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ADVANCED OXIDATION FOR GROUNDWATER REMEDIATION AND FOR SOIL DECONTAMINATION

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Abstract. The advanced oxidation process (AOP) used in this paper is based on EB irradiation of water in the presence and absence of ozone. The paper describes two distinct sets of experiments, one dealing with groundwater contaminated with perchloroethylene (PCE) and some genotoxic compounds, and the other dealing with soil contaminated with polycyclic aromatic hydrocarbons (PAHs). The combination of ozone and EB irradiation has shown to be able to mineralize trace amounts of PCE contained in groundwater in a single stage process without formation of any by-product to be disposed of. Moreover, experiments performed with real groundwater have demonstrated that the combined ozone/EB irradiation process is also apt for total removal of some genotoxic compounds detected in groundwater contaminated with PCE. The design of an ozone/EB irradiation plant for treating 108 m^3/h is presented. The issue concerning both the occurrences of genotoxic compounds in oxygen containing groundwater and possible processes for their removal is discussed. In the second part soil contaminated with PAHs has been treated in aqueous suspension using ozone and EB irradiation, respectively. Experiments were performed with low contaminated soil (total PAHs about 332 mg/kg soil). With an ozone consumption of 10 g O_3/kg soil a total PAH decomposition of about 21% was recorded. EB irradiation with a reasonable radiation dose of 100 kGy results in about 7% total PAH decomposition at room temperature and about 16%, respectively at 55 – 60°C. It was recorded that almost no transfer of the PAH takes place from the soil into the water when soil is merely suspended in water. Ozone mainly attacked the high molecular fraction (i.e. consisting of 5 or 6 aromatic rings) of the PAHs investigated while EB irradiation of the aqueous soil suspension mostly decomposed the lower fraction (i.e. consisting up to 4 aromatic rings).

SECTION A: OZONE/ELECTRON BEAM IRRADIATION FOR CONTROL OF PERCHLOROETHYLENE AND SOME GENOTOXIC COMPOUNDS IN GROUNDWATER

1. INTRODUCTION

Hydroxy free radicals are the strongest oxidants known to occur in water. Processes which generate hydroxy free radicals for the subsequent use of pollutant decomposition are generally referred to as "Advanced Oxidation Processes" (AOPs).

It has been found that the addition of ozone in combination with UV radiation or hydrogen peroxide can promote the decomposition of ozone and generate hydroxy free radicals. Combining hydrogen peroxide and UV radiation alone will achieve similar results as the aforementioned ozone based processes by generating hydroxy free radicals but with a considerably lesser yield [1]. What all these AOPs have in common is that the hydroxy free radicals originate from one single source only (ozone or hydrogen peroxide, respectively), i.e. the hydroxy free radical concentration obtained is comparatively low. On the other hand, groundwater very often is contaminated by rather small amounts of highly toxic compounds. To be effective in the treatment of groundwater containing trace amounts of pollutants high hydroxy free radical concentration is necessary. Combination of ozone with EB irradiation — which represents ionizing radiation — is able to produce much higher hydroxy free radical concentrations than the AOPs mentioned before because in this combination the hydroxy free radicals originate from two different but simultaneously working sources: (1) directly from the water to be purified by the action of the EB irradiation (so-called water radiolysis), and (2) from ozone decomposition accelerated by the reducing species formed during water radiolysis [2].

Table I shows the most important steps of all ozone based AOPs including also the combination of ozone and hydrogen peroxide. It clearly illustrates that O_3/UV and O_3/H_2O_2 processes are one and the same regarding hydroxy free radical generation: in the former, one is merely forming hydrogen peroxide in situ, rather than adding it from the outside. From this table it comes out clearly that two completely different mechanisms for OH free radical generation occur. UV radiation is absorbed by ozone (and, if present, by other organics absorbing UV at 254 nm) while the energy of the fast electrons is totally absorbed by water and not by any solute. In other words, under the conditions given, UV irradiation represents the direct effect of radiation while EB irradiation stands for the indirect effect of radiation.

TABLE I. OZONE BASED AOPs WITH REGARD TO THEIR MOST ESSENTIAL REACTIONS FOR HYDROXY FREE RADICAL FORMATION IN WATER

Irradiation of groundwater containing dissolved ozone	
UV - irradiation	Electron beam irradiation
INITIATION	
$O_3 \xrightarrow[254\ nm]{h\nu} O + O_2$	$H_2O \xrightarrow{e\text{-beam}} H_2O^+ + e^-$
PROPAGATION	
$O + H_2O \rightarrow H_2O_2$ $H_2O_2 \rightleftharpoons H^+ + HO_2^-$	$H_2O^+ + H_2O \rightarrow H_3O^+ + \mathbf{OH}$ $e^- + H_2O \rightarrow e^-_{aqu}$
O_3 - DECOMPOSITION	
$O_3 + HO_2^- \rightarrow O_3^- + HO_2$ $HO_2 \rightleftharpoons H^+ + O_2^-$ $O_3 + O_2^- \rightarrow O_3^- + O_2$	$O_2 + e^-_{aqu} \rightarrow O_2^-$ $O_3 + O_2^- \rightarrow O_3^- + O_2$ $O_3 + e^-_{aqu} \rightarrow O_3^-$
$O_3^- + H^+ \rightarrow HO_3$ $HO_3 \rightarrow O_2 + \mathbf{OH}$	
● Radiation is only absorbed **by ozone !**	● Radiation is only absorbed **by water !**
● The **only** source for OH free radicals is **ozone decomposition**.	● There are **two** sources for OH free radicals: - **water ionisation** **plus** - **ozone decomposition**

The latter produces hydroxy free radicals directly from water and simultaneously the promoters for ozone decomposition (by formation of the solvated electrons e^-_{aqu}) while the former only produces the promoter for ozone decomposition (by formation of hydrogen peroxide and its deprotonated anion, respectively). Accordingly EB irradiation must be more efficient regarding hydroxy free radical generation than any other ozone based process. Since UV irradiation of hydrogen peroxide is less effective than ozone/UV [1] it is obvious that ozone/EB irradiation is the most attractive AOP for groundwater remediation.

The present paper describes the design of the plant to be constructed and reports about pilot scale experiments performed to check the finished water regarding eventual formation of genotoxic compounds. Moreover, the mechanism in which the OH free radicals are generated in the ozone/EB process is discussed and compared with the OH generation in other ozone based AOPs.

2. EXPERIMENTAL

The polluted groundwater was transported from Bad Fischau-Brunn to Seibersdorf and treated in the existing 3 m^3/h pilot plant for continuous ozone/EB irradiation treatment of water. This facility has been already described elsewhere [6]. The groundwater to be treated contained 251 mg/L bicarbonate, 8 mg/L chloride, 15 mg/L nitrate and < 0.4 mg/L DOC and was polluted with about 61 µg/L PCE. Some preliminary experiments with synthetic Bad Fischau-Brunn groundwater (prepared from Seibersdorf tap water by dilution and subsequent adjustment to the corresponding solute content of the Bad Fischau-Brunn groundwater) have been performed, too, using the same facility.

PCE was measured by gas chromatography using cold on-column injection and electron capture detection.

To test water regarding genotoxicity a combination of three bioassays based on bacteria, plants and mammalian cells has been used. This combination represents a system with different genetic endpoints and the assays selected are complementary to one another with regard to various environmental genotoxins. As bacterial assay the Salmonella/microsome in vitro test (AMES test) with the strains TA 98, TA 100 and TA 102, with and without metabolic activation was used. As plant assay the Tradescantia clone 4430 in vivo was selected measuring the induction of micronuclei in the early pollen tetrads; in the in vitro test with mammalian cells the induction of micronuclei in cultures of primary rat hepatocytes has been determined. This combination of the three bioassays has been already used earlier to search for possible genotoxic effects in the aquifer of the "Mitterndorfer Senke". For more details see Ref. [3].

3. RESULTS AND DISCUSSION

Due to the results given in Fig. 1 a radiation dose of 200 Gy was found to be sufficient to reduce the PCE content in the water from about 61 µg/L to about 1 µg/L provided the ozone concentration in water before irradiation is ≥ 6 mg/L.

The unit of the radiation dose 1 Gray (Gy) is equivalent to an absorbed energy of 1 Joule/kg. Accordingly a radiation dose of 200 Gy means a very small energy transfer into the water. Would this energy of 200 J/L be converted totally into heat, which does not take place, the temperature of the water would increase by about 0.05°C only.

According to these dose and ozone requirements a 9 kW EB accelerator and 650 g O_3/h are necessary in theory to purify 108 m^3/h of the polluted groundwater. In reality a 20 kW accelerator and a 1 kg/h ozone generator have been chosen for the treatment process.

Figure 2 shows the block diagram of the planned 108 m^3/h water treatment plant in Bad Fischau-Brunn.

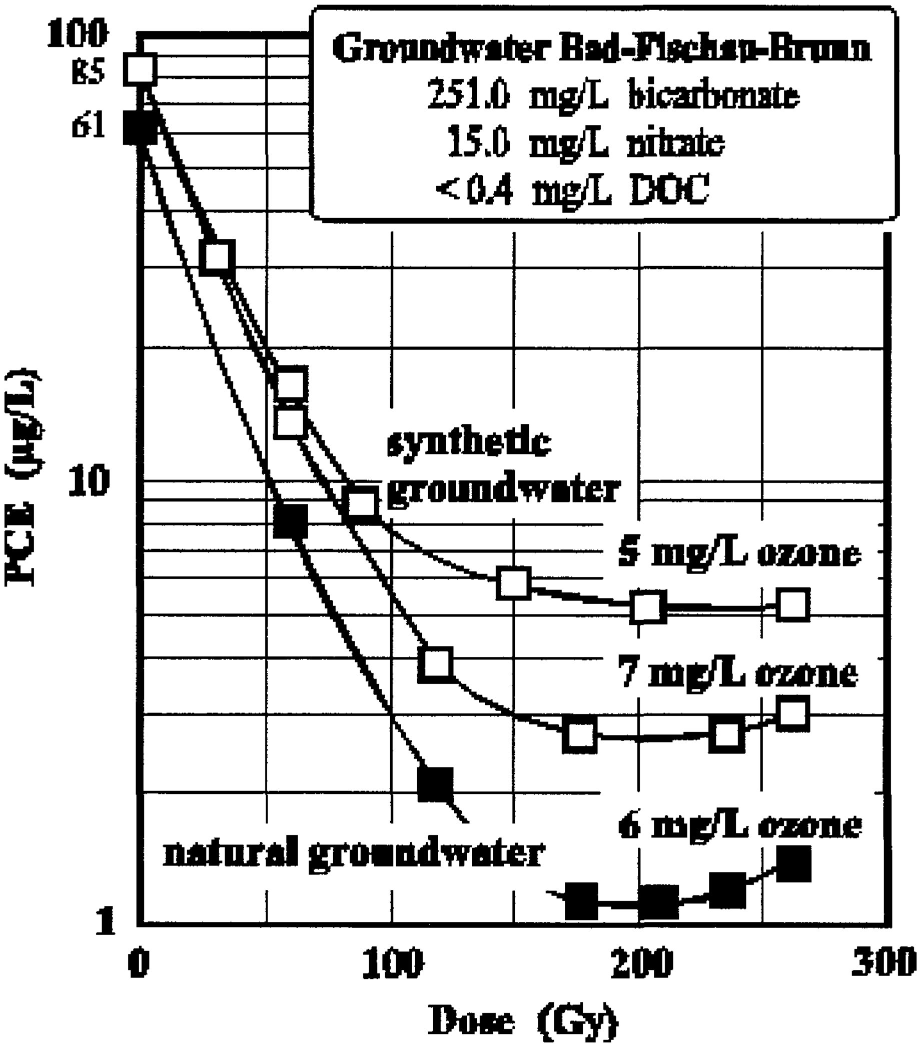


FIG. 1. Decomposition of perchloroethylene in Bad Fischau-Brunn groundwater by an ozone/EB irradiation treatment as a function of radiation dose and initial ozone concentration.

Ozone is made from pure oxygen, an ozone concentration of 13% per weight is planned. The ozone/oxygen stream is then compressed and mixed with the polluted groundwater at elevated pressure in a static mixing unit. Under the conditions given almost all ozone will be dissolved in the water but not all the oxygen. Therefore, most of the gaseous oxygen still present is released into the environment by means of a gas separator. Trace amounts of ozone are fed into an ozone destructor after the gas separator. Despite the inevitable ozone losses it is assumed that about 90% of the ozone produced remains in the water after oxygen release. The ozone containing polluted groundwater is then irradiated with 500 keV electrons in a closed irradiation chamber. The electrons penetrate into the chamber through a 30 µm thin titanium foil. Since the penetration of the 500 keV electrons in water is relatively short it is necessary to present the water to the EB in the shape of a thin, wide, fast-flowing stream. Accordingly the irradiation chamber will be 1.2 m wide but the thickness of the water stream in the chamber will be 3 mm only.

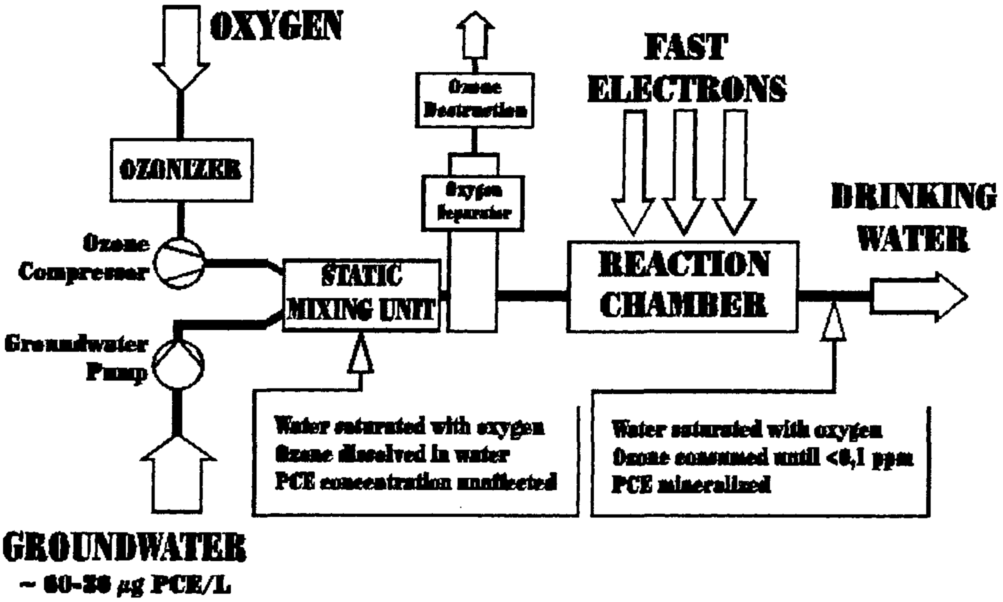


FIG. 2. Process schematic for Bad Fischau-Brunn's ozone/EB irradiation plant.

By the action of the EB irradiation in the presence of ozone, PCE is mineralized almost totally in the water [4]. The mineralization of PCE is of no influence to water quality; on the contrary, because of the ozone introduction the oxygen content of the water is increased — what can be classified as improvement of the treated water (see Table II).

TABLE II. CHANGE IN CONCENTRATION OF SOME NATURAL SOLUTES IN BAD FISCHAU-BRUNN GROUNDWATER AS A CONSEQUENCE OF THE TREATMENT PROCESS

Solute	Concentration in mg/L before the treatment	change by the treatment	after the treatment
Bicarbonate	251.0	0.06	251.06
Chloride	8.0	+ 0.068	8.068
Oxygen	8.7	+ 20.00 *	28.7 *

*can be roughly estimated only because of some degassing after treatment.

It has already been mentioned that the combination of ozone with EB irradiation is an AOP. However, compared with other ozone based AOPs the way in which the OH free radicals are generated is completely different. Groundwater can be described as a highly dilute aqueous solution of some inorganic and organic natural solutes. When dilute aqueous solutions are irradiated with fast electrons practically all the radiation energy is deposited in water molecules and the observed pollutant decomposition is brought about **indirectly** via the radicals formed from water (so-called water radiolysis). Direct action due to energy deposited directly in a solute is generally unimportant in dilute solutions, i.e. at solute concentrations below about 1 mol/L [5]. Roughly speaking the OH free radical generation in the combination of ozone with EB irradiation proceeds via 2 steps:

1. Water radiolysis:

$$H_2O \overset{\text{e-beam}}{\rightsquigarrow} OH^{\bullet};\ H^{\bullet};\ e^{-}_{aqu};\ H_2O_2$$

The action of fast electrons to water results in the direct formation of OH free radicals from the water to be purified. Beside the OH free radicals reducing species like solvated electrons and H-atoms as well as some hydrogen peroxide are formed. The reducing species and the hydrogen peroxide act now as promoter for the second step.

2. Ozone decomposition: The main reactions are:

$$\begin{array}{lll}
O_2 + e^{-}_{aqu} & \longrightarrow O_2^{-} & \\
O_2^{-} + O_3 & \longrightarrow O_3^{-} & \\
O_3 + e^{-}_{aqu} & \longrightarrow O_3^{-} & \\
O_3^{-} + H^{+} & \longrightarrow HO_3^{\bullet} & \longrightarrow OH^{\bullet} + O_2
\end{array}$$

For more details see [2, 6].

Just the opposite would take place if this groundwater is irradiated with non-ionizing UV radiation. In this case the radiation energy is deposited **directly** in ozone and not in water. The way in which the OH free radicals are formed is due to:

$$O_3 \underset{254\ \text{nm}}{\overset{h\nu}{\rightsquigarrow}} O^{\bullet} + O_2$$

$$\begin{array}{lll}
O^{\bullet} + H_2O & \longrightarrow H_2O_2 & \rightleftharpoons H^{+} + HO_2^{-} \\
O_3 + HO_2^{-} & \longrightarrow O_3^{-} + HO_2^{\bullet} & \\
O_3^{-} + H^{+} & \longrightarrow HO_3^{\bullet} & \longrightarrow OH^{\bullet} + O_2
\end{array}$$

Accordingly ozone/EB irradiation and ozone/UV irradiation represent the two ways in which radiation energy can be used. The indirect action generally is more efficient because all the radiation energy is taken by the water independent of the solutes present (as long as their concentration is < 1 mol/L). As a consequence the whole radiation energy is used for OH free radical production.

Although ozone/EB irradiation generates the OH free radicals necessary for pollutant decomposition in a total different way compared to that in the combination ozone/UV irradiation both treatment processes result in almost total mineralization of PCE. A 97% conversion of the organic chlorine into chloride for ozone/UV irradiation was reported [7], and that 96% of the organic chlorine is mineralized for the ozone/EB irradiation [4]. Moreover, it is known that PCE oxidation with OH free radicals may also produce trichloroacetic acid. Again, formation of trichloroacetic acid in trace amounts has been reported for both processes when used to decompose PCE in water [8, 4]. That means the product spectrum of PCE decomposition coincides for both AOPs even for the single organic by-product trichloroacetic acid on the ppb level. This is a clear indication that ozone/EB irradiation and ozone/UV irradiation decomposes PCE in water in exactly the same way. The only difference between both processes is the way in which the OH free radicals are formed. This includes moreover the combination ozone/hydrogen peroxide because in this process the OH free radical generation is exactly the same as in the combination ozone/UV irradiation [1]. Thus, the mechanism of PCE decomposition in water is the same for all three ozone based

AOPs. However, the ozone/EB irradiation process is able to generate more OH free radicals than any other of the ozone based AOPs. This is its crucial advantage.

The 100 m^3/h demonstration plant in Bad Fischau-Brunn was expected to be the first commercial ozone/EB irradiation plant for groundwater remediation to supply drinking water worldwide. Therefore, it was decided to test the purified water with respect to formation of genotoxic compounds. AMES and micronucleus tests with primary hepatocytes gave no indication of any genotoxic effect neither in the treated nor in the untreated water but the micronucleus test with Tradescantia (Trad-MCN) showed an unexpected result (Table III).

TABLE III. RESULTS OF TRAD-MCN TEST WITH WATER FROM THE WELL IN BAD FISCHAU-BRUNN BEFORE AND AFTER TREATMENT WITH OZONE/ELECTRON BEAM IRRADIATION

Sample	Genotoxic response in micronuclei (MCN) / 100 tetrads
Groundwater before treatment	33.2 ± 20.0
Groundwater after treatment	8.7 ± 4.1
Tap water (negative control)	7.0 ± 4.1
Tap water with 0.25 mM As_2O_3/L (positive control)	20.2 ± 6.5

Due to these results it is obvious that the contaminated groundwater does not only contain PCE but also some genotoxic compounds and, moreover, that the ozone/EB irradiation treatment for PCE mineralization totally removed also these genotoxic compounds.

Origin, structure and concentration of these genotoxic compounds are not yet known. The Trad-MCN test used for its detection needs about one month to yield results. Under these conditions activated carbon filtration alone is not apt for remediation of such contaminated water.

There are some data published concerning the contamination of the aquifer "Mitterndorfer Senke". About 6 km downstream of Bad Fischau-Brunn close to a big waste disposal site an activated carbon treatment plant for PCE removal from groundwater is located. Trad-MCN tests performed gave a positive response indicating that, besides PCE, genotoxic compounds are present in the water and in some cases also in the treated water after the carbon filter [9]. Accordingly activated carbon filtration could not control the genotoxic compounds present in the water. Furthermore, when UV irradiation was applied to the water after activated carbon filtration the genotoxicity of the water treated increased in all cases exponentially with the UV irradiation dose applied. Therefore, UV disinfection of such contaminated water is not possible. Beyond that, it is even questionable whether AOPs based on UV irradiation in combination with oxidants can be applied when the water to be purified contains such genotoxic substances and/or their precursors.

4. CONCLUSIONS

It has been demonstrated that groundwater polluted with trace amounts of PCE can be successfully purified by advanced oxidation without any loss in water quality. Moreover, experiments performed have demonstrated that the ozone/EB process is also apt for total removal of some genotoxic compounds detected in groundwater contaminated with PCE. Since the combination ozone/EB irradiation may generate the highest OH free radical concentration in water it is best apt for commercialization within all ozone based AOPs. Accordingly the first commercial full scale plant based on the combination ozone/EB irradiation for treating 108 m^3/h of water polluted with about 60 μg/L PCE and some genotoxic compounds was expected to be constructed in Bad Fischau-Brunn, Austria.

The mechanism of the OH free radical generation in the combination ozone/EB irradiation is fully understood. The identical product spectrum obtained for the processes ozone/EB irradiation and ozone/UV irradiation in case of PCE decomposition in water clearly indicates that ionizing radiation can be successfully used for OH free radical production without any side effects.

5. FINAL NOTE

In 1996 the community of Bad Fischau-Brunn was approached with a proposal to install and operate an ozone/EB irradiation plant for groundwater remediation to guarantee the long term drinking water supply. The total cost of the project was about 1,6 million US dollars. The European Union (EU) funded the project with 50% of the total cost within its LIFE programme. The municipal council of Bad Fischau-Brunn unanimously voted to accept the financial support from EU. The two year approval process followed the expected path of reviews by experts and authorities. The positive result regarding the removal of genotoxic compounds by the ozone/EB irradiation treatment convinced all about the outstanding potential of the process. The process itself was never questioned or under discussion. However, a controversy between the Mayor and the opposite party regarding some other issues ended in a new election of the municipal council and of the Mayor. In the campaign started before the election by the opposite parties it was now asserted that Bad Fischau-Brunn has enough water resources and does not need the contaminated well for its water supply. The ozone/EB process itself was never attacked directly. Nevertheless, the Mayor lost the election and the new elected council — in which the opposite parties got the majority — stopped the project because of no actual need. The commercialization of the ozone/EB irradiation process was hindered by a trifling political controversy not directly related to the technology itself.

SECTION B: OXIDATIVE TREATMENT OF SOIL CONTAMINATED WITH POLYCYCLIC AROMATICS (PAHs) IN AQUEOUS SUSPENSION FOR DECONTAMINATION

1. INTRODUCTION

Soil contaminated with polycyclic aromatics (PAHs) is a serious environmental problem in many parts of the world. It is known from the literature that PAHs react very fast and effectively with hydroxy free radicals in aqueous solutions. The reactions are diffusion controlled, the reaction rate constants for the reaction of PAHs with aqueous hydroxy radicals are in the order of $1 \times 10^{10} M^{-1}s^{-1}$ [10]. However, the transfer of the PAHs from the soil into water is very difficult. Therefore, it suggested to consider a direct treatment of the contaminated soil with aqueous hydroxy radicals, i.e. to suspend the contaminated soil in water and treat the suspension with an advanced oxidation process.

Advanced oxidation processes (AOPs) are those that promote the activity of the hydroxy free radical OH in oxidation reactions. It has been found that the addition of ozone in combination with UV radiation or hydrogen peroxide can accelerate the decomposition of ozone into OH. Combining hydrogen peroxide and UV radiation alone will achieve similar results as the ozone based processes by generating OH with a considerably less OH yields [11].

The most simple method to generate OH in water is its irradiation with ionizing radiation ("water radiolysis"). However, along with the OH reducing species like solvated electrons e^-_{aqu} and H-atoms are formed. Since the total amount of the reducing species is even somewhat more than the OH formation they often induce undesired side reactions and may reduce, moreover, the economy of an irradiation process considerably [12, 13]. Therefore, ozone is added to the water before or during irradiation what often converts the "hybrid" irradiation process into an almost pure AOP [6].

However, more recent investigations [14] concerning ozonation and AOP treatment of phenanthrene in aqueous solution have shown that the decomposition of this PAH is more effective by ozonation than by AOPs. This does not necessarily mean that ozonation in general is more effective for PAH destruction than AOPs are but it could be an alternative to AOPs in some cases.

The efficiency of AOPs with regard to PAH destruction obviously depends on the PAH structure. It cannot be excluded therefore that in certain cases the reducing species formed during water radiolysis may positively contribute to PAH destruction. Consequently EB irradiation of the suspended soil has also been included in the experimental programme.

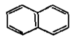
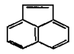
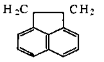
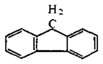
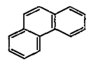
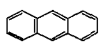
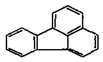
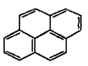
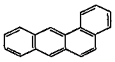
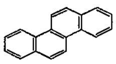
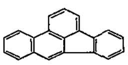
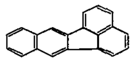
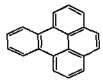
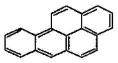
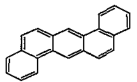
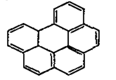
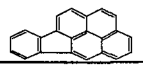
Due to these considerations the following have been established:

1. EB irradiation of aqueous soil suspensions at two different temperatures (20°C and 55–60°C, resp.).
2. Ozonation of the aqueous soil suspensions at room temperature.
3. EB irradiation of aqueous soil suspensions in the presence of ozone at room temperature.

2. EXPERIMENTAL

Assessment of the results obtained with the different treatment processes applied is based on the change in the total concentration of 17 selected PAHs. The selection of the PAHs is due the NIOSH list; the compounds are given in Table IV which also contains the concentration of each individual PAH on the original soil before treatment.

TABLE IV. THE PAHs OF THE NIOSH LIST AND THEIR ORIGINAL CONCENTRATION ON THE SOIL

No.	Name	Molecular formula	Molecular weight	Structure	Concentration mg/kg soil
1	Naphthalene	$C_{10}H_8$	128		2.1
2	Acenaphtylene	$C_{12}H_8$	152		0.6
3	Acenaphtene	$C_{12}H_{10}$	154		2.2
4	Fluorene	$C_{13}H_{10}$	166		2.5
5	Phenantrene	$C_{14}H_{10}$	178		13.3
6	Anthracene	$C_{14}H_{10}$	178		6.9
7	Fluoranthene	$C_{16}H_{10}$	202		53.2
8	Pyrene	$C_{16}H_{10}$	202		56.7
9	Benzo(a)anthracene	$C_{18}H_{12}$	228		17.2
10	Chrysene	$C_{18}H_{12}$	228		50.9
11	Benzo(b)fluoranthene	$C_{20}H_{12}$	252		44.6
12	Benzo(k)fluoranthene	$C_{20}H_{12}$	252		9.3
13	Benzo(e)pyrene	$C_{20}H_{12}$	252		19.3
14	Benzo(a)pyrene	$C_{20}H_{12}$	252		16.0
15	Dibenzo(a,h)anthracene	$C_{22}H_{14}$	278		2.9
16	Benzo(g,h,i)perylene	$C_{22}H_{12}$	276		20.9
17	Indeno(1,2,3-c,d)pyrene	$C_{22}H_{12}$	276		13.5

2.1. Procedure for the quantification of PAHs

2.1.1. Extraction from soil

The water suspension containing the PAH loaded soil was filtered and the filter residue extracted twice with 100 ml of acetone by ultrasonification for 1 h in each case. After additional filtering, the acetonic solution was brought to 200 ml. 200 µl internal standard solution (1 µg/ml of five deuterated PAHs in acetone: naphtalene-d8; acenaphtene-d10; phenanthrene-d10; chrysene-d12 and perylene-d12) were added to a 2 ml aliquot of the extract. After diluting this mixture by adding 1.8 ml acetone, it was ready for GC/MS analysis. The dry weight was determined by drying the extraction residue at 105°C overnight.

2.1.2. Extraction from aqueous solution

The filtered solution was extracted with 10 ml of cyclohexane twice. After adding 50 µl internal standard solution to a 1 ml aliquot, it was analysed by GC/MS.

2.1.3. Gas chromatography / mass spectrometry

Separation was performed on a DB5MS fused-silica capillary column, 30 m × 0.25 mm ID; 0,25 µm film thickness (J&W Scientific, Folsom, CA, USA), protected by a guard column DB1, 3 m × 0.32 mm ID, 0.5 µm film thickness, from the same manufacturer. Carrier gas was helium with an inlet pressure set to 100 kPa.

The mass spectrometer was operated in the electro impact mode (EI) using 70 eV ionisation voltage. The ion source temperature was 250°C, and the GC/MS-interface set to 280°C. The analyses were performed by selected ion monitoring (SIM).

3. DESCRIPTION OF THE EXPERIMENTAL SET-UP

The bench scale facility for treating the contaminated soil suspended in water consists of two storage vessels of glass S_1 and S_2 (volumes about 50 litres each) both equipped with a stirring apparatus to hold the soil in suspension. They are connected with each other via 3-way valves V_1 and V_2, respectively. V_1 also connects both vessels alternatively with a membrane pump MP made of stainless steel which pumps the suspension through the irradiation chamber and via the other valve V_2 into the corresponding vessel (for example, vessel S_1 contains the suspension to be treated, V_2 is adjusted then to conduct the suspension after treatment into the vessel S_2; when the run is finished almost all of the suspension is then in vessel S_2; now V_1 and V_2 are switched to the opposite position and another run starts pumping the suspension from S_2 via irradiation chamber into S_1). Just behind the pump is a small buffer vessel B to flatten the pulsation in the liquid which originates from the pump.

The irradiation chamber is designed for the irradiation of water layers with a thickness of 3 mm with simultaneous introduction of ozone (via frits in the bottom of the chamber) during irradiation. The window of the irradiation chamber is made of 25 µm titanium; its dimensions are 50 mm wide and 200 mm in length. The gas flow into the irradiation chamber is controlled by needle valves NV, flow meters FM and a pressure gauge P just as the flow of the aqueous suspension is controlled with regard to pressure and temperature. Heating of the suspension, when required, is provided in storage vessel S_1 by use of a heating bandage. To control the temperature in the irradiation experiments (both the room temperature and the elevated temperature) a heat exchanger HE in combination with a thermostat was used. The samples for analyses were taken using the 3-way valve V_3.

The EB accelerator is an ICT accelerator (500 kV, 25 mA, 120 cm scan width) manufactured by High Voltage Eng., USA.

Ozone was prepared from pure oxygen using a laboratory ozonizer (E. Sander Ltd., Germany). Ozone concentrations were determined routinely by measuring the UV absorption at 254 nm, calibrated against indigotrisulfonate method. The oxygen flow applied during the experiments was 140 L/h; the resulting ozone concentration was about 100 mg O_3/L O_2.

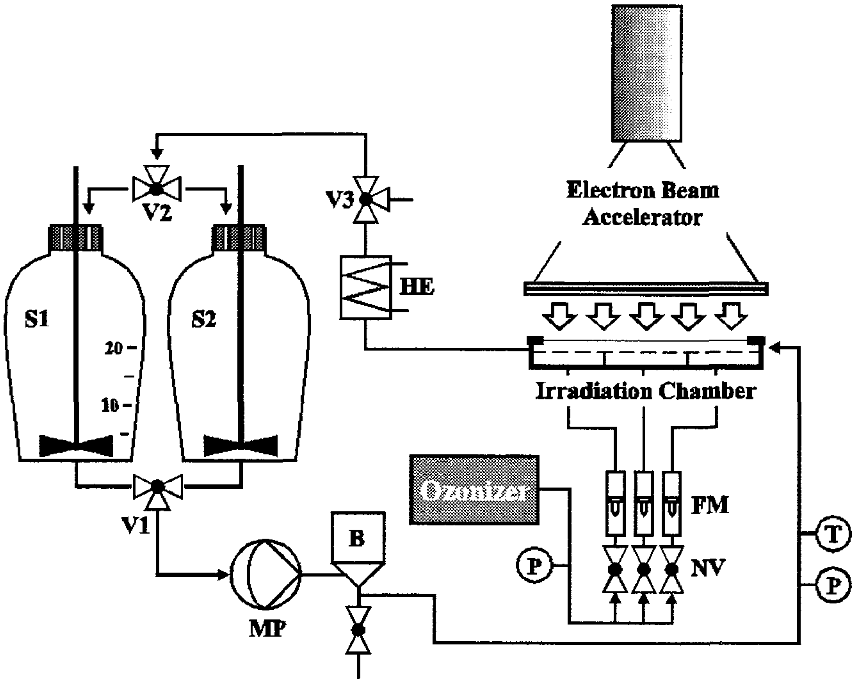


FIG. 3. Schematic view of the bench scale facility for treating soil in suspension.

This construction is very versatile and apt for the following treatment processes under complete identical conditions:

- EB irradiation
- ozonation
- combined ozone/EB irradiation (ozone introduction during irradiation)
- combination of ozonation and EB irradiation (ozone treatment before or after the irradiation, not simultaneously).

A schematic view of the experimental set-up is shown in Fig. 3.

Soil (particle diameter <1 mm) was suspended in Seibersdorf tap water and diluted with deionized water. The resulting mixture contains about 55 ppm bicarbonate. On the one hand, this is sufficient to stabilize ozone during ozonation; on the other hand, it does not scavenge too much OH radicals. The suspension contained 6% soil (per weight).

Twenty (20) litres of the suspension were used in one experiment (cycle). The flow rate was adjusted to 120 L/h what corresponds to a radiation dose of 10 kGy at 25 mA for each cycle when EB irradiation is considered. For ozonation each cycle is equivalent to an ozone dosage of 2 g O_3/kg soil. For the analyses about 150 ml of the suspension was taken for one sample.

Before starting the experiments the dead volume of the construction was determined. It was found to be about 1.5 litres. About 0.5 litres (~2.5%) of the suspension remains in the respective vessel because it is not possible to empty it totally. However, in the next cycle this non-treated part is again combined with the treated part and the effect is averaged by that due to the total of the cycles applied (at least 5 in case of the irradiation treatment processes). Moreover, there is another effect which reduced the efficiency of the process. Despite relative intense mixing by the stirring apparatus in the vessels it was not possible to hold all the soil totally in suspension. During one cycle about 10% of the total soil is precipitated on the bottom of the vessel. Again there is always an exchange of the soil precipitated and in suspension during different cycles so that the effect is averaged out. Nevertheless, these limitations resulted in a reduced efficiency of the process in the order of about 10–15% and are, moreover, most likely responsible in part for the scattering of the analytical results.

4. RESULTS AND DISCUSSION

4.1. EB irradiation at room temperature

Radiation doses of 50 kGy and 100 kGy have been applied (the unit of the absorbed radiation dose is 1 Gray (Gy). 1 Gy = 1 J/kg). However, even at the higher dose of 100 kGy, total PAH decomposition on soil did not exceed about 6.7%. Therefore, the following experiments have been performed at elevated temperature.

4.2. EB irradiation at 55–60°C

The results of these experiments are contained in Fig. 4. Radiation doses of 50, 100 and 200 kGy were applied corresponding to a total PAH decomposition of 3.5%, 15.8% and 18.4%, respectively. However, there is some inconsistency in results when the higher molecular components (above chrysene) are considered. The results obtained with 100 kGy show a much higher degree of PAH decomposition for the components above chrysene as was found for these components at the higher dose of 200 kGy. Since this is not very plausible the result obtained at 100 kGy most likely is not actual but due to the high scattering of the analytical data. This interpretation is supported by the rather high value found for the decomposition of dibenzo(a,h)anthracene which amounted to >10% at 50 kGy but only about 2% at 200 kGy. Similar results were also found for indeno(1,2,3-c,d)pyrene at these doses. Therefore, the results obtained with 200 kGy seem to be more reliable. Due to these results EB irradiation treatment seems to be more effective to PAHs of lower molecular weight (or PAHs consisting of less aromatic rings) while the PAHs with higher molecular weight (or more than 4 aromatic rings) are obviously more resistant against the attack of the free radical species formed during water radiolysis.

In the present case this is a clear disadvantage because the amount of the low molecular compounds (naphthalene until anthracene) on soil is rather small (only 8.3% of the total PAHs; see Table IV). The resulting net effect regarding total PAH decomposition must be small, therefore, although the amount of decomposition of these PAHs in general is almost 40% (at 200 kGy). However, it should be noted that doubling the radiation dose (from 100 kGy to 200 kGy) does not result in an analogous increase of the decomposition of these PAHs. The increase recorded at 200 kGy amounts to 10-20% only when compared with 100 kGy.

The more dominant PAHs on the soil to be treated are surprisingly more resistant to the irradiation process applied. The total PAH decomposition recorded is mainly due to the decomposition of fluoranthene and pyrene, which are located in the order of the PAHs

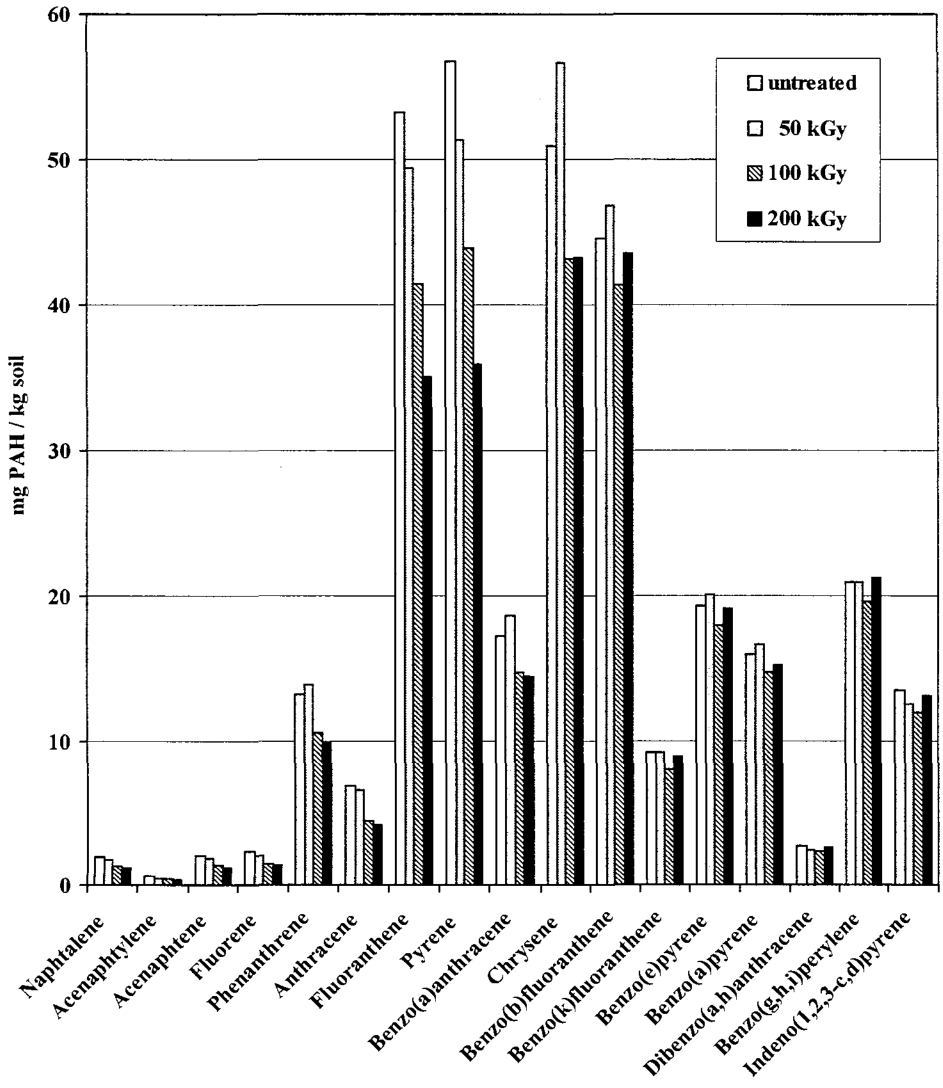


FIG. 4. Treatment of PAH contaminated soil in aqueous suspension by means of EB irradiation at 55–60°C. PAH decomposition as a function of radiation dose.

between the lower molecular weight range (until anthracene MG 178) and the higher range (above MG 228). For these two compounds also doubling of the radiation dose is more effective as it was for the compound mentioned with the lower molecular weight. However, all in all a radiation dose of 200 kGy seems to be too high to be justified with such a rather low decomposition (<20%) of the total PAHs.

It is supposed that the OH free radicals produced by the action of ionizing radiation on water play a dominant role in the decomposition of the PAHs on soil. Therefore, the next step logically is an irradiation treatment in the presence of ozone. The addition of ozone during irradiation converts the reducing species formed during water radiolysis into OH free radicals and by that the irradiation process into a pure Advanced Oxidation Process (AOP). However, before applying the AOP it was necessary to investigate the effect of ozonation alone with regard to PAH decomposition in order to determine the optimum ozone dose also for the AOP, i.e. the combination ozone/EB irradiation.

4.3. Ozonation at room temperature

The results obtained from ozonation of the PAH-containing soil in aqueous suspension are presented in Fig. 5 (except for low dose of 2 g O_3/kg soil).

At the low doses of 2 g O_3/kg soil and 6 g O_3/kg soil it is remarkable to note that mainly the high molecular PAHs are attacked by the ozone while the low and medium molecular PAHs are hardly attacked. There is an almost linear relation between the total PAH decomposition and the ozone dose applied; this is also true when the range is extended until an ozone dose of 10 g O_3/kg (corresponds to a total PAH decomposition of 20.9%). Unfortunately, above 10 g O_3/kg the linear relationship between ozone dose and total PAH decomposition considerably deviates from linearity. The corresponding value for total PAH decomposition at 20 g O_3/kg soil amounts to 27.3% only.

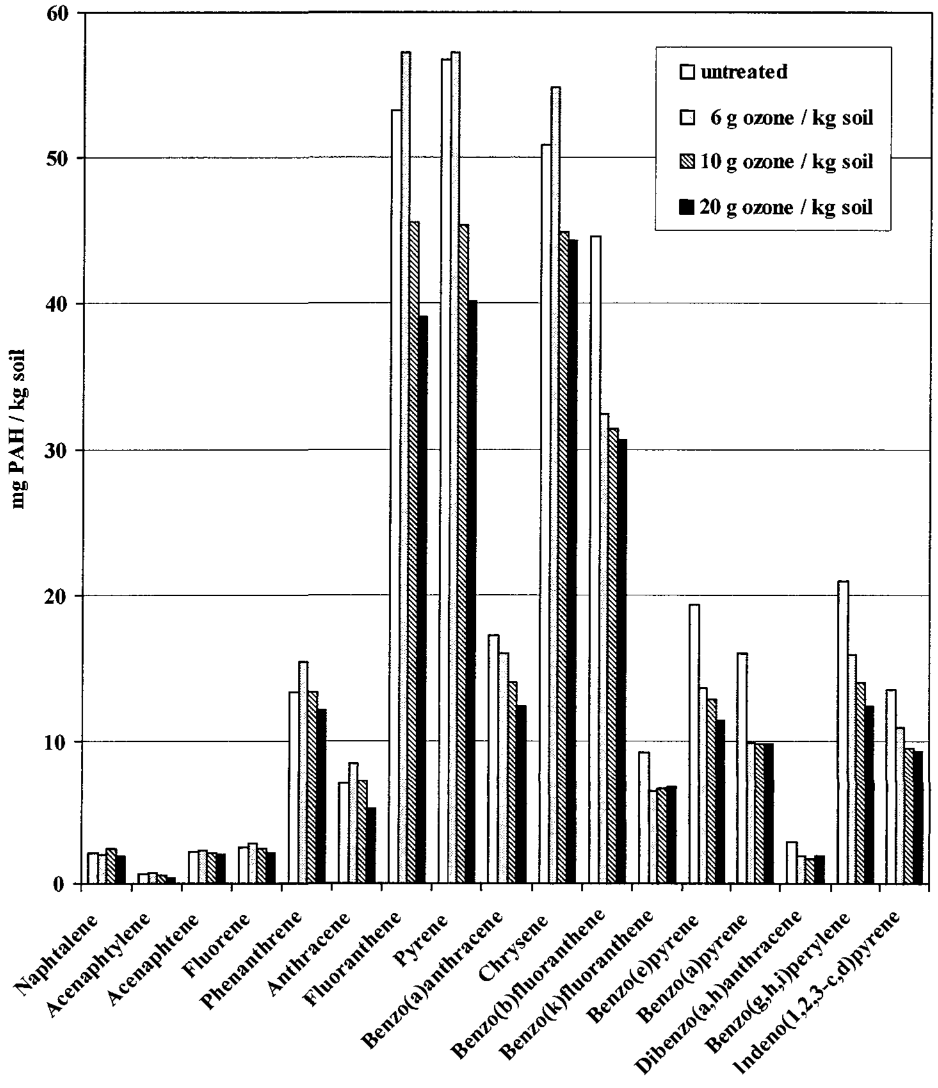


FIG. 5. Ozonation of PAH contaminated soil in aqueous suspension. PAH decomposition as a function of ozone dose applied.

Nevertheless, the results obtained from the ozonation experiments are quite expressive especially when compared with the findings from the EB irradiation experiments. At the lower ozone doses (2 g O_3/kg and 6 g O_3/kg) it was found that the high molecular PAHs were attacked by the ozone almost exclusively. In the EB irradiation treatment processes, however, it was noticed that the low molecular PAHs were essentially decomposed by that treatment.

At the higher ozone dose of 10 g O_3/kg soil the ozone obviously also attacks the PAHs in the medium molecular weight range (fluoranthene until chrysene); moreover, there is also some decomposition of the low molecular weight PAHs. At the highest ozone dose of 20 g O_3/kg all PAHs considered here are attacked. However, it is conspicuous that at the higher ozone doses the increase in the total PAH decomposition is caused by some decomposition of the low and medium molecular weight PAHs while decomposition of the higher molecular PAHs stagnated at ozone doses above 10 g O_3/kg. Since ozone itself is also a source for OH free radicals it seems possible that at higher ozone doses the soil acts as a promoter for the ozone decomposition into OH free radicals. This would mean that the decomposition of the PAHs in the low and medium molecular weight range is in reality an effect of OH free radicals originating from ozone decomposition.

It was, therefore, of interest to study the effect of the OH free radicals at higher concentrations; this can be done by using the combined ozone/EB irradiation treatment which represents as already mentioned an almost pure AOP provided that the ozone is introduced during irradiation.

4.4. Combined ozone/EB irradiation treatment

When ozone is introduced into water during irradiation most of the ozone is converted into OH free radicals. This is due to the action of the reducing species formed during water radiolysis which act as promoters for the ozone decomposition into OH free radicals. However, there is always a competition between direct ozone reactions with PAHs and ozone decomposition into OH free radicals but in this case the competition should be in favour of the ozone decomposition which means OH free radical generation.

We recorded that the combined ozone/EB irradiation treatment effected in both experiments performed better results when compared with irradiation alone but worse when compared with ozonation alone. (12.6% total PAH decomposition for the combination in comparison with 2% for the 50 kGy irradiation but 20.9% for the ozonation with 10 g O_3/kg soil ozone dose. 14.6% total PAH decomposition for the combination in comparison with 6.7% for the 100 kGy irradiation but 27.3% for ozonation with 20 g O_3/kg/soil ozone dose). It is further conspicuous that doubling both the irradiation dose and ozone dose hardly increases the total PAH decomposition (it only increases from 12.6% to 14.6%). Moreover, in both experiments total PAH decomposition obtained with the combined process is always less than the total PAH decomposition calculated by the sum of the individual processes. It is obvious, therefore, that ozone introduction during irradiation does not represent an improvement in search of a technical solution of the problem.

However, these results indicate that a combination of ozone with **subsequent** irradiation treatment could be more effective than the simultaneous treatment. On the one hand, ozonation with an ozone dose of 10 g O_3/kg soil has been found to be most efficient; on the other hand, irradiation at elevated temperature gave much better results than that obtained at room temperature. Therefore, ozonation with an ozone dose of 10 g O_3/kg soil was combined with a subsequent irradiation at 55-60°C applying radiation doses of 100 kGy and 200 kGy, respectively.

With a radiation dose of 100 kGy a total PAH decomposition of 32.8% was recorded while 43.6% was found when the irradiation dose applied was 200 kGy. Calculation of the total PAH decomposition by the sum of the individual treatment processes resulted in 36.7% (for 100 kGy) and 39.3% (for 200 kGy), respectively. Due to this result it is quite sure that the combination of ozonation with subsequent irradiation is not more than the sum of the two individual processes. In other words: **No synergistic effect exists.**

4.5. PAH decomposition in aqueous phase

It was found that there is almost no desorption of the PAHs from soil into water when soil was simply suspended (PAHs detected in water <0.1% of total PAHs on soil).

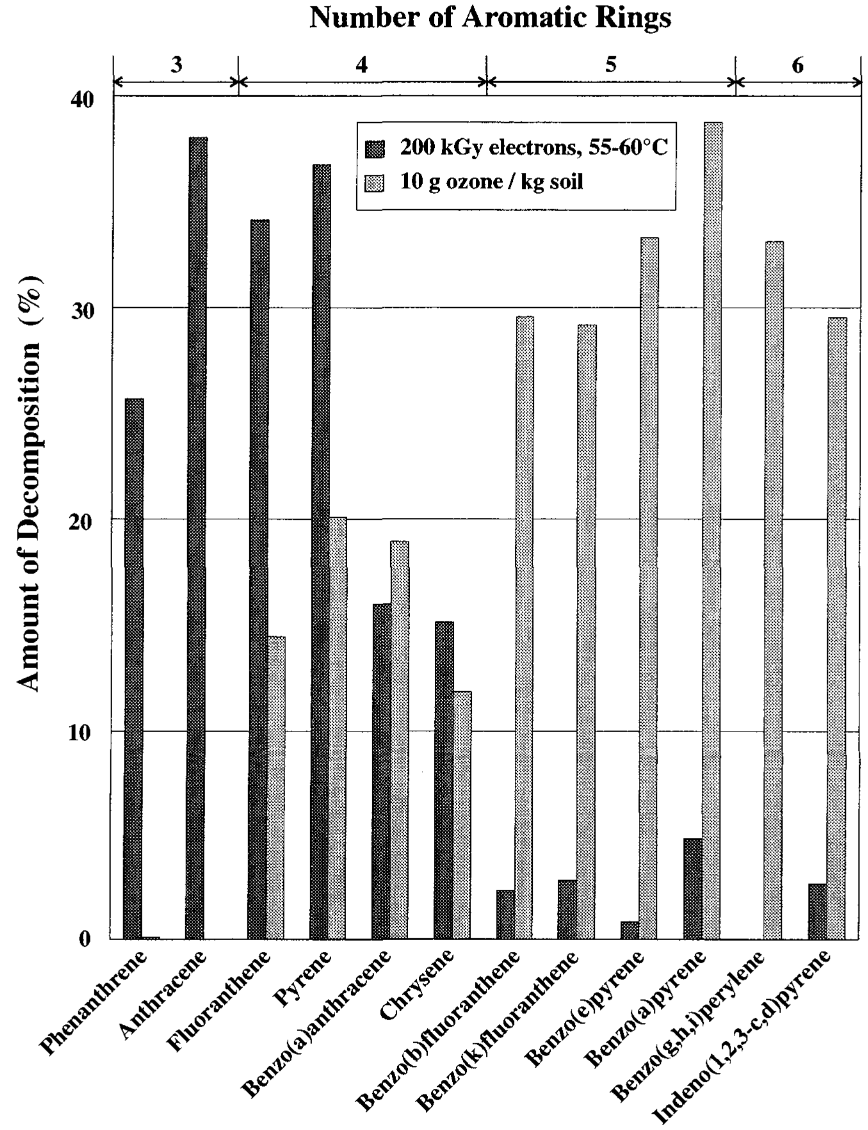


FIG. 6. Treatment of PAH contaminated soil in aqueous suspension. Effect of ozonation and EB irradiation, respectively on some selected PAHs.

5. SUMMARY

Oxidative treatment of the aqueous soil suspension reduces the total amount of the PAHs on soil but in different ways when individual PAHs are considered (see Fig. 6). It was found that ozone mainly attacked the high molecular fraction (i.e. consisting of five or six aromatic rings) of the PAHs investigated while EB irradiation of the aqueous soil suspension mostly decomposed the lower fraction (i.e. consisting up to 4 aromatic rings).

Under the conditions given irradiation of an ozonated soil suspension at 55–60°C was most effective and resulted in the highest total PAH decomposition. However, the total effect is only the sum of the effects of the two individual processes; accordingly there is no synergistic effect at all.

Using optimum conditions (10 g O_3/kg soil followed by a 100 kGy irradiation at 55–60°C) the total PAH decomposition would amount to about 33% of what corresponds to a total PAH decomposition of about 100 mg PAH/kg soil. A higher yield is hardly achievable according to the drastic yield reduction above the optimum conditions. An economic application seems to be very difficult to carry out, therefore.

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