

# Feasibility study for the remediation of groundwater contaminated by organolead compounds

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## Abstract

The aim of this research was to assess the effectiveness of chemical oxidation, Advanced Oxidation Processes (AOPs) and adsorption on granular activated carbon (GAC) for the ex situ remediation of a groundwater contaminated by organolead compounds, including tetraethyl lead (TEL), triethyl lead (TREL) and diethyl lead (DEL). The groundwater of concern was collected from the site of a former tetraalkyllead producing company in Trento (Italy), and showed an average total organic lead (TOL) content about 95.1  $\mu\text{g/L}$  (TEL 0.5  $\mu\text{g/L}$ , TREL 86.4  $\mu\text{g/L}$ , DEL 8.3  $\mu\text{g/L}$ ). The main target of the study was to find out which method was more effective in reducing the pollutant content. For this purpose, several laboratory tests were performed, including chemical oxidation tests with different reactants (hydrogen peroxide, modified Fenton's reagent, potassium permanganate, activated potassium persulfate, oxygen and combinations of potassium permanganate and modified Fenton's reagent), AOPs with ozone, UV radiation and hydrogen peroxide and filtration on granular activated carbon. A combination of chemical and physical treatments was also tested, with GAC filtration followed by chemical oxidation. According to the results achieved, the treatments which showed the best remediation performances were: chemical oxidation with modified Fenton's reagent, AOPs with hydrogen peroxide and ozone (perozone), AOPs with hydrogen peroxide and UV radiation, and the combined treatment with activated carbon filtration followed by chemical oxidation with perozone. All these treatments showed a 90% TOL removal, with excellent removals of both TEL and TREL, and final DEL concentrations below 5  $\mu\text{g/L}$ .

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## 1. Introduction

Tetraethyl lead (TEL),  $(\text{CH}_3\text{CH}_2)_4\text{Pb}$ , is an organometallic compound which was once commonly used as antiknock agent in gasoline. TEL was first prepared as a pure compound in 1859, but it started to be added to petrol in 1922, to improve the gasoline octane rating. Thanks to its capacity to improve engine performances, by the 1970s, almost all petrol produced around the world contained lead [1–4], but soon after the beginning of TEL production, its high toxicity emerged. Several very serious cases of lead poisoning occurred in all operating plants, and a number of workers died in an acute psychosis with hallucinations due to exposure to TEL gas or to contact with TEL oil [5].

Although organic lead compounds are not classifiable as to their carcinogenicity to humans [6], they are known to be highly

toxic and to have serious negative effects on human health, in particular seriously damaging the nervous system, adversely affecting the mental and neurological development in children and causing hallucinations, psychosis and cardiovascular problems in adults, being toxic even at low levels in blood, as 50  $\mu\text{g/L}$  [1,5,7–12].

Inhalation and ingestion represent the major routes of human exposure to TEL due to the dispersion in the atmosphere and deposition of lead-contaminated particulate [6–8], while for workers of TEL production industrial plants, the occupational poisoning can occur as a result of dermal contact, since organolead compounds can be easily absorbed through the skin [1,6]. On the whole, the toxicity of TEL is so high that no threshold has been identified under which adverse health effects cannot be detected [7].

Because of the important adverse effect of organolead compounds on the environment and on human health, many efforts have been made from the 1970s by most of countries to reduce organic lead emissions, the most important being the banning of

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leaded gasoline, with the introduction of the catalytic converter. Thanks to these efforts, most of lead sources have nowadays decreased, and, in spite of the persistence of lead in the environment, this has resulted in substantial decrease in human exposure, within few years from the banning of leaded gasoline, with a significant decline in blood lead levels [1,6,8,12,13]. But in the meanwhile, the widespread use of leaded gasoline had caused the dispersion of lead throughout the environment, causing serious exposure to human communities and to ecosystems [6], while spillages of large quantities of TEL during production, transportation or blending at oil refineries and petrol stations caused several cases of severe soil and groundwater contamination [14].

### 1.1. Organolead compounds

Under environmental conditions, TEL is a viscous colorless liquid. It is an apolar molecule, highly lipophilic and soluble in petrol and solvents. When TEL is released into the environment, it undergoes a series of dealkylation reactions [14,15]: at first, it is degraded to triethyl lead (TREL,  $(\text{CH}_3\text{CH}_2)_3\text{Pb}^+$ ), which is decomposed to diethyl lead (DEL,  $(\text{CH}_3\text{CH}_2)_2\text{Pb}^{2+}$ ), which can finally be turned, through the very unstable form of monoethyl lead  $((\text{CH}_3\text{CH}_2)_1\text{Pb}^{3+})$ , to inorganic, metallic, lead ( $\text{Pb}^{2+}$ ).

Organolead compounds are more toxic than inorganic lead, and their toxicity generally increases with the degree of alkylation, according to the following sequence:  $\text{TEL} > \text{TREL} > \text{DEL}$  [14,16,17].

In the atmosphere TEL can be rapidly photocatalytically decomposed by sunlight, by ozone or by hydroxyl radicals to TREL and DEL, which can be further decomposed in the same way, even if proved to be more stable species [14,16]. In soil organolead compounds may be persistent over decades, the natural chemical and biological degradation being very limited [18,19].

While TEL is a nonionic organic molecule, with low water solubility and a low potential for transport through soil, its degradation products, TREL and DEL, are cations, highly soluble in water, which can be easily be transported in groundwater [14,15]. On the whole, the mobility of organolead compounds in the subsurface is dominated both by sorption and by degradation reactions: while TEL is a typical DNAPL compound, and tends to be immobile and adsorbed into soil particles, TREL and DEL are quite mobile and tend to form large plumes in groundwater.

### 1.2. Remediation of organolead pollutants

Only a few remediation techniques for organolead soil and groundwater contamination have been investigated up to now. Since organic lead species can be extracted from water with the use of organic solvents [17], a possible way to remediate environmental media contaminated with TEL is a flushing with solvents and surfactants [15,20]. Some studies proved that enhanced bioremediation, with oxygen and nutrient addition, could effectively transform TEL into ionic alkyllead species, but

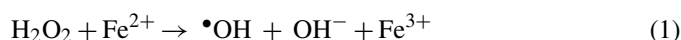
a complete TREL removal is more difficult to achieve [14,19]. Moreover, water soluble alkyllead compounds appeared to be toxic for non-adapted microorganisms [14]. Also the application of electrokinetic remediation led to poor results [21], while the thermal treatment proved to cause serious air pollution problems [22]. Recent studies [16] proved organolead compounds to be degraded by hydroxyl radicals  $\bullet\text{OH}$ , but the knowledge about the feasibility of using chemical oxidation for organolead compound remediation is limited.

The aim of this research was to evaluate the feasibility of using various chemical and physical treatments for the ex situ remediation of a groundwater contaminated by organic lead compounds (TEL, TREL, DEL), and to compare treatment efficiencies in order to assess the best remediation techniques and the most efficient treatment conditions. The processes considered in this study were: chemical oxidation, Advanced Oxidation Processes (AOPs) and adsorption on activated carbon, as well as combinations of these processes.

Chemical oxidation is a remediation technique which is based on the dosage of chemical reactants (oxidants) to mineralize organic pollutants from soils and groundwater, both in situ and ex situ applications. The oxidants most commonly used for environmental applications are hydrogen peroxide, Fenton's reagent, ozone, permanganate and persulfate [23–25].

The dosage of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) to a soil or groundwater leads to the production of hydroxyl radicals  $\bullet\text{OH}$ , which are very strong non-selective oxidant agents (standard oxidation potential, versus the standard hydrogen electrode SHE, of about 2.8 V), able to react with most of organic pollutants [24–26].

In Fenton's reagent, the production of hydroxyl radicals is enhanced by the dosage of ferrous ions ( $\text{Fe}^{2+}$ ), according to this catalytic reaction [24,26–29]:

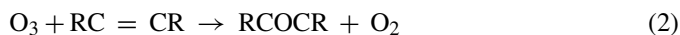


which is propagated by the  $\text{Fe}^{3+}$  reduction, which leads to the  $\text{Fe}^{2+}$  regeneration.

The availability of ferrous ions, which is usually limited under environmental conditions, can be promoted by the creation of very acid conditions (traditional Fenton's reagent) or by the addition of chelating agents (modified Fenton's reagent) [24,29–32]. A problem that is commonly encountered with Fenton's reagents is the consumption of the hydroxyl radicals for undesired side reactions (oxidant scavengers), as for the mineralization of natural occurring organic matter; in fact, when high concentrations of hydrogen peroxide are used, significant amounts of radicals can be consumed by the dosed reactants themselves (oxidant self-consumption) [28,31].

Ozone ( $\text{O}_3$ ) is a gaseous reactant having a standard oxidation potential of 2.1 V. It is considered very effective for the remediation of many organic pollutants, including chlorinated solvents, aliphatic hydrocarbons and aromatic compounds [23–25]. Ozone has been extensively applied for environmental applications, including the treatment of contaminated groundwater, saturated soils or the vadose zone [23–25,33–36]. Since it is an unstable compound, it must be generated on site.

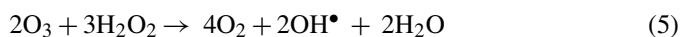
Ozone can attack organic pollutants in two ways [24,25]: through direct oxidation by ozone itself:



or through indirect oxidation, which is based on the ozone decomposition and on the formation of hydroxyl radicals. These radicals can be formed as a consequence of ozone reaction with hydroxide ions ( $\text{OH}^-$ ) at neutral or basic pH via reaction (3), or with water in the presence of UV radiation, via reaction (4):



Also the presence of hydrogen peroxide can highly enhance the radical formation, because of the very fast following process [25]:

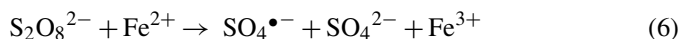


Usually the indirect oxidation process by hydroxyl radicals is faster than direct oxidation [24].

When used in water, ozone can be solubilized or used in the gaseous form, i.e. in bubbles; since ozone shows a relatively low solubility and higher decomposition rates in the aqueous phase than in the gas phase [25], its application in the gas phase is commonly preferred. As for hydrogen peroxide, carbonates and natural occurring organic matter can act as oxidant scavengers, resulting in a consumption of the dosed ozone and in an increase in the oxidant demand [24,25].

In the past few years, potassium and sodium permanganates ( $\text{K}_2\text{MnO}_4$  and  $\text{Na}_2\text{MnO}_4$  respectively) have been widely used to remediate petroleum hydrocarbons from soils and groundwater [24,25,37,38]. In aqueous systems the permanganate salts generate permanganate ions ( $\text{MnO}_4^-$ ), which show a standard oxidation potential of about 1.7 V. Despite their relatively low oxidation potential, the permanganate salts are considered effectively able to attack the carbon–carbon double bonds of aliphatic hydrocarbons and therefore to break organic molecules [24].

Persulfate salts, as sodium persulfate ( $\text{Na}_2\text{S}_2\text{O}_8$ ), recently started to be used as remediation agents [24,25,39,40]. Persulfate salts, when dissolved in water, dissociate into persulfate anions ( $\text{S}_2\text{O}_8^{2-}$ ), which, although strong oxidants (standard oxidation potential about 2.0 V), are kinetically slow in destroying most of organic contaminants. As for Fenton's reagent, also for persulfate the addition of transition metal ions (as ferrous ions) could activate the persulfate anions to produce the sulfate free radical ( $\text{SO}_4^{\bullet-}$ ) [23,24,40]:



Sulfate free radicals are more powerful oxidant agents than persulfate anions, having a standard redox potential of 2.6 V, and they may be able to oxidize many organic pollutants, as chlorinated solvents and aromatic hydrocarbons [26,40].

In AOPs, different combinations of chemicals are used to enhance the formation of highly reactive radical species, which may be able to mineralize even the most recalcitrant organic compounds. Most common AOP applications include combina-

tions of ozone, hydrogen peroxide and UV radiation, eventually with the contribution of catalysts, as titanium oxides [41–46].

The adsorption on activated carbons allows the removal of many organic and inorganic pollutants from the aqueous phase [46–51]. This process is widely applied for the treatment of drinking water, industrial and municipal wastewaters or for groundwater remediation.

Activated carbon particles are characterized by very high specific surfaces, due to the presence of micropores and macropores. The adsorption process is based on three steps [47], including the transport of the pollutants through the exterior surface film of the carbon particles, the diffusions within the activated carbon pores and the adsorption of the pollutants onto the interior surface of the carbon pores, thanks to Van der Waals forces.

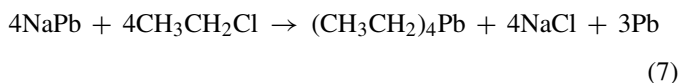
Granular activated carbons (GAC), which are characterized by a coarser grain size than powdered activated carbons (PAC) are commonly used for engineering applications, mainly in column filters. As polluted water flows through the activated carbon filter, chemicals are sorbed onto the carbon particles and therefore they are removed from the aqueous phase. The process is effective until the carbon is exhausted, i.e. no more surface is available for chemical sorption. The amount of chemicals which can be sorbed onto an activated carbon filter depends on the contaminant initial concentration and on temperature (according to the Freundlich isotherms) [46–48]. The exhausted carbon must be replaced or cleaned, for example by heating, to be reused [49]. Usually, GAC is preferred for real-scale column applications, because it allows its regeneration, thus decreasing the operation costs. Moreover, its performances in terms of contaminant removals are often higher than those of PAC.

For the clean up of a contaminated groundwater, activated carbon filtration can be used *ex situ*, as part of a pump and treat system, or *in situ*, using an underground permeable barrier. Usually, GAC systems are considered effective for the removal of many organic pollutants, as fuels and chlorinated compounds, and of selected metals [48–51].

## 2. Materials and methods

### 2.1. Contaminated site and groundwater samples

The groundwater samples for the experimental investigation were collected from a well from the site of a former tetraethyl lead producing company in Trento (Italy). In this site, TEL was commercially produced by reacting ethyl chloride ( $\text{CH}_3\text{CH}_2\text{Cl}$ ) with a sodium lead alloy (NaPb), according to the reaction:



The factory started its activities in 1940 and was closed down nearly 40 years later in 1978, after a major accident. At present, the site is abandoned. During the production, significant amounts of oil and organolead compounds were spilled and drained underground. After an investigation, the degree of environmental contamination by organolead compounds was found to be very high, especially in the areas where TEL was processed and

Table 1  
Contaminant concentrations in the groundwater samples used for the tests

Sample	TEL ( $\mu\text{g/L}$ )	TREL ( $\mu\text{g/L}$ )	DEL ( $\mu\text{g/L}$ )	TOL ( $\mu\text{g/L}$ )	Reference for tests
1	0.57	57.7	12.4	70.7	HP.1, MF.1, AP.1, PP.1
2	0.62	72.9	8.3	81.8	HP.2, MF.2, AP.2, PP.2
3	0.1	75.7	4.2	80.0	HP.3, HP.4
4	<0.005	125.1	5.3	130.4	MF.3, AP.3, PP.3
5	0.62	87.6	22.5	110.7	MF.4
6	0.02	86.1	7.2	93.3	MF.6, AP.4, PP.4
7	1.62	110.3	3.6	115.5	PPMF.1, PPMF.2
8	<0.005	69.4	3.0	72.4	O2.1, O3.2
9	0.86	75.3	6.8	83.0	O3.1
10	0.10	79.6	3.7	83.4	O3.3, O3.4
11	<0.005	69.4	3.0	72.4	UV.1, UV.2
12	<0.005	64.8	2.5	67.3	O3 + HP.1
13	0.009	95.9	4.4	100.3	O3 + HP.2, O3 + HP.3
14	0.10	75.7	4.2	80.0	UV + HP.1
15	<0.005	64.8	2.5	67.3	O3 + UV.1
16	<0.005	69.4	3.0	72.4	O3 + UV.2
Mean value	0.5	80.0	6.0	86.3	–

stored; the high soil contamination also resulted in the pollution of groundwater.

The soil profile in this site can be described from ground level as a thin layer of filling material (about 1 m), a horizon of silty sand (about 5 m), an aquifer characterized by gravel and sand (about 7 m), a layer of clayey and sandy lime with organic matter (about 2 m), another stratum of sands and gravel (about 5 m), and finally some alternations of fine sand and silt (about 15 m) to the total depth of about 35 m below the ground level. In this area the aquifer can be classified as semi-confined, the groundwater table starts at a depth of about 1.5 m and the groundwater flows from north to south with velocity of about 1 m per day.

The Italian law does not have a limit for the organolead content in soil and water. For this reason a toxicology study was carried out by the national sanitary service to establish a limit to be used as target level in the remediation process for the addressed contaminated site. As regards the contaminant content in groundwater, in 1997 the local sanitary service indicated 0.9  $\mu\text{g/L}$  as the maximum tolerable concentration for total organic lead (TOL), while in 2002 the national sanitary service stated the limit of 0.1  $\mu\text{g/L}$  for the TEL content.

The groundwater samples used for the laboratory tests were collected from a well located downstream the hotspots of soil contamination in the addressed site. To avoid the natural degradation of tetraethyl lead while the study was in progress, several groundwater samples were collected during the experimental investigation, by performing a weekly sampling. The pollutant contents of the groundwater samples are reported in Table 1.

After the collection, the groundwater samples were kept in closed bottles covered with aluminum foils to avoid the photolytic degradation of the organolead compounds. During the transport to the laboratory, the samples were kept in refrigerated containers at a temperature of about 4 °C. Moreover, the tests and the analysis were performed on the same day the sample was collected. During the tests, a certain degradation of the organolead compounds, e.g. due to the reaction with atmospheric oxygen, was unavoidable. For this reason, during the experiments the

original untreated samples (i.e. the blank samples, Table 1) were kept in the same conditions of the treated sample (i.e. in glass bottles covered with aluminum foils at room temperature), in order the calculated removal efficiencies not to be affected by the natural degradation processes.

The collected samples showed a certain variability in the pollutant content, due to the natural fluctuations of the flow direction and of the water table depth. The variability was higher for TEL, which is an apolar molecule having a low solubility, than for TREL and DEL, which are soluble species.

On the whole, the groundwater of concern proved to be contaminated by various forms of alkyl organic lead, with an average concentration about 0.5  $\mu\text{g/L}$  for TEL, 80.0  $\mu\text{g/L}$  for TREL and 6.0  $\mu\text{g/L}$  for DEL, which resulted in an average TOL content (summation of TEL, TREL and DEL in each sample) about 86.3  $\mu\text{g/L}$  (Table 1). Moreover, the groundwater showed a total lead concentration about 143.2  $\mu\text{g/L}$ , and, therefore, an inorganic lead content about 48.1  $\mu\text{g/L}$ . The groundwater pH ranged from 7.2 and 7.4.

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## 2.2. Experimental investigation

During this experimental investigation several laboratory tests were performed to determine the removal efficiency of the addressed methods on the target contaminants, and to assess the best treatment conditions, as contact times and reactant dosages. Three sets of experiments were performed. In the first set, several batch chemical oxidation tests with liquid reactants were

Table 2  
Chemical oxidation batch tests: reactant dosages, concentration and test duration

Oxidant	Test	Oxidant dose (mmol)	Contact time (h)	Reactant	Volume (mL)	Concentration (M)
Hydrogen peroxide	H2O2.1	0.2	1	Hydrogen peroxide	2	0.1
	H2O2.2	2	15	Hydrogen peroxide	20	0.1
	H2O2.3	10	3	Hydrogen peroxide	2.5	3.2
	H2O2.4	20	3	Hydrogen peroxide	5	3.2
Modified Fenton's reagent	MF.1	0.2	1	Hydrogen peroxide	2	0.1
				Ferrous chloride	0.2	0.1
				Catechol	0.22	0.1
	MF.2	2	15	Hydrogen peroxide	20	0.1
				Ferrous chloride	2.0	0.1
				Catechol	2.2	0.1
	MF.3	10	3	Hydrogen peroxide	2.5	3.2
				Ferrous chloride	0.8	0.5
				Catechol	0.88	0.5
	MF.4	10	15	Hydrogen peroxide	2.5	3.2
				Ferrous chloride	0.8	0.5
				Catechol	0.88	0.5
MF.5	20	3	Hydrogen peroxide	5	3.2	
			Ferrous chloride	1.6	0.5	
			Catechol	1.76	0.5	
MF.6	40	3	Hydrogen peroxide	10	3.2	
			Ferrous chloride	3.2	0.5	
			Catechol	3.52	0.5	
Activated persulfate	AP.1	0.2	1	Potassium persulfate	2	0.1
				Ferrous chloride	0.2	0.1
				Citric acid	0.22	0.1
	AP.2	2	15	Potassium persulfate	20	0.1
				Ferrous chloride	2	0.1
				Citric acid	2.2	0.1
	AP.3	10	3	Potassium persulfate	100	0.1
				Ferrous chloride	0.8	0.5
				Citric acid	0.88	0.5
	AP.4	20	3	Potassium persulfate	200	0.1
				Ferrous chloride	1.6	0.5
				Citric acid	1.76	0.5
Potassium permanganate	PP.1	0.2	1	Potassium permanganate	2	0.1
	PP.2	2	15	Potassium permanganate	20	0.1
	PP.3	10	3	Potassium permanganate	100	0.1
	PP.4	20	3	Potassium permanganate	200	0.1
Modified Fenton's reagent and potassium permanganate	PPMF.1	5 + 5	3	Hydrogen peroxide	1.25	3.2
				Ferrous chloride	0.400	0.5
				Catechol	0.44	0.5
	PPMF.2	5 + 5	15	Potassium permanganate	50	0.1
				Hydrogen peroxide	1.25	3.2
				Ferrous chloride	0.400	0.5
				Catechol	0.44	0.5
				Potassium permanganate	50	0.1

conducted. The oxidants tested in this experimental phase were: hydrogen peroxide, modified Fenton's reagent, activated persulfate and permanganate.

The second set of experiments included column tests with oxygen, ozone, and column tests with AOP (different combinations of hydrogen peroxide, ozone and UV radiation).

During the third experimental phase, adsorption on activated carbon was evaluated, and, at the end of these experimental trials, a test was performed in order to assess the efficiency of the combined use of chemical oxidation and adsorption on activated carbon.

### 2.2.1. Chemical oxidation batch tests

The chemical oxidation tests were performed at bench scale to assess the effects of different reactants, different oxidant dosages and different contact times. All the batch tests performed are summarized in Table 2. The trials include four tests performed with hydrogen peroxide (indicated as HP tests), six test performed with modified Fenton's reagent (MF tests), four tests performed with activated potassium persulfate (AP tests), four tests performed with potassium permanganate (PP tests) and two tests performed with the combined use of modified Fenton's reagent and potassium permanganate (PPMF tests).

The reactants used in this experimental phase were potassium persulfate ( $K_2S_2O_8$ ), potassium permanganate ( $KMnO_4$ ), ferrous chloride ( $FeCl_2$ ), catechol ( $C_6H_6O_2$ ), hydrogen peroxide ( $H_2O_2$ ) and sodium metabisulfite ( $Na_2S_2O_5$ ) for oxidation reaction quenching. All chemicals used for the tests were purchased from Sigma–Aldrich and were reagent grade. The deionized water used in the tests was produced with a Milli-Q system from Millipore.

For the production of modified Fenton's Reagent, hydrogen peroxide was dosed together with a solution of chelated iron ions. Ferrous chloride was used to provide iron ions, while catechol was used as chelating agent. In the first two tests performed with modified Fenton's reagent (tests MF.1 and MF.2), a iron:oxidant molar ratio equal to 1:10 was tested, while in the following tests, a molar ratio of 1:20 was used. In both cases the ferrous salt and catechol were dosed at a molar ratio iron:catechol equal to 1:1.1. To produce the activated persulfate oxidant, potassium persulfate was added to the reaction vessel together with the a solution of chelated ferrous ion; citric acid was used as chelating agent, with molar ratio iron:chelating agent equal to 1:1.1. In all tests performed with activated persulfate, the iron:oxidant molar ratio was 1:10.

For each reactant, tests were performed with the following oxidant concentrations: 0.2, 2, 10 mmol (two contact times: 3 and 15 h) and 20 mmol. An additional test was performed with modified Fenton's reagent, with a peroxide concentration of 40 mmol, and two tests were performed to assess the effects of the combined use of modified Fenton's reagent and permanganate (5 mmol of hydrogen peroxide and 5 mmol of permanganate, with two different contact times).

The catalyst:oxidant and iron:chelating agent molar ratios for the modified Fenton's reagent and in the activated persulfate processes were selected on the basis of literature values [24,30,32,40]. The oxidant doses were chosen in the same way in order to range from mild to strong oxidation conditions [24,25,28,33,36,37,40].

For each bench test, a groundwater sample having a volume of 800 mL was transferred into a 1000 mL glass reaction vessel. To avoid cross-contamination, before use all vessels were rinsed with HPLC grade acetone (>99.9%), and then rinsed several times with deionized Milli-Q water. In each experimental trial, after stirring the sample for a few minutes, the liquid oxidant was slowly added and the water samples were continuously magnetically stirred in order to obtain a complete mixing during all the test, and to allow a good contact between oxidant and polluted matrix. The oxidation reactions were quenched at the appropriate time by the addition of a sufficient amount of sodium metabisulfite solution. This sulfite salt acts as oxidant scavenger and results in a sudden drop of the oxidation reactions. To ensure the complete consumption of all the oxidant available, the amount of reductive agent added was equal to the total amount of oxidant dosed at the beginning of the test. The reaction between sodium metabisulfite and the oxidant agents are very rapid and tend to conclude within minutes. Here, the extent of the quenching process was measured for the hydrogen peroxide reactions only, with the use of peroxide test strips (EM Quant Peroxide Test Strips, EMD Chemicals

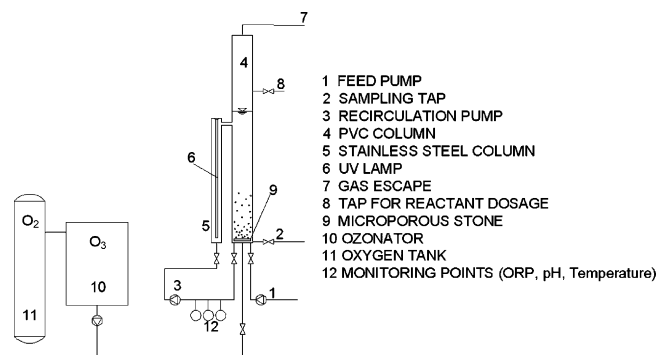


Fig. 1. Setup for chemical oxidation and AOP column tests.

Inc.) to measure the residual hydrogen peroxide concentration.

All tests were conducted at room temperature. During the tests the reaction bottles were covered with aluminum foils to avoid the photolytic degradation of the organolead compounds in the water samples.

### 2.2.2. Chemical oxidation and AOP column tests

The second set of experiments consisted in a series of column test performed with the use of oxygen, ozone, UV radiation and AOPs, which included the following combinations of treatments: hydrogen peroxide and ozone, hydrogen peroxide and UV radiation, ozone and UV radiation.

In order to perform these tests a special experimental setup was assembled. The setup, shown in Fig. 1, included a PVC transparent column and a stainless steel column, connected through a pipe and a peristaltic pump. The PVC column (internal diameter 8.5 cm, length 2.5 m) was equipped with several taps which allowed to dose liquid or gaseous reactants and to collect water samples during the tests. A microporous stone was placed at the bottom of the column, just above the entrance of the gaseous reactants, to enhance the diffusion of the inflowing gaseous reactant in the water sample and to avoid the formation of too big bubbles. During the tests the transparent plastic column was covered with aluminum foil to avoid sunlight to degrade the target compounds. The stainless steel column was used to contain a UV lamp (power 200 W, lamp length 160 cm, lamp external diameter 2.3 cm). A peristaltic pump was used to recirculate the water among the two columns and to ensure a good mechanical mixing of the treated water sample.

At the beginning of each test, a fixed volume of contaminated water (3.8 L) was inserted into the experimental setup by the peristaltic pump. Liquid oxidants, as hydrogen peroxide used for some AOP tests, were dosed by a tap in the upper part of the PVC column. For the tests with ozone and oxygen, the gaseous oxidant entered the system from the bottom of the PVC column, where the microporous stone could break the flux into small bubbles, thus enhancing the contact with the groundwater to be treated. The ozone-gas was produced by an ozonator (Microlab form Aeraque I.T. Srl, PV, Italy) from pure oxygen, provided by an oxygen tank, with an average ozone flow of 3 L/min; the same constant gaseous flow was used during the treatment with pure oxygen. During the tests, the gaseous oxidant, both oxygen or

ozone, flowed inside the wastewater with upflow stream and the exhaust gas, containing residual ozone and oxygen, could escape the setup through a vent in the upper part of the PVC column, to be diffused in outdoor air or to flow inside an active carbon bed to consume the excess of ozone. The treated wastewater could be sampled at different times during the experimental trials by a tap in the lower part of the PVC column: this allowed to evaluate reaction kinetics.

In the tests performed with UV radiation, oxygen and ozone, since the oxidant flow was maintained constant, the dosage of oxidant agent was regulated by changing the treatment duration: therefore, in the tests with the lower duration, the oxidant dose is minor than in the longer tests.

The tests performed with this experimental setup are summarized in Table 3.

### 2.2.3. Activated carbon column tests and combined treatments

The filtration tests on granular activated carbon were performed according to the ASTM procedure for the Rapid Small Scale Column Tests (RSSCT) [52], by using a stainless steel column (internal diameter 8 mm, length 25 cm). The granular activated carbon used was the “PICATIF TE 60”, with average diameter equal to 180  $\mu\text{m}$ . In the experimental setup, a sand filtration column was used before filtration on activated carbon to avoid the clogging of the carbon bed.

During each test, the groundwater sample was pumped through a peristaltic pump into the test columns, with upflow streams, while the outcoming flow was collected into a tank for sample analysis. The trials were conducted at room temperature (i.e. about 20 °C).

Two tests were performed, with two different treatment durations: 3 h (test GAC.3h) and 14 days (test GAC.14d). The aim of the two experiments was to assess the pollutant removal of GAC in case of a new carbon bed (shorter test) and after a significant filtration time (longer tests), so as to estimate the volume it was possible to treat before the carbon exhausted.

Besides these experiments, another test was performed, to assess the effects of the combined use of activated carbon and of AOPs. In this trial, the groundwater was at first filtered on the activated carbon bed, according to the same method used for the GAC tests, then it was treated with the use of ozone and hydrogen peroxide, using the same modalities described in Section 2.2 for the AOP trials.

### 2.3. Analysis

The TEL content was determined by purge&trap extraction followed by gas-chromatographic detection, using a AGILENT 5973 INERT gas chromatograph.

To determine the ionic alkyl lead (TREL and DEL) contents, the water samples were at first buffered at pH 8.5 with an ethylenediaminetetraacetic acid (EDTA), sodium diethyldithiocarbamate (NaDDTC) and ammonia solution, then extracted into *n*-hexane, derivatized with Grignard reagent, and then detected by GC–MS, using a VARIAN 4000 GC/MS.

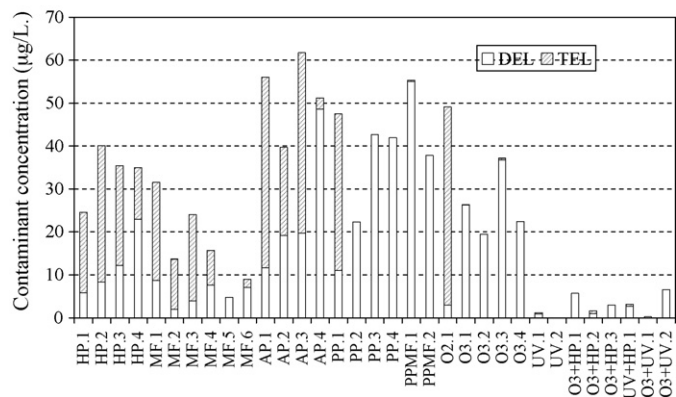


Fig. 2. Results of the chemical oxidation tests and AOP tests: contaminant concentration in the treated samples. TEL final concentrations are not shown because they are always inferior to 0.07  $\mu\text{g/L}$ .

Total lead concentrations were determined by ICP, using a VARIAN ICP-OES VISTA spectrometer. Before the analysis, the samples were mineralized with nitric acid, heated to 180 °C for 20 min, filtrated with 0.45  $\mu\text{m}$  filter, and extracted by sonication.

The detection limits were 0.005  $\mu\text{g/L}$  for TEL and 0.1  $\mu\text{g/L}$  for TREL and DEL.

## 3. Results and discussion

In order to assess the efficiency of the tested treatments, the removal percentages were calculated for TEL, TREL and for total organic lead. It was not possible to assess the removal of DEL, since this compound derives from the partial degradation of the other organic lead forms (tetraethyl and especially triethyl lead, which is the main part of the total organolead content); for this reason, its content in the treated samples can be higher than the content in the original samples. The main results achieved during the experimental investigation are shown in Table 4 and in Fig. 2.

### 3.1. Chemical oxidation batch tests

As can be seen from Table 4, all chemical oxidation tests resulted in a complete or very high removal of TEL, whose concentrations in most of the treated samples were below the detection limit (0.005  $\mu\text{g/L}$ ), but different reactants and different oxidant dosages led to different removal efficiencies for TREL and for TOL. For this latter parameter, the removal percentages were highly influenced by the accumulation of DEL, mainly caused by a partial decomposition of the tetraethyl lead content.

In the tests performed with hydrogen peroxide, the TREL removal percentages varied from 56 to 84%, while the TOL removal varied from 48 to 67%. The removal efficiencies did not show a definite trend, the highest TREL removal having been achieved in test HP.4 (oxidant dose equal to 20 mmol), while the highest TOL removal was achieved in test HP.1, with an oxidant dose of 0.2 mmol.

Table 3  
Chemical oxidation and AOP column tests: reactant dosages and contact times

Treatment	Test	Reactant dosage	Contact time (min)
Oxygen	O2.1	3L <sub>O<sub>3</sub></sub> /min	20
	O3.1	3L <sub>O<sub>3</sub></sub> /min	5
Ozone	O3.2	3L <sub>O<sub>3</sub></sub> /min	10
	O3.3	3L <sub>O<sub>3</sub></sub> /min	20
	O3.4	3L <sub>O<sub>3</sub></sub> /min	60
	UV.1	200 W <sub>UV</sub> lamp	5
UV	UV.2	200 W <sub>UV</sub> lamp	10
	(O3 + H2O2).1	3L <sub>O<sub>3</sub></sub> /min + 15 mmolH <sub>2</sub> O <sub>2</sub>	5
AOP ozone and H <sub>2</sub> O <sub>2</sub>	(O3 + H2O2).2	3L <sub>O<sub>3</sub></sub> /min + 5 mmolH <sub>2</sub> O <sub>2</sub>	20
	(O3 + H2O2).3	3L <sub>O<sub>3</sub></sub> /min + 15 mmolH <sub>2</sub> O <sub>2</sub>	20
AOP UV and H <sub>2</sub> O <sub>2</sub>	(UV + H2O2).1	200 W <sub>UV</sub> lamp + 15 mmolH <sub>2</sub> O <sub>2</sub>	20
AOP ozone and UV	(O <sub>3</sub> + UV).1	3L <sub>O<sub>3</sub></sub> /min + 200 W <sub>UV</sub> lamp	5
	(O <sub>3</sub> + UV).2	3L <sub>O<sub>3</sub></sub> /min + 200 W <sub>UV</sub> lamp	10

The results achieved with the use of modified Fenton's reagent were very satisfying, as they showed a nearly complete removal of both TEL and TREL, without accumulation of DEL. The removal efficiencies increased with the oxidant dose, the best results having been registered with an oxidant dosage of 20 mmol, which resulted in 91% TOL removal. A further increase in the oxidant dose (e.g. from 20 to 40 mmol) did not result in a contaminant removal improvement. It can be pointed out that as the contact time increases, as from test MF.3 (contact time 3 h) to test MF.4 (contact time 15 h), a limited improvement of system efficiency was encountered.

The removal efficiencies encountered with the use of activated persulfate were limited: a good TREL removal could be achieved only with higher oxidant dosages (e.g. 10–20 mmol) or with longer contact times. Moreover, with this reactant the TOL removal did not exceed 51%.

The use of permanganate led to a complete removal of TEL and TREL with all oxidant dosages except the lowest one (0.2 mmol), while the TOL removal did not exceed 66% even with the highest permanganate doses. This result is of concern, since this reactant proved to be able to decompose TEL and TREL even with low dosages, but seems to be unable to complete the organic lead decomposition, thus leading to a significant DEL accumulation. Based on these results, two more tests were performed, with a combined dosage of potassium permanganate and of modified Fenton's reagent. The results of these tests did not match the expectations, being of the same order of magnitude of trials performed with the sole use of permanganate, and even inferior to the remediation efficiencies achieved with a correspondent dosage of modified Fenton's reagent only. This was probably due to the excessive strength of the reactions achieved, which were very rapid, as indicated by a sudden increase in the solution temperature, and probably resulted in a significant oxidant self-consumption. It has already observed [53] that very fast and strong reactions could lead to a decrease in the contaminant removal efficiency, because of the rapid oxidant consumption.

On the whole, among all the chemical oxidation batch tests performed, the best remediation performances were achieved with the use of modified Fenton's reagent, with a peroxide con-

centration equal to 20 mmol (a molar ratio iron:oxidant equal to 1:20 was used) and a contact time of 3 h.

### 3.2. Chemical oxidation and AOP column tests

The use of oxygen as remediation agent led to a good removal of TEL only, with a limited removal of TREL and a consequent poor removal of TOL (32%), even if a significant accumulation of DEL was not encountered.

During all four tests performed with ozone a complete removal of TREL was encountered, but the TOL removal was limited, varying from 50 and 67%, mainly because of quite high DEL concentration in the final treated samples. In tests O3.3 and O3.4, the TEL removals were very limited, about 30–40%; these results can be considered as a consequence of sample heterogeneity, which caused a very high initial TEL content. The treatment performances did not seem to increase as the oxidant dose (i.e. the test duration) increases, since the results of the longest tests (O3.3 and O3.4) did not differ much from the results of the shortest tests (O3.1 and O3.2). On the whole, ozone proved to be able to oxidize TEL and TREL, but it seems unable to attack DEL, thus failing to reach a complete organolead removal.

The use of UV radiation as oxidant agent gave very good results, with a complete removal of TEL and TREL, and a TOL removal efficiency quite high, varying from 81 to 89%. Moreover, this treatment did not cause any accumulation of DEL. Among the target organolead compounds, DEL is the most refractory pollutant. Moreover, it can be produced as a result of TEL and TREL decomposition. DEL tends to accumulate in the treated water sample when the oxidation process attacks TEL and TREL, but it is unable to degrade DEL. If, as in the present case, TEL and TREL concentration significantly decrease and no DEL accumulation is encountered, it means that the oxidation process is strong enough to attack the DEL deriving from the partial oxidation of the other organolead compounds.

The combined use of hydrogen peroxide and ozone (peroxide treatment) resulted in an excellent removal of both TEL, TREL and TOL, without accumulation of DEL, even at the lower dose tested. Also the combined use of hydrogen peroxide and



Table 4  
Results of the performed tests

Treatment	Reactant	Test	TEL ( $\mu\text{g/L}$ )	TREL ( $\mu\text{g/L}$ )	DEL ( $\mu\text{g/L}$ )	TOL ( $\mu\text{g/L}$ )	TEL removal efficiency	TREL removal efficiency	TOL removal efficiency	
Chemical oxidation	Hydrogen peroxide	HP.1	<0.005	18.7	5.9	24.6	>99%	68%	65%	
		HP.2	0.02	31.8	8.3	40.1	>99%	56%	51%	
		HP.3	<0.005	23.2	12.2	35.4	>99%	69%	56%	
		HP.4	<0.005	12.0	23.0	35.0	>99%	54%	56%	
		MF.1	<0.005	22.8	8.7	31.5	>99%	60%	55%	
	Modified Fenton's reagent	MF.2	0.02	11.7	2.0	13.7	97%	84%	83%	
		MF.3	<0.005	20.0	4.0	24.0	>99%	84%	82%	
		MF.4	<0.005	8.1	7.6	15.7	>99%	94%	86%	
		MF.5	<0.005	<0.1	4.8	4.8	>99%	>99%	94%	
		MF.6	<0.005	1.9	7.1	9.0	>99%	98%	90%	
		Activated persulfate	AP.1	<0.005	44.3	11.7	56.0	>99%	23%	21%
	AP.2		<0.005	20.5	19.2	39.7	>99%	72%	51%	
	AP.3		<0.005	42.0	19.7	61.7	>99%	66%	53%	
	AP.4		<0.005	2.6	48.6	51.2	>99%	97%	45%	
	Potassium permanganate	PP.1	<0.005	36.5	11.0	47.5	>99%	37%	33%	
		PP.2	<0.005	<0.1	22.3	22.3	>99%	>99%	73%	
		PP.3	<0.005	<0.1	42.7	42.7	>99%	>99%	67%	
		PP.4	<0.005	<0.1	41.9	41.9	>99%	>99%	55%	
	Modified Fenton's reagent and permanganate	PPMF.1	<0.005	0.3	55.0	55.3	>99%	>99%	52%	
		PPMF.2	<0.005	<0.1	37.8	37.8	>99%	>99%	67%	
Oxygen	Oxygen	O2.1	<0.005	46.1	3.0	49.1	>99%	34%	32%	
		O3.1	0.05	<0.1	26.3	26.4	94%	>99%	68%	
	Ozone	O3.2	<0.005	<0.1	19.5	19.5	>99%	>99%	73%	
		O3.3	0.07	0.4	36.7	37.2	30%	99%	55%	
		O3.4	0.06	<0.1	22.4	22.5	40%	>99%	73%	
		UV.1	<0.005	0.3	0.9	1.2	>99%	>99%	98%	
		UV.2	<0.005	<0.1	<0.1	<0.1	>99%	>99%	>99%	
Chemical oxidation and AOP column tests	UV	O3 + HP.1	<0.005	0.0	5.7	5.7	>99%	>99%	92%	
		O3 + HP.2	<0.005	0.6	1.0	1.6	>99%	99%	98%	
	AOP ozone and H <sub>2</sub> O <sub>2</sub>	O3 + HP.3	<0.005	<0.1	3.0	3.0	>99%	>99%	97%	
		UV + HP.1	<0.005	0.4	2.7	3.1	>99%	99%	96%	
	AOP UV and H <sub>2</sub> O <sub>2</sub>	O3 + UV.1	<0.005	0.0	0.2	0.2	–	>99%	>99%	
		O3 + UV.2	<0.005	<0.1	6.6	6.6	–	>99%	91%	
	GAC adsorption	GAC	GAC.3h							
			Inflow—total mass ( $\mu\text{g}$ )	0.93	58	34	92	92%	99%	99%
			Outflow—total mass ( $\mu\text{g}$ )	0.07	0.8	<0.1	0.9			
			GAC.14d							
Inflow—total mass ( $\mu\text{g}$ )			50.0	20001	641	20692	>99%	>99%	70%	
Outflow—total mass ( $\mu\text{g}$ )			– <sup>a</sup>	– <sup>a</sup>	6271	6271				
GAC + perozone	Combined treatment GAC and AOP	GAC + AOP								
		Inflow	<0.005	97.3	2.7	100.0	–	>99%	74% <sup>b</sup>	
		Outflow first treatment	<0.005	<0.1	25.7	25.7				
		Inflow second treatment	<0.005	<0.1	25.7	25.7	–	>99%	93% <sup>b</sup>	
Outflow	<0.005	<0.1	1.7	1.7						

<sup>a</sup> Concentrations always below the detection limit.

<sup>b</sup> In test GAC + AOP, the sole GAC treatment resulted in 74% TOL removal, the sole AOP treatment resulted in 93% TOL removal, while the combined treatment achieved 98% TOL removal.

UV radiation resulted in an excellent contaminant removal, with complete degradation of TEL and TREL and 96% TOL removal, with low final DEL and TOL concentrations (2.7 and 3.1  $\mu\text{g/L}$  respectively). The two tests performed with ozone and UV radiation resulted in a good TOL removal, with a complete removal of TREL; in this case, however, a slight DEL accumulation was encountered, and the test performances were lower than in the other AOP tests, the TOL removal efficiency being of the order of 73–84%.

### 3.3. Activated carbon column tests and combined treatments

The filtration on the GAC bed resulted in a complete removal of all organic lead species in the short test (duration 3 h), but the longer tests had an average 70% removal for TOL, showing a rapid GAC consumption. Moreover, the groundwater treated by this method was characterized by significant residual DEL content.

When the groundwater filtered in the GAC column was also treated with perozone, the results were excellent, with a TOL removal about 98% compared to the initial TOL concentration (the sole GAC filtration resulted in a 74% TOL removal, while the perozone treatment showed a 93% removal). During this test, a complete removal of TEL and TREL was encountered, with a low final DEL concentration (1.7  $\mu\text{g/L}$ ).

#### 4. Conclusions

This research was undergone to assess the effectiveness of chemical oxidation, AOPs and filtration on activated carbon for the ex situ remediation of a groundwater contaminated by organic lead species, including TEL, TREL and DEL.

During the experimental investigation, several laboratory tests were performed, including chemical oxidation batch tests with different reactants (hydrogen peroxide, modified Fenton's reagent, potassium permanganate, activated potassium persulfate, oxygen and combinations of potassium permanganate and modified Fenton's reagent), AOP tests with ozone, UV radiation and hydrogen peroxide, and filtration on granular activated carbon. The effects of activated carbon filtration followed by chemical oxidation were also investigated.

Both chemical oxidation and AOPs proved to be effective for the remediation of the addressed contaminants. The treatments which showed the best remediation performances were: chemical oxidation with modified Fenton's reagent, AOPs with hydrogen peroxide and ozone (perozone), AOPs with hydrogen peroxide and UV radiation, and the combined treatment with activated carbon filtration followed by a chemical oxidation treatment with perozone. These treatments showed a 90% removal of TOL, with excellent removals of TEL and TREL (concentrations in treated samples below detection limits), without accumulation of DEL (final concentrations were below 5  $\mu\text{g/L}$ ). On the other hand, permanganate, persulfate, ozone, as well as the combination of permanganate and Fenton's reagent proved to be able to oxidize TEL and TREL, but it seems unable to attack DEL, thus failing to reach a complete organolead removal.

Also the filtration on activated carbon showed to be effective in the groundwater remediation, especially when used in combination with perozone as finishing treatment. In this case a 98% TOL removal was achieved, with a complete TEL and TREL remediation.

On the whole, both the use of AOPs, and of GAC filtration followed by chemical oxidation can be considered amenably applicable for the ex situ treatment of the contaminated groundwater of concern.

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