Article

Investigation of the Ozonation of Highly PAXHs Contaminated Soil Using Ultrahigh Resolution Mass Spectrometry

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Abstract: Ozonation is an effective chemical treatment technique for removing contamination from the environment. In some countries it is used to clean up drinking water instead of using chlorinated treatment. The contamination of soil with polyaromatic compounds (PAXHs with X = N, S or O) are some almost forgotten contaminants but describe very toxic and by now almost omnipresent chemical contaminations. The extremely high number of different PAXHs are strongly adsorbed on soil and a method is introduced where an organic solvent is used to facilitate the reaction of the contaminant with ozone. In this study ozone is applied for 6 or 18 h with addition of toluene and the different phases (organic, water, and extract of soil phase) are studied to understand the ozonolysis of polycyclic aromatic hydrocarbons and their derivatives. The reaction is studied using ultrahigh resolution mass spectrometry (UHRMS) allowing a comprehensive characterization of the initial contaminants as well as the various oxidation products. The results show that the ozonation treatment leads to continuous degradation of already oxidized compounds and a wide range of oxidation products can be detected.

Keywords: contamination; polyaromatic hydrocarbons; mass spectrometry

1. Introduction

Soil, air, and water pollution by polycyclic aromatic hydrocarbons or polyaromatic heterocycles that can contain different heteroatoms such as sulfur, nitrogen, or oxygen (PAXHs with X = N, S or O) originated from natural and anthropogenic sources has resulted in ubiquitous environmental damage all over the world. These compounds are known to be highly toxic to human health and to ecosystems [1,2]. Therefore, different soil remediation techniques were developed to remove the pollutants from soil. Besides thermal, physicochemical, and chemical remediation methods, biodegradation is the most widely used technique for treating PAXH contaminated soil [3]. Although biodegradation is both inexpensive and environmentally friendly, it has limited applicability regarding the solubility and accessibility of the contaminants. While low molecular weight compounds (LMW, means compounds with 2–3 rings) have a certain water solubility and higher molecular weight (HMW, >3 rings) PAXHs have a lower solubility in water and additionally can be more strongly sorbed to the soil organic matter. Both of those points reduce the accessibility to oxidants and therefore limits the effectiveness of biodegradation [4,5]. Besides the Fenton reaction [6–8] and photolysis [9–11], ozonation is used as a chemical (pre)treatment process to oxidize the recalcitrant HMW pollutants for enhancing the aqueous solubility and bioavailability. However, there are contradictory reports in the literature about the removal efficiency of PAHs by combining ozonation with bioremediation. Goi and Trapido observed that the combination of ozonation and bioremediation results in higher degradation of the pollutants than the respective treatment technique alone [12]. On the contrary, Scheper and co-workers pointed out that this combination does not improve the removal of PAHs, because ozonation is breaking the active binding sites for the microbial attack [13].

Ozone itself is as a strong electrophile and has a high reactivity towards PAXHs, because it attacks organic contaminants either by direct (bond attack) or indirect (atom

attack) mechanism. The direct pathway involves the 1,3-dipolar-cycloaddition of ozone to a double bond, which is the main reaction for PAHs degradation [14,15]. In the indirect ozonation, organic pollutants react with hydroxyl radicals, which are formed due to the self-decomposition of ozone in the presence of soil matrix [16], metal oxides [17], and/or water [18,19].

Soil remediation efficiency using ozone depends on various properties such as soil characteristics (soil moisture content, presence of soil organic matter, inorganic compounds, etc.), type of contamination (LMW and HMW PAHs), and treatment parameters (ozone flow rate and ozone concentration) [20]. Previous studies showed that the presence of soil moisture [21,22] and soil organic matter [12,17,23] leads to a higher ozone consumption due to the self-decomposition of ozone, side reactions, and also to the non-selectivity of oxidants such as ozone which react in multiple ways.

The reactivity of PAHs towards ozone depends on the number of fused aromatic rings and are studied in opposing reports [20]. Different authors in various studies observed that the removal of HMW PAHs is more efficient than that of LMW PAHs contaminated soil [17,24]. This is attributed to the lower bond localization energies of HMW pollutants, which are more easily attacked by ozone [25]. On the other hand, Carrere [26] and Nam and Kukor [4] investigated the improved degradation of LMW PAHs than HMW resulting from the better solubility in water and lower adsorption to the soil matrix. This adsorption is even stronger for aged soils, which makes the chemical remediation by ozonation considerably more challenging [22,27]. These conflicting reports indicate that for the ozonation reaction not only the direct reactants are important, but also the circumstances and their availability for the reaction. This problem can be solved by adding an organic solvent to water to desorb the pollutants from the soil organic matter for ozone accessibility. The first experiments for the ozonation of pyrene (without soil) were done in the 1930s adding different organic compounds like acetic acid [28], *tert*-butyl alcohol [29], dodecane [30], and acetic acid/heptane [31]. Jonsson and co-workers used a mixture of H_2O/EtOH (50:50 v/v) as a solvent system in the ozonation of nine different contaminated soils and analyzed 24 selected PAHs by gas chromatography coupled with mass spectrometry (GC-MS) [32]. Other authors investigated the addition of surfactants for the removal of naphthalene in Brij 30-containing solution [33] and removal of PAH contaminated sewage sludge [34]. Gas phase reactions of the ozonation reaction include studies of terpenes with ozone by gas chromatography-Fourier transform infrared spectroscopy (GC–FT-IR) and GC-MS [35].

GC-MS and high performance liquid chromatography (HPLC) are established analytical techniques for the ozone degradation studies of selected 16 EPA PAHs. This targeted and preferred method for PAHs analysis has the advantage of simple and comparable quantification of the results. However, the majority of the PAHs including higher molecular weight PAHs, alkylated PAHs and heteroatom-containing PAHs [36,37] are reacting with O_3 and should therefore be covered by the analysis method [38]. The combination of ultrahigh resolution mass spectrometry (UHRMS) with a non-target approach provides a much more comprehensive characterization of various oxidized and non-oxidized compounds obtained after ozonation. Based on high resolving power and mass accuracy UHRMS allows unique determination of the elemental compositions for each detected ion using Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) [39–44] or Orbitrap MS [45–49] due to its high accuracy and high resolution capabilities.

In this study, ozonation is used to degrade PAXHs from aged, contaminated soil using toluene as additional modifier solvents to make the contaminants available for oxidation. It has to be noted that the addition of toluene is not the best way to solve the issues here, because toluene is also a contaminant that can be removed by microbiological treatment. On the other side, the addition of an organic modifier has shown to be of help in making PAXH compounds accessible for the oxidation reaction [50]. Here, the advantages have to be taken with the disadvantages and the addition of toluene is necessary. For the understanding of the reactions, different phases (extracts from soil phase, organic and water phase) were analyzed after the ozonation using (+)-APPI Orbitrap MS to detect

the broadest range of PAHs and PAXHs (X = N, S, O) compared to atmospheric pressure chemical ionization (APCI) and electrospray ionization (ESI) [51]. The unique capabilities of ultrahigh resolution mass spectrometry allow a detailed observation of such a reaction and the detection of the oxidation products.

## 2. Materials and Methods

2.1. Chemicals

In this study toluene ($\geq$99.8%, Fisher Scientific, Loughborough, UK) and water (type I), which was tapped from a Clearwater dispenser Purelab Flex 2 (ELGA LabWater, Celle, Germany), were used for the ozonation.

2.2. Sample Preparation

An aged, contaminated soil sample was obtained from an industrial site in the German Ruhr area and 5 g of this sample was air dried at room temperature in a fume hood for 1 week. Afterwards, the sample was mortared for homogenization, sieved (2 mm pore size), and kept in a fridge at 4 °C for further treatment.

2.3. Experimental Procedure

Ozonation was performed by bubbling ozone continuously into a 25 mL vial with soil sample (85 mg), toluene (8 mL), and deionized water (10 mL) and stirred at room temperature for 6 and 18 h (Figure 1). Gaseous ozone was generated by BMT 803N ozone generator (BMT, Berlin, Germany) with maximum ozone generation power adjustment of 10 arbitrary units and a gas flow rate of 1 l/h. The excess not consumed ozone was passed through manganese dioxide (MnO_2) for removal.
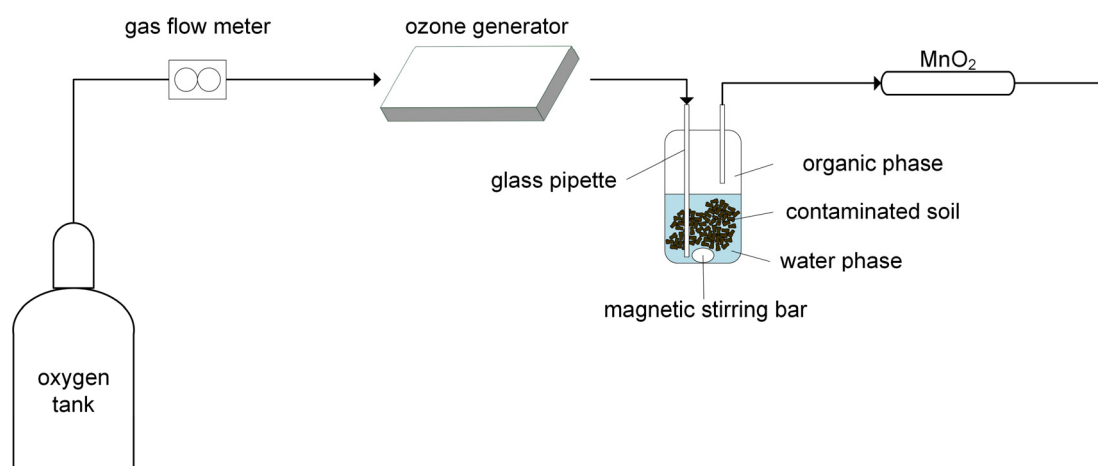
Figure 1. Schematic diagram of the ozonation experimental apparatus.

The soils from different reactions were filtered, dried in a fume hood and remaining PAXHs were extracted by Soxhlet extraction with dichloromethane (DCM, Fisher Scientific, Loughborough, UK) (50 mL) for 24 h. The solvent was then removed under reduced pressure and the residues stored for further analysis.

The liquid layers were separated by liquid-liquid extraction and the organic layer was dried over magnesium sulfate ($MgSO_4$, Sigma Aldrich, Darmstadt, Germany) and filtered. Both the water and toluene phases were concentrated under reduced pressure and residues stored for further analysis.

A control reaction without ozone was performed by stirring the contaminated soil in toluene (8 mL) and deionized water (10 mL) for 18 h at room temperature. The different layers were separated and prepared for the analysis as described before.

2.4. Instrumentation and Data Analysis

The different residues were diluted in toluene:methanol (1:1, v/v) to a final concentration of 150 ppm and analyzed using a research-type Fourier transform Orbitrap Elite mass spectrometer (Thermo Fisher Scientific, Bremen, Germany). Mass spectra were recorded with a transient of 1.5 s, resulting in a resolving power of R = 480,000 at m/z 400 in a mass range of m/z 150–1300 using a spectral stitching [46,52,53] method with mass windows of 30 Da and 5 Da overlap. For the ionization with APPI, a Krypton VUV lamp (Syagen Technologies, Tustin, CA, USA) was used with photon emission at 10.0 and 10.6 eV. The diluted samples were introduced by direct injection at a flow rate of 20 µL/min and ion source conditions were set as follows: capillary temperature of 275 °C, vaporizer temperature of 250 °C, sheath, auxiliary, and sweep gases of 20, 10, and 2 arbitrary units.

Acquired mass spectra were analyzed using Composer V1.5.0 (Sierra Analytics, Modesto, CA, USA) to assign the elemental compositions to detected signals. Peak Assignments were applied on the following criteria: H: 0–300, C: 0–100, O: 0–20, N: 0–2, S: 0–1, double bond equivalent (DBE): 0–80 and mass error $\leq$ 1.5 ppm. For further data evaluation and graphical visualization Excel (Microsoft Office Professional Plus 2010, Microsoft Excel 2010) and Origin (v9.2.0, OriginLab Corporation, Northhampton, MA, USA) were used.

3. Results

The direct ozonation of aged, contaminated soil without organic solvent showed no significant removal of contamination. This can have different reasons, as the ozone does not interact with the PAH or that the PAH are bound to the soil matrix. Whatever the reason, to make the contaminants available for biodegradation they have to be accessible.

Therefore, to carry out the ozonation of contaminated soil an additional modifier needs to be added and here toluene was added to enhance accessibility of pollutants towards oxidants. The detailed reaction was then investigated using high resolution mass spectrometry as this is the method of choice to analyze complex mixtures of pollutants and complex soil organic matter as well as the effects of the ozonation on contaminated soil.

The different APPI mass spectra of different extracts (control reaction, 6 h ozonation in toluene and 18 h ozonation in toluene) are compared in Figure 2. The mass spectrum of the control reaction (top trace, black) contains prominent signals, of which some ($m/z \leq 278$) correspond to pollutants from the 16 EPA-PAH list. However, dominant signals are also detected above m/z 278 indicating the presence of higher aromatic compounds that are not present on the 16 EPA-PAH list [54].

After ozonation with addition of toluene (second and third trace, red and orange), new oxygen containing species are formed, indicating the increased effectiveness of removing PAHs is more effective with the addition of toluene as an organic solvent. Detailed changes are presented in the zoomed-in spectra between m/z of 367.10 and 367.16. Here, $C_{29}H_{18}[H]$ is detected with lower intensities by increasing the reaction time from 6 h to 18 h, while an almost complete removal of the nitrogen compound $C_{28}H_{17}N$ is observed. Additionally, multiple oxygenated species such as $C_{21}H_{18}O_6[H]$, $C_{25}H_{18}O_3[H]$ and $C_{22}H_{22}O_5[H]$ are detected with significant intensities in comparison to the intensities of polycyclic aromatic hydrocarbons.

Figure 3 shows the detailed results of the distribution for selected signals, which are arranged in different heteroatom classes based on the number of assigned elemental compositions. APPI is able to ionize PAXHs [51,55] forming protonated [M+H]$^+$ and/or radical cation [M]$^{+\bullet}$ species [56]. Each compound class contains the number of all individual signals of each phase (organic, water and extract of soil phase) and the intersections of these different phases, so that each individual composition from all phases is represented exactly once.
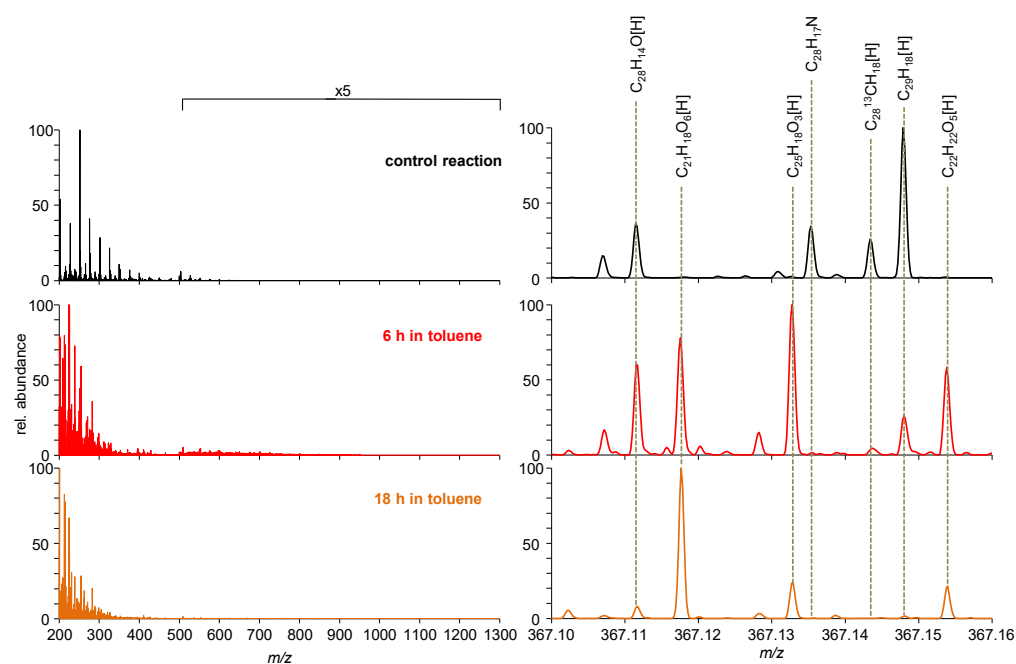
Figure 2. Mass spectra of organic phases from control reaction (black), ozonation within 6 h in toluene (red), within 18 h in toluene (orange), and corresponding zooms into *m/z* 367.10–367.16 (**right**).
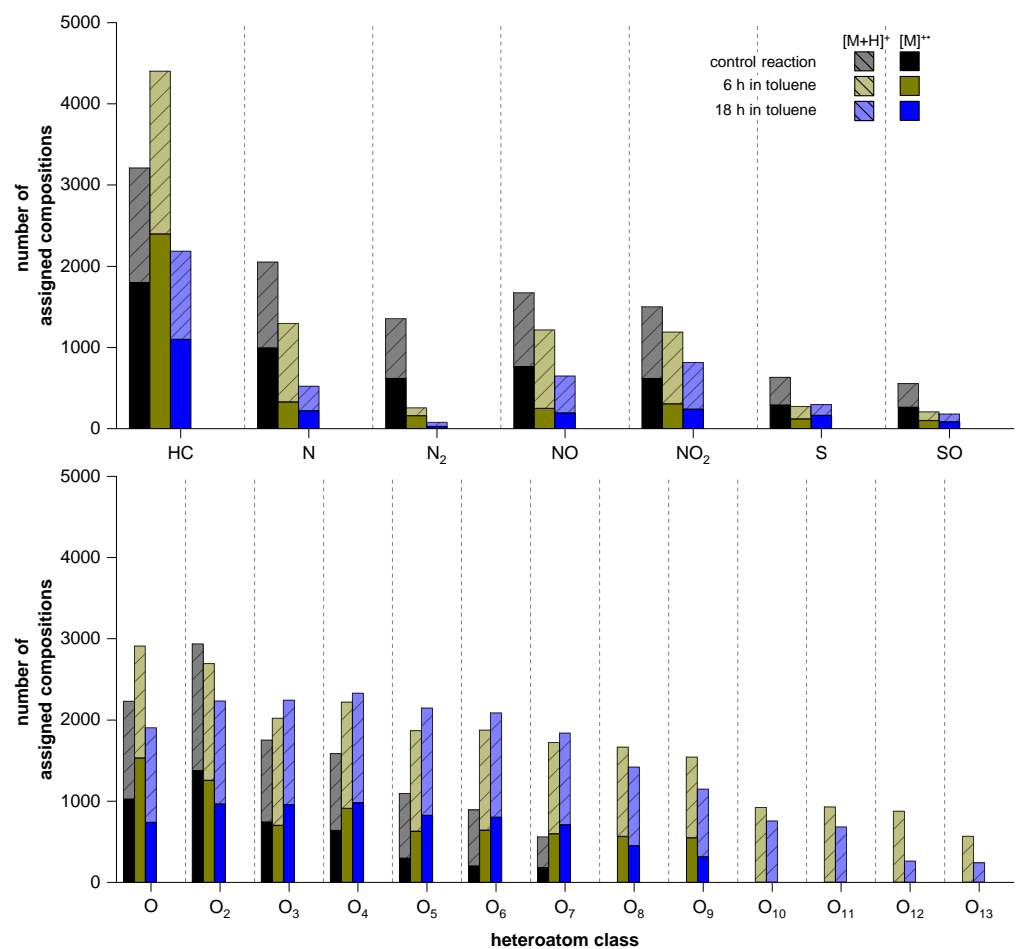
Figure 3. Population-based class distribution of the most prominent heteroatom classes (**top**) and oxygenated compounds (**bottom**) for control reaction (black), ozonation within 6 h in toluene (dark yellow) and within 18 h in toluene (blue).
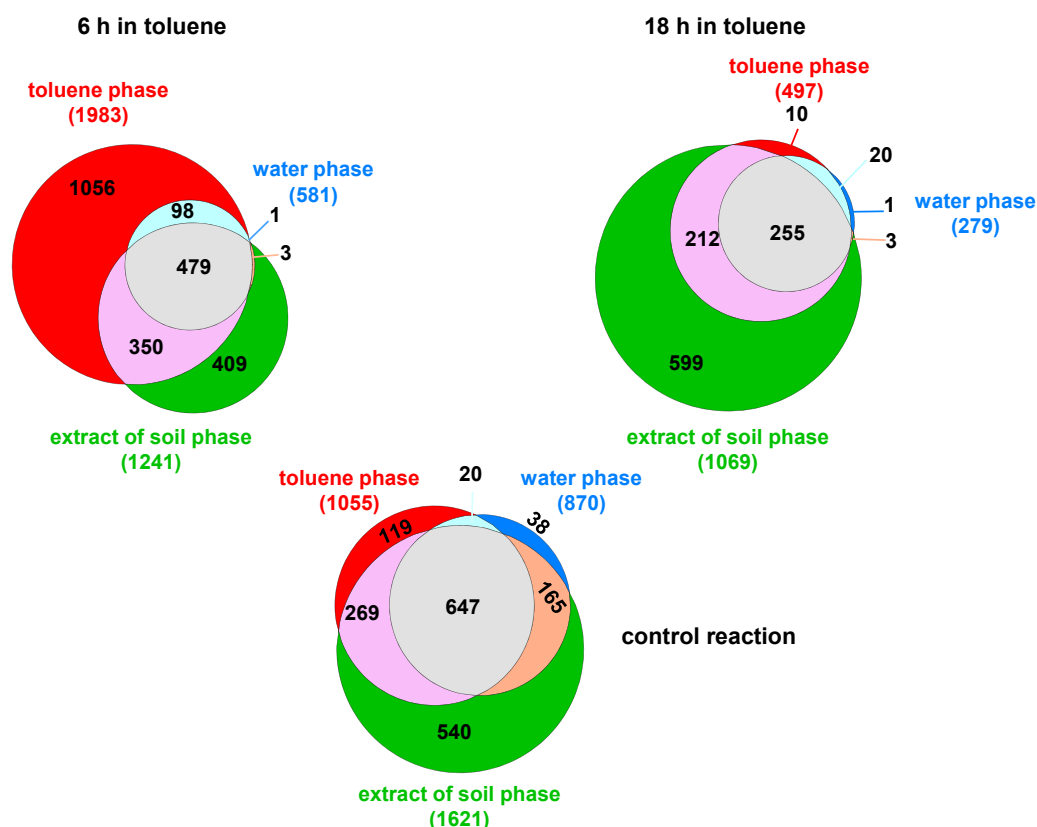
Results from the measurements of the control sample show that HC class is the most abundant class followed by NO, NO_2, and N_2. The comparison of the control reaction with the ozonation reactions show a significant decrease of the populations for hydrocarbons, N-containing compounds, and S-containing compounds. The most efficient removal of PAHs (reduction from 3211 to 2183 hydrocarbon species) and PANHs (from 2052 to 522 nitrogen species) is achieved by adding toluene and using a reaction time of 18 h, due to longer contact time with O_3. However, after the 6 h ozonolysis with addition of toluene an increase of the HC class is observed. This increase might be the consequence of the enhanced extraction of pure hydrocarbons from the soil under these conditions. Adsorption of PAH to soil matter can be strong especially in aged soil and both the addition of toluene can dissolve the contaminations better while O_3 can weaken the adsorption [22]. A similar observation was reported by Choi et al. showing the improved extraction of humic substances with longer contact time with ozone [23].

Performing the ozonation reactions multiple oxygenated compositions up to O_{13} are detected. When performing 18 h of toluene-based ozonation, less O_x (x > 8) are detected compared to 6 h toluene-based ozonolysis. This decrease of number of O_x species with increasing time of ozonation can be explained by further reaction and decomposition of by-products with O_3 [21]. Various compounds with a high average of molecular weights are formed during ozonation, and interestingly with longer treatment time, high molecular weight compounds are degraded to smaller ones [23].

For a detailed presentation about the differences in the population between the phases, a Venn diagram for the radical HC class is shown in Figure 4. Comparison of the control reaction with toluene-based ozonation after 6 h illustrates a decrease in the individual and common assignments in different phases, except for the toluene phase (red circle) and common assignments for extract of soil phase and toluene phase (pink circle). This increase of the assignments in the toluene phase explains the enhanced extraction of hydrocarbons after a certain reaction time, which are individually detected in the toluene phase only. These compounds are then further oxidized due to the strong reduction of assignments of 1983 (6 h reaction time, toluene phase) to 497 (18 h reaction time, toluene phase). After 18 h of ozonation, a population decrease is achieved for common, individual and total detected phases demonstrating the continuous removal of PAHs. Comparing the individual assignments of the extracts from soils, 599 hydrocarbon species were detected after 18 h of ozone injection. This increase can be explained by the fact that the degradation of PAHs in toluene and water phase is faster than in the soil probably due to oxidation of PAHs at the water-toluene phase boundary.

For a more detailed understanding of chemical changes after the ozonation, Kendrick plots of HC, O_3, and O_7 of different reactions and phases are shown by representation of assigned compositions as a dot with a certain DBE and #C (carbon number) per molecule. In addition, the total relative intensity for a given DBE is connected to a line. Figure 5 illustrates these results for HC species. The extract of the soil phase from control reaction covers PAHs with maximum DBE of 73 and #C of 94. Additionally, a narrow distribution with high relative intensities (red dots) is obtained for the toluene and the extract of soil phase, which indicates the higher concentration of these hydrocarbons in the soil. Highly aromatic hydrocarbons with DBE > 55 and #C > 70 are not extracted by toluene during 18 h of stirring, while PAHs with DBE $\leq$ 47 and #C $\leq$ 58 are detected in the water phase sample. These HMW PAHs have a poor solubility in water [32,57,58] and therefore the relative intensities of assigned PAHs with DBE $\geq$ 20 are much lower than to corresponding assigned ones in the extract of soil and toluene phase.
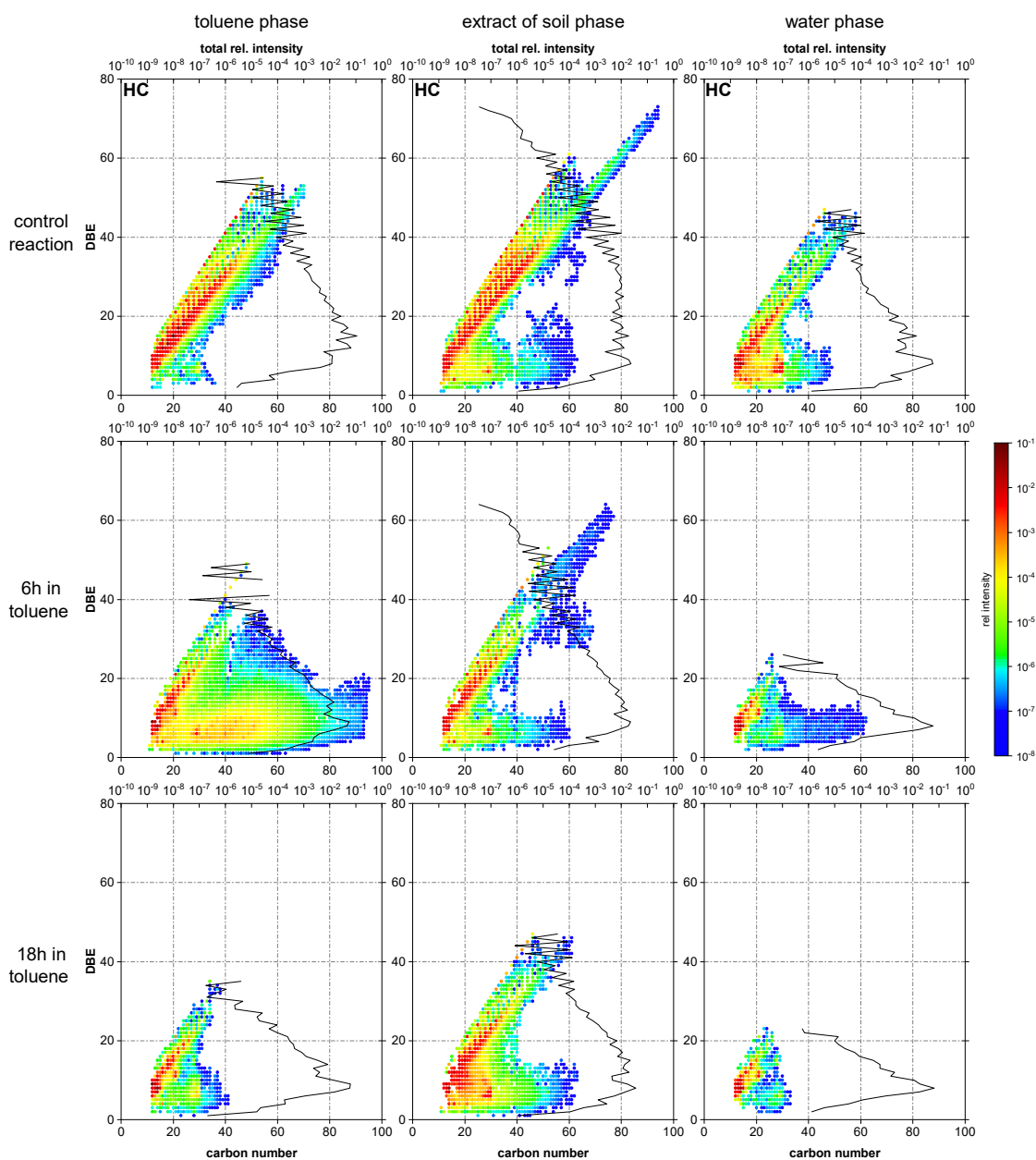
6 h in toluene

toluene phase
(1983)

1056
98
1
479
3
350
409

water phase
(581)

extract of soil phase
(1241)

18 h in toluene

toluene phase
(497)
10
20
212
255
1
3
599

water phase
(279)

extract of soil phase
(1069)

toluene phase
(1055)
20
119
269
647
38
165

water phase
(870)

control reaction

540

extract of soil phase
(1621)

Figure 4. Population-based area-proportional Venn diagrams for radical HC species of different phases from control reaction (**middle**), ozonation within 6 h in toluene (**top left**) and within 18 h in toluene (**top right**).

After the 6 h ozone treatment of contaminated soil and with addition of toluene, a broader range of PAHs with #C up to 95 are detected in the toluene phase. These hydrocarbons are adsorbed very strongly to the soil and after a certain time of ozonation they can be extracted by toluene. Furthermore, a significant decrease of the high relative intensities from the narrow distribution with DBE values higher than 20 is achieved for toluene and the extract of soil phase hinting an effective removal of these pollutants from soil. Meanwhile, less HC species are detected in the water phase after 6 and 18 h ozonation in toluene, which especially explains the limited phase transfer of PAHs with DBE < 27 and the high implementation of O_3 in wastewater treatment due to the effective oxidation of contaminants in water [59,60].

After 18 h of toluene-based ozonation, highly aromatic PAHs with DBE > 52 were completely removed from the soil. Additionally, a reduction of relative intensities for PAHs with DBE 20–40 was observed when injecting ozone for 18 h suggesting the partially degradation of these compounds. The faster degradation of HMW and high carbon content PAHs may be declared by the fact that these PAHs are likely to be present in lower concentrations in the soil than LMW PAHs.

The same reactions comparisons are shown in Figure 6 for $O_3[H]$ and $O_7[H]$ classes. Regarding the results of the control reaction, O_3 species were detected in all three phases, while O_7 species were only found in the water phase. After toluene-based ozonation for 6 and 18 h an increase of relative intensities for the narrow distributions is observed in all phases, but an increase in reaction time does not lead to any significant change in O_7 class. A closer look into the Kendrick plots reveals a second high intensity region (DBE $\leq$ 10 and #C $\leq$ 30) in O_3 and O_7 classes, only found in the toluene and the extract of soil phases. These multiple oxygen containing compounds with DBE $\leq$ 26 are transferred into the water phase and this explains the significant high intensity region in the water phases.
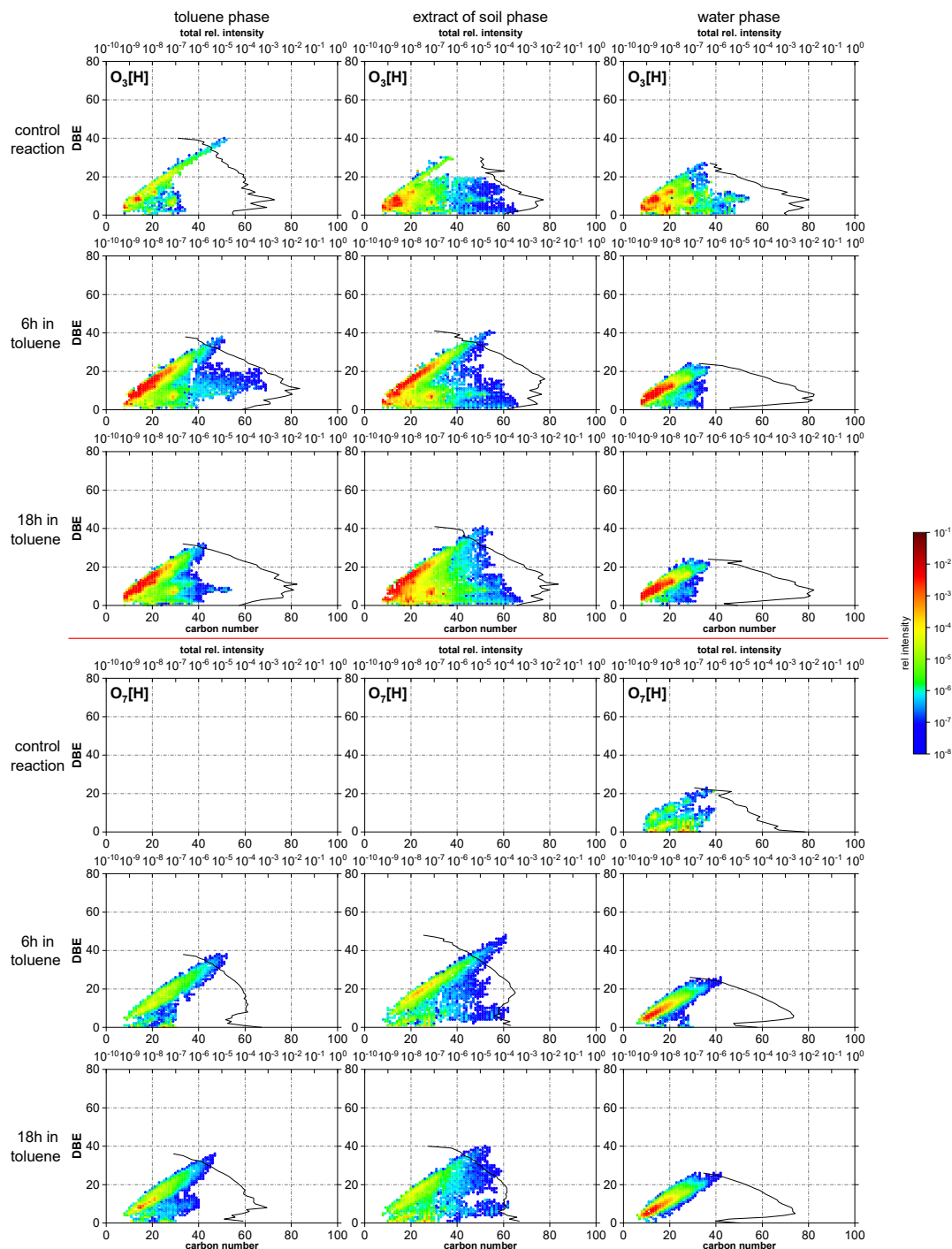
Figure 5. Kendrick plots for HC class in the different phases of control reaction, ozonation within 6 h in toluene and ozonation within 18 h in toluene. The total relative intensity for a given DBE is represented on the upper y-axis, while the number of carbon atoms is plotted on lower y-axis.

Since ozonation of only toluene results in formation of hydrocarbons and oxygenated compounds (Figure 7), the presence of toluene plays an important role in understanding the ozonation of contaminated soil. Nevertheless, results from ozonation of only toluene show the formation of hundreds of compounds and demonstrates, how complex the reaction can be even when ozonating a single compound. The production of such polymers by ozonation of only toluene can be a reason for enhanced extraction of pollutants from aged, contaminated soil, as polymers have surfactant-like properties [61]. This continuous formation of oxidized compounds is eventually the reason for less significant changes in the O_7 class shown in Figure 6. When comparing the Kendrick plots of ozonation of only toluene with both toluene phases, obtained from control reaction and 6 h ozonation, a perfect overlap of the high intensity regions is obtained. This overlap clearly shows the increase of the relative intensities in O_3[H] class is caused by indirect attack (atom attack) of high abundant PAHs with hydroxyl and/or toluene like radicals. Beside this, the high

intensity region (DBE $\leq$ 10 and #C $\leq$ 30) in $O_3[H]$ and $O_7[H]$ (Figures 6 and 7) class could originate from the mechanism of direct attack (bond attack) of ozone with highly aromatic PAHs, which causes ring openings and the decrease of DBE values.

Figure 6. Kendrick plots for $O_3[H]$ (**top** graph) and $O_7[H]$ (**bottom** graph) classes in the different phases of control reaction, ozonation within 6 h in toluene and ozonation within 18 h in toluene. The total relative intensity for a given DBE is represented on the upper y-axis, while the number of carbon atoms is plotted on lower y-axis.
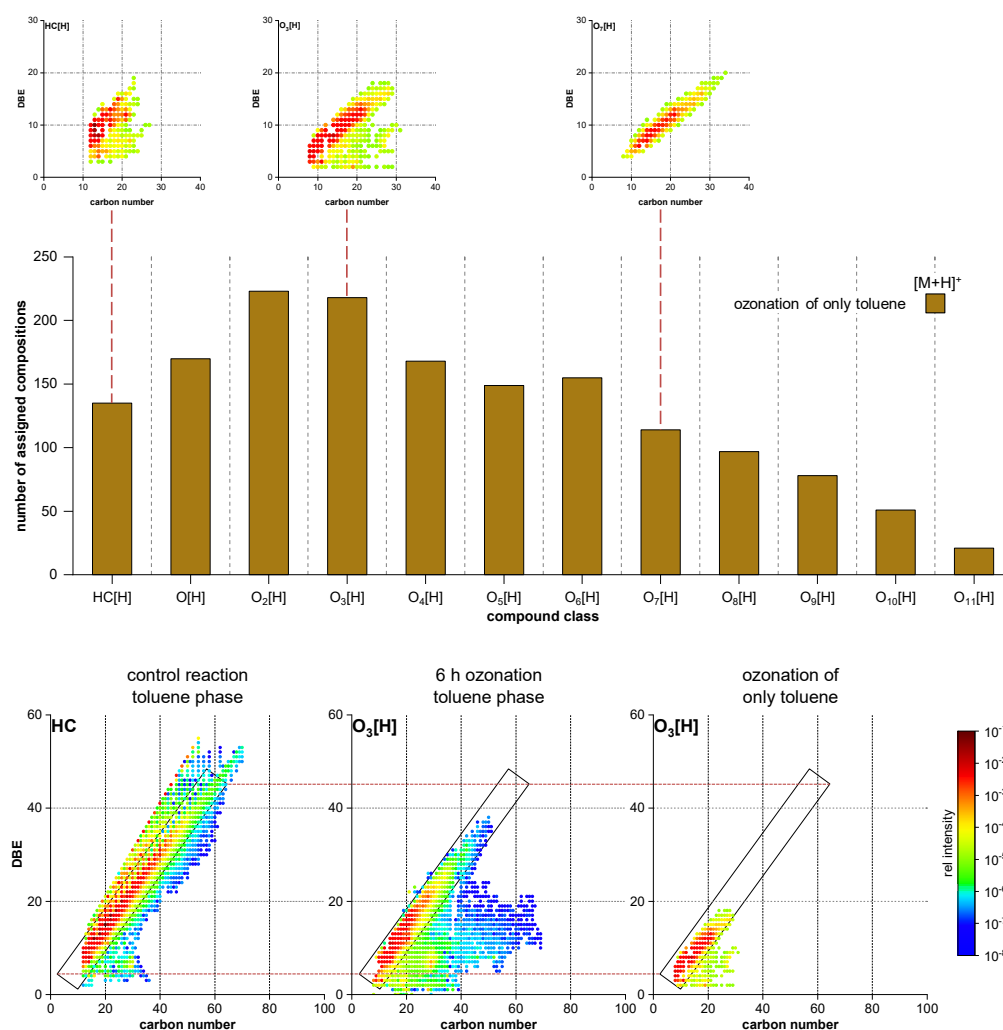
Figure 7. Kendrick plots for HC[H], O$_3$[H], and O$_7$[H] classes and population based class distribution of hydrocarbons and oxygenated compounds after ozonation of only toluene (**top** graph) and Kendrick plots of control reaction, 6 h ozonation, and ozonation of only toluene (**bottom** graph).

4. Conclusions

In this study, a combination of non-target analysis by using ultrahigh resolution mass spectrometry of the different phases achieved from ozonation of PAXHs contaminated soil with addition of toluene is demonstrated. For effective oxidation of PAHs and nitrogen-containing PAHs, the addition of toluene is required probably due to creation of surfactant-like products, which can further enhance desorption of contaminants, and addition of toluene moiety to pollutant molecules. Overall, the accessibility of the contaminants is improved by the additions of toluene.

Sophisticated analytical method such as ultrahigh resolution mass spectrometry allow a detailed coverage of the molecular changes that occur during the ozonolysis reaction. Due to the extremely accurate and highly resolved data, it is possible to detect the oxidized species and differentiate them from non-oxidized species. Detailed molecular information about such a complex reaction can be gained. Here, high molecular weight polyaromatic compounds with a double bond equivalent of more than 52 are successfully removed by performing 18 h of toluene-based ozonation with formation of highly oxidized compounds. With increasing reaction time, a decrease in the number of O$_x$ species is observed which is explainable by further reaction and decomposition of oxygen containing compounds with O$_3$. The achieved results confirm both mechanistic pathways (direct and indirect ozonation) for highly complex mixtures with both, a complex mixture of pollutants, and a complex

soil matrix. Further investigation can include the possibility of biodegradation of highly oxidized PAHs for an effective combination of chemical and biological treatment.

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