REPORT

Treatment of Dioxin Contaminated Soils

Literature Review and Remediation Method Development

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Report Summary

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This report includes a literature review of documented soil remediation techniques tested for dioxins. It is noted that more options are desirable if remediation of dioxin-contaminated sites shall be carried out in any larger scale in Sweden. More options that means a more effective reduction of the contaminant, but also a smaller environmental footprint for the process itself. The experiments indicate that dioxins in less weathered organic matter are easier to extract than from more the weathered material. Furthermore, it was observed that the harsh treatment that NaOH-extraction at 100°C does have effect on dioxin congeners, where one can observe formation of an individual congener. Furthermore, it was observed that the harsh treatment that NaOH-extraction at 100°C does have effect on dioxin congeners, where one can observe formation of an individual congener. What is more interesting is that the pretreatment with 90°C water, which was conducted to remove chlorophenols from soil which then can form dioxins when they are in an alkaline environment, in fact, was also effective for extracting dioxins. The oxidation with titanium dioxide was also conducted in laboratory scale. The results revealed no differences in oxidation rate which could be related to the different soil types. However, the oxidation rate depended on the amount of particles in the extract.

Keyword
Dioxins, furans, chlorophenols, titanium dioxide, soil remediation

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Foreword

It is quite illogical, that the main difficulty when it comes to remediation of soil contaminated by dioxins is that they are too strongly adsorbed to the soil to be treated in an easy way. It's illogical since mobility is one of the main factors when risk for environmental and human health is assessed. From that perspective, it might seem like a contaminant that is too strongly sorbed to be treated would also be stable enough to not constitute a risk. But recently it has been observed that dioxins do move in the soil matrix. This is when the particles they are stuck to move. And since dioxins are highly toxic even in low concentrations, this is why it's still relevant to find a cost effective and environmentally sound method to deal with dioxins in soil - even though they constitute a soil remediator's challenge.

Very few methods for remediation of these contaminants are available. Common practice today is thermal treatment, i.e. when soil is heated to approximately 800°C when dioxins combust. This is expensive and in cases when the excess heat is not taken care of, the overall environmental performance is poor. The hypothesis of this project is that the dioxins can be extracted into an aqueous solution and thereafter oxidized to eliminate the contaminants. If successful, it has the potential to be affordable option to improve environmental performance considerably.

The project was co-funded by MB Enviroteknik, M-Real, Holmen, Kramfors kommun, Västerås Stad, Södra Skog and EKA Chemicals. and the Foundation for IVL Swedish Environmental Research Institute (SIVL) via grants from the Swedish Environmental Protection Agency and the The Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning (Formas).

Summary

Dibenzodioxins and dibenzofurans, often referred to as dioxins, are among the most toxic substances that humans emit into our environment today, with its carcinogenic effects in humans and animals. Common sources of dioxins are; incomplete combustion, earlier use of chlorine bleaching process in paper industry and the wood impregnating industry where dioxins and furans are found as contaminant in the chlorophenols used in the process. Since the dioxins are very hydrophobic they will be bound to particles in different forms, but mainly to the soil organic fraction. Transport of dioxins from soil to a nearby water recipient will largely depend on transport of the particle that the dioxins are sorbed to.

This report includes a literature review of documented soil remediation techniques tested for dioxins. It is noted that more options are desirable if remediation of dioxin-contaminated sites shall be carried out in any larger scale in Sweden. More options that means a more effective reduction of the contaminant, but also a smaller environmental footprint for the process itself.

The study investigates the possibility of using a photolytic catalyst (titanium dioxide), which in combination with UV light oxidizes organic substances into water and carbon dioxide, and thus removes the dioxins. In this method, pollutants are extracted into an aqueous solution which then treated by the oxidizing combination of UV-light and TiO_2 catalyst. . An efficient transfer into solution is accomplished by increasing the colloid formation using a solution of sodium hydroxide (NaOH). After oxidation, the NaOH solution is recycled to the extraction phase and utilized again as far as possible. A sub-study was conducted to optimize the colloid formation, where temperature, time of extraction and concentration was varied in two types of soils.

The results of the bench scale experiments show that the efficiency of extraction varies greatly, probably depending on how dioxins sorb to particles and in which stages of decomposition the organic material is. In the most effective case, which was a soil with 6% relatively new organic material only 20% of dioxins remained after extraction (measured in ng/kg WHO-TEQ). In the worst case, a sandy soil containing 2% organic matter, the dioxin content doubled (measured in ng/kg WHO-TEQ) after treatment. The experiments indicate that dioxins in less weathered organic matter are easier to extract than from more the weathered material. Furthermore, it was observed that the harsh treatment that NaOH-extraction at 100°C does have effect on dioxin congeners, where one can observe formation of an individual congener. What is more interesting is that the pretreatment with 90°C water, which was conducted to remove chlorophenols from soil which then can form dioxins when they are in an alkaline environment, in fact, was also effective for extracting dioxins. Almost equally good results were achieved with water extraction in comparison to NaOH extraction, which is interesting because it is much easier to handle than NaOH and these results thus indicate new opportunities for manageable soil remediation.

The oxidation with titanium dioxide was also conducted in laboratory scale. The results revealed no differences in oxidation rate which could be related to the different soil types. However, the oxidation rate depended on the amount of particles in the extract. Initially an increasing dioxin oxidation rate was observed with increasing particle concentration, but this effect disappeared at higher particle concentrations. Most likely, the initial observations can be explained by increasing contact between the dioxin-containing particles and the titanium oxide surfaces. At higher particle concentrations, the penetration of UV light is limited thus decreasing the oxidising capacity in the solution.

Sammanfattning

Dibensodioxiner och dibensofuraner, vilka ofta benämns som dioxiner, är bland de mest toxiska ämnen som människor släpper ut i vår miljö idag, med dess cancerogena effekter hos människor och djur. Vanliga källor är ofullständig förbränning, äldre tiders klorblekningsprocess i pappersmassaindustrin samt träimpregneringsverksamhet där dioxiner och furaner funnits som en förorening i de klorfenoler som använts i processen. Genom att dioxinerna är mycket vattenskyende kommer de i mark att finnas bundna till partiklar i olika former, men främst till jordens organiska fraktion. Spridning av dioxiner från mark till exempelvis ett vattendrag kommer till största delen vara beroende av att partikeln som dioxinerna sitter på transporteras.

I rapporten finns en litteraturgenomgång av de dokumenterade tekniker som testats med avseende på dioxiner. Det kan konstateras att fler alternativ är önskvärda om efterbehandling av dioxinförorenade områden ska kunna ske i någon större skala i Sverige. Alternativ som är både reducerar föroreningen bättre och samtidigt innebär en lägre miljöpåverkan för själva processen.

Studien undersöker möjligheten att använda en fotolytisk katalysator (titandioxid), vilken i kombination med UV-ljus oxiderar bland annat organiska ämnen till vatten och koldioxid, för att ta bort dioxinerna. För att kunna använda katalysatorn måste föroreningarna extraheras ut i en vattenlösning som sedan oxideras. Detta åstadkoms genom att öka kolloidbildningen med hjälp av natriumhydroxid (NaOH). Efter oxidationen återförs NaOH till extraktionssteget och den utnyttjas så långt som är möjligt. I studien genomfördes försök för att optimera kolloidbildningen, där temperatur, extraktionstid och koncentration varierades på två typjordar.

Resultaten av bänkskaleförsöken visar att effektiviteten hos extraktionen varierar kraftigt, troligen beroende på hur dioxinerna binder in till partiklarna och i vilket stadie av nedbrytning som det organiska materialet är. I det bästa fallet vilket var en jord med 6 % relativt nytt organiskt material var endast 20 % av dioxinerna kvar efter extraktion (mätt i ng/kg WHO-TEQ). I det sämsta fallet, en sandig jord innehållande 2 % organiskt material hade halten ökat till det dubbla (mätt i ng/kg WHO-TEQ). Försöken indikerar att mindre vittrat organiskt material är lättare att extrahera än vittrat material. Vidare kan man se att den tuffa behandling som lut-extraktionen vid 100°C innebär har effekter på själva dioxinkongenerna, där man kan konstatera en bildning av en enskild kongen.

Vad som mer är intressant är att den förbehandling med 90°C vatten, som genomfördes för att ta bort klorfenoler från jorden vilka sedan kan bilda dioxiner när de kommer i en alkalisk miljö, faktiskt också var effektivt för att extrahera dioxiner. Nära nog lika bra resultat uppnåddes med vatten som extraktionsmedel, vilket är intressant då det är betydligt lättare att hantera än NaOH och skulle kunna erbjuda nya möjligheter.

Oxidationssteget med titandioxid genomfördes också det i laboratorieskala. Resultaten visade inte på några skillnader i oxidationshastighet som kan härröras till jordtyp. Däremot berodde oxidationshastigheten på hur mycket partiklar som fanns i extraktet. Till en början ökar hastigheten eftersom fler partiklar kommer att träffa ytan, men när partiklarna blir så många att UV-ljuset begränsas av det kommer hastigheten att minska. Försöken visade dock att principen fungerar, förutsatt att dioxinerna sitter på det organiska materialet i extraktet.

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1 Introduction

A large part of the polluted premises in Sweden are polluted with hydrocarbons or halogenated hydro carbons. There is a great necessity to find cheap and large scale technologies to treat these large amounts, on site or off site. These technologies also need to contribute to a sustainable development so that the environmental benefits exceed the environmental costs, which is not always the case when large amounts of energy or chemicals are consumed in the process.

Titanium dioxide (TiO_2), is a photolytic catalyst that can be used to destroy hydro carbons in a resource effective way. Since TiO_2 is a catalyst it will not be consumed during the process, which implies that the running cost and the environmental stress for the destruction itself will be very low. For this technology to succeed the pollutants must be extracted into a liquid phase. The liquid must be inorganic since an organic solution would compete with the pollutant that is to be destroyed by the TiO_2

As hydrophobic organic contaminants (HOC) are believed to sorb onto organic matter and organic matter has the ability to form colloids, the HOC can move in soil and threat the environment. Due to the toxicity of dioxins it is relevant to find an environmentally correct and cost effective method to remediate contaminated soils. The process is composed of two principal steps, the first is the organic matter extraction into inorganic solution and the second is the oxidation of the contaminants using titanium dioxide (TiO_2) as a catalyst.

1.1 Aims and limitations

This project aims to find a more cost effective and environmentally friendly method to remediate soils contaminated with dioxins or other hydrophobic contaminants.

The project addresses the two process steps; extraction and oxidation (destruction) in a laboratory scale in order to observe the success of basic mechanisms. The main aims are to find;

1. Ratio of extracted natural organic matters and dioxins as a function of selected soil properties using sodium hydroxide as extracting agent.

2. Oxidation rate of soil organic matter in an alkaline solution using titanium dioxide as a photo catalyst.

Since all experiments are being carried out in a laboratory scale results are merely indicators of the mechanisms involved. Further up scaling and optimization work will be needed based on the results of this study.

2 Literature review

The first section of this report is a review of existing knowledge relevant to the project. This is in principle, dioxins and their behaviour in soil, titanium dioxide as a photo catalyst and now existing methods for treatment of soils contaminated with hydrophobic hydrocarbons.

2.1 Dioxins and furans

Dioxins are organic contaminants classified as persistent organic pollutants (POP), which has been considered to be a historical problem due to the fact that they persist in the environment for centuries or even longer, becoming a challenge for future generations (Weber et al., 2008). Dioxins are important environmental contaminants due to the high toxicity of some congeners and the difficulty of its degradation process which leads to a great concern in the environmental community. Research has been carried out with the intention to clarify the dioxins' toxicity, especially after an explosion in a chemical factory, a chlorophenol producer in Seveso, Italy, in 1976 (Wilson, 1982). Dioxins can be spread not only through soil but also primarily through air and water. The sources are for example metallurgical activities, combustion processes, unwanted by-products from the synthesis of organochloride agents such as pentachlorophenol (PCP), chlorine bleaching of paper and pulp, chlor-alkali production and wood-impregnation activities using chlorophenol (CP) agents, and many others (Figure 1). The last three processes have been described as the most important, responsible for heavy contamination of soils with PCDD/Fs.

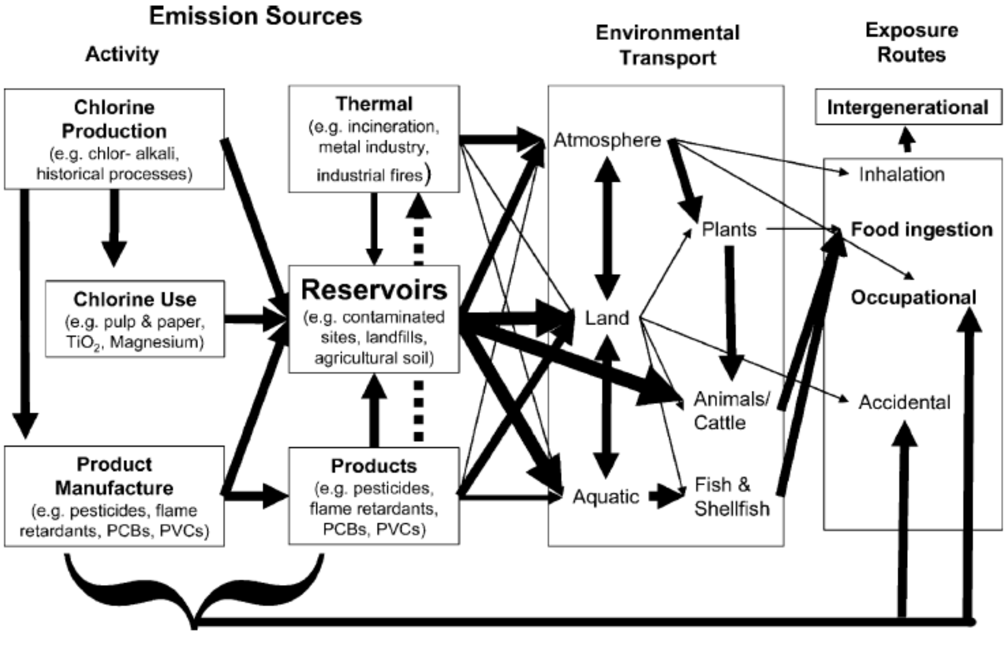

Figure 1 Sources of emission, environmental transport and human exposure routes of PCDD/Fs (Weber et al., 2008).

Besides in contaminated soil, extremely high levels of dioxins can be detected in animals like ducks, fishes and chickens. This situation generates a concern because one of the primary cause of contamination in mammals and other animals is through the food (Fiedler et al., 2000; Baccarelli et al., 2002). Dioxins can be transferred to vegetal, animals and humans mainly by the alimentation process producing an exposure for different levels of the food chain (Weber et al., 2008). Salmon for example, and others fatty fishes, are susceptible to dioxin intoxication because the toxic dioxins can be strongly accumulated by the high fat content (Wiberg et al., 1992).

Generally, exposure means a mixture of congeners that can generate different possible effects, some still under investigation, like for example problems in the reproductive process and carcinogenicity. Researches are also analysing the possibility of the neonatal thyroid function being modified due to maternal exposure to dioxins (Baccarelli, 2008).

Dioxins and furans are a family of chlorinated aromatic compounds, polychlorinated dibenzo-para-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) respectively. These two groups cover a total of 210 compounds, differing in the numbers of chlorine substituents and with similar characteristics (Rappe, 1994) (Figure 2). The congeners which present higher toxicity are those with substituents in the positions 2, 3, 7, 8, according to the concept of Toxic-Equivalent Factors (TEF) (Kulkarni et al., 2008) (). Besides the high resistance of POP's to metabolic and environmental degradation, POP's are easily bio-accumulated due to the presence of lipophilic characteristics, presenting the capacity to be accumulated by higher organisms in fatty tissues (Fiedler et al., 2000). The high hydrophobic property is represented by their high octanol-water partition coefficients (K_{ow}), being higher as more chlorine substituents it has, and their low water solubility (Orazio, 1992). For instance the range of Log K_{ow} values for tetra- through octa-chlorinated dioxins is 6.91-8.75 (Jackson et al., 1993; Govers and Krop, 1998).

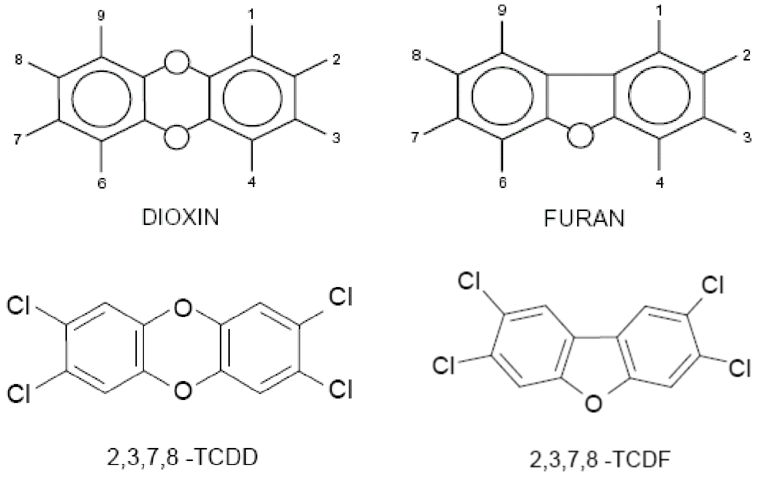

Figure 2 The general formula of dioxins and furans and the formulas for 2,3,7,8 – TCDD and 2,3,7,8 – TCDF.

2.1.1 Dioxins in soil

Due to its high hydrophobicity, the dioxins are also classified as hydrophobic organic contaminants (HOC). The high hydrophobicity of HOC is determinant in the case of sorption onto natural organic matter (NOM), the higher the hydrophobicity, the higher the sorption onto NOM (Chiou et al., 1979). Hydrophobic organic contaminants are believed to sorb onto the organic matter, which determine their fate and environmental impact, presenting a quick sorption which is believed to be induced by hydrophobic interactions (Means and Wijayaratne, 1982; Rivas et al., 2008). The sorption process has been suggested to be a partitioning process between the surfaces of the aqueous phase, the immobile matrix particles and mobile colloidal particles providing a usually high correlation between K_{ow} and K_{om} which is the partition coefficient between aqueous phase and soil organic matter (Chiou, 1989). The specific surface area of the organic matter is also a relevant soil characteristic (Chiou et al., 1979). Research has been carried out in order to model the sorption process with simple mathematical equations, but the soil heterogeneity is a complicated property to be considered (Huang et al., 2003).

In general, the fate of organic contaminants such as dioxins in soil is determined by their physicochemical properties (e.g. contaminant persistency in soil and its capacity to be strongly sorbed onto mineral or organic solid phases) as well as by the soil properties (e.g. the biological activity, water regime, and organic matter content, etc.) (Kretzschmar et al., 1999). As hydrophobic organic contaminants (HOC) do not have affinity to the soil aqueous phase, they would not have a significant mobility in soil, as being strongly sorbed and retained. However, they can have a relevant mobility due to the colloid formation capacity of the organic matter containing sorbed HOC, although the hydrophobic colloids formed are less mobile than hydrophilic colloids present in soil (Means and Wijayaratne, 1982; Kretzschmar et al., 1999).

Since the association of dioxins to the solid phase in the soil matrix is so strong, mobilisation either in nature in order for it to constitute a hazard or in a remediation method to treat the soil is dependent on the mobilisation of solid material. Therefore it is of importance to understand the dynamics of the smallest solid components in soil - the colloids.

2.2 Colloids in soil solutions

Even though the colloid behaviour in soil is not completely understood yet, the formation of colloidal carriers in soil has been studied carefully due to the colloid's ability to enhance the transport of contaminants (Kretzschmar et al., 1999). Consequently, the rapid transport of strong sorbing pollutants facilitated by colloids can certainly play the role of the dominant transport pathway (Figure 3) (Grolimund et al., 1996).

Moreover, there are important characteristics which lead the colloidal transport of contaminants to become environmentally important, such as the significant pollutant toxicity, which not even trace concentrations of it can be detected in the groundwater, the availability of great concentrations of mobile colloidal particles, the strong pollutant sorption onto the mobile particles and its slowly desorption, and the pollutant transport over large distances reaching uncontaminated areas (Kretzschmar et al., 1999).

Due to the transport possibility of HOC through the soil sorbed onto colloidal organic matter, the presence of colloidal particles is necessary. Colloidal particles from the solid matrix can be formed by silica, carbonates, aluminosilicate minerals, oxides and oxyhydroxides of Fe, Al, and Mn, and natural organic matter. Commonly, the *in situ* mobilized colloids are composed likewise to the natural fine fractions of the porous medium, even though the mineral or organic phases have different proportions. (Kretzschmar et al., 1999). Organic matter and mineral particles present different sizes, organic matter are smaller particles and mineral particles are bigger, contributing to different mobility in solution (Lead J.R. et al., 1999).

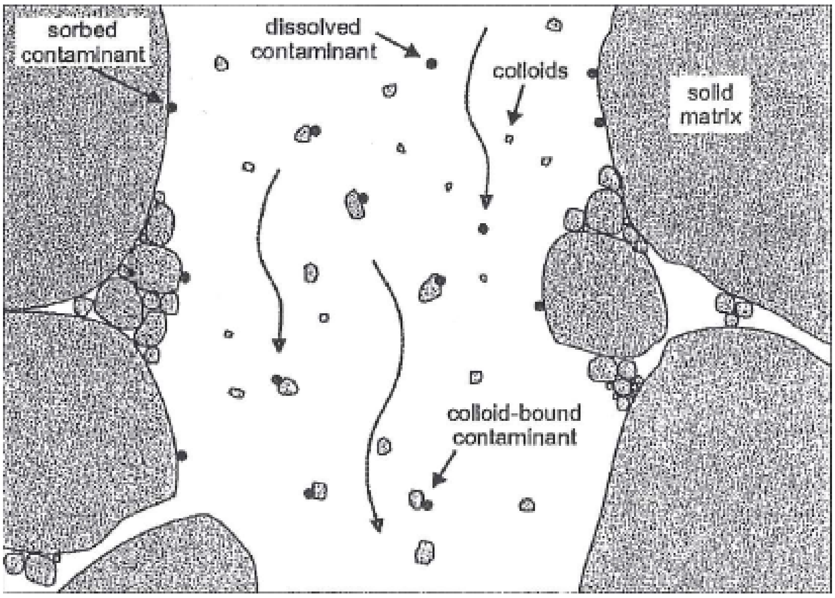

Figure 3 Representation of colloid facilitated transport of contaminants in porous media

Research has analysed the mobile colloidal particles in groundwater aquifers and soils, demonstrating that inorganic colloids are normally associated with natural organic matter (NOM) (Ryan and Gschwend, 1990; Ronen et al., 1992; Kaplan et al., 1993). The natural organic matter adsorbed onto inorganic colloids has an effect on the colloidal stability and surface characteristics of the inorganic particles (O'Melia, 1989; Tiller and O'Melia, 1993). This effect in the colloidal stability is achieved by the contribution of the NOM negative charge, what decreases the particles deposition, maintaining them in suspension (Ryan and Gschwend, 1990; Ronen et al., 1992). The NOM is mainly constituted of humic and fulvic acids negatively charged by their phenolic and carboxylic groups. Besides the negative charge contribution of the NOM, the humic-coated mineral surfaces also add stability to the colloidal particles by the steric repulsive forces between them (Tipping and Higgins, 1982; O'Melia, 1989; Tiller and O'Melia, 1993).

2.2.1 Colloid formation

Colloid formation is an important issue regarding colloidal particles in soil, but still it is poorly understood. Studies have detected that the colloid formation in soil is mostly due to perturbations in the system. According to McCarthy and Degueldre (1993), colloidal particles can be detected in a large diversity of aquifers. However, the concentration of the colloidal particles is very low in natural (undisturbed) aquifer systems (<1mg/L). Higher colloid concentrations are detected mainly in natural sites disturbed by some physical or chemical perturbations what consequently mobilizes naturally existing colloidal particles. Examples of these perturbations are waste disposal, groundwater recharge, irrigation and groundwater pumping (Kretzschmar et al., 1999). Sampling of mobile colloids is an example of physical perturbation that mobilizes colloidal particles due to the devices installation, the drilling mud utilization, the high flow rates and/or the atmospheric exposure which can result in changes in the redox potential (Backhus et al., 1993). However, in order to prevent the colloid generation and mobilization and not to provide wrong results in the sampling, special sampling techniques were elaborated (Backhus et al., 1993; McCarthy and Degueldre, 1993; Weisbrodn et al., 1996).

In general, the responsible mechanism to release colloidal particles under an alteration of the solution chemistry is the changes in the forces between the colloid surfaces and the grains to which they are attached. The generation of repulsive forces between them is the important result. Chemical perturbations, such as the pH increase, the change in the mineral surface charge by macromolecules and ions adsorption, and the ionic strength decrease, are responsible for colloids generation and dispersibility. Nevertheless, the variations in the solution chemistry result in effects on the colloid detachment which can only be predicted qualitatively (Ryan and Elimelech, 1996). Usually, with the intention to release the colloids, the decrease in ionic strength is the used change in groundwater chemistry generated by, for instance, infiltration of dilute precipitation water or artificial recharge of fresh water. According to Ryan and Elimelech (1996), the solution that can decrease hydraulic conductivity and mobilize colloids in flow-through columns and in saturated soils, with a great effect, are the dilute solutions consisted of monovalent ions. On the contrary, solutions consisted of bivalents ions and high ionic strength solutions were also tested and they were not able to mobilize colloidal particles. In addition, the decrease of soil hydraulic conductivity by increasing the pH of infiltrating water (from pH 6 to 9) and the injection of surfactants, in order to enhance oil recovery, can also mobilize colloidal particles (Muecke, 1979; Suarez et al., 1984).

The pH of the solution affects substantially the surface charge of the particles due to the protons exchange between the solution and the surface functional groups. Minerals particles normally have amphoteric surface charge, presenting negative charge when the pH solution is high and positive charge when it is low. The amphoteric surface charge can also reach the zero value, at an intermediate pH, when it is in the point of zero charge (pH_{pzc}) (Ryan and Elimelech, 1996). Moreover, addition of sodium ions (Na^+) to the soil solution is responsible to enhance the colloids dispersibility. The sodium ions are sorbed onto the colloidal particle surfaces generating a thick diffusive double layer around them. Consequently, strong repulsive forces among the particles exceed the van der Waals attractive forces and the dispersibility is enhanced (Rengasamy and Olsson, 1991). As quoted before, the solution ionic strength is also an important chemical perturbation that results in colloid mobilization. It regulates the dimension of the double layers that extent from the surface into the bulk solution (Hunter, 1981).

The principle of colloid release from porous media is described mainly in two steps and its kinetics is affected by the flow field hydrodynamics and the particle surface interactions. The double layer repulsion or attraction, the short–range forces ("non-DLVO" forces e.g. steric repulsion and hydration) and the London-van der Waals attraction are forces between the surfaces that can be responsible for the colloid mobilization. However, under chemical perturbations, the most relevant force is the double layer repulsion or attraction (Verwey, 1947). The Derjaguin, Landau, Verwey and Overbeek theory (DLVO theory) describes the effect of these forces in the intersurface interactions.

The first step of the colloid generation process is the diffusional transport of the colloidal particles from the matrix surface through an energy barrier (interaction boundary layer). Subsequently, in the second step the released particles are transported across stationary water film existent around the matrix grains (the diffusion boundary layer) (Kretzschmar et al., 1999). Some physical factors and soil characteristics have a decisive influence in how thick is the diffusion boundary layer. For instance, regarding the physical factors, the fluid viscosity, the flow velocity and the geometry of the flow field are important. Concerning the soil characteristics, the irregular pore geometry and the surface roughness have influence in the thickness of the diffusion boundary layer in natural porous media (Ryan and Gschwend, 1994). The release and mobilization of colloidal particles can also be influenced by shear forces and hydrodynamic drag in particles with large diameters and also in quite thin diffusion boundary layers such as at high flow velocities (Cerda, 1987).

The first step can be extremely slow under chemical perturbations due to the presence of a primary energy minimum, and consequently, this step can rate-limits the overall kinetics of the process (Figure 4). Equation 1 describes the exponential relation between the particle release rate (K_r) and the detachment energy barrier (ΔV_r). The equation shows that K_r decreases while ΔV_r increases (Kallay and Matijevic, 1981; Nelligan et al., 1982).

Equation 1 : $$K_r \propto \exp\left(\frac{-\Delta V_r}{K_b T}\right)$$

Where:
K_b is the Boltzmann's constant;
T is the absolute temperature.

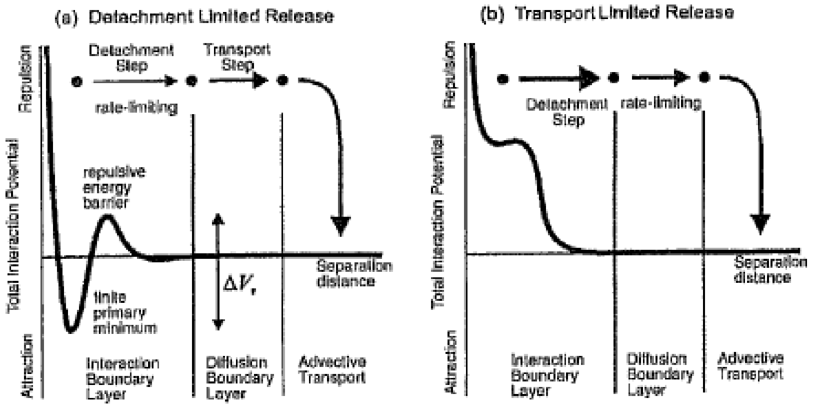

Figure 4 Principles of colloid release. (a) Detachment limited release. (b) Transport limited release.

The detachment energy barrier is calculated by subtracting the energy corresponding to the primary energy minimum (in which the particles are attached) from the energy corresponding to the repulsive energy barrier (Dahneke, 1975). An important characteristic of the theory, which describes the behaviour of the colloids generation, is that the theory (the DLVO theory) was modified in order to take into account the short-range repulsion forces. This modification result in a finite depth of the primary minimum, which was infinite when the theory was considering only the attractive van der Waals forces and the double layer forces (Kretzschmar et al., 1999).

The second step can also be rate-limiting for the overall kinetics of the colloids release process. The transport of the colloidal particles through the diffusion boundary layer is the decisive step of the process when the forces between the matrix grains and the colloidal particles are predominantly repulsive. In this case, the repulsive forces remove strongly the colloidal particles from the surface and the detachment step is fast, resulting in high overall release rates (Figure 4) (Kretzschmar et al., 1999).

According the modified theory, the colloids release rate may increase with increasing ionic strength if the potential boundary conditions are assumed constant for the matrix surfaces and for the colloids. If the charge boundary conditions are assumed constant, the behaviour may be the opposite (Kallay et al., 1986).

The success of an extraction of dioxins from soil into a solution or a suspension will be dependent on the fact that dioxins do stick to the solid phase and preferably to the organic constituents. It is also important that an extraction media generates a colloid release and not a destruction since it is not desirable that the dioxins find new, non-breakable, surfaces of minerogenic origin. This calls for an optimization of parameters such as pH and ion strength.

2.3 Titanium dioxide

Titanium makes up a quite high percentage of the earth's crust and is generally spread. The most common and most commonly occurring source is ilmenite. Titanium dioxide (TiO_2) occurs naturally as rutile (TiO_2) but can also be produced from ilmenite (Vannerberg, 1989). It is widely used as white pigment when colouring concrete, paints and tooth paste amongst others (Taoda, 2008). It is not toxic and it is stable throughout the pH scale. TiO_2 has shown to be photochemically active in the presence of sunlight for many different kinds of chemicals. Because of these properties, and despite that it only utilizes about 3-4% of the energy in the solar UV spectrum, it is the most widely used photochemical catalyst for photo-destruction of organic matter (Rababah and Matsuzawa, 2002). Toxic chemicals dissolved in water can easily be decomposed and detoxified by TiO_2 and light (Taoda, 2008).

2.3.1 Production of TiO_2

To be able to evaluate the environmental aspects of the methods for oxidation of PAH's that consumes titanium dioxide the entire production process must be considered. Therefore an overview of the mining and production of titanium dioxide is given here.

Titanium is a commonly occurring part of many minerals (NGU, 2005). Only two minerals are relevant from an economical point of view: Ilmenite ($FeTiO_2$) (52.7% theoretical TiO_2 content) and Rutile (TiO_2) (100% theoretical TiO_2 content). Leucoxen, a fine titanium rich conversion product of ilmenite is also of interest. TiO_2 occurs in three different types dependent on the crystal structure. This will be further explained but initially TiO_2 will be referred to as rutile, the most common of the three.

Mining is done both in conventional mines and through dredging of beaches and sediments where the ore exists as sand (NGU, 2005). Even though this process has some environmental impact, the crucial environmental impact comes from the enrichment and pigment production. Bad quality ilmenite, ilmenite with low titanium dioxide content (the TiO_2 content can vary between 44 and 70%), requires the most processing. How the processing is done is described schematically in Figure 5.

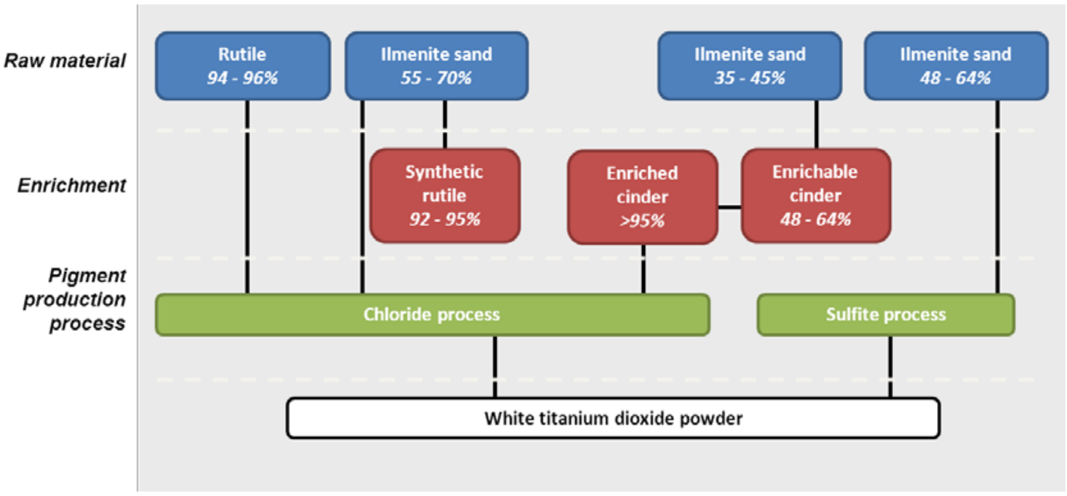

Figure 5 Schematic description of how the quality of the ore affects the production process for the white titanium dioxide pigment (according to NGU, 2005), the percentage accounts for the titanium dioxide content in the material.

In the enrichment process, gravitation and flotation enrichment are used in the first step to separate ilmenite and rutile sand from other grains of sand (Kronos, 2005). After the first step of enrichment the pigment production process takes place. There are two different processes to choose from, the chloride or the sulphite process. The chloride process requires a high TiO_2 content and if it is used low value sand is enriched through different acid leaching processes. This results in synthetic rutile or enriched ilmenite which can later in the production process form titanium tetrachloride by exposure to high temperatures and high pressure at the same time as adding chlorine gas and carbon. This process separates titanium from iron, after which the titanium tetrachloride is allowed to react with oxygen to form titanium dioxide. The chlorine gas is not consumed during the process and can be reused.

The sulphate method is not very common today (NGU, 2005) as it results in large amounts of cinder (iron sulphate is sold to waste water treatment facilities as a sediment chemical). The principal is that the sand, after the first enrichment, is solved in sulphuric acid and titanic dioxide, divalent iron and sulphate ions are formed. No pre-treatment is necessary since the method can handle low value sand.

Even if the chloride method generates less slag it consumes more energy because of the high temperature needed for the reactions both in enrichment and pigment production. Common for both methods is that after solving the TiO_2 it needs to be dried which is done in hot roasting pans. The conclusion is that the environmental impact during production is much dependent on what energy source that is used during production. India and Australia, which are large producing countries, both use large parts of fossil fuel based energy. Norway uses the sulphate method in the two Titanium works (Kronos, 2005; Tinfos, 2005; NGU, 2005) despite their cheap hydro power that has made it favourable to produce aluminium in the country.

CPM at Chalmers University uses so called ELU-value (Environmental Load Unit), to describe the environmental impact a substance has, where a higher number means a higher degree of environmental impact (Steen, 1999). The model considers both the willingness to pay today and in the future. It also considers the rarity of the substance - a rare substance as silver or gold gives a high ELU-value. The ELU can be seen as an indication in this case, where titanium can be compared to other metals to get an understanding of the environmental impact. Table 1 states the ELU-values for a selection of metals.

Table 1 ELU-number for a selection of substances, where a higher value means a higher environmental impact (Steen, 1999).

Substance	ELU-value (ELU/kg)
Titanium	0,953
Iron	0,96
Aluminium	0,44
Copper	208
Silver	54 000
Gravel	0,002

The conclusion is as previously mentioned that the environmental impact during production depends on the energy source, even if all methods mean a substantial environmental burden. This implies that all consumption of TiO_2 should be avoided if possible.

2.3.2 TiO_2 as a catalyst

TiO2 has a number of surface properties that are interesting for the industry because of the high oxidative ability, amongst other things metal oxides can form on the surface of TiO2 (Diebold, 2003). It was the high oil prices in the seventies that made Fujishima and Honda (1972) discover that TiO2 could be used to photolytically separate water molecules. The discovery was meant to be used to produce hydrogen gas, but was never commercialized, even if research on the method is being carried out today (Diebold, 2003). Today TiO2 is used in a number of different areas thanks to its photolytic properties. Windows are coated to become "self-cleansing", car tunnels are coated to improve the air standard, sun lotion contains TiO_2 to give a physical protection towards UV light (Carp et al., 2004). The impression is that the market is just in the beginning where many questionable applications are introduced without considering the consequences. The photo catalytic mechanisms are not fully understood. Even in review articles from the latest three years it is stated that there are gaps in the understanding of the mechanism.

The principle for photochemical is based on the semiconductor, i.e. ZnO, CdS, Fe_2O_3 and ZnS amongst others, electron configuration, which means a filled valence band (bottom of Figure 5) and an empty conduction band (top of Figure 6) (Diebold, 2003). When a photon with an energy that exceeds the gap between these tapes hits the metal oxide surface an electron transition occurs and conduction band electrons (e^-_{cb}) and valence band positive holes (h^+_{vb}) are formed, so called electron/hole pair. The hole in the valence band has a high oxidating power (+1.0 to +3.5V compared to NHE) whilst the electron pare in the conduction band is a good reducing agent (+0.5 to -1.5V compared to NHE).

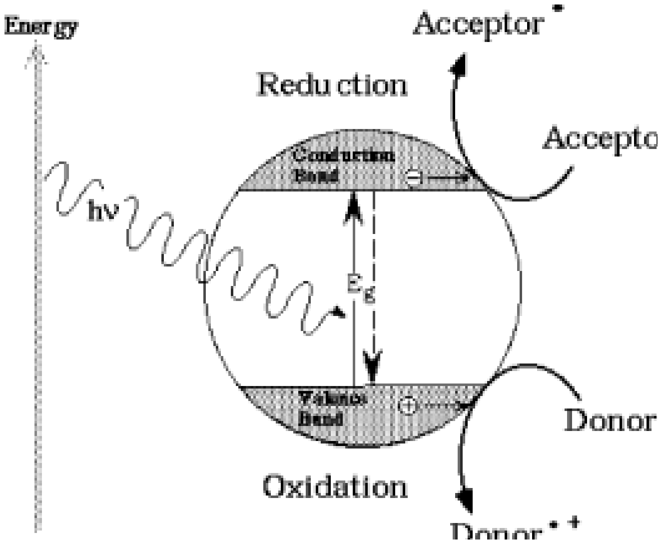

Figure 6 Principal picture of the photo catalyzation.

Titanium dioxide is what could be called a non-selective oxidant that can oxidize most substances (Carp et al., 2004, Diebold, 2003). Both organic and inorganic compounds, both in gas and liquid phase, can be adsorbed to the surface and be oxidized. It is in other words possible to apply a pollutant directly to the surface to oxidize them. An organic molecule will be minimized to carbon dioxide and water, if enough time is allowed to pass. In practice the molecule needs to adsorb-oxidize-desorb a number of times before the final products are reached. Principal reactions for adsorbents on titanium dioxide can be seen in Equation 2 to Equation 7.

Equation 2: $\mathbf{TiO_2 + h\nu \rightarrow TiO_2 (e^-, h^+)}$

Equation 3: $\mathbf{TiO_2 (h^+) + RX_{ads} \rightarrow TiO_2 + RX_{ads}^{\bullet +}}$

Equation 4: $\mathbf{TiO_2 (h^+) + H_2O_{ads} \rightarrow TiO_2 + OH_{ads}^{\bullet} + H^+}$

Equation 5: $\mathbf{TiO_2 (h^+) + OH_{ads}^- \rightarrow TiO_2 + OH_{ads}^{\bullet}}$

Equation 6: $\mathbf{TiO_2 (e^-) + O_{2\,ads} \rightarrow TiO_2 + O_2^{\bullet -}}$

Equation 7: $\mathbf{TiO_2 (e^-) + H_2O_{2\,ads} \rightarrow TiO_2 + OH^- + OH_{ads}^{\bullet}}$

The free radicals that are formed are very reactive and short-lived and only exist at the surface since they react with almost any compound (Diebold, 2003). Hydroxide radicals ($OH^{\bullet}$) with an oxidation potential of -2.80V, only exceeded by fluoride, (Carp et al., 2004) are considered by some scientists to be the most important ion of the above mentioned for oxidation of organic compounds (Diebold, 2003). Other scientists consider super oxide (O_2^-) to be the most important (Carp et al., 2004).

Regardless of the mechanisms involved, water seems to be an important component in these processes. Kakinoki et al. (2004) studied the relation between the degradation of famotidine and the relative humidity (RH) in a test vessel. A linear relationship was found where higher RH gave higher degradation. The reason is assumed to be the hydroxyl radicals that are formed from the divided water molecules that interacts in the oxidation and degrades the molecules. The conclusion therefore becomes that water is a good solvent to use for degradation of pollutants through photo catalysis.

Many studies indicate the difference in efficiency between different types of TiO_2 (Kakinoki et al., 2003). There are three different forms of titanium dioxide in nature. Rutile is the most common, after that follows anatase and most rarely, brookite. The difference in crystal structure gives efficiency for degradation of different compounds. For water, it has been found that anatase is 1.5 times for efficient than rutile.

Based on available literature it becomes clear that two key questions must be solved to maximize the oxidation of organic compounds over a titanium dioxide surface: 1).The organic molecules must be in direct contact with the surface. 2) The formation of radicals at the surface must be high.

2.4 Existing soil remediation Methods

Due to the recognition of environmental problems of polluted areas, different soil remediation technologies have been studied and developed. The treatment of soils contaminated with persistent organic pollutants (POP's) can be carried out by one of many available techniques. There is a great variety of remediation techniques and applications. This report will describe the most commonly occurring technologies. The techniques described are divided in groups of chemical, biological, physical and thermal methods, focussed on remediation of soils contaminated with polycyclic aromatic hydrocarbons (PAH's), dioxins and furans.

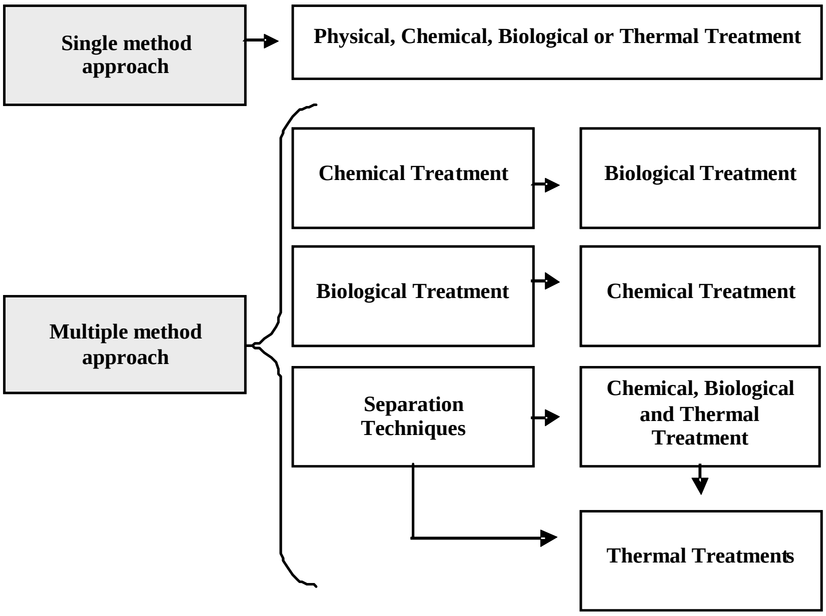

Figure 7 Possible remediation technique combinations

These remediation techniques can be performed either in a "singular method approach", when one technique is performed alone, or as a part of "multiple method approach", when more techniques are performed in conjunction. Another characteristic is that they can be performed either *ex situ* (after the contaminated material has been removed, either on-site or off-site) or *in situ* (in the ground) (Figure 7).

2.4.1 Chemical treatment methods

There are mainly two chemical treatment methods: the reductive dehalogenation techniques and the oxidation techniques.

Reductive Dehalogenation Techniques aims to detoxify chlorinated contaminants through dechlorination using reducing conditions. A possible option is to use nucleophilic substitution and oxidative dehalogenation (Chen et al., 1997). Alkali metal hydroxide/polyethylene glycol process

(APEG) is a technique frequently used to remediate contaminated soils, sediments, oils and sludge, by using polyethylene glycol (PEG) (reducing agent) and potassium hydroxide (KOH) (Freeman and Harris, 1995). However, the Base-catalysed decomposition (BCD) process is cheaper and faster than APEG. In addition, APEG is not an appropriate method to remediate soil contaminated with dioxins, while BCD can be used to treat aqueous dioxin-contaminated soils (Haglund, 2007). The BCD process needs alkali addition from 1-20% and also needs the temperature around 315-420ºC. As hydrogen ions are required for the BCD reaction, if the contaminated soil does not provide hydrogen donor, suitable hydrogen donors are added (Kulkarni et al., 2008).

In the oxidation methods, the contaminants are destroyed through a chemical reaction between them and an oxidant. There are different oxidants suitable for these methods, but the strongest one among them is the hydroxyl radical, being used in many oxidation methods (Table 2).

Table 2 – The strength of different oxidant (ITRC, 2005).

Chemical Species	Standard Oxidation Potential (Volts)	Relative strength (Chlorine=1)
Hydroxyl radicals (OH•)	2.8	2.0
Sulphate radical (SO_4•)	2.5	1.8
Ozone	2.1	1.5
Sodium persulphate	2.0	1.5
Hydrogen peroxide	1.8	1.3
Permanganate (Na/K)	1.7	1.2
Chlorine	1.4	1.0
Oxygen	1.2	0.9
Superoxide ion (O•)	-2.4	-1.8

The strongest oxidant, the hydroxyl radical (OH•), have the capacity to react unselectively and quickly with unsaturated organic compounds, for instance aromatic structures. Various methods can generate (OH•) radicals in different ways but the generation via iron-catalysed decomposition of hydrogen peroxide under low pH (2.5-4.5) is commonly used. The reaction is called Fenton's reaction (Equation 8) (ITRC, 2005).

Equation 8 $H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH\bullet$

This reaction is performed at low pH because under these conditions (pH < 5) iron (III) is transformed back into iron (II) and remains in solution. Fenton's reaction has been modified with respect to the peroxide concentration. Previously it was performed with 0.03% concentration but now concentrations are normally ranging from 4% to 20% for *in situ* treatments. Other changes have also been made; the reaction has been performed without the addition of iron and at neutral pH (Goi et al., 2006; Palmroth et al., 2006). However, according to Tang and Huang (1996), if iron is used in the reaction, there is an optimal concentration of hydrogen peroxide as well as an optimal peroxide and Fe^{2+} ratio. Optimal conditions of Fenton's reactions are vital as high concentration of ferrous ions will lead to the hydroxyl radicals consuming the ferrous ions resulting in a less efficient oxidation (Equation 9).

Equation 9 $Fe^{2+} + OH\bullet \rightarrow Fe^{3+} + OH-$

Due to the high oxidation efficiency of Fenton's reaction, there is a large interest for it in soil remediation which is shown in the high number of publications with this approach. Many researchers have analysed the Fenton's reaction and Fenton-like applications and it is described to work properly for remediation of both groundwater and contaminated soils and also for wastewater treatments (Watts et al., 1999; Pérez et al., 2002; Flotron et al., 2005).

Permanganate is also an oxidation agent that is been used. It is characterized for having high affinity for organic compounds presenting aldehyde groups, hydroxyl groups or carbon-carbon double bonds, and it can be used in two of the most common forms: potassium permanganate ($KMnO_4$) or sodium permanganate ($NaMnO_4$). The main difference between them is the concentration of the supplied form. The sodium permanganate agent is supplied with concentration of 40% and in used in solution, while the potassium permanganate agent has a maximum concentration of 4%, being prepared from a crystalline product. Consequently, the $NaMnO_4$ agent allows the use of greater concentrations (ITRC, 2005). Research have suggested that the utilization of permanganate oxidation is suitable to remediate both contaminated soils and sediments, and also contaminated groundwater, but normally it is used in combination with other techniques (Ferrarese et al., 2008; Tsai et al., 2009).

Ozonation is a traditional technique to treat municipal water. The numbers of studies about this method has been increasing during the last 20 years and have indicated that ozonation is a successful technique to treat contaminated water and soil by degrading complex organic contaminants (ITRC, 2005). The ozonation method has a particular characteristic when comparing it to many other chemical remediation techniques: the introduction of a gas in the process followed by the oxidation either directly or indirectly. In the direct oxidation, the reaction occurs directly between the contaminant and the ozone molecules, while in the indirect oxidation there is a production of hydroxyl radicals. The indirect oxidation increases its relative importance when the pH increases and in presence of minerals, since both improve the hydroxyl radicals production (Sreethawong and Chavadej, 2008). As quoted before, hydroxyl radicals react unselectively and quickly with organic contaminants. Comparing the direct and indirect oxidation the indirect oxidation is faster due to the presence of hydroxyl radicals, which have higher oxidation strength than ozone. The ozone concentration is an important parameter as it can act as sterilizing agent if the concentration is too high. In the other hand, if the ozone concentration is low, it has the advantage of improving microbial activity, as a result of oxygen introduction into the soil, which would improve the efficiency of bioremediation if it is to be used as a next remediation step (ITRC, 2005).

Supercritical water oxidation (SCWO) or pressurized hot water oxidation (PHWO) is another oxidative technique which involves formation of hydroxyl radicals. The difference is that in the PHWO method the oxidants are introduced in the beginning, under supercritical conditions. The reagents being used include persulphate and oxygen but the most frequently used oxidant is air. PHWO is a suitable technique to remediate soils contaminated with hydrophobic pollutants which present high chemical stability, but the technique needs to be carried out under harsh conditions. The costs to perform this method can vary from cheap to expensive depending on the organic contaminant concentration. The cheapest option is to treat wastewater with contaminant concentrations varying from 1% to 20% using heat exchangers, because the oxidation process releases heat which can be used to preserve the required temperature reaction. When the concentration is lower, the costs are more expensive and when it is higher the incineration method is competitive. The important characteristics which make this technique relatively expensive are the equipment and the high energy consumption (Thomason and Modell, 1984).

Photolytic oxidation works with ultraviolet (UV) light and it works properly to remediate contaminated groundwater. Soils cannot be remediated directly because the photo degradation of dioxins, for example, is negligible. In order to be suitable for soil treatment, it needs to be performed in conjunction with a solubility-enhancement method such as extraction using surfactants or vegetable oils, or solvent-washing. The photo degradation is fast when used in combination with ethanol. The photolytic oxidation can also be performed in conjunction with other oxidative techniques, using Fenton's reagent for example (Pérez et al., 2002; Lee et al., 2005).

2.4.2 Biological treatment methods

Biological treatments involve the utilization of microorganisms (MO) which use the contaminant as carbon source. With the intention to degrade hazardous organic contaminants, MO are used to transform contaminants ideally into water and carbon dioxide under favourable environmental conditions for the degradation process. Defined by the MO chosen to run the treatment, the process can be performed under either aerobic or anaerobic conditions. Different microorganisms have been analysed to be used in biological treatments. Biological treatments can be performed *in situ* if the microorganisms can have access to the pollutants. However, in order to circulate oxygen and nutrients, soil flushing and groundwater pumping are commonly used in combination with *in situ* biodegradation (Freeman and Harris, 1995). Even if it is possible to use *in situ* biologic treatment, Wilson and Jones (1993) described that for most PAHs it has limited effect, requiring a combination with other methods.

The use of bio-slurries or bioreactors is an option to perform biological treatments, especially for highly contaminated material (Freeman and Harris, 1995). In the bioreactors, water is mixed with the contaminated soil, and aerobic biodegradation takes place under controlled conditions. This system has the advantage to be easily managed and hence easy to maximize the efficiency. However, it does not treat the more hydrophobic PAHs properly (Wilson and Jones, 1993).

Composting is a biological method which involves the addition of naturally occurring microorganisms, with environment control, water, nutrients, oxygen and highly organic material (straw, sawdust or wood chips) into the contaminated soil. The high organic matter concentration achieved after these additions results in high microbial activity that provides a temperature increase and consequently, a more efficient degradation and higher degradation rates (Freeman and Harris, 1995).

Land farming is also a remediation method involving biological treatment. This technique is performed by spreading a thin layer of contaminated soil onto the treatment area surface. When MO are added there is also addition of moisture, nutrients and minerals with the intention to increase their activity. Besides this, it is also important to carefully mix the soil to be sure that the supply of oxygen is sufficient for the aerobic biological degradation and to provide a greater contact between the microorganisms and the organic content. The land farming technique is a suitable method to decrease concentrations of PAHs with three or less aromatic rings (Wilson and Jones, 1993).

As the contaminants can have low bioavailability and limit the biological techniques, a promising option is to combine separation techniques (with the use of surfactants for example) or chemical oxidation with the biological methods. Many researchers have shown that it can improve the efficiency and speed of PAHs removal (Zheng et al., 2007). Besides this, the combination of pre-oxidation using Fenton's reagent and biodegradation has presented great results (Kao and Wu, 2000).

2.4.3 Phytoremediation treatment methods

Phytoremediation is an option for biological treatment which is relatively new. This new technique is performed *in situ* and utilizes the ability of plants to remediate contaminated soils, normally with heavy metals, by extracting, sequestering and detoxifying the existing contaminants. Additionally, phytoremediation is also a technique to remove PAH's from soil. Much research has been carried out since 1991 concerning the endogenous genetic, physiological and biochemical abilities of plants to produce non-toxic compounds (like nitrate, ammonia, carbon dioxide and chlorine) from many complex organic contaminants by mineralizing them (Vidali, 2001). Examples of the biochemical and bio physical process performed by plants which enhance the soil remediation are (Parrish et al., 2005):

- Chemical alterations of toxic compounds through the plant metabolisms resulting in inoffensive forms;
- Sequestration and storage of pollutants in the range of 0.1-1% of the plant dry weight;
- Changes in the plant capture of contaminants by generating a more acidic soil;
- Adsorption of pollutants by adsorbing the nutrients to which they are bound;
- The increase in bioavailability of contaminants by using enzymes released from plants as surfactants.

In addition, persistent organic pollutants can also be remediated by a synergistic interaction between microorganisms in the rhizosphere and plants (Chaudry et al., 2005).

Phytoremediation is commonly performed using grass, trees or in combination with biological methods. There are some important characteristics of the plants which enable them to remediate polluted soils such as their ability to adapt to soil conditions, to cover a considerably great root surface area, and to survive without advanced and frequent maintenance like trimming of fertilizing. Based on those characteristics studies have described the feasibility to use the Graminaeae family (grass) due also to their fibrous root system which penetrate deeper into the soil.

Rezek et al. (2008) monitored the remediation of fifteen PAHs in soil by using ryegrass (Lolium perenne) for eighteen months. During the process it was performed soil fertilization using N-P-K fertilizer every fourteen days being the soil at 5-10°C in the winter and 12-27°C in the summer. After remediation the PAH concentrations were substantially reduced to 50%, except for the high molecular weight PAHs such as indeno(1,2,3-c,d)pyrene, benzo(g,h,i)perylene and dibenzo(a,h)anthracene. Examinations of the remediated soil regarding the PAH content in different soil layers showed that PAH concentrations were lower mainly in the samples from the bottom layers (18 centimetres deep soil). These results described that PAHs have a heterogeneous degradation in soil since the extent covered by roots and its depth are not known and complicated to measure in field sites.

Another observation is that even if there was a good germination of seedlings in the PAH polluted soil for phytoremediation, there was also a decrease in the ryegrass growth comparing it to seven other species of legume and grass (Smith et al., 2006). The explanation lies not only in the PAH toxicity but also in the reduction of biomass production in highly polluted soil reducing nutrients and water supply for plants. There are also other plants which can remove PAH from contaminated soils, such as switchgrass (Panicum virgatun) and tall fescue (Festuca arundinacea). They are able to remove all PAHs by approximately 40%, excluding indeno(1,2,3-c,d)pyrene which were only 1.5% (Cofield et al., 2008). Echinogalus crus-galli and native Korean grass (species Panicum bisulcatum) have efficient extra cellular production of enzymes and robust growth that enable them to be used for phytoremediation of soils contaminated with PAH (Lee et al., 2008). Remediation using these species was able to degrade 77-94% of pyrene and more than 99% of the phenantrene after a treatment for eighty days.

Grass has been extensively used for phytoremediation but trees are also an alternative to treat contaminated soils due to their large root systems (Mueller and Shann, 2006). A wide range of trees have the capacity to remediate soils contaminated with PAHs, for instance black willow, black locust, red mulberry, sycamore and rooted hybrid poplar. The method is performed by fertilizing and watering the pot planted trees keeping it under ventilation at temperatures varying between -4°C and 39°C for twelve months. The reduction of PAH content from aged soils was dependent on the compound. Phenanthrene showed the fastest and the most complete degradation when comparing it to pyrene and anthracene. The feasibility to use white pine (Ponus strobus), red pine (Pinus resinosa) and jack pine (Pinus banksiana) for phytoremediation was also studied and they presented great results. They were able to degrade 74% of pyrene in soil during eight weeks while an unplanted soil could degrade around 40% or less (Liste and Alexander, 2000). The disadvantages of phytoremediation method in practice are the difficulties of calculating the duration of the remediation treatment needed, measuring the remediation rates and deciding monitoring dates (Newman and Reynolds, 2004). In order to do that it is necessary to develop models which take into account many interactions.

A combination of phytoremediation and biological methods are an option that can improve the removal of PAHs from contaminated soils. A multi-process was performed involving land-farming, during 120 days keeping a constant moisture level, followed by a treatment using PAH-degrading bacterial culture, which were mixed into the soil, performed for 120 days more and the last process was phytoremediation using tall fescue (F. arundinacea), which were sown into the soil which was also performed for 120 days (Huang et al., 2004). However, before the multi-process, a plant growth promoting rhizobacteria (PGPR) was used in the plant seeds to promote biomass production and plant growth. The multi-process showed positive results having an increase of 23% in comparison to the phytoremediation process alone. This treatment reached a removal efficiency of 78% of sixteen priority PAH being also able to remove the higher molecular weight PAH, especially those composed of more than five rings, such as benzo(a)pyrene (removal efficiency of 58%), benzo(g,h,i)perylene (43%), dibenzo(a,h)pyrene (42%) and indeno(1,2,3,c,d)pyrene (32%).

Another multi-process was also carried to evaluate the removal efficiency of PAHs of those treatments and it included two biological methods, as a soil pre-treatment, which were on-site land-farming with biosolids and composting in drum reactors, followed by the phytoremediation process using three cool season forages, yellow sweet clover (Melilotus officinalis), annual ryegrass (Lolium multiflorum) and tall fescue (F. arundinacea) (Parrish et al., 2005). After that, a secondary phytoremediation process was performed for twelve months in a greenhouse. The results of this multi-process were in accordance with the previous one described, there was a substantial reduction in PAH content particularly those with 4- and 5-rings (Huang et al., 2004).

2.4.4 Physical treatment methods

Common physical treatments are the separation techniques which mainly involve the separation of contaminants from the polluted matrix. The separated contaminant is transferred to another medium, for instance to an adsorbent from a polluted liquid, or into a liquid from a polluted soil, and consequently, the contaminated material frequently has reduced its volume.

Supercritical water extraction (SCWE) or also called pressurized hot water extraction (PHWE) is a separation technique that utilizes water as the only solvent. As the name implies, this method is performed under particular temperature conditions and high pressure due to the water properties in this situation. When the pressure and temperature are higher than critical values (221bar and 374°C) the water assumes a "supercritical" state and its properties change substantially. Under these critical conditions dielectric constant of the water reduces significantly and the water presents its polarity such as that of organic solvents, becoming efficient to extract even PAH, dioxins and other highly hydrophobic contaminants (Freeman and Harris, 1995; Hashimoto et al., 2004).

A frequently used physical technique is the soil washing which is performed with water-based solvents and commonly used as an "extraction technique" (Freeman and Harris, 1995). Research has shown that soil washing is a suitable method to remediate soils with coarse material but it does not work properly on soils with high clay, silt and organic matter content (Freeman and Harris, 1995). This is due to the high permeability of coarse soil for liquids and as well as the lower capacity of the soil to establish bonds with the contaminant owing to its smaller particles surface areas per unit volume. Consequently, if the coarse soil (gravel and sand) is separated from the fine soil (silt and clay), what can be performed prior to or during the soil washing remediation, the volume of contaminated material can be substantially reduced (Cheng et al., 2007). Soil washing technique can be performed in multiple stages in order to increase the process efficiency (Figure 8).

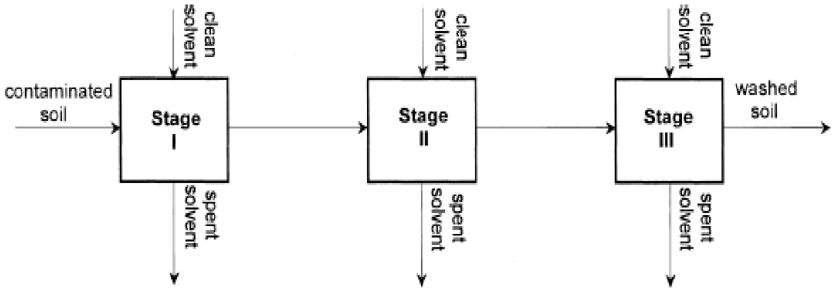

Figure 8 Soil washing in three cross-current stages (Khodadoust et al., 2005).

Solvents of low molecular weight alcohols have been tested and they have also shown to be appropriate solvents for soil washing remediation, in order to extract organic pollutants from soil (Khodadoust et al., 2000). Besides, the utilization of another extracting solution can allow the extraction of both organic contaminants and metals (Khodadoust et al., 2005). Vegetable oils, surfactants and cyclodextrins are alternative solvents which can also be used to perform separation of PAH and dioxins from soil (Brusseau et al., 1994; Yeom et al., 1996; Isosaari et al., 2001).

As described previously, separation techniques involve only the removal of the contaminant from the polluted matrix, there is no degradation involved. Thus, a post-treatment of the removed media is required, for instance the use of UV-degradation, activated carbons to adsorb the extracted pollutants and also the use of distillation to regenerate the solvent (Isosaari et al., 2001; Ahn et al., 2007). A post-treatment for the remaining soil is also necessary in order to have a safe disposal.

2.4.5 Thermal treatment methods

The thermal treatments for soil remediation that are being used are thermal desorption, vitrification and incineration.

Using thermal desorption, temperatures in the range of 100°C to 600°C are being used to heat the contaminated soil and vaporize the pollutants which have their boiling points between these temperatures. Since the contaminants are just vaporized, there is no destruction of them. Hence, if they need to be destroyed an after step is needed. Due to the absence of contaminants destruction, this method can be seen as a thermal separation technique.

Thermal desorption techniques can be performed at low or high temperatures (Wait and Thomas, 2003). When it is performed at low temperatures, low temperature thermal desorption, the volatile components are vaporized, and when it is performed at high temperatures there is a possibility to vaporize the compounds with a higher boiling point. Another process that can occur when the high temperature thermal desorption is performed is the oxidation of compounds instead of the volatilization. However, even if the oxidation takes place, the method should not be seen as an incineration process because there is no intention to destroy the contaminants. The disadvantages of the thermal desorption are the high demand for energy and costs related to that (Freeman and Harris, 1995).

Vitrification and stabilization/solidification are two remediation methods included in the stabilization techniques which are being used to treat soils contaminated with inorganic pollutants. It is called stabilization techniques due to the transformation of the contaminants into less mobile and less soluble compounds. The process is performed at very high temperatures, in the range of 1600°C to 2000°C. Since the temperatures needed are extremely high, it is possible to remediate soil contaminated with inorganic and organic pollutants, which are vaporized or pyrolysed (Freeman and Harris, 1995). An example of solid matrix contaminated with both pollutants is ash, usually containing high concentrations of PAH, dioxins and heavy metals. Thus, when vitrification is performed in soils contaminated with a mixture of the three, inorganic pollutants are stabilized and the concentration of organic pollutants is reduced (Kuo et al., 2003). The process is performed by melting the soil at extremely high temperatures and cooling it later, resulting in a hard, chemically inert, monolithic, crystalline product and stable glass with low leaching properties (Freeman and Harris, 1995). However, the vitrification process does not solve the final disposal problem of the contaminants and another remediation technique is required.

Incineration is the most known and the most effective method to treat PAHs and chemically stable contaminants like PCDD/Fs. The incineration process is performed at temperatures higher than 1000°C which consequently result in a high energy demand and extensive costs. However, if soils with high concentration of organic material are treated in the process, it will produce energy which can be used in the combustion decreasing the demand for energy. Thus, incineration is a great option as a technique to remediate soils with high total organic content, exceeding 20-25% (Thomason and Modell, 1984).

2.4.6 Electrokinetic Treatments

Low permeable soils can be treated with *in situ* electrokinetic method to remove radio nuclides, heavy metals and some organic contaminants. Electrokinetic remediation is performed by applying a direct current electric potential of low level through electrodes placed into the polluted soil (Figure 9 and Figure 10). Electromigration is the mechanism responsible to transport ionic pollutants to the electrode of opposite charge. Besides, soluble pollutants also move due to a driving force produced from electro-osmotic flow. This technique has already been applied for more than ten years; however it has recently been used to remediate low permeable soils contaminated with hydrophobic and strongly adsorbed contaminants like PAHs. Additionally, in these cases solubilising agents have also been applied to improve the PAH removal. Research has been carried out about this method and its feasibility to treat soils contaminated with PAHs.

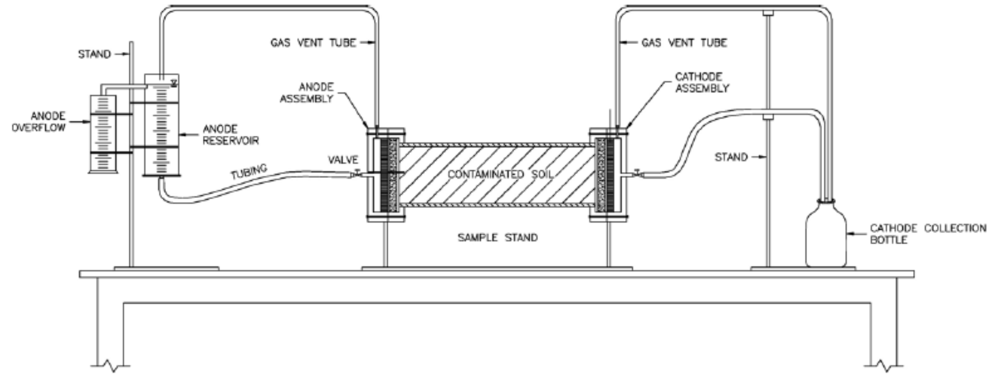

Figure 9 Scheme of electrokinetic test, side view (Reddy et al., 2006).

Reddy et al. (2006) has studied this technology using bench scale experiments using soil from a manufactured gas plant (MGP soil) performed with cyclodextrin (10% HPCD), co-solvent (20% n-butylamine) and surfactants (5% Igepal CA-720 and 3% Tween 80) as flushing agents; conducted at 1.4 hydraulic gradient and at 2.0 VDC/cm voltage gradient. When 20% n-butylamine co-solvent was used followed by 10% HPCD, the electroosmotic flow achieved the maximum point. However, regarding the PAHs migration towards the cathode it was more significant and efficient when the PAHs were solubilised using surfactants and HPCD. The surfactant Igepal CA-720 provided the highest removal efficiency of PAHs.

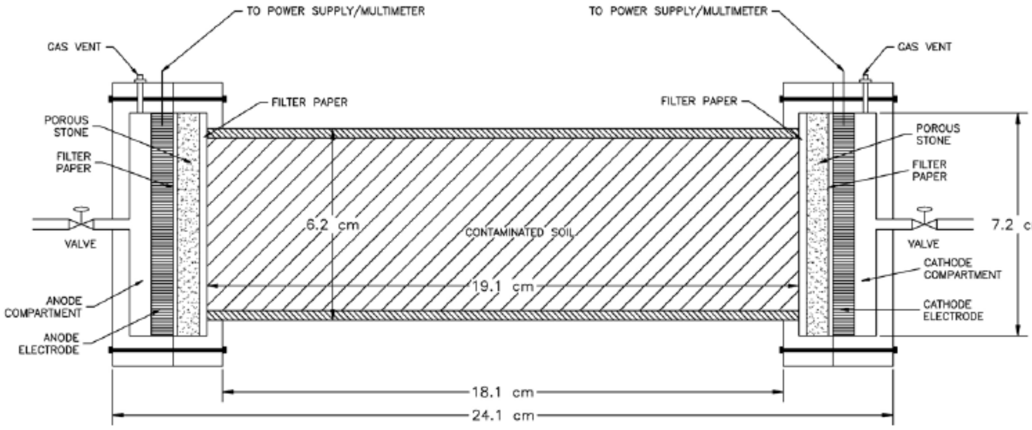

Figure 10 Scheme of electrokinetic test, top view (Reddy et al., 2006).

The efficiency of HPCD at high (10%) and low (1%) concentrations to remediate kaolin soil (clayey soil) contaminated with phenanthrene has also been analysed (Maturi and Reddy, 2006). A sodium hydroxide solution of 0.01M was used in the experiments to achieve neutral pH conditions at the anode and according to previous results phenanthrene migrated from anode to cathode (Reddy et al., 2006).

When the experiments were performed with 1% HPCD the phenanthrene removal was higher than when it was performed with 10% HPCD also including deionized water. This behaviour is due to the high electro osmotic flow produced in the first case. In the presence of deionized water phenanthrene, which presents hydrophobic characteristic, could not be solubilised, even with relatively high electroosmotic flow. Another important parameter in the remediation of phenanthrene is the pH, which may be controlled in order to increase solubilisation of pollutants and migration of pollutants from the soil (the region adjacent to the anode) (Saichek and Reddy, 2003). However, there was contaminant deposition and low removal efficiency represented by high concentrations of pollutants in the cathode soil regions or in the middle as a result of subsequent changes in the solution chemistry or in the soil.

2.4.7 Innovative treatment methods

Mechano-chemical degradation is an innovative technique for degrading organic contaminants and studies have described the feasibility to treat soils contaminated with many different organic compounds, including PAHs and dioxins (Nomura et al., 2005; Napola et al., 2006). To implement this method, the contaminated matrix in ground in a ball mill at ambient temperature with addition of a dechlorinating agent (CaO) (Figure 11). During the process thermal energy is produced due to the energy transference from the milling bodies to the solid system. The thermal energy generated increases the surface reactivity and also highly active radical are produced which reacts directly with the contaminants (Birke et al., 2004). As there is no need for extra energy and the technique is simple the technology is economically attractive.

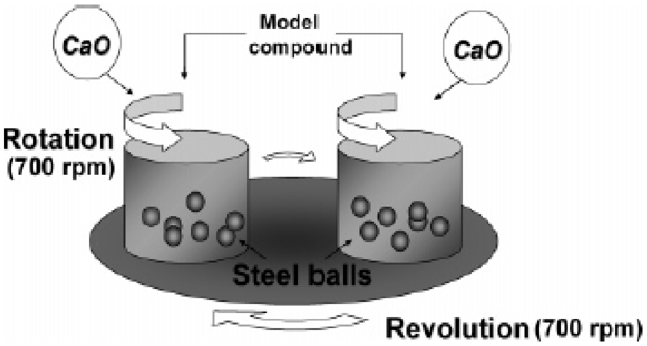

Figure 11 Illustration of mechanochemical treatment (Nomura et al., 2005).

Nano scale degradation is another innovative technique for soil remediation. Recent studies have analysed the potential of nano scale iron particles and the conclusion is that they have high potential regarding environmental remediation (Zhang, 2003). The innovative techniques involving nano scale particles have the advantage to be a cost-effective remediation method due to the low operational costs, but more research is needed in order to develop a cost-effective process to produce the nano material (Savage and Diallo, 2005). The nano scale particles have a high capability to degrade many environmental pollutants frequently detected in contaminated soils, even the chemically stable compounds like dioxins (Kim et al., 2008). This is due to their large surface reactivity and large surface area enabling them to work really well for remediation treatments and it is possible to remediate contaminated soils with nano scale degradation using *in situ* application (Figure **12**). Zero valent ions systems have been used for nano scale treatments and it has been deeply analysed along with the possibility to introduce a second metal in the treatment, enhancing the DE chlorination rates substantially. The use of a second metal leads to a bimetallic system which is composed of zero valent iron and a catalytic noble metal (Pd or Ni) (Zhang et al., 1998). Hydrogen atom transfer is the dehalogenation mechanism which takes place when a bimetallic system is used, but electron transfer is responsible when only zero valent iron is used (Kim et al., 2008).

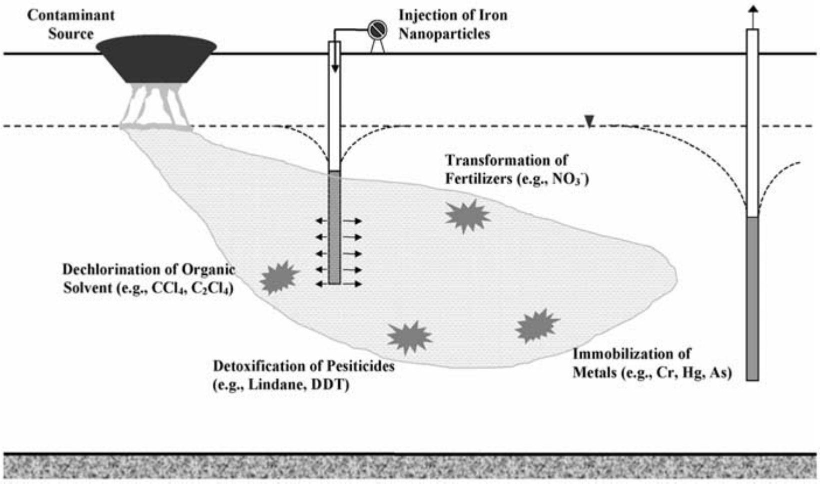

Figure 12 Example of *in situ* remediation application using nano scale iron particles. (Zhang, 2003).

It is important to note that nanotechnology has been of great importance in many scientific areas such as biotechnology, physical sciences and electronics, and it is a promising growing technology (Whitesides, 2003). However, along with this new technology, environmental problems are also coming out due to the increasing release of nano material in great amounts into the environment. The consequences of human exposure to nano material still needs to be well analysed but some attractive nano material characteristics already causes a concern regarding human health (Savage and Diallo, 2005; Fleicher and Grunwalg, 2008). Thus, investigations about environmental and exposure consequences to nano material should be carried out along with nano scale material research.

As quoted before, all the techniques described can be applied in conjunction with one or more techniques in order to achieve better results.

3 Materials and method

The extraction of dioxins to a NaOH solvent was performed using five different soils to represent different soil matrixes. Basic soil properties are described in Table 3. The soils were taken from industrially polluted sites in Sweden, where different types of activities historically caused the contamination. This has given the soils different congener patterns and levels of concentrations. For the extraction trials soils W, I and E were investigated and for the oxidation supernatants from W, B, I, and K where treated and analysed.

Table 3 Properties of investigated soils.

Soil	LOI	Water content	C:N quota	Fine material
W	6%	6%	137	2%
B	100%	30%	82.2	N/A
I	2%	8%	19.3	6%
K	36%	11%	31.7	25%
E	7%	21%	-	-

It should be noted that the supernatant treated in the oxidation did not come from the extraction process described here but was taken from previously performed experiments. The extraction experiments and the oxidation experiments are thereby separate to each other.

3.1 Extraction

3.1.1 Method development

Two method development trials were executed as pre-studies to adjust the final trial process, examining different parts of the process. The first aimed to investigate whether dioxins and poly aromatic hydrocarbons (PAH) can be extracted into an alkali water solution. The results showed that there were great variations in the extraction between different soils and resulted in some propositions for further investigations. This part of the development process is further described in Appendix I.

The second method development trial was carried out with the purpose of optimizing the organic matter extraction process from the soil based on the initial experiments. This resulted in two optional settings for the optimized extraction. The extraction should be performed at higher temperatures and median concentration or median temperatures and higher concentrations. This is further described in Appendix II. The results gained from the method development experiments (Appendix II) were used to make a model to be able to find the right circumstances for the wanted LOI and turbidity. This can be found in appendix III.

3.1.2 Execution

The extraction was constructed after consulting the method development results (Appendix I, II and III). By using the model described above the correct parameter values of temperature, time and concentration could be decided so that the LOI and the turbidity for the supernatant was high. The relative LOI was set to range between -55 and -45 and the turbidity to range between -90 and -80 based on previous results (Appendix II). This gave T=100°C, C=5.5 M, t=1.5h

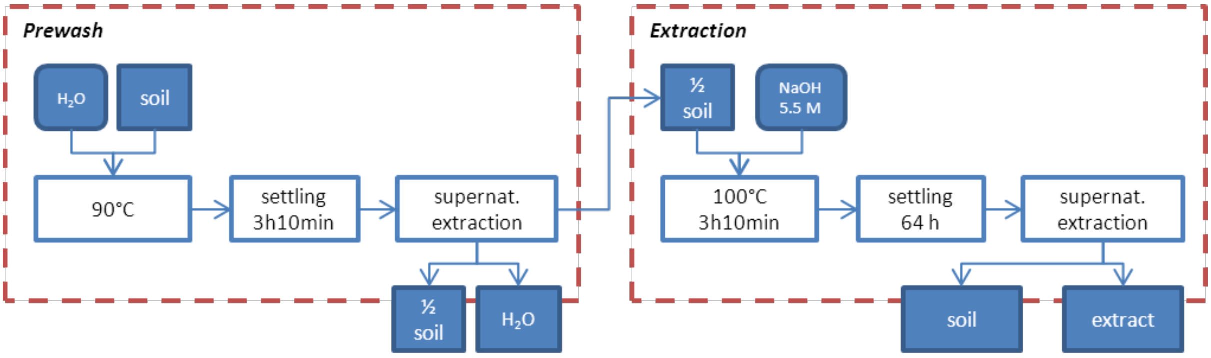

Figure 13 Schematic description of the extraction laboratory execution, where samples in the bottom of the figure were analysed.

A pre-washing step was added to remove as many chlorophenols as possible from the soil sample before the extraction phase as they may form dioxins during this process. Since the chlorophenols have a dipole tendency the idea was that they could be extracted to the water phase with the addition of heat. Three different soils were analysed, W, I and E, all described earlier in this chapter.

Triplet samples were done for the W soil sample. All soils were washed and extracted using a liquid:solid ratio of 1:20 (L/S 1:20). Dependent on the type of soil different starting amounts were used as the soils had different material reduction percentages in alkali extraction (Appendix I).

During the washing, water was added to the soil sample and was heated to 90°C and set to settle at 40-50°C for 3 hours and 10 minutes. After that the supernatant was extracted and sent for analysis with regard to chlorophenols and dioxins as was a soil sample as was a part of the soil sample.

For the extraction 5.5 M NaOH was added to the washed soil. This was heated to 100°C in an oil bath where it was kept for 1.5 hours with stirring done for 1 minute every 15 minutes. It was then set to settle for 64 hours after which the supernatant was removed and sent for analysis with regard to chlorophenols and dioxins, as was the remaining soil.

Due to the characteristics of the E sample there was no pre-wash in this extraction. Except for that, the extraction followed the same agenda as the above described experiments.

3.2 Oxidation

In a water reactor made up of two concentric glass cylinders between which the fluid was streamed, photo catalytic measurements were carried out. In the centre of the reactor an UV lamp (Sylvania BLB-18W-T8; λ=368 nm, FWHM=20 nm) was placed. The output effect from the UV lamp was about 2.7 mW/cm^2 which gave an effect of 2 mW/cm^2 after passing through the reactor. A peristaltic pump pumped the water from the reservoir through the reactor. The tank had a volume of 2 l and the pumping speed was approximately 140 ml/min. After passing through the reactor, the water was recirculated to the reservoir where it was mixed by a magnetic stirrer. Aluminium fittings and end caps were replaced by stainless steel fittings and end caps to avoid erosion. To ensure high enough oxygen concentration air was bubbled through the reservoir.

The experiment was carried out in the following way. The delivered soil samples were allowed to sediment 24-48 hours. The suspension was thereafter diluted with four parts of water to a total volume of between 1400-1600 ml and stirred in the reservoir with a magnetic stirrer. To this the titanic dioxide (ca 0.64 g/l; Hombikat UV100, Sachtleben Chemie) was added to the water. The water and particle suspension were stirred an additional 15 minutes. A blank sample was removed before the pump was started. When the fluid started to circulate in the system the UV-light was turned on. After 8 hours the light was turned off and a final sample was removed. The same procedure was carried out for all soil samples. For the sample K20 an intermediary sample was taken after 4 hours. For the soil sample B1 a trial setup without TiO_2 powder addition was also used. In this experiment the reactor was filled with spiral shaped column seals covered with a thin layer of TiO_2 film. In that way practical complications when particle-water separation after treatment is avoided.

4 Results and discussion

It can be seen in Table 4 that the soils chosen for the experiment derives from different contaminant sources, since the congener patterns differ between the three samples. The E soil is a chlorine-alkali industry, while the other two are related to the forestry industry.

Table 4 Initial dioxin and furan concentrations in tested soils. Three individual samples of the W soil was used during treatment as a triplicate, but only analysed once for initial concentration.

ELEMENT		I	W	E
2,3,7,8-tetraCDD	ng/kg DW	2.3	9.2	<0.94
1,2,3,7,8-pentaCDD	ng/kg DW	40	96	<2.8
1,2,3,4,7,8-hexaCDD	ng/kg DW	27	210	<2.8
1,2,3,6,7,8-hexaCDD	ng/kg DW	430	7100	<2.8
1,2,3,7,8,9-hexaCDD	ng/kg DW	120	780	<2.8
1,2,3,4,6,7,8-heptaCDD	ng/kg DW	1700	177000	45
oktachlorodibensodioxin	ng/kg DW	2800	920000	240
2,3,7,8-tetraCDF	ng/kg DW	9.8	16	220
1,2,3,7,8-pentaCDF	ng/kg DW	51	22	190
2,3,4,7,8-pentaCDF	ng/kg DW	430	71	83
1,2,3,4,7,8-hexaCDF	ng/kg DW	2000	610	160
1,2,3,6,7,8-hexaCDF	ng/kg DW	720	150	64
1,2,3,7,8,9-hexaCDF	ng/kg DW	700	240	<3.5
2,3,4,6,7,8-hexaCDF	ng/kg DW	26	20	4.7
1,2,3,4,6,7,8-heptaCDF	ng/kg DW	52900	109000	160
1,2,3,4,7,8,9-heptaCDF	ng/kg DW	880	1500	14
oktachlorodibensofuran	ng/kg DW	60300	226000	160
sum WHO-PCDD/F-TEQ lowerbound	ng/kg DW	1200	4000	77
sum WHO-PCDD/F-TEQ upperbound	ng/kg DW	1300	5000	80

The value which is often used to describe dioxins is called WHO TEQ. It is a normalized count of the 17 different types of dioxins (congeners) that are analysed. The congeners are normalized with respect to their toxicity which gives a weighted mean for WHO TEQ.

4.1 Extraction

The extraction is meant to affect the soil physically, by destroying the material to which the dioxins are sorbed, to enable that the hydrophobic dioxins can exist in water. Table 5 shows that the extraction has a major physical effect on the soils. The material loss from the W and I soils are around 30 %. The loss of material is both from organic matter and fine minerogenic material. The latter, since ion strength in the solution is raised considerably. This will cause charged aggregates to separate and particles disperse into solution. This is the desired effect for humic material, but will affect minerogenic material the same way. The E soil, which mainly consists of fine minerogenic material, shows that this effect is substantial, where the material loss is 77 %. The E soil was not treated with water, which is why no data is available for water extraction.

Table 5 The effect of extractions on the basic properties of the soils such as loss on ignition (LOI) or the loss of material where fine particles is the dominating fraction.

Soil	LOI Before treatment	LOI after water extraction	LOI after NaOH extraction	Total material loss
W	6	9.4 ±1.5	4.8 ±0.6	28 % ±2
I	2	3.5	6.5	33 %
E	7.4	-	9.0	77 %

The figures of LOI are considered not to be reliable, since the total amount of organic matter in the soil cannot rise due to this treatment. It can however be an effect of sampling since treatment will mean a certain degree of sorting. The expected development is that LOI decreases especially during treatment using NaOH. Why this is effect is not present cannot be explained. Figures of total material loss however show that extraction effectively takes away fine material and that soil with high representation of fine grains might not be suited for NaOH extraction. Hot water extraction might be a better alternative or the use of lower ion strength.

4.1.1 Dioxins

The concentrations of dioxins remaining in soil after treatment using both hot water and NaOH are shown in Table 6.

Table 6 Dioxin concentrations in the soil after extraction using both water and NaOH.

ELEMENT		I	2W	3W	4W	E
2,3,7,8-tetraCDD	ng/kg DW	<0.81	42	32	24	<0.81
1,2,3,7,8-pentaCDD	ng/kg DW	40	240	180	84	<1.9
1,2,3,4,7,8-hexaCDD	ng/kg DW	56	100	160	220	<3
1,2,3,6,7,8-hexaCDD	ng/kg DW	860	1800	2300	1300	<3
1,2,3,7,8,9-hexaCDD	ng/kg DW	290	540	870	620	<3
1,2,3,4,6,7,8-heptaCDD	ng/kg DW	3700	41000	72000	30000	330
oktachlorodibensodioxin	ng/kg DW	9800	700000	800000	360000	4400
2,3,7,8-tetraCDF	ng/kg DW	14	9.6	8.4	2.6	590
1,2,3,7,8-pentaCDF	ng/kg DW	72	16	17	7.5	330
2,3,4,7,8-pentaCDF	ng/kg DW	450	26	50	25	190
1,2,3,4,7,8-hexaCDF	ng/kg DW	2000	110	240	51	300
1,2,3,6,7,8-hexaCDF	ng/kg DW	1400	53	79	26	92
1,2,3,7,8,9-hexaCDF	ng/kg DW	33	<2.5	<5.5	<2.1	<2.6
2,3,4,6,7,8-hexaCDF	ng/kg DW	1200	72	290	54	1.3
1,2,3,4,6,7,8-heptaCDF	ng/kg DW	170000	16000	21000	7300	230
1,2,3,4,7,8,9-heptaCDF	ng/kg DW	1200	160	380	160	31
oktachlorodibensofuran	ng/kg DW	73000	33000	16000	7500	380
sum WHO-PCDD/F-TEQ lowerbound	ng/kg DW	2600	1400	1800	820	170
sum WHO-PCDD/F-TEQ upperbound	ng/kg DW	2600	1400	1800	820	170

It can be seen that concentrations are still considerable, well above the guideline value from Swedish EPA of 20 ng/kg DW WHO TEQ for residential land use or 200 ng/kg DW for industrial land use. These figures, however, are to be seen as indicative, since they are not performed during the proper full scale circumstances.

In Figure **14**, the remaining fraction of dioxins (WHO TEQ) is illustrated, as remaining concentration divided by the initial concentration of dioxins. This shows a residual concentration of 16 % in the best case and 213 % in the worst case. It can be concluded that the method is indeed efficient during certain conditions although there is a great difference in-between different soils, where some contain higher concentration after treatment.

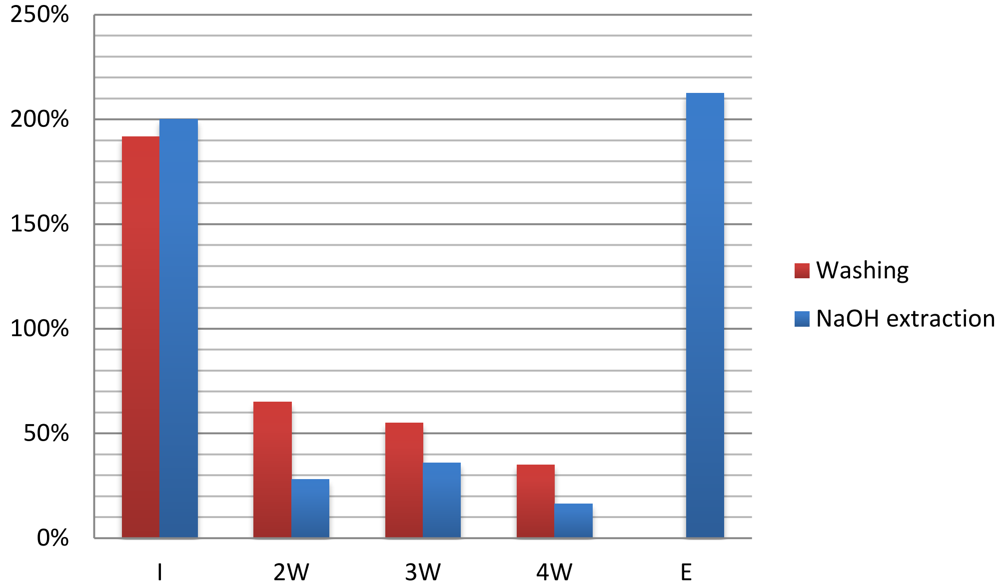

Figure 14 Remaining fraction of dioxins (sum WHO-PCDD/F-TEQ) after hot water washing and NaOH extraction compared to initial concentrations. The "Wes" samples is a triplicate.

A possible explanation to the good result of the W samples is that they contained higher start concentrations of which a greater portion was not weathered or leached before. This hypothesis is supported by the fact that the C:N quota is the highest for the W soil, which indicates that it contains the youngest organic material of the soils. In other words – the dioxins that are still stuck on the particles of I and E after treatment might have been too well sorbed or integrated into the soil matrix.

For the W samples it can also be concluded that hot water is a rather efficient extraction solution, since the difference between the water and the NaOH extractions is not more than 35 % units in any of the soils. What was thought of being a treatment mainly for the chlorophenols to avoid dioxin formation in the alkaline environment also showed to be effective for dioxins. It is not considered to be likely that water affects the dioxins themselves, but that it rather gets the carriers into solution or suspension.

The I and E samples behave differently leaving a doubled concentration in the soil after treatment. Since 77 % of the material in the E soil was taken away, this means that the extraction left dioxins being still in the solid phase and to a lesser extent followed the suspended minerogenic material into solution. Further discussion on this topic will follow below.

The amounts of dioxins that were used for the calculations above are based on the toxicologically weighted WHO TEQ unit, which does not reveal the details behind the figures. In Figure **15** and Figure **16**, the changes of 17 individual congeners are displayed, first after water treatment and second after NaOH treatment. They show that in all soils, the 2,3,4,6,7,8-hexaDBF congener increase by 100 to 1100 %. The toxic 2,3,7,8-tetraCDD increases in one of the W samples but is reduced in the others. This effect is achieved using water as extract. The NaOH does mean changes to this picture, but no radical ones. This result differs from the results of the initial pre trials, where furans were formed more generally and not as specific as in this trial where concentration, temperature and time of extraction were optimized. The fact that furans were formed during the water extraction implies that chlorophenols forming furans in alkaline environments do not constitute the major pathway. Also, the I sample increase is more than 1000 % while W samples less than 200 %, which is remarkable since W samples contained 10 times higher concentration of chlorophenols than the I sample from the beginning. This also strengthens the hypothesis that chlorophenols does not transform into furans.

For the data analysis below, concentrations below limit of detection were adjusted to limit of detection divided by 2. This is important since the congener 1,2,3,6,7,8-hexa CDF decreased below limit of detection in the W samples. The distinct bend of the curve in the furans implies that rearrangement of chlorine atoms occur during the treatment. Any chemical transformation of normally stable compounds like dioxins requires energy to break bonds or to create new ones and this rearrangement takes a relatively small amount of energy.

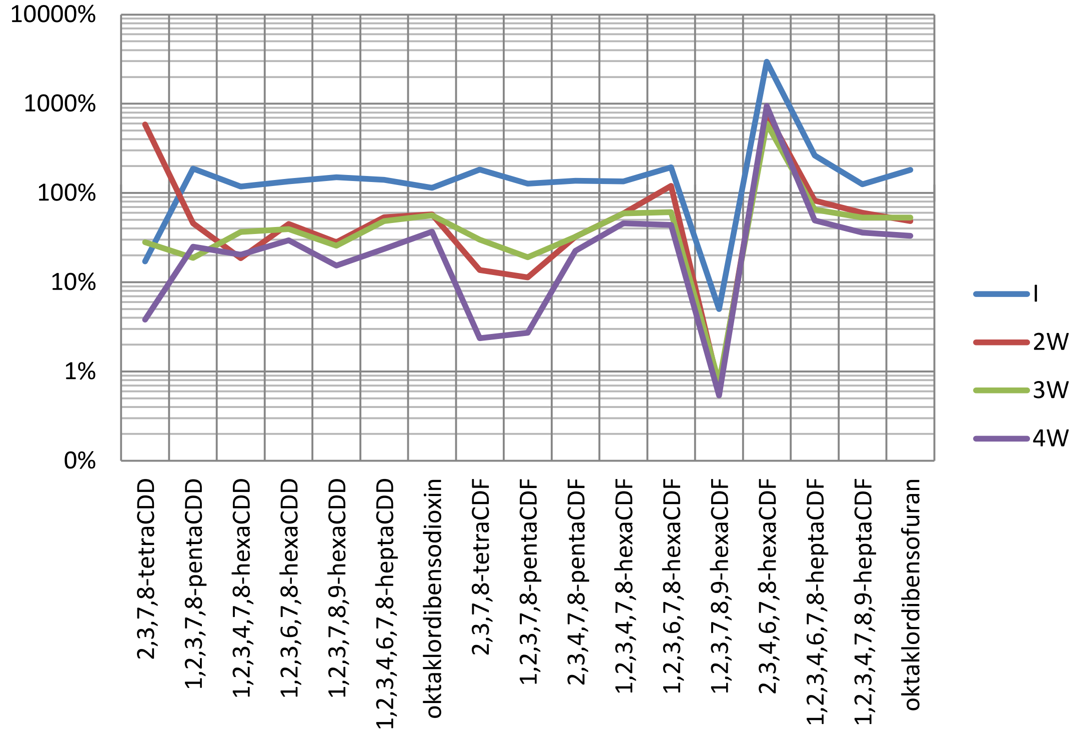

Figure 15 Remains of individual dioxin congeners after water extraction compared to initial concentrations. The “Wts” samples is a triplicate.

If the furans are believed to simply swap between congeners during treatment, this does not mean any major effects to the total toxicity of the soil. A change, however, that is of great concern, since this is the most toxic congener, is the supposed increase of the 2,3,7,8-tetra CDD congener in the W soils. After water treatment, only one of the samples in the triplicate rise, but after NaOH treatment all samples increase by more than 100 %. This effect is not observed in the I soil at any of the treatment steps.

There is no concentrations decrease of chlorophenols that corresponds with the increase of 2,3,7,8-tetra CDD. Also, formation of dioxins from chlorophenols cannot occur in the absence of an alkaline environment. This is why this mechanism cannot be responsible for the increase during water treatment.

The I samples shows a relatively stable general increase of the concentrations except for the 2,3,4,6,7,8-hexaDBF congener and its supposed corresponding congener. This implies that the raised concentrations derive from material separation rather than formation of dioxins. If the material which does not sorb dioxins is being removed, concentration profile will be unaltered since dioxins remain although raised since uncontaminated material is taken away.

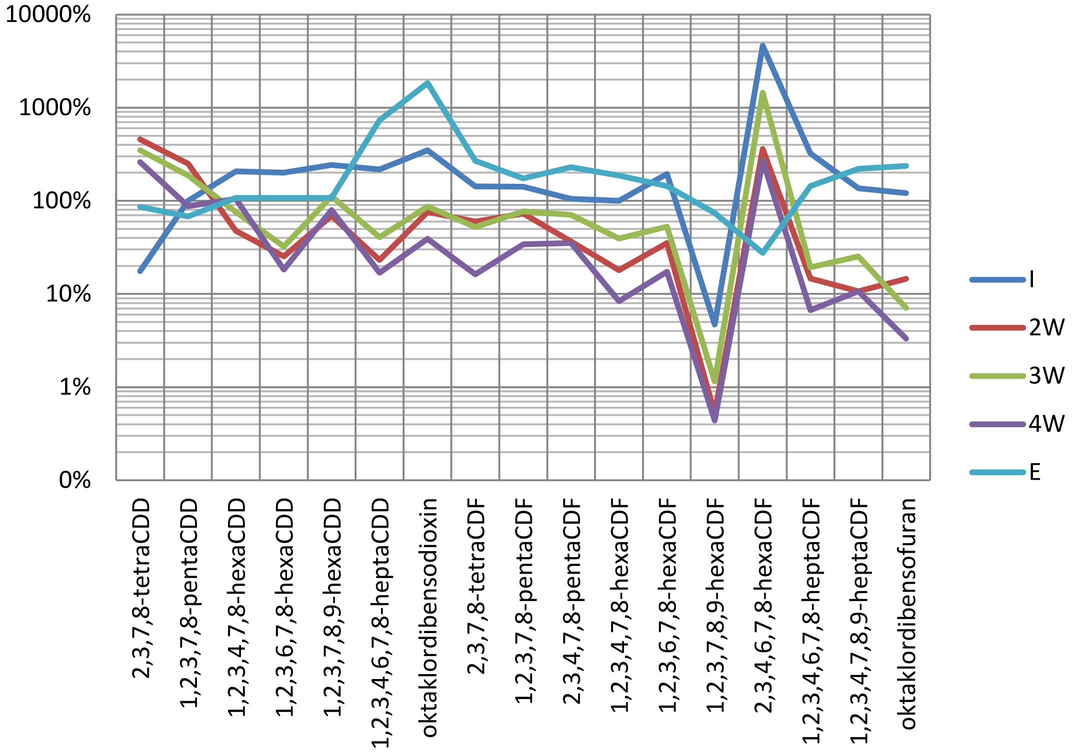

Figure 16 Remains of individual dioxin congeners after NaOH extraction compared to initial concentrations. The "Wes" samples is a triplicate.

E sample represents a totally different soil and congener pattern. The initial concentrations are below limit of detection in several congeners, which is also the case after treatment (results in 100 % remaining after treatment). According Figure **16** concentrations increase where initial concentrations are high. 2,3,4,6,7,8-hepta CDF seems to be decreasing, although this concentration is close to the limit of detection, which means great uncertainty. So is also 1,2,3,6,7,8-hepta CDF, which means that all present congeners increase. These figures could imply the same reason as the I soil, although it should be stressed that only 23 % of the soil remains in the solid phase which means that there are greater uncertainties regarding the E soil due to small sample amounts. These soils however does not seem to be treatable in this manner due to its fine grained nature.

The hypothesis for extraction of the dioxins was that extraction of the solid material that sorbs the dioxins would also bring them into solution. It seems, however, like dioxin sorption mechanisms to soil is not as straight-forward as they are believed to be, or that the age of dioxins do play an important role in their behaviour in soil.

4.1.2 Chlorophenols

The concentrations of chlorophenols were studied with special interest since the reaction pathway from chlorophenols to dioxins in an alkaline environment is well known. Table 7shows the concentrations before during and after treatment.

Table 7 Concentrations of total chlorophenols in treated samples. All concentrations given in mg/kg DW

	I	2W	3W	4W	E0
Before treatment	0.485	4.71[1]	4.71[1]	4.71[1]	<0.2
After water treatment	0.413	0.015	1.4	1.19	N/A
After NaOH treatment	0.409	0.912	1.25	1.27	<0.35

[1] Only one sample represents the initial concentrations of the W triplicate sample.

Water treatment has an effect on the soil, although there still are remains in the soil of pentachlorophenols that constitute the most hydrophobic chlorophenols. The conclusion is that water treatment step should be developed further, since it is effective both for dioxins and chlorophenols.

Figure **17** shows that also chlorophenols are being removed from the soil leaving just about 20 % of the starting amount in the soil after treatment in the best case and below 95 % in the worst case. Since chlorophenols are detected in mg/kg compared to ng/kg for dioxins, it is of interest to reduce these amounts further, to avoid any unwanted chemical transformations.

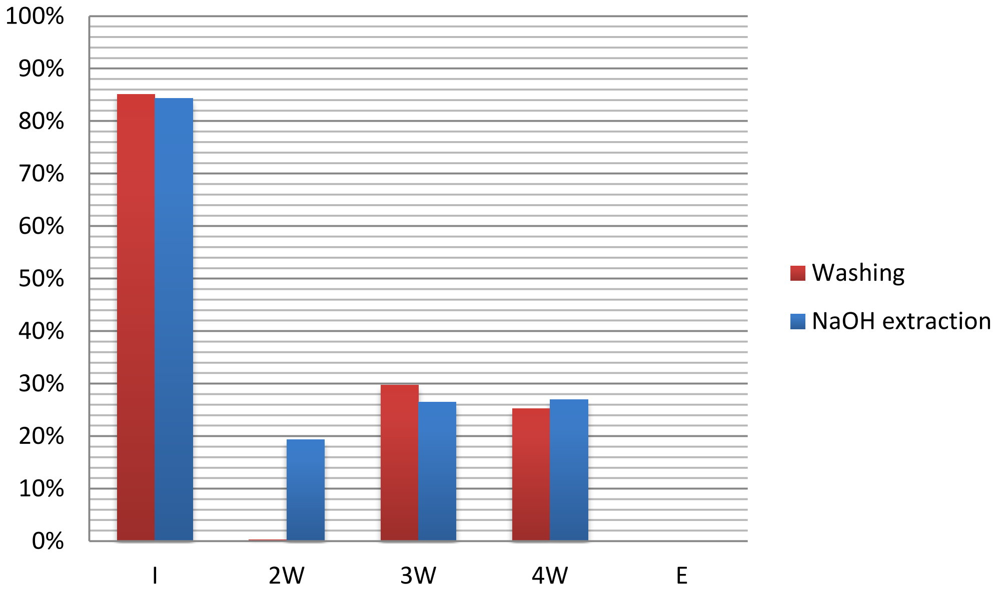

Figure 17 Remaining fraction of total chlorophenols after hot water washing and NaOH extraction compared to initial concentrations. The "Wes" samples is a triplicate.

It can be seen that extraction from the I soil is less effective than the W soils. Based on previous experiences it could be assumed that W soils are easier to leach either due to the soil matrix or the age of the contaminants. The complete reduction seen in 2W is assumed to be an outlier due to sampling, since other samples are well assembled.

4.1.3 Mass balance

During laboratory treatment, losses or sources of contaminants can always pose an uncertainty to the final result interpretation. This is why mass balances are shown below. The mass balance is the initial amount in the soil prior to experiments, compared to the total amount after extractions in both aqueous phase and soil phase, which is shown in Figure **18** for chlorophenols and in Figure **19** for individual dioxin and furan congeners.

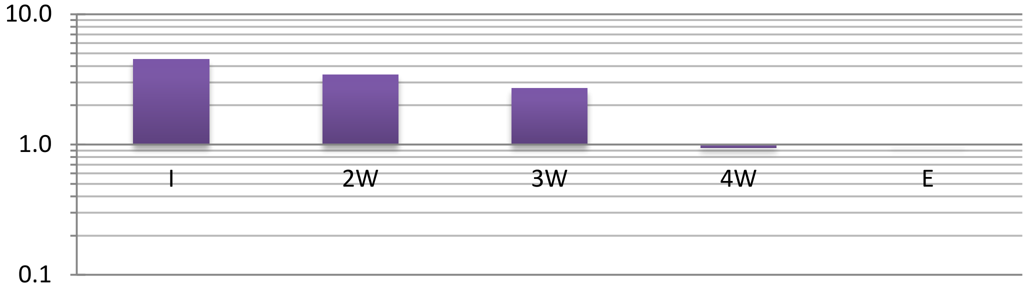

Figure 18 Mass balance for the total chlorophenols, shown as the quotient between the initial amount plus all extracted chlorophenols and remaining chlorophenols. A quotient of 1 indicates that no losses or gains of substances were achieved during the experiment. E soil is not included since concentrations were below limit of detection in all samples.

Quotients for losses or gains of chlorophenols vary in-between samples in the triplicate from 3.4 to 0.95, which implies that handling and/or sampling affect losses and gains more that general reaction mechanisms. Further, the difference between mass balances of chlorophenols for W samples makes the correlation between dioxin formation and chlorophenols weak since the mass balance pattern for dioxins do not show the corresponding pattern. Dioxin mass balance in Figure **19** and shows low spread within the W soil triplicate for gains. It further supports the conclusions drawn in previous sections.

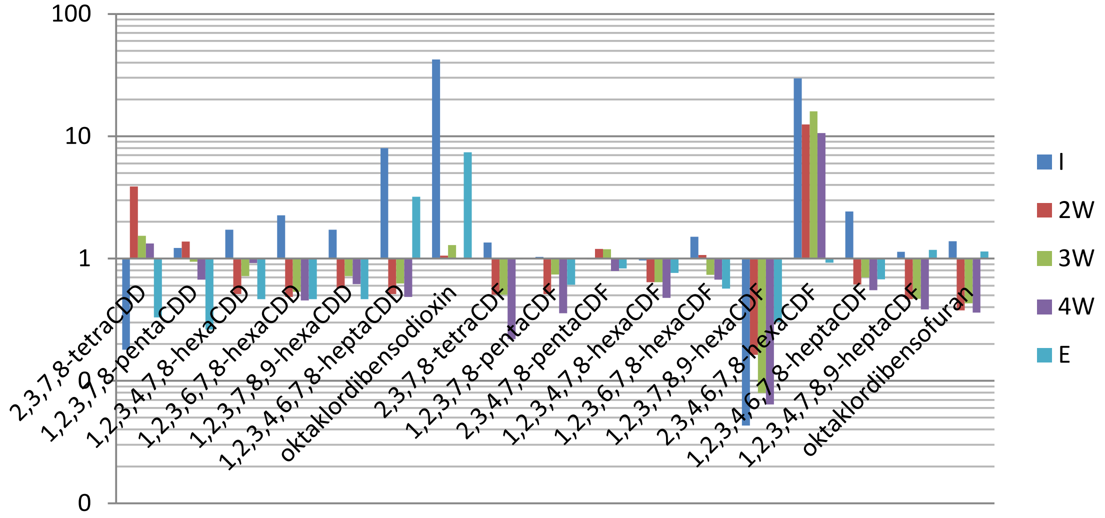

Figure 19 Mass balance for individual dioxin congeners after water and NaOH treatment, shown as the quotient between the initial amount and all extracted dioxins plus remaining dioxins. A quotient of 1 indicates that no losses or gains of substances were achieved during the experiment.

4.2 Oxidation

Figure 3 shows the water extract before and after 8 hours of photo catalytic treatment. Because of the high particle content in the water samples the measuring was done after it had settled for at least 14 hours. Samples taken in the beginning of the experiment had to settle longer. In Figure **21** there is a noticeable difference in colour in the B1 and I1 sample. The difference is smaller for K20. For the W2 sample the difference in tone cannot be noted as the fluid was clear from the beginning. The COD content of the different samples can be seen in the following table, Table 8. The given values are for the diluted samples used in the photo catalytic experiments. The initial COD content in the original samples is obtained by multiplying by a factor of 5. COD was being used as the indicating figure, since it is a more cost-effective measurement assumed to have a fair correlation to the dioxin concentration of the sample. If COD is affected by the oxidation, so is also the dioxins assumed to have.

Table 8 COD content before and after 8 hours of photo catalytic treatment. The COD content is decided through using potassium dichromate (COD Cr). In the table the reduction of COD per hour is given as well as the time needed to halve the original amount of COD.

Sample	COD (mg/l)			ΔCOD (mg/l,h)	ΔCOD (mg/l,h,W, g_{cat})	$t_{1/2}$ sunlight (h)	$t_{1/2}$ 100 mW/cm^2 (h)*
	T=0 h	*4 h*	*8 h*				
B	112		94	2.25	2.9	24.9	0.7
I	62		55	0.875	1.1	35.4	1.0
W	20		19	0.125	0.3	80	2.2
K20	305	303	298	0.875	1.1	174.3	4.7

*) Extrapolated values

The result shows a large variation in how effective the method is to reduce the COD amount in the different samples. The largest absolute decrease in COD is in the B1 sample. This sample becomes noticeably clearer after photo catalytic purification (Figure **21**). The sample I1 is clear after the treatment but still gives a lower COD reduction. This sample has a higher turbidity than B1 which probably consist of particulate substances containing carbon compounds which would explain the difference to I1. The K20 sample has a much higher initial COD amount and gives the same magnitude of reduction as the other samples. This gives a substantially lower relative reduction than the other samples.

There are three limiting factors for an effective photo catalytic degradation. The first one is the organic component's access to the photocatalytic particles, since the oxidation takes place in the boundary layer between the particles and the surrounding medium. Secondly, the form of the organic material, since particulate organic components in the water therefore takes long time to degrade photocatalytically. Third, particles and SOM spread light and reduce the available light effect in the water. Figure **20** shows the relationship between the reduction speed and the initial concentration. This shows the low reaction velocity of the B1 sample due to the high turbidity. And it shows that these contradicting limiting factors will result in an optimum initial COD concentration somewhere in the range of 100 to 300 mg/l COD.

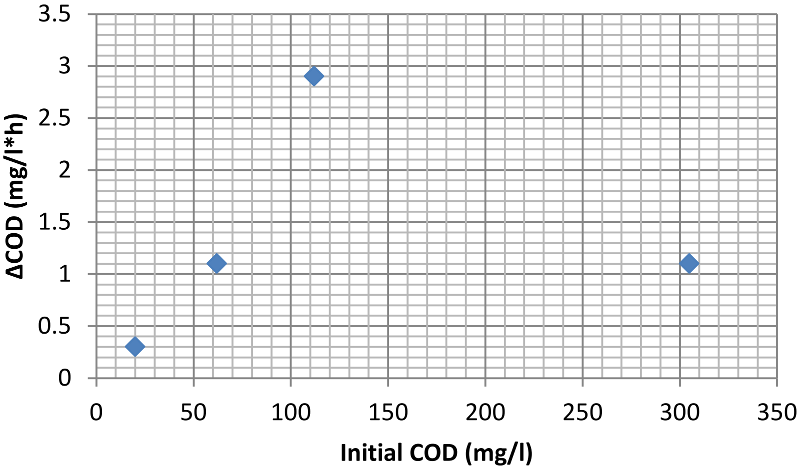

Figure 20 The COD reduction speed of the extract as a function of the initial COD concentration, for the four tested soil extracts.

Thorough sedimentation and eventual mechanic filtering should therefore be considered. Addition of hydrogen peroxide is commonly added to supplement photo catalytic oxidation and should be considered at the high concentrations of organic material in the water samples.

A known fact is that the intensity, I, for the UV lamp, that is the flow of photons in the reactor, scales in a linear to the photocatalytic reaction velocity up to a certain effect limit after which the increase flattens out according to I^x, where $x \approx 0.7$. To increase the light effect within the linear area from 2.7 mW/cm^2 to 100 mW/cm^2 would result in an increase in the turnover 40 times. An adjustment in the efficiency like that would give a half-life time, $t_{1/2}$, of 1 – 5 hours (Table 8). UV lights with higher efficiencies are available in your average store and should be considered in following attempts.

Figure 21 Water extract before (left) and after (right) photo catalytic processing. From left to right in the picture: B1, I1, W2, K20.

5 Conclusions

The effectiveness of the extraction varies significantly between different soil samples, both as a consequence of laboratory handling and sampling but to a greater extent as a result of the soil matrix and its effect on contaminant sorption. In the executed trials, the soil containing organic matter with the highest C:N ratio, indicating young material, was extracted most effective. Dioxins in soils with less or older organic material was not able extract from the soil into solution or showed an increase of dioxins after extraction. Whether this shows that the dioxins are too stable to extract at all is not possible to deem after these trials.

Water at 90°C was used primarily to reduce the amount of chlorophenols, who are more water soluble than dioxins, before NaOH treatment in order to avoid dioxin formation in the aggressive alkaline environment. The water however showed to be rather effective in one of the soils also for dioxin removal. This area should be further developed since it is important both for risk assessments of contaminated sites as well as for treatment.

The oxidation process works as anticipated, although there are areas for improvement when taking the whole process including both extraction and oxidation into account. Now, each step has been optimised separately.

Concluding, the extraction step is the most critical one in this process, which will have to be developed and customised for the specific soil intended to extract. In the cases where the extraction works as anticipated the total process will most likely be cost-effective from both a monetary and an environmental point of view compared to other methods available.

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Alkaline extraction of heavy hydrocarbons from soil

A pilot study

Johan Strandberg
Jan 2009

Table of Contents

1 Introduction

Treatment of dioxin contaminated soils is in great need of cheap and large scale technologies that can handle pollution in a good way. Titanium dioxide is a catalyst that enables degeneration of dioxins in the presence of UV-light. To be able to use this technology the dioxins must be extracted to a liquid phase. Many factors can have an impact on the extraction and should therefore be measured to be able to draw any conclusions from them. Some examples of factors are: clay content, organic content, pollutant type (halogenated and non halogenated carbohydrates) and the C:N quota, which gives the degree of degradation of the organic material. The hypothesis is that the degree of extraction will be dependent on one or many of the mentioned factors and most likely as combinations of each other.

By adding NaOH to the soil the organic material will be hydrolysed and go into suspension. A small part of can leave as carbon dioxide. Mineral particles will also go to suspension, since the cohesive forces between the particles will disappear when the monovalent cations are added. Part of the mineral particles will stay in the supernatant. This part is interesting since it will be of importance to the process.

2 Aim

The aim was to investigate whether dioxins and poly aromatic hydrocarbons (PAH) can be extracted into an alkali water solution.

3 Material and method

Soil samples were dried in 105°C over night. About 25 grams of soil was weighed and added to a glass bottle. Larger stones and gravel were removed. A fractional sample was sent to be analysed in respect to the total content of pollutant, LOI and C:N quota. At IVL the proportion of fine materials was analysed.

A NaOH solution of 45% was added to the bottle with soil so that the liquid/solid ration was 1:20 (L/S 1:20). The bottle was placed in an over end tumbler for shaking for approximately 3 hours. After that the particles were allowed to settle until the mixture had reached steady state. The supernatant was removed from the bottle with a pipette and put in another bottle to be saved. The procedure, from the point where NaOH was added was repeated four times. After the last extraction with NaOH the bottles were filled with deionized water after which the soil/water slurry was filtered with suction filtration on a glass fibre filter with 0.7 µm pore size. This was done to wash the soil and minimize the amount of NaOH that would crystallize during drying.

The remaining soil was weighed. The remaining soil was made up of mineral components and larger organic material. The soil was sent off for analysis with respect to the total concentration of pollutant.

4 Results

In Table 1 the results from the experiments can be found. They show that there are great variations in the extraction between different soils. There are even some cases where the amount of pollutant has increased in the residue that was compared to that blank sample. This is theoretically impossible. The concentration of the pollutant after extraction could increase if there was an extraction of non-contaminated material during the process, but the total amount of pollution in the sample cannot increase. The most probable source of error is that the hydrophobic pollutants are hard to sample for analysis do to their lump formation preference.

Table 1 Information on the soil sample properties before extraction and reduction of material and contaminants after extraction.

	Before					After			
	Loss on ignition	Soil water content	Soil C:N quota	Soil fine mtrl**	Contaminant Conc*(ng/kg TS)	Loss of soil material	Contaminant Conc* (ng/kg TS)	*Contaminant conc. change*	*Contaminant mass change*
W	6%	6%	137	2%	4000	-14%	8400	*110%*	*81%*
B	100%	30%	82.2	-	60100	-28%	11000	*-82%*	*-87%*
I	2%	8%	19.3	6%	1200	-2%	1000	*-17%*	*-18%*
K 06100	36%	11%	31.7	25%	5100	-27%	479	*-91%*	*-93%*
K 0620	95%	25%	38.5	-	1800	-80%	20	*-99%*	*-100%*
V	4%	6%	15.7	7%	2.1	-37%	6.5	*210%*	*96%*

*For V the concentration is given in mg/kg TS of carcinogenic PAH, whilst in the other cases the dioxin is measured in ng/kg TS WHO TEQ.

** Fine material is defined as particles <0.063 mm, which is the finest sifting that can be done with dry material.

The concentration of dioxins in the samples is actually not a concentration. The value used, and that often is used when having to do with dioxins, is something called WHO TEQ. It is a normalized count of the 17 different types of dioxins (congeners) that are analysed. The congeners are normalized with respect to their toxicity which gives a weighted mean for WHO TEQ. I the W case it can be seen that the 2,3,7,8-TCDD has increased with more than 300 % after extraction. 2,3,7,8-TCDD has a large impact on WHO TEQ since it has the highest toxicity out of the congeners. It is the most toxic substance the human has ever made. There are other congeners that have a higher concentration after extraction, but these do not show as much on the WHO TEQ since they have a lower toxicity.

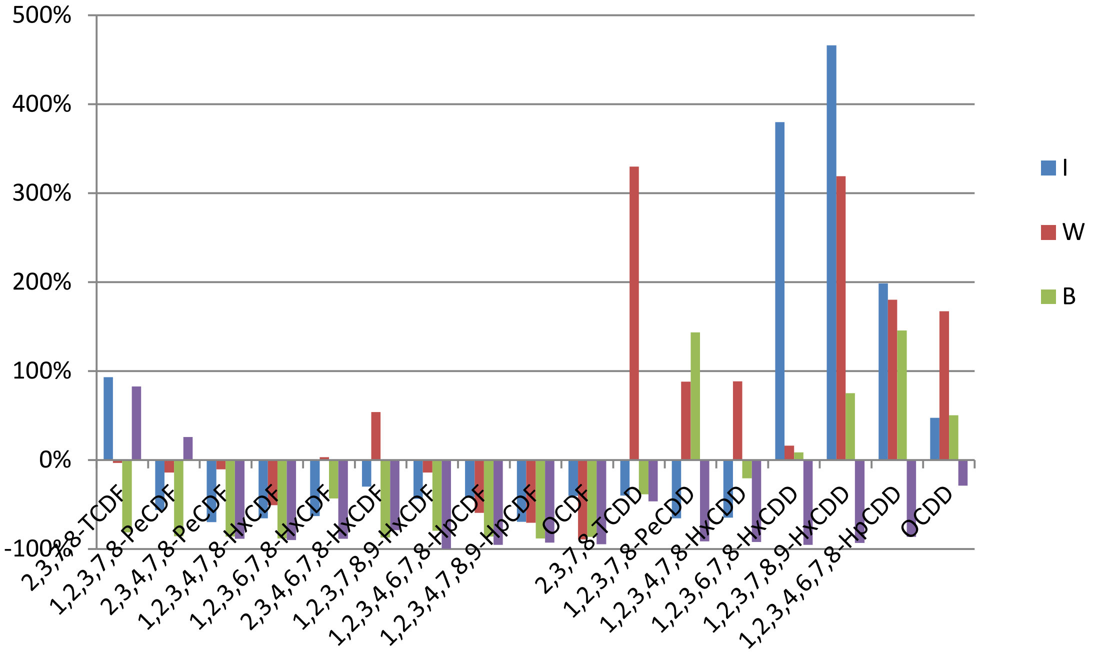

Figure 1 Change, given in percent, in the amount of dioxin congeners after extraction with alkali solution in four different soils. The values given as “less than” have been converted to absolute values, which implies that the extraction was underestimated.

The results from soil sample V are interesting when studying the material reduction that was 37% despite the fact that LOI was a mere 4%. This shows that the fine mineral particles go to suspension through addition of monovalent cat ions, completely in line with the theory. Retrospectively it has been noted that material had settled at the bottom of the bottles, which shows that an increase of gravity through using cyclones or finding ways to get the particles to cluster without addition of unwanted substances in a natural soil or affecting the organic particles / colloids that are to remain in the suspension, are necessary. That the amount of PAH in the sample increased after extraction seems unlikely since the high concentration of NaOH dissolves PAH.

Both B and K basically gives the answer expected. The reduction of dioxin relates fairly well to the LOI. There is little shifting between congeners and the organic carbon goes to suspension and the dioxins follow. Worth noting is that B works well in spite of the high C:N quota that shows that the material has a low degradability. For some congeners an increase can be noted, comparable to the W-material that also had a high C:N quota.

The loss of mass in the I-soil was more than 2% which represents the total organic content. This indicates that the NaOH has caused the organic material to go to suspension which is consistent to the colour loss of this sample throughout the extraction phases. The reduction of WHO TEQ is, even though all the organic material is gone, only 17%. This is mostly due to the decrease of the congener 2,3,7,8-TCDF that is weighted 0.1 in the count. This is interesting because dioxins are assumed to prefer binding to organic material to such a great extent that mineral particles could be ignored if the organic content of the soil is over 2%. Since dioxins still exist in the I-sample though all organic material is extracted this could imply that the assumption is wrong or that the sorption mechanism is different than previously assumed.

5 Discussion and conclusions

The increase in dioxin content could be explained by the presence of chlorophenols in the soil. These can form dioxins when in contact with a base such as NaOH, Figure 2 and Figure 3.

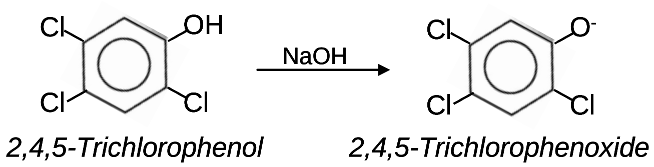

Figure 2 Formation of chlorophenoxide (Conell D. W., 1997)

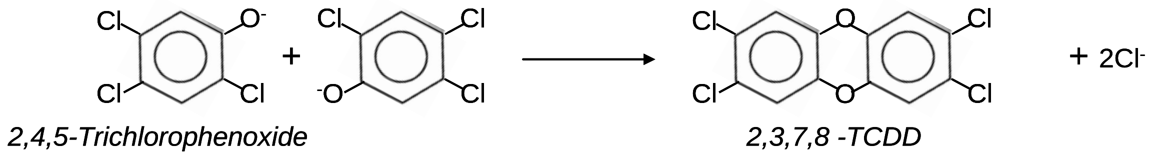

Figure 3 Formation of dioxins from two chlorophenoxides (Conell D. W., 1997)

The most interesting thing about the results is that the extraction of furans (congeners that end with F) is effective in all types of soils, whilst many dioxins (congeners that end with D) occur in larger amounts after extraction.

Four conclusions can be made from the preformed experiments:

1. Extraction of dioxins with NaOH is highly appropriate for soils with a high degree of organic, somewhat humified, material.
2. Extraction of dioxins from soils with a high C:N quota needs improvement, either through heating or possibly electric current, alternatively through simple mechanical separation.
3. Extraction of dioxins from soils with a low degree of organic material needs improvement, either through the methods described above or through addition of a surfactant.
4. The study suffers from uncertainties due to the few number of samples analysed and due to the small amount of soil included in each sample. This makes the interpretation of the results difficult.

6 Further investigations

To be able to further optimize the method the following is proposed.

Oxidation with TiO_2 is tested on the extracts from the K-soils, which contain high concentrations of dioxins and has high coloration because of the organic material, which is a hard test for the last treatment step.

Improved extraction with heat to be tested on the W soil since the heat is expected to have an impact on wood residues.

Improved extraction with electric current could prove to have an effect on the extraction, since it has been observed for PAH's.

Method securigy and mass balances should be carried out with higher certainty. Specially for the mineral soils which proved to be more complex than expected. This could be done through constructing twin samples in higher volumes which would enable analyzes on the remainder (LOI, C:N-quota), and analysis of the supernatants.

The importance of the soil matrix seems to be large for the extraction why more sample should be carried out in the same way to see if it is consistent with the already investigated soils.

7 References

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Optimization of organic matter extraction from soil into inorganic solution

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January 2010

Table of Contents

1 Introduction

As hydrophobic organic contaminants (HOC), as dioxins, are believed to sorb onto organic matter and organic matter has the ability to form colloids, the HOC can move in soil and threat the environment. Due to the toxicity of dioxins it is relevant to find an environmentally correct and cost effective method to remediate contaminated soils. This is the aim of the overall project of which this method development is a part of. The overall project is composed of two principal steps, the first is the organic matter extraction into inorganic solution, described here, and the second is the oxidation of the contaminants. Thus, if the project succeeds, the resulting method has the potential to be relatively cheap and to improve the environmental performance considerably.

Regarding the extraction process, if the organic matter containing sorbed contaminants can form colloidal particles, contaminants can be separated from the soil and thereafter mineralized. Thus, if the extraction of organic matter is optimized, the first step of the whole project can be performed faster and cheaper, improving the method in total.

This research aims to optimize the organic matter extraction from soil into an inorganic solution through analyzing of the colloid formation. In order to do that, the influence of four parameters, temperature, time, solution concentration and soil type were studied, being the process performed in a single extraction step. The intention is to use other tools to optimize the organic matter extraction excluding the necessity for more than one step.

2 Aim

This research aims to optimize the organic matter extraction from soil into an inorganic solution through analyzing of the colloid formation. In order to do that the influence of four parameters are to be investigated. The parameters are:

Temperature

Time

Solution concentration

Soil type

3 Material and method

For the purpose of optimizing the organic matter extraction process from the soil, the experiments described below were performed.

3.1 Experimental Design

Two different soils were used in order to analyze the influence of these parameters on soils with different characteristics; a sandy artificial soil (30% sand-poor, granulated clay; 40% peat moss; 30%

sand) and an organic material (bark, approximately 100% organic matter). The variables are summarized below.

Temperature: 50ºC, 80ºC, 100ºC;

Time: 1.5 hours, 3.0 hours;

Solution concentration: 5M, 16,7M;

Soil: sandy artificial soil and organic material.

The solution of use was sodium hydroxide in accordance with previous experiments within this project.

3.2 Experimental procedure

The experiment was performed in five main steps, all performed in the same way for all samples:

Heating soil and extract;

Washing remaining soil;

Sedimentation of supernatant;

Measurement of turbidity in extract;

Measurement of loss on ignition (LOI) on remaining soil.

The first step, the heating process, started with the addition of the sodium hydroxide solution to the selected soil. 25g of soil were used for 500g of solution, mixed in a heat resistant beaker with a total volume of 1L (Fig. 1). The liquid:solid ratio (L:S ratio) 20 was selected according to previous experiments within the project. The beaker containing the solution and the soil was placed on a heating plate at the chosen temperature (at 50°C, at 80°C or at 100°C) which was constant during 1.5 hours or 3.0 hours. The fourth temperature, 20°C, was the ambient temperature. The use of a magnetic stirrer was not possible, consequently, during the heating process, the samples were mixed every 15 minutes using a glass rod.

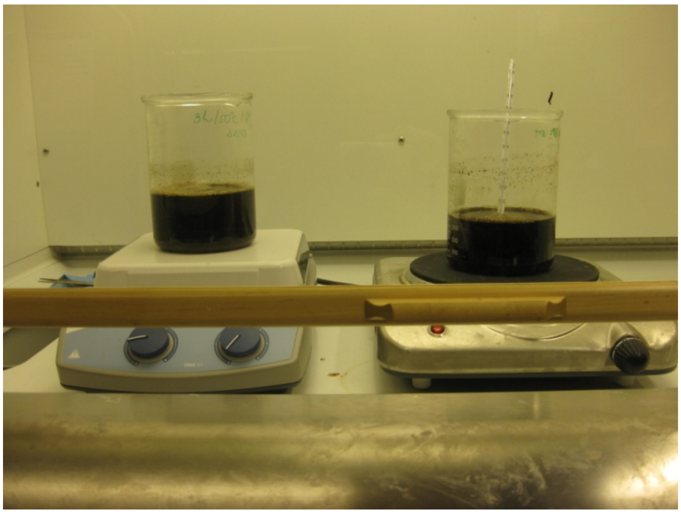

Figure 1 First step, heating soil and extract.

After 1.5 hour or 3.0 hours, depending on the time selected, the heating process was stopped and the samples were put aside for approximately 20 min with the objective of achieving the ambient temperature. Then, the supernatant was removed by suction device, placed in plastic bottles and saved. Glass bottles were not used due to the corrosive property of the sodium hydroxide.

After removal of supernatant, the remaining soil was washed. The washing has the aim of reducing the sodium hydroxide content, which otherwise will crystallize resulting in an erroneous dry weight of the soil. The lower the sodium hydroxide content, the lower the error resulted from the crystallization of it. Practically, washing was performed after the supernatant removal, where 500 mL of demineralised water was added to each sample and mixed with the glass rod. The samples were put aside after that for approximately 20 min. Then, the new supernatant was removed by a suction pipette and discarded. This procedure was repeated three times for each sample.

A complicacy of this process was to remove the supernatant using a suction pipette. The organic soil made the pipette clog frequently due to large particles in suspension. After the third washing, it started the sedimentation process.

Due to the darkness of the first supernatant removed, containing the sodium hydroxide solution after the extraction, it was not feasible to measure the turbidity. Therefore, sedimentation was necessary. The sedimentation was performed just after the washing. 500 ml of demineralised water were added and mixed with the glass rod. Then, the samples were put aside and observed for one week (Fig. 2). After sedimentation, samples were less dark and turbidity could be measured.

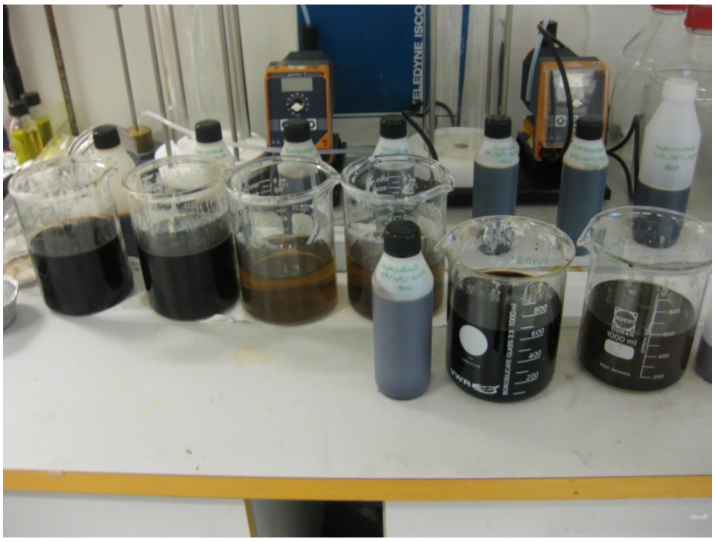

Figure 2: Third step, sedimentation, and plastic bottles containing the first supernatant removed.

3.3 Analysis

The turbidity measurement was performed by sampling a small portion of each sample from the beaker with the suction pipette to the turbidimeter (Laboratory Turbidimeter Model 2100AN IS/ISO Method 7027). Then, the small portion was poured carefully back to the same beaker from where it was sampled. After approximately 20 min, the supernatant was removed again and the loss on ignition process could be executed.

All results were compared to the results of samples extracted at 20ºC, i.e. the negative control (Table 1 and Table 2). They were calculated according to Equation 1 and means that the higher the absolute values of the difference related to the control, the higher the extraction process effect.

Equation 1

$$D = \left(\frac{x_2 - x_1}{x_1} \right) \times 100\%$$

Where:

D is the difference related to the control;

x_1 is the result obtained at 20ºC;

x_2 is the result obtained at the selected temperature.

The loss on ignition analysis has the objective to determine the organic matter content remaining in the soil after extraction. The process was performed according to the standard (prEN

15935:2009:E., 2009). In order to perform the loss on ignition on dried samples, the drying process according to the standard (prEN 15934:2009:E., 2009) was also carried out.

The loss on ignition process starts by the pre-ignition of the crucibles that are going to be used. They were placed in the furnace and heated at 550ºC for 30min. After the pre-ignition they were transferred to a desiccator in order to achieve the ambient temperature and, after that, their weight was measured (m_a). Next step was to transfer the remaining soil, after the last removal of the supernatant, to the pre-ignited crucibles for drying. The crucible containing the soil samples were placed in a drying oven at 105ºC overnight. The importance of washing derives from the corrosive nature of the sodium hydroxide solution that will corrode the sample and the crucibles during drying if this is not made to sufficient extent. After drying, the samples were weighed (m_b) and then, the actual loss on ignition process was performed where samples were placed in the furnace at 550ºC for 2 hours and then transferred to the desiccator in order to achieve the ambient temperature. The samples were weighed again (m_c) and the loss on ignition could be calculated according to Equation 2.

Equation 2

$$W_{LOI} = \left(\frac{m_b - m_c}{m_b - m_a} \right) \times 100\%$$

Where:

W_{LOI} is the loss on ignition of the dry mass of a solid sample, in percentages;

m_a is the mass of the empty crucible in grams;

m_b is the mass of the crucible containing the dry matter in grams;

m_c is the mass of the crucible containing the ignited sample in grams.

4 Results

The results of LOI after the extraction process were compared both to the LOI for the same soil without any treatment (the negative control) and with the samples extracted at 20ºC (Table 1 and table 2). The difference was calculated according to the equation 1 and describes that the higher the absolute values of LOI difference, the higher the extraction process effect.

The effect of the three parameters, temperature, time and solution concentration, were analyzed by the turbidity and loss on ignition indicators. The first observation was regarding the sedimentation process. After the third washing, when the samples were allowed to sediment, it could be seen that the sandy samples extracted with sodium hydroxide solution 16.7 M resulted in a sample solution that was very dark in the day of extraction, turning to varying shades of brown solutions after one week. Except for the samples using 5 M solution, it was consequently seen that longer extraction time and higher temperature resulted in greater difference after sedimentation. In the 5 M samples the difference between various temperatures and extraction times were obvious even before sedimentation. There was no obvious difference over time with respect to colour in the first supernatant containing sodium hydroxide.

The sedimentation process did not have any notable results for the organic soil. Even though the samples still being very dark after one week of sedimentation it was possible to measure the turbidity, which was not the case before the washing.

For a clear understanding of the results described, it is important to note the difference between the description of results obtained directly from the turbidity and LOI analysis, and the results obtained from the comparison of these with the negative control.

Table 9 Turbidity and LOI results compared to the negative control for the sandy soil.

	Sandy Soil								
	Turbidity compared to the negative control (%)			LOI compared to the negative control (%)			LOI compared to 20°C (%)		
Time (h), [NaOH] / Temperature (°C)	50	80	100	50	80	100	50	80	100
1.5h/5M	-44	-84	-92	-50	-71	-75	-11	-48	-55
3.0h/5M	-80	-96	-98	-59	-73	-76	-31	-54	-59
1.5h/16.7M	-74	-76	-84	-57	-69	-77	-3	-30	-48
3.0h/16.7M	-54	-81	-80	-63	-71	-77	-29	-43	-55

Table 10 Turbidity and LOI results compared to the negative control for the organic soil.

	Turbidity compared to the negative control (%)			LOI compared to the negative control (%)			LOI compared to 20°C (%)		
Time (h), [NaOH] / Temperature (oC)	50	80	100	50	80	100	50	80	100
1.5h/5M	-5		-26	-23		-12	-1		13
1.5h/16.7M	43	126	47	-22	-16	-27	3	12	-3

4.1 Temperature

The temperature effect for different times and concentrations is described and it is showed that all sandy samples show less turbidity than the negative control and that higher temperature leads to a greater difference in comparison to the negative control (Fig. 3). For samples extracted for 1.5 hours using a solution of sodium hydroxide 5M, the turbidity decreased 44% when treated at 50ºC, 84% when treated at 80ºC and 92% when treated at 100ºC (Table 1). In the samples extracted using the same sodium hydroxide concentration, but for 3.0 hours, the turbidity decreased up to 98% when treated at 100ºC. So, for the sandy soil, samples extracted at lower temperatures, during the same time using the same sodium hydroxide concentration, resulted in a higher turbidity reading than those extracted at higher temperature. Comparing the results in general, it was also observed that shorter time of extraction and lower sodium hydroxide concentration meant a bigger relative contribution from temperature.

Regarding the loss on ignition (LOI) analysis for the sandy samples, all samples showed an expressive decrease in the LOI demonstrating a noteworthy extraction of the organic matter (Fig. 4). It can be seen that samples extracted at lower temperatures, during the same time, using the same sodium hydroxide concentration, had a higher LOI than those extracted at higher temperature, i.e. organic material were more effectively removed from the soil at higher temperatures. The comparison to the negative control shows this effect in Figure 5. Samples extracted for one and a half hours using a sodium hydroxide solution of 5M had a decrease in the LOI of 50% for the sample extracted at 50ºC relative to the control, 71% for the samples extracted at 80ºC and 75% for the sample extracted at 100ºC (Table 1).

The same effect was seen for samples extracted for one and a half hours but using a solution of 16.7M, where the decrease of the LOI were 57% when extracted at 50ºC, 69% when extracted at 80ºC and 77% at 100ºC.

For all samples analyzed with respect to the three parameters the best reduction of LOI, i.e. organic matter, was 77% at 100^{o}C. However, at this temperature all the samples showed similar LOI reduction compared to the negative control, around 75% (Table 1), meaning that at such high temperature, time of extraction and the solution concentration did not have a considerable effect. Thus, the same general observation as for the turbidity analysis is applicable on the loss on ignition, i.e. shorter time of extraction and lower concentration of the sodium hydroxide increased the importance of the temperature.

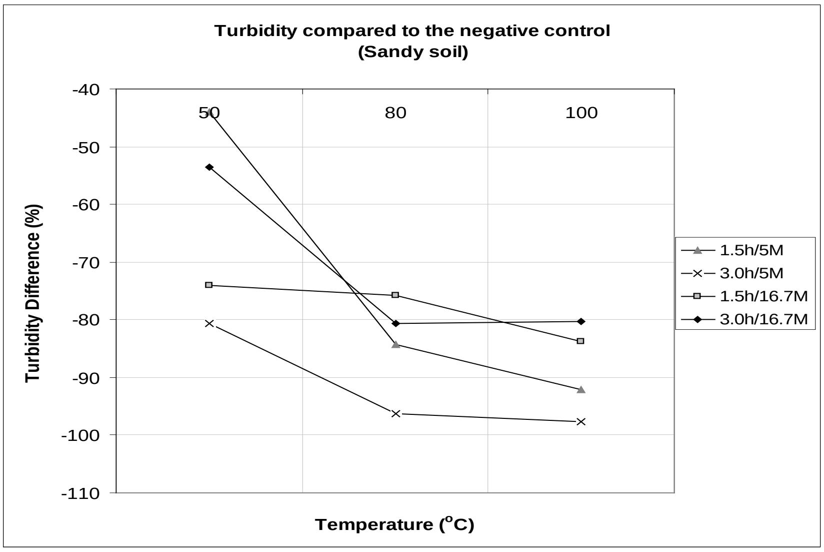

Figure 3 - Turbidity compared to the negative control for the sandy soil.

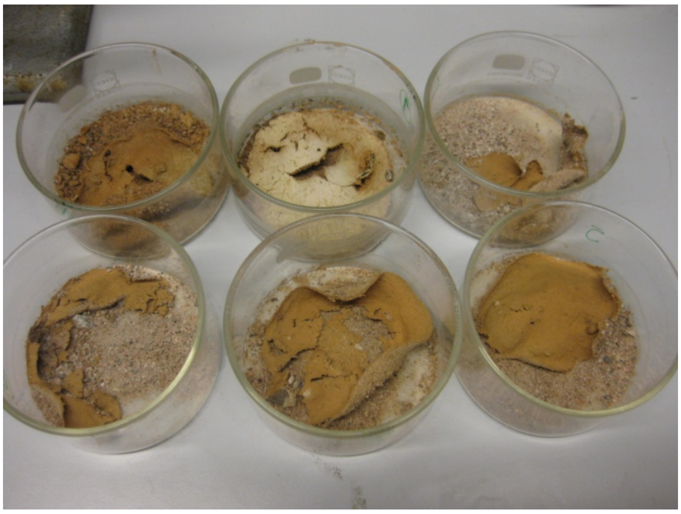

Figure 22 - Sandy samples after loss on ignition analysis.

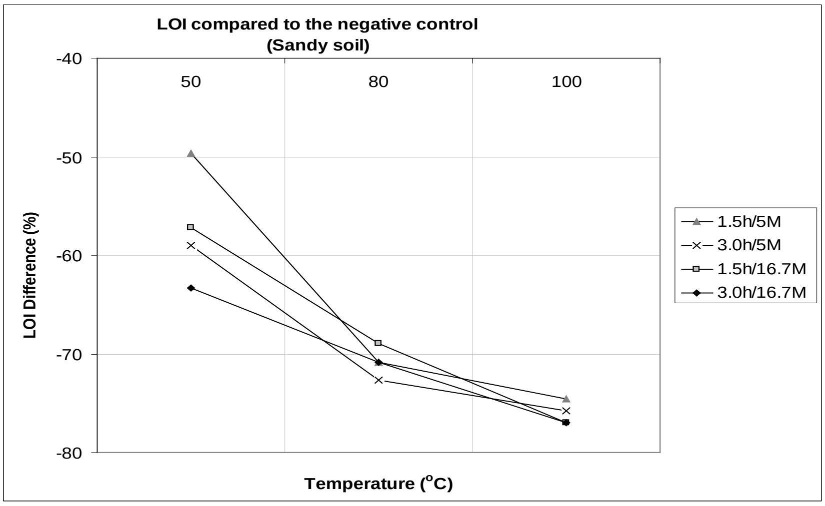

Figure 5 - LOI compared to the negative control for the sandy soil.

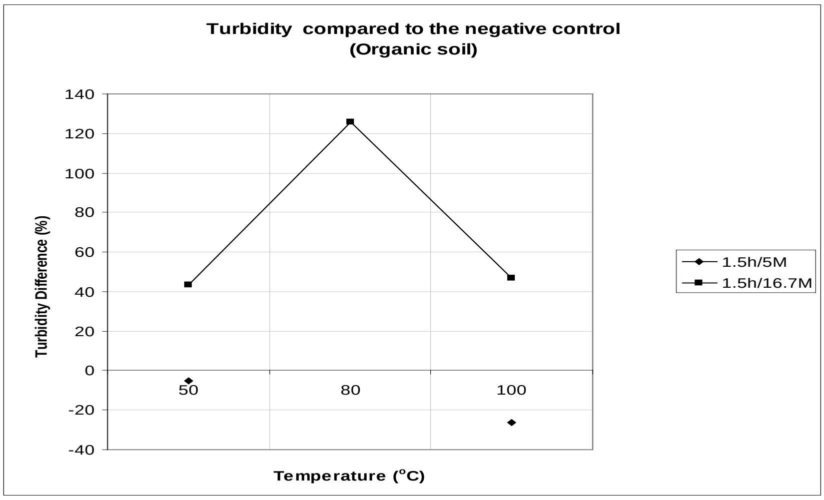

Figure 6 - Turbidity compared to the negative control for the organic soil.

For the soil samples with a high organic matter content which were extracted using sodium hydroxide 16.7 M, turbidity showed a positive correlation to temperature. However, for samples extracted using a 5 M solution, turbidity showed a slight decrease with increased temperature. The difference in turbidity relative to the negative control for the organic soil was also analyzed (Fig. 6). It shows higher differences at higher temperatures for all samples, although it does not follow a linear trend such as the sandy soil. For instance, in the samples extracted for 1.5 hours using a 16.7M solution, the increase of turbidity was 43% at 50ºC and 126% at 80ºC, but 47% at 100ºC (Table 2). For the samples extracted with the solution of 5 M the turbidity decreased 5% at 50ºC and 26% at 100ºC.

The loss on ignition for the organic soil samples did not follow the same trend as the turbidity. Comparing the LOI for the samples after extraction with the negative control indicates the efficiency of the studied parameter which in this case is temperature (Fig. 7). The sample that was extracted using the 5 M solution at 50ºC had a decrease of LOI relative to the control of 23% and the sample extracted at 100ºC had a decrease of 12% (Table 2). For samples extracted using 16.7 M solution, the relative difference compared to the negative control for the sample extracted at 50ºC was 22%, the one extracted at 80ºC left 16% less in the sample to be ignited and the last one extracted at 100ºC reduced it by 27%. Thus, there was no consistent behavior with respect to the temperature neither for turbidity nor for the loss on ignition analysis on the organic rich soil.

The sandy soil and the organic soil showed similar behavior when considering temperature and turbidity relative to the control. Both soils showed a positive correlation between temperature and turbidity, in all samples (Fig. 8). The main difference was to which extent temperature influenced each sample. For both soils it is clear that a lower sodium hydroxide concentration means a higher influence from the temperature.

However, with respect to the comparison with the negative control, the sandy samples were more affected than the organic samples. Moreover, the sandy soil showed greater difference between samples and control, which means that they were more affected by the temperature than the organic soil. Thus, according to the turbidity results, the temperature affected more the sandy samples than the organic samples.

Concerning the effect of temperature, the sandy and the organic soil did not show similar behaviour regarding the LOI. The sandy soil presented a clear positive correlation with the temperature while the organic soil presented a slightly positive correlation for the samples extracted with solution of 16.7 M and a negative correlation for the samples extracted with solution of 5 M. However, it is still possible to observe that the lower the sodium hydroxide concentration, the higher the influence of the temperature (Fig. 9). Moreover, the sandy soil showed larger deviance from the negative control with respect to LOI. Thus, according to both the LOI and turbidity, the temperature affected the sandy samples more than the organic samples.

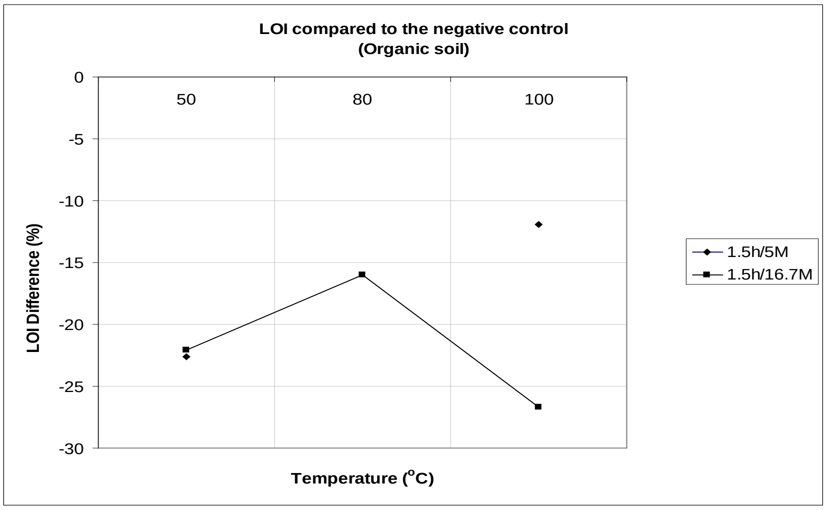

Figure 7 - LOI compared to the negative control for the organic soil.

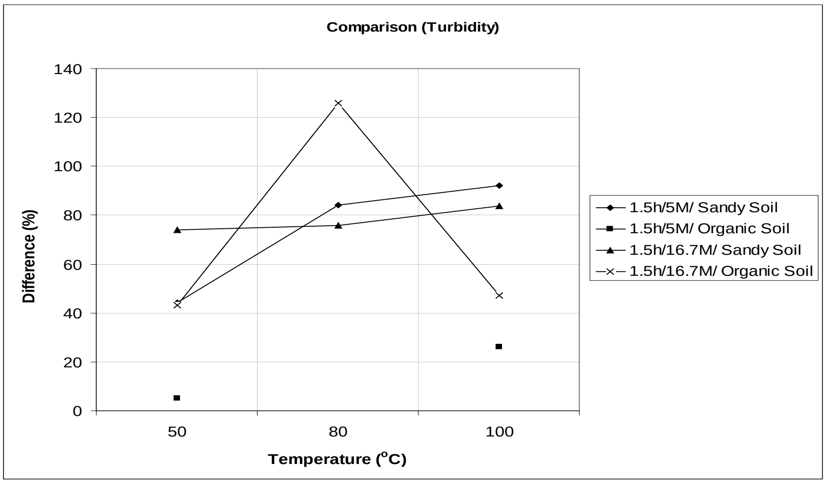

Figure 8 - Comparison between sandy and organic soil regarding temperature and turbidity relative to control.

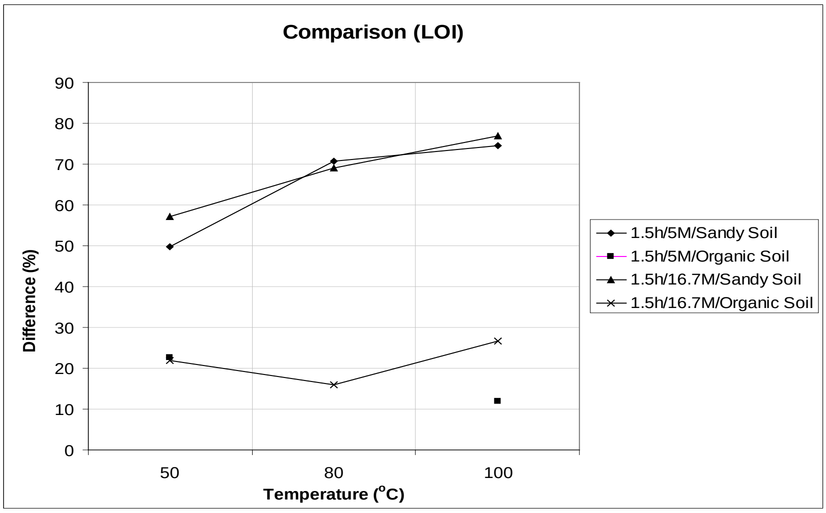

Figure 9 - Comparison between sandy and organic soil regarding the temperature and LOI relative to *control.*

4.2 Time

The duration of extraction showed a similar trend as the temperature for the sandy soil samples with respect to the turbidity. The samples extracted for one and a half hours showed higher turbidity than those extracted for three hours, using the same temperature and concentration. Comparison with the negative control indicates that samples extracted using two different concentrations showed diverse trends over time (Fig. 3).For the samples extracted using the 5 M solution, longer duration of extraction resulted in a greater difference in comparison to the control for the turbidity. For example the samples extracted at 100ºC using a sodium hydroxide solution of 5 M, turbidity was 92% less than the negative control when extracted for one and a half hours and 98% when extracted for three hours. But, samples extracted using the solution of 16.7 M behaved in an opposite way; longer time of extraction resulted in a smaller difference between samples. For example, the samples extracted at 100ºC using a sodium hydroxide solution 16.7 M, the turbidity decreased 84% when extracted for one and a half hours and 80% when extracted for three hours (Table 1). Thus, the difference with respect to turbidity did not have a consistent behavior.

The loss on ignition results for the sandy samples showed similar behavior like the turbidity; samples extracted during shorter time showed higher loss on ignition and less difference in comparison to negative control. For example, in comparison to the control, samples extracted at 50ºC using solution concentration of 5M had a LOI decrease of 50% when extracted for one and a half hours and 59% for three hours (Table 1). According to the results for the samples extracted at 100ºC, it is possible to notice less influence of the time effect. For the samples extracted with solution of 5 M at 100ºC, the difference between the results of the samples extracted for different times was only 1%. For those extracted with 16.7M solution at 100ºC during the two different times there was no difference (Table 1). Thus, the time of extraction showed more effect in samples extracted at lower temperatures and solution concentration.

4.3 Solution concentration

Sandy samples extracted with a less concentrated solution, at the same temperature during the same time, displayed higher turbidity than those extracted with a more concentrated solution. The turbidity difference compared to the negative control for the sandy soil was analyzed (Fig. 3). The difference decreased when the concentration of the solution increased. It can be seen that samples extracted for 1 and a half hours at 80ºC, turbidity decreased 84% in comparison to the control when extracted with a sodium hydroxide solution of 5 M and 76% when the concentration was 16.7 M (Table 1). In the samples extracted for three hours the results were similar. Therefore, as for the others variables, the turbidity was lower at higher concentrations. However, in contrast to the other parameters, the relative differences to the control were smaller at higher concentrations of the solution. A general observation from the data is that the effect of the concentration becomes more important at low temperatures and short extractions.

The loss on ignition analysis for the sandy samples showed that higher concentrations, lead to lower LOI in the soil residues, but also a larger difference compared with the control, proving the efficiency of the NaOH. Samples extracted at 50ºC for one and a half hours demonstrate a decrease in the relative difference to the control of 50% when using a solution of 5 M and 57% when using a solution of 16.7 M (Table 1). A general observation is therefore that the concentration of the solution had a more substantial effect in samples extracted for shorter time and at lower temperatures.

In the case of the organic soil with respect to the turbidity analysis, the behaviour was the opposite of the sandy samples; the samples extracted with a less concentrated solution indicated lower turbidity than those extracted with a more concentrated solution, during same time and same temperature. The difference relative to the negative control followed the same trend; higher solution concentrations meant the greater difference (Fig. 6). It was, however, observed that when lower solution concentrations were used, there was a decrease relative to the negative control, and when higher solution concentrations were used, there was an increase relative to the negative control. As an example, the samples extracted at 100ºC the turbidity decreased 26% when extracted with sodium hydroxide solution 5 M and increased 47% when it was 16.7 M (Table 2). Thus, the turbidity values were higher at higher concentrations of the solution and in the same way the difference relative to the negative control were also higher at higher solution concentrations but with a unique behavior.

The LOI results also showed a unique behaviour for samples extracted at 50ºC. Samples extracted at 50ºC had a decrease relative to the control of approximately the same, around 22% for both concentrations of extraction, 5 M and 16.7 M but it was expected to have higher difference for the samples extracted at 16.7 M concentration (Table 2). At 100ºC the decrease was of approximately 12% when extracted using the solution of 5M and 27% when it was 16.7 M, showing a higher difference related to the negative control at higher concentrations. Thus, as only samples at one temperature presented useful results, no significant trend could be seen with respect to the LOI for the analyzed samples.

To conclude it, the sandy and the organic soil revealed opposite trends regarding the turbidity results and concentration. The turbidity for the organic soil indicated a positive correlation with the sodium hydroxide concentration while the sandy soil generally presented a negative correlation, with an exception for the sandy sample extracted at 50ºC (Fig. 10).

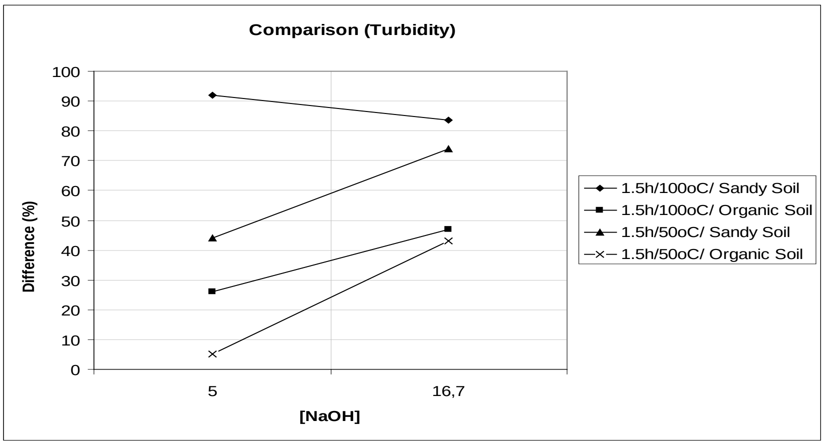

Figure 10 - Comparison between sandy an organic soil regarding the solution concentration and turbidity relative to control.

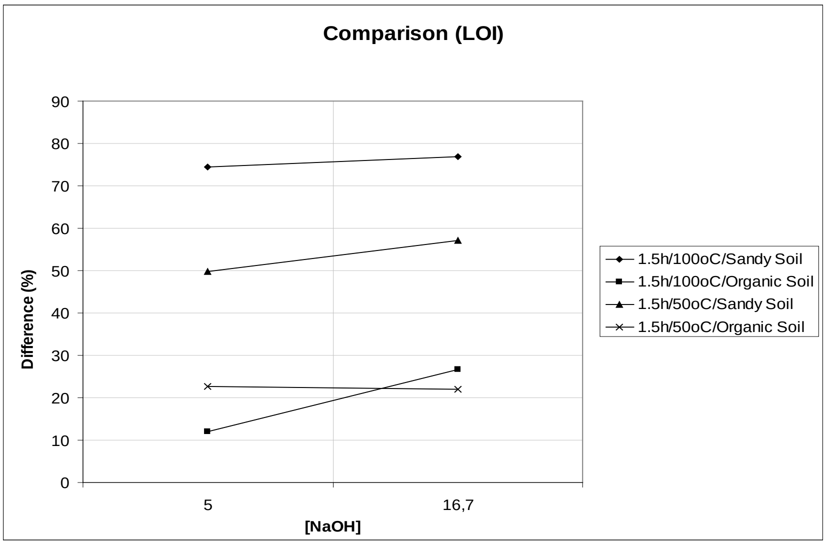

Figure 11 Comparison between sandy an organic soil regarding the solution concentration and LOI relative to control.

Similarly to the temperature analysis, it is clear that the turbidity point out that the extraction process affected the sandy samples more than the organic soil, since the difference related to the negative control was higher.

It is notable that almost all samples had a positive correlation between LOI and concentration. The exception was the organic soil extracted at 50ºC where concentration did not seem to have an effect (Fig. 11). In addition, the high results for the sandy soil described the higher effect of the extraction for these samples than for the organic samples. Thus, according to the loss on ignition analyses, the sodium hydroxide concentrations influence more the sandy than the organic soil.

4.4 Relative importance of variables

In order to better analyze the effect of the temperature, time and solution concentration in the extraction process, a comparison among these different parameters was carried out. The first observation is the different behavior of the two soils used when analyzing the parameters, being the sandy soil more affected. However, generally, the temperature and solution concentration are the parameters which affects in higher levels the extraction process.

For all parameters a general behavior was observed, the one being analyzed showed more effect in the extraction under lower conditions of the others. At extreme conditions of all parameters, each influence is lower.

Comparing the turbidity and the LOI results, the higher the turbidity results, the higher the LOI results, what means the higher the turbidity, the lower the organic matter extracted, showing an opposite behaviour to that expected.

5 Discussion and conclusions

The parameters, temperature, time and solution concentration showed noticeable effects in extraction of organic matter.

Temperature was a parameter which presented a great effect. This effect can be explained by the DLVO theory, which describes the presence of an energy barrier for the detachment step of colloids. As more energy available in the process easier is the detachment step. Consequently, under higher temperatures, more particles, both bigger like mineral particles and smaller like organic matter, could be extracted. The smaller particles extracted were removed in the washing but probably not the bigger ones, because of the suction device. This fact reflects in the results for the sedimentation, turbidity and LOI. As higher particles were also extracted at higher temperatures, the sedimentation was easier and faster for these samples, showing greater difference. Then, turbidity showed lower results at higher temperatures as less particles, organic matter and mineral particles, were in suspension. Due to the great extraction of organic matter from soil and its removal at higher temperatures, the LOI showed lower organic matter remaining in soil. The three analyses confirm the great extraction of particles at higher temperatures.

The second parameter cited, time of extraction, did not showed an impressive effect. Among the three parameters, the time was the one which contributed less for extraction. However, even though the time influence was not great, its low influence is possibly due to the energy barrier existent for the colloid detachment. As described in the DLVO theory, the colloid detachment can be extremely slow under chemical perturbations. Consequently, the time chosen to run the experiment was not enough to show a significant influence in the sedimentation, turbidity and LOI analysis.

As the temperature, the solution concentration also showed a great effect in extraction. According to Ryan J.N. and Elimelech M. (1996), the high pH produced by addition of sodium hydroxide and the high content of sodium ions are responsible for colloids generation and dispersibility. In the sedimentation analysis, even if more particles were extracted, the behavior was not the same as temperature owing to the high colloid dispersibility in solution. At lower concentrations, the difference between various temperatures and extraction times were obvious even before sedimentation. The fact is that at higher concentrations the colloid dispersibility was higher even after washing and difference between the solutions was greater after sedimentation.

Regarding concentration and turbidity, its behavior after sedimentation was similar as for the temperature. The turbidity showed lower results at higher concentrations. More particles were extracted from soil, they were removed and fewer particles remained in suspension. The LOI was also lower at higher concentrations, showing that higher solution concentrations of sodium hydroxide can extract more organic matter, as explained by Ryan J.N. and Elimelech M. (1996).

The soil characteristics were also a substantial parameter to be considered in the extraction of organic matter. The sandy soil showed to be more affected by the parameters than the organic soil, being more difficult to extract the organic matter from the organic soil. This behavior is because the organic soil has stiff particles, much harder to be affected by the solution, and in the sandy soil the organic matter is more vulnerable.

Therefore, in order to optimize the organic matter extraction, the temperature and solution concentration are the effectives parameters. At higher temperatures and solution concentration greater is the extraction. However, as the efficiency does not have extremely great increase under the highest conditions of both of the parameters, median temperatures and concentrations should be used.

Thus, the optimized extraction could be performed

either at higher temperatures and median concentration

or at median temperatures and higher concentrations.

Modelling of experimental data from "Treatment of dioxin contaminated soils" using experimental design software

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Aug 2011

Table of Contents

1 Introduction

A post analysis was made of the experiments perform in this project.

2 Aim

The aim was two-fold; 1) create a model for predicting the relative LOI and Conductivity and 2) thereby find optimal extraction settings.

3 Material and method

The experimental plan was as follows:

Part

1. For two soils A and B concentration of NaOH was varied in two levels 5M and 16.7M at the same treatment-time 1.5h.
2. Additionally trials with soil A was performed long treatment-time 3h while varying concentration at two levels 5M and 16,7M.

The parts 1 and 2 were performed at the temperatures 20, 50, 80 and 100C. The experimental plan can be seen as a temperature-layer design in one continuous variable (concentration) and one categorical variable the soil-type. Due not performing trials on soil B in part 2 we have a slightly unbalanced trial plan. However, based on soil expertise an assumption was made that further treatment time could be regarded as an additive factor, not dependent on the soil type.

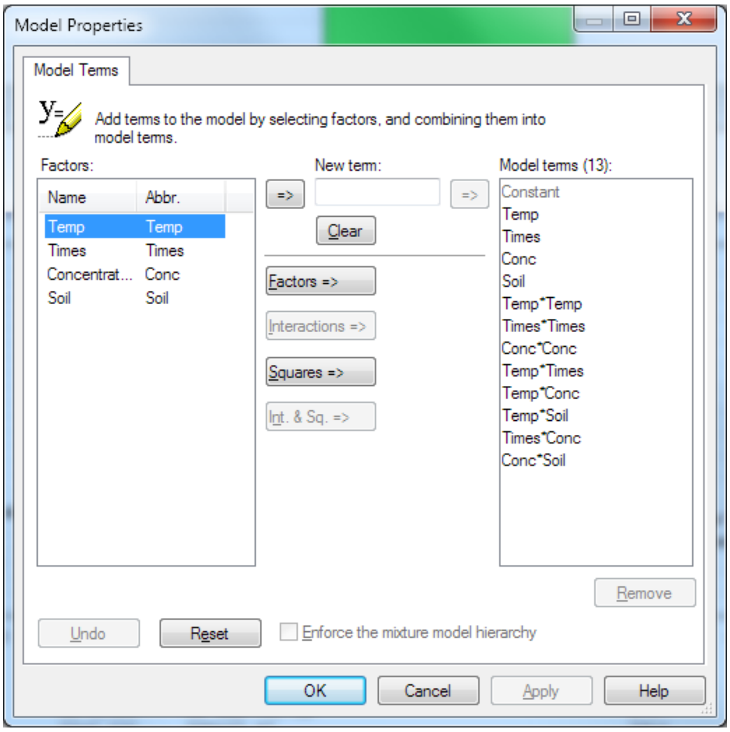
Two responses were measured LOI and Conductivity after performed experiments. Both a visual inspection and simple linear regression was applied as data analysis (see Appendix II). In addition to that a multi linear regression type of modell was used, this model was estimated using Parial least square (PLS) in the software MODDE8 from Umetrics, Sweden. In both approaches used for data analysis the different soils different starting points was a problem for both LOI and Conductivity. Grouping of results was detected in the predicted versus measure graphs in MODDE8 for instance and the model not so good.

In order to circumvent this problem it was chosen to calculate a relative LOI and Conductivity using the experiments performed at 20C as the basis. After this transformation the model estimated in MODDE8 had sufficient quality.

It is chosen here to present the output of final model and using the model in the built in optimizer that MODDE has. It was decide that target for Relative Turbidity should be -90 (±5) and for Relative LOI -55 (±5). As measure how well the proposed parameter are is indicated by the **Log(D).** A Log(D) less than -1 means that all result should be within specification, Log(D) of -10 mean all response are on target.

4 Results and discussion

The model includes these model terms shown in figure 1 below.



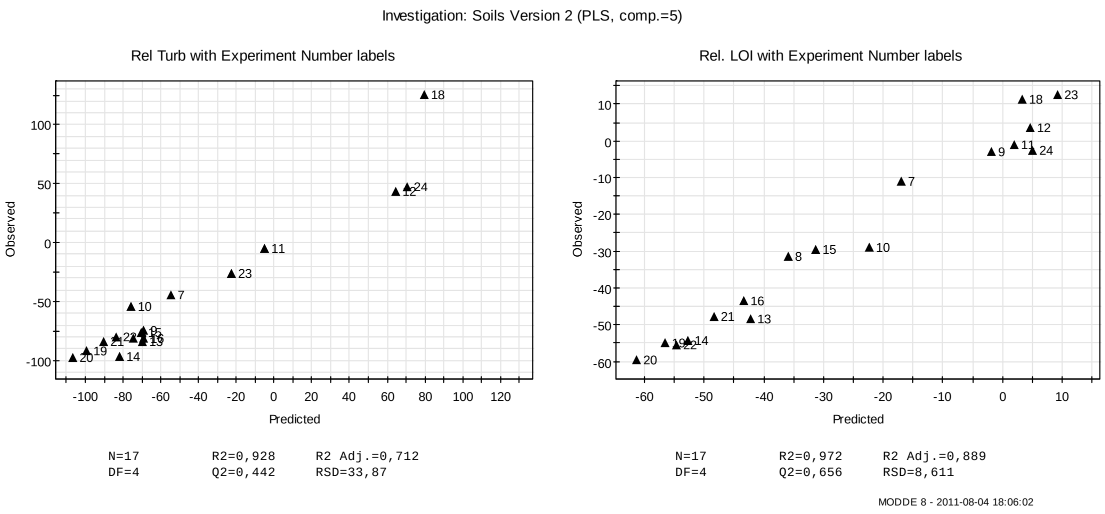
Add terms to the model by selecting factors, and combining them into model terms.

Name	Abbr.
Temp	Temp
Times	Times
Concentrat...	Conc
Soil	Soil

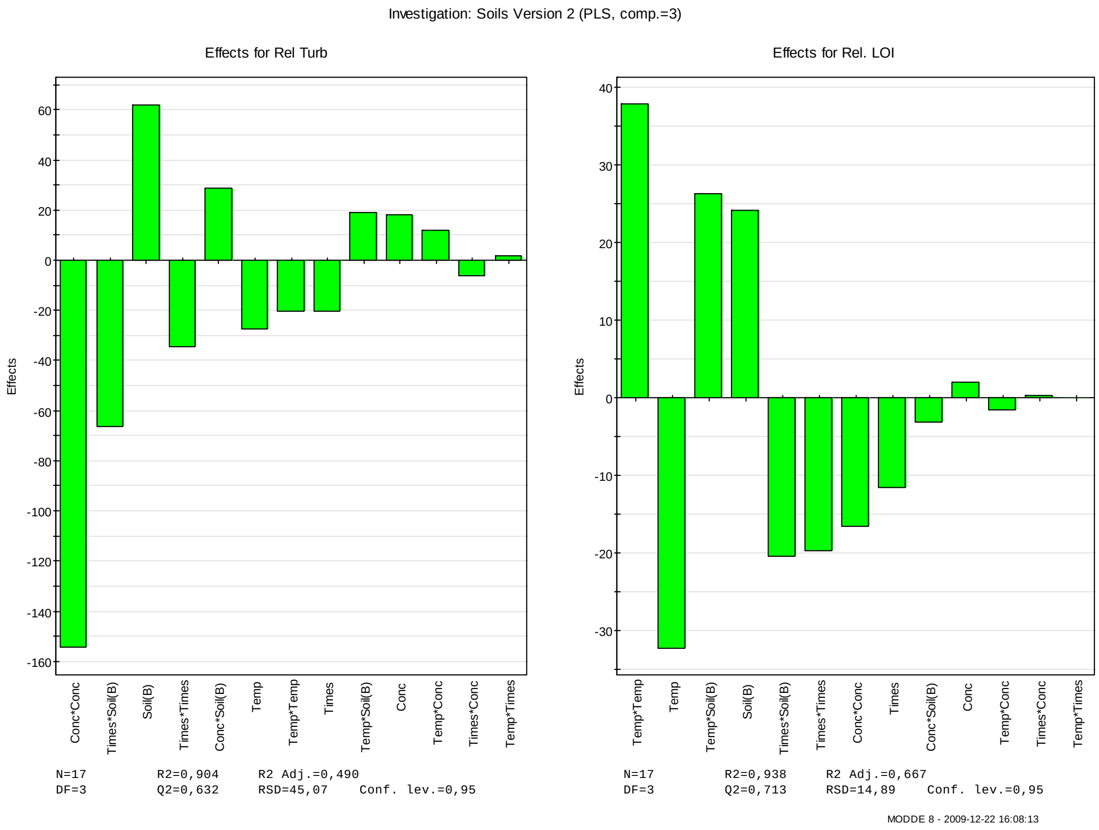
Model terms (13):
Constant
Temp
Times
Conc
Soil
Temp*Temp
Times*Times
Conc*Conc
Temp*Times
Temp*Conc
Temp*Soil
Times*Conc
Conc*Soil

☐ Enforce the mixture model hierarchy

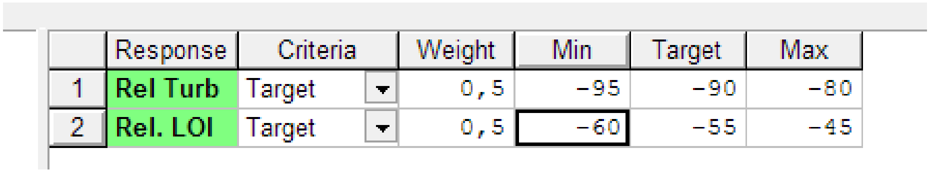
Figur 1 Model terms for the common model for Soil A and B built for Relative Turbity and Relative LOI.



Figur 2 Predicction of Rel Turb and Rel. LOI based on the PLS model built in MODDE.



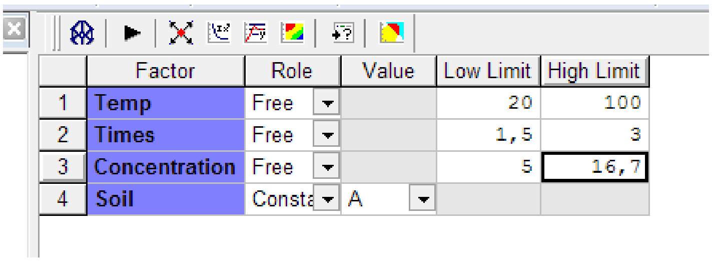
Figur 3 Effect plot obtained for analyis in MODDE for a combined model for Soil A and Soil B.



	Response	Criteria	Weight	Min	Target	Max
1	**Rel Turb**	Target	0,5	-95	-90	-80
2	**Rel. LOI**	Target	0,5	-60	-55	-45

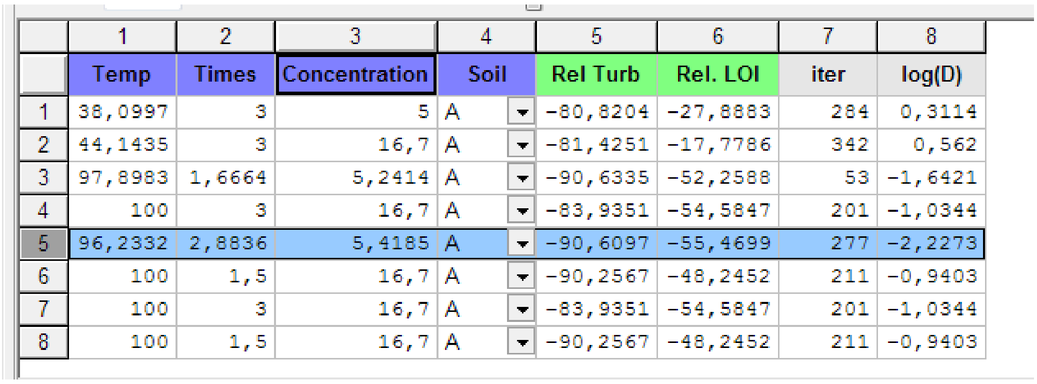
Figur 4 Targets and boundaries for optimization of Rel.. Turb. and Rel.. LOI for both soils A and B.

4.1 Optimization for soil A



	Factor	Role	Value	Low Limit	High Limit
1	Temp	Free		20	100
2	Times	Free		1,5	3
3	Concentration	Free		5	16,7
4	Soil	Consta	A		

Figur 5 Constraints for optimization Rel. Turb andRel. LOI for Soil A.

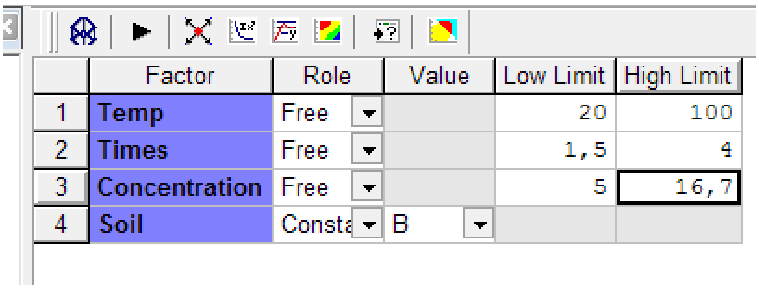


	1	2	3	4	5	6	7	8
	Temp	Times	Concentration	Soil	Rel Turb	Rel. LOI	iter	log(D)
1	38,0997	3	5	A	-80,8204	-27,8883	284	0,3114
2	44,1435	3	16,7	A	-81,4251	-17,7786	342	0,562
3	97,8983	1,6664	5,2414	A	-90,6335	-52,2588	53	-1,6421
4	100	3	16,7	A	-83,9351	-54,5847	201	-1,0344
5	96,2332	2,8836	5,4185	A	-90,6097	-55,4699	277	-2,2273
6	100	1,5	16,7	A	-90,2567	-48,2452	211	-0,9403
7	100	3	16,7	A	-83,9351	-54,5847	201	-1,0344
8	100	1,5	16,7	A	-90,2567	-48,2452	211	-0,9403

Figur 6 Optimizer results for Soil A. The marked row (no 5) is the optimal solution found.

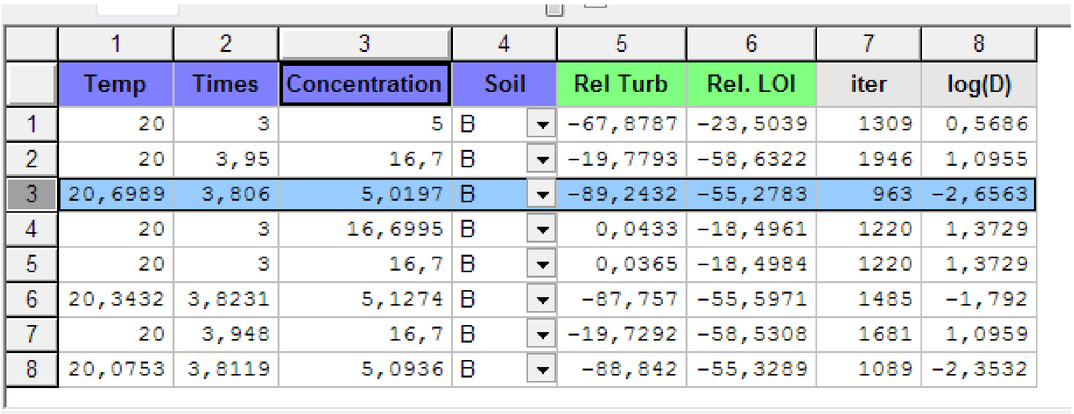
4.2 Optimization for Soil B

For soil B it was impossible to reach the target without extrapolate on the model. These boundaries were used.



	Factor	Role	Value	Low Limit	High Limit
1	Temp	Free		20	100
2	Times	Free		1,5	4
3	Concentration	Free		5	16,7
4	Soil	Consta	B		

Figur 7 Constraints for optimization Rel. Turbity and Rel. LOI for Soil B.



	1	2	3	4	5	6	7	8
	Temp	Times	Concentration	Soil	Rel Turb	Rel. LOI	iter	log(D)
1	20	3	5	B	-67,8787	-23,5039	1309	0,5686
2	20	3,95	16,7	B	-19,7793	-58,6322	1946	1,0955
3	20,6989	3,806	5,0197	B	-89,2432	-55,2783	963	-2,6563
4	20	3	16,6995	B	0,0433	-18,4961	1220	1,3729
5	20	3	16,7	B	0,0365	-18,4984	1220	1,3729
6	20,3432	3,8231	5,1274	B	-87,757	-55,5971	1485	-1,792
7	20	3,948	16,7	B	-19,7292	-58,5308	1681	1,0959
8	20,0753	3,8119	5,0936	B	-88,842	-55,3289	1089	-2,3532

Figur 8 Optimizer results for Soil AB The marked row (no 3) is the optimal solution found.

5 Conclusions

In order to obtain sufficient results for soil A the temperature should be around 96C, the times 2.9 and the concentration 5,4 M.

In order to obtain sufficient results for soil B the temperature should be around 21C, the times 3,8 and the concentration 5 M. Note that there is a minor extrapolation regarding times here (from 3 to 3,8).

6 References

User Guide to MODDE 8, Umetrics AB, Umeå, Sweden