Effect of ozonation on polychlorinated biphenyl degradation and on soil physico-chemical properties

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ARTICLE INFO

ABSTRACT

The objectives of this study were to investigate the effectiveness of ozone treatment on degradation of polychlorinated biphenyl (PCB) contaminated soils and to observe the subsequent changes in soil physico-chemical properties. Furthermore, the ability of plants to grow on the ozone-treated soils was evaluated. Soils with different physico-chemical characteristics spiked with seven PCB congeners in two different time periods were chosen. Ozonation was more efficient for PCB degradation in freshly spiked soils and the removal efficiency increased with increasing ozonation time. The highest decrease was found in the soil with a lower soil organic matter (SOM) content and a coarser soil structure indicating the substantial effect of soil characteristics on the efficiency of ozonation. The composition of individual PCB congeners changed in all treatments in terms of higher accumulation rate of highly chlorinated biphenyls with a higher ozonation time. Increased mobility of several elements, changes in SOM content and in soil pH were detected after ozonation. Vulnerability of plants to these modifications was documented on rape seedlings. No inhibition in growth during any treatment and predominantly higher concentration of PCB in non-ozonated treatments were observed. Results suggest that this method can present a promising environmental friendly remediation technology for PCB contaminated soils.

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1. Introduction

Contamination of soils with polychlorinated biphenyls (PCB) has often resulted from manufacture, handling, use, and disposal of these chemicals. If released into the environment, these persist for years because they are resistant to degradation by chemical or biological processes. Therefore, their extreme persistence in the environment and ability to bioconcentrate in the food chain present a great environmental risk.

Several physico-chemical effective methods exist for clean up of soils contaminated by these pollutants, but they are often too costly [1]. More feasible and environmentally friendly methods of bioremediation are time consuming and usually require higher portion of pollutants in more bioavailable forms. Thus, chemical degradation of organic compounds by strong oxidation agents such as ozone (ozonation) could be a feasible solution. The costs associated with in situ ozonation were stated to be relatively small compared to conventional soil remediation techniques such as incineration, thermal desorption and chemical extraction due to significantly lower energy consumption and simplicity of the tech-

nique applied [2,3]. Moreover, oxidation using ozone can also be an effective pre-treatment to enhance the subsequent bioremediation step since ozone-treated organic compounds are transformed to oxygenated intermediates that are usually less toxic, more water-soluble and thus more biodegradable [4–6]. The additional benefit of this method over the others lays mainly on a possible reuse of the ozonated soil. Ozone can be applied either as a gas phase or as an aqueous phase. To use of gaseous ozone for the treatment of unsaturated soils contaminated with PCB may have a significant potential over the aqueous form since the diffusivity of the ozone gas in soils is higher and thus, the amount of ozone that can react with the contaminants is much greater. Moreover, gaseous ozone has been found to be readily delivered through columns packed with a number of geological materials and soils and is effective in removing contaminants such as hydrocarbons, polyaromatic hydrocarbons (PAH), diesel fuels, pesticides and chlorinated solvents [2,5–9].

In the most cases the pre-oxidation seems to be the only solution since the parent compounds are often resistant to bioremediation. However, the effectiveness of ozonation may be limited by factors such as competing reaction with soil organic matter (SOM), moisture content, particle size, metal oxides and pH [7,9,10]. There are also potential concerns that ozonation may possibly cause nutrient mobility changes and affect the mobilization of some metals

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by destroying the SOM or by changing the oxidation state of some metals, such as U and Cr [11,12].

Because most of the studies were carried out with PAH and pesticides as model substances, data about other organic pollutants are scarce. The lack of research investigating gaseous ozone treatment of soils contaminated with PCB allows to set up the following objectives of this study: (i) to investigate the effectiveness of ozone as a chemical oxidant for soils contaminated with different PCB congeners; (ii) to consider the influence of different physical and chemical soil characteristics during ozonation on degradation and/or removal efficiency of PCB; (iii) to monitor the changes of soils properties and (iv) to investigate the response of plants grown on the studied soils after the ozonation treatment.

2. Materials and methods

2.1. Soil characteristics and sample preparation

Soil samples with different physico-chemical properties and particle-size distribution (Table 1) classified as Chernozem and Fluvisol were used for the ozonation. Before sampling, soils were analysed for particle-size distribution (hydrometer method), cation exchange capacity (BaCl$_2$ extraction) and organic matter (Sims and Haby colorimetric determination). Soil pH was measured in suspension using a 1:5 (w/v) ratio of soil and deionised water/0.2 M KCl.

Soils were spiked with seven indicator PCB congeners (100 µg of each PCB congener per 1 kg of soil) purchased from Analytika Ltd (Prague, Czech Republic) dissolved in petroleum benzene. The PCB congeners investigated in this study are summarised in Table 2. The studied soils were spiked at two different times prior to ozonation: 36 months before the ozone treatment (Chernozem 36, Fluvisol 36) and 6 months before the ozone treatment (Chernozem 06, Fluvisol 06).

2.2. Ozonation procedure

An amount of 400 g of air-dried and sieved (2 mm) soil was weighed into a 250 mL polypropylene column with porous space
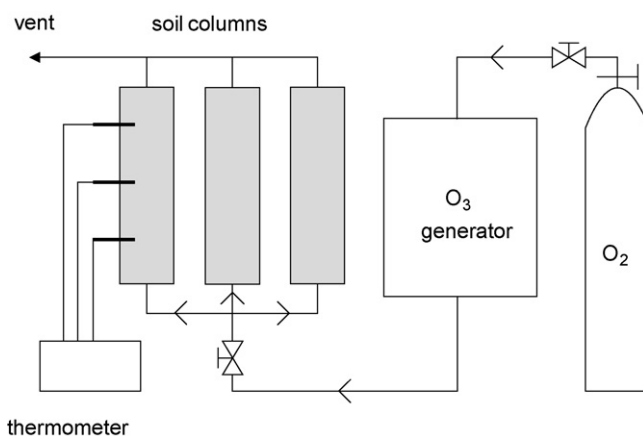

Fig. 1. Schematic diagram of the ozonation procedure using columns filled with PCB contaminated soils.

for the gas in the bottom. The experiment was conducted in triplicates. Ozone was generated from pure commercial oxygen by an ozone generator (V 4, Crystal Air, Canada Inc.) and the final mixture of ozone–oxygen was blown into each of the three flasks at a flow rate of 0.15 L min^{-1}, controlled by flowmeters. The flow rate of oxygen through the ozone generator was 0.45 L min^{-1} corresponding to a concentration in the gas phase of 60 g m^{-3} (according to the disclaimer of the ozone generator producer). The produced gases were transported outside of the column. The ozonation procedure was carried for 2.5, 4 and 6 h. Temperature changes in the soils during ozonation were measured by a K-type thermocouple thermometer (Hanna Instruments, Portugal). Three temperature probes were placed into the column at 1.5, 2.0 and 7.5 cm from the bottom. The scheme of ozonation procedure is shown in Fig. 1.

2.3. Plants cultivation

After the ozonation procedure, soil samples were put into 150 mL plastic containers (150 g per container) and three replicates were set up for each treatment. Pots were sown with approximately

Table 1
Agrochemical characteristics of the studied soils

Soil type	Particle-size distribution (%)			CEC[a] (cmol kg^{-1})	pH$_{KCl}$	SOM[b] (%)
	Clay (<0.002 mm)	Loam (0.002–0.02 mm)	Sand (0.02–2 mm)			
Chernozem 36	36	28	36	25.5	7.4	3.8
Fluvisol 36	12	7	81	8.90	4.5	1.2
Chernozem 06	31	30	39	21.4	7.1	2.2
Fluvisol 06	10	5	85	6.30	5.5	1.0

[a] Cation exchange capacity.
[b] Soil organic matter.

Table 2
Chemical structure and analytical characteristics of the seven PCB congeners

PCB IUPAC no.	Structure	Vapour pressure (Pa)[a]	log K_{ow} [b]	SIM[c] ions	Retention time (min)
PCB 28	2,4,4′-Trichlorobiphenyl	0.0245	5.67	256, 258	16.81
PCB 52	2,2′,5,5′-Tetrachlorobiphenyl	0.028	5.84	290, 292	18.57
PCB 101	2,2′,4,5,5′-Pentachlorobiphenyl	0.00231	6.38	324, 326	23.11
PCB 118	2,3′,4,4′,5-Pentachlorobiphenyl	n.a.[d]	6.74	324, 326	25.60
PCB 138	2,2′,3,4,4′,5′-Hexachlorobiphenyl	0.000431	6.83	360, 362	27.25
PCB 153	2,2′,4,4′,5,5′-Hexachlorobiphenyl	0.0008	6.92	360, 362	26.38
PCB 180	2,2′,3,4,4′,5,5′-Heptachlorobiphenyl	0.000136	7.36	394, 396	29.18

[a] Data from Ref. [35].
[b] Octanol–water partition coefficient; data from Ref. [36].
[c] Selected ion monitoring.
[d] Value not available.

10 seeds of rape (*Brassica napus* L.) and slightly watered. After germination, plants were thinned to three plants per pot, moved to an outdoor weather-controlled vegetation hall and watered every day with deionised water. Plants were harvested after 30 days of growth. Roots and shoots were separated and carefully rinsed with deionised water to remove all soil particles.

2.4. Analysis of PCB

Congener-specific analyses of both soil and plant samples were performed using the modified EPA 1668 method [13]. Preparation of soil and plant samples for PCB determination is precisely described [14].

Samples were analyses for PCB on the gas chromatography coupled with mass spectrometry detection (GC/MSD) using the HP 6890N/5975 (Agilent Technologies, USA). Samples were separated on a 30 m × 0.25 mm, 0.25 μm, HP5-MSI capillary column (J&W Scientific, USA) under following temperature program: 2 min at 70 °C, from 70 °C to 150 °C at 25 °C min^{-1}, to 200 °C at 3 °C min^{-1}, to 270 °C at 8 °C min^{-1}, to 290 °C at 25 °C min^{-1} and 5 min at 290 °C. The carrier gas used was pure helium with a flow rate of 1 mL min^{-1}. The injection volume was 1.0 μL in the splitless mode. The injector temperature was kept at 250 °C; a pressure of 8.31 psi during 1.5 min was applied. A SIM (selected ion monitoring) mode acquisition method with two characteristic ions was chosen for the detection of analytes. The seven PCB congener structures, the SIM ions and the retention times under the given experimental conditions are listed in Table 2.

2.5. Statistical analysis

One-way analysis of variance (ANOVA) with further Duncan test was performed for the evaluation of the data (Statistica 7.0, StatSoft). The results were evaluated on the basis of homogeneous groups at the level of significance $p < 0.05$.

3. Results and discussion

3.1. PCB removal by ozone treatment

The laboratory experiment showed that ozonation of soils contaminated with PCB led to their degradation and the removal efficiency increased with increasing ozonation time. The disappearance of the sum of PCB congeners (PCB$_7$) from the soils exposed to ozone within time is shown in Fig. 2. The initial concentration

(c_0) of PCB$_7$ just before ozonation was lower than the concentration spiked to the soils. These losses can be attributed to a strong (non-extractable) binding to the soil sorption complex and due to a variety of mechanisms, including biodegradation, photodegradation, leaching and volatilization [15,16] since these soils were placed in an experimental outdoor hall in order to better simulate natural conditions. A period of 2.5 h of ozone treatment did not show significant decreases of PCB$_7$ concentration among the treatments. Longer ozonation led to rapid decreases in PCB$_7$ mainly in Fluvisols. While Fluvisols showed a statistically different decrease after each ozonation time, Chernozems showed it only between 0 and 2.5 h and between 2.5 and 6 h of ozonation (Chernozem 06) or did not show any (Chernozem 36). This variation can be attributed to the different SOM content of individual soils since competing reaction of ozone with SOM was found to reduce contaminant removal rates [5,9,17]. Cornelissen et al. [18] indicated that the presence of SOM significantly increased the sorption of PCB and chlorobenzenes. Chernozems contain more SOM competing with ozone, and thus less ozone is available for the degradation of PCB. Results of study performed by Cassidy et al. [19] showed that the presence of SOM resulted in a slower reaction rate of the di- and hexachlorbiphenyls with ozone.

Fig. 3 shows how soil temperature, measured in 1.5 cm distance from the bottom, rose in the beginning of ozonation. Larger differences in temperature, more than 10 °C, with the maximum reached after 1.3 h was found in Fluvisols. Similar findings were performed by Leštan et al. [12] where soil temperature reached the maximum after 1 h of ozonation of soils contaminated predominantly with Pb. This can be attributed to an exothermic oxidation reaction with soil organic matter and possibly reaction with sand and hydroxyl radicals formation during the process. For that reasons, no significant differences in PCB degradation were observed among treatments after 2.5 h of ozonization since the SOM oxidation could prevail over PCB degradation. After the maximum temperature was reached, it remained stable or slightly declined which can also explain different PCB removal rates among the treatments. The results also showed that the temperature growth was slower further from the ozone source. Moreover, in all treatments, temperature did not achieve its maximum at 7.5 cm from the bottom of the column (data not shown).

Other explanation of increased PCB$_7$ removal from Fluvisols could be attributed to a higher content of the sand fraction and/or sesquioxides in these soils since the catalytic properties of the
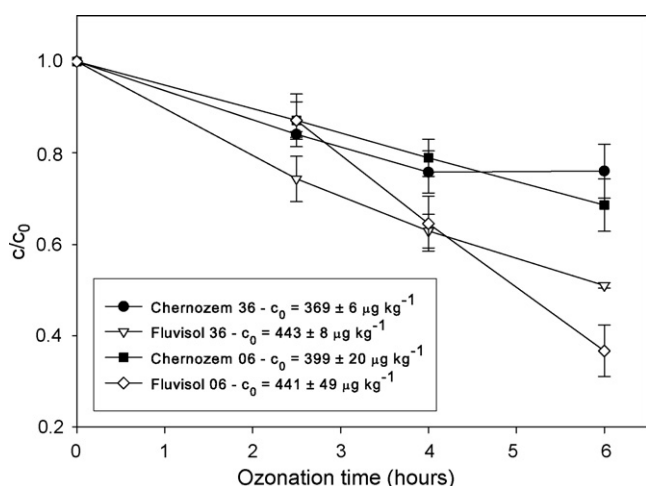

Fig. 2. Relative concentration of PCB$_7$ found in the studied soils before (0 h) and after 2.5, 4 and 6 h of ozonation.
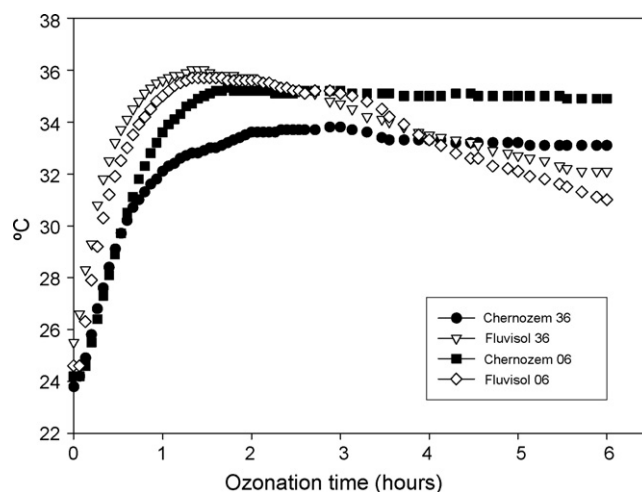

Fig. 3. Temperature evolution during ozonation in the studied soils measured by probes placed into the column in 1.5 cm distance from the bottom.
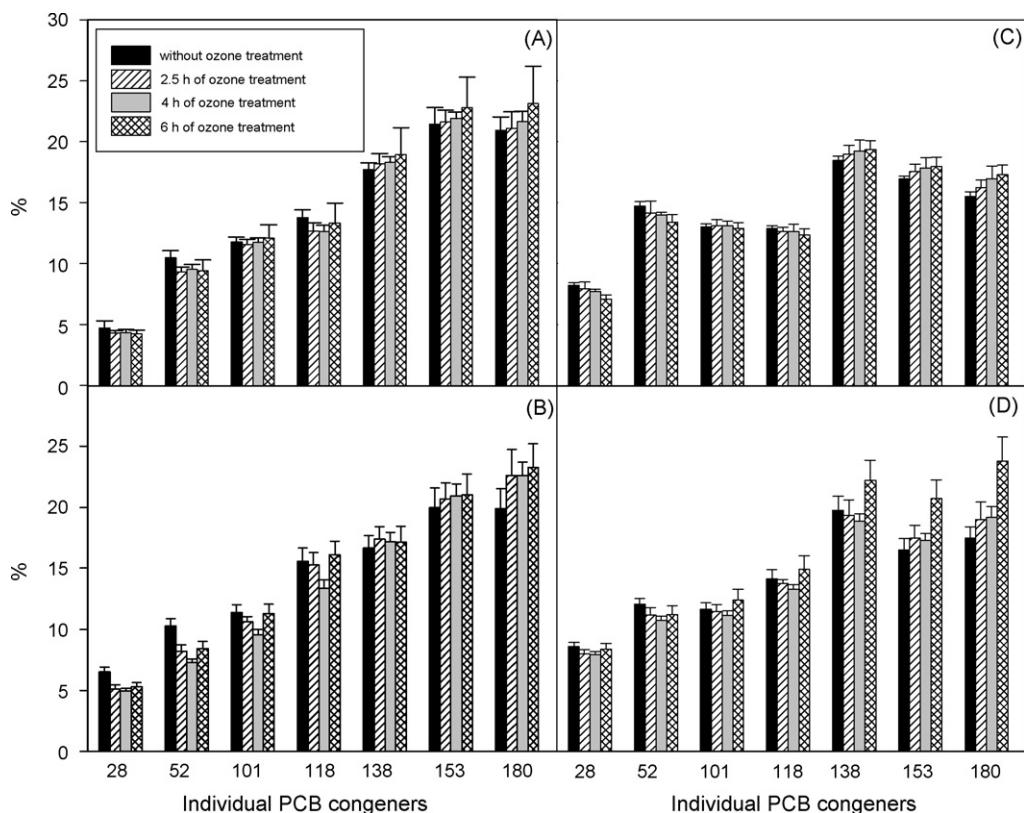
Fig. 4. Percentual contents of individual PCB congeners in the studied soils from (A) Chernozem 36, (B) Fluvisol 36, (C) Chernozem 06, and (D) Fluvisol 06 with/without ozone treatment.

sand surface (caused by presence of metal oxides) enhance the self-decomposition rate of ozone generating more OH radicals (OH•) in the system [7,20]. The radicals OH• are known to be non-selective and stronger oxidants of organic compounds than ozone itself [6,21]. In the study performed by Choi et al. [22], 22% of the enhancement in phenanthrene removal was achieved by OH• generated by catalytic reactions of ozone with the reactive sites of the sand. Moreover, a higher level of PCB_7 removal from Fluvisols may result from the fact that these soils have a larger pore spaces than the Chernozem clayey soils, facilitating thus the transport of gaseous ozone through the soil [23]. Several authors reported that high soil pH favour the decomposition of ozone and thus increased

Fig. 5. Soil organic matter content measured in the studied soils with/without ozone treatment.

generation of OH• [24,25]. Since we used air-dried soil samples, the effect of different soil pH could be neglected. Approximately 37% and 69% of PCB_7 remained in the Fluvisol 06 and Chernozem 06 in contrast to Fluvisol 36 and Chernozem 36 where 50% and 76% of the initial PCB_7 concentration remained. This could be explained by the fact that soils contaminated in a long term developed more resistant bonds leading to high sequestration of contaminants. Therefore, they exhibit very slow desorption and removal compared to freshly contaminated soils [26,27].

The distribution of individual PCB congeners in the studied soils before ozonation is similar to our previous findings [14]. A lower percentage ratio of lower chlorinated biphenyls (LCB) and a higher percentage ratio of highly chlorinated biphenyls (HCB) was detected in all treatments even that all soils were spiked with same amount of each PCB congener (Fig. 4). The stronger linear relationship detected in soils spiked 36 months before ozonation is attributed to the formation of stable bonds of HCB and easier degradation of LCB in soils. The composition of individual PCB congeners changed at all variants in terms of higher accumulation rate of HCB with increasing ozonation time. This trend is more evident in Fluvisols. Our results are consistent with those obtained by Manzano et al. [28] where the degree of elimination depended on the level of congener chlorination in soils treated with the Fenton reagent. The LCB congeners have been found to have higher vapour pressures (Table 2) than the HCB congeners [29]. Therefore, the lower sorption tendency of LCB in soils can increase their availability to react with ozone. Furthermore, air-dried soils were used in our experiments containing possibly some traces of pore moisture (up to 3%). The higher removal rate of LCB compared to HCB can be thus partly attributed to their different log K_{ow} values (Table 2). Nam and Kukor [5] reported that the efficiency of ozonation in the degradation of PAH decreased as the log K_{ow} increased.
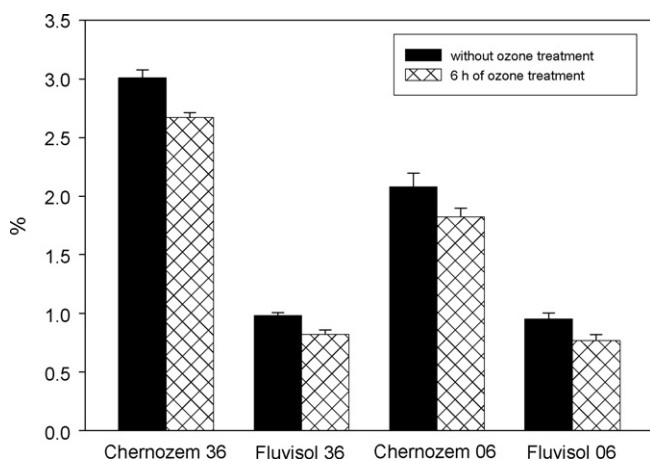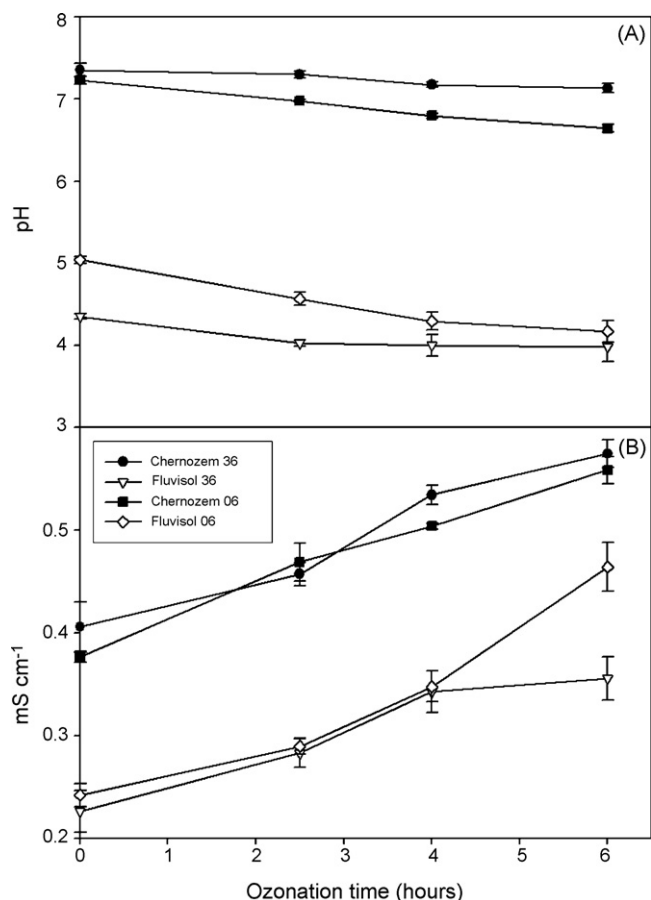
Fig. 6. Soil pH (A) and electrical conductivity (B) changes in the studied soils measured before (0 h) and after 2.5, 4 and 6 h of ozonation.

Fig. 7. Concentration of PCB_7 in rape plants grown on the studied soils with/without ozone treatment.

3.2. Influence of ozone treatment on soil characteristics

Beside the fact that ozonation significantly degrades PCB congeners in soils, its side effect on soil properties has to be carefully watched since secondary use of treated soil is expected. Therefore, several soil parameters were investigated before and after ozonation. As mentioned earlier, ozonation leads to the degradation of SOM [9,17]. Haapea and Tuhkanen [17] found that SOM content decreased by 40% after ozonation. The reduction in SOM content in all tested soils ranged between 10% and 20% with differences between soil types (Fig. 5). Higher decreases were found in Fluvisols.

Soil pH was measured before and after individual ozone treatments. All tested soils showed a statistical decrease in soil pH between treatments without ozone procedure and after 6 h of ozonation (Fig. 6). The soil pH declines during ozonation can be explained by the changed characteristics of SOM. Organic matter becomes more acidic and hydrophilic due to the formation of carboxylic functional groups [30].

As mentioned earlier, ozonation may possibly change the nutrient mobility and cause the mobilization of some metals e.g., by destroying the SOM or by changing the oxidation state of some metals [11,12]. In order to estimate the total amount of dissolved ions before and after ozonation, electrical conductivity (EC) measurements were performed. The EC of soil solutions measured in demineralised water before ozonation and after different ozonation time is shown in Fig. 6. As the ozonation time increased, the EC of soil solutions increased. This fact can be related to the destruction of SOM by ozone and subsequent release of ions into the soil solutions. Furthermore, Naddeo et al. [31] observed that increasing the oxidation rate leads to increased EC through SOM decomposition. Almost a twofold increase of EC after 6 h of ozone treatment compared to the untreated variant was found in Fluvisol 06. This can be related to the highest reduction of SOM content found in this soil.

In order to obtain more data about changes of easily extractable elements before and after ozonation, the 0.11 M acetic acid extraction [32,33] was performed (Table 3). Almost no statistical differences were observed in the case of K, Mg and Ca. Increased concentration of other elements in the soil solution, which were even more than 2.5-fold higher in some cases, could be attributed to the degradation of soil organometallic complexes by ozone [12].

3.3. Growth of plant on ozonated soils

Vulnerability of plants to grow on soils treated with ozone was documented on rape seedlings. Plant biomass production and concentration of PCB in shoots were investigated. Statistical analyses did not show any inhibition of plant growth after any treatment. It is in contrast with the study performed by Stehr et al. [34] who found that the growth of garden cress grown on PAH contaminated

Table 3
Content of elements extracted by 0.11 M acetic acid measured before (0 h) and after 6 h of ozonation; data marked by the same letter did not significantly differ at $\alpha = 0.05$

Sample	Cu (mg kg^{-1})	Fe (mg kg^{-1})	Mn (mg kg^{-1})	Zn (mg kg^{-1})	P (mg kg^{-1})	Ca (mg kg^{-1})	Mg (mg kg^{-1})	K (mg kg^{-1})
Chernozem 36 (0 h)	2.63[a]	49.5[a]	71.9[a]	2.62[a]	179[a]	10913[a]	566[a]	172[a]
Chernozem 36 (6 h)	3.59[b]	44.4[a]	202[b]	3.31[b]	240[b]	10329[a]	584[a]	187[a]
Fluvisol 36 (0 h)	0.30[a]	64.1[a]	57.9[a]	6.59[a]	189[a]	478[a]	28.6[a]	149[a]
Fluvisol 36 (6 h)	0.53[a]	158[b]	72.5[a]	8.89[b]	279[b]	530[a]	34.1[a]	169[a]
Chernozem 06 (0 h)	0.98[a]	77.7[a]	71.3[a]	1.79[a]	32.5[a]	4336[a]	263[a]	114[a]
Chernozem 06 (6 h)	1.87[b]	91.8[a]	182[b]	2.17[b]	61.6[b]	3430[b]	285[a]	127[a]
Fluvisol 06 (0 h)	0.36[a]	94.2[a]	48.0[a]	5.67[a]	216[a]	638[a]	48.7[a]	166[a]
Fluvisol 06 (6 h)	0.93[b]	231[b]	76.4[b]	7.39[b]	324[b]	773[a]	44.3[a]	187[b]

soils was hindered after ozonation. The authors attributed this fact to the formation of toxic substances during the phenanthren ozonation. However, it was demonstrated only on root length measured after 2 days of growing. Fig. 7 presents the amount of PCB_7 found in shoots of rape plants grown on ozonated/non-ozonated soils. From the statistical point of view, no differences were observed among individual ozone periods but differences were detected between ozonated and non-ozonated treatments. Even more than 3.3- and 2.4-fold higher concentrations of PCB_7 were detected in rapes grown on Fluvisol 36 and Chernozem 06 soils without ozone treatment compared to those grown on soils treated with ozone for 6 h. Distribution of individual PCB congeners followed the same trend in all treatments (higher accumulative level of HCB in rape biomass; data not shown). Since rapes were harvested during the elongation stage, our result confirms the ability of rape to grow on ozone-treated soils. For the determination of the degradation potential further research has to be performed with plants harvested in pure maturity.

4. Conclusions

The main following conclusions and suggestions for further investigations have arisen from the presented study:

1. Ozonation led to PCB removal from contaminated soils with the higher degradation rate of LCB congeners.
2. Prolongation of the ozonation period led to different PCB removal rate among treatments indicating the substantial effect of soil physico-chemical properties on the efficiency of ozonation.
3. PCB in soils contaminated in a long-term (Chernozem 36, Fluvisol 36) are more strongly bound to the soil sorption complex leading to lower PCB removal compared to freshly (Chernozem 06, Fluvisol 06) contaminated soils.
4. Changes in soil characteristics and composition of elements were detected after the ozone treatment.
5. First results carried out with plants growing on ozonated soils showed decreased amounts of PCB in rape seedlings point out that ozonation is a promising remediation method.
6. More research is needed to maximise PCB degradation keeping soil parameters sufficient for optimal plant growth.

Acknowledgements

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