

**Investigation of chemical remediation techniques for
polycyclic aromatic compounds contaminated soil by
high resolution mass spectrometry**

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“Either seem as you are or be as you seem.”

*Dschalāl ad-Dīn
Muhammad Rūmī*

Kurzfassung

Die Funktionsfähigkeit des Bodens – als Bestandteil des Ökosystems – ist für die Existenz des Lebens und der Umwelt äußerst essenziell. Infolgedessen sind in den letzten Jahren die Bedenken über die permanente anorganische und organische Schadstoffbelastung des Bodens erheblich gestiegen. Der Substanzklasse der polyzyklischen aromatischen Kohlenwasserstoffe (PAKs) kommt als Kontamination aufgrund ihres starken krebserregenden und toxischen Potenzials eine bedeutende Rolle zu. Die weitere Nutzung dieser verunreinigten Böden ist kaum oder gar nicht mehr möglich und müssen daher einer Dekontamination unterzogen werden, welches sich als sehr schwierig erweist. Deshalb wird die Bestimmung relevanter chemischer und physikalischer Parameter für die Sanierungsbehandlung durch die Komplexität des Umweltmediums Boden sowie die Existenz tausender unbekannter Schadstoffe erschwert.

Ziel dieser Arbeit war die Etablierung von chemischen Verfahren für die Oxidation von hochmolekularen PAKs, die aufgrund der höheren Anzahl an aromatischen Ringen eine schlechtere Wasserlöslichkeit aufweisen, um die mikrobiologische Sanierung dieser Verbindungen zu verbessern. Hierbei wurden verschiedene Oxidationsverfahren wie Fenton-Reaktion, Ozonolyse und Photooxidation auf einen hochgradig schadstoffbelasteten Boden angewandt und mittels ultrahochauflösender Massenspektrometrie (UHRMS) die erhaltenen Endprodukte untersucht. Diese Analysemethode ermöglicht eine umfassende Charakterisierung der verschiedenen oxidierten und nicht oxidierten Verbindungen und ein detailliertes Verständnis der chemischen Reaktion auf molekularer Ebene.

Ein wichtiges Ergebnis dieser Arbeit zeigte, dass kein signifikanter Abbau von hochmolekularen PAKs in chemischen Sanierungsmethoden mit Wasser als einziges Lösungsmittel beobachtet werden konnte. Daher war der Einsatz eines Lösungsvermittlers notwendig, um die Verfügbarkeit von hochmolekularen PAKs für die chemische Sanierung zu erhöhen. Der Zusatz von 5 Vol% Toluol als Lösungsvermittler verbesserte in der Fenton-Reaktion und Ozonolyse erheblich den Abbau von PAKs durch Bildung von hochoxidierten Kohlenwasserstoffen.

Abstract

The functionality of soil – as a part of the ecosystem – is extremely essential for the existence of life and environment. Therefore, concerns about the permanent inorganic and organic pollution of the soil have dramatically increased in the last few years. The substance class of polycyclic aromatic hydrocarbons (PAHs) plays a significant role as a contaminant since they exhibit high carcinogenic and toxic potential. Further use of these contaminated soils is hardly or not at all possible and therefore must undergo decontamination, which turns out to be very challenging. The complexity of soil, as an environmental medium, coupled with the presence of thousands of unknown pollutants complicates the identification of the relevant chemical and physical parameters for remediation.

The aim of this work was to establish chemical processes for the oxidation of high molecular weight PAHs, which are relatively insoluble in water due to higher number of aromatic rings, in order to enhance the microbial remediation of these compounds. Various oxidation techniques, like the Fenton reaction, ozonolysis and photooxidation, were applied to a highly contaminated soil and the obtained products were analyzed using ultrahigh resolution mass spectrometry (UHRMS). This analytical method facilitates a comprehensive characterization of various oxidized and non-oxidized compounds and a detailed understanding of the chemical reaction on a molecular level.

A key result of this work revealed that no significant degradation of high molecular weight PAHs was observed in chemical treatments using water as sole solvent. Therefore, the addition of a co-solvent was necessary to increase the availability of high molecular weight PAHs for chemical remediation. The addition of 5% v/v toluene as a co-solvent significantly improved the degradation of PAHs in Fenton reaction and ozonolysis by promoting the formation of highly oxidized hydrocarbons.

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1. General introduction

Soils are essential for various functions such as support, protection, nutrients and filtration, and therefore the entry of harmful chemical compounds into the soil has damaging consequences for humans, animals, plants and ecosystems. The contamination of soil was exacerbated by the Industrial Revolution, which started in England and spread between the eighteenth and nineteenth centuries to a certain number of developed countries in Europe, USA and Japan.¹ The release of contaminants into the soil became even larger with growing population and industrial production as well as the use of fossil fuels. According to the European Environment Agency (EEA), the number of potentially polluted soil in the 39 EEA countries was estimated at 2.5 million sites for 2011.²

Soil pollution can be caused by different sources and activities that contribute various contaminants to the soil (Figure 1-1). The greatest contribution to soil contamination is made by waste disposal and treatment, which covers the disposal of municipal and industrial waste, followed by industrial and commercial activities like mining, oil extraction and production, and power plants. Among the pollutant types, heavy metals and mineral oil are the most important classes with about 60% contribution. Heavy metals are generally defined as those metals and metalloids with a density higher than 5 g/cm³ and toxicity even at low concentrations. These heavy metals enter the soil mainly through mining, smelters and foundries and other metal-based industrial processes.³ The remaining contaminant groups (mineral oil, PAH, BTEX, CHC and phenols) and components, like alkylated, higher molecular weight and otherwise mono- or polysubstituted aromatics (N, S, O or halogens), are encompassed by polycyclic aromatic compounds (PACs).⁴

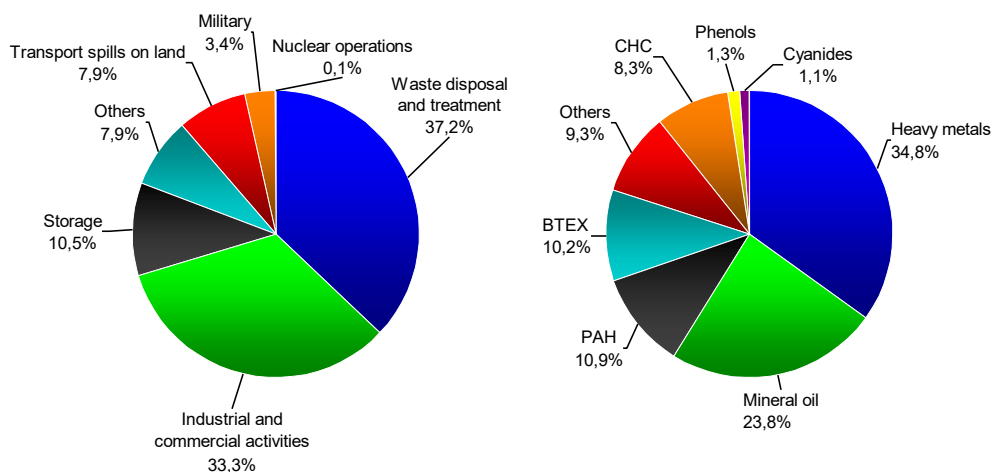


Figure 1-1: Distribution of sectors and contaminants for polluted soil in Europe.²

1.1 Polycyclic aromatic compounds (PACs)

PACs comprise a varied group of thousands of organic compounds with two or more annulated aromatic rings and have attracted more interest of the global scientific community due to toxic effects on human health and ecosystems and their ubiquitous occurrence in natural media.^{4, 5} They are distributed in the environment such as groundwater,⁶ sewage sludge,⁷ sediments of lake and river,⁸ soil⁹ and air.¹⁰ In Figure 1-2, some examples of selected PACs are shown.

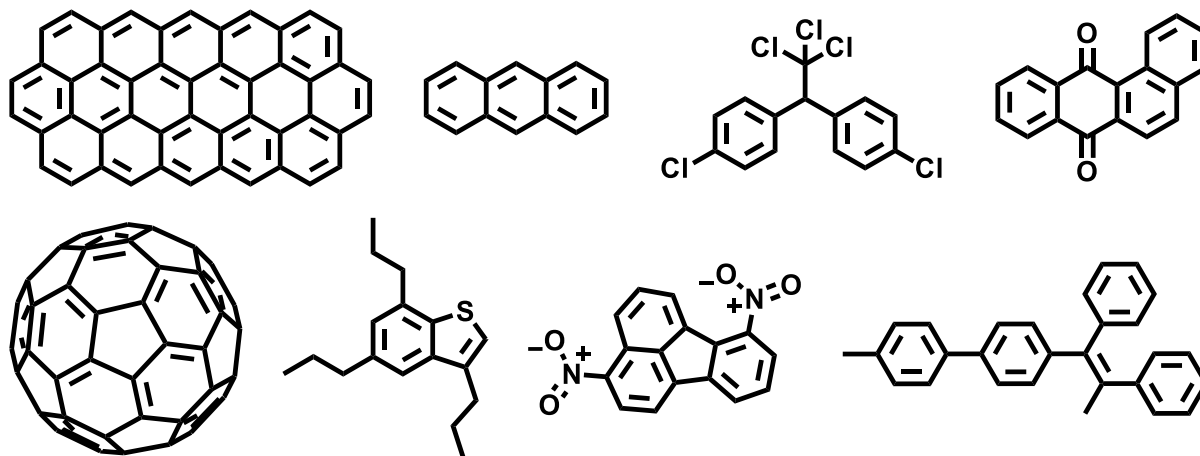


Figure 1-2: Examples of selected PACs.

PACs are originated from both anthropogenic and natural sources including petrogenic, pyrogenic and biogenic processes.^{5, 11} Petrogenic and pyrogenic PACs can be produced from anthropogenic and natural sources, while biogenic PACs are formed through natural activities. Anthropogenic activities associated with the combustion of wood or oil products and natural activities related to volcanic eruption or forest fire leading to creation of pyrogenic (combustion derived) PACs. Petrogenic (petroleum derived) PACs are produced by anthropogenic (e.g. oil spills or petroleum industrial processes) or natural activities (e.g. oil seeps).^{12, 13} Therefore, high molecular weight and less heteroatomic PACs are dominantly found in pyrogenic sources, while low molecular weight and more alkylated and heteroatomic PACs are present in petrogenic sources.¹⁴

It is very well known that PACs have negative consequences for human health and environment. But studies regarding toxicity are very often focused on the 16 EPA-PAHs which were created in 1976 by the Environmental Protection Agency (EPA) to represent all PACs.¹⁵ The introduction of the 16 EPA-PAHs provides the following benefits: (A) Decrease of analytical complexity and cost; (B) Commercial availability of the selected standards; (C) Good comparability and practicability of the analysis.¹⁴ Nevertheless, the 16 EPA-PAHs are

considered in many recent studies as priority toxic pollutants. The extension of the 16 EPA-PAHs list seems necessary, because other PACs, such as alkylated and heterocyclic aromatic compounds (NSO-PACs), found in the soil and are reported to be toxic and/or mutagenic.^{13, 14, 16-18} Furthermore, the hazard potential is strongly affected by interactions between different PACs and other compounds present in environmental mixtures (e.g. soil matrix).⁵

PACs are absorbed by various exposure routes (inhalation, ingestion and dermal contact) and the symptoms to humans are well known when exposed to PAHs.^{19, 20} Short-term exposure to PAHs results in symptoms to humans like nausea, eye irritation, diarrhoea, vomiting, and confusion, while long-term exposure leads to impaired lung and immune function, liver and kidney damage, asthma-like symptoms and respiratory problems.²¹⁻²⁴ Apart from unmetabolized PAHs, metabolized ones also cause health-damaging effects. These active metabolic products are reacting with cellular proteins, DNA or RNA leading to formation of mutations, tumors and cancer.²⁵

As a result of the highly toxic effects of PACs on human health and ecosystems, remediation efforts are required to remove these compounds from the environment.

1.2 Remediation of PACs contaminated soil

1.2.1 Behavior of PACs in soils

Given their harmful effects on human health and ecosystems, PACs contaminated sites must be cleaned up before the sites are considered to be safe for further usage. The complexity and characteristics of soil (moisture content, presence of soil organic matter and mineral fractions, interactions between contaminant and soil, etc.) together with the existence of thousands of unknown pollutants in complex mixtures have a great impact on the remediation.²⁶ One of the main factors negatively influencing the removal of PACs is the aging time of pollutants in soil, which describes the increased contact time between the pollutants and soil.²⁶⁻²⁹ With prolonged residence of contaminants in soil, the interactions (mainly diffusion and sorption) between organic compounds and soil increase and become more complex, which promote occlusion of contaminants within soil micropores and significantly decline the availability of the contaminants for diverse remediation processes.^{30, 31} Here the amount³² and the nature³³ of soil organic matter (SOM) as well as the type of contaminant (and its physico-chemical properties)³⁴ have a large influence on the rate and extent of the aging process.

The different interactions of SOM and mineral fractions with the pollutants are demonstrated in Figure 1-3.^{35, 36} When organic contaminants are entering the soil, they slowly diffuse through

the soil and become adsorbed by organic matter and/or mineral fraction due to hydrogen bonds or van der Waals forces.³⁵ By aging, stable and nearly irreversible covalent bonds are formed between pollutant compounds and organic matter facilitated by enzymatic and/or (photo)chemical catalysts.^{35, 37} This aging process further leads to sequestration of organic compounds in pores,³⁸ which can reduce the toxicity of contaminants³⁹ but also makes the complete removal of pollutants from soil even more difficult.⁴⁰ Therefore, it is not easy to answer the question whether it is necessary to remove PACs from highly aged contaminated soil because of the complicated sequestration process of a complex mixture of organic compounds and their different toxicity effects.⁴¹

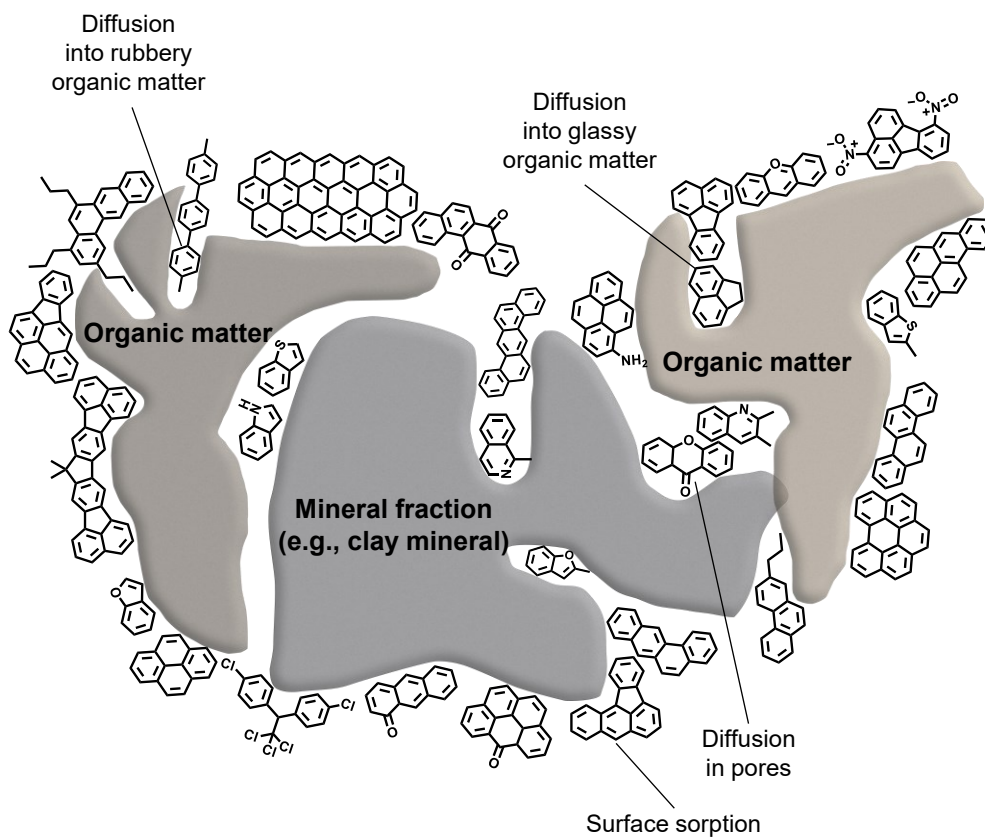


Figure 1-3: Diffusion and sorption process of various organic compounds within organic matter and mineral fraction, adapted from Semple et. al.³⁵

1.2.2 Remediation techniques

Over the last thirty years, more than 270 studies have been published on the remediation of only contaminated soil by searching for “PAH” (or polycyclic aromatic hydrocarbon) or “PAC” (or polycyclic aromatic compounds), “soil” and “remediate”, which show the considerable effort invested in the development of remediation techniques.⁴² Soil reclamation strategies are

classified into physical, biological and chemical methods, and are performed either by “on-site” or by “off-site” treatment (Figure 1-4).⁴³ Among these various remediation techniques, biological treatment is regarded as a safe, eco-friendly and inexpensive remediation method that leads to a decrease in concentrations of organic compounds by ideally converting them into CO₂ and H₂O.⁴⁴ Pollutants can be potentially addressed by living microorganisms (bioremediation) or plants (phytoremediation or plant-assisted bioremediation) resulting in environmental clean-up of contaminated soil.¹² However, biological treatment is a time consuming process⁴⁵ and often shows limited applicability on poorly water soluble compounds with higher molecular weight⁴⁶ and heavily contaminated soils.⁴⁷ Therefore, thermal remediation is widely used to effectively remove organic pollutants from heavily contaminated soil by destruction or volatilization.¹² Mainly three different techniques are applied namely incineration, thermal desorption and microwave frequency heating.⁴⁸ Due to the utilization of high temperatures, these processes entail drawbacks, such as high costs, production of air pollutants and deterioration of soil quality.⁴⁹

Organic contaminants are strongly attached to soil components as a result of their hydrophobic character, which can be broken by using single or mixture of solvents. Consequently, solvent extraction/soil washing is a frequently applied separation technique for removing pollutants from soil and concentrate them in liquid phase.⁵⁰ Typical extraction agents are studied for cleaning contaminated soil including mixtures of water and co-solvents,⁵¹ surfactants,⁵² cyclodextrins,⁵³ subcritical⁵⁴ and supercritical fluids⁵⁵ and vegetable oils.⁵⁶

Many researchers have invested extensive work in the development of chemical remediation methods, placing more emphasis on advanced oxidation processes (AOPs).⁵⁷⁻⁵⁹ Highly reactive and non-specific hydroxyl radicals (OH[•]) are formed during AOPs and react with nearly all types of organic pollutants either to transform them to biodegradable compounds or ideally degrade them down to CO₂ and H₂O.⁶⁰

Besides the studies on remediation efficiencies when using individual technologies, several combinations of biological, physical and chemical remediation techniques were applied to enhance the removal of contaminants from soil. Solvent extraction is mostly utilized as pre-treatment prior to chemical⁶¹ or biological⁶² degradation to overall reduce the pollutant concentration and increase the availability of pollutants. Meanwhile, the application of chemical remediation technique as a first⁶³ or secondary step⁶⁴ has been demonstrated.

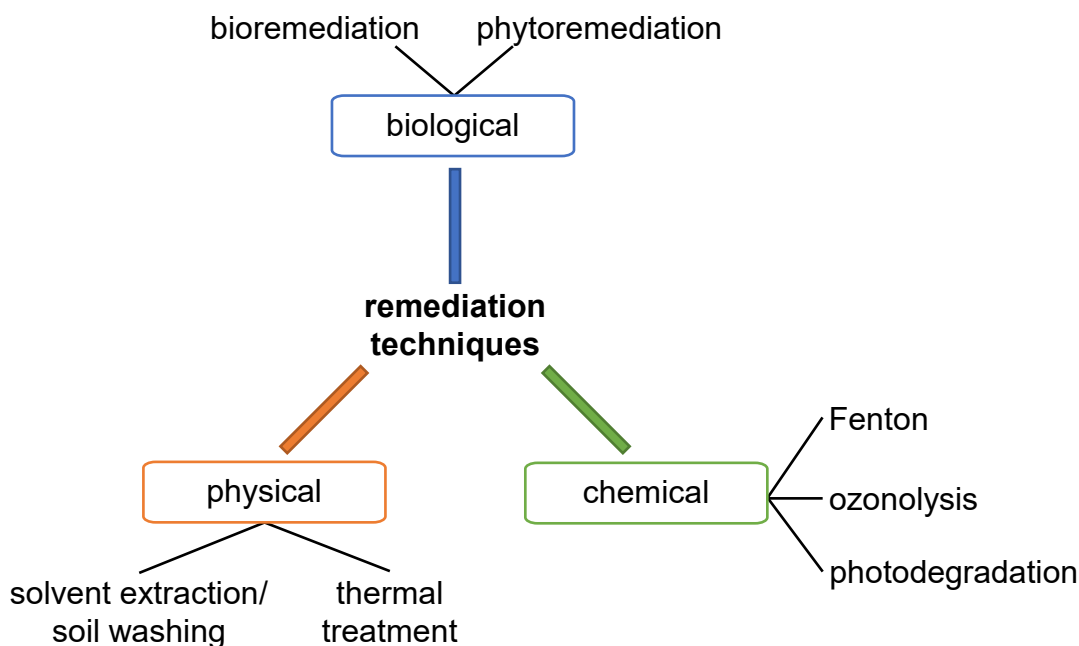
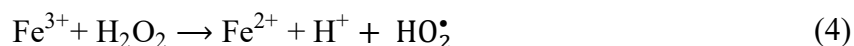


Figure 1-4: Remediation techniques for cleaning-up contaminated soil.

1.2.3 Chemical treatment of contaminated soil

AOPs were first introduced for wastewater treatment in the 1980s and have attracted much interest in recent decades due to the versatile processes for OH^\bullet production.⁶⁵ The extremely high oxidizing capability of OH^\bullet is harnessed to induce a series of oxidation reactions, which results in complete mineralization of organic pollutants to CO_2 and H_2O .⁶⁰ The formation of highly reactive OH^\bullet through Fenton reaction, ozonation and photocatalytic degradation is illustrated in Scheme 1-1.

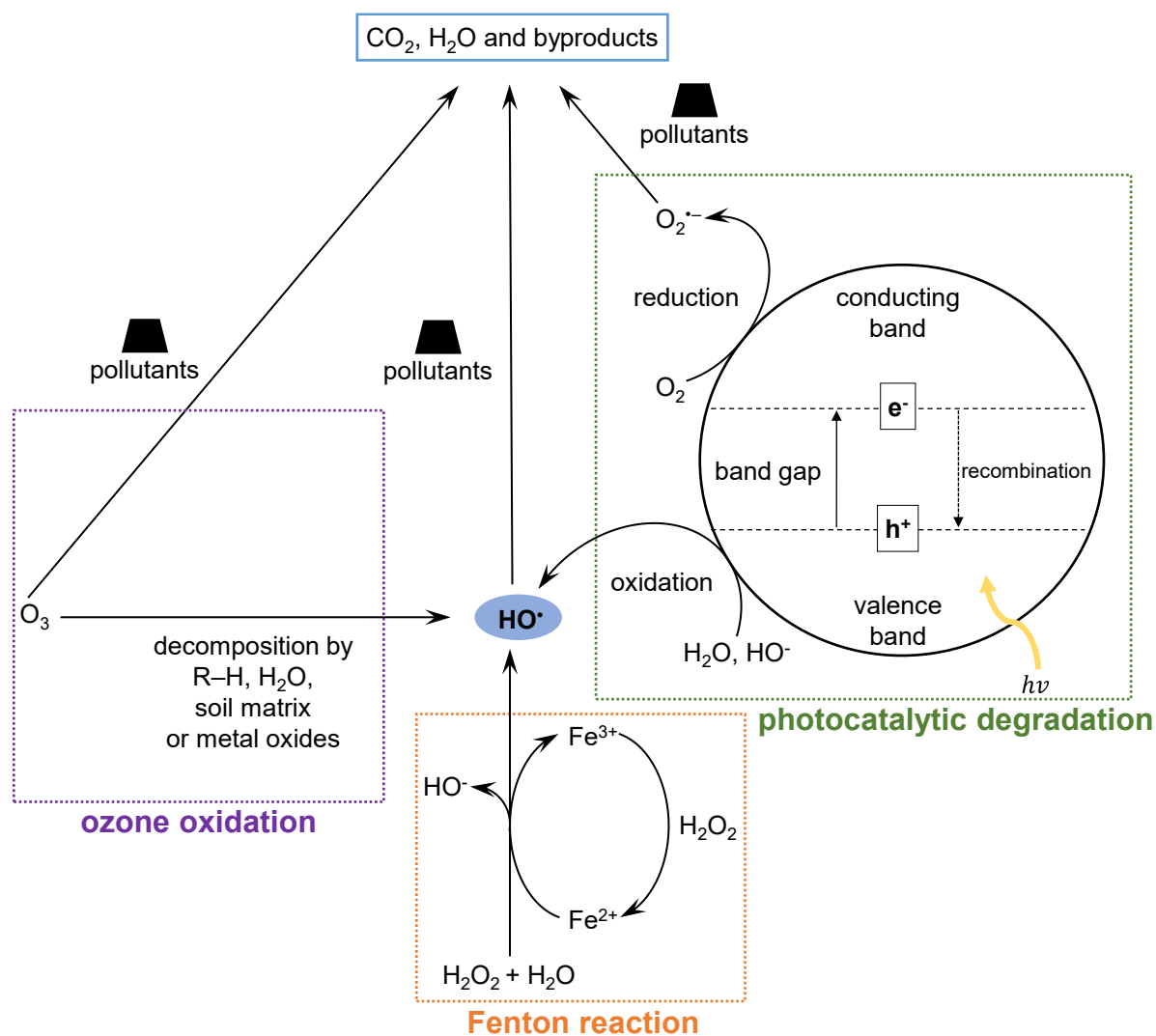
Fenton's reagent was invented in the 1890s by Henry John Horstman Fenton, who studied the oxidation of tartaric acid in the presence of ferrous salt (Fe^{2+}), and is nowadays used to degrade PACs in the environment.⁶⁶ In the presence of Fe^{2+} , OH^\bullet are generated by the decomposition of hydrogen peroxide (H_2O_2) under acidic conditions (eq. (1)) and are able to oxidize PACs either by OH^\bullet addition (eq. (2)) or hydrogen abstraction (eq. (3)).⁶⁷ The Fe^{3+} ion reacts with H_2O_2 to regenerate Fe^{2+} and form HO_2^\bullet , which can also act as reactive species (eq. (4)).⁶⁸



Conventional Fenton oxidation is performed in a very acidic medium (pH around 3) for optimal degradation results. A decrease or increase of the pH value leads to a reduction of the efficiency of Fe^{2+} - H_2O_2 system (solvation of protons by H_2O_2 at low pH values)⁵⁷ or to precipitation of $\text{Fe}(\text{OH})_3$ (at neutral or alkaline conditions).⁶⁹ In order to avoid precipitation and acidic conditions, Fenton-like and modified Fenton processes are applied using metal oxide minerals⁷⁰ or chelating agents.⁷¹

Ozonation has been shown as one of the most successful technologies for treating wastewater and contaminated soils and can be achieved by introducing gaseous or aqueous ozone.⁴¹ In the aqueous phase, the degradation pathway of organic pollutants is highly effected by pH of aqueous solution.⁷² When operating ozonation under low pH conditions, direct oxidation (bond attack) of PACs by O_3 via nucleophilic, electrophilic or dipolar addition reactions takes place.^{73, 74} Indirect oxidation (atom attack) involves the reaction of organic contaminants with OH^\bullet , which are formed through ozone decomposition in the presence of SOM,⁷⁵ metal oxides⁷⁶ or OH^- (with increasing pH).⁵⁴

Photocatalytic degradation is based on the application of semiconductor metal oxides or sulfides as photocatalysts to promote oxidizing reactions for the destruction of organic contaminants. This process has been investigated in detail by several authors for the treatment of wastewater and its usage has been expanded to the clean-up of contaminated soil.^{77, 78} Many semiconductors, viz. TiO_2 , ZnO , ZrO_2 , CeO_2 , WO_3 , Fe_2O_3 , ZnS and CdS have been studied for photocatalysis, whereby TiO_2 (in the anatase form) is the most used photocatalyst due to its chemical inertness, low cost and high photoactivity.^{79, 80} The general mechanism of photocatalysis is illustrated in Scheme 1-1. Semiconductor materials have a band gap for separating the valence band from the conduction band.⁸¹ The absorption of photons with energy matching or greater than the band gap of a photoconductor leads to a excitation of an electron from the valence band to a vacant conduction band, thus forming electron-hole pairs.⁷⁸ These photo-generated holes can react with water or OH^- to create OH^\bullet , while strong oxidant superoxide radical anions ($\text{O}_2^\bullet^-$) are produced through reduction of molecular oxygen by photoelectrons in the conduction band.^{82, 83}



Scheme 1-1: Schematic illustration on PACs degradation by Fenton reaction, ozone oxidation and photocatalytic degradation, adapted from Jin et al.⁸⁴ and Zeng and Huang et al.⁵⁷

Unfortunately, chemical treatment of PACs from the polluted soil is not an easy task. Many authors confirmed the decreased removal efficiencies of PACs from field contaminated soils than artificially (spiked) ones due to the presence of soil matrix and various types of organic pollutants.^{53, 56, 61, 85-88} Here, SOM acts as radical scavenger and reservoir for sequestration of pollutants limiting the degradation extent.^{44, 89, 90} In case of the various contaminants, each of the individual compound has different chemical reactivity towards oxidants, which impedes the complete mineralization. Therefore, higher oxidant amount is generally needed to degrade sorbed PACs.⁹¹ The addition of co-solvents addresses the problem of sequestration by desorbing them from the soil matrix and increasing their accessibility for different AOPs.^{45, 92, 93}

1.3 State of the Art in soil contamination analysis

Although the complexity of PACs contaminated soils is considerable, many soil remediation studies are based on the quantification of 16 EPA-PAHs analyses. These various compounds are oxidized by AOPs, which, if the mineralization is incomplete, result in the formation of numerous new products and even an increase in overall complexity. The determination of PACs and transformation products can be achieved by both target and non-target analysis.

For the success of an applied chemical remediation method, the concentration of individual or all 16 EPA-PAHs was often measured using targeted gas chromatography coupled with flame ionization detector (GC-FID)⁴⁵ or mass spectrometry (GC-MS).⁹⁴ Also total petroleum hydrocarbons (TPH) and/or selected alkanes were determined to provide information on the remediation efficiency of oil contaminated soil.^{63,95} For the analysis of transformation products and other polar PACs, organic molecules were derivatized and detected with GC-MS⁹⁶ or analyzed using liquid chromatography (LC) hyphenated to different detectors, such as quadrupole time-of-flight mass spectrometer (Q-TOF MS), triple quadrupole (QqQ), photometric diode array detector (PDA) or fluorescence detector (FLD).^{97,98} Regarding the identification of compounds in complex mixtures, the availability of suitable standards is necessary. Aitken et al. could determine the structure of C₁₅H₈O₂, which was responsible for the increase in genotoxicity, by synthesis of 2*H*-naphtho[2,1,8-*def*]chromen-2-one.⁹⁸

A non-target approach allows a wider presentation of possible transformation products in complex mixtures by simultaneously recording a broad mass range. The development of non-target approach has even increased with the introduction of benchtop high resolving mass spectrometers, including Q-TOF MS, Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS) and Fourier transform Orbitrap mass spectrometer (FT Orbitrap MS). These instruments, coupled with a chromatographic separation, were extensively used for non-target screening of unknown organic pollutants and transformation products in complex environmental samples.⁹⁹

1.4 Analytical techniques used in this study

1.4.1 Ultrahigh resolution mass spectrometry

The understanding of oxidation processes in a complex mixture consisting of soil matrix and thousands of organic compounds is a challenging task. Here, the application of ultrahigh resolution mass spectrometry (UHRMS) allows a better understanding of oxidation reactions occurring during AOPs of highly PACs contaminated soil on a molecular level.

$$R = \frac{m}{\Delta m} \quad (5)$$

$$\text{mass error} = \frac{m_{\text{experimental}} - m_{\text{theoretical}}}{m_{\text{theoretical}}} * 10^6 \quad (6)$$

For the analysis of such complex mixtures, seen in Figure 1-5, ultrahigh resolving power (eq. (5)), high mass accuracy (eq. (6)) and dynamic range are crucial for precise assignment of unique molecular compositions including those with low abundances.¹⁰⁰

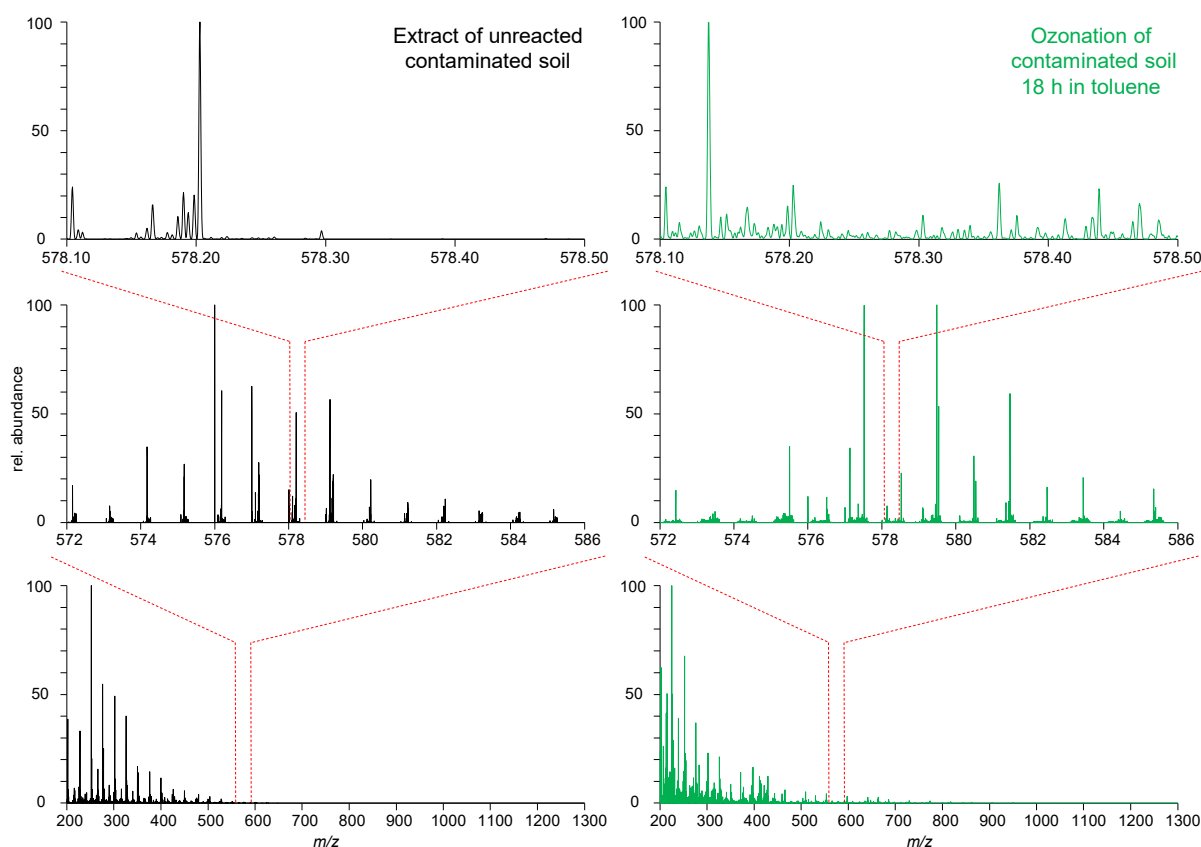


Figure 1-5: Averaged mass spectra (bottom) of extract from unreacted contaminated soil (left), ozone treated contaminated soil within 18 h in toluene (right) corresponding zooms into m/z 572-586 (middle) and into 578.10-578.50 (top).

The above-mentioned FT-ICR MS and FT Orbitrap MS are the only mass spectrometers that meet the requirements of ultrahigh resolving power and high mass accuracy. In both instruments, ions are stored in ultrahigh vacuum via electromagnetic field in a Penning trap (FT-ICR MS)¹⁰¹ or by electrostatic field in a variant of a Kingdon trap.¹⁰² The detection of ions is performed by their image current as a function of time recorded as free induction decay (FID) or transient.¹⁰³ Once the frequency-domain signal is obtained by mathematical Fourier transform operation of time-dependent FID, it can be converted to m/z . Therefore, the m/z

values are dependent on ion oscillation frequencies and independent of ion velocities.¹⁰⁴ The resolving power of both instruments is increased with longer acquisition time or – in case of FT-ICR MS – with stronger superconducting magnet.¹⁰⁵ Furthermore, the application of spectral stitching method enhances the dynamic range, mass accuracy, resolving power and sensitivity leading to an increase in the number of assigned compositions. Here, a collection of several mass windows with a certain overlap is used to achieve a complete picture of all species present in the sample.¹⁰⁶⁻¹⁰⁹

Figure 1-6 shows a schematic view of a research type Orbitrap Elite (Thermo Fisher Scientific, Bremen, Germany) used in this study. It is built up of a linear trapping quadrupole ion trap (LTQ) Velos Pro and a high-field Orbitrap mass analyzer. The LTQ comprises a dual pressure configuration, in which a high pressure cell is used for ion accumulation, trapping, isolation and fragmentation. Afterwards, the ions are passing a low-pressure cell for further registration with the detectors.¹¹⁰ In order to reduce space-charge effects and improve mass accuracy, transfer of the ions into Orbitrap mass analyzer can be regulated by automated gain control (AGC) of the linear quadrupole ion trap.¹⁰⁷ For ultrahigh resolution measurements, ions are transferred via a quadrupole ion guide to an external storage device, called C-trap. Here the ions are kept in the middle part of the C-trap by radio frequency (RF) and are accumulated by a rapid loss of their kinetic energies due to collisions with N₂. Finally, ions are entering the Orbitrap by high-voltage electric pulses.¹¹¹ The Orbitrap mass analyzer is a “Knight-style” Kingdon trap and is composed of two opposing cup-like outer electrodes (split in two halves) and spindle-shaped central electrode. After generating an electrostatic field by utilization of high voltage at the central electrode, ions are circling around the central electrode and simultaneously moving in a reciprocating motion along it. The frequency ω of the reciprocating movement is only dependent on the inverse m/z and field curvature k (eq. (7)).

$$\omega = \sqrt{k * \frac{z}{m}} \quad (7)$$

With a research type Orbitrap Elite, an increase in the transient time from 1.5 s to 3.04 s is possible, which can theoretically result in a resolving power higher than 960,000 at m/z 400. Here, a compact high field Orbitrap mass analyzer with an inner electrode radius (R_1) of 5 mm and outer electrode Radius (R_2) of 10 mm is installed instead of the standard Orbitrap mass analyzer ($R_1 = 6$ mm and $R_2 = 15$ mm) resulting in higher field strength at a constant voltage.^{112, 113}

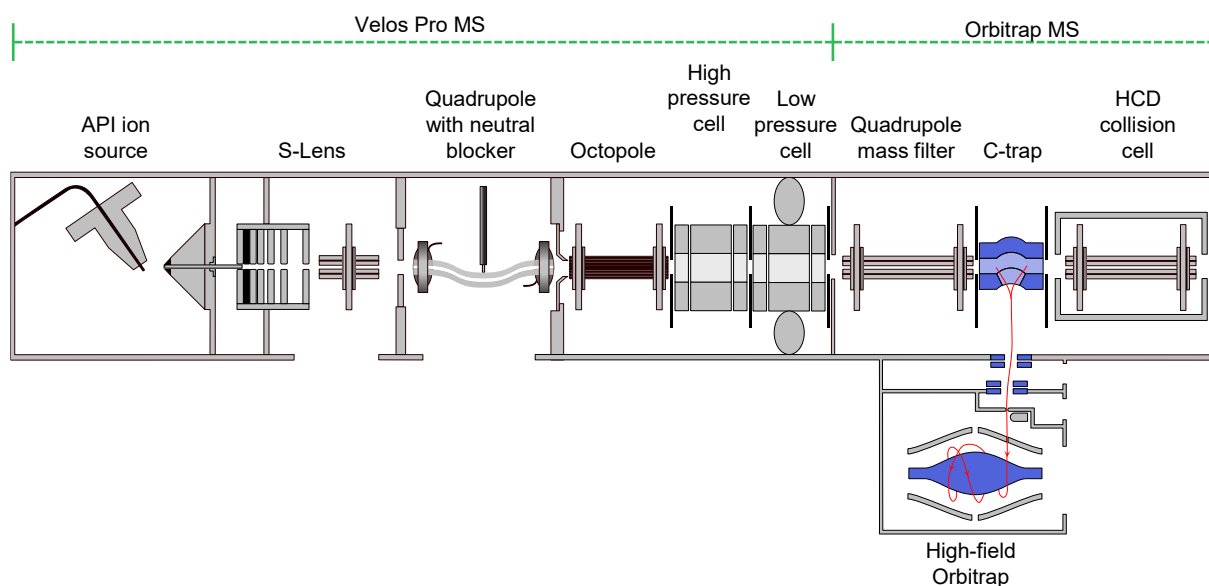


Figure 1-6: Schematic view of an Orbitrap Elite mass spectrometer, adapted from Gross.¹¹⁴

1.4.2 Ionization techniques

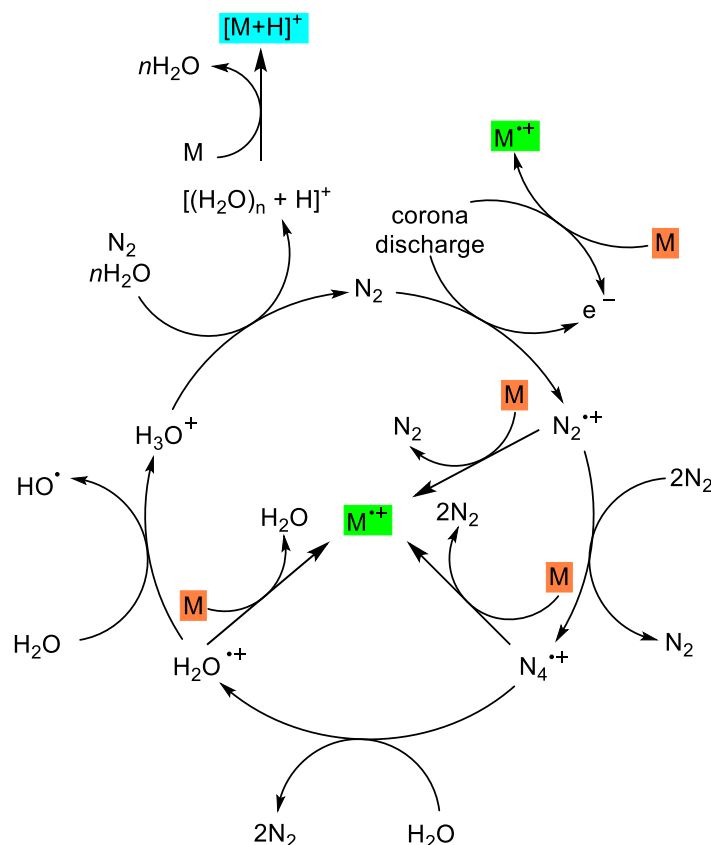
In 1973, Horning et al. introduced the atmospheric pressure ionization (API), which facilitated a direct connection of the analyte in solution phase with mass analyzer, as an alternative ionization method to electron impact (EI).¹¹⁵ With API, a solution of the analyte is directly injected into a hot stream of nitrogen at atmospheric pressure for a rapid vaporization of the solvent. The vapor is exposed to radioactive ^{63}Ni and the emitted electrons initiate a complex sequence of ionization processes. Meanwhile, API is used as a collective term for different ionization techniques producing ions at atmospheric pressure. These techniques have been applied for the analysis of different compounds in complex mixtures that allow less or no fragmentation of generated ions (soft ionization).¹¹⁶ The most frequently used ionization methods include electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI) and atmospheric pressure photoionization (APPI). Each ionization method exhibits both selectivity (and sensitivity) and discrimination based on the type of the analyte.¹¹⁷

ESI is the most established method among the group of API techniques that ionizes acidic polar compounds in negative and basic polar compounds in positive mode by forming deprotonated $[\text{M}+\text{H}]^-$ or protonated $[\text{M}+\text{H}]^+$ species. Under certain conditions (suitable choice of solvent and capillary voltage), non-polar PACs can be detected as radical cations by using ESI in asphaltene fraction of crude oil.¹¹⁸ The ionization process starts with the input of analyte solution into the ESI needle to which high potential (usually between ± 3 to ± 5 kV) is applied. At the capillary tip of the sprayer, a Taylor cone is formed emerging a fine mist of electrically charged

droplets.¹¹⁹ The production of the charged droplets is increased by introduction of sheath and auxiliary gas, which results in evaporation of the solvent. The formation of gas-phase ions is described with two models namely charged-residue model (CRM) and ion evaporation model (IEM). In CRM, charged droplets successively lose solvent molecules leading to shrinkage of droplets and simultaneous increase in charge density at the droplet surface until the Rayleigh limit.¹¹⁹ Once the Rayleigh limit is exceeded, the electrostatic repulsion surpasses the surface tension and the parent droplets are split into much smaller droplets by the Coulomb explosion.¹²⁰ In case of IEM it is thought that desolvated molecular ions are emitted into the gas phase from highly charged microdroplets.¹²¹

After the presentation of API by Horning et al. in 1973, the same group introduced one year later the refined API replacing the electron source (radioactive ^{63}Ni) by a corona discharge source.¹²² Here, the analyte solution is injected into the source via a silica capillary and solvent is rapidly evaporated by using a heated sprayer (max. 500 °C). Between the sprayer and the sharp tip of the corona needle, an ion plasma is generated by corona discharge inducing a complex sequence of reactions (Scheme 1-2). Firstly, nitrogen molecules (N_2) are ionized by electrons, which are emitted from the corona needle, and the produced nitrogen radical cations react with water to finally form H_2O cluster ions $[(\text{H}_2\text{O})_n + \text{H}]^+$. These cluster ions transfer protons to analyte molecules M forming protonated species $[\text{M}+\text{H}]^+$.¹²³ The creation of radical cations M^+ can be explained either by direct ionization of analyte molecules through corona discharge or charge transfer reactions from ionized reactive species (N_2^{*+} , N_4^{*+} and H_2O^{*+}) to organic molecules.^{124, 125}

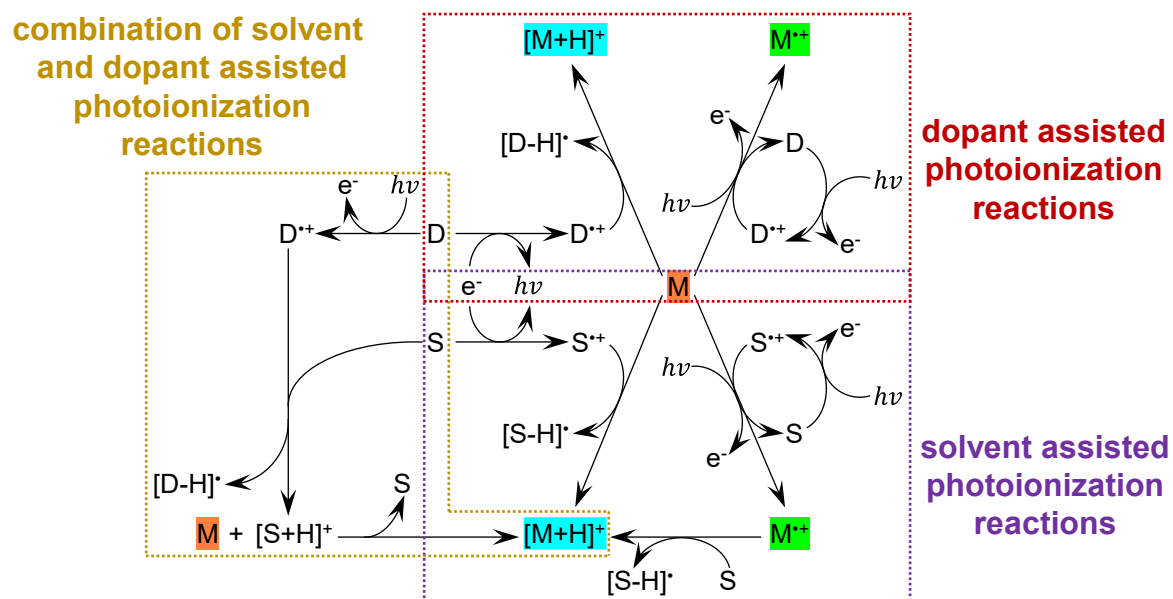
The ionization of pure hydrocarbons using APCI is still discussed. Vaz and Romao demonstrated the application of APCI for the detection of *n*-paraffins using isooctane as reagent,¹²⁶ while Gardinali et al. showed a significant limitation in the characterization of aliphatic hydrocarbons with APCI.¹¹⁶ These studies indicate that the analysis of aliphatic hydrocarbons is possible under certain conditions (sensitivity of the instrument, source conditions, addition of reagents and/or solvents and nature of sample).



Scheme 1-2: Reaction sequences for the formation of radical $M^{\bullet+}$ and protonated species $[M+H]^+$ by APCI.¹²³⁻¹²⁵

In 2000, two independent studies were published by Syage et al.¹²⁷ and Robb et al.¹²⁸ on the use of LC-MS with APPI to analyze polar and non-polar compounds. Different discharge lamps are employed for photon emission, such as Xenon lamp (photon emission at 8.4 eV), Krypton lamp (10.0 and 10.6 eV) or Argon lamp (11.2 eV). The use of the krypton discharge lamp prevents the ionization of some solvents (e.g. methanol, acetonitrile and hexane) and essential air constituents (water, nitrogen or oxygen), because the photon emission energy of the krypton lamp is lower than the ionization energies (IE) of the solvents and air components.¹²⁹ During APPI, radical cations $M^{\bullet+}$ and protonated species $[M+H]^+$ are formed from analyte molecules by different mechanisms involving solvent (S) and/or dopant (D), which is shown in Scheme 1-3. Radical cations are created in two distinct pathways. The first one describes the direct absorption of a photon by organic molecules M and subsequent release of an electron when IE of the molecule is lower than the energy of photon.¹²⁹ The second pathway suggests the ionization of solvent or dopant and reaction of these radical ions with analyte compounds.¹³⁰ Protonated molecules are created by proton transfer between various species (dopant or solvent assisted) and analyte molecules/analyte ions.¹³⁰ If photoionization of respective solvent is not possible, the addition of a dopant leads to creation of solvent ions, which then react with the analyte by proton transfer.^{128, 130} The comparison of APPI and APCI shows an efficient

ionization and detection of some compound classes by APPI, but both still allow the ionization of non-polar compounds in comparison to ESI.¹¹⁶



Scheme 1-3: Reaction sequences for the formation of radical ($M^{\bullet+}$) and protonated species ($[M+H]^+$) by APPI.¹²⁸⁻¹³¹

1.4.3 Tandem mass spectrometry

Tandem mass spectrometry (or MS/MS, MS_n) is a technique for gaining structural information of unidentified compounds.¹³² Generally, two main concepts are existing for carrying out tandem MS measurements, which are tandem-in-time or tandem-in-space. Tandem-in-time instruments involve a single mass analyzer (ion trap, FT-ICR and Orbitrap), in which the different stages (ion selection, activation and analysis of product ions) are occurring in time sequence.¹³³ In tandem-in-space instrumentation (QqQ, TOF and double focusing mass analyzer), the previously mentioned stages are taking place in physically separated mass analyzers.¹³³ In this study, MS/MS experiments were performed using collision-induced dissociation (CID), the most well-known collision method, to understand the effect of co-solvent addition on chemical degradation.¹³⁴ In CID, gaseous ions are kinetically accelerated and then collide with neutral gases (H_2 , He, Ar, N_2 or Xe)¹³⁵ leading to a formation of activated species and conversion of part of their kinetic energy into internal energy.¹³⁶ The final step encompasses a dissociation of the activated species at this level of internal energy causing bond breaking and fragmentation processes.^{136, 137}

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2. Scope of work

The successful remediation of an aged highly contaminated soil with thousands of unknown compounds is associated with multiple challenges. Therefore, the aim of the study is to investigate a chemical treatment for cleaning-up contaminated soil and understand the reaction in detail using UHRMS methods. Here, the first three chapters cover the application and understanding of the Fenton reaction of a contaminated soil, while the following two chapters are dealing with ozonation and photooxidation as an alternative chemical treatment method.

In Chapter 3, Fenton oxidation was applied to a highly contaminated soil using various co-solvents such as methanol, ethanol and toluene. The results of the reactions were analyzed by a research type FT Orbitrap Elite with APPI(+) and compared with the original soil sample. This chapter is the starting point for further optimization of the reaction conditions and the development of alternative chemical remediation methods.

Based on the results of previous chapter, Chapter 4 was focusing on the conditions of the Fenton oxidation such as toluene amount and comparison of toluene with dichloromethane (DCM) as co-solvents. Furthermore, a nitrogen-containing model compound was reacted under Fenton conditions with different co-solvents and structural elucidation experiments with MS/MS measurements were performed to verify the proposed reaction mechanism.

A method for the extraction efficiency of the products obtained after toluene-based Fenton oxidation of contaminated soil was developed in Chapter 5. For this, DCM and water were used as extraction solvents and the obtained various phases were separately analyzed by using UHRMS.

Chapter 6 demonstrates a successful combination of toluene-based ozonation of contaminated soil and non-target analysis using UHRMS. Here, the obtained phases (organic, water and soil phase extract) were physically separated and individually studied to gain a better comprehension of the ozonation of PAHs and their derivatives. In addition, toluene (as single compound) was treated with ozone and results were compared to ozonated polluted soil to assess the influence of the co-solvent.

The impact of various co-solvents and TiO_2 on photodegraded contaminated soil is covered in Chapter 7. For this purpose, the effect of TiO_2 as a catalyst and toluene or DCM as co-solvent was investigated by analyzing the different phases individually.

An overall conclusion of this work is presented in Chapter 8.

3. Studying the Fenton treatment of polyaromatic compounds in a highly contaminated soil with different modifiers by high resolution mass spectrometry

Redrafted from:

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3.1 Abstract

Remediation of polycyclic aromatic compounds (PAHs) contaminated soil is highly challenging, because of the complex soil matrix and immense number of various pollutants. These PAHs have a low polarity, which separates them from the surrounding soil. To make those non-polar compounds accessible for biological treatment, those compounds need to be made water soluble. One way to achieve this is the use of a Fenton reaction. The reaction is observed in a non-target approach with high resolution mass spectrometry as method for detection. The Fenton reaction is studied with addition of modifiers (methanol, ethanol and toluene) for a widespread understanding of the oxidation process of PAHs in a highly contaminated soil. The results show that the most effective soil remediation was achieved using toluene as a modifier, which leads to a significant decrease of PAHs and polyaromatic nitrogen heterocycles (PANHs) in the soil. After the toluene-based Fenton reaction, the number of oxygen atoms in the products increased up to O₁₈, which makes them better soluble in water and allows a better removal from the soil matrix. Similar hydrocarbon distributions were detected on the molecular level in Soxhlet extracted soil phase and toluene phase, while smaller PAHs with double bond equivalents (DBE) ≤ 38 are transferred into the water phase.

3.2 Introduction

Environmental contamination with PAHs is a serious and widespread issue with consequences to human health.¹ Apart from the non-polar PAHs with different ring size, other heteroatom-containing species are present, which include oxygen, sulfur or nitrogen, and sometimes even halogenated compounds.² These contaminations are often found at industrial sites³ in soils and sediments.⁴ Anthropogenically, such compounds are mostly created during incomplete oxidation, pyrolysis of carbon-containing fossil fuels and as byproducts in industrial processes.^{5, 6} Depending on the number of the condensed aromatic rings, a differentiation exists between low (LMW, 2-3 rings) and high molecular weight (HMW, > 3 rings) molecules.^{7, 8}

To date, various remediation techniques have been investigated for the degradation of PAHs including thermal,^{9, 10} physicochemical,^{11, 12} biological,^{13, 14} and chemical treatment.¹⁵⁻¹⁷ From all these remediation techniques, biodegradation is among the most frequently employed one, because it is a cost-effective, eco-friendly and economical approach, that requires less energy and/or chemicals than thermal, physicochemical or chemical treatments.¹⁸⁻²⁰ Nevertheless, bioremediation efficiency is depending on the number of condensed rings.²¹ LMW pollutants are soluble in water at least to some extent, which makes them more bioavailable than HMW PAHs that are more hydrophobic and tightly adherent to soil. Using chemical oxidation as a pretreatment step increases the solubility in water and therefore the bioavailability of the organic pollutants.

Especially in wastewater treatment starting from the 1980s,^{22, 23} chemical oxidation is commonly employed in the form of one or more so-called “advanced oxidation processes” (AOPs), which is classified into chemical, photochemical, sonochemical, electrochemical and other treatments (e.g. nonthermal plasma, supercritical water oxidation or ionizing radiation).²⁴ Over the last years, the Fenton oxidation has been of increasing interest, as it is a simple one-pot reaction that only involves the use of cheap, environmentally benign and abundant chemicals.²⁵⁻³⁰ During the conventional Fenton reaction, OH[•] are produced by decomposition of H₂O₂ in the presence of Fe²⁺ (eq. (1)).³¹ Besides the conventional Fenton reaction, various modified Fenton processes have been explored and these modified processes include the combination of Fenton with other processes (photo-Fenton,²⁹ electro-Fenton³²), alternative sources of oxidants³³ or catalysts³⁴ and the application of heterogeneous catalysts.³⁵



It has been shown that the remediation of PAHs by Fenton reaction can be of low efficiency for aged polluted soil. This is attributed to the contaminants being incorporated deeply into the soil matrix, which makes them unavailable to OH^\bullet being formed within the aqueous medium.^{36, 37} This problem can be addressed by using organic co-solvents as modifiers. Due to the increased solubility of the pollutants in those solvents, these are more easily removed from the inner soil matrix and therefore more accessible for the oxidation reaction.³⁸ Different solvents have been employed for this purpose, most commonly ethanol, which improves the treatment of polluted soil as well as of PAHs spiked soil compared to the reaction in a purely aqueous medium.^{39, 40} Gan and co-workers pointed out that the Fenton treatment with addition of ethyl lactate instead of ethanol improves the degradation of phenanthrene, anthracene, fluoranthene and benzo[*a*]pyrene due to the enhanced solubility.⁴¹ However, degradation kinetic studies for selected PAHs (naphthalene, fluorene, phenanthrene, fluoranthene, pyrene and anthracene) using methanol and ethanol have shown that the removal of PAHs is inhibited by these solvents, probably by their acting as a radical scavenger.⁴²

Studies regarding the efficiency of the Fenton reaction for PAHs remediation have so far been mostly conducted by a targeted GC-MS analysis of one or more members of the 16 EPA-PAHs list.⁴³ While this approach might be suitable for comparative reasons and enable a relatively simple quantification of results, it still neglects major parts of a contaminated sample. Many pollutants, such as alkylated PAHs, higher molecular weight PAHs and heteroatom-containing PAHs are typically not covered,⁴⁴ but are still part of the contamination and need to be considered. Most of the initial compounds, let alone their reaction products are, to date, unknown and a large portion of them is not amenable to gas chromatography due to their molecular weight. Ultrahigh resolution mass spectrometry (UHRMS) – with Fourier Transform ion cyclotron resonance mass spectrometry (FT-ICR MS)⁴⁵⁻⁵⁰ and Orbitrap MS⁵¹⁻⁵⁴ – has shown to be an excellent tool for studying complex mixtures of polyaromatic compounds in a non-target approach and is more suitable for achieving a comprehensive characterization of the initial pollutants as well as the various oxidized products obtained after the reaction.^{55, 56} UHRMS allows the unambiguous determination of the elemental composition of each detected ion through its high resolving power and mass accuracy.⁵¹

Zhang and co-workers studied the efficiency of a Fenton-like reaction for the degradation of petroleum contaminated soil using ESI(-) FT-ICR MS.⁵⁷ While the oxidized products of the reaction are easily analyzed this way, the method neglects the majority of unreacted, non-polar compounds. In order to not only understand what products are formed, but also which

compounds are recalcitrant to the reaction, APPI is the method of choice for the detection of non-polar species.^{58, 59}

This study presents the application of a Fenton oxidation of polycyclic aromatic compounds (PACs) in highly contaminated soil, using different co-solvents, including methanol, ethanol and toluene as modifiers to make them better accessible for bioremediation. These modifiers are chosen because they can be removed during an industrial biological treatment. Results from the reaction were compared with results from the original soil extract. APPI(+) Orbitrap MS was chosen as a non-target analysis method for gaining a detailed characterization of the products on a molecular level.

3.3 Materials and Methods

3.3.1 Chemicals

The reagents used for the experiments were toluene ($\geq 99.8\%$, Fisher Scientific, Loughborough, UK), hydrogen peroxide (30%; J. T. Baker, Sowinskiego, Poland), sulfuric acid (95-98%, J. T. Baker, Deventer, Netherland), methanol ($\geq 99.8\%$; J. T. Baker, Sowinskiego, Poland), ethanol ($\geq 99.8\%$; Merck, Darmstadt, Germany) and deionized water (type I) taken from a Clearwater dispenser Purelab Flex 2 (ELGA LabWater, Celle, Germany).

3.3.2 Sample preparation

Highly contaminated soil⁵³ was received from an industrial site in the German Ruhr area. The soil is an inhomogeneous mix of different types of materials. Especially noticeable was some dark and sticky clumps that were analyzed and found to contain especially high amounts of PAHs. Overall, the average amount of the solvent extractable organics was determined at $64.5 \pm 9.5 \text{ g kg}^{-1}$. Details of the analytical procedures and characterization of the soil can be found here.^{53, 54} For the experiments, 5 g of the sample were air dried for one week in a fume hood at room temperature. After drying around 61% of weight loss was observed resulting from drying off the humidity, the soil was ground in a mortar for homogenization, sieved (2 mm pore size) and stored in a fridge at 4 °C.

3.3.3 Experimental procedures

Fenton reactions were carried out without modifier or with methanol, ethanol or toluene as organic modifiers, respectively. For each reaction, a sample of soil (300 mg) was transferred into a 1000 mL single-neck flask and the respective modifier (29 mL, 5% v/v) was added, where applicable. While stirring, deionized water (434 mL) was added, and the mixture acidified with H₂SO₄ (1.3 M) to pH ~ 3. Afterwards FeSO₄·7H₂O (4.8 g, 17.27 mmol) was added, the flask was stirred at 0 °C (using a bath of ice and water) till the iron salt was dissolved. Then H₂O₂ (3*50 mL, 0.45 mol, 3 M) was added dropwise every 30 minutes⁶⁰ at 0 °C and the reaction mixture was stirred for additional 48 h at room temperature. After the reactions, the soil was filtered, dried in a fume hood and adherent organic matter was recovered by Soxhlet extraction with DCM (50 mL) for 24 h. Afterwards the solvent was removed under reduced pressure using a rotary evaporator and the residues stored for further analysis.

In case of the reaction with toluene as modifier, the layers of the filtrate were separated, and the organic layer was dried over MgSO₄ and filtered. Both water and toluene phase were concentrated under reduced pressure using a rotary evaporator and residues stored for further analysis.

For comparison of the reactions with the untreated sample, a Soxhlet extraction of the contaminated sample (300 mg) with DCM (50 mL) was performed for 24 h without prior reaction. The solvent was then removed under reduced pressure using a rotary evaporator and the residue stored for further analysis.

3.3.4 FT Orbitrap MS and data analysis

Mass analysis was performed on a research type FT Orbitrap Elite (Thermo Fisher Scientific, Bremen, Germany). The mass spectra were collected with a resolving power of $R = 480,000$ at m/z 400 in a mass range of m/z 150-1300 using APPI. Spectral stitching^{51, 61, 62} was used as a scan technique with mass windows of 30 Da with 5 Da overlap. For APPI a Krypton VUV lamp (Sygen Technologies, Tustin, CA, USA) was used with photon emission at 10.0 and 10.6 eV. The different extracts (Figure 3-1, purple bordered) were diluted in toluene:methanol (1:1, v/v) to a final concentration of 150 ppm and analyzed by direct injection at a flow rate of 20 μ L/min. Ion source conditions were adjusted as follows: capillary temperature of 275 °C, vaporizer temperature of 250 °C, sheath, auxiliary and sweep gases of 20, 10 and 2 arbitrary units. It has to be noted that the addition of toluene as a solvent also make it possible to use toluene as a dopant in dopant-assisted APPI analysis.

Recorded mass spectra were imported into Composer (V1.5.0, Sierra Analytics, Modesto, CA, USA) for assignment of elemental compositions to detected signals. Assignment was performed based on the following limits: H: 0-300, C: 0-100, O: 0-20, N: 0-2, S: 0-1, DBE: 0-80 and mass error ≤ 1.5 ppm. Excel (Microsoft Office Professional Plus 2010, Microsoft Excel 2010) and Origin (v9.2.0, OriginLab Corporation, Northhampton, MA, USA) were used for further data evaluation and graphical visualization.

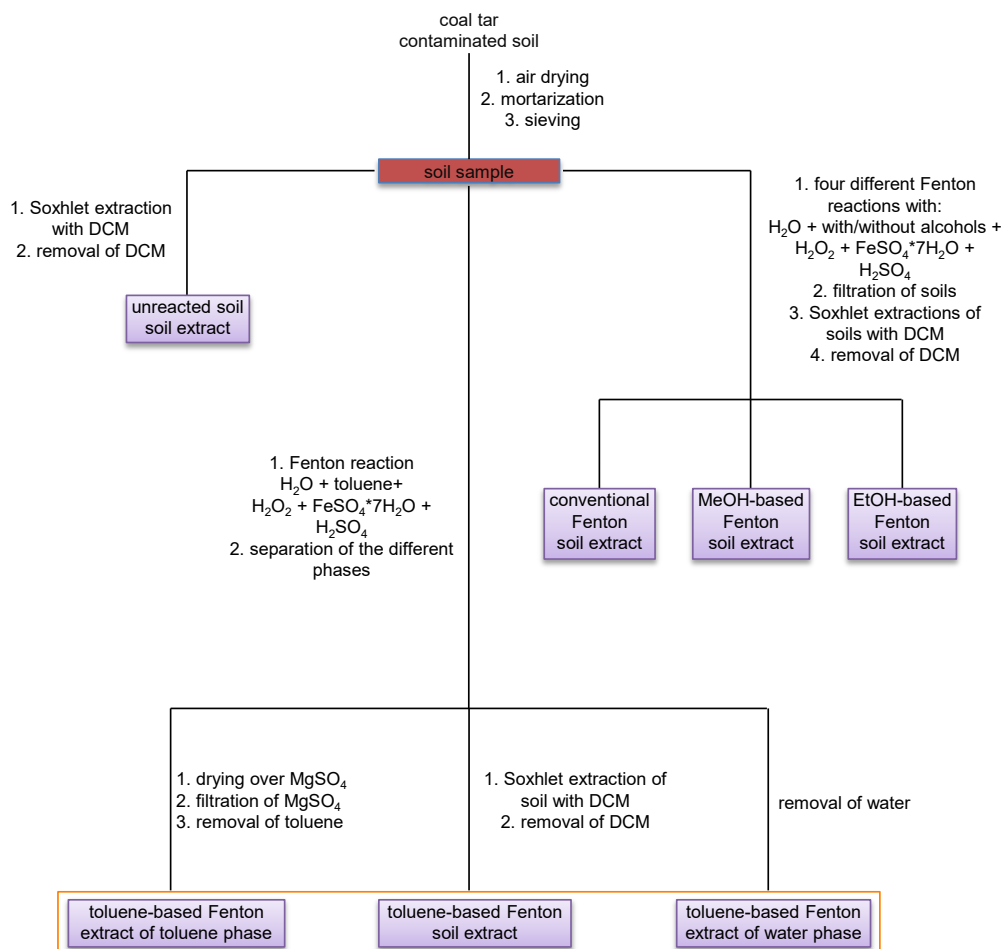


Figure 3-1: Reaction and chemical workout for the Fenton reaction of contaminated soil with different modifiers.

3.4 Results and Discussion

Soxhlet extracts of the contaminated soil before (unreacted) and after Fenton reactions were analyzed and compared to evaluate the efficiency of the reaction. As both, the original sample as well as the sample after Fenton reaction are highly complex mixtures and high resolution mass spectrometry is the method of choice to analyze the outcome of the Fenton reaction down to the molecular level. Figure 3-2 shows the APPI mass spectra of the different extracts. The spectrum of the unreacted soil extract (top trace, black) shows dominant signals that belong to

radical hydrocarbon species. The corresponding chemical compositions partly fit to compounds from the 16 EPA-PAHs list or their derivatives with only little alkylation.

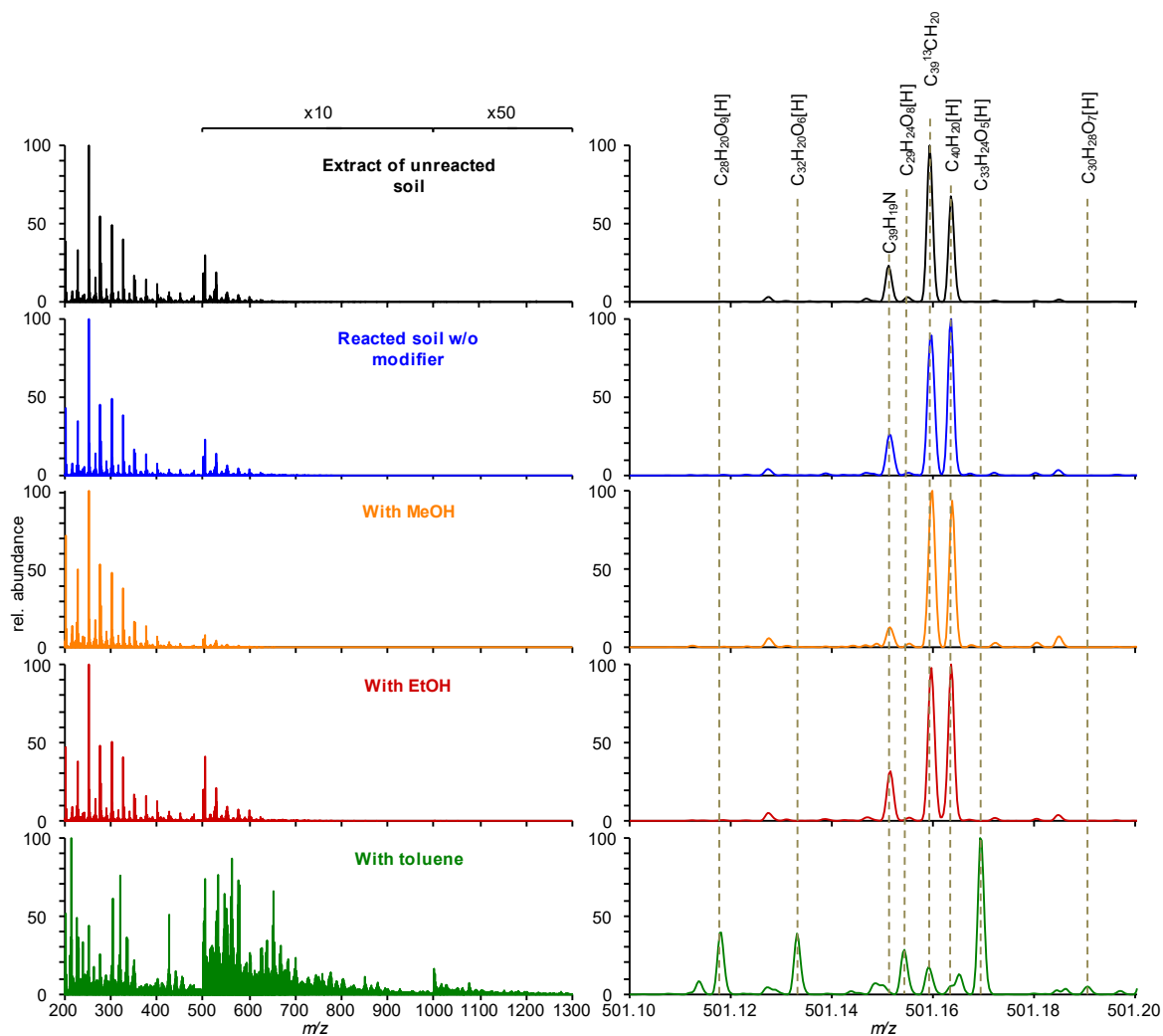


Figure 3-2: Mass spectra of Soxhlet extract from unreacted soil (black), Fenton reaction without modifier (blue), Fenton reaction with additional modifier methanol (yellow), Fenton reaction with additional modifier ethanol (red) and Fenton reaction with additional modifier toluene (green) and corresponding zooms into m/z 501.10-501.20 (right).

The same is observed for the spectra of the extracts after Fenton reaction without modifier (second trace, blue) and with methanol (third trace, yellow) or ethanol (fourth trace, red) as modifiers, respectively. Overall, no significant changes are observed within these spectra. The addition of toluene (bottom trace, green) improves the solubilities of the PAHs, makes them better accessible for the reaction and that way increases the efficiency of the Fenton reaction by formation of a wide variety of oxygenated species. The formerly dominating PAHs signals in the lower mass range are now showing signals with lower intensity, while new signals are appearing, also in the higher mass ranges. The zoomed-in spectra between m/z 501.10 and 501.20 exhibit some major changes between the different reactions. Multiple oxygen-

containing species like $C_{33}H_{24}O_5[H]$, $C_{32}H_{20}O_6[H]$, $C_{30}H_{28}O_7[H]$, $C_{29}H_{24}O_8[H]$ and $C_{28}H_{20}O_9[H]$ are detected with significant intensities in comparison to the intensities of polycyclic aromatic hydrocarbons.

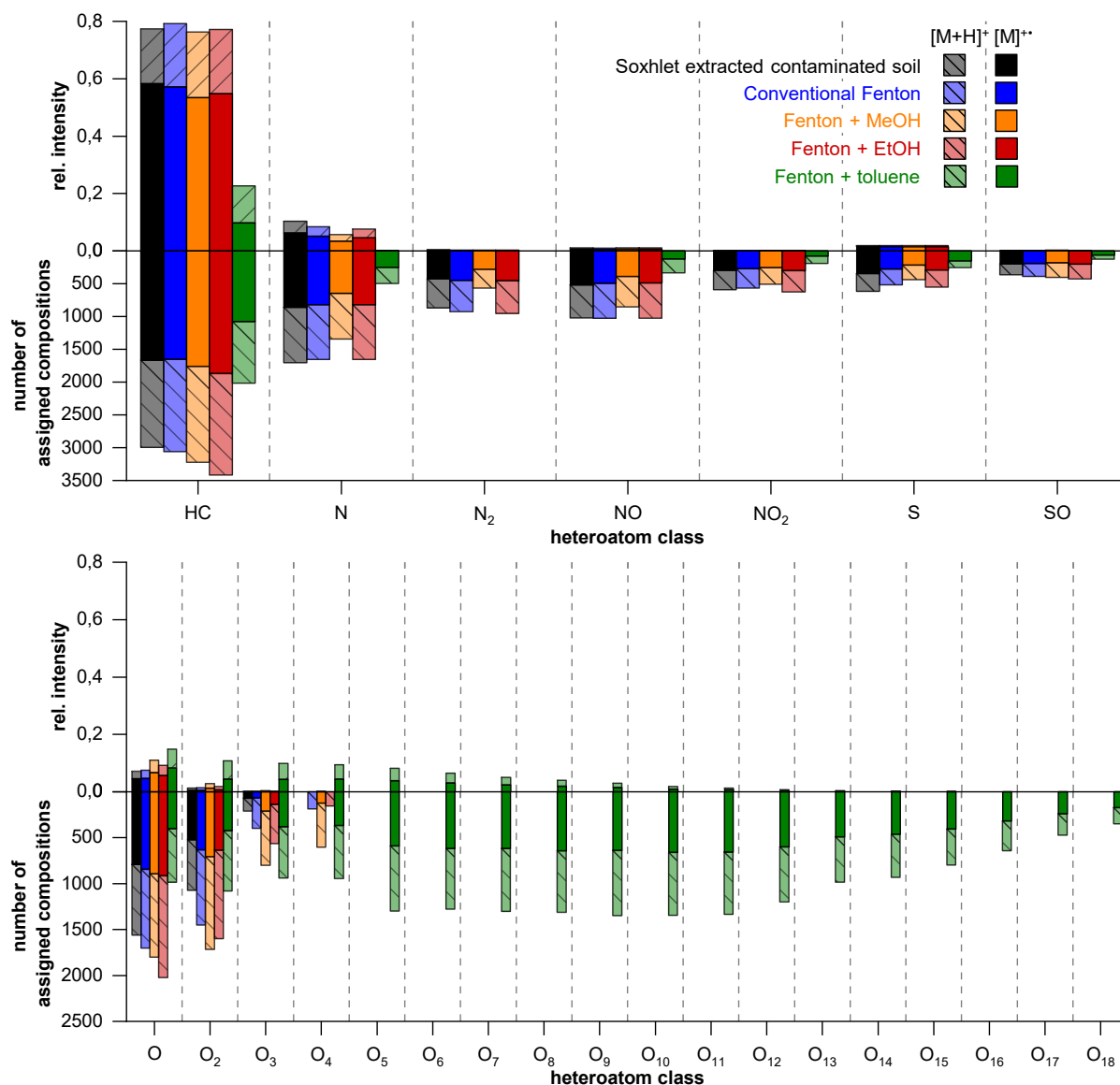


Figure 3-3: Relative intensity (upwards graph) and population-based (downwards graph) class distributions of the most prominent heteroatom classes (top) and oxygenated compounds (bottom) for Soxhlet extract of unreacted soil (black), soil reacted without modifier (blue), with additional methanol (yellow), with additional ethanol (red) and with additional toluene (green). Results from both radical ions and protonated molecules are shown.

Once elemental compositions are assigned to individual signals, these can be represented in different ways. In Figure 3-3, the detected signals were categorized into different heteroatom classes (i.e. the amount of heteroatoms per molecule) and plotted either based on the classes summed relative intensities or based on the total number of assigned compositions (population) within each class. Both methods of data interpretation offer certain benefits. The (relative)

intensity of a signal is dependent on the response factors of individual compounds^{63, 64} and can be largely affected by ion suppression,^{65, 66} thus overestimating few concentrated or easily ionized compounds. In a population plot, every signal has the same importance and even low intensity signals are counted equally. Therefore, a population plot overestimates the majority of many low abundant and difficult to ionize compounds. In general, after the Fenton reaction of contaminated soil, organic pollutants are either completely or partially transformed into oxygenated products. Completely removed or newly formed compounds are easily identified in population plots, while the data from relative intensities is needed for the representation of partially degraded contaminants.

Using APPI as ionization technique, PACs are easily ionized⁶⁷ by forming either their radical cation $[M]^+$ or the corresponding protonated species $[M+H]^+$.⁵⁸ Here, oxygen-containing classes from O₁-O₁₈ (Figure 3-3, bottom) are illustrated separately from the most abundant heteroatom classes, namely HC, N, N₂, NO, NO₂, S and SO (Figure 3-3, top). Comparing the Soxhlet extracts from the untreated soil with those after the Fenton reactions without or with addition of alcohols does not show any significant changes in relative intensity or population for the hydrocarbons. However, a slight reduction of N and S classes can be observed using methanol as co-solvent. In the extract of the unreacted sample, low oxygenated compositions with O₁-O₃ were detected.

When performing the Fenton reaction with addition of alcohols, the low oxidized classes O₁ to O₄ increase in intensity and population, while no significant degradation of hydrocarbons is observed. Here, maybe different solubilities from the PAHs and the Fenton oxidants in alcohols can play a role that the CH class distribution is not affected but the N-classes are. A strong degradation of hydrocarbons, nitrogen and sulfur containing compounds was achieved by Fenton oxidation using additional toluene. A closer view on the HC class points out the importance of different data representations. Considering the relative intensities of the different experimental setups, a decrease from 77.4% (untreated soil) to 29.3% (Fenton with toluene) was observed. This decrease corresponds to a loss of 37.9% regarding the total intensity of hydrocarbons.

In contrast, comparing the number of assigned hydrocarbon compositions before and after the reaction shows a reduction by 32.7%, while a share of 67.3% of the elemental compositions is still present. These include compounds that were only partly degraded (thus losing signal intensity) but are still present in the sample (and therefore show up in the population). These results are based on mass spectrometric measurements. While high resolution and accuracy are decisive advantages of this method it has to be noted that only overall elemental compositions

can be obtained. This means that structural isomers with the same mass and formula cannot be distinguished. Here, one point that cannot be decided is if the amount that is reacted are isomers that react more easily while one or more additional isomers remain unaffected.

In total 980 hydrocarbon compositions were removed completely by running the Fenton reaction with addition of toluene. Furthermore, this reaction has led to an increase of the relative intensities of all classes of oxygen-containing compounds, up to O₁₈ (Figure 3-3, bottom). Beginning from O₂ also the population of these classes increases dramatically compared to the unreacted sample. The decrease of the population in the O₁ class indicates that singly oxidized hydrocarbons, which are produced when the reaction is performed with alcohols, are more easily degraded when using toluene. Moreover, a maximum of 1530 newly created compositions were observed within the O₉ class, which confirms the efficient oxidation of contaminants in the presence of toluene.

Variations of structure and molecular weight are among the most important factors that influence a pollutants oxidation rate during a remediation reaction.⁶⁸ Thus the large variety of hydrocarbons present in a typical PACs contamination renders the remediation of contaminated soil a difficult task. One molecular parameter that can be helpful for the categorization of structural types is the DBE, which refers to the total number of π -bonds and rings within a molecule. In Figure 3-4, assigned compositions are grouped according to the corresponding DBE and the detailed DBE distributions based on the relative intensity (left) and population (right) are shown for hydrocarbon species that were detected as radical ions. The Soxhlet extracts of the untreated contaminated soil contain highly aromatic hydrocarbons up to a DBE of 73. While the highest intensities are observed in the DBE range between 10 and 30 (around 3-10 aromatic rings), the highest population, i.e. the broadest distribution of alkylations is observed between DBE 30 and 50.

After Fenton reaction, compounds with the highest DBE are removed in all cases, the reactions with additional methanol (max. DBE 58) or toluene (max. DBE 60) being more efficient than with additional ethanol (max. DBE 64) or without any modifier (max. DBE 65). Regarding signal intensities, only the reaction with addition of toluene shows a significant reduction throughout the entire DBE range, while in all other cases no significant change can be observed. When considering the population-based plot, the addition of methanol leads to some loss of compounds in the DBE range above 30, while the use of toluene leads to a significant loss of compounds with a DBE above 20. In case of all tested modifiers however, newly created hydrocarbon species with a DBE below 20 are detected. These must be either related to the

reaction (i.e. they are reaction products) or a result of more efficient dissolution of compounds from the soil.

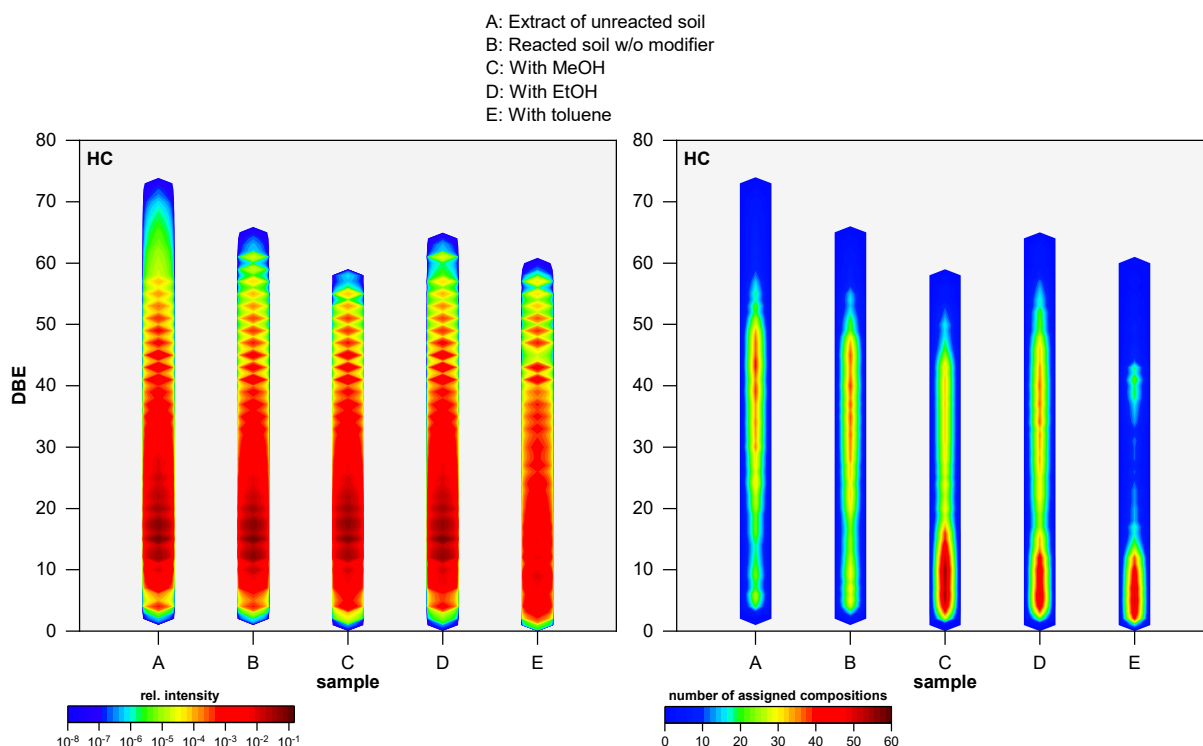


Figure 3-4: Relative intensity (left) and population-based (right) DBE distributions of hydrocarbons detected as radical ions of a Soxhlet extract from the unreacted soil (A), soil reacted by Fenton without modifier (B), with additional methanol (C), with additional ethanol (D) and with additional toluene (E).

Combining the ultrahigh resolution mass spectrometry with usage of Kendrick plot for data visualization allow a deeper understanding of chemical changes in the oxidation of PACs. In these plots, the assigned compositions within in a class are represented as a dot with a certain DBE and number of carbon atoms per molecule. In Figure 3-5, results from different samples are summarized for the selected classes HC, N and O₁₋₅. The unreacted contaminated soil contains HC species from C₉ to C₉₆ and DBE from 2-73. In addition, compounds up to O₃ species were detected with a narrow distribution, which is achieved also for the N radical class. By calculating the linear regression equation for the hydrocarbon compositions with the highest relative intensities, a slope of around 0.76 (Figure 3-5, black line) is determined. This slope points out the linear expansion of the aromatic cores with several aromatic rings.^{53, 69, 70}

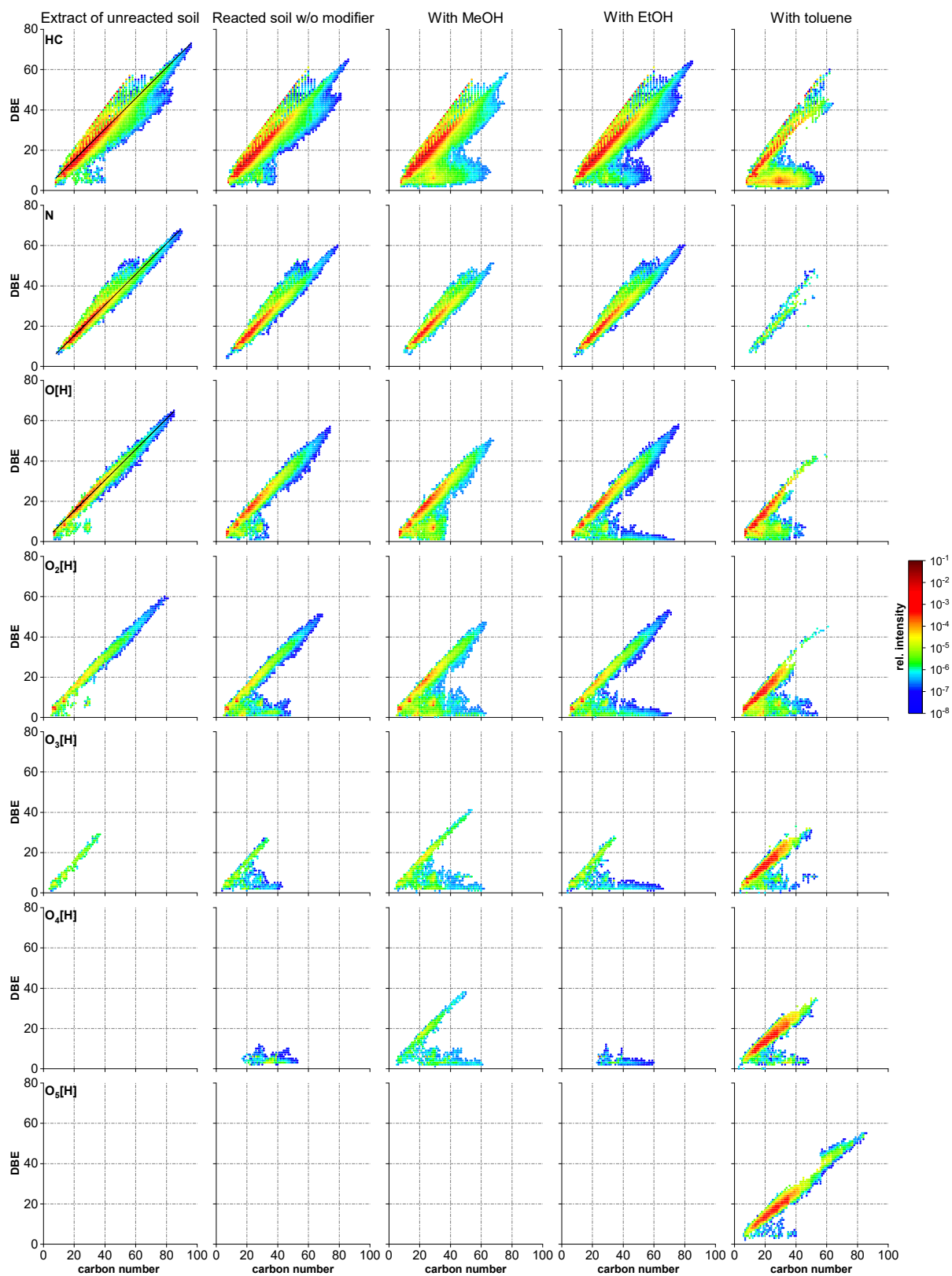


Figure 3-5: Kendrick plots of HC, N and O_{1-5} classes measured with APPI(+) of Soxhlet extract of unreacted soil, soil reacted by Fenton without modifier, with additional methanol, with additional ethanol and with additional toluene.

A similar DBE versus carbon number distribution, like for HC species, was obtained for N and O containing compositions including the same slope gained for the highest relative intensities. The obtained results can be explained by the soil contamination with coal tar, which contain highly fused aromatic compounds with higher DBE values than e.g. petroleum-contaminated soil.⁷⁰ After treating the contaminated soil without any modifier, no changes in HC and N class distributions are visible. Nevertheless, newly formed O₁₋₃ species with DBE around 1-15 and C₅-C₄₈ were discovered. Whenever a modifier is used in the Fenton reaction, HC species with high carbon number (until C₆₆ for methanol-based Fenton reaction) in lower DBE ranges (DBE ≤ 19) were detected (Figure 3-5). The extraction of these pure hydrocarbons from the soil is favored through the combination of OH[•] and modifier by enhanced desorption of the compounds from the soil matrix. Apart from this extraction capacity, there is no significant difference in the degradation process of PAHs regarding to the use of different alcohols. However, after the methanol-based Fenton treatment, compounds in O₄ class were detected and the corresponding non-oxygen-containing HC compositions were assigned with the highest relative intensities in the Soxhlet extracted contaminated soil. These compounds, detected as O₄ species, are formed through the oxidation of PAHs and/or further oxidation of PAOHs with oxygen number 1-3.

The removal efficiency of PAHs and PANHs was significantly increased by addition of toluene as modifier. Highly aromatic PAHs with DBE 43-73 and carbon number 64-96 were completely degraded. The less DBE containing hydrocarbons (DBE 20-40) were fully removed after a certain number of carbon atoms. The reason for the rapid oxidation of compounds with higher carbon count for a certain DBE is that the increase of carbon atoms for a given DBE is structurally possible only by inserting side chains to the aromatic core part.

These substituted PAHs are probably more reactive towards OH[•] than the unsubstituted ones and therefore removed completely after toluene-based Fenton reaction.^{71, 72} An efficient decrease for N class in relative intensity and number of assigned compositions was only reached with Fenton with addition of toluene.

For the extraction of PAHs from contaminated soil, toluene is also used as a solvent^{73, 74} and it is recommended by the International Organization for Standardization (ISO) for the elution of highly contaminated soils using Soxhlet extraction.⁷⁵ Therefore, the comparison of different phases (extracted soil, toluene and water phase) obtained after the reaction is necessary for the conformation of the chemical treatment apart from the extraction of PACs with additional toluene (Figure 3-1, orange rectangle). Kendrick plots of the hydrocarbon class of the different phases are illustrated in Figure 3-6. Soxhlet extracted soil sample and separated toluene phase

show similar hydrocarbon distributions, which verifies the reaction of PAHs in the presence of toluene. However, hydrocarbons with low DBE ($\text{DBE} \leq 19$) and high carbon number per molecule are detected only in Soxhlet extracted soil. PAHs with $\text{DBE} \leq 38$ and carbon number ≤ 42 are transferred into the water phase, because of the poor solubility of HMW hydrocarbons in water.^{4, 76, 77} Furthermore these transferred PAHs with DBE higher than 20 are detected with lower relative intensities in comparison to the Soxhlet extracted soil sample and toluene phase.

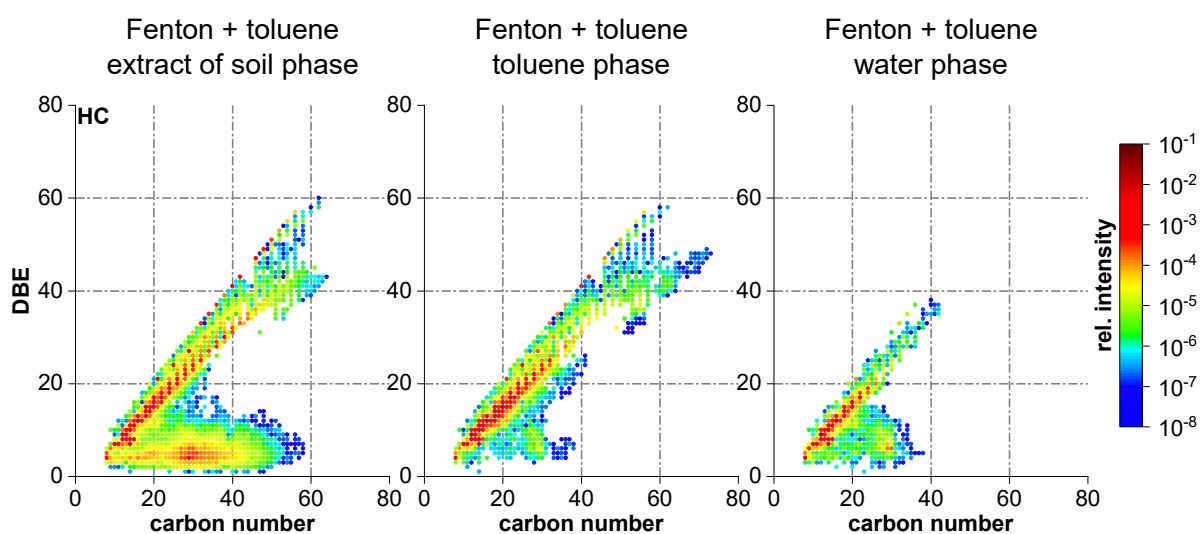


Figure 3-6: Kendrick plots of HC class measured with APPI(+) of the extract of soil phase (left), toluene (middle) and water phase (right) got after the Fenton + toluene reaction.

Considering all results shown here, the effect of adding a modifier such as toluene has a large effect on the reactivity of the Fenton reaction towards polyaromatic hydrocarbons. While methanol and ethanol do not really show a better efficiency of the reaction, the addition of toluene to the mixture really makes the oxidation reaction much more effective. At this point it is speculative to discuss the detailed molecular mechanism, but the effect of toluene is important. Most likely here the addition of toluene dissolves the aromatic species much better into the organic phase. Now, while they are dissolved, the reaction partners have a much better chance to meet at the phase boundaries between the toluene and water phases, where the oxidation can take place. For a better understanding of the molecular mechanism, these phase boundary interactions need to be better understood.

3.5 Conclusion

Toluene is from an environmental perspective certainly not the best and most wanted modifier for making PAHs contaminations from soil accessible for remediation. But it has other advantages. For one it is biodegradable for microbiological remediation. And then, this study demonstrated the successful Fenton-based pretreatment of highly PACs contaminated soil by comparing toluene with other modifiers. And here, toluene is making contaminants accessible for a remediation process in a manner that is not possible with other modifiers. Pure hydrocarbons with maximum DBE of 70 are present in the soil – used in this experiment – and are efficiently oxidized in the presence of toluene, while the addition of methanol and ethanol has not resulted in significant soil remediation probably due to scavenging effects of reactive radicals by alcohols.⁴¹ This oxidation step makes the contaminants available for microbiological degradation. Here, the detection of similar HC distribution patterns in the different phases (extract of soil, toluene and water phase) obtained after the Fenton + toluene reaction has clearly shown the improved removal of PAHs from the soil. The results indicate that the addition of toluene improves the solubilities and makes the polyaromatic compounds accessible for the oxidation reaction. With more oxygen they become much more polar and water soluble, making them accessible for biological treatment.

3.6 References

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4. Investigation of Fenton oxidation of aged and highly PACs contaminated soil with addition of toluene or DCM analyzed by ultrahigh resolution mass spectrometry

Redrafted from:

Satilmis, I. and Schrader, W. “*Investigation of Fenton oxidation of aged and highly PACs contaminated soil with addition of toluene or DCM analyzed by ultrahigh resolution mass spectrometry*” will be submitted to *Environments*.

4.1 Abstract

Contaminated soil consists of a complex mixture of thousands of polycyclic aromatic compounds (PACs) making the remediation extremely difficult. Modified Fenton reaction is the method of the choice for removing pollutants from the soil. Due to low water solubility of the contaminants, an organic co-solvent is necessary for increased accessibility of PACs towards oxidation reaction. In this work, the impact and amount of the modifier (DCM or toluene) added to the Fenton reaction of aged highly contaminated soil was investigated by using ultrahigh resolution mass spectrometry.

The obtained results show the improved degradation of polycyclic aromatic hydrocarbons (PAHs) and PANHs in soil using toluene instead of DCM. This can be attributed to the formation of surfactant-like products and/or addition of toluene to PACs. Furthermore, a certain amount of toluene (5% v/v) is required for efficient PAHs removal, while further increase in the toluene amount lead to any significant benefit of the degradation process.

4.2 Introduction

PACs, which comprise PAHs and heteroatom-containing compounds (N, S, O and/or halogens),¹ are highly toxic and carcinogenic compounds and ubiquitously present in natural media including soil, sediments, water and air due to anthropogenic contamination. For the removal of recalcitrant PAHs from soil, various remediation techniques have been applied including biological, (physico)-chemical and thermal treatment. Here, bioremediation plays an important role, but biological amendment of polluted soil depends on the number of fused rings. Low molecular weight PAHs (2-3 rings) can be digested by microbes, but higher molecular weight PAHs (> 3 rings) have been shown to be resistant towards biodegradation due to very low solubility in water and strong adsorption onto the soil organic matter.²⁻⁴ While soil adsorbed PAHs usually are no ecotoxicological threat, the free PAHs can represent a toxicological problem. Therefore, various chemical treatment methods were examined for pre- or post-treatment in combination with bioremediation, either forming more biodegradable compounds or further removing of the remaining pollutants.^{2, 5-8}

Among the chemical techniques, such as ozonation,⁹⁻¹¹ photooxidation,¹²⁻¹⁴ persulfate,^{15, 16} or permanganate,^{15, 17, 18} the Fenton reaction is the most extensively studied chemical oxidation method for cleaning-up contaminated soil. During the Fenton process, catalytic decomposition of H₂O₂ in presence of ferrous ion (Fe²⁺) generates OH[•], which are highly reactive and non-specific oxidants.¹⁹ These strong radicals are attacking organic compounds by abstraction of H-atom or through an addition to C-C double-, triple bonds or aromatic rings.²⁰ Nevertheless, using Fenton reaction is still being challenged in many studies, because the remediation efficiency depends on various factors: (A) Aged contaminated soil are more difficult for treatment than artificially spiked soil due to stronger sequestration into the soil matrix and less availability to OH[•];^{6, 19, 21-25} (B) In addition to adsorption process, the presence of soil organic matter causes the consumption of OH[•] as scavenger;^{15, 22, 26} (C) The removal of LMW PAHs is more favored than HMW because of increased solubility and decreased binding to soil organic matter with decreasing molecular weight.^{21, 24, 27, 28} These factors point out that the organic matrix has the greatest impact on PAH accessibility toward oxidant,²⁴ and therefore a higher desorption efficiency is necessary for the successful degradation of pollutants.

Watts et al. studied the application of vigorous Fenton reaction to enhance the desorption of PAHs from soil organic matter by producing additional radical and anion species.²⁹ Furthermore, the implementation of organic additives (solvents, vegetable oils or surfactants) was investigated for removing the hydrophobic compounds from the soil matrix to facilitate a successful degradation. Gan and co-workers found that the addition of ethyl lactate rather than

ethanol results in improved removal of selected PAHs due to less scavenging impact of OH[•] and enhanced solubility of PAHs.³⁰ Bogan et al. documented the efficient treatment of HMW PAHs including vegetable oils through dissolution and oxidation of HMW PAHs in vegetable oils.²⁸ In addition, the oxidation of vegetable oils during Fenton reaction generates surfactants, which are also capable of desorbing the pollutants from soil.²⁷ Rafin et al. investigated the cyclodextrin-based Fenton reaction of benzo[a]pyrene (BaP) and found out that the existence of cyclodextrin-BaP-iron-complex leads to focused attack of OH[•] on BaP.³¹ These examples show that the Fenton oxidation is an important reaction, where new insights can still be found. Recently we showed a successful combination of non-target approach using ultrahigh resolution mass and Fenton oxidation of aged highly contaminated soil with addition of various modifiers (MeOH, EtOH or toluene), whereby the highest removal of PAHs was provided with toluene. This combination allows an achievement of extensive characterization of the parent pollutants together with different oxidized products.

For investigating the efficiency of Fenton oxidation in PACs contaminated soil, almost targeted GC-MS analysis of the 16 EPA-PAHs was performed.³² This approach allows a simple and comparable quantification of the results, but neglects the majority of PACs that also react during oxidation process.³³ Here, many of the unknown PACs, as well as their reaction products, have high molecular weights and are not detectable by gas chromatography. Combining UHRMS with a non-target approach provides a comprehensive characterization of the initial PACs and various oxidized a non-oxidized compounds on a molecular level. FT-ICR MS³⁴⁻³⁹ and Orbitrap MS⁴⁰⁻⁴² are the benchtop mass spectrometers allowing the unique determination of elemental compositions for each detected ion based on the high resolving power and high mass accuracy. This study is the follow-up to the previous one (Chapter 3) by investigating the chemical conditions such as amount of toluene used as co-solvent and difference between addition of toluene and DCM. Fenton reaction of 9-ethylcarbazole in presence of different co-solvents (without, DCM or toluene) was performed to study the impact of the different co-solvents on the degradation process for deeper understanding the Fenton oxidation of PACs contaminated soil in the presence of co-solvents.

4.3 Material and Methods

4.3.1 Chemicals

The reagents used for the experiments 9-ethylcarbazole (99%, Thermo Fisher, Kandel, Germany), toluene ($\geq 99.8\%$, Fisher Scientific, Loughborough, UK), DCM (99%, Fisher Scientific, Loughborough), hydrogen peroxide (30%; J. T. Baker, Sowinskiego, Poland), sulfuric acid (95-98%, J. T. Baker, Deventer, Netherland), and deionized water (type I) taken from a Clearwater dispenser Purelab Flex 2 (ELGA LabWater, Celle, Germany).

4.3.2 Sample preparation

A highly contaminated soil was received from an industrial site in the German Ruhr area. 5 g of the sample were air dried for one week at room temperature in a fume hood. Then the sample was mortared for homogenization, sieved (2 mm pore size) and kept in a fridge at 4 °C for further experiments.

4.3.3 Experimental procedure

For each Fenton reaction, the respective sample (85 mg of contaminated soil or 10 mg of 9-ethylcarbazole) was transferred into a 500 mL single-neck flask and the respective modifier (8.4 mL, 5% v/v) was added where applicable. While stirring, deionized water (124 mL) was added, and the mixture acidified with H_2SO_4 (1.3 M) to pH ~ 3 . Afterwards $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (4.8 g, 17.27 mmol) was added, the flask was stirred at 0 °C till the iron salt was dissolved. Then H_2O_2 (3*14 mL, 0.13 mol, 3 M) was added dropwise every 30 minutes⁴³ and the reaction mixture was stirred for additional 48 h at room temperature.

In case of the Fenton reactions of contaminated soil, the soils from different reactions were filtered, dried in a fume hood and remaining compounds were extracted by Soxhlet extraction with DCM (50 mL) for 24 h. Then the solvent was 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 MgSO_4 and filtered. Both water and toluene phase were concentrated under reduced pressure and residues stored for analysis. However, only residues of Soxhlet extracted soils and residues of organic phases were further analyzed.

For comparison of the reactions with the untreated sample, a Soxhlet extraction of the contaminated sample (300 mg) with DCM (50 mL) was performed for 24 h without prior reaction. The solvent was then removed under reduced pressure and the residues stored for further analysis.

In case of the Fenton reactions of 9-ethylcarbazole, the layers were separated and the water phase was extracted with DCM (3x). The combined organic layers were dried over MgSO₄, filtered, concentrated under reduced pressure and stored for analysis.

4.3.4 FT Orbitrap MS and data analysis

Mass analysis was performed on a research type FT Orbitrap Elite (Thermo Fisher Scientific, Bremen, Germany). The mass spectra were collected with a resolving power of $R = 480,000$ at m/z 400 in a mass range of m/z 150-1300 using APPI. Spectral stitching^{41, 44, 45} was used 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 different residues of the various reactions were diluted in toluene:methanol (1:1, v/v) to a final concentration of 150 ppm and analyzed by direct injection at a flow rate of 20 μ L/min. Ion source conditions were adjusted as follows: capillary temperature of 275 °C, vaporizer temperature of 250 °C, sheath, auxiliary and sweep gases of 20, 10 and 2 arbitrary units. MS/MS measurements were performed using CID with an isolation window of 0.4 Da and high energy (around 35%) by applying helium as collision gas.

Recorded mass spectra were imported into Composer (V1.5.0, Sierra Analytics, Modesto, CA, USA) to assign the elemental compositions to detected signals. Peak Assignment was performed based on the following limits: H: 0-300, C: 0-100, O: 0-20, N: 0-2, S: 0-1, DBE: 0-80 and mass error ≤ 1.5 ppm. Excel (Microsoft Office Professional Plus 2010, Microsoft Excel 2010) and Origin (v9.2.0, OriginLab Corporation, Northhampton, MA, USA) were used for further data evaluation and graphical visualization.

4.4 Results and Discussion

4.4.1 Comparison between toluene- and DCM-based Fenton reaction

Earlier studies from our group demonstrated a successful recovery of over 95% for PACs, using toluene or DCM, for crude oil spiked on sand⁴⁶ as well as the most efficient removal of PAHs from aged heavily contaminated soil with addition of toluene (beside MeOH and EtOH) as modifier to the Fenton reaction.⁴⁷ Therefore, Fenton experiments of contaminated soil with additional toluene or DCM are performed to determine the best solvent for the removal of PAHs from soil. Comparison of the organic and extract of the soil phases, obtained for toluene- and DCM-based Fenton, with extract of unreacted soil are shown in Figure 4-1. Here, the detected signals were grouped in different heteroatom classes and presented either by using the summed

relative intensities or according to the total number of assigned compositions (population) for each class. Both methods of data interpretation are required due to complete or partial conversion of PACs into oxidized compounds. The fully degraded or newly created components can be represented in population diagrams, whereas the partially oxidized compounds are visualized in the relative intensity data.

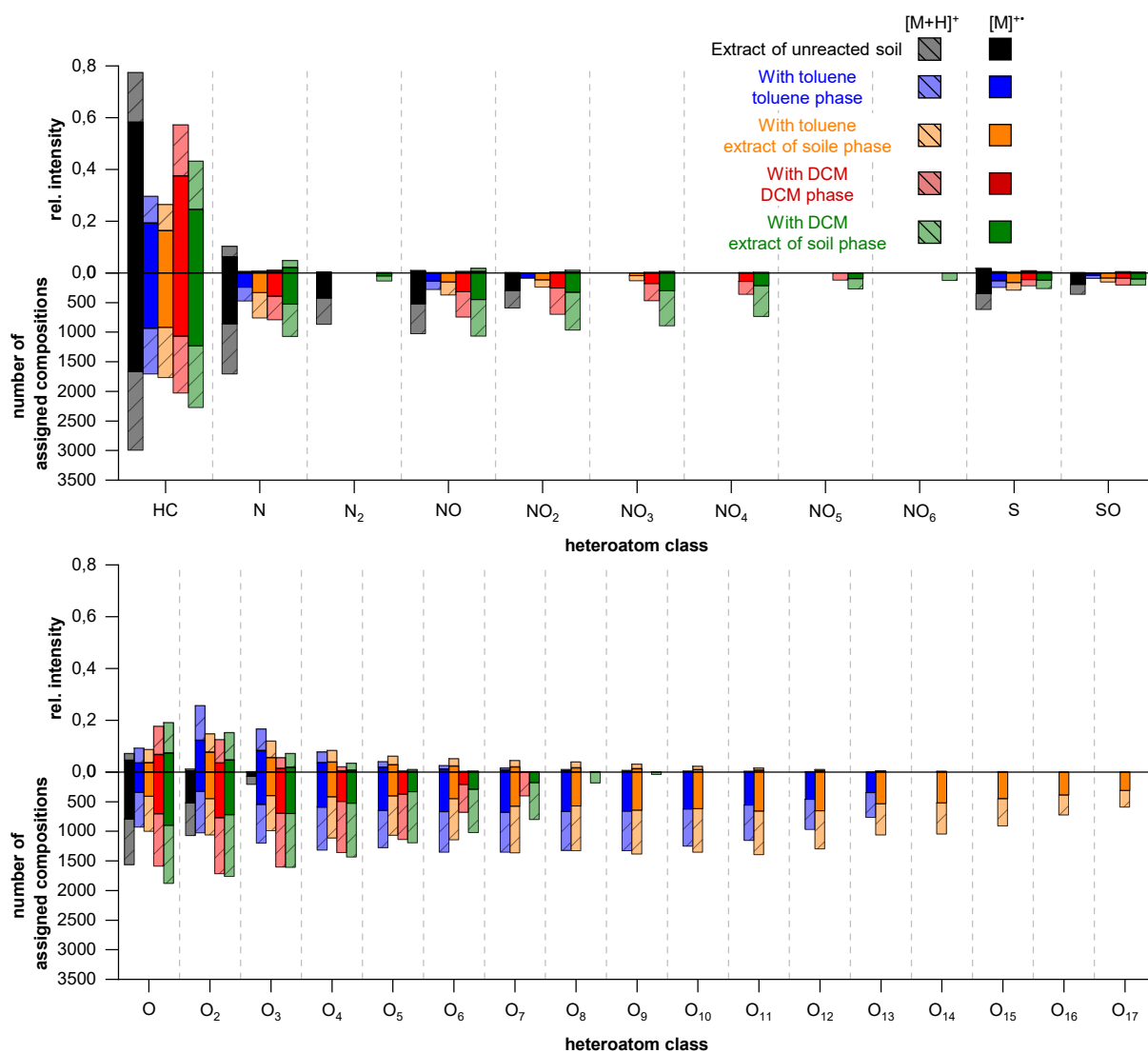


Figure 4-1: Relative intensity (upwards graph) and population-based (downwards graph) class distributions of the most prominent heteroatom classes (top) and oxygenated compounds (bottom).

In general, Fenton treatment with toluene or DCM resulted in removal of PAHs, PANHs and PASHs. The oxidation of PAHs and PANHs was more efficient when toluene was added as co-solvent which is indicated by lower relative intensity and population for the HC and N classes (Figure 4-1, top). Here, a decrease for HC class in relative intensities from 77.4% (unreacted soil) to 29.6% (Fenton with toluene; toluene phase) and 26.4% (Fenton with toluene;

extract of soil phase) was obtained. Regarding the population, a reduction of the assigned hydrocarbon compositions from 2999 (unreacted soil) to 1709 (Fenton with toluene; toluene phase) and 1772 (Fenton with toluene; extract of soil phase) was observed. It is important to mention that structural isomers with the same formula and mass cannot be distinguished and thus no clear prediction can be made about reactivities of different isomers.

Low oxygenated compositions containing O₁-O₃ were detected in the extract of the unreacted sample. Running the Fenton reaction with addition of toluene leads to production of up to O₁₃ containing products in toluene phase and up to O₁₇ in the extract of soil phase, while the creation of PAOHs after DCM-based Fenton oxidation is much less prominent (Figure 4-1, bottom). After toluene-based Fenton oxidation compounds with O₁₄₋₁₇ were only detected in the extract of the soil phase. Similar, but less obvious, trend can be observed in the DCM-based Fenton oxidation. These results imply the increasing strength of hydrophobic interactions between PAOHs and soil organic matter with higher oxygen number in the molecule requiring stronger extraction methods such as Soxhlet extraction.

A more detailed understanding of the chemical changes is provided by the Kendrick diagrams, where the assigned compositions are plotted as a dot with a specific DBE and #C (carbon number) per molecule. Figure 4-2 illustrates the different samples for HC, N and O₆ species. PAHs with DBE ≤ 73 and #C ≤ 96 are found in the extract of unreacted soil. The narrow distributions with high relative intensities in HC and N classes result from soil contamination with coal tar and from the high concentrations of the corresponding PAHs.⁴⁸ In both reaction types, HMW PAHs and PAHs with higher carbon numbers for a certain DBE are degraded faster than the remaining contaminants, probably due to lower concentration of these PAHs compared to LMW PAHs. Many studies regarding Fenton oxidation of PAHs contaminated soil have proven superior degradation of LMW PAHs than HMW ones arguing with poor solubility and higher adsorption on soil organic matter.^{21, 24, 27} However, inclusion of organic additives enhanced Fenton oxidation of HMW pollutants by increasing solubility and desorption of HMW contaminants.²⁸ The removal efficiency of PANHs was increased after toluene-based Fenton due to lower relative intensities in the narrow distribution range. Interestingly, the addition of toluene instead of DCM resulted in a serious increase in the relative intensity and population of O_x (Figure 4-2 and O₆ as an example in Figure 4-3). This result strongly indicates that apart from the oxidation of the PACs, the toluene is also oxidized since it is added in large amounts to the reaction.

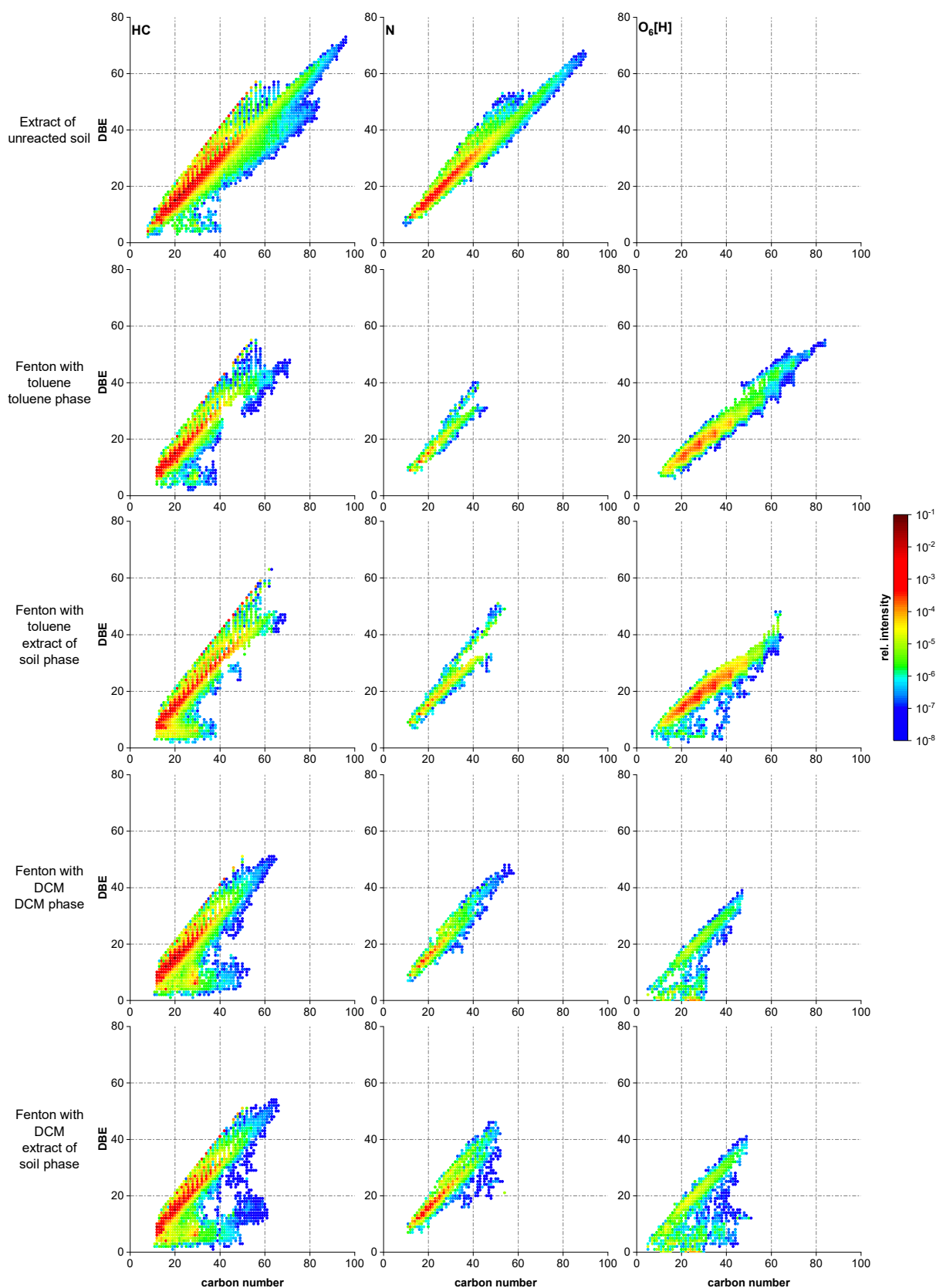


Figure 4-2: Kendrick plots of HC, N and O₆[H] classes before and after co-solvent-based Fenton reactions achieved for different phases.

To verify this assumption, a Fenton reaction of only toluene was performed to compare the high intensity regions between the different reactions (Figure 4-3). Here, the high intensity region of HC class (unreacted soil) has only an overlap with the O₆ class of the DCM-based Fenton (Figure 4-3, upper dashed line). The high intensity region of O₆ class (toluene-based Fenton) matches with the O₆ class of the Fenton reaction of only toluene and a similar distribution pattern were obtained for both reaction types (Figure 4-3, bottom dashed line). Therefore, the high intensity regions of O_x class, received from the toluene-based oxidation of contaminated soil, is resulting either by polymerization of toluene or addition of toluene radicals to the compounds. This production of polymers may be a reason for the improved toluene-based Fenton oxidation, as the polymers have surfactant-like properties.⁴⁹

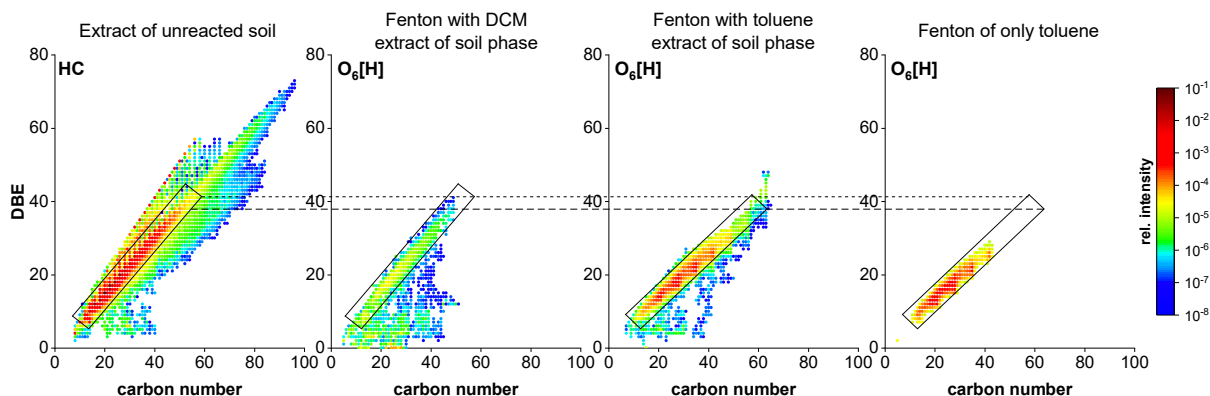


Figure 4-3: Kendrick plots of HC before chemical treatment, O₆[H] class after DCM-based Fenton, O₆[H] class after toluene-based Fenton and O₆[H] class after Fenton of only toluene.

4.4.2 Fenton reaction of 2-ethylcarbazole and MS/MS measurements

As shown above, the addition of toluene to the Fenton oxidation results in the formation of highly oxidized compounds either through polymerization of toluene or the addition of toluene moiety to the pollutants. The polymerization of toluene is indicated by Fenton reaction of only toluene, where similar highly oxidized compounds, like in the Fenton oxidation of contaminated soil, were obtained (Figure 4-3). Regarding the reaction of toluene with PACs, it is extremely difficult to make a prediction due to the complex mixture of thousands of PACs in soil and the polymerization of toluene. For this purpose, the complexity of the Fenton system has to be reduced, which can be achieved by using a single component in the Fenton oxidation. Here, a nitrogen-containing compound was chosen as a reactant in order to distinguish the created nitrogen-containing products from the polymerization products achieved during the Fenton oxidation of toluene.

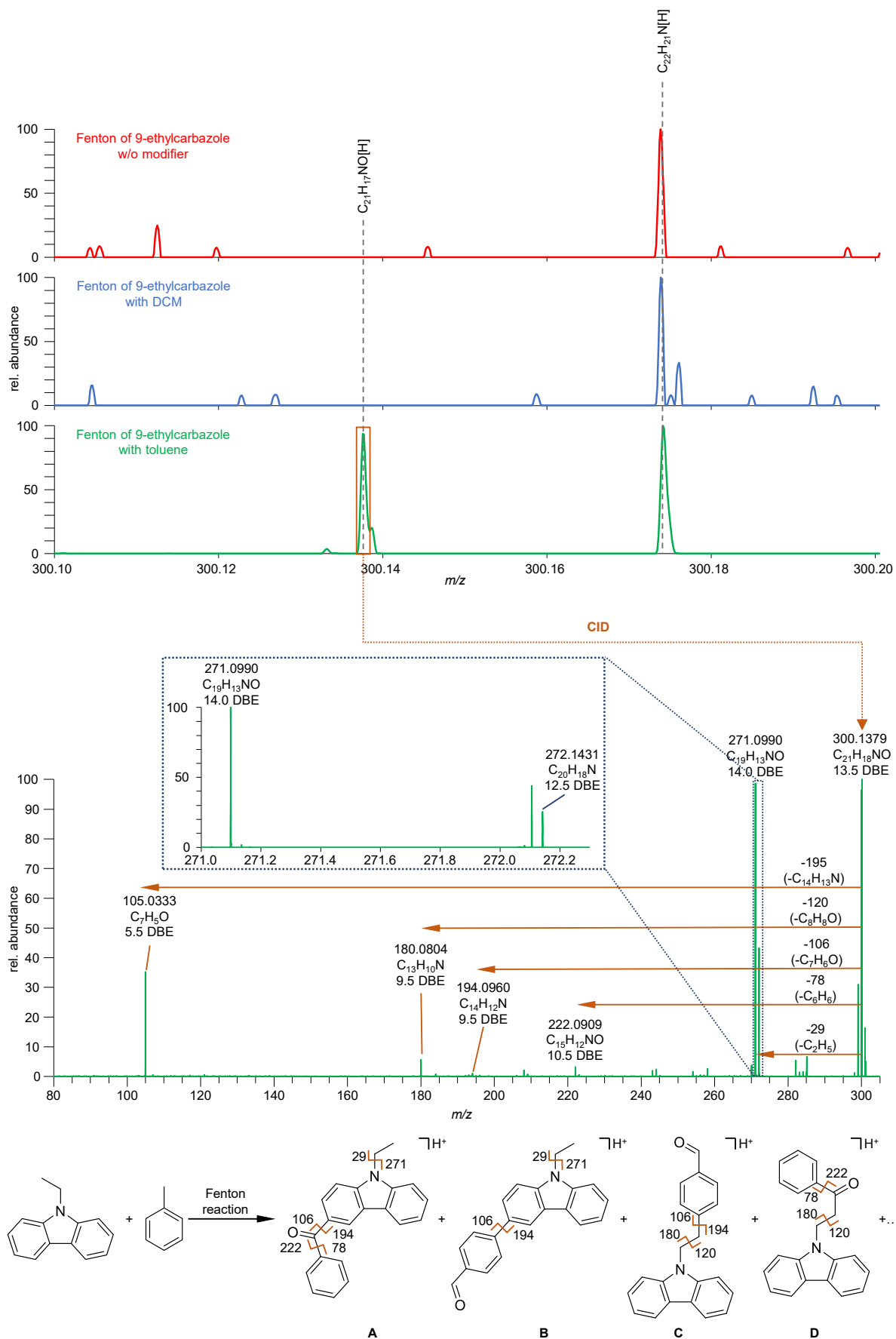


Figure 4-4: Comparison of the mass spectra from different Fenton reactions of 9-ethylcarbazole (top), CID spectrum of $C_{21}H_{18}NO$ and possible structures regarding addition of toluene to 9-ethylcarbazole (bottom).

A Fenton reaction of 9-ethylcarbazole was performed w/o modifier, with addition of DCM or with toluene under the same conditions as for the Fenton reaction of contaminated soil and the resulting mass spectra of each reaction is shown in Figure 4-4. In the mass range of m/z 300.1-300.2 a nitrogen compound $C_{21}H_{17}NO$, detected as protonated species, is formed only in the Fenton reaction of toluene-based Fenton of 9-ethylcarbazole. For structural elucidation, a CID experiment (normalized collision energy of 35%) for the ion at m/z 300.14 was carried out and the obtained fragmentation pattern is presented in Figure 4-4. This CID study indicates a connection of toluene molecule to 9-ethylcarbazole in different ways and the presence of a carbonyl group, which is shown by loss of CO (m/z 272). The loss of ethyl group ($-C_2H_5$) from 9-ethylcarbazole can only happen, if toluene is connected to 9-ethylcarbazole either by terminal methyl-ring bond (Figure 4-4 bottom, molecule A) or ring-ring bond (Figure 4-4 bottom, molecule B). The cleavage of phenyl group ($-C_6H_6$) leads to formation of an ion with m/z 222 and can only be observed if an addition of toluene to 9-ethylcarbazole through the terminal methyl group has taken place (Figure 4-4 bottom, molecules A and D). The nitrogen-containing fragment $C_{13}H_{10}N$ can be only achieved when toluene is connected to the side chain of 9-ethylcarbazole (Figure 4-4 bottom, molecules C and D) and therefore cleavage of oxidized toluene moiety is occurring.

4.4.3 Different amounts of toluene

The addition of toluene instead MeOH, EtOH and DCM to the Fenton oxidation of aged highly contaminated soil induced an increase in the removal of PAHs (Chapter 3). Therefore, Fenton experiments with different amounts of toluene (0.5, 1, 5, 10 and 15% v/v) were performed to achieve the best volumetric ratio of water and toluene. Figure 4-5 illustrates the class distributions for the most prominent heteroatom classes and oxygenated compounds based on relative intensity and population. The addition of 0.5% v/v toluene does not significantly degrade PACs. Increasing the toluene content to 1% v/v causes a slight decrease in relative intensity for the HC class and population for the N and S class. A significant removal of hydrocarbons was achieved by introducing 5% v/v toluene leading to a decrease of the relative intensities from 77.4% (unreacted soil) to 26.4% (Fenton with 5% v/v toluene). The additional toluene amount of 10% v/v results in minor benefit in PAHs degradation; instead, nitrogen-containing compounds are further oxidized. With increase of toluene amount of 15% v/v, Fenton reaction became inefficient regarding to the degradation of PAHs and PANHs. This effect is expected to be due to consumption of the oxidants by toluene and therefore less available reactant for the contaminants.

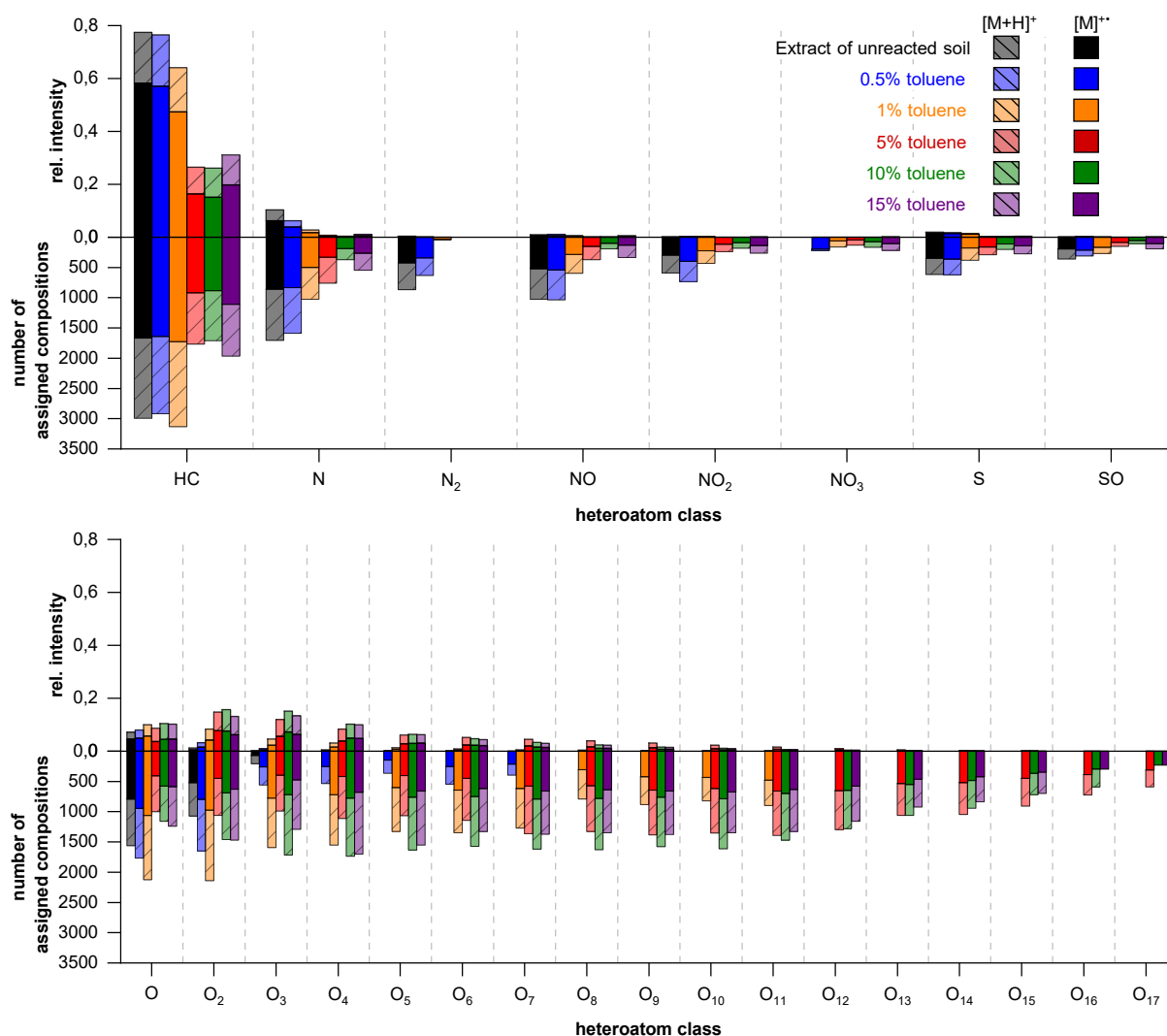


Figure 4-5: Relative intensity (upwards graph) and population-based (downwards graph) class distributions of the most prominent heteroatom classes (top) and oxygenated compounds (bottom) obtained from the extracts of the soil phases.

The formation of multiple oxygenated compounds after Fenton oxidation strongly depends on the amount of toluene. Less amount of toluene (0.5 and 1% v/v) causes less production of O_x-containing compounds, while higher amounts dramatically increase the creation of PAOHs. When toluene content was increased to 10% or 15% v/v, less high oxygenated compositions with O₁₂-O₁₇ were detected as compared to 5% v/v. This implies that with increasing toluene amount, the oxidation of toluene is more likely than the production of high oxygenated compounds with O₁₂-O₁₇.

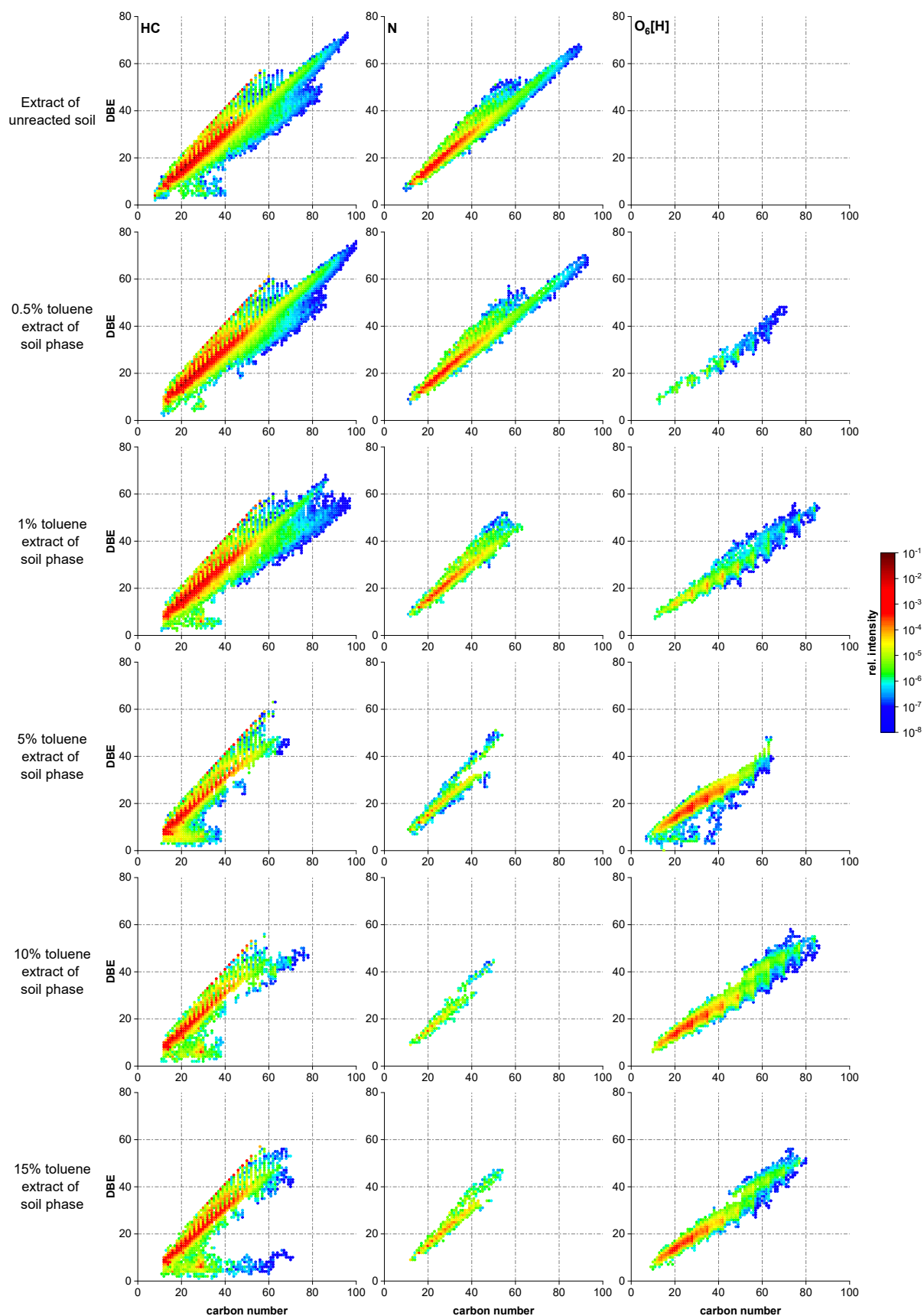


Figure 4-6: Kendrick plots of HC, N and O₆[H] classes before and after toluene-based Fenton reactions with addition of various amounts of toluene.

In Figure 4-6, Kendrick plots from extracts from the soil phases, which were obtained from unreacted soil and different Fenton reactions, are summarized for HC, N and O₆ classes. The Fenton oxidation with toluene in amounts of $\geq 5\%$ v/v resulted in both the almost complete removal of highly aromatic PAHs with DBE ≥ 60 and #C ≤ 70 and an effective decrease in population and relative intensity for N class. A closer look into the Kendrick plot of the 1% v/v toluene-based Fenton reveals a series of compounds with higher relative intensity and a range of 7 carbon numbers and DBE 4, which fits very well to the moiety of toluene. This defined range amplifies the assumption that toluene reacts with PACs in the presence of oxidants and/or that polymerization reaction of toluene takes place.

The studies from the various amount of toluene experiments (Figure 4-6) clearly demonstrate that the availability of the pollutants is a major parameter for the successful degradation, which can be achieved with addition of a certain amount of co-solvent to increase the solubility of pollutants towards the water-soluble reactants.

4.5 Conclusion

This present work showed the necessity of additional co-solvents to Fenton treatment of PACs contaminated soil, because the physico-chemical properties (e.g. molecular structure and weight, hydrophobicity, polarity, solubility in water and affinity for soil organic matter) of different pollutant molecules have an important effect on the solubility and degradation process. Especially for aged polluted soils, contaminants were penetrated deeper into the soil matrix becoming less accessible to oxidants. Here, the addition of defined toluene amount leads to effective removal of PAHs and PANHs probably due to creation of surfactant-like products, which can further enhance desorption of contaminants, and/or addition of toluene moiety to pollutant molecules. Interestingly, the treatment of PAHs could not be significantly improved with higher amounts of toluene (10 or 15% v/v), which can be explained by the reaction of OH[•] with toluene. The most efficient degradation was achieved for HMW PAHs and PAHs with side chains, which were transformed to oxidized compounds. Therefore, future work should focus on the biodegradability of these oxidized compounds for a successful treatment of aged and highly contaminated soil combining chemical and biological treatment.

4.6 References

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5. Studying the behavior of highly PAOHs achieved after toluene-based Fenton oxidation of aged coal tar contaminated soil by high resolution mass spectrometry

Redrafted from:

Satilmis, I. and Schrader, W. “*Studying the behavior of highly PAOHs achieved after toluene-based Fenton oxidation of aged coal tar contaminated soil by high resolution mass spectrometry*” will be submitted to Environmental Research.

5.1 Abstract

In this study, a method for Soxhlet extraction of highly oxidized compounds, which were created after toluene-based Fenton oxidation of contaminated soil, was established. Here, toluene-based Fenton oxidation was applied to remove PAHs from contaminated soil. After reaction, different phases (toluene, water and extract of soil phase) as well as Soxhlet extract of Fenton applied soil using DCM or water as extraction solvent were separately analyzed using ultrahigh resolution mass spectrometry (UHRMS). Oxidized compounds up to O₁₈ are newly created and preferably transformed into the water phase. The further removal of these compounds from the soil was accomplished with DCM as extraction solvent, while the highly oxidized ones (O_x > 10) were not removable with water-based Soxhlet extraction.

5.2 Introduction

Between the eighteenth and twentieth centuries, many coking and industrial gas plants were built in Europe to meet the huge growth in energy demand and these coal related processes resulted to the formation of coal tar, which caused global coal tar contamination of groundwater and soil. Coal tars contain a complex mixture of thousands of PACs comprising heteroatom-containing compounds (N, S, O and/or halogens) and PAHs, which are known to exert mutagenic, carcinogenic and toxic effects.¹ These PAHs are divided into low (2-3 rings) and high molecular weight (> 3 rings) compounds, whereby the LMW ones are more biodegradable due to their certain water solubility.²⁻⁶ The combination of bioremediation with chemical methods as pre- or post-treatment enhances the overall removal of PAHs,^{2, 7-10} but remediation of aged contaminated soil is more challenging than artificially spiked soil due to the deep integration of hydrophobic pollutants into the soil particles.^{11, 12}

To date, various oxidation methods, such as permanganate,¹³⁻¹⁵ persulfate,^{13, 16, 17} photooxidation,¹⁸⁻²⁰ ozonation²¹⁻²³ or Fenton reaction are studied to decontaminate polluted soil by ideally transforming the PAHs into final products CO₂ and H₂O.⁷ However, this transformation is a difficult task for aged contaminated soil with pollutants, whose real compositions and numbers are unknown. Therefore, the examination of the exact amount of oxidants required for the mineralization of PAHs is more difficult for PAH mixtures than for individual compounds, which ends up in the formation of oxygenated PAOHs.¹² Further formation of PAOHs takes place during natural oxidation (biotic and abiotic) resulting in their presence in various environmental sources.²⁴

Fenton treatment is achieved by combining H₂O₂ and ferrous ion (Fe²⁺) for generating non-selective and highly reactive OH[•] with short lifespan.²⁵ In addition, the problem of strong adsorption of pollutants to the soil matrix, which leads to lower availability of the contaminants to OH[•], can be solved by adding different organic additives (surfactants, vegetable oils or organic solvents) to Fenton reaction of aged contaminated soil leading to enhanced desorption and more effective oxidation of PAHs.²⁶⁻²⁸

For the preparation of soil samples preceding the instrumental analysis, different extraction methods were investigated which can be an important point for sample handling. These studies include methods like Soxhlet extraction,²⁹ ultrasonic-assisted extraction,³⁰ pressurized liquid extraction,³¹ microwave-assisted extraction³² or supercritical fluid extraction³³ to analyze different PAHs. In addition, different solvent systems were used for the extraction of PAHs, depending on the PAH class being investigated. Here, pure DCM, hexane/DCM or hexane/acetone was used to mainly extract PAHs and/or carbonyl group containing PAHs, while

ethyl acetate, methanol, acetonitrile or water was chosen for enhanced extraction of hydroxyl or carboxyl group containing PAHs.³⁴⁻³⁶

The combination of gas chromatography (GC) or liquid chromatography (HPLC/UHPLC) with mass spectrometry is an established analytical technique for targeted analysis of PAHs after environmental sample remediation. For the analysis of compounds with hydroxyl or carboxyl groups, LC-MS is preferred over GC-MS, since the analysis of these compounds is performed without derivatization and the use of lower operating temperatures can reduce various rearrangement reactions. Letzel et al. documented the more effective ionization of PAOHs using both APCI and APPI over ESI.³⁷ Although ESI is more sensitive than APCI and APPI, the application of APCI or APPI is more preferred to ESI due to the matrix suppression achieved with ESI.³⁸

In the targeted analysis of Fenton treated soil contaminated with PAHs, a large part of the oxidized compounds is neglected. Therefore, this study presents the application of Fenton oxidation of coal tar contaminated soil adding toluene as modifier and non-target analysis of the different phases (organic, water and extract of soil phase) using APPI(+) Orbitrap MS. Soxhlet extractions of degraded soil was performed using DCM or water as solvents gaining a detailed analysis for the extraction efficiencies of PAOHs.

5.3 Materials and Methods

5.3.1 Chemicals

The reagents used for the experiments were toluene ($\geq 99.8\%$, Fisher Scientific, Loughborough, UK), DCM (99%, Fisher Scientific, Loughborough), hydrogen peroxide (30%; J. T. Baker, Sowińskiego, Poland), sulfuric acid (95-98%, J. T. Baker, Deventer, Netherland), and deionized water (type I) taken from a Clearwater dispenser Purelab Flex 2 (ELGA LabWater, Celle, Germany).

5.3.2 Sample preparation

Highly aged coal tar contaminated soil was taken from an industrial site in the German Ruhr area. 5 g of the sample were air dried for one week in a fume hood at room temperature. After drying, the soil was crushed in a mortar for homogenization, sieved (2 mm pore size) and kept in a fridge at 4 °C.

5.3.3 Experimental procedure

Fenton treatment of coal tar contaminated soil was carried out using toluene as modifier and described in detailed in Chapter 3, while further chemical workout conditions are presented in Figure 5-1. Briefly, the soil was filtered and halved for a first Soxhlet extraction using DCM or water as solvent. The different extracts were collected and concentrated under reduced pressure to obtain the residues for analysis. Meanwhile, a second Soxhlet extraction step of the halved soils was carried out using the opposite solvent and the collected extracts were concentrated under reduced pressure for analysis.

The liquid layers were separated by liquid-liquid extraction and the organic layer was dried over MgSO_4 and filtered. Both water and toluene phase were concentrated under reduced pressure and residues stored for further analysis.

A control reaction without Fenton reagents was performed by stirring the contaminated soil in toluene (29 mL) and deionized water (434 mL) for 48 h at room temperature. The different layers were separated and prepared for the analysis as described before.

5.3.4 FT Orbitrap MS and data analysis

Mass analysis of the different residues, which were diluted in toluene:methanol (1:1, v/v) to a final concentration of 150 ppm, was performed on a research type FT Orbitrap Elite (Thermo Fischer Scientific, Bremen, Germany). Mass spectra were recorded in a mass range of m/z 150-1300 and with a resolving power of $R = 480,000$ at m/z 400 using spectral stitching method³⁹⁻⁴¹ with mass windows of 30 Da with 5 Da overlap. APPI was chosen for ionization and for this a Krypton VUV lamp (Syagen Technologies, Tustin, CA, USA) was applied with photon emission at 10.0 and 10.6 eV. The diluted samples were analyzed by direct injection at a flow rate of 20 $\mu\text{L}/\text{min}$ and with adjusted ion source conditions 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 imported into Composer (V1.5.0, Sierra Analytics, Modesto, CA, USA) to assign the elemental compositions to detected signals. Peak Assignments were set on the following criteria: H: 0-300, C: 0-100, O: 0-20, N: 0-2, S: 0-1, DBE: 0-80 and mass error ≤ 1.5 ppm. Excel (Microsoft Office Professional Plus 2010, Microsoft Excel 2010) and Origin (v9.2.0, OriginLab Corporation, Northhampton, MA, USA) were used for further data evaluation and graphical visualization.

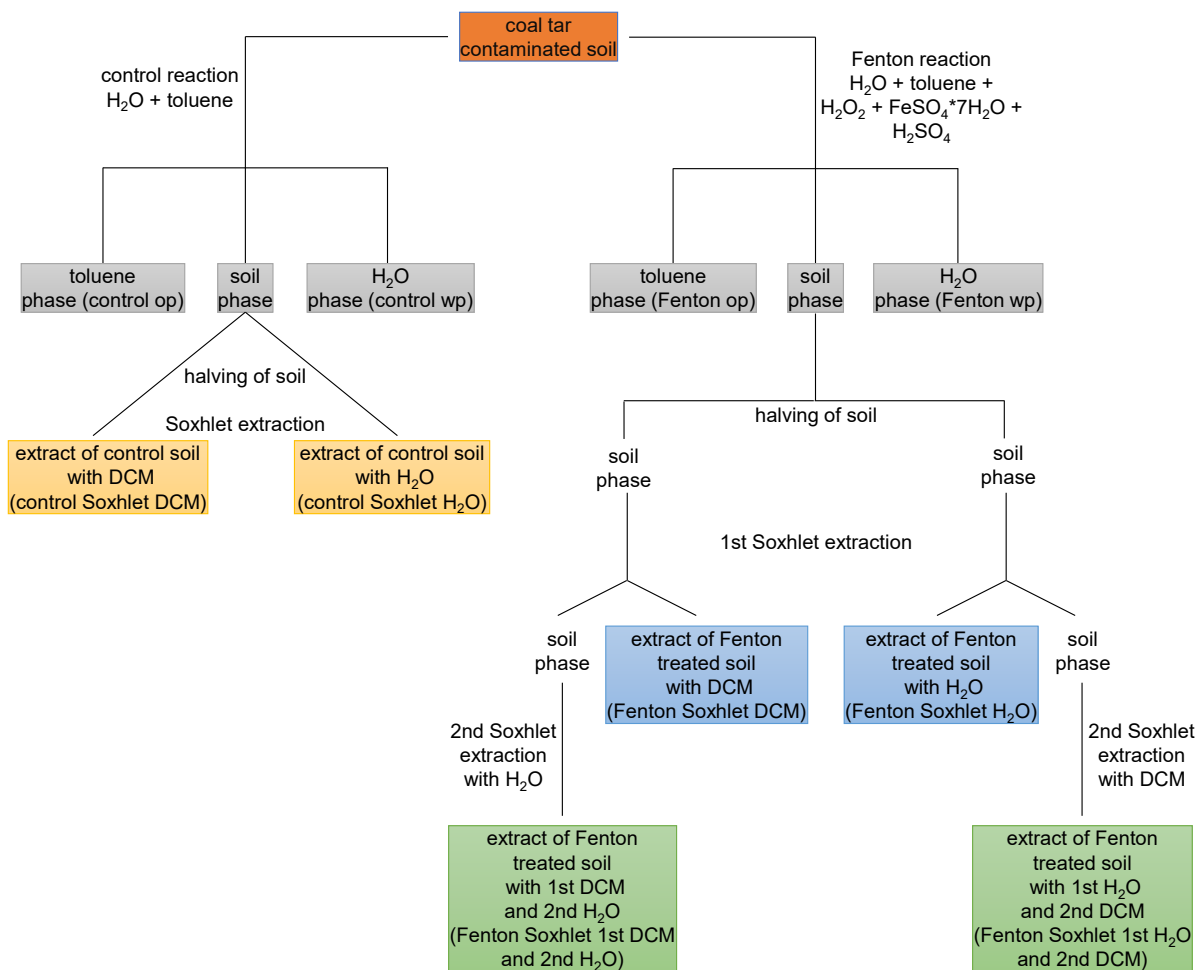


Figure 5-1: Reaction and chemical workout procedure of coal tar contaminated soil.

5.4 Results and Discussion

Fenton oxidation with addition of toluene needs a detailed comparison of the different phases (toluene, water and extract of soil phase). Figure 5-2 presents the results of the distribution for hydrocarbons and oxidized compounds based on the number of assigned elemental compositions obtained from the toluene and water phases. The advantage of showing relative intensity and population as data interpretation methods is explained in Chapter 3. The usage of APPI leads to the formation of protonated species $[M+H]^+$ or radical cations $[M]^+$.⁴²

Comparing the toluene and water phase of the control reaction highlights the increased relative intensity and population in HC class for the toluene phase, whereas PAOHs with maximum O₉ were detected in the water phase. This can be explained with lower solubility of PAHs in water as well as the reduced solubility of highly oxidized compounds in toluene. The strong oxidation of hydrocarbons after toluene-based Fenton is proved by significant decrease of relative intensity and population for HC class in toluene and water phase, which leads to increased

formation of highly oxidized compounds compared to the control reaction. These PAOHs are created during the reaction of PAHs with hydroxyl and/or non-hydroxyl radicals,⁴³ which are produced with higher excess of H₂O₂, and are preferably transferred into the water phase as a result of greater solubility of these compounds in water.

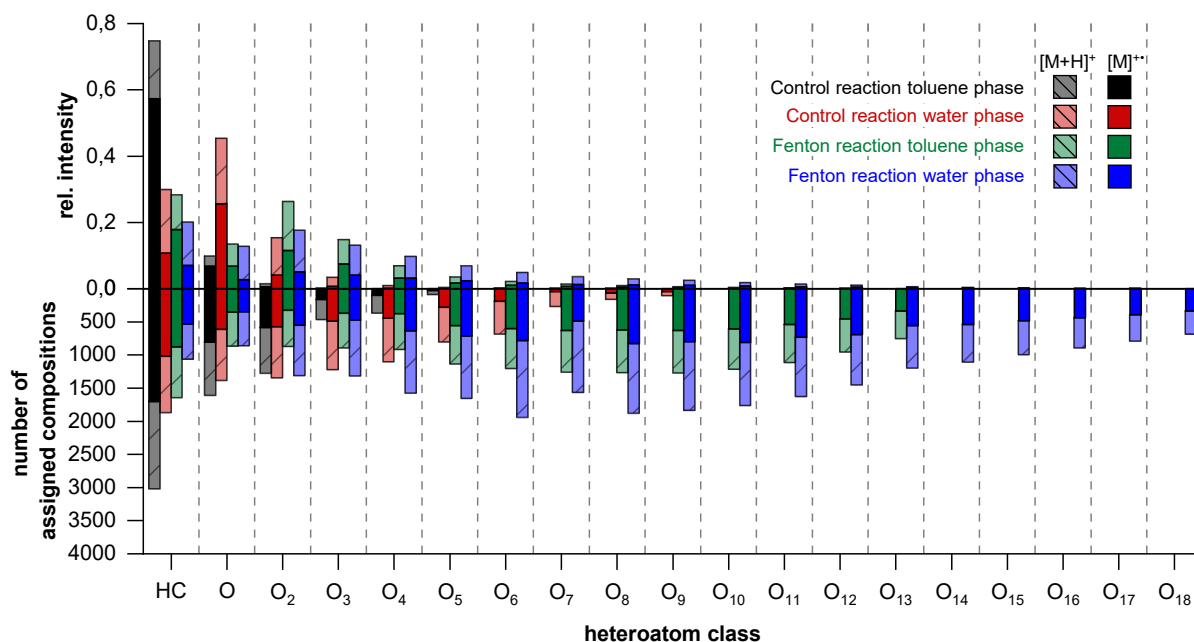


Figure 5-2: Relative intensity class distribution of HC and O_x classes for toluene phase of control reaction (black), water phase of control reaction (red), toluene phase of Fenton reaction (green) and water phase of Fenton reaction (blue).

Figure 5-3 illustrates the utilization of DCM or water in the Soxhlet extraction of the different soils received from control reaction and Fenton oxidation. After Soxhlet extraction of the soil obtained from control reaction, the relative intensity of the hydrocarbon class decreased dramatically compared to the toluene phase of the control reaction. The reason for this decrease is that toluene has already extracted most of the PACs, but the complete removal of these contaminants from aged contaminated soil is hindered by extremely strong adsorption onto hydrophobic surface.¹² In contrast, the number of assigned compounds after Soxhlet extraction with DCM increased from 3032 (control reaction toluene phase) to 3497. These results suggest the extraction of some PAHs is only possible by applying stronger extraction methods than just stirring in toluene. After toluene-based Fenton oxidation of soil contaminated with coal tar, compounds containing up to O₈ were removed by Soxhlet extraction with water, while higher PAOHs (up to O₁₇) were obtained only with DCM as extraction solvent. This seems to be primarily inconsistent with that of Figure 5-2, but a differentiation is required between solubility of the pollutants and their desorption from soil matrix. PAHs and PAOHs are sorbed to the soil

matrix due to hydrophobic interactions, which can be broken by organic solvents.^{44, 45} Therefore, the extraction of hydrophobic PAHs and (highly) oxidized compounds is more prominent using DCM as solvent. Once they are desorbed from the soil and further oxidized, they are significantly transferred into the water phase due to their higher water solubility. Another interesting point of the data gained from the Soxhlet extraction of the Fenton applied soil (extracted with water) is the limited removal of oxidized compounds up to O₈. One reason for this might be that with addition of further oxygen atoms, the adsorption of the oxidized compounds onto soil matrix becomes stronger, and thus water is not sufficient as extraction solvent.

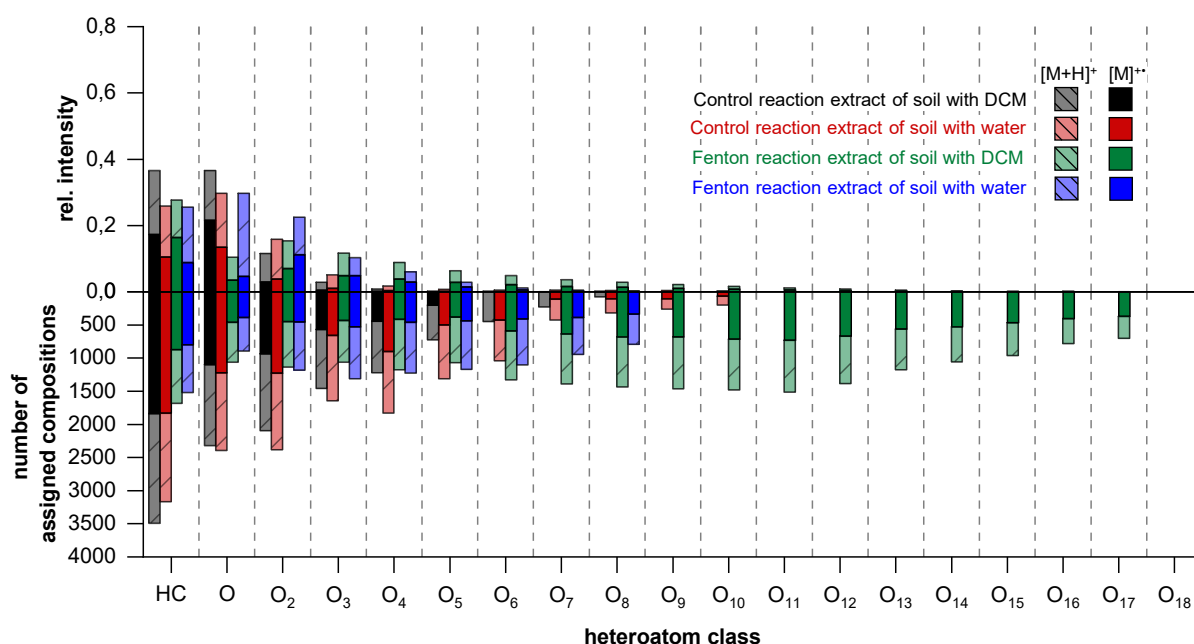


Figure 5-3: Relative intensity class distribution of HC and O_x classes for DCM-based Soxhlet extraction of control reacted soil (black), water-based Soxhlet extraction of control reacted soil (red), DCM-based Soxhlet extraction of Fenton reacted soil (green) and water-based Soxhlet extraction of Fenton reacted soil (blue).

The comparison between the different Soxhlet extraction steps of the Fenton treated soil is shown in Figure 5-4. Here, the Fenton degraded soil was halved and both parts of the soil were exposed to a stepwise Soxhlet extraction using the one solvent in the first step and the opposite solvent in the second step. For both sequences, application of DCM-based Soxhlet extraction enhances the removal of highly oxidized compounds. The use of water instead of DCM in the Soxhlet extractions lead to an increased removal efficiency of PAOHs up to O₈. Higher oxidized compounds are more effectively extracted with DCM, which amplifies the assumption of stronger hydrophobic interactions with increasing number of oxygen atoms. Depending on the

aging and the properties of the soil, which are the main factors for the release of hydrophobic pollutants,⁴⁶ further extraction steps are needed to enhance the contaminants removal.⁴⁵

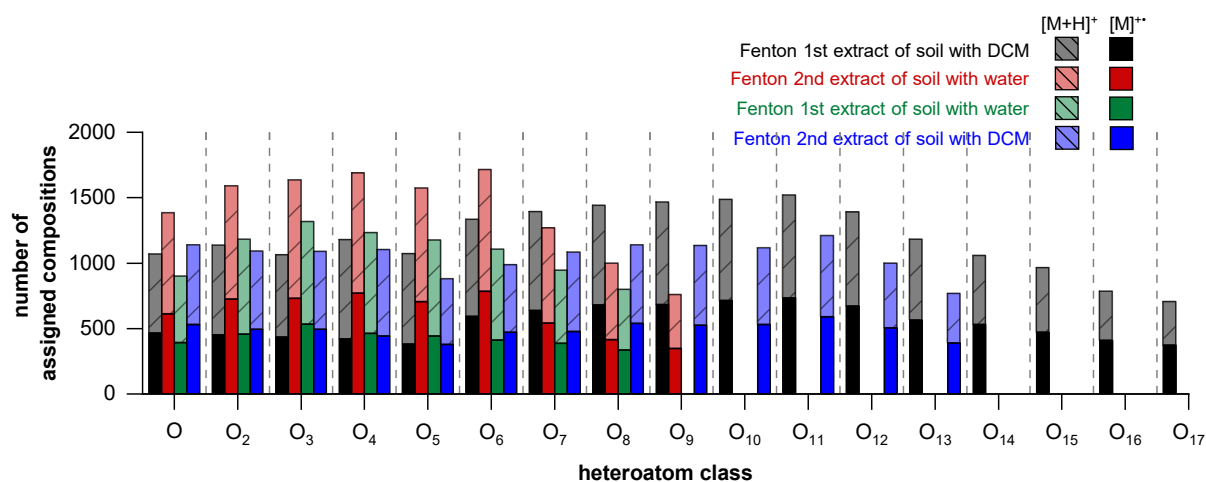


Figure 5-4: Relative intensity class distribution of multiple oxygen classes for 1st DCM-based Soxhlet extraction of Fenton reacted soil (black), 2nd water-based Soxhlet extraction of Fenton reacted soil (red), 1st water-based Soxhlet extraction of Fenton reacted soil (green) and 2nd DCM-based Soxhlet extraction of Fenton reacted soil (blue).

For a deeper exploration of the chemical changes, data plotting using Kendrick plots is an excellent method, where the assigned formulae are illustrated by a given DBE and carbon number per molecule.

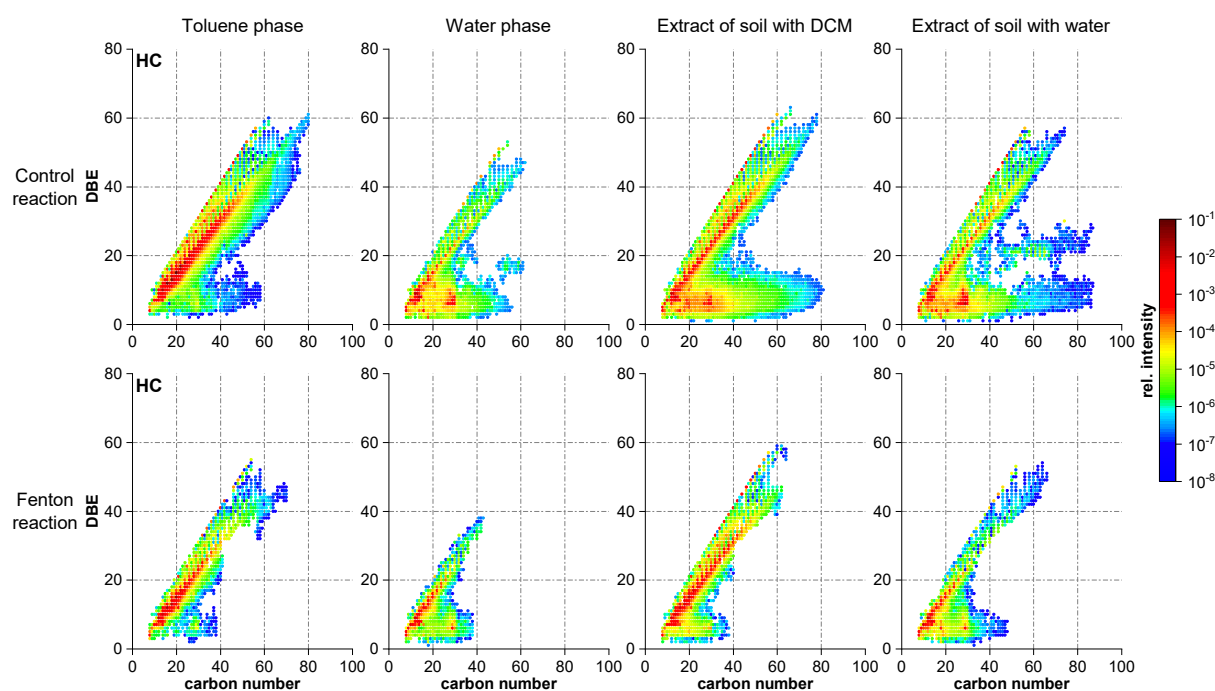


Figure 5-5: Kendrick plots of HC class for different phases of control reaction and Fenton oxidation.

In Figure 5-5, different phases and various extracts are shown for HC class. Highly fused PAHs are found in the coal tar contaminated soil, which can be proved by the narrow distributions with high relative intensities.⁴⁷ Furthermore, less assignments were obtained in the water phase of the control reaction due to poor solubility of PAHs in water, but Soxhlet extraction of control reaction applied soil with water led to further extraction of PAHs. Whenever a DCM-based Soxhlet extraction of the control reaction applied soil is performed, hydrocarbons with high carbon numbers ≤ 81 in lower DBE ranges ($\text{DBE} \leq 21$) were assigned. These hydrocarbons are deeply partitioned in pores of soil particles and were not be extracted by stirring the contaminated soil in toluene and water.^{44, 48} The high intensity region in the distribution of the DCM extract is less prominent compared to the toluene phase, because toluene already extracted most of the PAHs with certain DBE values and carbon numbers. Toluene-based Fenton treatment led to a significant removal of PAHs with certain alkyl chains and high DBE values. Similar to control reaction result, limited PAHs with $\text{DBE} \leq 38$ and carbon number ≤ 43 are detected in the water phase and further hydrocarbons with higher DBEs and carbon numbers were extracted using water-based Soxhlet extraction.

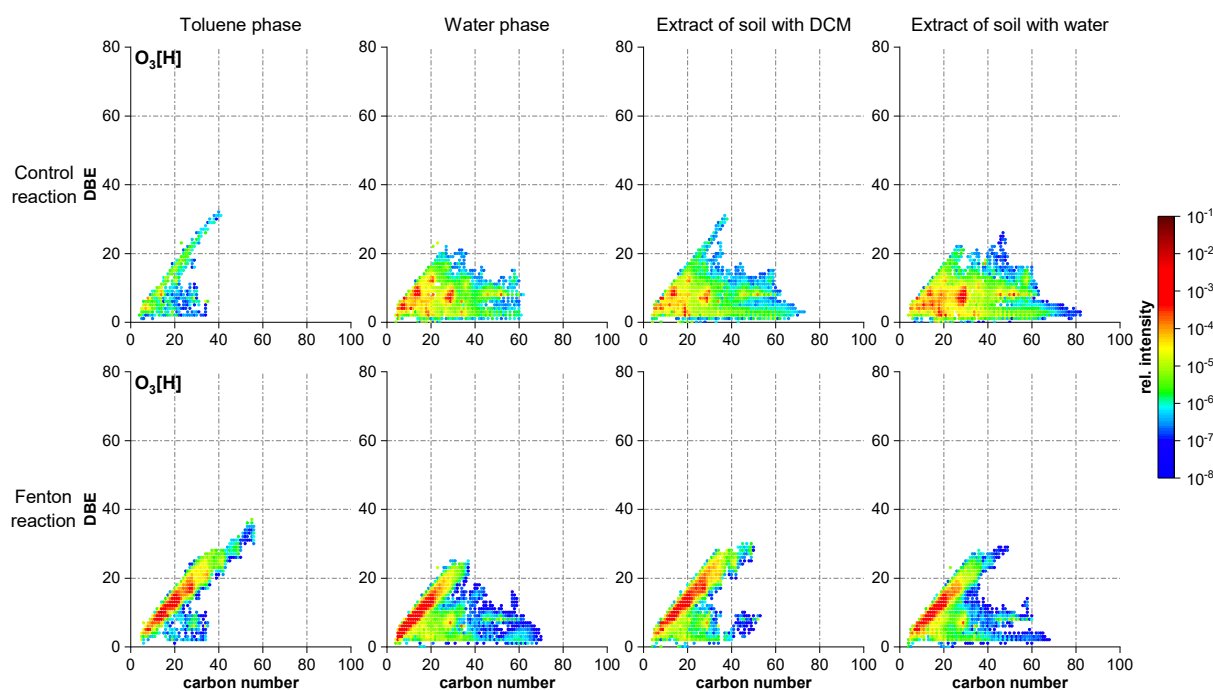


Figure 5-6: Kendrick plots of $\text{O}_3[\text{H}]$ class for different phases of control reaction and Fenton oxidation.

In Figure 5-6, Kendrick plots of $\text{O}_3[\text{H}]$ are shown for various phases and different extracts. Except in the toluene phase, significant O_3 species were detected in the water phase and in the extracts of DCM- and water-based Soxhlet extractions of control reaction applied soil. Here, the Kendrick plot of water-based Soxhlet extraction shows higher relative intensities for some

assigned compositions than for DCM-based ones due to better extractability. After the Fenton oxidation, high intensity regions are present in DBE range 2-20 and carbon numbers 5-28. Our studies demonstrated that these oxygen compounds are formed by polymerization of toluene, addition of toluene moiety to PAHs and/or direct reaction of PAHs with oxidants. Especially the O_3 species with DBE below 20 and carbon number up to 65 are transferred into the water phase and preferably extracted with water-based Soxhlet, which were similar results as for the control reaction. The comparison between the control reaction and Fenton oxidation regarding $O_7[H]$ class demonstrates a significant production of oxidized compounds in all various phases (Figure 5-7). Furthermore, O_7 species from the water phase were detected with higher relative intensities than that ones from the toluene phase due to better solubility of the oxidized compounds in water than in toluene. But the extraction of these oxidized PAHs from soil was more favored with DCM than with water. O_7 species with $DBE \leq 41$ were able to be removed with water-based Soxhlet extraction, while higher ones were able to be recovered using DCM-based Soxhlet extraction.

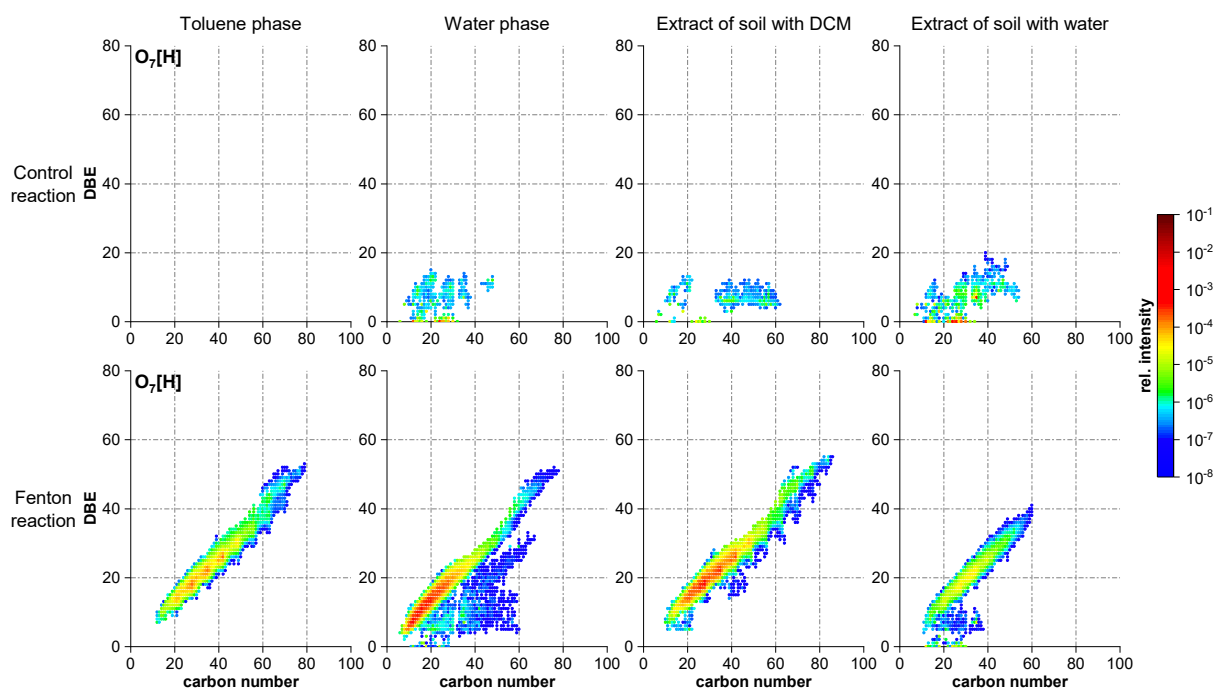


Figure 5-7: Kendrick plots of $O_7[H]$ class for different phases of control reaction and Fenton oxidation.

With the increase of DBE, the hydrophobic interactions also increase leading to stronger adsorption of PAOHs and therefore making them less available for extraction with water.⁴⁹ Similar results of limited extraction of highly oxidized PAHs with water-based Soxhlet extraction were achieved from the stepwise extraction of Fenton applied soil using DCM or water as extraction solvent (Figure 5-8).

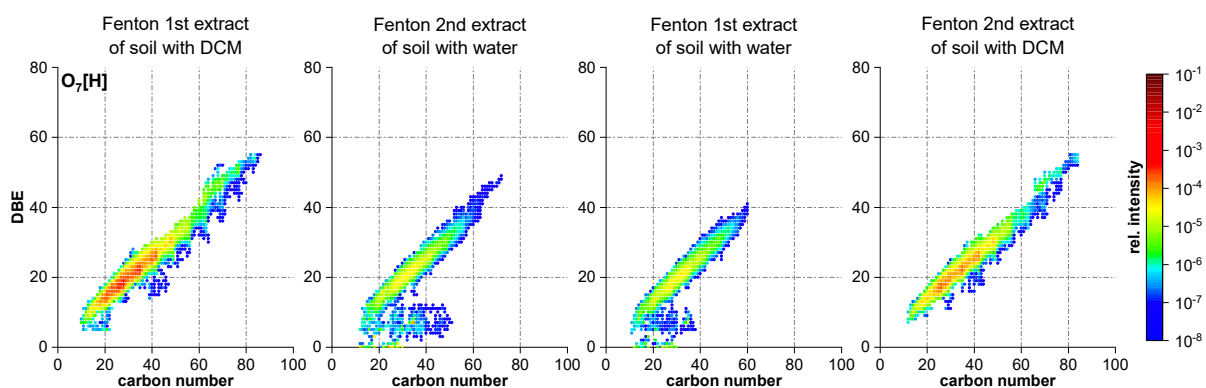


Figure 5-8: Kendrick plots of $O_7[H]$ of stepwise DCM or water-based Soxhlet extraction from Fenton applied contaminated soil.

5.5 Conclusion

The different phases (organic, water and extract of soil phase) obtained from toluene-based Fenton oxidation of coal tar contaminated soil as well as the Soxhlet extraction of highly oxidized PACs, which were formed after toluene-based Fenton oxidation, were studied using UHRMS. In aged soil contaminated with coal tar, PAHs are extremely strong adsorbed onto the soil matrix and deeply embedded in pores of soil particles resulting in poor availability for the oxidants. Treatment of these contaminated soils with toluene-based Fenton removes pollutants by transforming PAHs into oxidized compounds readily for further biodegradation. After Fenton reaction, PAOHs with high oxygen number were predominantly found in the water phase due to better solubility in water. On the other hand, these highly oxidized compounds were preferably removed from soil using DCM-based Soxhlet extraction. These results indicate that with increasing oxygen number within the molecule, the hydrophobic interactions also increase and therefore difficult to extract with water. In addition, multiple runs of Soxhlet extraction are recommended for complete removal of PAHs from aged contaminated soil. With ageing of contaminated soil, the adsorption of the pollutants to the soil matrix increases and their diffusion into the soil pores deepens further.

5.6 References

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6. Investigation of the Ozonation of highly PAXHs contaminated soil using ultrahigh resolution mass spectrometry

Redrafted from:

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6.1 Abstract

Ozonation is an effective chemical treatment technique for removing contaminations from the environment. In some countries it is used to clean up drinking water instead of using chlorinated treatment. This shows that ozonation is an effective method to remove contaminations. The contamination of soil with PACs – and here especially all kinds of polyaromatic hydrocarbons – 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 contaminants 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 PAHs and their derivatives. The reaction is studied using 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.

6.2 Introduction

Soil, air and water pollution by polycyclic aromatic hydrocarbons or polyaromatic heterocycles that can contain different heteroatoms like sulfur, nitrogen or oxygen (PAXHs with X = N, S or O) originated from natural and anthropogenic sources, has resulted in ubiquitous environmental damages 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 PACs 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 (2-3 rings) have a certain water solubility, higher molecular weight (> 3 rings) PAXHs have a lower solubility in water and additionally can be stronger adsorbed to the soil organic matter. Both of those points reduce the accessibility to oxidants and therefore reduces the effectiveness of biodegradation.^{4, 5} Besides the Fenton reaction⁶⁻⁸ and photolysis,⁹⁻¹¹ ozonation is used as 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 PACs, 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 OH[•], which are formed due to the self-decomposition of ozone in the presence of soil matrix,¹⁶ metal oxides¹⁷ 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 and side reactions.

The reactivity of PAHs is depending 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, Carrere²⁶ and Nam and Kukor⁴ 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 contaminated 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 dodecane³⁰ and acetic acid/heptane.³¹ Jonsson and co-workers used a mixture of H₂O/EtOH (50:50 v/v) as a solvent system in the ozonation of nine different contaminated soils and analyzed 24 selected PAHs by GC-MS.³² Other authors investigated the addition of surfactants for the removal of naphthalene in Brij 30-containing solution³³ and removal of PAHs 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 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 O₃ and should therefore be covered by the analysis method.³⁸ The combination of 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 FT-ICR MS³⁹⁻⁴⁴ or Orbitrap MS⁴⁵⁻⁴⁹ due to its high accuracy and high resolution capabilities.

In this study, ozonation is used to degrade PACs from aged contaminated soil using toluene as additional modifier solvent to make the contaminants available for oxidation. For the understanding of the reactions, different phases (extract of 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 APCI and ESI.⁵⁰

6.3 Materials and Methods

6.3.1 Chemicals

The solvents used for the ozonation toluene ($\geq 99.8\%$, Fisher Scientific, Loughborough, UK) and deionized water (type I) tapped from a Clearwater dispenser Purelab Flex 2 (ELGA LabWater, Celle, Germany).

6.3.2 Sample preparation

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

6.3.3 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 stirring at room temperature for 6 and 18 h (Figure 6-1). 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 and not consumed ozone was passed through manganese dioxide (MnO_2) for removal.

The soils from different reactions were filtered, dried in a fume hood and remaining PACs were extracted by Soxhlet extraction with DCM (50 mL) for 24 h. Then the solvent was 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 MgSO_4 and filtered. Both water and toluene phase 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.

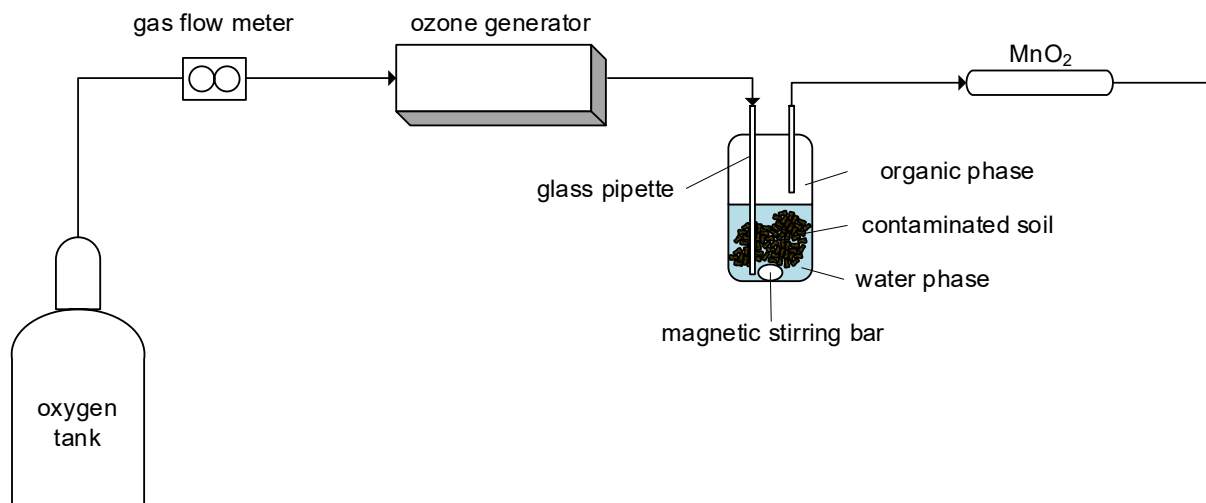


Figure 6-1: Schematic diagram of the ozonation experimental apparatus.

6.3.4 FT Orbitrap 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 FT Orbitrap Elite (Thermo Fisher Scientific, Bremen, Germany). Mass spectra were recorded with a resolving power of $R = 480,000$ at m/z 400 in a mass range of m/z 150-1300 using spectral stitching^{46, 51, 52} method with mass windows of 30 Da and 5 Da overlap. For the ionization with APPI, a Krypton VUV lamp (Sygen 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 $\mu\text{L}/\text{min}$ 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, DBE: 0-80 and mass error ≤ 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, Northampton, MA, USA) were used.

6.4 Results and Discussion

The direct ozonation of aged contaminated soil without organic solvent showed no significant removal of contaminations. This can have different reasons, as the ozone does not interact with PAHs or that PAHs 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 6-2. 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 in the 16 EPA-PAH list.⁵³

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 like $C_{21}H_{18}O_6[H]$, $C_{25}H_{18}O_3[H]$ and $C_{22}H_{22}O_5[H]$ are detected with significant intensities in comparison to the intensities of polycyclic aromatic hydrocarbons.

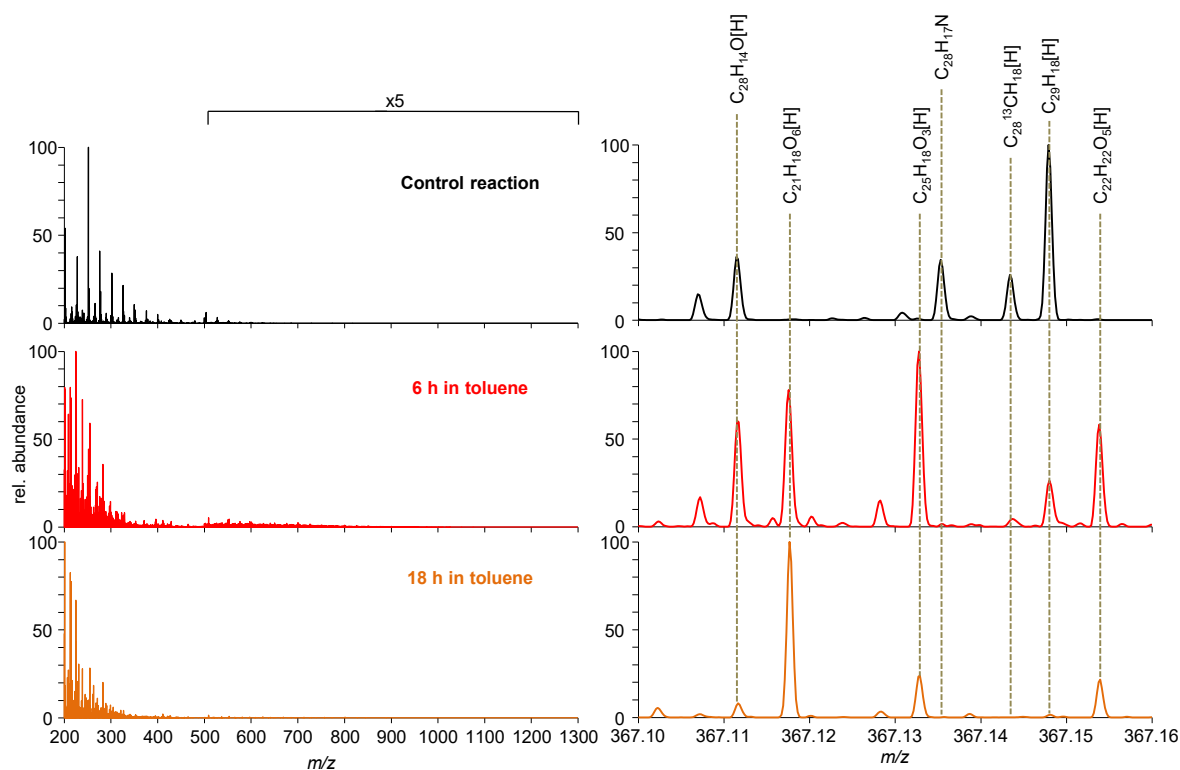


Figure 6-2: Mass spectra of organic phases from control reaction (black), ozonation within 6 h in toluene (red), within 18 h in toluene (orange), and corresponding zooms into m/z 367.10-367.16 (right).

Figure 6-3 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 PACs^{50, 54} forming protonated $[M+H]^+$ and/or radical cation $[M]^{\bullet+}$ species.⁵⁵ 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.

Results from the measurements of the control sample show that HC class is the most abundant class followed by NO, NO₂ and N₂. The comparison of the control reaction with the ozonation reactions show a significant decrease of the populations for hydrocarbons, N-containing 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 O₃. 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 PAHs to soil matter can be strong – especially in aged soil – and both the addition of toluene can dissolve the contaminations better, while O₃ 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. After O_7 , less O_x ($x > 8$) are detected with longer toluene-based ozonation reaction. 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

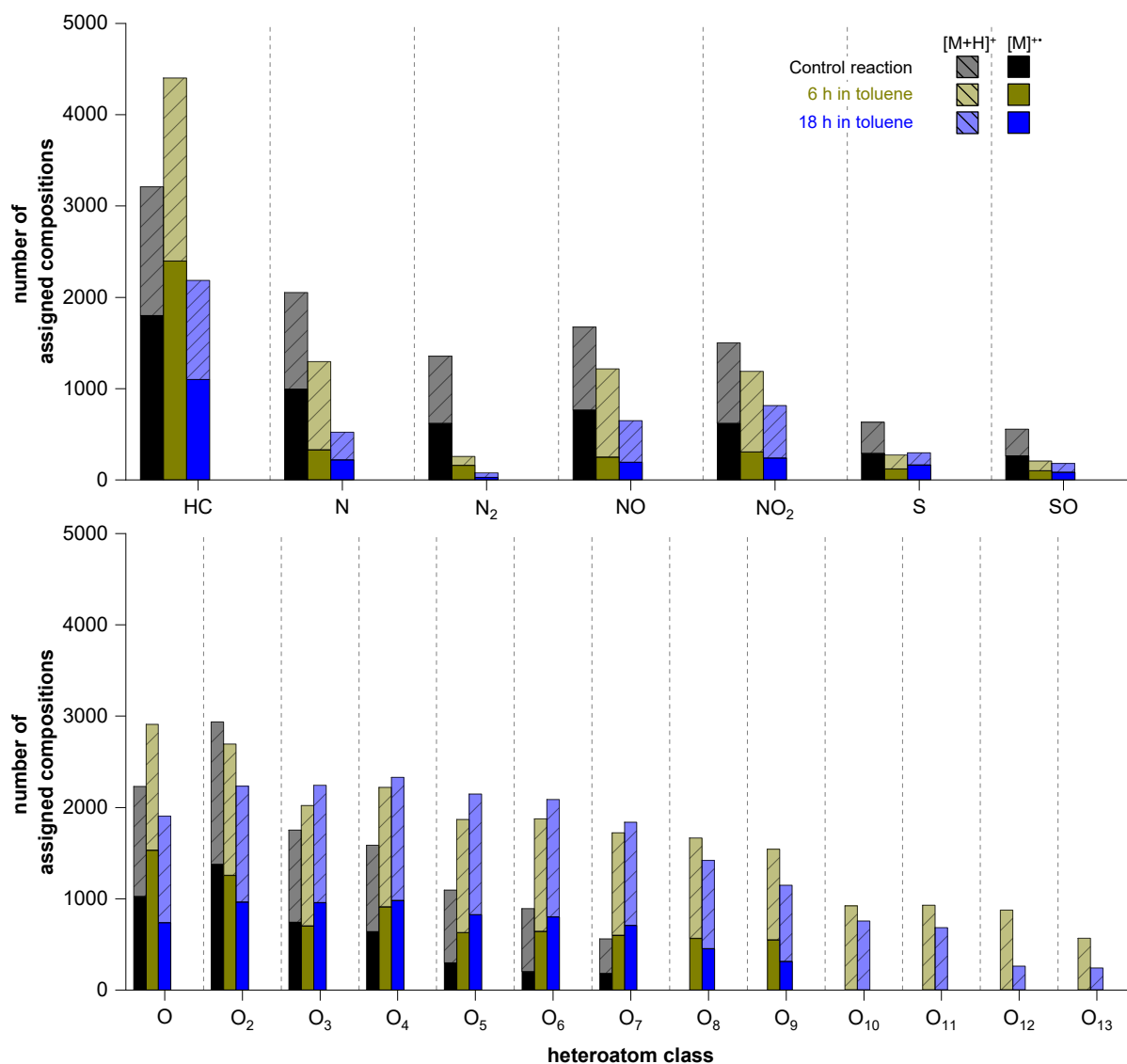


Figure 6-3: Population-based class distribution of the most prominent heteroatom classes (top) and oxygenated compounds (bottom) for control reaction (black), ozonation within 6 h in toluene (dark yellow) and within 18 h in toluene (blue).

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 6-4. 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.

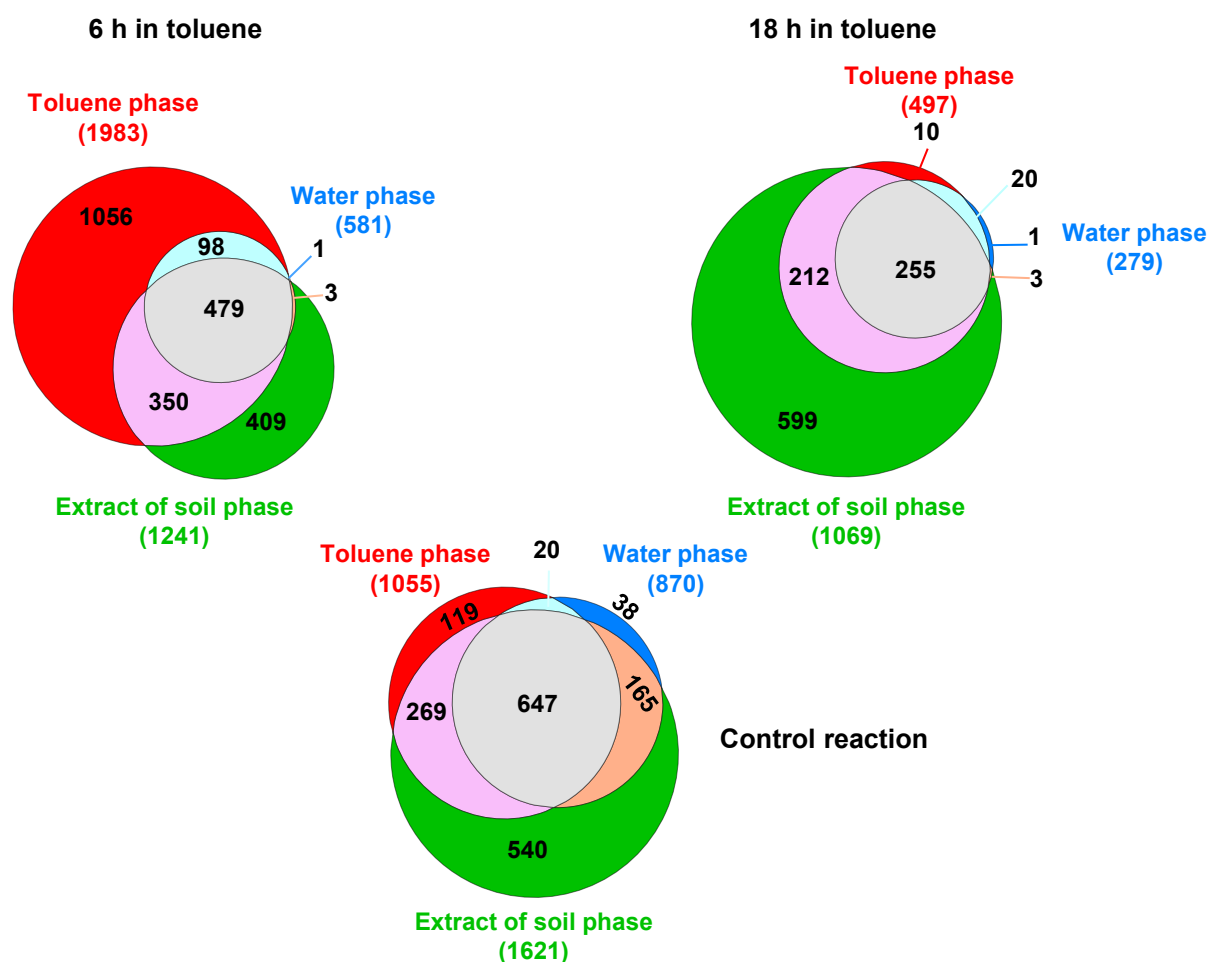


Figure 6-4: Population-based area-proportional Venn diagrams for radical HC species of different phases from control reaction (middle), ozonation within 6 h in toluene (top left) and within 18 h in toluene (top right).

For a more detailed understanding of chemical changes after the ozonation, Kendrick plots of HC, O₃ and O₇ 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 intensities for a given DBE is connected to a line. Figure 6-5 illustrates these results for HC species.

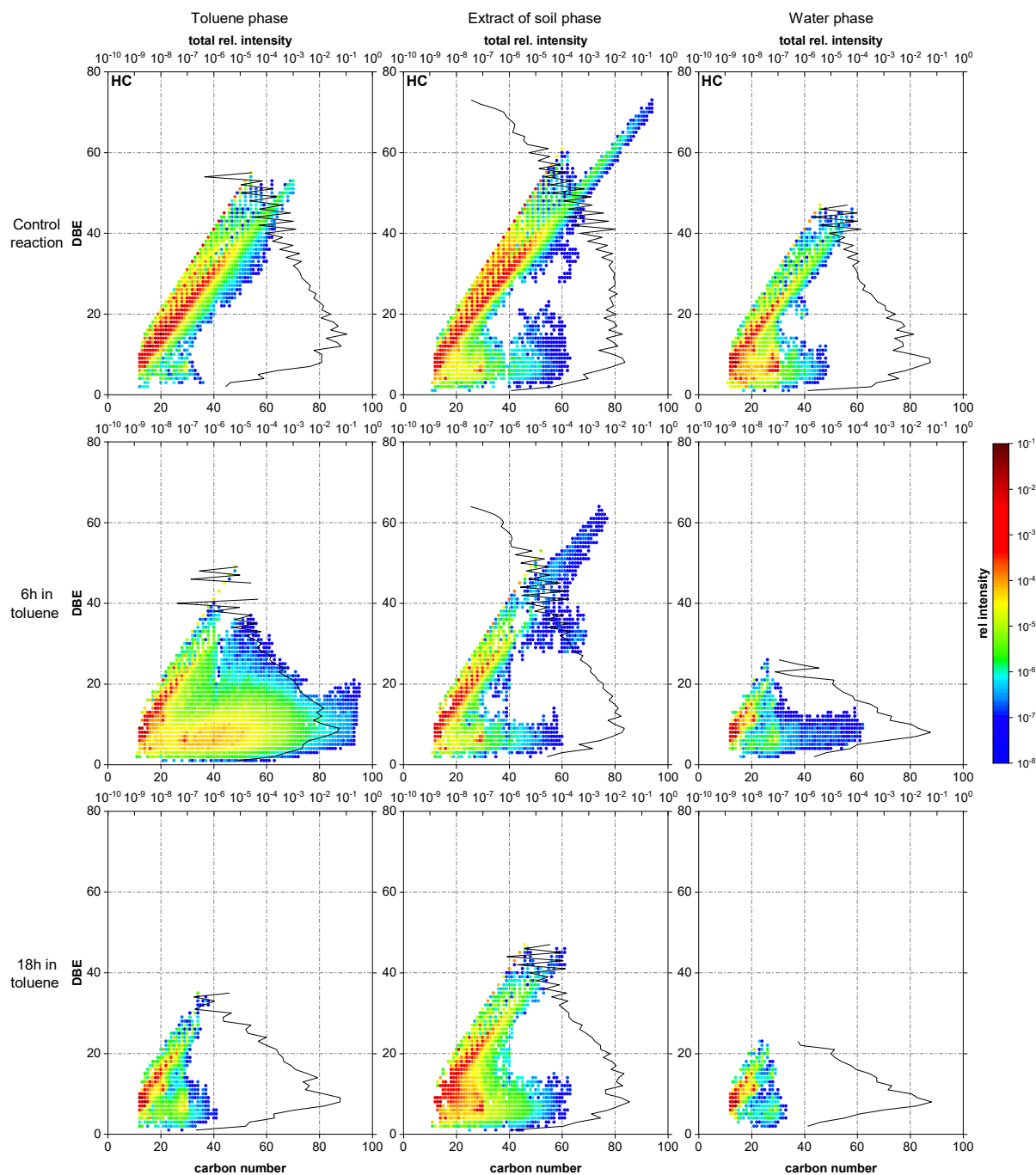


Figure 6-5: Kendrick plots for HC class in the different phases of control reaction, ozonation within 6 h in toluene and ozonation within 18 h in toluene. The total relative intensity for a given DBE is represented on the upper y-axis, while the number of carbon atoms is plotted on lower y-axis.

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 $\text{DBE} > 55$ and $\text{\#C} > 70$ are not extracted by toluene during 18 h of stirring, while PAHs with $\text{DBE} \leq 47$ and $\text{\#C} \leq 58$ are detected in the water phase sample. These HMW PAHs have a poor solubility in water^{32, 56, 57} and therefore the relative intensities of assigned PAHs with $\text{DBE} \geq 20$ are much lower than to corresponding assigned ones in the extract of soil and toluene phase.

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 extremely strong 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 the 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 $\text{DBE} < 27$ and the high implementation of O_3 in wastewater treatment due to the effective oxidation of contaminants in water.^{58, 59} After 18 h of toluene-based ozonation, highly aromatic PAHs with $\text{DBE} > 52$ 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 reaction comparisons are shown in Figure 6-6 for $\text{O}_3[\text{H}]$ and $\text{O}_7[\text{H}]$ 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 ($\text{DBE} \leq 10$ and $\text{\#C} \leq 30$) in O_3 and O_7 class only found in the toluene and the extract of soil phases. These multiple oxygen-containing compounds with $\text{DBE} \leq 26$ are transferred into the water phase and this explains the significant high intensity region in the water phases.

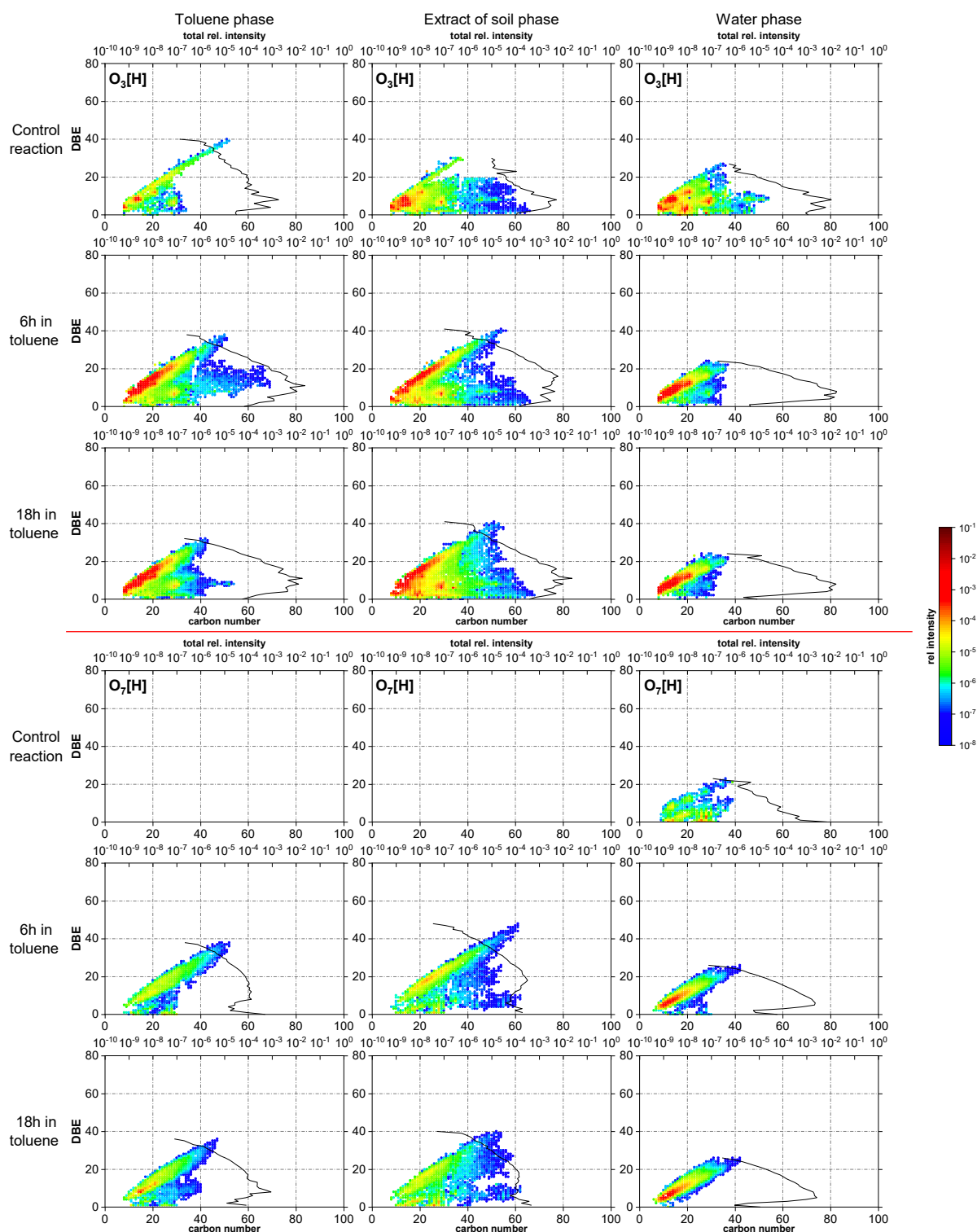


Figure 6-6: Kendrick plots for $O_3[H]$ (top graph) and $O_7[H]$ (bottom graph) classes in the different phases of control reaction, ozonation within 6 h in toluene and ozonation within 18 h in toluene. The total relative intensity for a given DBE is represented on the upper y-axis, while the number of carbon atoms is plotted on lower y-axis.

Since ozonation of only toluene results in formation of hydrocarbons and oxygenated compounds (Figure 6-7), 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.⁶⁰ This continuous formation of oxidized compounds is eventually the reason for less significant changes in the O₇ class shown in Figure 6-7.

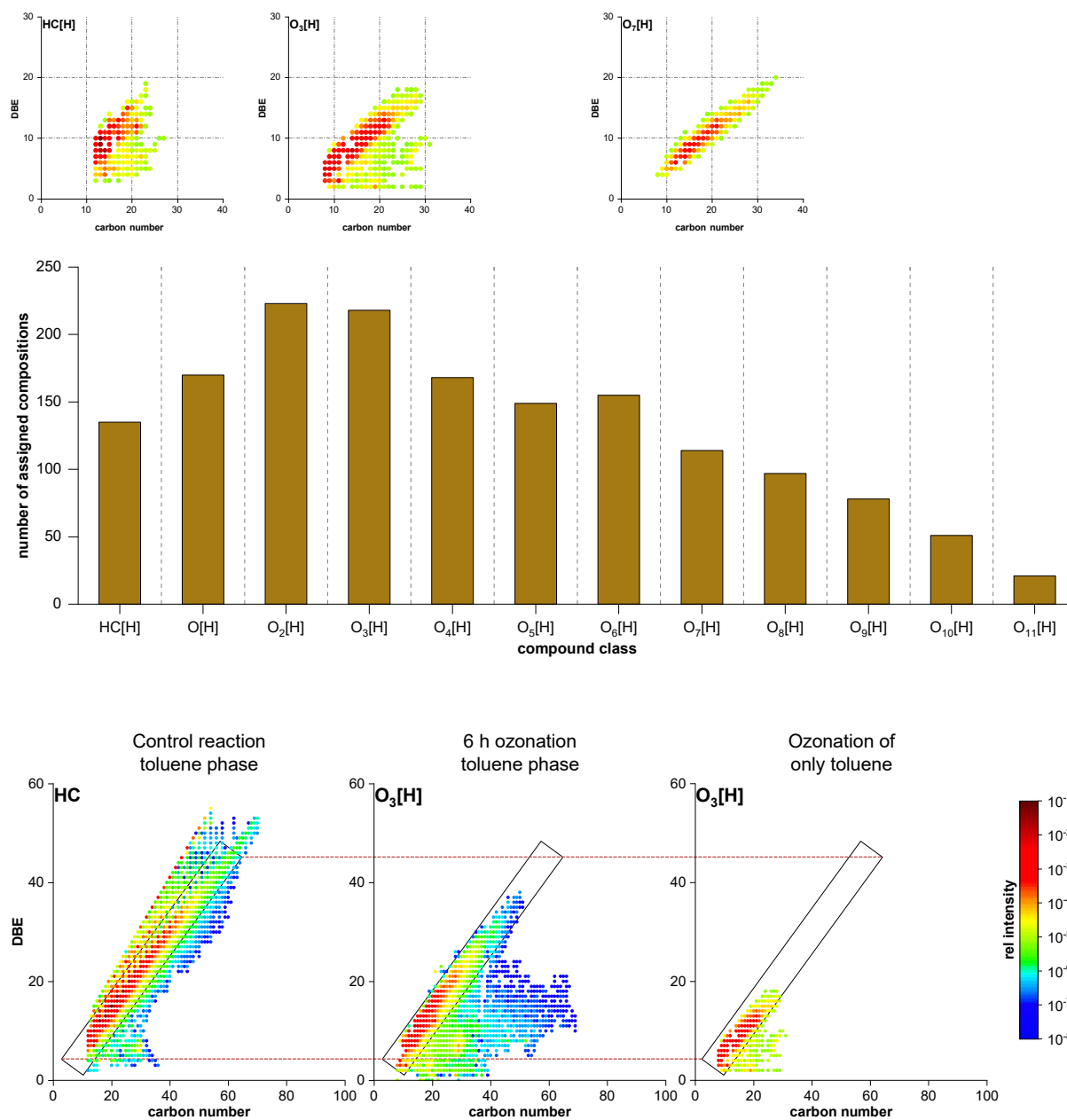


Figure 6-7: Kendrick plots for HC[H], O₃[H] and O₇[H] classes and population-based class distribution of hydrocarbons and oxygenated compounds after ozonation of only toluene (top graph) and Kendrick plots of control reaction, 6 h ozonation and ozonation of only toluene (bottom graph).

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 OH^\bullet and/or toluene like radicals. Beside this, the high intensity region ($DBE \leq 10$ and $\#C \leq 30$) in $O_3[H]$ and $O_7[H]$ (Figure 6-6 and Figure 6-7) class could originate from the mechanism of direct attack (bond attack) of ozone with highly aromatic PAHs, which causes ring openings and decrease of DBE values.

6.5 Conclusion

In this study, a combination of non-target analysis by UHRMS of the different phases achieved from ozonation of PACs contaminated soil with addition of toluene is demonstrated. For effective oxidation of PAHs and PANHs, 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 contaminants are being made much better accessible by the additions of toluene. Here, HMW PAHs ($DBE > 52$) are successfully removed by performing 18 h of toluene-based ozonation with formation of highly oxidized compounds. With increasing reaction time, a decrease of 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.

6.6 References

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7. Effect of toluene or DCM on the photocatalytic degradation of coal tar contaminated soil

Redrafted from:

Satilmis, I. and Schrader, W. “*Effect of toluene or DCM on the photocatalytic degradation of coal tar contaminated soil*” will be submitted to *Environmental Science: Processes & Impacts*.

7.1 Abstract

In this present study, the effect of different modifiers (toluene or DCM) and TiO₂ on PACs contaminated soil was investigated. The different phases (extract of soil, organic and water phases) were individually analyzed with an ultrahigh resolution mass spectrometer enabling a comprehensive characterization of a complex mixture of soil matrix and unknown pollutant compositions on a molecular level. For a deeper understanding of various modifiers on the photodegradation of aged contaminated soil, further photochemical experiments of 9-ethylcarbazole were accomplished. The obtained results reveal that toluene molecules are added to pollutants during photooxidation to form highly oxidized PAOHs. Furthermore, polycyclic aromatic hydrocarbons (PAHs), PANHs and PASHs were more effectively removed in the presence of TiO₂.

7.2 Introduction

Polycyclic aromatic compounds (PACs) contamination is widely found in all environmental compartments such as air, water, sediments and soil and these pollutants have a diverse range of carcinogenic, mutagenic and toxic effects on human health and ecosystems. One of the major cases of soil damage is coal tar contaminated soil comprising a complex mixture of thousands of PACs that include polycyclic aromatic hydrocarbons (PAHs) and heteroatom-containing compounds (N, S, O and/or halogens).^{1, 2} These compounds are released into the environment by both natural (e.g. volcanic activity or wildfires)³ and anthropogenic (e.g. incomplete combustion or pyrolysis of carbon-containing organic materials)⁴ processes.

PAHs are hydrophobic, persistent and bioaccumulative organic compounds with two or more annulated aromatic rings bonded in linear, cluster or angular structures and are persistent in the environment mainly due to poor solubility in water and strong adsorption onto solid substances.⁵ The water solubility of PAHs decreases with increasing number of condensed aromatic rings, which explains the limited implementation of widely used biodegradation to remove high molecular weight (> 3 rings) PAHs than low molecular weight (2-3 rings) ones.⁶ Here, various combinations of remediation techniques (biological, physicochemical and chemical) have been reported to increase availability and removal efficiency of PAHs.⁷⁻⁹ In recent years, the research interest in AOPs as pre- or post-chemical treatment with biodegradation for the clean-up of contaminated soil has been increased.¹⁰⁻¹³ Highly oxidant and non-selective OH[•] are liberated during AOPs destroying the most of recalcitrant organic pollutants to ideally mineralize them to CO₂ and H₂O or form more biodegradable compounds.¹⁴ The main types of oxidants in AOPs for the remediation of contaminated soil include Fenton oxidation,¹⁵⁻¹⁷ persulfate,¹⁶⁻¹⁸ ozone,¹⁹⁻²¹ permanganate^{15, 16, 18} and photooxidation.

Photodegradation has the potential to be an efficient way to remove PAHs and its use in water is broadly investigated.²²⁻³⁰ In contrast, studies on the photocatalytic degradation of PAHs in soil is rather limited.³¹⁻³⁶ In the presence of the complex soil matrix, the degradation of PAHs is significantly impeded by additional parameters (e.g. sorption strength of PAHs to the soil, soil particle size and humic acids), which leads to lower PAH degradation rates.³¹ Two main pathways are involved in the photolysis of organic pollutants named as direct and indirect photodegradation. The direct photodegradation starts with absorption of light by PAHs leading to excitation of PAHs and formation of PAH radical cations and solvated electrons. Meanwhile, reaction of solvated electrons with oxygen from water creates superoxide radical anion (O₂^{•-}) and singlet oxygen that react with organic molecules to form oxidized products.^{37, 38} Indirect

photolysis (photocatalytic degradation) is based on the addition of semiconductor metal oxides^{39,40} or sensitizers,⁴¹ which interact with light for the formation of reactive species. In the past few years, the photocatalytic degradation of PAHs in the presence of TiO₂ under UV-irradiation or solar light has been extensively used in different environmental systems due to high photoactivity, photochemical inertness and low cost of the TiO₂.⁴² TiO₂ has a gap energy of 3.2 eV correlating to a wavelength around 380 nm. Irradiation of TiO₂ with ultra-violet (UV) light (wavelength < 380 nm) results in the excitation of the electrons (e⁻) from the valence band to create holes in the valence band and e⁻ in conduction band.⁴³ These hole-electron pairs are involved in the production of OH[•], O₂^{•-} and hydroperoxyl radicals (HO₂[•]) as main reactive species and are responsible for the photocatalytic decomposition of PAHs.⁴⁴

The clean-up of aged coal tar contaminated soil using photodegradation is more challenging than spiked soil with PAHs. This can be explained by the fact that aging has a great impact on the reduction of pollutants release from the soil to water.⁴⁵ In addition, the number and composition of contaminants in a real soil contaminated with coal tar are unknown making the complete removal of these contaminants even more complicated.³⁵ The use of water/organic solvent mixtures^{46, 47} or only organic solvents⁴⁸⁻⁵⁰ can enhance the photooxidation of hydrophobic PAHs due to increased accessibility and solubility.

Although many PAHs are highly toxic and carcinogenic to human and environment, 16 PAHs are listed by the EPA as representative pollutants.⁵¹ Therefore, many photodegradation studies were based on targeted GC-MS or HPLC coupled with spectroscopic and spectrometric techniques (UV/VIS, FLD, DAD, PAD, MS). However, a non-targeted approach using UHRMS is required to extensively characterize degradation products after photooxidation of a coal tar contaminated soil with major unknown pollutants on a molecular level. Here, FT-ICR MS and Orbitrap MS were utilized in different studies for deeper understanding of weathering and photochemical processes of crude oil.⁵²⁻⁵⁷

In this study, we compared the influence of different modifiers (toluene or DCM) and the addition of TiO₂ as photocatalyst by having a closer look into the different phases (extract of soil phase, organic and water phase) using APPI(+) Orbitrap MS. Furthermore, photooxidation of 9-ethylcarbazole with addition of different modifiers (without co-solvent, DCM or toluene) was studied to understand the details of the photocatalytic reaction of PAHs in soil.

7.3 Material and Methods

7.3.1 Chemicals

The reagents used for the experiments were 9-ethylcarbazole (99%, Thermo Fisher, Kandel, Germany), toluene ($\geq 99.8\%$, Fisher Scientific, Loughborough, UK), DCM (99%, Fisher Scientific, Loughborough), titanium dioxide (99.7%, Merck, Darmstadt, Germany) and deionized water (type I) taken from a Clearwater dispenser Purelab Flex 2 (ELGA LabWater, Celle, Germany).

7.3.2 Sample preparation

Coal tar contaminated soil was obtained from an industrial site in the German Ruhr area and 5 g of this sample were air dried for one week at room temperature in a fume hood. After the drying process, the soil was ground in a mortar for homogenization, sieved (2 mm pore size) and stored in a fridge at 4 °C for further experiments.

7.3.3 Experimental procedure

For each photolysis experiment, a sample of soil (85 mg) was transferred into a quartz glass vial and respective modifier (3 mL), deionized water (12 mL) and TiO₂ (1.2 mg) were added, where appropriate. Three different reactions were carried out: (A) Water + toluene; (B) Water + toluene + TiO₂; (C) Water + DCM. The vials were placed in a laboratory-made photoreactor consist of 8 UV lamps (PL-S 9W UV-A/2P, Philips, Amsterdam, Netherlands) and 4 emitting visible wavelength light lamps (MASTER PL-C 26W/865/2P, Philips, Amsterdam, Netherlands) and stirred for 545 h (Figure 7-1). During the photoirradiation, the temperature was kept below 40 °C.

After the reactions, the soil obtained from different reactions were filtered, dried in a fume hood and remaining compounds were extracted by Soxhlet extraction with DCM (50 mL) for 24 h. Afterwards the solvent was removed under reduced pressure and the residues stored for further analysis. The liquid layers were separated by liquid-liquid extraction and the organic layers were dried over MgSO₄ and filtered. Both water and organic phase were concentrated under reduced pressure and residues stored for further analysis.

In order to compare the various photooxidation reactions with the untreated sample, a Soxhlet extraction of the contaminated sample (85 mg) with DCM (50 mL) was performed for 24 h. Afterwards, the solvent was removed under reduced pressure and the residues stored for further analysis.

For the photoirradiation of a model compound, 9-ethylcarbazole (10 mg) was transferred into a quartz glass vials to perform three different reactions: (A) Photooxidation in presence of water; (B) Water + toluene; (C) Water + DCM. After stirring for 168 h, the layers were separated and the water phase was extracted with three times DCM. The combined organic layers were dried over MgSO_4 , filtered, concentrated under reduced pressure and stored for analysis.

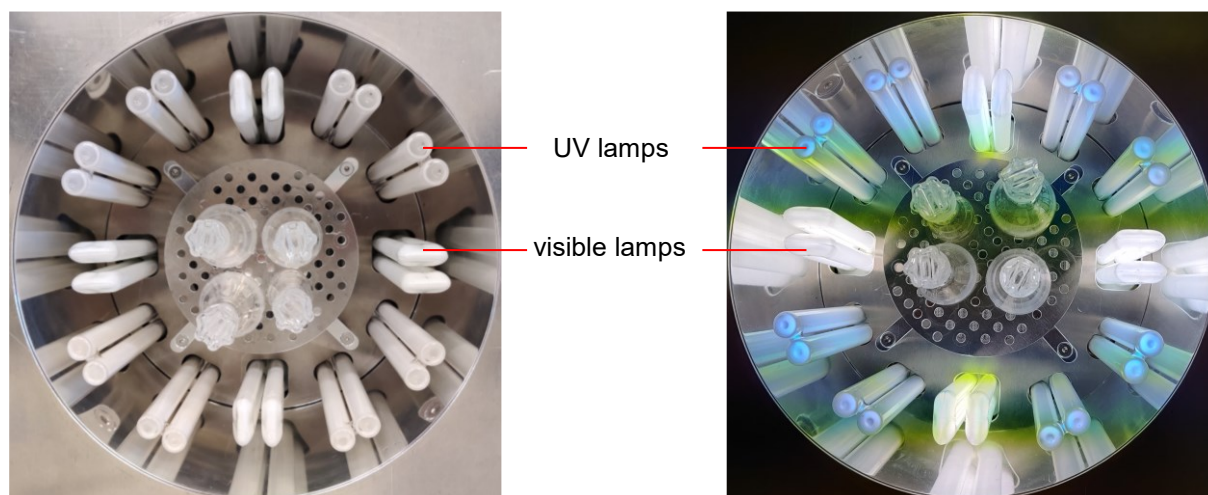


Figure 7-1: Photoreactor with UV and visible light lamps.

7.3.4 FT Orbitrap and data analysis

The different residues achieved from different reactions and different phases were diluted in toluene:methanol (1:1, v/v) to a final concentration of 150 ppm and analyzed using a research type FT Orbitrap Elite (Thermo Fisher Scientific, Bremen, Germany).⁵⁸ Mass spectra were recorded with a mass resolution of $R = 480,000$ at m/z 400 in a mass range of m/z 150-1300 using APPI(+) and spectral stitching method of 30 Da mass windows with 5 Da overlap.⁵⁸⁻⁶⁰ For APPI measurements, 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 analyzed by direct injection at a flow rate of 20 $\mu\text{L}/\text{min}$ and with adjusted ion source conditions as follows: capillary temperature of 275 $^{\circ}\text{C}$, vaporizer temperature of 250 $^{\circ}\text{C}$, sheath, auxiliary and sweep gases of 20, 10 and 2 arbitrary units.

Recorded mass spectra were exported into Composer (V1.5.0, Sierra Analytics, Modesto, CA, USA) and processed on the following criteria: H: 0-300, C: 0-100, O: 0-20, N: 0-2, S: 0-1, DBE: 0-80 and mass error ≤ 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, Northampton, MA, USA) were used.

7.4 Results and Discussion

UHRMS was used to investigate the details of the photodegradation reaction of contaminated soil with additional modifiers. Here, UHRMS is the method of the choice to analyze such complex mixtures of pollutants and complex soil matrix down to the molecular level. In Figure 7-2, the mass spectra of the extract of unreacted soil and the organic phases from different reactions are shown. APPI was chosen as ionization method due to detection of wider range of PAHs compared to electrospray ionization ESI and APCI.⁶¹ The 16 EPA-PAH list contains compounds with $m/z < 279$ and these compounds (and including isomers) are detected with higher relative intensities in the extract of unreacted soil. Nevertheless, further dominant signals of higher molecular weight PAHs with $m/z > 279$ were observed, which underlines the importance of extending the 16 EPA-PAH list.⁵¹ A significant decrease of dominating PAHs after m/z 400 is obtained in the organic phases of the different photo-induced reactions indicating the favored removal of HMW PAHs. Having a closer look at the zoomed-in mass spectra between m/z 367.10 and 367.16 reveals detailed changes regarding the reaction conditions. As a result of various photooxidation reactions, $C_{28}H_{17}N$ and $C_{24}H_{18}N_2S[H]$ are detected with lower intensities. Furthermore, oxidized species like $C_{21}H_{18}O_6[H]$ (red and blue spectrum) and $C_{25}H_{18}O_3[H]$ are found after photooxidation, which implies the continuous oxidation of already oxidized PAHs. The addition of TiO_2 to toluene-based photooxidation reverses the ratio of $C_{28}H_{14}O[H]$ to $C_{29}H_{18}[H]$ and leads to increased production of oxygenated species $C_{24}H_{17}NO_3$, which can be explained either by increased formation of oxygen compounds or the increased degradation of the hydrocarbons. In general, the addition of TiO_2 enhances the degradation of pollutants due to increased formation of reactive species.^{33, 62} However, Wilcke et al. found out that the addition of TiO_2 did not necessarily improve the degradation in soils, as the different minerals in soils have also a catalytic effect.³¹

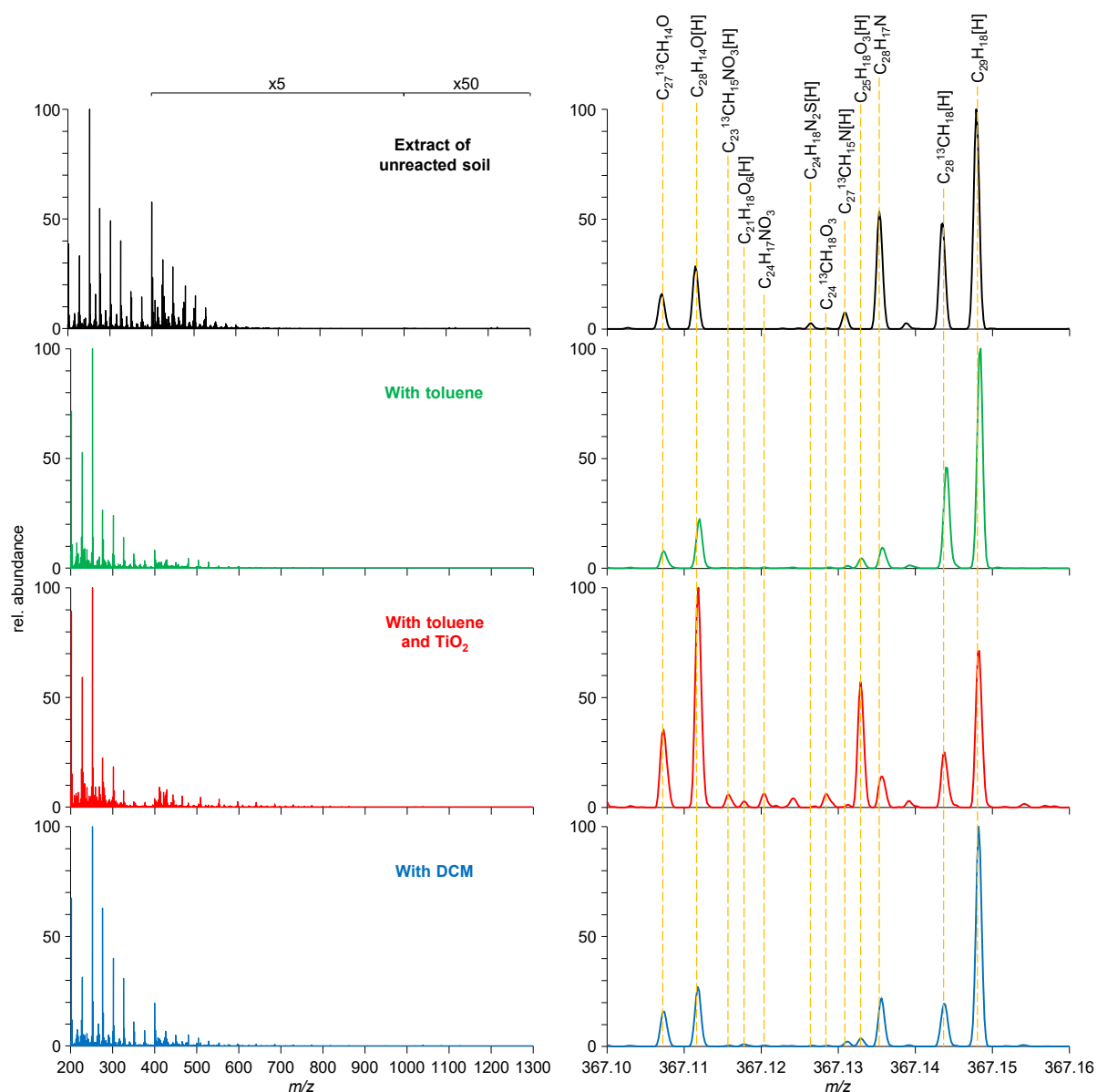


Figure 7-2: Mass spectra of Soxhlet extract from unreacted soil (black) and the organic phases of soil reacted with addition of toluene (green), with addition of toluene + TiO_2 (red) and with addition of DCM (blue).

The high number of selected signals, which is achieved by the combination of UHRMS and non-target analysis, can be arranged in different heteroatom classes based on the number of assigned elemental compositions. Both protonated $[\text{M}+\text{H}]^+$ and radical cation $[\text{M}]^{\bullet+}$ species are listed, which are formed by using APPI as ionization technique.⁶³ In case of the different photodegradation reactions, each compound class contains both the individually assigned compositions (from each organic, water and extract of soil phase) and those that occur in two and all three different phases. This data evaluation enables us the representation of each individual composition from all phases exactly once (Figure 7-3).

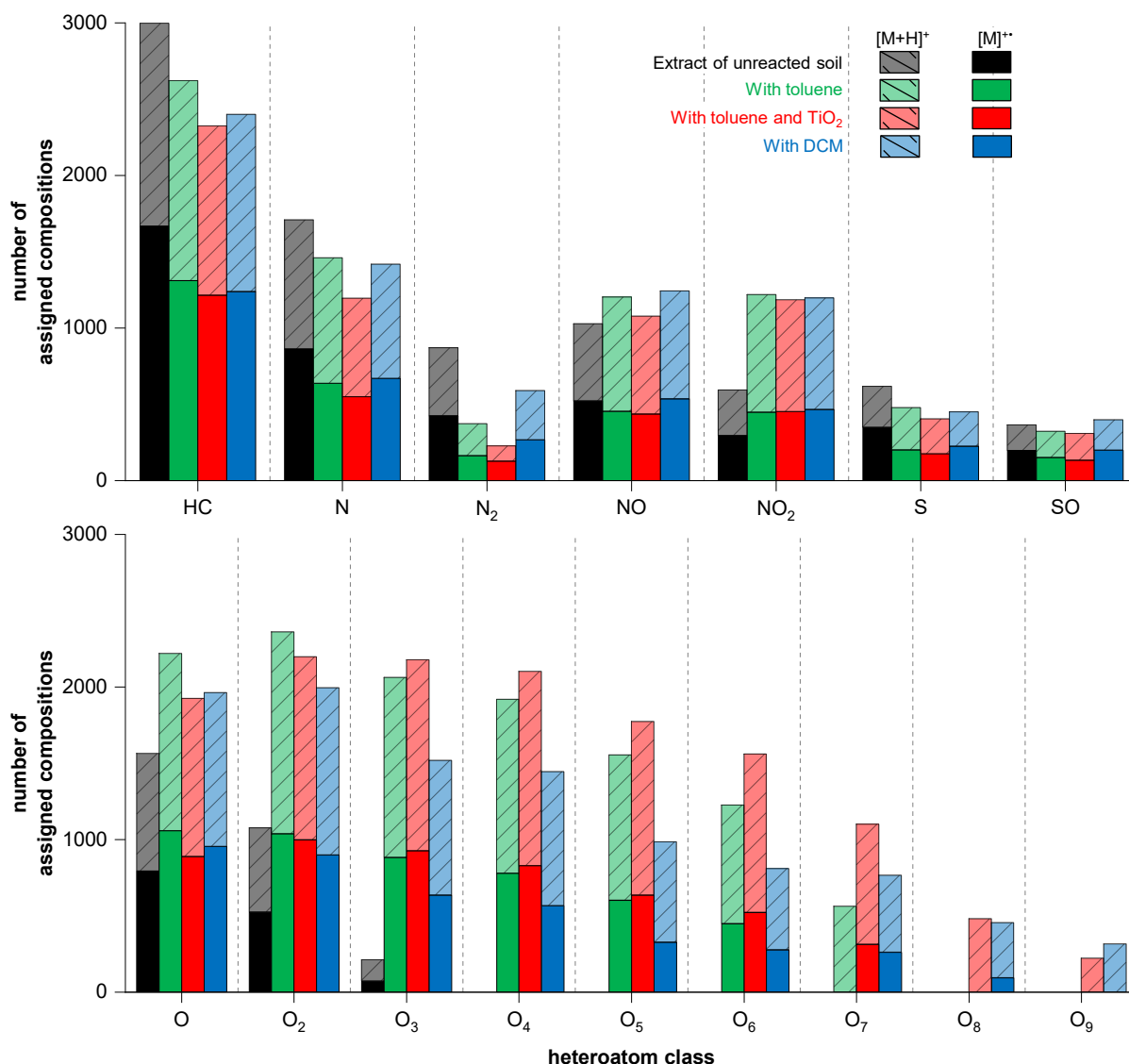


Figure 7-3: Population-based class distributions of the most prominent heteroatom classes (top) and PAOHs from extract of unreacted soil (black), photodegradation in toluene (green), in toluene + TiO₂ (red) and in DCM (blue).

After the photooxidation of contaminated soil, a reduction of HC, N, N₂ and S classes as well as an increase in NO_x and O_x classes were obtained. Using DCM instead of toluene as modifier leads to a slightly higher number of removal of hydrocarbons sulfur- and nitrogen-containing compounds, but higher number of assignments for oxygen-containing classes from O₁-O₆ were observed with addition of toluene (without TiO₂). These results must be related to the addition of toluene moiety to organic compounds or the reaction of reactive species with toluene forming highly oxidized compounds and oligomers. The addition of TiO₂ significantly improves the degradation of PAHs by formation of oxidized compounds. One possible explanation is the higher sufficient production of reactive intermediates, which are attacking the pollutants. On the other hand, these active intermediates can react with toluene creating higher concentrations of oxygenated oligomers and thus facilitate the desorption of PAHs due to having surfactant-

like properties.⁶⁴ Furthermore, phenolic compounds can serve as photosensitizers and hence accelerate the photodegradation of PAHs.⁶⁵

UHRMS provides elemental composition assignments of organic molecules and therefore the usage of Kendrick plots for data representation allows a deeper insight into the chemical transformations occurring after photooxidation of contaminated soil. Here, the assigned formulae are visualized as spots by a given DBE and carbon number per molecule (Figure 7-4). Highly aromatic PAHs with $\text{DBE} \leq 73$ and PANHs with $\text{DBE} \leq 68$ are found in the contaminated soil confirming the pollution of soil with coal tar.⁶⁶ The comparison of the unreacted soil with the different photooxidation reactions shows preferential removal of compounds with high DBE values and highest carbon numbers for a certain DBE. High aromatic PAHs were detected with lower relative intensities in the extract of the soil phase, which was photodegraded in the presence of toluene and TiO_2 , evidencing the enhanced removal of PAHs with the addition of TiO_2 . These highly aromatic PAHs were detected with low relative intensities in the extract of unreacted soil indicating the lower concentration of these hydrocarbons in the unreacted contaminated soil. The organic phases of each photooxidation reaction contain less and limited hydrocarbons and nitrogen-containing compounds compared to the extract of soil phases. These results reveal that due to increased hydrophobicity, compounds with high DBE values are strongly adsorbed onto the soil matrix and therefore be extracted using Soxhlet extraction. In the case of the O_6 class, the same correlation between increasing soil affinity with increasing DBE (and thus hydrophobicity) is observed resulting in fewer PAOHs detection in the organic phases of the different photodegradation reactions. The creation of oxygen-containing species was most significant with addition of TiO_2 , as justified by increased population and relative intensities. These higher oxidation efficiencies are achieved by higher production rates of reactive species in the presence of TiO_2 , so different reaction scenarios have to be considered: (A) Direct attack of reactive species to PACs; (B) Reaction of active species with toluene; (C) Recombination of both PACs and toluene radicals.

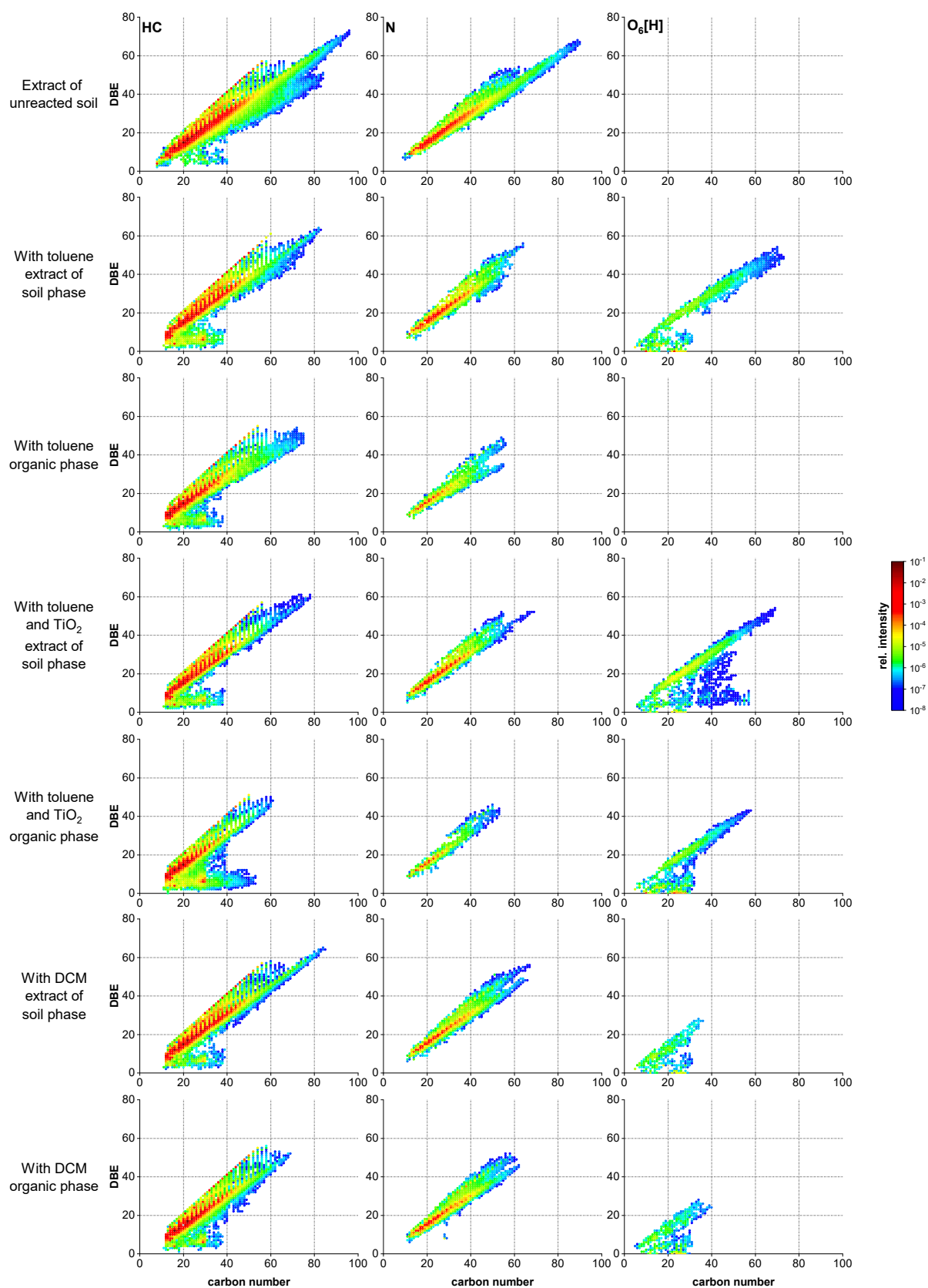


Figure 7-4: Kendrick plots of HC, N and O₆[H] classes of extract of unreacted soil, extracts of soil after reaction and organic phases obtained from different photodegradation reactions.

In case of the water phases, much less PACs with $\text{DBE} \leq 49$ were detected compared to organic and extract of soil phases. Furthermore, a significant reduce of the relative intensities for $\text{DBE} > 20$ was observed in the different water phases (Figure 7-5). The results verify the decrease in solubility of organic compounds in water with increasing DBE.⁶⁷

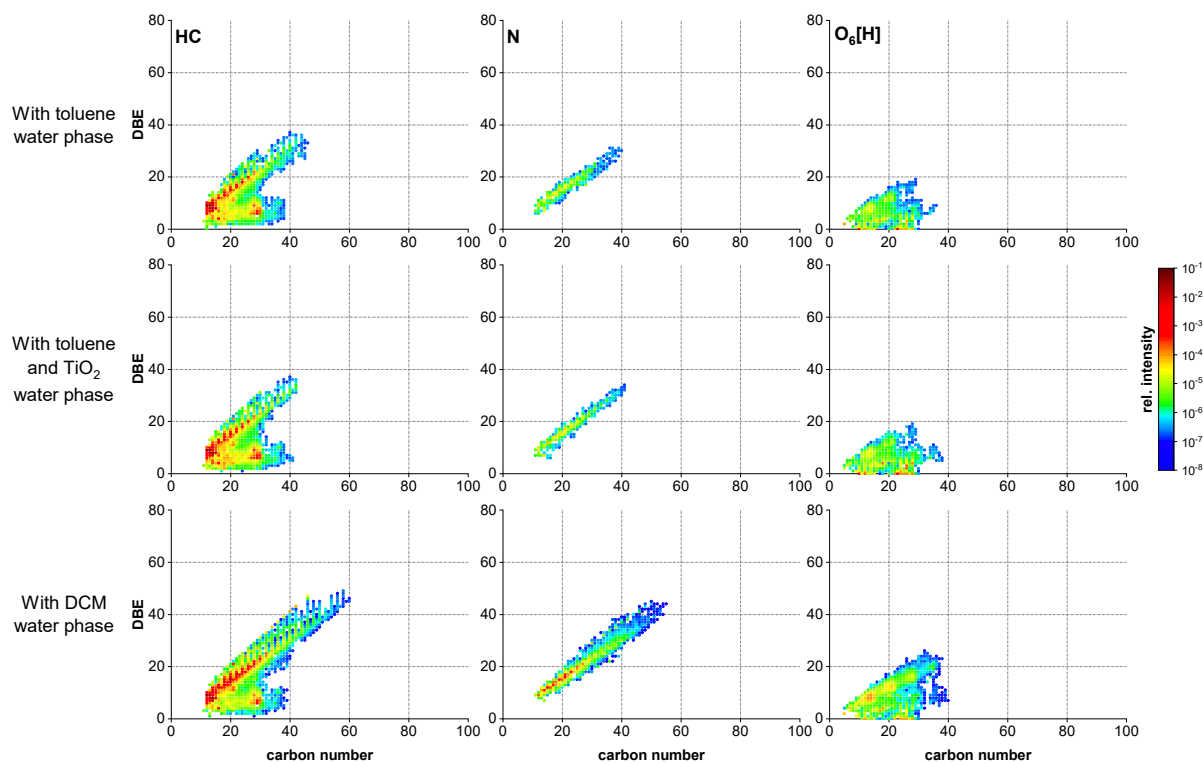


Figure 7-5: Kendrick plots of HC, N and $\text{O}_6[\text{H}]$ classes of the water phases obtained from different photodegradation reactions.

The results from Figure 7-4 indicate the formation of toluene oligomers and addition of toluene moiety to organic compounds. Unfortunately, making a prediction for the reaction of toluene with pollutants in the complex sample is extremely difficult. Here, further investigations using different modifiers for the photochemical reaction of a single component are required. Therefore, photooxidation of 9-ethylcarbazole was performed in water, DCM or toluene. The standard nitrogen-containing compound was chosen on purpose to differentiate NO_x products from toluene-adducts. Figure 7-6 presents the selected elemental compositions in the mass range of m/z 310.10-310.15 occurring only after toluene-based photooxidation of 9-ethylcarbazole. The NO compound probably results from the addition of toluene moiety to a nitrogen compound, which is formed during photodegradation of 9-ethylcarbazole. The detection of the reaction product with elemental composition $\text{C}_{23}\text{H}_{18}\text{O}$ was only found after toluene-based photooxidation and can be explained by polymerization of toluene molecules.

The results of the photooxidation of 9-ethylcarbazole in the presence of various solvents indicate that during the toluene-based photooxidation of PACs contaminated soil both the addition of toluene structure to PACs and self-reaction of toluene adducts occurs.

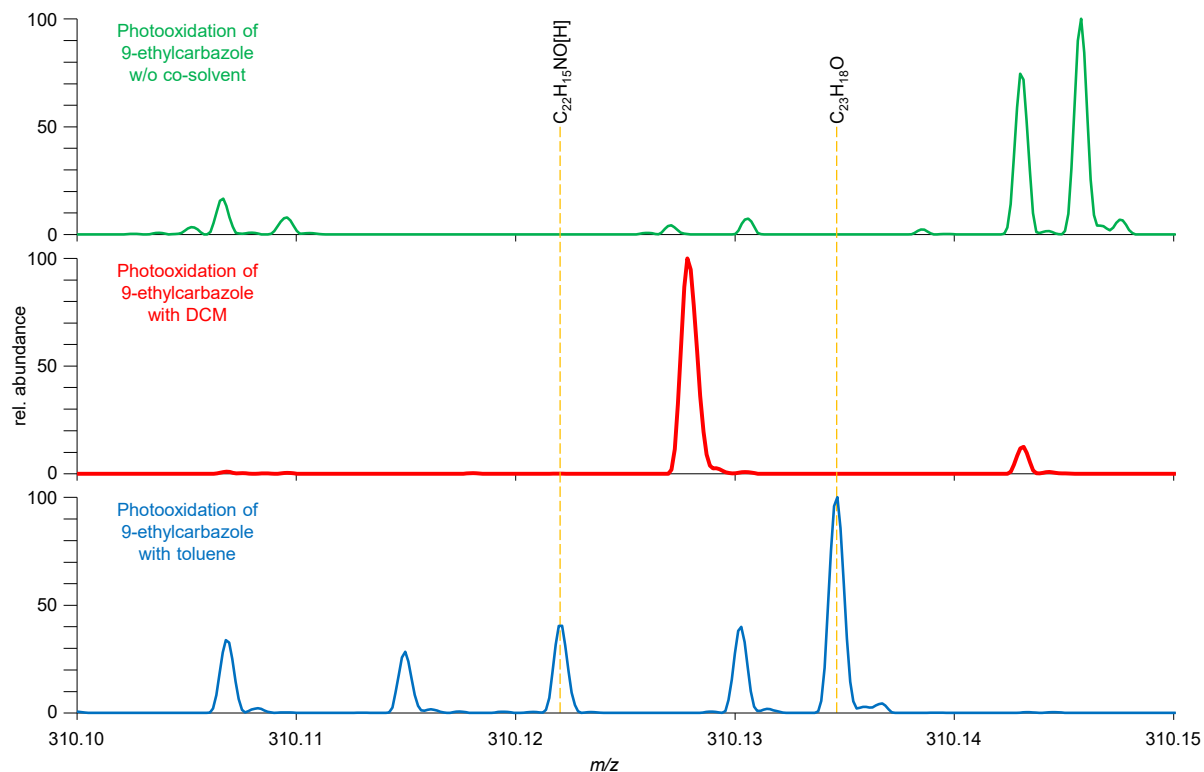


Figure 7-6: Comparison of the mass spectra from different photooxidation reaction of 9-ethylcarbazole without modifier (green), with addition of DCM (red) and with addition of toluene (blue).

Our results show the photocatalytic remediation of aged contaminated soil is less effective than Fenton oxidation⁶⁸ or ozonation.⁶⁹ One explanation may be the light transmission of the soil. Here, the soil organic matter absorbs light or deals as radical scavenger which leads to less light penetrating into deeper soil layers and less production of reactive species.³¹ Furthermore, the complex mixture of thousands of organic pollutants makes it more difficult to determine the parameters for photochemical degradation, e.g. reaction time, temperature and amount of TiO₂.

7.5 Conclusion

The effect of different modifiers (toluene or DCM) and TiO_2 on the photooxidation of coal tar contaminated soil was investigated on the molecular level using ultrahigh resolution mass spectrometry. PAHs with DBE up to 73 were detected in the contaminated soil, which illustrates the pollution of the soil with large and highly aromatic compounds. These large PAHs were removed using toluene- or DCM-based photodegradation and removal efficiency was even improved with the addition of TiO_2 . Soxhlet extraction of phototreated contaminated soil was necessary to remove highly aromatic compounds and highly oxidized PAOHs, which were much less present in the organic and water phase. Due to polymerization of toluene and addition of toluene molecules to organic compounds, PAOHs with higher DBE numbers were predominantly observed after toluene-based photodegradation.

7.6 References

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8. General Conclusion

Despite the ongoing threat of contaminated soil to ecosystems and human health, its remediation still remains a challenging and difficult undertaking, which is related to the intricate nature of soil and the existence of thousands of unidentified pollutants. At this point, our study aims to develop a chemical remediation method for a highly contaminated soil and analyze the changes after the reaction using ultrahigh resolution mass spectrometry as a powerful tool.

We started our research with the application of Fenton oxidation to real and heavily contaminated soil. This sample contains PAHs up to a DBE of 73 and #C of 96, which points out the strong contamination with coal tar. The Fenton reaction of this sample with water – as the only solvent – was not effective at all for the oxidation of PACs, so the inclusion of various co-solvents (methanol, ethanol and toluene) was necessary. While methanol and ethanol showed no efficiency in the oxidation reaction, this became much more effective when toluene was added and the substituted PAHs were preferably oxidized than the unsubstituted ones. It is well known that the contaminants in aged soils are deeply incorporated into the soil matrix making the removal from the soil more difficult. The addition of toluene dissolves the organic compounds improving accessibility for chemical remediation.

Further studies focused on the detailed understanding of the Fenton reaction with a such complex mixture to optimize the chemical conditions. Based on the previous studies by our group that reported a successful recovery of $\geq 95\%$ for crude oil in spiked sand by using toluene or DCM as extraction solvent, Fenton experiments with addition of these solvents were performed to determine the best solvent. Here, oxidation of PAHs and creation of highly oxidized hydrocarbons (up to O_{17}) were more prominent with toluene than with DCM. Therefore, the data from Fenton oxidation with the soil sample were compared to those from Fenton oxidation with only toluene. The perfect overlap of these data showed that highly oxidized PAHs, obtained after toluene-based Fenton of contaminated soil, were formed either by polymerization of toluene or by radical addition of toluene to pollutants. The production of these polymers can be assumed as the reason for the increased oxidation of PAHs in toluene-based Fenton due to their surfactant-like properties. However, higher amounts of toluene did not improve the treatment of PAHs, which can be attributed to the consumption of the oxidizing agents by toluene.

Due to the formation of highly oxidized PAHs after toluene-based Fenton oxidation, we further investigated the extraction efficiency of these compounds using DCM or water as extraction solvent. After the Fenton treatment, PAOHs with high oxygen number were mainly detected in the water phase, whereas the extraction of these compounds was more effective using DCM as extraction solvent. These results reflect the enhanced solubility of PAOHs in water and the increase in hydrophobic interactions with higher oxygen numbers within a molecule. Furthermore, several Soxhlet extraction cycles are required to completely remove PACs from contaminated soils.

After the intensive studies of Fenton oxidation of highly PACs contaminated soil, we shifted our interest to ozonation as treatment method and transferred our knowledge from the Fenton experiments to the ozonolysis. The experiments were performed using toluene as co-solvent, since no significant removal of PAHs was observed without any organic solvent. Similar results to the toluene-based Fenton process were obtained in toluene-based ozonation for 18 h, where PAHs (DBE > 52) and PANHs effectively transformed into highly oxidized compounds due to formation of polymers during ozonation of toluene. As the reaction time increased, a reduction of oxidized components was noticed possibly caused by the continuous reaction (and degradation) of PAOHs with ozone.

The last part of the work dealt with the influence of toluene or DCM (as co-solvents) and the addition of TiO_2 on the photooxidation of PACs contaminated soil. High molecular weight PAHs are oxidized by addition of toluene or DCM and the overall degradation efficiency of contaminants was further enhanced with TiO_2 . The comparison of the results from the various chemical treatment methods demonstrated a lower efficiency for PAHs degradation with photooxidation. This can be explained by absorption of light by soil organic matter reducing the generation of oxidizing agents.

To sum up, the development of chemical and analytical methods provides new perspectives for the mechanisms of remediating contaminated soil.

9. Appendix

9.1 List of Abbreviations

°C	degree Celsius
Δm	mass deviation
μL	microliter
AGC	automated gain control
AOP	advanced oxidation processes
APCI	atmospheric pressure chemical ionization
API	atmospheric pressure ionization
APPI	atmospheric pressure photoionization
BTEX	benzene, toluene, ethylbenzene, xylenes
CHC	chlorinated hydrocarbon
CID	collision-induced dissociation
CRM	charged-residue model
Da	Dalton
DAD	diode array detector
DBE	double bond equivalent
DCM	dichloromethane
DNA	deoxyribonucleic acid
e^-	electron
e.g.	<i>exempli gratia</i> (lat.), for example
EEA	European Environment Agency
EI	electron impact
EPA	Environmental Protection Agency

ESI	electrospray ionization
et al.	<i>et alia</i> (lat.), and others
eV	electron Volt
FID	flame ionization detector
	free induction decay
FLD	fluorescence detector
FT	Fourier transform
FWHM	full width at half maximum height
g	gram
GC	gas chromatography
h	hour
HC	hydrocarbon
HMW	high molecular weight
HPLC	high performance liquid chromatography
i.e.	<i>idem est</i> (lat.), that being
ICR	ion cyclotron resonance
IE	ionization energies
IEM	ion evaporation model
IR	infrared
ISO	International Organization for Standardization
kg	kilogram
kV	kilovolts
L	liter
LC	liquid chromatography
LMW	low molecular weight

LTQ	linear trapping quadrupole
<i>m</i>	mass
<i>m/z</i>	mass-to-charge ratio
max.	maximum
mbar	millibar
MeOH	methanol
mg	milligram
mL	milliliter
mm	millimeter
MS	mass spectrometry
MS/MS	tandem mass spectrometry
nm	nanometer
PAC	polycyclic aromatic compound
PAH	polycyclic aromatic hydrocarbon
PAXH	polycyclic aromatic heterocycle
PDA	photometric diode array detector
ppm	parts per million
Q	quadropole
QqQ	triple quadrupole
<i>R</i>	resolving power
RF	radio frequency
RNA	ribonucleic acid
s	second
SOM	soil organic matter
TOF	time of flight

TPH	total petroleum hydrocarbon
UHRMS	ultrahigh resolution mass spectrometry
UV	ultraviolet
V	volume
V	Volt
v/v	volume fraction
VIS	visible
VUV	vacuum ultraviolet
ω	frequency

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9.4 List of Publications

9.4.1 Reviewed articles

Satilmis, I.; Schrader, W., *Investigation of the Ozonation of Highly PAXHs Contaminated Soil Using Ultrahigh Resolution Mass Spectrometry*, *Environments* **2023**, 10, (2), 18.

Satilmis, I.; Schrader, W., *Studying the Fenton treatment of polycyclic aromatic compounds in a highly contaminated soil with different modifiers by high resolution mass spectrometry*, *J. Hazard. Mater. Adv.* **2022**, 8, 100200.

9.4.2 Oral presentations

Satilmis, I.; Schrader, W., *Investigating the Fenton oxidation of polycyclic aromatic hydrocarbon contaminated soil by high resolution mass spectrometry*, Fachgruppe FTMS und hochauflösende Massenspektrometrie, Berlin, Germany, 19-20 September **2019**.

Satilmis, I.; Schrader, W., *Studying the Fenton based oxidation of polycyclic aromatic hydrocarbons (PAXHs) as a tool for soil remediation*, 17th International Conference on Chemistry and the Environment, Thessaloniki, Greece, 16-20 June **2019**.

Satilmis, I.; Schrader, W., *Effects of cosolvents in Fenton oxidation as clean-up procedure for polycyclic aromatic hydrocarbon (PA(X)H)-contaminated soil*, 52nd Annual DGMS Conference, Rostock, Germany, 10-13 March **2019**.

9.4.3 Posters

Satilmis, I.; Schrader, W., *Oxidation of polyaromatic hydrocarbons (PAXHs) from contaminated soil*, Umwelt 2018, Münster, Germany, 09-12 September **2018**.

Satilmis, I.; Schrader, W., *Fenton versus Ozone: Oxidation of PAHs in contaminated Soil as clean-up procedure*, European mass spectrometry conference (EMSC), 51st Annual DGMS Conference Saarbrücken, Germany, 11-15 March **2018**.

Satilmis, I.; Schrader, W., *Fenton based oxidation of crude oil in supercritical CO₂*, 50th Annual DGMS Conference, Kiel, Germany, 5-8 March **2017**.

9.5 Curriculum Vitae

Der Lebenslauf ist in der Online-Version aus Gründen des Datenschutzes nicht enthalten.

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