

Integrated treatment of PAH contaminated soil by soil washing, ozonation and biological treatment

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Abstract

The aim of the study was to optimise three different treatment methods and to find out if the integration of soil washing, ozonation and biological treatment could be a feasible method for the remediation of aged oil contaminated with PAHs. Three different ozone doses and soil washing were studied in different pHs in order to assess their effect to the degradation and enhancement of biodegradability of PAH in the soil and water phase. Main target of the study was to find out a method with which the PAH concentrations could be decreased below the Finnish guideline level for total PAHs. In this case, the initial concentration of PAHs was 1200 mg kg⁻¹ and therefore almost 85% degradation of PAHs was required. Any of the methods studied was not able to reach this target level alone, but by several combinations of the methods studied achieved 90% reduction of PAHs. The consumption of ozone was 5–10 times lower in the integrated treatments of soil washing, ozonation and biological treatment than without prewashing.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) constitute a group of hydrophobic organic compounds (HOCs) [1], which are related to the incomplete oxidation and combustion [2] and also to the uncontrolled environmental pollution practically present everywhere. The PAHs structures differ in the number and placement of aromatic rings and their physicochemical properties can vary widely [3].

Soil extraction and washing are potential and economically feasible technologies for cleaning the contaminated soils on-site. A lot of research has been done to investigate the effectiveness of these techniques for removal of HOCs from contaminated soils and the effect of soil washing for the biodegradability of PAHs (e.g. [4–6]).

Besides the bioavailability, the efficiency of the bioremediation depends also on toxicity, environmental conditions and the presence of suitable microorganisms. Many microorganisms,

including bacteria, algae and fungi have been shown to be able to degrade PAHs [7–14]. The degradation of PAHs by composting and by land treatment has also been studied (e.g. [15–17]). Even though bioremediation is one of the most cost-effective technologies, most of the studies have resulted decreased concentrations of PAHs with 2–4-ring in their molecular structure, but no reduction was observed of 5–6-ring PAHs since 5- and 6-ring PAHs are very recalcitrant due to their low water solubility and the resonance energies of their structure [7,11,17–19]. Final removals after biological treatment based on the sum of all PAHs are observed to be in the range between 50 and 70% [17]. The results are not consistent with the studies, in which surfactants have been employed to increase the bioavailability and mobilization of bounded PAHs [4–6,16].

Chemical oxidation is quite widely studied method for the treatment of waters and slurries including refractory compounds. The effect of ozonation for the degradation and kinetics of soil contaminated with PAHs has also been studied [20–24]. Among technologies for the removal of PAHs, ozonation is a good alternative, since PAHs, due to their molecular structures, react very fast with ozone. The ozone (O₃) is attacking and degrading aromatic organic pollutants in the aqueous phase, which broke the

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hydrophobic PAHs into more simple, soluble and biodegradable form via aromatic ring cleavage and/or via hydroxylation of the aromatic rings due to radical reactions [7,20–23].

pH has a great influence on the ozonation of PAHs in the liquid media. The rate of PAHs disappearance is usually decreased when the pH is increased [24]. Against these results can be suggested that direct ozonation is the main reaction of PAHs decomposition, and that in alkaline environment more hydroxyl radicals appear due to ozone decomposition and degradation of PAHs is slower [25]. In direct ozone reactions each PAH-molecule needs two ozone molecules to disappear, but intermediate compounds can consume much more ozone [24]. Also the organic (like humic substances) and inorganic (like carbonates) matters of matrix may act as a scavengers and consume ozone [22,26].

The studies of the integrated ozonation-biological treatment for different PAHs have shown that ozonation improved the bioavailability and biodegradability of the contaminants rendering PAHs more soluble and thus biologically accessible [1,26–28]. At higher ozone doses, biodegradable compounds, both initially present and formed as a result of ozonation, compete for the available ozone [22,29–33]. Therefore it is not always worthwhile to increase the ozone dose too much, and it is important to determine the optimum ozone dose so, that a higher fraction of dissolved matter can be eliminated, e.g. by, usually more economical, biological post treatment. The amount of dissolved humic matter is usually increased during ozonation, which implies that ozone break down the soil matrix and aid the dissolution of particulate and colloidal humic matters from the soil surface, which also release PAHs to the aqueous phase [1]. So, a chemical pre-treatment is also useful for promoting the soluble intermediates from otherwise highly insoluble PAHs.

The aim of the study was to optimise and integrate soil washing, ozonation and biological treatment in an economically feasible way for the remediation of the aged soil contaminated with PAHs. The effect of ozonation was studied in three different pH values (3, 7 and 10) for the untreated soil, pre-washed soil and for the washing water separated after soil washing. All samples were biologically post-treated. Compared with the Finnish guideline value for the soil, 200 mg PAHs kg⁻¹, almost 90% removal of the initial concentration of total PAHs (1200 mg kg⁻¹) should have been obtained. Most of the experiments were done in laboratory scale, but also the soil washing and treatment of washing water was repeated in a pilot-scale.

2. Materials and methods

2.1. Description of the site and the characteristics of the aged PAH-contaminated soil

The soil studied was collected from the wood impregnation plant of Haapamäki, owned by the Finnish State Railways. The industrial impregnation activity started at the site in 1956 and the capacity of the plant is 35,000 m³ year⁻¹ of sleepers which is equivalent to (around) 350,000 sleepers/year. The plant has produced almost all the impregnated sleepers needed by the Finnish railways. The soil studied was collected from the vicinity of the

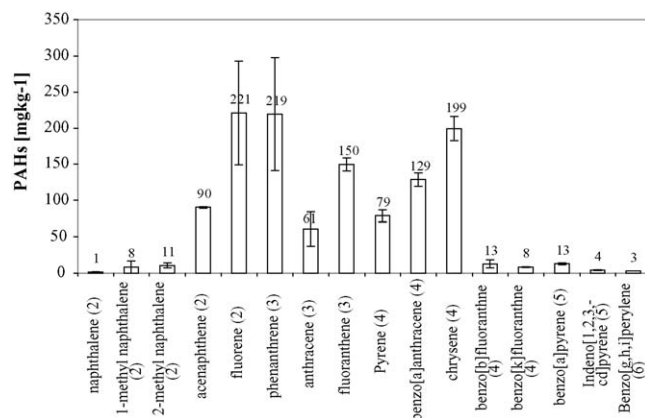


Fig. 1. The concentrations of 16 different PAHs analysed of the sieved <4 mm soil studied.

creosote loading station where the soil has been classified highly contaminated. Since the soil was very heterogeneous containing, e.g. big rocks, the soil was sieved for the laboratory study.

The concentrations and standard deviations of 16 different PAHs analysed in <4 mm diameter soil fraction is represented in Fig. 1. The moisture content of the soil was 8% and the amount of organic matter was quite high, 2%. The total PAH-concentration was about 1200 mg kg⁻¹, which is about 10% of the organic matter in soil. The relative amount of 2- and 4-ring PAHs was about 97% of the total amount of PAHs analysed. Less than 2% of the PAHs analysed had 5- and 6-aromatic rings in their structure.

2.2. Integrated soil washing, ozonation and biological treatment

The schematic diagram of the integrated treatment of PAH contaminated soil involving sequential soil washing, chemical oxidation and biological degradation is represented in Fig. 2.

2.3. Soil washing experiments

The pre-screened soil (<4 mm) was washed in soil:water mixture of 1:2 (w:w) in three different pH values (3, 7 and 10). A rotary shaker agitated the soil–water mixture for 45 min in glass containers with Teflon caps. After mixing, the soil and water phases were separated by decantation. Most part of the detached fines and organic matter was transferred into the liquid phase. Some of the results of laboratory tests were transferred into the pilot scale in which 25 kg of soil was first washed with 50 l of water, pH adjusted to 10. The washing was repeated with 25 l of water without pH adjustment. The soil and water phases were separated.

2.4. Ozonation

The schematic diagram of the ozonation apparatus is represented in Fig. 3. Essentially the same equipment was used both in the laboratory and pilot scale experiments. The laboratory scale ozone tests were carried out in a glass container

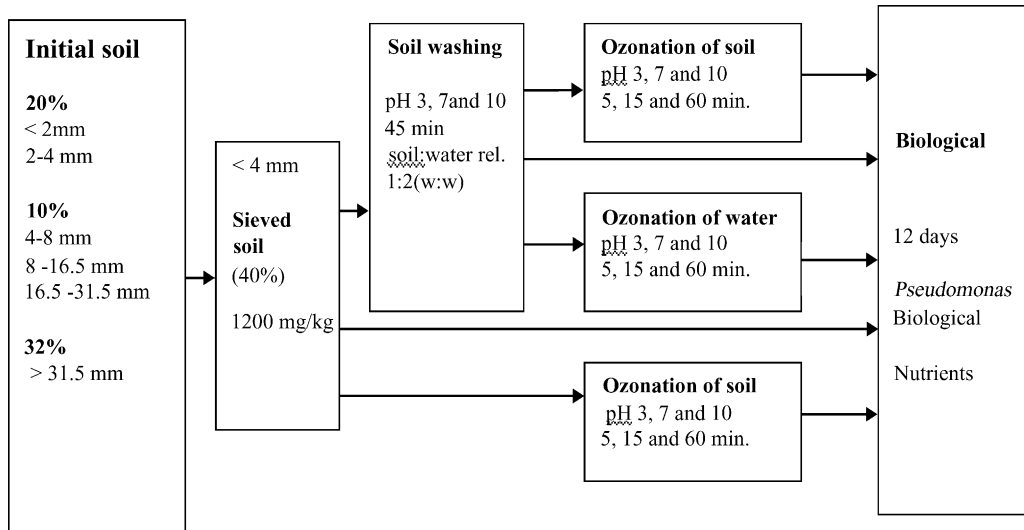


Fig. 2. The diagram of the different integrated processes studied. Only the results of the treatments for <4 mm soil fraction are represented.

(volume 21), which was agitated in a vertical shaker (200 rpm). Ozone was generated with a Pacific Technology generator from synthetic dry air. The influent ozone concentration was about 2000 ppm and the flow rate was 5 l min^{-1} . The ozone concentration in the gas phase was measured from the gas streams of influent and effluent by using a Dasibi 1008 analyser. The ozone analyser was connected to a computer, which calculated automatically the amount of fed ozone (mg l^{-1} of water) and transferred ozone (%). The ozone doses versus organic matter were $0.6\text{--}0.93 \text{ mg O}_3 \text{ mg}_{\text{org}}^{-1}$ ($53\text{--}790 \text{ mg l}^{-1}$) for the unwashed soil and much lower, $0.02\text{--}0.34 \text{ mg O}_3 \text{ mg}_{\text{org}}^{-1}$ ($20\text{--}287 \text{ mg l}^{-1}$)

for the washed soil. The ozone dose for the liquid phase was $0.16\text{--}2.9 \text{ mg O}_3 \text{ mg}_{\text{org}}^{-1}$ ($36\text{--}640 \text{ mg l}^{-1}$). The ozone values represented are the consumed doses. The transfer efficiency of ozone, varied in the different test series due to the organic matter content in the soil samples. The laboratory scale ozonation tests were performed in three different pH values for untreated and pre-washed soil–liquid mixtures and for washing water separated after soil washing experiments.

The pilot scale ozonation tests were done in a semibatch mode for washing waters from the pilot scale soil washing experiments. Pasific Technology G-22 generator generated the ozone.

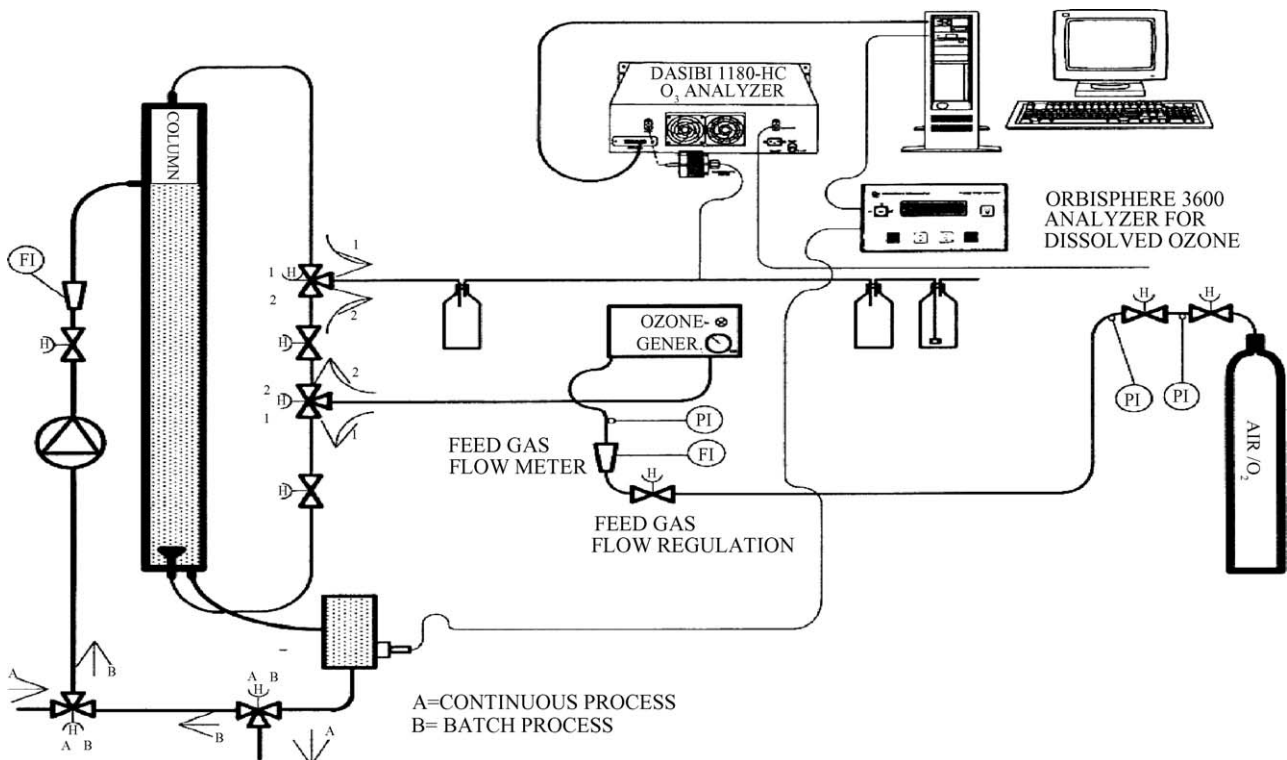


Fig. 3. A Schematic diagram of ozonation apparatus.

The influent ozone concentration was about 5000 ppm and the gas flow rate was 7.5 l min^{-1} . The water was circulated through a dissolved ozone measurement chamber where residual dissolved ozone was measured by Orbisphere 3600 analyser. The ozone concentration was increased in relation of initial COD up to a concentration of $0.5 \text{ mg O}_3 \text{ mg COD}^{-1}$.

2.5. Biodegradation tests

The respirometric biodegradation tests were done in the dark incubation flasks (WTW BOD Trak Oxitop) for the initial soil and treated soil and water samples. The method provides a direct measurement of the oxygen consumed by microorganisms in a closed vessel in which the inbuilt datalogger records and calculates BOD readings in every 4 h. The amount of PAH contaminated soil in the incubation flasks was 20 g. In addition, 77.23 g of PAH-free soil and 8 mm long glass pipes about 22 g were added. The glass pipes were added to avoid the anaerobic conditions during the incubation. The moisture content was adjusted to 30% with nutrient water (mixture done according to SFS 5508). The inoculums were prepared by mixing 8 g of compost from municipal composting plant and earlier isolated *Pseudomonas* sp. into a 100 ml of sterile 1% NaCl–water and added with the nutrient water. The samples were incubated in the dark at $20 \pm 0.5^\circ\text{C}$ for 12 days. The same procedure was used for the water sample biodegradation tests. The volume of PAH containing water was 40 ml and the amount of nutrient/inoculums water added was 325 ml. If needed, pH of the samples was adjusted to 6–8. During incubation, the water samples were mixed with a magnetic stirrer.

2.6. Analytical methods

The amount of total solids (dry matter) and organic matter in water and soil samples were determined according to SFS 3008. The amount of PAHs was analysed according to the Nordtest method (Nordtest TechRep 329). Before the extraction (sodium pyrophosphate and toluene) the internal standard (Supelco: Semivolatiles Internal Standard Mix) was added into the vial and the mixture was agitated in a shaking table for 16 h in sealed glass bottles. The extract was analysed by GC/MS (Hewlett Packard HP 6890/5972) equipped with HP-5 column ($30 \text{ m} \times 0.25 \mu\text{m} \times 0.25 \mu\text{m}$, with 5% phenyl siloxan film). The feed gas (helium) flow was 1 ml min^{-1} . The splitless injection

was done in 40°C . After injection, the oven temperature was increased from $25^\circ\text{C min}^{-1}$ to 140°C and from $10^\circ\text{C min}^{-1}$ to 320°C . The concentrations of 16 different PAHs were determined by comparing the chromatograms with 3 different calibration curves (Supelco: Polynuclear Aromatic Hydrocarbons Mix) and the response of known amount of internal standard. Approximately every fifth sample was analysed duplicate, the averages of the standard deviations for single PAHs are shown in Table 1.

3. Results and discussion

3.1. Ozonation

3.1.1. Ozone transfer

The ozone transfer efficiencies during ozonation of the washed and unwashed soils in different pH values are represented in Fig. 4. The amount of transferred ozone was the highest (about 70%) for the soil without washing. The transfer-% during the ozonation of the pre-washed soil was much lower. When pH was not adjusted, the ozone transfer efficiency was less than 10% after 20 min of ozonation of the unwashed soil. In acidic environment, the ozone transfer-% increased from 20 to 30% after about 25 min ozonation. The soil washing had removed part of the organic matter and fine particles to the water phase, and the remaining inorganic fraction of soil was fairly inert for ozone.

3.1.2. Solid matter and volatile organic carbon

The dry matter content of the untreated soil was 92%, and of that the amount of organic matter was 1.7%. After washing and during the ozonation of unwashed soil the organic matter

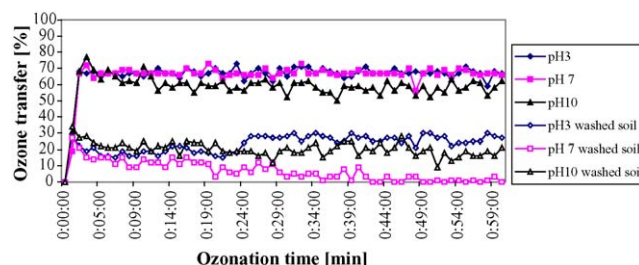


Fig. 4. The ozone transfer efficiencies during ozonation of washed and unwashed soils in different pHs.

Table 1
Averages of standard deviation for analysed PAHs ($n = 5-9$)

	Average of standard deviation	Minimum	Maximum		Average of standard deviation	Minimum	Maximum
Naphthalene	0.101	0.002	2.413	Pyrene	7.672	0.453	10.299
1-Methyl naphthalene	0.765	0.051	1.945	Benzo(a)anthracene	4.867	1.323	8.945
2-Methyl naphthalene	0.468	0.051	1.482	Chrysene	10.001	1.506	21.325
Acenaphthene	3.933	0.122	1.085	Benzo(b)fluoranthene	2.065	0.272	5.422
Fluorene	10.037	1.355	22.170	Benzo(k)fluoranthene	1.634	0.016	4.229
Phenanthrene	6.030	0.368	11.623	Benzo(a)pyrene	0.655	0.064	1.267
Anthracene	3.569	0.807	8.994	Indeno(1,2,3,-cd)pyrene	0.238	0.052	0.509
Fluoranthene	11.972	2.161	21.773	Benzo(g,h,i)perylene	0.138	0.003	0.326

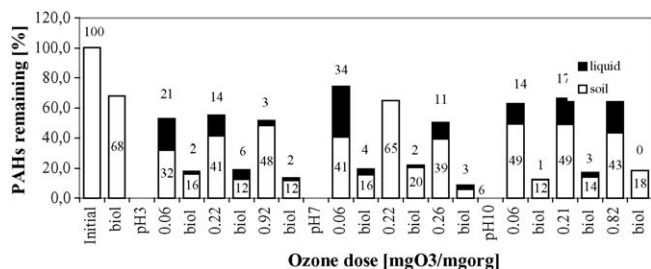


Fig. 5. The effect of pH and ozone doses for the mass balances of PAHs remaining in the liquid and solid phases after ozonation and biological treatment of PAH contaminated soil. The initial concentration was 1580 mg kg⁻¹ PAHs.

content of a dry matter decreased about 40% in a soil phase. The ozonation of washed soil did not effect notably to the amount of the organic matter content.

3.1.3. Ozonation and biological treatment of the unwashed soil

Fig. 5 shows the relative amount of PAHs remaining in the soil- and water phases compared to the untreated soil in different pH values and ozone doses after ozonation and biological post-treatment. After 12 days of biological degradation the amount of untreated soil's extractable PAHs decreased just about 30%.

When the degradation of PAHs by ozonation alone is considered, there were no notably differences in the degradation with the highest and lowest doses, the average degradation/transformation of PAHs in soil was 50–60%.

The ozonation enhanced the biodegradability of the soil PAHs. When biological step followed the ozonation, the overall degradation was always more than 80% and up to 94% with the highest ozone dose in acidic pH. These results are in congruence with the literature, which indicates that ozonation can enhance biodegradability of PAHs by desorbing them from the soil matrix into more bioavailable form.

3.2. Soil washing, ozonation and biological treatment of soil

The relative amounts of extractable PAHs after soil washing, ozonation, and biological treatment are presented in Fig. 6. The relative amount of total PAHs in the soil was decreased about 50% in the soil washing where the PAHs were transferred into the washing water. The ozonation of washed soil was not very

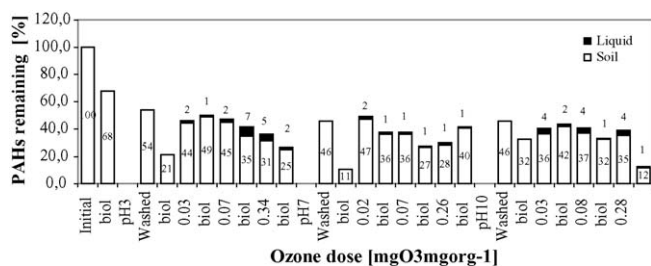


Fig. 6. The effect of pH and ozone doses for the mass balances of PAHs remaining in the liquid and solid phases after ozonation of pre-washed soil:water mixture and after biological treatment. The initial concentration of total PAHs was 1580 mg kg⁻¹.

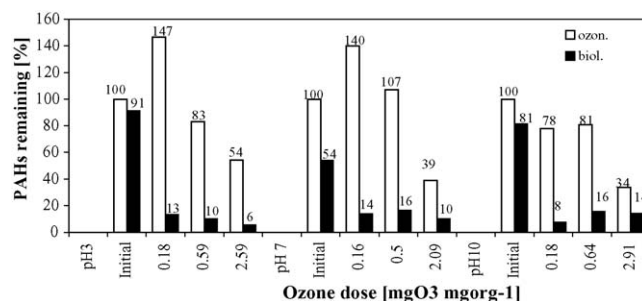


Fig. 7. The effect of pH and ozone doses for the mass balances of PAHs remaining in the liquid phase after ozonation and after biological treatment of washing water. The initial concentration of total PAHs was about 200 mg l⁻¹.

useful since most of the oxidable material had been removed into the water. During ozonation, the amount of PAHs in the soil decreased to just 0–20%. The ozonation seemed to have only slight or even inhibitive effect on the biological degradation of the PAHs in the soil. This can be explained by the removal of the most bioavailable part of PAHs and organic matrix of the soil in the washing stage.

After biological treatment of the washed soil, the relative amount of PAHs remaining in the soil was decreased more than after the ozonation, except by the highest ozone dose (0.26 mg O₃ mg_{org}⁻¹) in pH 10.

3.3. Ozonation and biological treatment of washing water

The relative amounts of extractable PAHs in the soil washing water after ozonation and biological treatment can be seen in Fig. 7. The PAHs in the washing water were recalcitrant to the biological treatment, which can be explained by the assumption, that they were probably strongly bound into the colloidal matter and fine particles. This hypothesis is supported by the observation that during the ozonation in neutral and acidic environment, the total amount of extractable PAHs seemed to increase more than 40%, in the lower ozone doses. This might be due to the better extraction efficiency of PAHs, which are trapped, e.g. in the humic polymer which are released after a mild ozonation. This phenomenon is in the consistence in the study done by Eschenbach et al. [34]. The degradation of PAHs by ozone required higher ozone doses. On the highest ozone doses the relative amount of total PAHs in the washing water was decreased approximately 45–65%.

The best results were obtained after the biological post-treatment step. Ozonation improved the biodegradability of the washing water. Without ozonation only 10–45% of PAHs degradation in the washing waters was achieved, while even with the lowest ozone dose, the amount of PAHs remaining after 12 days of incubation was only 6–16% of initial.

3.4. Biodegradation of organic matter in soil

Besides of the concentration of PAHs, also the biodegradable part of the soil was monitored by BOD measurement. Daily BOD values analysed during the 12 days of incubation of an ozonated (in pH 7) unwashed and pre-washed soils

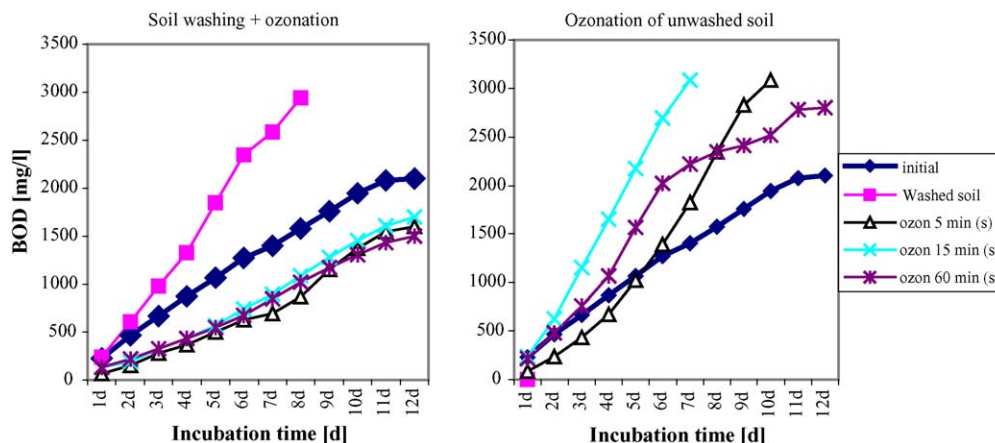


Fig. 8. The BOD during 12 days of biological treatment in soil phase after soil washing and ozonation done in pH 7.

are represented in Fig. 8. Soil washing alone enhanced the biodegradability of organic matter in the soil phase significantly but after by ozonation the biodegradability and/or the amount of biodegradable matter in soil phase was lower than in initial soil matrix. Ozonation of unwashed soil enhanced the biodegradability of the organic matter. This trend was increased to a certain level and after that, further ozonation started to decompose also the biodegradable organic matter.

4. Summary

The concentrations of the sum of analysed PAHs remaining achieved with the selected two treatment trains are represented in Fig. 9. The purification of a soil under the target level ($200 \text{ mg PAHs kg}^{-1}$ in soil) was not achieved with any of the individual methods studied under the used conditions. By combining different methods the target value could be attained. Soil washing transferred approximately 50% of soil PAHs into the washing water and also improved the biodegradability of soil PAHs, especially when the washing was done in the pH 7 and 3. After biological treatment of soil, the concentration of PAHs was only 10% of the initial soil and half of the PAHs were transferred into the washing water. The improvement of the biodegradation is assumed to be mainly a consequence of increased mobilization of PAHs from the aged soil matrix, which contribute the biodegradation.

After biological treatment of ozonated soil samples, 90% reduction of PAHs was achieved. The target was attained only

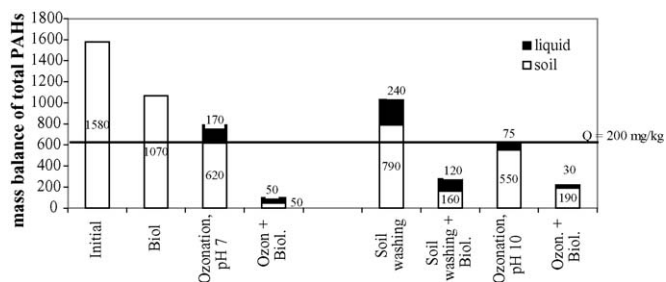


Fig. 9. Concentrations of PAHs the soil and liquid phases after ozonation + biological treatment and soil washing + ozonation + biological treatment.

after ozonation done in pH 3 for unwashed soil and integrated soil washing + ozonation in pH 10 with the highest ozone dose studied.

Unwashed soil included more organic matter competing with ozone, and thus less ozone is available for the degradation of PAHs. The ozone dose needed was 50–70% smaller for the washed than unwashed soil. The study also endorse the other studies reported by the literature, that degradation of PAHs in soil by ozonation is more efficient in acidic and neutral environment than in alkaline conditions.

5. Conclusions

When selecting the most suitable method for the purification of aged soil contaminated by PAHs, the most important parameters are the initial contaminant concentration and the required purification efficiency. If 50% reduction of PAHs is sufficient, all the studied methods are adequate. However, by integration of different methods studied, the desired 90% target value could be obtained. Soil washing and ozonation with small ozone doses increased the biodegradation and/or mobilization of the PAHs, which makes the biological post treatment efficient. The study demonstrates that integrated soil washing/ozonation with biological post-treatment can be an economically efficient method by lowering the consumption of ozone, when designing the process for soils contaminated with PAHs.

Main conclusions and suggestions for further studies are:

- the biodegradability of PAHs in aged soil was 30% even after addition of nutrients and inoculum;
- soil washing and ozonation increased the biodegradation of PAHs although pH adjustment in full scale applications will increase total costs during operation and restrict post-treatment and reuse of soil;
- 90% removal of PAHs was obtained by biological treatment of ozonated soil even though the possible formation of toxic oxidation intermediates should be detected;
- soil pre-washing did not improve the degradation of PAHs during ozonation but it decreased the amount of ozone dose

needed 50–70% and sifted the ozone demand into the water phase;

- much less ozone for the 90% level of purification was required when the pre-washed soil and washing water were biologically post-treated;
- the more detailed analysis of different PAHs, their intermediates and degradation products as well as impact of soil washing and ozonation on the PAHs “trapped” in the humic matter should be detected;
- the detailed economical cost analysis comparison with individual and alternation of integrated processes including practicability and feasible analysis.

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