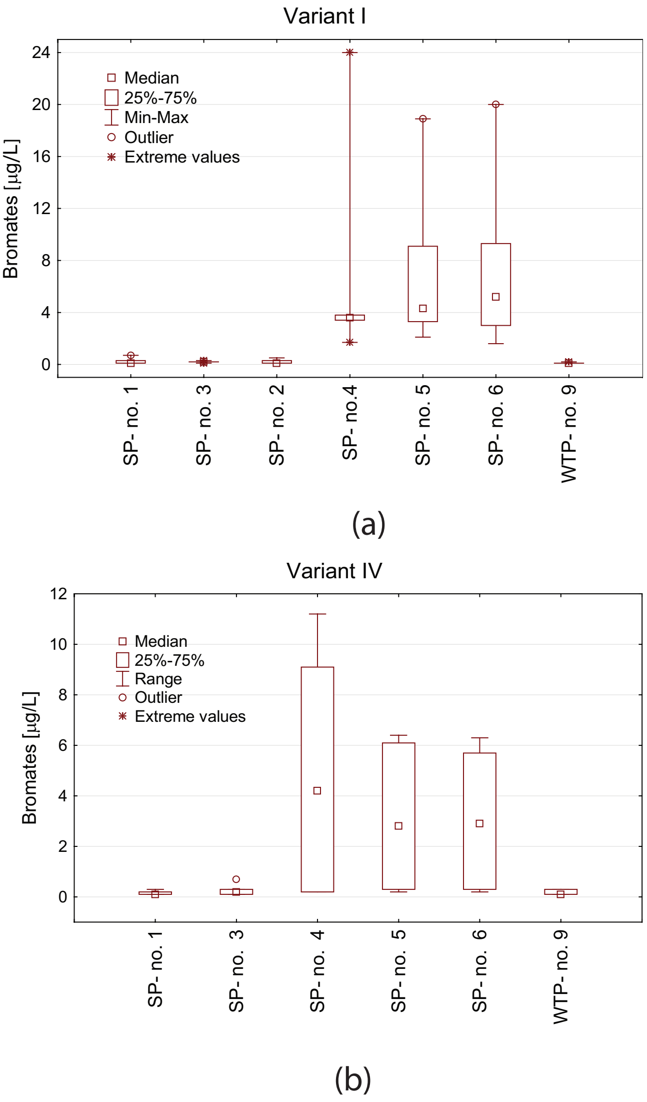


Fig. 13. Comparison of UV$_{254}$ removal during study.



(a)

(b)

Fig. 14. Variability of bromates concentration in the pilot system and water treated in Maczki WTP (a) Variant I and (b) Variant IV; SP – sampling point, WTP – water treatment plants.

Table 7
Changes of THM concentration during study

Variant		THM concentration (μg/L)	
		Point 6	TW
Variant I	Minimum	2.2	7.5
	Mean	2.6	10.7
	Maximum	3.1	15.4
Variant II	Minimum	1.0	5.6
	Mean	1.7	7.4
	Maximum	2.4	8.3
Variant III	Minimum	2.2	6.6
	Mean	2.3	8.1
	Maximum	2.3	9.6
Variant IV	Min	1.3	6.0
	Mean	1.6	6.6
	Maximum	1.9	7.5

TW, Treated water, at Maczki WTP.

The analysis of trihalomethanes (THM) concentrations for all variants (Table 7) confirmed the effectiveness of ozonation and sorption of activated carbon on NOM removal, thus, justifying the necessity of modernisation of Maczki WTP. In all pilot systems reduction of ingredients of NOM was higher than at Maczki WTP. This resulted in the lowest concentrations of precursors of oxidation by-products, which was three times lower than after disinfection at Maczki WTP. In the period of conducted studies, the highest concentration of chloroform in water after disinfection in Maczki WTP was noted on 22.08 and was equal to 15.4 μg/L. On that day, at Point 6 (Variant I) the highest concentration of chloroform, equal to 3.1 μg/L, was also observed, which was five times lower than in water pumped into the pipe network. The highest processing effectiveness in NOM removal was achieved for Variant IV, which resulting in low content of DBP in treated water characterised by average concentration of chloroform at the level of 1.57 μg/L (variability range from 1.3 μg/L to 1.9 μg/L).

An integral element of the research was the assessment of the cost of development of Maczki WTP's water treatment line. Cost of investment in one level of ozonation (post-ozonation) and filtration using an activated carbon filter was estimated to be at least 5 million Euro. While an investment including only ozonation has been estimated at 2.5 million Euro. This would cause significant increase in the unit cost of water production at Maczki WTP. Another effective solution that is much cheaper is usage of powdered activated carbon which requires an investment of approximately 0.5 million Euro.

4. Conclusions

The odour of water obtained in Maczki WTP is most likely caused by action of bacteria in water. The perceptible odour is earthy-mouldy by nature; however, it cannot be traced down to a specific water contamination. It is presumably caused by a mix of different substances resulting from biochemical transformations.

The purpose of model studies was to evaluate whether it is possible to reduce the odour to the level acceptable by consumers (1 TON) with lower funds and without the necessity of advanced development of the processing line. The conducted studies showed high risk of generation of cancerogenic ozonation by-products that are harmful for health (Variant III and IV). Therefore, ozonation without sorption should not be considered as a viable option for Maczki WTP development.

The results of presented studies, conducted in the pilot station, find a compatibility with a results of another researchers [18,23]. Undoubtedly, the most effective method of removal of odour from water would be the implementation of at least one level of ozonation and filtration using an activated carbon filter. Those processes are definitely effective methods to reduce TON. However, they are not the best solution from an economical point of view as they require large financial investment in case of expansion of the existing technological water treatment line. Therefore, that justifies the necessity of continuation of studies with application of powdered activated carbon to reduce TON parameter down to value 1. Implementation of such a solution will not generate significant costs for the development of Maczki WTP.

Our studies have shown that for raw waters of high actual absorption (SUVA ca. 4 m^3/gC m), the technological treatment trial, including coagulation and filtration using active carbon (without ozonisation), guarantees a high odour removal of up to 1 TON. For existing WTPs, for which an unacceptable odour occurs periodically in surface water sources, use of powdered activated carbon only during periods of deterioration of water quality is the best from both a technological and economic point of view.

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