



Hot water extraction with in situ wet oxidation: PAHs removal from soil

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Received 27 November 2001; received in revised form 8 February 2002; accepted 9 February 2002

Abstract

We are reporting the results of a small-scale batch extraction with and without in situ wet oxidation of soils polluted with polycyclic aromatic hydrocarbons (PAHs) using subcritical water (liquid water at high temperatures and pressures but below the critical point as the removal agent). Two types of soil; one spiked with four PAHs, and an aged sample were used. Experiments were carried out in a 300 ml volume reactor in the batch mode. In each experiment, the reactor was filled with 45–50 g of soil and 200–220 ml of double distilled water. For extraction without oxidation, the reactor was pressurized with nitrogen, while for those with the oxidation, an oxidizing agent (air, oxygen or hydrogen peroxide) was used.

The extraction only experiments were carried out at 230, 250 and 270 °C for spiked soil samples, and at 250 °C for aged soil samples, while all of the combined extraction and oxidation experiments were carried out at 250 °C. Removal of PAHs from spiked soil in extraction-only experiments was from 79 to 99+% depending on the molecular weight of the PAH. This was in the range of 99.1% to excess of 99.99% for the combined extraction and oxidation. While 28–100% of extracted PAHs can be found in water phase in case of extraction alone, this reduces to a maximum of 10% if the extraction is combined with oxidation. With aged soil similar or comparable results were obtained. Based on these results, extraction with hot water, if combined with oxidation, would probably reduce the cost of post treatment for the water and can be used as a feasible alternative technique for remediation of contaminated soils and sediments.

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Keywords: Polycyclic aromatic hydrocarbons; Hot water extraction; Wet oxidation; Soil remediation; Water treatment

1. Introduction

Major remediation techniques available currently for solid matrices like soils, sediments and sludges which are contaminated with heavy organic compounds like polycyclic aromatic

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hydrocarbons (PAHs), include processes like incineration, thermal desorption, soil washing/solvent extraction, disposal at hazardous land fills, or deep well injection [1]. While each of these techniques has some advantages, there are concerns regarding their usage either from environmental or economical points of view. Incineration is the only destruction technology that completely degrades the toxic residues on soil, but is extremely expensive. Solvent extraction requires expensive solvent regeneration and thermal desorption produces air pollutants, which necessitates secondary treatment of the off gases [2]. Finally, regarding land fills and deep well injections, these methods are more a postponement of the problem to the future generations rather than a true solution.

The use of organic solvents in processes ranging from analytical extractions to chemical synthesis to environmental remediation is being reduced for both environmental and political reasons. Water is an “environmentally-friendly solvent” and has the additional advantages of being readily available, non-toxic, and very low in cost. However, water in its “natural” state is not a good solvent for most organics, but it becomes good to excellent solvent at its supercritical conditions. Historically water has received very little attention as an extraction solvent for contaminated soils, because it was considered to be too polar to dissolve most organic compounds. At ambient conditions, the dielectric constant of water is ~ 80 which is much too polar to solvate most organic pollutants of interest such as PAHs and PCBs. The PAH solubilities in water at ambient conditions are low and decrease rapidly with molecular weight [3,4]. On the other hand, supercritical water has a low dielectric constant and is therefore, an extremely effective solvent for most organic contaminants [5–8]. Supercritical water, however, is extremely corrosive and necessitates very special material of construction in addition to the added cost of high temperatures and pressures. The dielectric constant of water is a very strong function of temperature and it can be lowered significantly even at mild conditions. Hawthorne et al. [9] have compared the dielectric constant of water at different temperatures and pressures to some known solvents. From their results it can be noted that (a) at temperatures below ~ 325 °C the dielectric constant is not a strong function of pressure; and (b) the dielectric constant changes very little from 250 to 325 °C, but the difference in pressure required to maintain water in the liquid state is significant. Therefore, in this temperature range water has an excellent potential for being a very effective solvent for extraction of organics from soils and sediments.

Hawthorne and co-workers pioneered the use of hot water for extraction of organics from solid matrices [9–12]. Their interest was mainly in soil/sediment analysis in the laboratory and use of hot water extraction for quantitative determination of soil contamination. In soil extraction, they reported recoveries exceeding the certified values based on conventional Soxhlet and sonication extraction (EPA SW-846, methods 3540 and 3550). For all of the PAHs there was a little increase in extraction when the temperature was increased from 250 to 300 °C. Another advantage of using hot water for extraction was possibility of class selective extraction [11]. As the temperature of water increases its polarity decreases. Hence more polar contaminants will be extracted at lower temperatures and as the polarity of contaminants decrease, they will be extracted at higher temperatures. Similar results on analytical applications of hot water extraction were also reported by Hartonen and co-workers from Finland [13–16]. They have also shown that for extraction of a variety of chemicals (PCBs, polychlorinated dibenzofurans and naphthalenes, PAHs, *n*-alkanes) hot water extraction (which they call pressurized hot water extraction) was superior to other extraction techniques.

Lagadec et al. [1] recently reported on pilot scale hot water extraction of PAHs and pesticides from soils. Extractions were carried on 8 kg of soil contaminated at 2200 ppm total PAHs ranging from naphthalene to benzo(g,h,i)perylene at concentration levels ranging from 7 to ~100 ppm. At 275 °C all PAHs were removed to below detection levels (approximately <0.5 ppm) in 60 min of extraction. Pesticide contaminated soil had 73–400 ppm levels of six different pesticides. Again, 1 h extraction at 250 °C reduced all pesticides to below detection levels (<0.1 ppm). This was a unique study in one respect; hot water extraction was compared to bioremediation and supercritical CO₂ extraction. Bioremediation process was done by placing the contaminated soil in a lined pit and tilling frequently for a year. Although removal efficiencies were high for low molecular weight PAHs, little or no removal was observed for high molecular weight PAHs. However, even for low molecular weight PAHs, removal rates during 1 year of bioremediation were much lower than those obtained in 60 min of hot water extraction. The original PAH or pesticide contaminated soils used in this study could not support plant growth before treatment with hot water extraction, but both soils were fertile without additional treatment after extraction. In addition, earthworm toxicity was reduced from 100% for contaminated soils to 0% for treated soils. This is the only pilot scale study on hot water extraction that shows that the process is feasible.

Wet oxidation is a water treatment process for oxidation of organics dissolved in water. If no catalyst is used in the process, it is called homogeneous wet oxidation and it usually takes place at 200–325 °C temperature and 20–200 atm pressure with a typical residence time of 15–60 min to achieve high (>99%) destruction for many compounds [17]. The technology is commercialized and the Zimpro Process [18], the Wetox Process [19] and Vertech Technology [20] are all homogeneous wet oxidation processes, which are currently used for treatment of wastewater from multitude of industries, especially in Europe. In the literature, there are vast amount of studies on catalytic or non-catalytic wet oxidation of phenol, phenolic waste, chloro- and nitrophenols, chlorobenzenes, pyridines, some aliphatic compounds (such as glycols, organic acids, aldehydes, amines), certain dyestuff and dyestuff precursors, etc. and recent reviews are available [21,22]. These compounds are common water contaminants with appreciable solubilities in water at ambient conditions; hence wet oxidation is an alternate technology for their destruction. On the other hand, there are no studies on subcritical wet oxidation of PAHs or PCBs dissolved in water. Due to solubility limitations (very low concentrations at ambient conditions), these compounds are not typical contaminants in water at ambient conditions, which are candidates for catalytic or homogeneous wet oxidation, conventional technologies, such as carbon adsorption or advanced oxidation (ozone and/or H₂O₂ with UV light), would be more feasible alternatives for remediation.

There are no studies on combined extraction/in situ oxidation using subcritical hot water. Brunner [23] reported on a process that combines supercritical water extraction with supercritical water oxidation. The process, however, operated in series. The soil was packed in a bed and extracted with supercritical water by passing water over the bed. The effluent was then mixed with the oxidizing agent and fed to the oxidation reactor. They used an aged soil with ~10% by weight hydrocarbons. After extraction, the residual concentrations were below 100 ppm in soil. For reaction experiments they used halogenated compounds and observed good efficiency in destruction, however they did not present any data on combined operation of the extractor/reactor unit. The only relevant study is by Hawthorne et al.

[24] on pilot scale destruction of high explosives (TNT, RDX and HMX) contaminated soil (12% TNT, 0.32% RDX, 0.08% HMX) using subcritical water. Basically, they have placed soil and water (4–6 kg soil with 4 l water) in a vessel and heated to 275 °C with ~2 h heat-up period and 1 h reaction time at 275 °C. They have observed >99.9% destruction of TNT and RDX and ~98% destruction of HMX. They have also shown by Microtox acute toxicity test that there was no significant residual toxicity in either the process waters or in the leachates from the treated soils. This study confirms our findings on high explosives contaminated wastewater as well [25]. We have shown that at temperatures above 200 °C wet oxidation was complete for TNT, RDX and HMX. With a catalyst present in the system (Pt/TiO₂) RDX and HMX oxidation was complete at 120 °C, whereas TNT required ~170 °C.

In this study, we report on our findings on hot water extraction combined with in situ wet oxidation. We used two types of soil contaminated with PAHs; spiked and aged soil. As oxidant air, oxygen and hydrogen peroxide were employed for spiked soil and for aged soil only oxygen and hydrogen peroxide were used. To the best of our knowledge this is the only study that combines hot water extraction and wet oxidation for environmental remediation.

2. Experimental section

2.1. Soil preparation

2.1.1. Spiked soil

A sample soil from west Seattle sediments was used for the experiments. It had a dark brown color and sandy clay texture. It was dried, milled and autoclaved for homogeneity. Four solutions of phenanthrene, anthracene, chrysene and benzo(a)pyrene were prepared by dissolving 500 mg of each PAH into 100 ml of methylene chloride. These solutions were then spiked on 1 kg of soil and thoroughly mixed with periodic addition of methylene chloride in order to get a homogenized mixture. Prepared spiked soil then was transferred into two 500 ml glass jars and stored in the refrigerator in the dark and aged for over 3 months. Samples from this spiked soil as well as treated soil (after extraction/oxidation experiments) was taken and analyzed for PAH content. Initially integrated soxhlet unit similar to Foss Tecator Soxtec Avanti 2055 was used for 6 h to extract the PAHs. Later this was replaced by extraction using an accelerated solvent extractor ASE[®] 200 by Dionex (Sunnyvale, CA).

2.1.2. Aged soil

For experiments on aged soil, a soil sample was obtained from a railroad tie manufacturing plant located in the northeastern United States, the soil type was a sandy loam. This sample was milled and sieved with a no. 40 mesh (420 μ opening) and stored in a glass jar, covered with aluminum foil and stored in the refrigerator for later use. This soil was characterized similar to that of the spiked soil. Solvent extracts from this soil were tested against a standard of 16 priority PAHs and 6 substances were selected based on the abundance and also to represent a wide range of molecular weights. Table 1 summarizes the PAHs identified in the aged soil together with the ones followed in extraction/oxidation experiments marked with an asterisk.

Table 1
Concentration of PAHs in aged soil, as is determined by GC after calibration with 16 priority PAH standard

PAH	Concentration ($\mu\text{g/g}$ soil)
Naphthalene	7
Acenaphthylene	2
Acenaphthene*	29
Fluorine	11
Phenanthrene*	46
Anthracene	21
Fluoranthene*	184
Pyrene*	148
Benzo(a)anthracene	41
Chrysene*	65
Benzo(b)fluoranthene	22
Benzo(k)fluoranthene	32
Benzo(a)pyrene*	25
Indeno(1,2,3-c,d)pyrene	11
Dibenz(a,h)anthracene	3
Benzo(g,h,i)perylene	9

*: Selected for treatment studies.

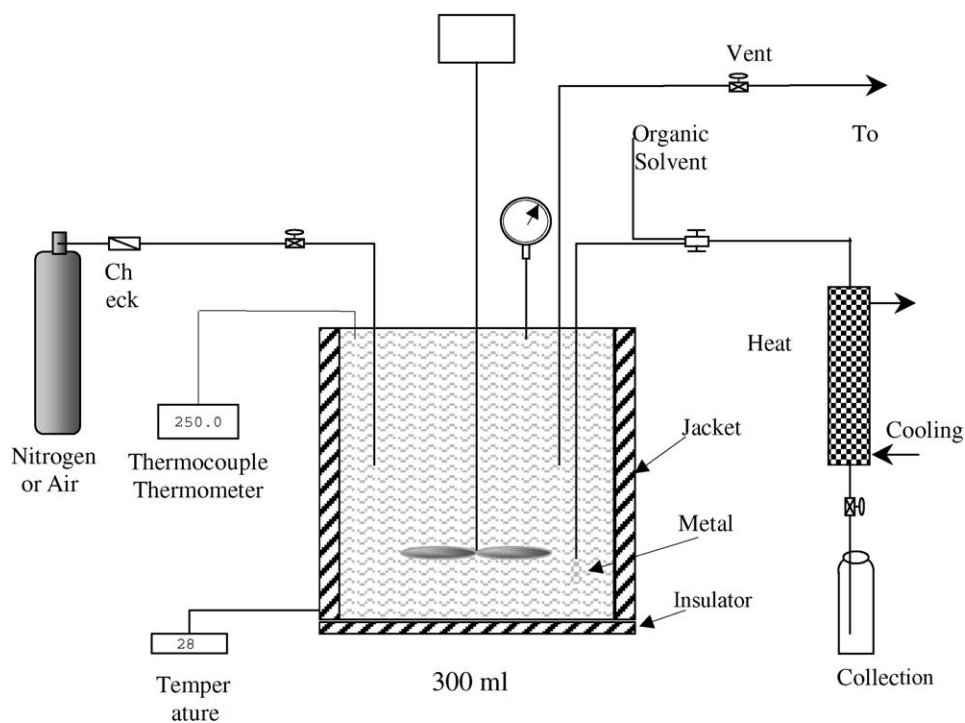


Fig. 1. Equipment set-up.

2.2. Hot water extraction

A 300 ml stainless steel bolted closure type reactor by Autoclave Engineering was used in all experiments. An experimental set-up diagram is shown in Fig. 1. The reactor was modified from its original design to enable us for loading and unloading it without disassembling of any tubing or sensor probes. This reduces the leak problems and equipment wear and tear, which is associated with this type of work. In each run, about 45–50 g of soil was weighed in a balance, a sample taken for analysis, and added to the reactor. After taking out the glass jar containing the spiked soil from the refrigerator, it was left in dark until it reached room temperature and it was thoroughly shaken before opening its cap. This step was done to avoid condensation of water on the soil and in order to homogenize the soil. Then once again soil was mixed thoroughly with the stainless steel scoop before placing the appropriate amount of soil on the balance. Double distilled water, 200–220 ml was then added on top of the soil in the reactor. These amounts reduced the dead volume in the reactor to a minimum. The reactor vessel was bolted to the main body, which supported the tubing, temperature sensor and mixer. All reactor exit valves were closed and the reactor was pressurized with nitrogen to an initial pressure of 400–450 psig. Heating was provided by a cylindrical ceramic heater, which surrounded the reactor body. A temperature controller was connected to the heater thermocouple rather than the thermocouple measuring the inside reactor temperature. The heater was turned on while monitoring the temperature inside the reactor. When the temperature approached 10–20 °C below the set point, the mixer was started at 300–500 rpm. Initial heating period usually took between 45 and 90 min. Extraction time then was started when the reactor temperature was at the desired set point ± 5 °C.

During the initial runs, samples were taken hourly for 4 h, followed by a second sample at the end of 4 h. This was done to determine the extent of extraction with time and to find the proper reaction time for the experiments. As shown in Fig. 2, based on these initial experiments, it was decided to limit the other runs to 3 h and taking samples only at the end of 3 h.

Sampling was done by first stopping the mixer for a period of 20–30 min while keeping the heater on. This was done to settle the soil particles, while keeping the water near the set point in order to keep the PAHs from precipitation. Then valve 1 was opened for about 1 min

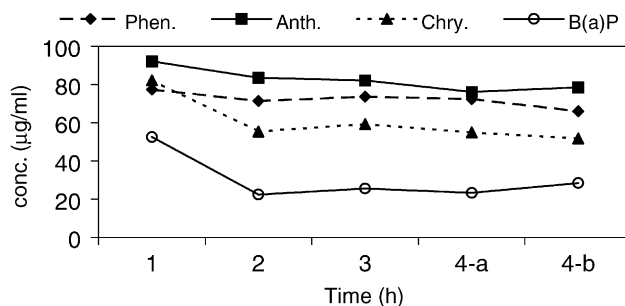


Fig. 2. Extent of PAHs extraction by hot water with time.

and closed in order to trap the sample between two sampling valves, where it was cooled down by the circulating water in the heat exchanger. Then by opening valve 2 the sample was transferred to a 22 ml vial with 2 ml of methylene chloride in it. Sampling vials were then shaken by hand and the lower portion (methylene chloride with the dissolved PAHs) was separated using a syringe. The sample trap was washed a few times with methylene chloride to collect any PAHs that may have been precipitated out on the walls. All washes were collected together with the initial sample, the amount of solvent reduced by evaporation, and a sample is injected to HP-5890 GC for analysis. A Zebtron ZB-5 column by phenomenex (Torrance CA) was used in the GC. Column specifications are 30 m length, 0.53 mm i.d. and 1.50 mm film thickness. Injection port and FID temperatures were 300 and 325 °C, respectively, and temperature program that was used is as follows: initial temperature: 150 °C, initial time: 2 min, heating rate: 20 °C/min, final temperature: 300 °C, final time: 30.5 min. Helium was used as carrier gas, and the column head pressure was 10 psi.

At the end of each run, while the reactor was still at the reaction conditions, the water in the reactor was discharged to a collection vessel and the dry soil was taken out of the reactor after that. Ten grams of this treated soil was extracted again by methylene chloride in an ASE 200 extractor as mentioned earlier. Extraction by ASE takes about 15 min and uses much less solvent. Extraction performances are comparable or better than 18 h soxhlet extraction [26–28]. The difference between the initial and the final soil analyses gives the extent of PAHs removal from the soil. The difference between the total amount of PAHs removed (soil analysis difference between before and after extraction) and the amount of PAHs dissolved in water (water sample analysis) gives the amount of PAHs destructed by oxidation.

2.3. Hot water extraction combined with oxidation

These series of extraction/oxidation experiments are basically similar to the hot water extraction experiments explained above. An oxidizing agent was added to the water/soil mixture instead of nitrogen. The oxidizing agents were air, oxygen and hydrogen peroxide. When air or oxygen was used, the amount of soil placed in the reactor was slightly less in order to make room for excess oxygen needed for PAHs' oxidation. However the soil/water ratio was kept constant at 45–50 g soil to 200–220 ml water as before. Air or oxygen was used to pressurize the vessel instead of nitrogen. In case of hydrogen peroxide, while keeping the soil/water ratio the same as before, a part of the water was replaced by an equivalent volume of 30% hydrogen peroxide. The hydrogen peroxide volume was calculated to release oxygen in excess of required amount for total oxidation.

3. Results and discussion

3.1. Spiked soil experiments

Table 2 shows the operating conditions and initial concentrations for different experiments on spiked soil. Pressures are the initial pressures at room temperature. When reactor vessel was heated, the pressure range was from 1500 to 1900 psig. The feed concentrations

Table 2
Operation conditions and initial concentrations of PAHs on the spiked soil

Run ID	Temperature (°C)	Pressure (psi)	Soil weight (g)	Water (ml)	Initial PAH concentrations in soil (µg/g soil)			
					Phenanthrene	Anthracene	Chrysene	Benzo(a)pyrene
230-N ₂	230	425	49.96	220	399	448	525	386
250C-N ₂	250	400	50.05	220	399	448	525	386
270C-N ₂	270	400	50.14	220	399	448	525	386
250C-air	250	450	45.87	200	399	448	525	386
250C-O ₂	250	450	45.54	200	399	448	525	386
250C-H ₂ O ₂	250	450	50.22	217	372	409	433	261

Table 3
Concentration of PAHs in spiked soil before and after the extraction with hot water and using nitrogen as pressurizing gas with no oxidant

Soil sample	Concentration of PAHs in soil (µg/g soil)			
	Phenanthrene	Anthracene	Chrysene	Benzo(a)pyrene
Untreated soil	399	448	525	386
Treated soil at 270C-N ₂	2.74	1.89	37.41	42.18

for these experiments are calculated as the average of several extractions of different untreated soil samples to get a representative concentrations of PAHs in the spiked soil. Later in experiments with aged soil, it was decided to measure feed concentrations from a representative part taken from the sample before adding it to the extraction vessel.

Table 3 and Fig. 3 compare the PAHs' concentrations in the untreated spiked soil and soil after hot water extraction at 270 °C under nitrogen atmosphere. It is clear that for lighter PAHs, phenanthrene and anthracene, the extent of extraction is almost to completion (<3 mg/g soil), while for heavier ones, chrysene and benzo(a)pyrene, although results are encouraging, the remaining amounts in soil are still high (chrysene concentration ~37.5 mg/g soil, and benzo(a)pyrene concentration ~42 mg/g soil). This is due to lower

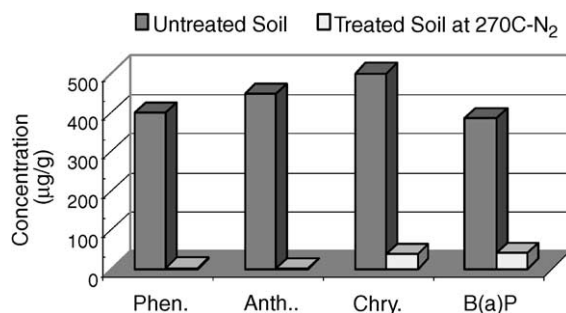


Fig. 3. Concentration of four PAHs in soil before and after extraction with water at 270 °C under nitrogen atmosphere.

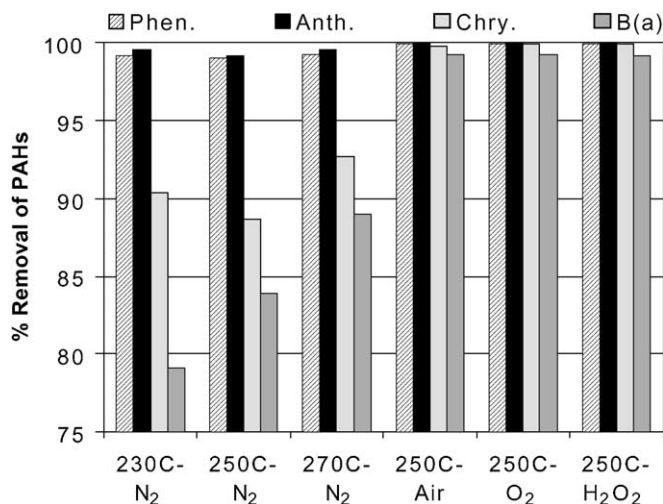


Fig. 4. Extent of removal of PAHs from soil at different operating conditions.

solubility of these heavier substances in the hot water at that temperature resulting in low partition coefficients. However, it should be noted that this is a single equilibrium stage batch extraction, even for chrysene and benzo(a)pyrene percent extraction is about 90% (Fig. 4). Thermodynamically, if one assumes that the partition coefficients will remain the same, a couple more equilibrium extraction stages would result in percent removal in excess of 99.9% even for benzo(a)pyrene.

As mentioned above the experiments were done in two series: first, extractions under inert gas atmosphere at different temperatures, and second, extraction at 250 °C using different oxidizing agents. Extents of PAHs removal from soil under all experiments are shown in Fig. 4. It can be seen that extraction efficiencies (difference between concentrations in untreated and treated soil) for phenanthrene and anthracene are above 99% for all treatments, while they decrease as the molecular weight goes up. The extraction efficiencies for chrysene are from 88.7 to 92.7% for extraction under nitrogen atmosphere (without oxidation) and increases to 99.80–99.96% when using oxidizing agents. For benzo(a)pyrene these ranges are 79–89 and 99.2–99.3%, respectively.

Fig. 5 shows the water phase PAH content after each treatment, expressed as weight of each PAH per gram of initial soil added in the extraction vessel. This shows how much of each PAH, which initially were in the soil, could be found in the water phase at end of the experiment. As expected the concentrations of PAHs in water increased with the operating temperature to a level near the initial contamination level in the soil for extraction under nitrogen atmosphere indicating that extracted PAH from soil are now in the water phase. On the other hand, when an oxidant is used, PAH concentrations in water sharply fall down to levels near zero concentration indicating destruction of the extracted components. Among the different oxidizing agents used, H₂O₂ is a better oxidant than O₂, which is better than air. The liquid extract had a brown color when extraction was done under nitrogen, which became light brown with air, pale yellow with oxygen and almost colorless (very pale

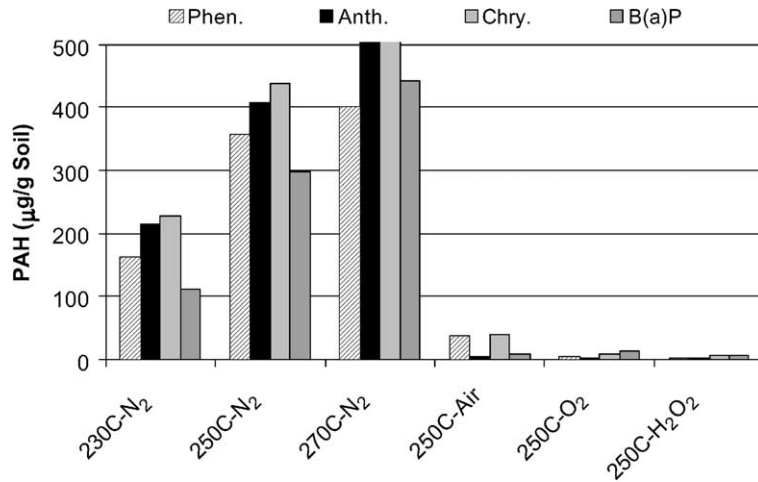


Fig. 5. PAHs content of water after each treatment of spiked soil.

yellow) with H₂O₂. For hydrogen peroxide the range of residue PAHs in the soil was from 0.9 to 6.9 mg/g soil. It may be thought that the oxidizing power would be proportional to oxidizing agent concentration. Hence using a larger excess of oxidizing agents may decrease the residual PAH concentrations in soil. It should also be noted that in addition to the spiked PAHs, soil organic matter is also extracted and oxidized, which explains the color change.

Extent of organic oxidation was calculated based on the material balance on each PAH. It is assumed that all disappeared material is oxidized to non-organic products. One indicator supporting this assumption was that no new peaks were observed in the chromatograms. Results are shown in the Fig. 6. The extent of oxidation is highest for anthracene and lowest

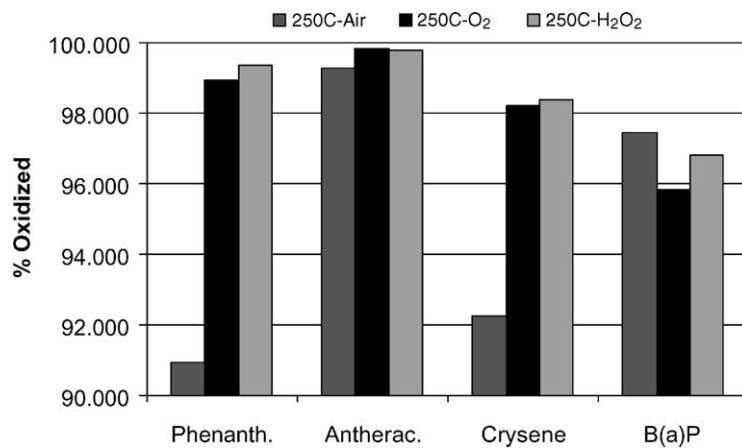


Fig. 6. Extent of organic oxidation in spiked soil.

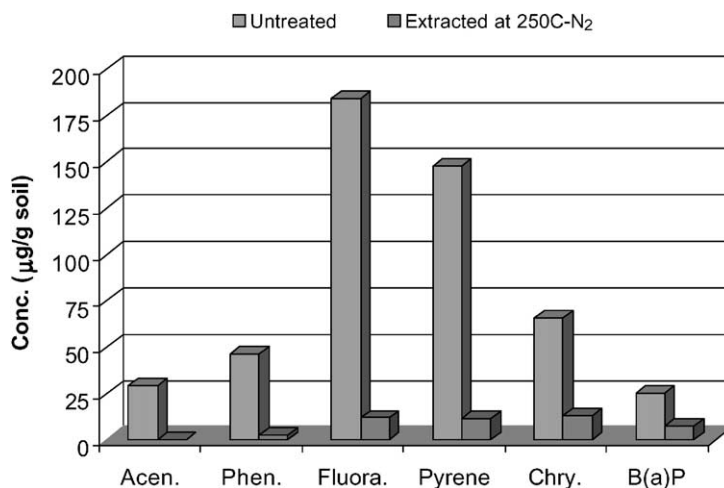


Fig. 7. Concentration of PAHs in aged soil before and after extraction with water at 250 °C under nitrogen atmosphere.

for benzo(a)pyrene. Longer reaction times and/or higher oxidant concentrations should result in almost complete mineralization of the PAHs.

3.2. Aged soil experiments

Before running each experiment, a representative sample of soil was taken for extraction with ASE200 extractor and then the sample was identified by gas chromatograph analysis. For all analyses concerning aged soil, gas chromatograph was calibrated with a standard containing 16 priority PAHs. Concentrations of 16 PAHs in aged soil is shown in Table 1. Six out of those sixteen PAHs were selected for treatment studies as is described earlier.

Fig. 7 compares the PAHs concentrations in the untreated aged soil and soil after hot water extraction at 250 °C under nitrogen atmosphere. This shows a significant reduction in each PAH over the original concentration in the soil. However, due to difference in concentrations of PAHs in the aged soil sample to find a clear trend, the same data are presented in Fig. 8 in the form of percentage of each PAH remaining in the soil after extraction, based on its concentration in the untreated soil. It is clear that for lighter PAHs, like acenaphthene, the extent of extraction is almost to a completion (less than 1% residue), whereas it is between 6 and 8% for intermediate ones like phenanthrene, fluranthene and pyrene. For heavier ones like chrysene and benzo(a)pyrene, although results are encouraging, the remaining amounts in soil are still high (chrysene residue ~20%, and benzo(a)pyrene residue ~30%). Fig. 9 compares the extent of PAH removal from aged soil by extraction-only and by two extraction/oxidation methods. By comparing Figs. 4 and 9, it is clear that extent of PAH removal from aged soil by combined hot water extraction and oxidation is comparable or even better than those of spiked soil. It should be noted that the concentrations of PAHs in the aged soil were lower than those in the spiked soil. Extent of organic oxidation using oxygen

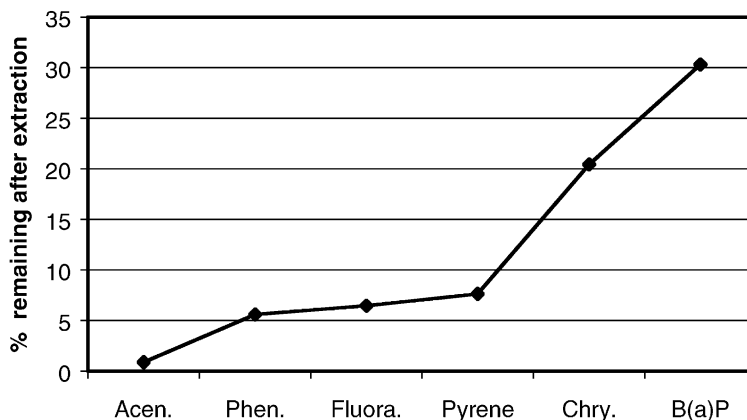


Fig. 8. Percentage of each PAH remaining in the soil over the original concentration, after 3 h extraction at 250 °C and under nitrogen atmosphere.

and hydrogen peroxide for aged soil is shown in the Fig. 10. Calculation method is the same as that for spiked soil and in this part no new peaks were observed in the gas chromatograph charts. While the extent of oxidation for acenaphthene is almost to a completion, it takes a general downward trend based on the increasing molecular weight for the other PAH components. The question about oxygen being a better oxidizing agent than hydrogen peroxide, depends on the individual PAH and no general conclusion could be reached.

Finally, it should be noted that the reported data are taken in a batch process. We had to first stop the mixer for 15–20 min for settlement of the soil, take the water samples and then evacuate the water from the vessel to remove the extracted soil for analysis. Stopping the mixer normally resulted in 10–20 °C temperature drop in the vessel. Then until the

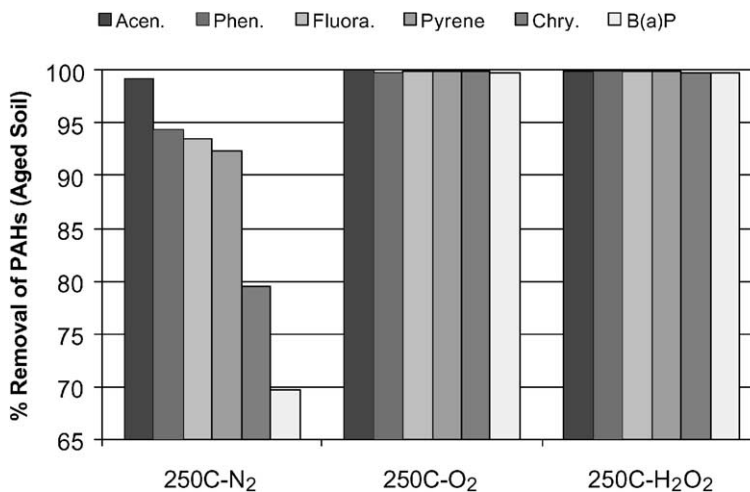


Fig. 9. Extent of removal of PAHs from aged soil at different operating conditions.

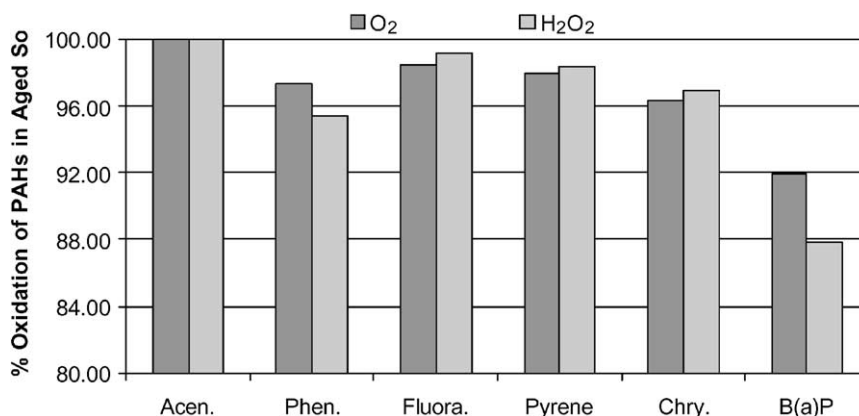


Fig. 10. Extent of organic oxidation in aged soil.

water in the vessel is evacuated, it could take about 45 min to 1 h to return to the operating temperature since mixer was stopped. In addition, during water drainage, pressure was also decreasing. At some point the pressure inside the vessel could be below the vapor pressure of water inside the vessel, which results in exit of remaining water as steam. All of these result in the decrease of solubility of PAHs in hot water, hence during this process it is quite possible that some of the extracted PAHs could precipitate from the water phase on to the soil. Hence the reported data, in fact, represent the worst case scenario. Actual extractions could have been higher at all conditions since we expect some recrystallization of the PAHs during water evacuation. In a continuous process, it would be possible to get much lower residual concentrations of PAHs in the soil.

Acknowledgements

This project has been funded by Grant 069TAM0769 in part with Federal Funds as part of the program of the Gulf Coast Hazardous Substance Research Center which is supported under cooperative agreement R815197 with the United States Environmental Protection Agency and in part with funds from the State of Texas as part of the program of the Texas Hazardous Waste Research Center. The contents do not necessarily reflect the views and policies of the US EPA or the State of Texas nor does the mention of trade names or commercial product constitute endorsement or recommendation for use. We specially thank to Professor K.C. Donnelly and Dr. L.Y. He for providing the soil sample and for consultations, and to Professor R.L. Autenrieth and Dr. T. McDonald for giving access to their ASE 200 extractor unit and helping in analytical work.

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