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Effectiveness of ozone as a decontaminant in soils containing DDT and lindane

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Summary

This work focused on the application of an advanced oxidation process (AOP) such as ozonation in soils with sandy texture and little organic matter, contaminated with the pesticides lindane and DDT. The O3 flux was applied in triplicates for each treatment, with the independent variables: Dry Soil or Wet Soil, and ozone treatment time (0.012 g per minute) of 30min and 60min (each treatment with its respective control). The results showed a decrease of 30.72% of DDT and 26.24% of lindane corresponding to the 60-minute dry soil treatment. A previous analysis of soil organic matter showed a 70% decrease in relation to the control, in dry soil. In a test on the biological activity of soils subjected to the treatments: contaminated soil treated with ozone and decontaminated soil inoculated with non-contaminated soil extract, the results reveal that non-contaminated and contaminated soils showed normal microbial activity, with differences in dynamics, and visible adaptation and selection phases in those subjected to ozone treatment. Basal respiration and metabolic quotient qCO2 values were also obtained, showing an increase in the ozone and re-inoculated soil treatments, in which a certain degree of stress can be observed.

Key words: Soils, Advanced Oxidation Processes (AOP), Ozone, Dichloro diphenyl trichloroethane (DDT), hexachlorocyclohexane (HCH), Organic Matter.

1. INTRODUCTION Soil Contamination

Soil performs essential environmental functions for maintaining biogeochemical and organic matter cycles, and providing food and other ecosystem services (Lopez, Poch, & Porta, 2019). The term "ecosystem services" is defined as the benefits that humans obtain from ecosystems (Millennium Ecosystem Assessment, 2005), which directly or indirectly support our survival and quality of life. There are 4 types of ecosystem services, the first is the Provisioning Service (food and raw materials), the second is the Regulating Service (air quality and local climate, carbon sequestration, moderation of extreme events, water purification, etc.), the third is the Supporting Service (habitat for species, conservation of genetic diversity). Fourth and last is the Cultural Service where recreation, mental and physical health activities are highlighted (FAO, 2017).

Soil is a key component in the ecosystem, its protection is fundamental and constitutes one of the most sensitive and vulnerable receiving environments. The Rio Summit, 1992, declared the importance of soil

protection and its potential uses for sustainable development (Chen, et al., 2016); (Ministry of the Presidency, 2005).

Soil degradation processes pose a risk to ecosystem functioning and, therefore, a threat to health. Among the different degradation processes suffered by soils, contamination from anthropogenic activities is a widespread problem (FAO, 2015). Royal Decree 9/2005, on contaminated soils Ministry of the Presidency (2005), defines a contaminated soil as one whose characteristics have been negatively altered by the presence of chemical components of a hazardous nature of human origin, in such concentration as to generate an unacceptable risk to human health or the environment, and so declared by express resolution. When a soil is contaminated, a chain reaction is triggered. Soil biodiversity is disturbed, reducing the organic matter present and its filtering action. In addition, the water stored in the soil and groundwater is contaminated, generating an imbalance of its nutrients (FAO, 2019). Soil contamination happens from a variety of causes. Excessive application of pesticides on croplands, industrial wastewater, accidental releases of toxic pollutants and leaching from landfills have been serious perpetrators in the contamination and deterioration of soil quality (Chen, et al., 2016). The presence of contaminants in the environment, is usually due to anthropogenic activities (Rodriguez, McLaughlin, & Pennock, 2019). There are some groups of contaminants that are commonly found in different soils (Fig1).

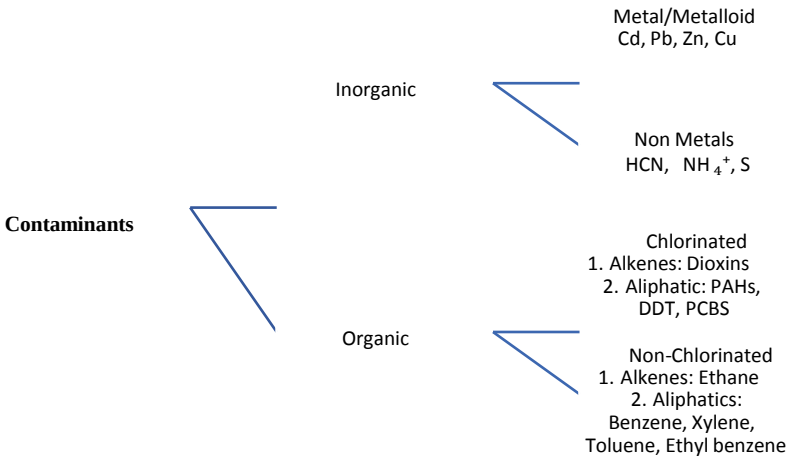


Figure 1. Categorization of common contaminants in soils. Adapted from FAO, 2019.

1.2. Persistent organic pollutants

Currently, more than 200,000 synthetic chemicals are used and produced for domestic, agricultural and industrial purposes (Derek & Philip, 2006). Many of these substances are released into the environment generating harmful effects on the ecosystem. The presence and persistence of this immense quantity of substances causes changes in the chemical structure of the biosphere (Dachs & Méjanelle, 2010). Among these synthetic chemicals are persistent organic pollutants (POPs), which are part of a large group of toxic compounds, subject to bioaccumulation and long-range transport. POPs are part of all phases of ecosystems and in all living beings that inhabit them (Navas, 2017). In order to safeguard human health and the environment from POPs, the United Nations Environment Programme (UNEP) promoted the adoption of the Stockholm Convention. The objective of this convention was to reduce or eliminate the use or production of 12 preferred POPs; other compounds were added later, until there are currently 25 (Table 1). Similarly with the Convention on Long-range Transboundary Air Pollution (CLRTAP) belonging to the United Nations Economic Commission for Europe (UNECE), from which similar restrictions were practiced from a list of 16 POPs that was also later expanded (Table 1) (Casal, 2018).

Table 1. List of persistent organic pollutants present in the Stockholm Convention and Convention on Long-range Transboundary Air Pollution (Casal, 2018).

Stockholm Convention			
Disposal		**Prohibition**	**Unintentional production**
Aldrin	Hexachlorobenzene	Perfluorooctane sulfonic acid	Dioxins and furans
Chlordá	Hexachlorocyclohexane	Salts and fluoride from sulfonyl	Hexachlorobenzene
Chlordecone	Lindane	Perfluorooctane	PCBs
Dieldrina	Mirex	DDT	
Ether of Pentabromodiphenyl	PBB		
Endrin	PBDE		
Endosulfan	Pentachlorobenzene	Heptachlor	Toxafe

Convention on Long-range Transboundary Air Pollution		
Sulfonic acid from perfluorooctane	Endosulfan	Mirex
Sulfonyl fluoride	Endrina	PBDE
Perfluorooctane	Hexachlorocyclohexane	PCB
Aldrin	Heptachlor	Pentachlorobenzene
Chlordane	Hexabromobiphenyl	Naphthalenes
Chlordecone	Hexachlorobenzene	Polychlorinated
DDT	Hexachlorobutadiene	Chlorinated kerosenes
9Dieldrina	Lindane	short-chain
Ether from hexabromodiphenyl	Toxaphene	

Once emitted, POPs accumulate in different reservoirs such as oceans, soils, glaciers, depending on factors such as: the site where they were released a priori, the transport process and the specific characteristics of POPs (hydrophobicity, persistence, volatility). Then these reservoirs manage to re- emit POPs for transport, this process being a secondary source (Hung, et al., 2016).

Organochlorine compounds. DDT and Lindane

Organochlorine compounds are potentially contaminating chemical substances whose main characteristic is their high chemical stability, and which are insoluble in water and soluble in fats. They comprise different chemical groups; such as ethane derivatives as is the case of DDT, cyclodienes including dieldrin, chlordane, aldrin, endrin, heptachlor and toxaphene and hexachlorocyclohexanes as is the case of lindane (Zaragoza, et al., 2016).

Organochlorine compounds have a high permanence in the soil due to their hydrophobic nature, thus facilitating their bioconcentration and bioaccumulation in the trophic chain (Barrera, et al., 2006). The adsorptive-desorptive behavior of hydrophobic organic compounds plays a very important role in the transport and availability of contaminants in soils and sediments (Barrera, et al., 2006).

Soil organic matter and POPs form stable bonds, where they remain non-extractable. However, environmental modifications to the soil can change the rates of persistent organic compounds in the soil, causing them to become extractable (Rodriguez, McLaughlin, & Pennock, 2019).

1.3.1. DDT

One of the most widely used insecticides for pest control during the 20th century is the classically named dichlorodiphenyltrichloroethane (DDT, 1,1,1-trichloro-2,2bis(trichlorophenyl)-ethane), which is highly harmful and bioaccumulative (Fig. 2, Table 2). Despite its ban, it is still used in some countries. DDT is a colorless, crystalline organic compound, soluble in apolar solvents and fats and poorly soluble in water. Since it is insoluble in water and very lipophilic, it accumulates in the trophic chain (Mora, 2011). Even when not used, DDT and its metabolites (DDE, DDD) are present in different environmental matrices, tend to accumulate in lipid-rich tissues, and are excreted/secreted in different ways including breast milk, so it is necessary to evaluate the risks associated with exposure to DDT and other organochlorine compounds through ingestion (Fig. 3) (Oddy, 2001). (Fig. 3) (Oddy, 2001).

Molecular **formula**

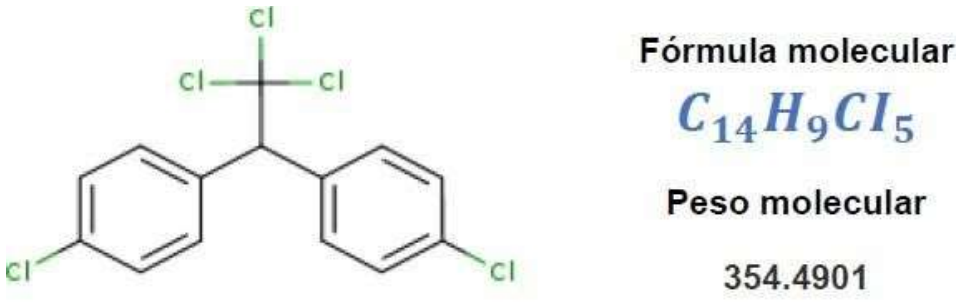


Figura 2. Molécula DDT (National Library Medicine)

Figure 3. DDT decomposition, a) HCl elimination to form DDE under aerobic conditions b) reductive dechlorination to form DDD under anaerobic conditions. Adapted from (Wenming, Mengling, Hongming, Mingyong, & Yu, 2020).

Table 2. Physical properties of the substance

Physical property	Value	Units	Temp (degrees C)
Melting point	108,5	grade C	
log P (octanol-water)	6,91	(none)	
Water solubility	0,0055	mg / L	25
Vapor pressure	1.60E07	mm Hg	20

Henry's Law Constant	8.32E06	atm-m^3 / mol	25
Atmospheric OH rate constant	3.44E12	cm3 / moleculesg	25

1.3.2. Lindane

In addition to DDT, lindane or gamma hexachlorocyclohexane (HCH) is another pesticide that is widely used despite the fact that its application has been banned. This substance is present in the environment in different isomeric forms (alpha, beta, gamma and delta) (Fig. 4). It is a slightly volatile, solid, off-white compound with a musty odor under ordinary pressure and temperature conditions (Table 3). It dissolves in organic solvents, is chemically stable and non-polar (ECHA, 2020). The global application of lindane has been considered to be 600,000 tons in the second half of the 20th century. In addition, the manufacture of one ton of lindane generates approximately 6-10 tons of wastes exhibiting other HCH isomers. According to a recent estimate, 4.8 million tons of lindane production waste may still be present in the environment (Faure, Hanna, Rybnikova, Tascone, & Usman, 2017).

Molecular formula

$C_6H_6Cl_6$

Molecular weight **290.831**

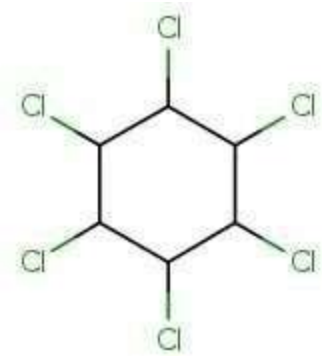


Figure 4. Lindane molecule (National Library Medicine)

Table 3. Physical properties of the compound

Physical property	Value	Units	Temp (degrees C)
Melting point	112,5	grade C	
log P (octanol-water)	4.260	(none)	
Water solubility	8	mg / L	25
Vapor pressure	7.83E04	mm Hg	25
Henry's Law Constant	2.56E04	atm-m3 /mole	25
Atmospheric OH rate constant	5.73E13	cm3/ moleculesg	25

1.4. Advanced Oxidation Processes

Currently, potential hazards to the environment and human health have been recorded due to the use of organic compounds such as pesticides, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), among others (Chen, et al., 2016). It is because of the above that there is a high interest in the development of research and technologies to reduce the presence of persistent organic pollutants in the environment (Navas, 2017). Advanced oxidation processes (POAs) are suitable for degrading all types of

organic pollutants into harmless products and almost all rely on the production of reactive hydroxyl radicals (-OH) with a redox potential of 2.8 V (Chen, et al., 2016).

In recent years POAs are part of a promising technology for the removal of organic compounds present in the soil that could be easily combined with another type of technology such as bioremediation (Derudi, Lombardi, Nano, Rota, & Venturini, 2007). There are different processes to generate -OH radicals and thus allow a better treatment result. The techniques frequently used in POAs (Fig.5) are Fenton Oxidation, Photocatalysis, Plasma Electrooxidation and Ozonation (Chen, et al., 2016), and involve different types of media (water, soil, air). They are described in Figure 5.

There are soil decontamination processes based on chemical oxidation and applicable "in situ", the so-called ISCO (In situ Chemical Oxydation) (Huling & Pivetz, 2006); (Kluck & Achari, 2015); (Ranc, Faure, Crozec, & Simmonot, 2016). This group includes treatments with permanganate, persulfate, in addition to those previously mentioned, Fenton and Ozone.

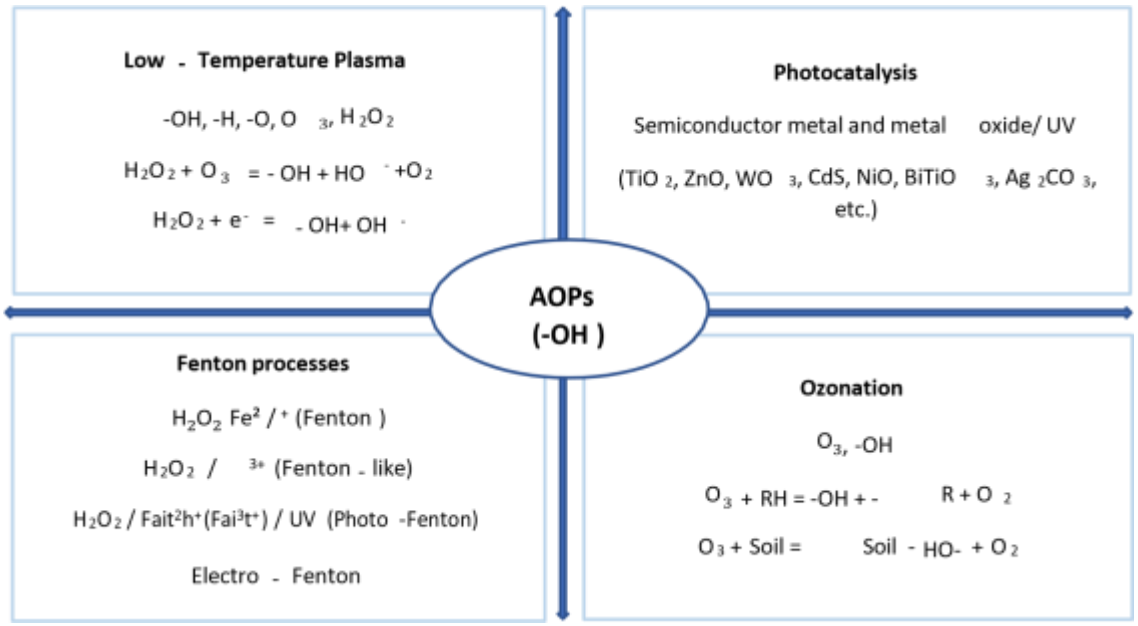


Figure 5. Hydroxyl radicals formed according to advanced oxidation technologies. Adapted from Chen, et al. 2016.

1.4.1. Fenton's method

The Fenton method is a common method to generate HO- radicals through the application of iron salts in the presence of H $O_{22.}$. This process occurs through the reaction between H O_{22} and ferrous iron in an acid medium (pH 2.5 - 4). Due to the catalytic function of iron, it is not consumed or diminished during the procedure, quite the contrary, Fe^{2+} is regenerated from Fe^{3+} (Bengoa, Bes, & M,T Silva, 2018).This method is effective in the treatment of wastewater with the presence of organochlorine contaminants and dyes (US Peroxide, LLC, 2009). Also in soils it has been used to decontaminate, for example, polycyclic aromatic hydrocarbons (Chiew, Gana, Kiat, & Yapa, 2011) or other groups of pollutants (biphenylpolychlorinated compounds, dioxins, fuel oil, etc.), sometimes combined with bioremediation techniques (Huang, et al., 2017). This technique has been used to eliminate pesticides (including DDT and Lindane), although one of the collateral effects (apart from the degradation of organic matter and microorganisms) the increase of metals in the soil (Morillo & Villaverde, 2017). The presence of by-products is a problem in some of the AOP techniques (Huling & Pivetz, 2006).

1.4.2. Ozone Techniques

Ozone-based POAs involve ozone in combination with techniques such as UV irradiation and the use of hydrogen peroxide to increase the generation of -OH radicals and thus obtain greater pollutant removal (Beltran, 2013). Ozone is used to mineralize organic molecules. In the ozonation process the efficiency depends on the contamination of the soil or water to be treated, concentration of O_3 and contact time (Bengoa, Bes, & M,T Silva, 2018). Ozone is produced through an O_3 generator and a feed gas that can be pure oxygen or air. The O_3 concentration at the output of the system is different when using air and pure oxygen, for the former the concentration varies between 1 and 4% and for pure oxygen it usually ranges between 4 and 12 %. There are three types of methods for ozone generation, UV methods, electrochemical discharge and corona discharge or also called

"Silent electrical discharges" which is the most commonly applied method. It is important that the ozone has contact with the material to be treated and is dispersed as much as possible. Currently, ozonation has a wide range of applications, it can include oxidation of recalcitrant organic pollutants (pesticides, pharmaceuticals), water purification and purification, oxidation of inorganic pollutants (sulfites, manganese, iron) (Bengoa, Bes, & M, T Silva, 2018). Applying ozone is recommended for the treatment of chemical species with the presence of sulfur, oxygen, nitrogen, or phosphorus, therefore, compounds such as pesticides, aromatic species can through ozone be transformed and pass to a biodegradable phase (Bablon, et al., 2001). The ozone flux may be lower when only increasing biodegradability, rather than total mineralization of organic matter, is intended. Ozone can react through two mechanisms, one of them is the direct way that frequently reacts with organic matter with double bonds, or amines, and the indirect way that is a free radical process carried out at a higher speed. The parameters to be taken into account are pH (the higher the pH, the lower the stability of O_3), dosage and optimum contact time. Regarding the advantages, the raw material is easily accessible, it reacts efficiently with organic and inorganic compounds thanks to its high reactivity and redox potential, among the disadvantages are, it must be performed in situ, generating ozone in high concentrations is toxic and irritating, it also has high costs (Bengoa, Bes, & M, T Silva, 2018).

1.5. Application of POA techniques for the remediation of contaminated soils.

with pesticides and other persistent organic pollutants.

POAs techniques have been used for the remediation of soils with persistent organic pollutants. Table 4 shows some experiments applying the POAs techniques already mentioned in section 1.4. For the treatment of soils contaminated with DDT, the photocatalysis and fenton techniques have been applied. In the first technique, the experiment was based on UV application at 25ºC for a period of 24h and application of TiO_2 at different concentrations (0%,0.5%,1%,2%,3%). In this experiment there was an increase in photodegradation in alkaline medium, in addition the addition of TiO_2 improved DDT degradation unlike HS^- (bisulfide) which inhibited the degradation of the pollutant (Quan, Chen, Chen, Zhao, & Zhao, 2005). For the Fenton technique a study with diuron was based on the use of H O_{22} (60,000 mg kg^{-1}), neutral pH, citrate, Fe3+ (600mg kg^{-1}). The treatments were efficient with 80% removal of the contaminant when Fe^{3+} and citrate were applied. In the aqueous phase, stable Fe chelates are produced which, together with citrate, allow diuron removal (Vicente, et al,

2012). The Fenton technique has also been used for the removal of HCH (β HCH, γ-HCH). This experiment was performed in a neutral pH medium, with several reagents: H O_{22} alone, H O_{22} +Fe ll, Na S O_{228} alone and Na S O_{228} +Fe ll. The results showed 70% degradation β HCH and 95% γ- HCH with H O +Fe_{22}^{2+} ; 40% degradation β HCH and 90% γ-HCH with Na S O_{228}^{2+} +Fe.The experiment showed favorable results under saturated and unsaturated flow conditions, although in the presence of flow the contaminant degradation decreases when the flow rate is increased (50% - 0.5mL/min^{-1} and 30% - 2mL/min^{-1}) (Muhammad, Oriane, Victoria, Pierre, & Khalil, 2017). As for plasma oxidation, in a work with pentachlorophenol (PCP) was used in conditions of 95% concentration, humidity 20%, and 18kV for 60min, showing that increasing voltage

generates degradation products (oxalic acid, tetrachlorohydroquinone, formic acid), depending on the intensity and time of application (Tie, Na, Jie, & Yan, 2010).

1.5.1. Ozone application

As regards the use of ozone as an oxidant in soil decontamination techniques, different studies have been carried out. Richland (1992) in a study with phenol and trichlorobenzene (TCB) managed to reduce up to 97% of the phenol content and 67% TCB in the top layer of soil. They worked at pH of 6.4 to 6.7 and times of 1 to 1.5 hours. The greater the depth, the higher the percentage of removal, 93% for TCB. In another study with PAH, up to 95% of the compounds were removed (except the larger ones) in a few weeks for concentrations of 3g kg^{1} of young and aged soil, the latter showing lower reductions. There is greater effectiveness when mixing oxidation techniques with biological treatment (Derudi, Lombardi, Nano , Rota, & Venturini , 2007). Table 4 shows a summary of the above data. Decontamination by ozone techniques has some advantages over other ISCO modalities, such as the absence of metal by-products or ions (Fenton, persulfate, or permanganate) (Morillo & Villaverde, 2017). In addition, as it is a technique that is developed via gas it achieves better access to the active site and the possibility of treating soil in unsaturated and saturated zone (by bubbling). These authors consider ozone a promising technique for soil decontamination by chlorinated pesticides and point out the possibility of combining it with biological techniques. In another work, Ranc, Faure, Crozec, & Simmonot (2016), review ISCO methods for PAHs, suggesting some aspects to take into account, in view of effectiveness, such as the presence of organic matter, and some metals, or anions such as carbonates and sulfates, which can consume radicals and decrease their availability. The presence of colloids (clays, organic matter) reduces the oxidizing effect, because it allows sorption and protection of the pollutant, and the working pH is maintained in the physiological zone. Another observable effect in this type of oxidation is the remanence of ozone molecules and the increased concentration of oxygen in the soil matrix (product of the reaction) that facilitates, together with the initial fragmentation effect of the molecules themselves, the subsequent biodegradation (Kluck & Achari, 2015).

Table 4. Methodological Summary for soil remediation through AOPs

Technique	**Pesticide**	**Result**	**Reference**
Degradation by photocatalysis	DDT	Alkaline medium increased photodegradation - HS inhibiting pollutant degradation	(Quan, Chen, Chen, Zhao, & Zhao, 2005)
Fenton	DDT (diuron)	Fe^{3+} +citrate decreases 80% of the contaminant.	(Vicente, et al., 2012)
Plasma (pulsed crown)	*pentachlorophenol*	64 to 90 % for 60 min^{-1} of treatment.	(Tie, Na, Jie, & Yan, 2010)
Fenton	HCH (β HCH, γ-HCH)	70% degradation β HCH and 95% γHCH with H O +Fe_{22}^{2+} ; 40% of. degradation β HCH and 90% γ- HCH with Na S O +Fe $_{228}^{2}$	(Muhammad, Oriane, Victoria, Pierre, & Khalil, 2017)
Ozone	Phenol, 1,2,4 trichlorobenzene	The greater the depth, the higher the percentage of removal, 93% for TCB	(Richland, 1992)

Ozone	PAH (Aromatic hydrocarbons polycyclic)	95% removal for all contaminants in young soils. 80% removal in old soils	(Derudi, Venturini, Lombardi, Nano, & Rota, 2007)

2. Objectives

The objectives of this work are as follows:

1. To develop an experimental system for soil decontamination by ozone treatment at laboratory scale, to remove organic pollutants from contaminated soil.
2. Check the operation of the system, evaluating the reduction of contamination, and controlling two variables: time of ozone application and humidity status of the sample, as a preliminary phase.
3. To observe the effects on the biological activity of the treated soils, in order to evaluate the possibility and conditions for linking an oxidation and a bioremediation treatment process.

2.1. Methods

2.1.1. Ozone Calibration

In order to calibrate the ozone generator to ensure a comparable flow rate in the different experiments, we proceeded as described below. The dry oxygen flow, regulated at 0.75 L/min, was connected to the inlet of the ozone generator. The output of the ozone generator was connected with the input to a bubbler bottle containing a volume of 80 ml of 0.5M potassium iodide. After the ozone contact time had elapsed (10 minutes, 15 minutes), 1 mL aliquots were withdrawn for titration with 0.05 M sodium thiosulfate solution. Three calibration repetitions were performed so that the configuration would generate a stable ozone concentration at the system output (Morera, 2004).

2.1.2. Soil organic matter analysis

In order to preliminarily evaluate the effects of ozone on soil organic materials, the soil organic matter was quantified before and after ozone application, under different conditions, as they would be applied in the decontamination part. The two parameters used were oxidizable organic matter and water-soluble organic matter. The amount of ozone applied to the soil was 0.012 g O_3 per minute**.**

2.1.2.1. Oxidizable organic carbon

Soil organic carbon was analyzed using the Walkley & Black method (Page, et al., 1996). This method is based on the wet oxidation of organic carbon (Cox) in soil (Carreira & M.M, 2010). Aliquots (2g) of dry soil subjected to the different ozone treatment conditions (dry soil, wet soil) and untreated soil were analyzed in triplicate with the respective blanks.

2.1.2.2. Soluble organic matter

Soil extracts were made in water at a 1:10 ratio (w/v). After 24 hours of agitation and contact at room temperature, they were filtered through Whatman 42 paper. Aliquots of the extracts were analyzed for organic matter by the wet method, using potassium dichromate in sulfuric acid medium (150ºC, 2 hours) and subsequent titration with ammonium ferrous sulfate in the presence of ferroin.

2.1.3. Preparation of contaminated soil

100 g of soil were contaminated with the mixture of the insecticides DDT and lindane in acetonitrile. The theoretical concentration of contaminants in the soil was 100 mg per kg of dry soil for both contaminants. It was left in contact in an open container under extraction, long enough for the solvent to evaporate and the contaminant to settle in the soil matrix. At the end of the evaporation time, the sequence of ozone treatments was carried out as detailed below, or the soil was kept at -22ºC while awaiting the corresponding treatment.

2.1.4. Ozone treatment

To carry out the decontamination treatment, and based on the result obtained in the application of ozone on clean soil, 50 g of contaminated soil were weighed (reference to air-dry soil), to be subjected to a stable ozone flow of 0.000256 mol Ozone/min (0.012 g Ozone/min) for a period of 30 minutes or 60 minutes.

This process was carried out in dry soil and wet soil, in separate processes. In the case of wet soil, the same procedure was applied by adding 7 ml of H_2O to each 50 g of soil (equivalent to approximately 30% of the field capacity of the soil). This low moisture level was set to have water present in the system, but without over-occupying the porosity. In some works, moisture is shown as an incident factor that can favor the degradation of contaminants (Muhammad, Oriane, Victoria, Pierre, & Khalil, 2017). Table 5 shows a summary of the experimental approach. Ozone applications were performed in triplicate, sequentially. Two controls were worked with (one for the 30-minute treatment and one for the 60-minute treatment), although the treatment received is the same (absence of ozone), in order to decrease the influence of the contaminant contact time variable with the soil matrix and the effect of sample heterogeneity in the contamination and sampling process. In this way, each treatment has its own control with which to make the comparison. Therefore, the cases analyzed in triplicate, would be the following. i) Witness/Control ii) Dry Soil 30 min O_3 iii) Wet Soil 30min O_3; iv) Witness/Control v) Dry Soil 60min O_3 vi) Wet Soil 60min O_3.

Table 5. Summary of experimental approach.

Reference	Process	No. Samples
SSC30	Control	3
SS30	30' dry	3
SHC30	Control	3
SH30	30' wet	3
SSC60	Control	3
SS60	60' dry	3
SHC60	Control	3
SH60	60' wet	3

2.1.5. DDT/lindane extraction

Once the decontamination processes were completed, the extraction and quantification of contaminants in the treated soils was performed. A QuEChERS type extraction was performed (Martínez & Páez, 2016). This type of extraction is a modern, fast and simple technique used in multi- residue analysis of pesticides.
5 g of soil were used, to which 4 ml of H_2O were added, this mixture was shaken for 3 min^{-1} and subjected to rest for 15 min^{-1}. Once the previous procedure was done, 25 ml of acetonitrile and salts (magnesium sulfate and NaCl) were added. These mixtures are placed in ultrasound and then centrifuged for 6 minutes at 3000 rpm. This method takes advantage of the high salinity generated by the salts to force the migration of the organic compounds to the organic phase, acetonitrile, which under these conditions is not miscible in water and can be separated by decantation. Among the different solvent options, different studies show different

degrees of analyte recovery (Braganca et al., 2013), and in the present work one of them, acetonitrile, was chosen in order to facilitate the process and that it can be analyzed without changing the solvent, both by liquid and gas chromatography.

2.1.6. Contamination monitoring by HPLC-UVvis.

Given the time limitation in the experimental development, in order to have information on the changes in the contamination level of the different samples that were being treated, it was decided to monitor one of the two pollutants by HPLC-UVvis, due to the easy availability of the technique in the laboratory. This monitoring was carried out on one of the two contaminants (DDT), which is the one that can be quantified by this type of technique. Lindane lacks chromophores that could facilitate such monitoring.

It can be assumed that a rather unspecific oxidation treatment such as ozonation will affect both pollutants in parallel. The determination was carried out semi-quantitatively using a flow rate of 1 ml per minute in an isocratic regime with a mobile phase consisting of acetonitrile and water in a ratio of 80:20 and detection at 254 nm**.**

2.1.7. Quantification by gas chromatography

Once all the extracts of the series were obtained, the quantitative analysis of contaminants in the extracts was carried out by gas chromatography with mass spectrometry detection. The chromatographic analysis was carried out in SCAN mode, Splitless, with an injector temperature of 250ºC, detector temperature of 280ºC and source temperature of 230ºC. The mobile phase consisted of Helium, with a flow rate of 1ml/min, and a temperature ramp starting at 50ºC (1min) and a gradient of 10ºC/min up to 310ºC (5min). Mass spectrometry also allows qualitative observation of the presence of other compounds, metabolites or by-products that may have been generated during the process**.**

2.1.8. Respirometry

In view of the results obtained and the nature of the decontamination process (oxidation of organic matter), the aim was to evaluate the state of the system once ozone had been applied. For this purpose, it was considered appropriate to evaluate the biological activity with a respirometric experiment. For this purpose, 50 g of soil samples, treated as described in section 3.2.4, were placed in oxitop (WTW) respirometers moistened to 70% of the field capacity. They have been kept in incubation at 25 ºC and absence of light. The accumulated oxygen consumption of the samples was recorded for 4 weeks. Once completed, the Substrate Induced Respiration (SIR) value was quantified after the addition of an aqueous glucose solution (4mg/kg). A possible number of samples were tested based on the availability of treated soil, establishing as reference the treatment that seemed to have the greatest effect on the pollutant, known from the monitoring during the process.

2.1.9. Statistical analysis

An exploratory analysis consisting of graphs of means and curves by contaminants and an inferential analysis of comparison of means of each treatment with its corresponding control was used and consists of the t-Student test for independent samples. Results were considered significant when $p<0.05$.

$$_0 : H\ \mu_1 = \mu_2\ vs.\ H_1 : \mu_1 < \mu_2$$

μ_1 is the mean of the treated group. μ_2 is the mean of the control group.

3. RESULTS AND DISCUSSION

3.1. Ozone Generator Calibration Test

The results of the ozone calibration are shown in Table 6. From the average results the installation is adjusted and tested to obtain a stable ozone flux of 0.000256 Mol O_3/min^{-1} (0.012g O_3/min). $^{-1}$

Table 6. Ozone calibration test results

Repetitions	Time Min	Mol O_3	Mol O_3 min $^{-1}$ g O_3 min	
1	15	0,0039	0,000264	0,0126
2	15	0,0038	0,000253	0,0121
3	15	0,0038	0,000253	0,0121

3.2. Effect of O_3 on Oxidizable Organic Carbon and Soluble Organic Matter.

The results of the organic matter analysis of the uncontaminated soil samples subjected to ozone treatment are shown in Table 7. As can be seen from the results obtained, ozone treatment on dry soil causes a decrease in soil organic matter of approximately 70%, which is significant with respect to the control, only when the soil is treated dry. When the ozone treatment is carried out in the presence of moisture, the differences are not significant. This could be due to the worsening of the ozone-organic matter contact due to the presence of water (Tie, Guangzhou, Jie, & Na, 2014). On the other hand, if we take into account the presence of soluble organic matter, it does vary quantitatively in the treated soil under wet conditions, the effect being significant and reaching a 35% increase. This apparent contradiction is due to the different concentration dimensions of soluble and total organic matter. If the soluble organic matter is expressed as a fraction of the total organic matter, it can be seen that in the control soil there is 8.16% of soluble carbon in relation to the total oxidizable carbon, while in the samples treated with ozone this percentage is 11.55% and 11.04% respectively in dry and wet treated soil. Consequently, we can speak of an increase in the soluble carbon fraction, as expected, when organic matter is treated with an oxidant such as ozone, due to its fragmentation. This proportion, on the other hand, is not significantly different between dry and wet samples. In general, therefore, we found a higher overall effect of ozone on dry soil, while maintaining a similar soluble carbon profile (with a 3% excess in treated soils compared to the control soil). A high content of organic matter in soils could consume more ozone and cause less pollutant removal. Soil particles become coated when water is present, interfering with the reaction caused by ozone with organic matter (Tie, Guangzhou, Jie, & Na, 2014). When advanced oxidation techniques are used there is a decrease in organic matter due to the effect of oxidation (Muhammad, Oriane, Victoria, Pierre, & Khalil, 2017).

Table 7. Organic Matter of ozone-treated soil samples, under wet and dry conditions, with variation in percentage relative to the control, and soluble C. fraction. *Statistically significant differences ($p<0.05$). $\bar{X}$ Mean σ Standard deviation.

Muestra	M.O soluble (mg C kg suelo^{-1})		Variación	C.O oxidable (% C)		Variación	C sol/C ox
	X	σ	%	X	σ	%	%
Control	886,99	91		1,087	0,071		8,16
Suelo Seco	892,022	33	100	0,772	0,038	71*	11,55
Suelo Húmedo	1 194	66	135 *	1,081	0,050	99	11,04

3.3. Contamination monitoring by HPLC-UVvis

The values obtained through HPLC-UVis monitoring are shown in Table 8. This procedure was used as a pre-analysis of the different treatments to determine the efficiency of the ozone treatment. The results showed heterogeneity among the different controls and when comparing each treatment with its respective control, the treatment with the highest removal was SS60 with 20.5% removal with respect to its control followed by SS30 with 20.2% for DDT. The treatment with the lowest removal was SH60 with 14.4% removal with respect to its corresponding control. This analysis showed that the application of ozone in the experimental conditions had a certain percentage of effectiveness in the elimination of the pollutant, and also gave an idea of the variability in the results. The variability in the controls is around 13% coefficient of variation in the dry controls, in a homogeneous way. The variations in the wet sample controls were less homogeneous. In any case, it appeared that the dry treatments were somewhat more effective.

Table 8. DDT concentration (mean and standard deviation) obtained in the monitoring of ozone- treated samples.

Reference	Process	Mean conc mg/kg	Desv est
SSC30	Control	78,3	9,8
SS30	30' dry	58,1	3,8
SHC300	Control	81,9	8,2
SH30	30' wet	62,5	2,9
SSC60	Control	70,3	9,6
SS60	60' dry	49,8	5,1
SHC60	Control	57,9	2,7
SH60	60' wet	43,5	7,6

3.4. Chromatographic analysis of extracts

This section shows results of the effect of O_3 applied during two different time intervals on soils contaminated with DDT and Lindane. Table 9 shows the means, standard deviation and percentages of the contaminants recovered in the extract relative to the control.

Table 9. Quantification of DDT and Lindane in the soil samples subjected to the different ozone treatments and percentages of residual contamination in relation to the corresponding control. Mean and standard deviation (*): Significant differences ($p<0.05$).

Reference	Average soil conc. mg/kg		Desvest		Residual contamination	
	Lindane	DDT	Lindane	DDT	Lindane	DDT
SSC30	59,4	53,2	1,7	3,9		
SS30	46,2	40,4	7,1	4,6	77,8 (*)	75,9 (*)
SHC30	59,9	57,5	8,4	7,2		
SH30	55	49,4	7,5	3,3	91,8	85,9
SSC60	73,4	55,1	5,0	1,3		
SS60	54,1	38,2	11,6	9,1	73,7 (*)	69,3 (*)
SHC60	40,8	37,7	5,2	1,7		
SH60	38,4	31,3	1,7	1,5	94,1	83,0

First, we analyzed the recovery of the analyte in the extraction and analysis process (Figure 7) taking into account the different controls of each treatment. The figure shows differences in the recovery data between controls, due to different probable causes. One of them is the heterogeneity of the sample. Another is the presence of moisture in some of the samples, which can induce changes in the contaminant dynamics and in aspects such as biodegradation or sorption during contact time. The lowest values correspond to the wet soil controls at 60 minutes, a situation in which the time and humidity factors are at maximum conditions in this experiment. On the other hand, greater extraction of lindane is observed in relation to DDT, and this would respond to the particular dynamics between analyte and solvent in the working medium. The difference between the extraction capacity of different analytes for the same solvent has already been mentioned; organic solvents such as acetonitrile are not capable of extracting all compounds in the same way (Espín, Martínez-López, Mojica, & García-Fernández, 2010). In sum, this variability observed in the quantification of contamination in the control soils (not subjected to the ozone variable) corroborates the suitability of having a specific control for each treatment situation, in order to measure with less error the variables operated: ozone time and humidity.

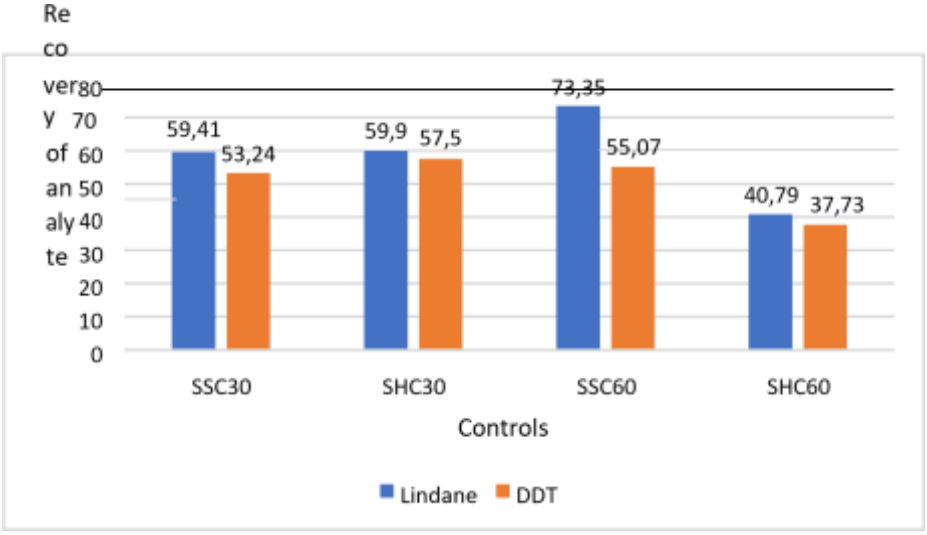


Figure 7. Recovery of analytes in the different treatment controls.

Regarding the results on decontamination, and looking at the data in comparison with the corresponding controls, there is a significant difference ($p<0.05$) in the treatments applied in dry soils for both contaminants, that is, the mean contamination of the sample with the applied treatment is lower than the mean of the control group. As for the treatments in wet conditions where the p values are 0.32082, 0.3166 for

lindane, respectively for 30 and 60 minutes and 0.153 for DDT in SH30 there is no significant difference between the control and the sample, that is, the mean contamination of the sample with the applied treatment is equal to the mean of the control group. Table 10 shows that the mean of Control and Sample differ mostly at 30' dry, while at 60' wet the difference is relatively small.

In view of the existence of significant differences in concentrations compared to the controls, some of them being significant, Figure 8 shows the removal percentages of the different pollutants compared to the ozone treatments. The most favorable values correspond to the dry soil treatment with 60' of O_3. In this research a decrease of 30.72% of DDT and 26.24% of lindane was achieved, while the lowest values are in the wet environment for both pollutants. The reactivity of the pollutant with ozone could be affected by its distribution in soil organic matter (Derudi, Venturini, Lombardi, Nano, & Rota, 2007), and by other factors such as the presence of inorganic elements or matter consuming radicals (Ranc, Faure, Crozec, & Simmonot, 2016). According to Tie, Guangzhou, Jie, & Na

(2014), after 30' of O_3 treatment at 0.5 $Lmin^{-1}$ obtained a pnitrophenol (PNP) removal of 51.8%. The ozonation method in soils with organic contaminants gives rise to metabolites that are more readily biodegradable than the parent compound (Richland, 1992).

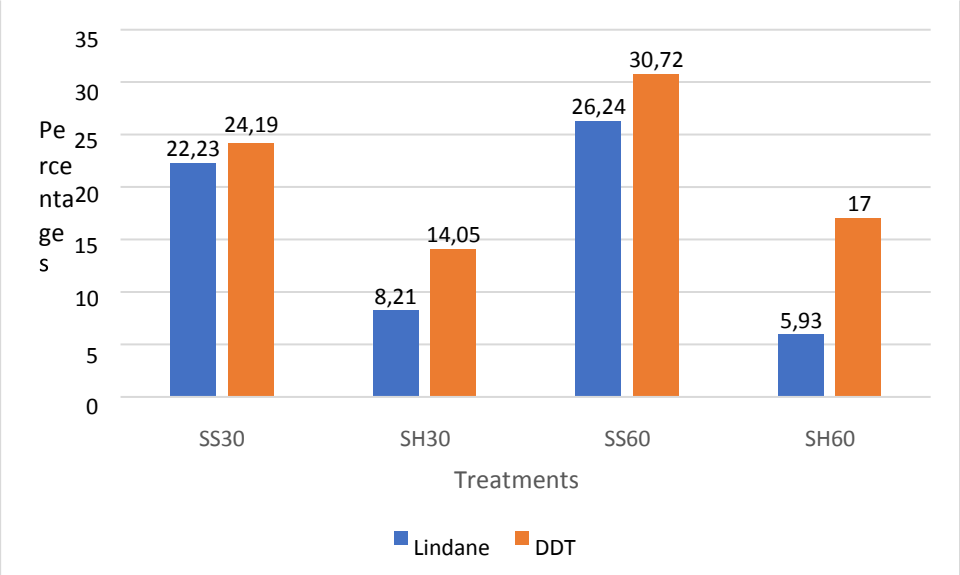
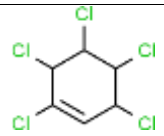
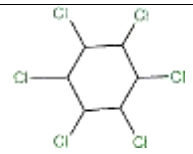
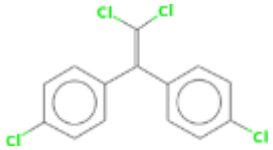
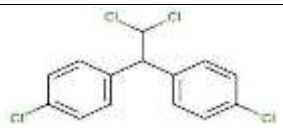
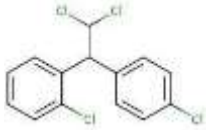
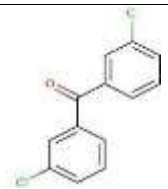


Figure 8. Percentage removal of DDT and lindane against different O_3 treatments.

In addition to the decreases in the concentration of contaminants in some of the treatments, the spectra obtained in the GC-MS analysis have been analyzed in order to locate possible by- products, of which the most relevant are shown (Table 10). The by-products generated by some of the contaminants present in the soils after treatment are not necessarily repeated or coincided in all the replicates of the same treatment. These by-products coincide with some metabolites already described from degradation processes in the medium (ECHA, 2020) (Wenming, Mengling, Hongming, Mingyong, & Yu, 2020). Substances such as pesticides, amines and aromatic species can be transformed in the presence of ozone and brought to a state where it is easily degradable (Bengoa, Bes, & M,T Silva, 2018).

DDT and lindane by-products (National Library Medicine).

By-product	Structure	Treatment
Pentachlor - Cyclohexene		SSC30
Alpha - lindane		All samples
DDE		SSC30 SHC30 SS30 SH30 SHC60 SSC60 SH60 SH60
DDD		SSC30 SHC30 SS30 SH30 SH30 SSC60 SHC60 SS60
Mitotane		SSC30 SSC60 SH60
Chlorophenyl-methanone		SS30

Some of the metabolites found in the control no longer appear in the treated samples (DDE in SS60, DDD in SH60, chlorophenylmethanone in SS30 and pentachlorocyclohexane in SSC30), indicating that the oxidation process is not the main process involved in the transformation, but rather the physicochemical and biological processes of the soil. Moreover, the effects are not consistent, due to the low specificity of oxidation. In the data obtained in gas chromatography, mitotane has been identified, but it has not been quantified, it is present in dry soil controls and it is formed when ozone is present in a humid medium for 60 minutes. Mitotane is a drug used to treat cancer in adrenal glands (The American Society of Health-System Pharmacists, 2016). Regarding the biotransformation of this drug in human metabolism assays, metabolites such as acetic acid (DDA) have been identified along with small amounts of DDE. Safety data for this drug state that DDT and other polychlorinated diphenyl-like compounds have deleterious effects on pregnancy and fertility, and the same could be expected for mitotane (Laboratoire HRA Pharma, 2004).

3.5. Respirometry

The purpose of the respirometry test is to examine the microbial activity in the affected soil, taking into account that it is a relatively vulnerable soil (low level of organic matter, sandy), which has been subjected to a contamination process and an aggressive oxidation treatment.

In relation to accumulated respiration, graph 9 shows that the values in uncontaminated soil and contaminated soil show similar respiratory activity from the beginning and throughout the follow-up time. In each of the 4 groups, an increasing trend in the values is observed, and these values become closer as the days elapsed, resulting in an accumulated activity that does not show significant differences in the different treatments. The values of the samples subjected to contamination and ozone, with or without inoculation with non-contaminating soil extract indicate a low initial respiratory activity, showing an adaptation process. With the passing of the days, the microbial activity improves, obtaining steep slopes that at the end of the period are equal to the rest of the treatments. The inoculated sample is the one that shows a tendency to a more difficult recovery.

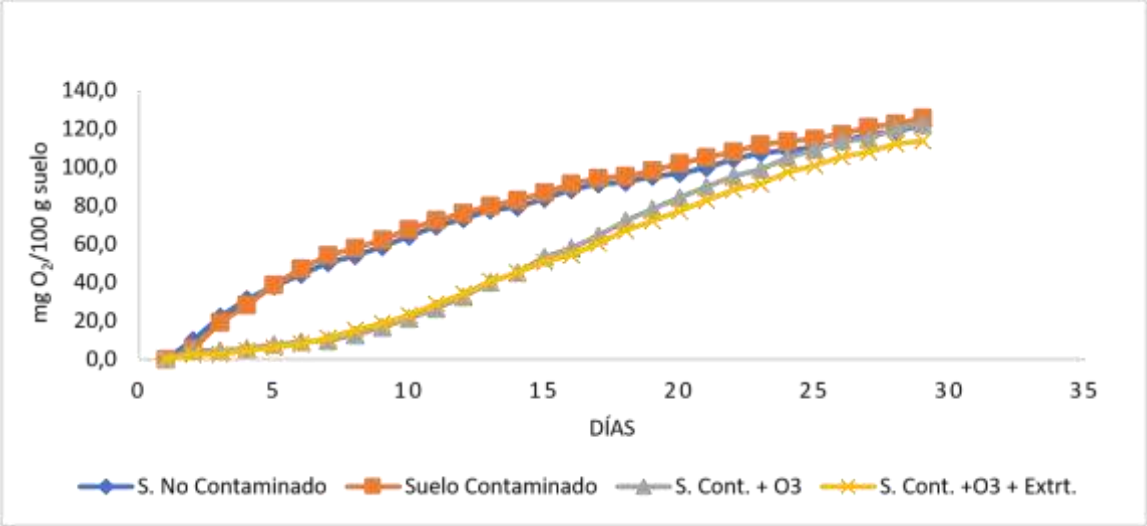
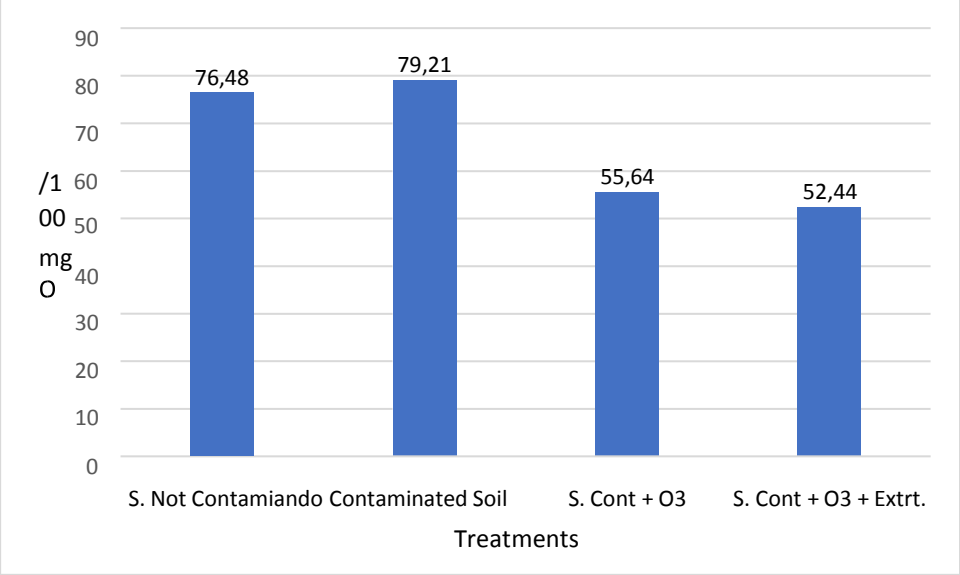


Figure 9. Respiration accumulated in 28 days of soil subjected to different treatments: uncontaminated soil; soil contaminated with DDT and lindane under experimental conditions; contaminated soil treated with ozone (S. Cont. + O_3), and decontaminated soil inoculated with uncontaminated soil extract (S. Cont. + O_3 + Extrt.).

Figure 10 shows the average respiration values for each treatment over the total time analyzed. The highest average is for the contaminated soil, while the lowest is for the ozone-treated and reinoculated soil. The results obtained therefore show an increase in biological activity in the medium with DDT and lindane, which indicates that this soil is able to adapt relatively quickly to the contamination situation (the adaptation phase is 24 hours in relation to the control). We could infer that this soil contains microorganisms capable of using these organochlorine compounds as nutrients or energy (Betancur, 2013) or at least survive in their presence and use carbon sources available under these conditions, including possible dead organisms.

As for ozone treatment, taking into account that it is a powerful, non-specific oxidant and that we have already proven its capacity to degrade organic matter, it is to be expected that the microbiota will be affected. The reduction of respiration in the ozone-treated samples is shown by the lower values in the initial and adaptation phase. The organisms that survive do so due to two factors. On the one hand, the presence of pollutant, on the other hand, the oxidation treatment. In both cases they adapt and can use as a carbon source

the remains of organisms and also the half degraded remains of soil organic matter. In the last sample there was low microbial activity compared to the sample treated with ozone, probably due to the competitiveness between inoculated microorganisms and microorganisms present in contaminated soils. We could expect that the organisms adapted in the contaminated sample and capable of surviving oxidation are not the same as those in the uncontaminated soil, so incorporating these into the system (with the a priori intention that it could mobilize biological activity after an oxidizing attack) has even been an added stress factor. It would have been interesting to test a fifth treatment with a contaminated soil extract and with the adapted microbiota. Ohlenbusch, Hesse, & Frimmel (1998) in their research express that the application of O_3 on contaminated soils leads to an increase in activity, although there may be a lag phase and a selection of microorganisms during this regrowth process, further indicating that this may be due to a small proportion of residual O_3 that is concentrated in the extract after the ozonation process.



Mean accumulated respiration in soil subjected to different treatments.

The respiratory activity that has been analyzed gives an idea of activity. In order to visualize the volume of active biomass, the SIR (ISO, 2002) is usually used, the values of which are shown in Table 11 shows the highest value in unpolluted soil, while the contaminated soil treated with ozone and reinoculated, still has the lowest value of active biomass. As for the mean values of basal respiration, there is no significant difference between treatments, and the metabolic quotient qCO_2 (ISO, 2002), on the other hand, shows an increase in the ozone and inoculated soil treatments, while the values for unpolluted and polluted soil remain relatively low. This parameter is used in some studies as an indicator of microbiota stress. In this case values above 0.3 are associated with stress. As we can see, all treatments exceed this value (which is that of unpolluted soil) and especially where ozone treatment has been carried out, and when inoculated with unpolluted soil extract.

3.6. Final considerations

The results of both the decontamination treatment and the evaluation of the biological activity in the treated samples are considered positive within the objectives set and taking into account the context in which they took place. It would have been desirable to continue with a quantification in the samples incubated in the respirometry, in order to, based on the results, be able to move on to the next experimental phase, adapting and increasing the number of variables (in the chemical oxidation and in the biological phase) in order to optimize the decontamination process in the laboratory.

Basal respiration, SIR and metabolic coefficient in different treatments.

Treatments	**R. Basal**	**SIR**	**qCO2**
S. Uncontaminated	2,8	4,6	0,33
S. Contaminated	2,8	4,1	0,37
S. Cont.+O3	2,9	2,5	0,61
S. Cont + O3 +Extrt	2,7	2,0	0,72

4. CONCLUSIONS

1. A system for decontaminating soil by means of ozone flow has been developed. Although some aspects remain to be improved, performance in terms of pollution reduction has been satisfactory.

2. The application of an ozone flux of 0.000256 Mol O_3 /min^{-1} (0.012g O_3 /min^{-1}) to a soil contaminated by lindane and DDT at a concentration of 100 mg kg^{-1} reduces the pollutant concentration by 6 to 26% in the case of lindane and 14 to 30% in the case of DDT.

3. The greatest reductions were achieved by treating the soil dry, and 60 minutes, followed by the same conditions for 30 minutes. The presence of humidity causes less effectiveness of the treatment, achieving non-significant differences in relation to the controls.

4. Some pollutant metabolites were identified. These metabolites are those usually identified in the literature, and cannot be associated exclusively with ozone treatment, since they are found in control and treated samples, indistinctly.

5. By means of the respirometric test it has been possible to observe changes in the biological activity of the treated samples. The changes are smaller in the untreated contaminated soil sample than in those samples that have received the oxidation process. Stress has been observed in the surviving microbiota of the treated samples.

6. Some modifications are proposed to improve the efficiency of the treatment, as well as the need to increase the variables (pollutant concentration, reduction of the ozone flow and improvement of the contact time).

7. In relation to the assembly of advanced oxidation techniques with bioremediation processes, it is necessary to extend the study with trials that include the two serial phases and modifying variables (time, nutritional recovery of the soil after oxidation, etc.) in order to establish the optimum conditions.

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