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ABIOTIC TREATMENT OF PCP-CONTAMINATED WATER WITH METALLIC IRON

By

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ABSTRACT

The removal of PCP from aqueous solution in contact with metallic iron was investigated by laboratory batch experiments. The decline in PCP concentration as well as inorganic parameters were monitored over time. Removal of up to 90 % of the initial PCP was observed within 24 hours. The initial geochemical conditions of the PCP solution changed rapidly to basic and reductive conditions when in contact with metallic iron. Organic degradation by-products were not found during the removal of PCP using two distinct analytical procedures. Chloride ions analyzed in the solution after PCP removal were relatively low and showed high variability between experiments. The extraction of iron with solvents showed that a maximum of 37% PCP was sorbed. The effectiveness of iron on PCP removal appeared to be limited by the number of contacts with a fresh PCP solution. The rate constant in PCP removal appeared to be directly proportional to the iron to solution ratio. The PCP removal behaviour fitted well two sorption models (Freunlich, Langmuir). The results indicate that the process involved in the removal of PCP does not seem to be dechlorination because of the lack of by-products and low level in chloride ion, and is not completely sorption because of the lack of reversibility.

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1. INTRODUCTION

Contamination of groundwater has been identified as an important problem in North America since the early 1980's. One major source of contamination is caused by the release of organic compounds such as petroleum hydrocarbons and synthetic chemicals into the environment. Pentachlorophenol (PCP), a chlorinated aromatic organic compound utilized in the wood preservation industry, is a common contaminant in soil and groundwater at numerous sites. Because of its toxicity, PCP has to be removed from soil and groundwater to acceptable concentrations defined by environmental regulations. Typically, the acceptable limits are in the range of 30-60 ppb for drinking water and 0.05-5 ppm for soil (CCME, 1991).

The contamination of soil by PCP is a common problem that can be solved with a limited number of remediation technologies. For example, one recently developed method in laboratory uses Fenton's Reagent (hydrogen peroxide (H_2O_2) combined with a catalyst Fe^{2+}) which, when mixed with contaminated soil produces a strong oxidant, hydroxyl radical ($OH\cdot$) that will oxidize PCP to produce Cl^- and carbon (Tyre et al., 1991; Watts et al, 1990.). This technology obtained very good results in degrading PCP in soil at relatively high concentration (200 mg/kg) in a short period of time (up to 99% in 3 hours). However, this degradation needs to occur at very low pH (pH = 3) and large additions of iron (400 mg/L) and hydrogen peroxide (120,000 mg/L) are needed. The application of this technology to in situ remediation problems would be limited by the very low pH requirements. This would require the use of large volumes of strong acid in aquifer, where soils have large buffering capacity.

The remediation technologies developed to treat contaminated soil with PCP are different than those for groundwater problems. Clean up criteria for soil are usually in the range of ppm while for water, criteria are in the range of ppb. By treating contaminated soil to clean up criteria there is still a potential for contaminating the groundwater by infiltration of rain

water and dissolution of the PCP left in the soil. Hence, by transporting the contaminant in the groundwater flow, drinking water wells located in the vicinity of the site could be impacted. Therefore, treating the contaminated soil does not automatically treat the contaminated groundwater and groundwater remediation technologies need to be more efficient in removing contaminants due to the lower water clean up criteria.

The need to develop groundwater remediation technologies arose concomitant with the discovery of a large number of contaminated sites. Groundwater contaminated with organics is commonly remediated by pumping the water from the aquifer and treating it above ground with various methods. This technology called Pump and Treat is relatively simple, but has had limited success. The major difficulty with Pump and Treat lies in the limited efficiency to pump out the contaminant. Because the majority of organic contaminants have a relatively low solubility and an acceptable water concentration that can be orders of magnitude below the solubility limit, a small amount of pure product can contaminate vast quantities of water. Typically the concentration of organics in the pumped water will be high at the beginning but will decline rapidly and level off with time (Mackay and Cherry, 1989). It was also shown that in some cases the organic contaminant concentrations in the pumped well increased after the Pump and Treat system was turned off. The long time involved in the remediation of groundwater by Pump and Treat is an important factor that can make the clean up criteria difficult to achieve at a reasonable cost.

The contaminated water can be treated at ground surface by one or a combination of three types of methods: physical, chemical or biological.

The most common treatment type is physical treatment involving the flow of contaminated water through activated carbon, where the organic contaminant is adsorbed onto the carbon particles. Because PCP has an affinity to sorb on organic material, good results in removing the PCP are observed. The main disadvantage of carbon adsorption is that the contaminant

is not destroyed, it is simply transferred from the water to the activated carbon. Disposal or regeneration of the carbon will be necessary and often problematic. Another important disadvantage is the high operating costs to replace the activated carbon. These costs increase with the level of contamination (Sullivan and Lenzo, 1989).

The chemical treatment of organic contaminants and PCP in particular can be achieved by oxidation. One of the most recent chemical oxidation technology's consists of mixing contaminated groundwater with hydrogen peroxide and exposing the mixture to UV light. The process involves the direct UV photolysis of the hydrogen peroxide resulting in the production of hydroxyl radicals (OH·). These radicals are strong oxidants that degrade PCP into carbon dioxide, water and in some cases organic acids. In one particular study, where PCP photooxidation was performed in TiO_2 particles suspensions, p-chloranil, tetrachlorohydroquinone, H_2O_2 and o-chloranil were the principal intermediates. The final products were HCO_2^-, $CH_3CO_2^-$, CO_2, H^+ and Cl^- (Mills and Hoffman, 1993). This technology is appealing because relatively high PCP concentrations can be destroyed to very low levels without producing toxic byproducts. However, the costs are relatively high considering the energy consumption, the long duration of the treatment and the pretreatment necessary for each specific site (USEPA, Report: EPA/540/AR-93/501, 1993).

The biological treatment of PCP-contaminated water may be done in anaerobic reactors (fixed film, upflow sludge blanket) or in aerobic reactors (fluidized bed) in which bacteria attached to a fixed film or in the form of a granular sewage sludge are acclimatized to PCP for a few months. The contaminated groundwater is then pumped through the reactors at a rate that will achieve a predefined retention time. The biodegradation pathways in the case of anaerobic treatment follow reductive dechlorination, reviewed by several authors such as Hendriksen and Ahring (1993) and Nicholson et al., (1992). In the case of aerobic treatment, the degradation of PCP is achieved by mineralization and produces carbon dioxide and hypochloric acid (Puhakka and Järvinen, 1992, and Mäkinen et al., 1993). The main

disadvantage is that the treatment efficiency can be extremely variable depending on many factors (temperature, initial PCP concentration, variability of the inlet PCP concentration and the production of inhibitors).

Because of the difficulties and costs of Pump and Treat methods, recent research efforts have focused on in situ methods for treating aquifers contaminated with organic substances. In situ methods preclude the need to pump out the groundwater. The methods that are principally developed are biotic or abiotic treatments that destroy the contaminants. They both involve the addition of nutrients or reactants into the subsurface to enhance the degradation of the organic compounds. These technologies offer great advantages. They eliminate the need to bring the contamination out of the subsurface minimizing the exposure. The cost is reduced because there is no external energy needed, no disposal of the contaminant and the equipment is limited. Only periodic maintenance and monitoring is necessary.

One abiotic in situ technology for halogenated organics has been investigated since 1990 at the Institute for Groundwater Research in Waterloo, Ontario. The method called metal-enhanced abiotic degradation consists of using a permeable wall, made of a mixture of granular metallic iron and sand, installed across the path of the contaminant plume. The plume passively flows through the permeable wall, where the halogenated organic compounds are degraded by abiotic chemical reactions. During field tests, the groundwater coming out of the permeable wall was shown to contain much less halogenated organic compounds, preventing the down gradient migration of the contaminant plume. The details of this method are given in a later section. Some of the advantages of this technology are that the treatment is passive, requiring no external energy supply; the contaminants are degraded, requiring no further treatment and the cost is very competitive with conventional pump and treat methods. The method has been tested for the degradation of a wide selection of chlorinated aliphatic compounds (Gillham and O'Hannesin 1992). The time required for complete degradation depends on the contaminant, the groundwater flow rate and the thickness of the wall.

Metal-enhanced abiotic degradation is therefore extremely promising and offers potential for other halogenated organics such as PCP. PCP is a member of the chlorinated aromatic compounds that are structurally different than chlorinated aliphatics. PCP thus represents a logical contaminant to further test the potential of that method.

The objective of this research is to determine the feasibility of the method for the treatment of PCP. This study focusses on determining if PCP can be degraded from water in contact with iron in controlled laboratory experiments. The specific objectives of the study are:

- to determine the rate and the extent of PCP removal;
- to verify if by-products are produced during removal of PCP;
- to estimate the fraction of PCP removal caused by other surface processes such as sorption;
- to compare the PCP removal behaviour with adsorption isotherms.

2. LITERATURE REVIEW

2.1 Chemical and physical properties of Pentachlorophenol

Pentachlorophenol (PCP) is a polychlorinated aromatic compound (C_6HCl_5O) that as been used as biocide for wood preservation since 1930 (Jackson and Bisson 1990). In 1982, the Canadian production of PCP was 1800 t (CCME, 1993). PCP was usually mixed at a concentration of 5 % volume in different petroleum derived liquids and was sprayed over the wood logs. The industrial production and utilization of PCP has resulted in the contamination of soil and groundwater at several sites in North America. For example, in the Central United States a wood preserving plant used PCP over a 40 year period contaminating a large land surface. Soil and groundwater investigations at the plant showed that soil was contained with up to 1 % PCP and groundwater contained between 13-90 mg/L (Litchfield et al., 1994).

The chemical and physical properties of PCP are presented in Table 1. PCP is a relatively large organic compound (266.34 g/mol) composed of one benzene ring with 5 chloride ions an one hydroxyl group. The solubility in water is relatively low (15mg/L at 25°C and at pH=5,1) and depends upon the temperature and pH. PCP is a weak acid (pKa= 4.74) and therefore partially dissociates in water to form the negatively charged phenolate ion. The degree of dissociation is pH controlled; as pH increases, the degree of dissociation and solubility increases (Schellenberg et al.,1984). The low vapour pressure (1.7×10^{-5} mmHg at 25°C) and Henry's law constant values (2.8×10^{-7} atm·m^3/mol) of PCP indicate that it does not volatilize easily and prefers to stay in the aqueous phase.

The USEPA maximum concentration in drinking water is 200 µg/L (MOE, 1992), while the Canadian Council of Ministers of the Environment drinking water criteria is 60 µg/L (CCME, 1991).

The mobility of PCP in groundwater is readily affected by adsorption onto organic matter in soil according to the log Kow(5.01) (Banerji et al. 1986). From laboratory batch adsorption experiments, the removal of PCP in contact with soil was confirmed to be due to adsorption which fitted a Freundlich isotherm (Parker and Jenkins 1986). PCP adsorbs more readily to organic matter than other chlorinated phenols. However, the degree of adsorption decreases as pH increases.

Biodegradation is also a process participating in PCP removal in natural groundwater under aerobic and anaerobic conditions. In the study of Smith and Novak (1987), PCP at a concentration of 25 mg/L was found to be completely biodegraded after 3 months in contact with soil under aerobic conditions in controlled microcosm experiments. The biodegradation of PCP was slower than phenol and monochlorophenol (2-CP) and followed a first order kinetic reaction. However, it is unclear that the effect of PCP sorption was accounted for during these experiments. Speltel et al. (1989) also concluded that PCP was biodegradable, but its degradation rate was somewhat slower than the rate of other organic compounds such as less chlorinated phenols. A study in which PCP was degraded in aerobic and anaerobic conditions in aquariums containing natural swamp sediment and water showed that PCP was more rapidly degraded under aerobic conditions than under anaerobic conditions (1 day versus 192 days) (Boyle et al., 1980).

2.2 Background on metal-enhanced degradation

2.2.1 History

The use of zero-valence metals for degrading halogenated organic carbon was first reported in 1972 in the U.S. patents literature (Sweeny and Fisher, 1972-73 as reported in Gillham and O'Hannesin, 1994). The method utilized metallic zinc for removing pesticides from aqueous solutions. The study concluded by suggesting that this method could be used in reactor

vessels and that it could be applicable to a wide range of halogenated organic compounds.

In 1988, researchers in Japan working on the degradation of chlorinated aliphatics, such as 1,1,2,2-tetrachloroethane (1,1,2,2-TECA) and trichloroethene (TCE) in aqueous solutions in the presence of iron powder (Senzaki and Kumagai, 1988-89 as reported in Gillham and O'Hannesin 1994) showed that the rate of degradation of 1,1,2,2-TECA increased as the surface area to solution ratio increased. They showed that the reaction rate declined at pH values greater than 8. They also reported the formation of a headspace in the reactive hypovials containing the iron powder and the chlorinated aliphatic compound. The headspace was mainly composed of nitrogen and hydrogen.

2.2.2 Waterloo Research Group Experiments

In a study examining the sorption of organic contaminants on well casing materials, some chlorinated aliphatics, namely tetrachloroethene (PCE) hexachloroethane (HCE) and bromoform (TBM) were found to completely disappear at a relatively high rate from solution in the presence of galvanized metals and aluminium (Reynolds et al., 1990). At that time, the disappearance of the halogenated organic compound was attributed to reductive dehalogenation rather than sorption.

In recent studies (1992) performed by a group of researchers at the Waterloo Centre for Groundwater Research, the zero-valence metallic iron was used to enhance the degradation of selected chlorinated aliphatics (chloromethanes, chloroethanes and chloroethenes) in aqueous solutions (Gillham and O'Hannesin, 1992). Iron was used because of its low cost and the relatively high rates of degradation it produced in preliminary experiments. Three types of experiments were performed to evaluate the effect of iron on the degradation of chlorinated aliphatics: laboratory batch tests; laboratory column tests; in situ permeable wall test.

In the batch tests, fourteen chlorinated aliphatics in solution were put in contact with metallic iron (Gillham and O'Hannesin 1994). All except dichloromethane degraded, with half lives ranging from 0.22 to 432 hours. The degradation process was consistent with a first order degradation model. Rates of degradation were generally higher for the more highly oxidized organic compounds and were generally three to eight orders of magnitude higher than natural abiotic and biotic rates reported in the groundwater literature (Vogel et al., 1987). Degradation products were detected during the experiments including chloroform, methane, ethane and chloride (Cl^-) (O'Hannesin, 1993). The pH increased from neutral to basic conditions while Eh declined from oxidizing to reducing conditions.

In the present study, the use of iron to degrade PCP is expected to produce similar results as reported above. For example, the degradation rate is expected to be rapid, degradation products are expected to be found (less chlorinated phenols, phenol and chloride), and the chemistry conditions are expected to change to basic and reductive conditions.

The column tests were performed to observe the rate of degradation under dynamic flow conditions. In this test, the chlorinated aliphatic solutions flowed through a cylinder (3.8 cm diameter by 50 cm long) containing a mixture of silica sand and metallic iron. Results showed that the chlorinated aliphatic concentrations declined exponentially with distance travelled into the column.

In the in situ permeable wall test, a groundwater contamination plume containing TCE (253 mg/L) and PCE (43 mg/L) was allowed to flow through a vertical permeable wall composed of a mixture of 22% wt. of metallic iron and 78% wt. of concrete sand (O'Hannesin and Gillham 1992). Monitoring of the plume downgradient of the wall showed that the concentrations of TCE and PCE declined by 95% and 91% respectively. Degradation by-products, such as 1,1-DCE, cis-DCE and trans-DCE and Cl^-, were detected downgradient of the wall. These observations were consistent with the laboratory tests. Over the 474 day

study period, no apparent decrease in the performance of the wall was observed.

The Waterloo Research Group concluded that the degradation process was abiotic and electrochemical in nature, involving oxidation of the iron and reductive dechlorination of the halogenated aliphatic compounds (Gillham and O'Hannesin, 1994). The following equations were proposed based on the presence of water, zero-valence iron and a chlorinated organic compound $X\text{-}Cl^-$:

$$2\ Fe^0 \rightarrow 2\ Fe^{2+} + 4e^-$$
$$3\ H_2O \rightarrow 3\ H^+ + 3\ OH^-$$
$$2\ H^+ + 2\ e^- \rightarrow H_2\ (g)$$
$$X\text{-}Cl + H^+ + 2\ e^- \rightarrow X\text{-}H + Cl^-$$

$$2\ Fe^0 + 3\ H_2O + X\text{-}Cl \rightarrow 2\ Fe^{2+} + 3\ OH^- + H_2(g) + X\text{-}H + Cl^- \quad (1)$$

For each mole of Cl^- produced there are 2 moles of Fe^{2+} introduced in solution, when hydrolysis of water is included in the process.

3. MATERIALS AND ANALYTICAL METHODS

3.1 Metallic iron

Laboratory batch tests were conducted using iron filings (Master Builder Blend B, granular iron) obtained from the Waterloo Centre for Groundwater Research. The iron was collected as a waste product from machining and foundry operations, and after processing, was marketed primarily as an additive to improve the wear characteristics of concrete. The fillings were composed of 95% iron (Fe^0) and carbon (C) and 5% impurities (silica, other metals) and consisted of irregularly shaped metallic iron particles with a grain size ranging from 0.57 to 2 mm. The specific surface area was about 1.1 m^2 /g (determined by the BET method (Brunauer, Emmett, Teller)), the particle density was 6.97 g/cm^3, the bulk density was 3.17 g/cm^3, and the porosity was 55% (Gillham and O'Hannesin, 1994).

3.2 Organic compound and solution

The organic compound used in this study, pentachlorophenol (PCP), was Purity Grade (99%) from Sigma Chemical Company. The PCP solids were dissolved in 1 M NaOH and diluted to obtain a target concentration of approximately 25 mg /L with 0.01 M NaOH. The pH of the solution was then adjusted to pH 7.5 with dilute H_2SO_4.

The organic solution was prepared in a 5 L glass bottle with a spigot at the bottom and was placed on a magnetic stirrer for 30 minutes before use. The concentration of the organic solution was around 23 mg/L and remained constant throughout the entire experiment period.

The water (Control) solution used in all the experiments was prepared with organic free water to which dilute sodium hydroxide (NaOH) was added to adjust the pH to neutral. In one experiment (preliminary batch test), calcium carbonate ($CaCO_3$) was added to the solution

with dilute H_2SO_4 to help dissolve the $CaCO_3$. The final $CaCO_3$ concentration was 40 mg/L and the final pH was neutral (6.8).

3.3 Analytical methods

3.3.1 Organic analyses

The analysis of PCP and other chlorinated phenols in solution was performed by HPLC (High Performance Liquid Chromatography) using a reverse-phase column (Shandon Hypersil ODS C18) and a diode array detector. Detection wavelengths were 280 and 324 nm and the column was maintained at 40°C. The solvents used in the HPLC were methanol and sodium acetate both HPLC grade. For each HPLC analysis, 25 µL of the sample liquid was withdrawn from the HPLC vial. The analytical method used in this study was developed by Kennedy et al., (1992) and the detection limit for all chlorinated phenols was 0.5 mg/L. All analyses were measured in duplicate and the average of the duplicates were used in the plots of concentration versus time. The variability, expressed as the coefficient of variability (cv=(standard deviation/mean)x100), was generally less than 2 % between the analysis duplicates, but the variability between analytical runs was much larger. One analytical run corresponds to an event during which the HPLC is turned on, performs the analysis of a set of samples and is turned off at the end of the analyses. The variability caused by the HPLC (between analytical runs) was estimated using standards of known concentrations. The details of the error calculations are given in Appendix A. The error varied between 8.2% at concentrations around 20 mg/L to 14.3% at 10 mg /L. At concentrations above 1 mg/L the error appeared randomly distributed around the standards, but for concentrations below 1 mg/L the error was consistently lower than the standards (Graph APX-1-1 in Appendix A).

3.3.2 Open characterization

Open characterizations for volatile organic compounds and for semi-volatile extractable organic compounds was performed by a commercial laboratory (Paracel Ltd) for one composite sample, in an attempt to identify potential degradation products. The composite sample was a mixture of three Reactive hypovials with a solution-iron contact time of one week. The volatile open characterization was conducted by purge and trap to find potential degradation compounds such as chlorobenzene, dichlorobenzene, and other chlorinated compounds, whereas the extractable open characterization consisted of an acid/base extraction method to find compounds such as chlorophenols. In both open characterizations, the samples were analyzed using gas chromatography with mass spectrometry detection in full scan mode. The open characterization itself consists of identifying and quantifying mass spectra by comparing them with those found in the National Bureau of Standards (NBS) Library of Mass Spectra. The concentrations are estimated semi-quantitatively from the response of toluene-d8 for the volatile analysis and phenanthrene-d10 for the semi-volatile analysis.

3.3.3 Inorganic analyses

Chloride (Cl^-) was analyzed using ion chromatography, with a detection limit of 0.1 mg/L. The pH measurements were performed with a combination pH reference electrode and a Fisher Accumet model 620 pH meter, calibrated with a buffer solution of pH=7 and with the appropriate buffer solution of pH=4 or 10. Since many of the pH measurements were around 11, the use of buffer 10 (rather than a higher pH buffer) will produce a slight uncontrollable error. However, this error is likely very small compared to the observed pH trends. The redox potential of the solution was determined using a combination Ag/AgCl and platinum electrode and a Cole Parmer model 5985-80 Digi-Sense meter. The electrode was verified with a Zobell solution. Millivolt readings (E) were later converted to the redox

potential (Eh) using the standard potential of the electrode at a given temperature (Eh = $E_{measured}$ + 248 - 44, T° = 20°C).

3.3.4 Gas analyses

The gases in the headspace produced in Reactive hypovials was analyzed with a GC using a Hewlett Packard model 5710A GC equipped with a thermal conductivity detector and a Hewlett Packard integrator model 3386A. The column was a Porapack T 50/80 mesh, which was maintained at 70 °C. Helium at a flow rate of 40 mL/min was the carrier gas. The detector temperature was held at 150°C and the temperature of the injection port was set at 100°C. A sample volume of 0.5 mL was injected into the column. The column allowed the detection of four types of gas, namely nitrogen (N_2), oxygen (O_2), methane (CH_4) and carbon dioxide (CO_2).

4. EXPERIMENTS

4.1 Experimental design

Five distinct tests were carried out during the course of this study: batch tests, extraction tests, iron loading tests, iron to solution tests, and sorption isotherm tests. The main objective was to evaluate the effect of iron for the removal of PCP from the solution.

The batch tests were used to evaluate the effect of iron on PCP removal with time and to monitor changes in the chemistry of the solution during the test. The extraction tests were completed to determine if the PCP removal was due at least in part to some sort of sorption onto the metallic iron. The iron loading tests were performed to verify if the same metallic iron could repeatedly remove the same amount of PCP from successive fresh PCP solutions. The iron-to-solution ratio tests were accomplished to see the effect of the mass of iron on the equilibrium PCP concentration and on the time to equilibrium. The sorption isotherm tests were performed to see if the removal of PCP could be compared to isotherms of existing sorption models. The experiments were usually carried out once but sometimes twice (batch tests) and always in duplicate or triplicate. Replicates were used because they allow to calculate the variability at each time (i.e. it gives an error bar for each plotted point). All tests were performed in hypovials containing predetermined amounts of iron and solutions.

For each test, measurements are the results of duplicate or triplicate hypovials, and each hypovial was analyzed twice on the HPLC. Therefore, each measurement corresponding to a point on the graphs is the average of 4 to 6 analyses on the HPLC.

Replicate hypovials were used to estimate the variability in the laboratory procedure and duplicate analyses to estimate the variability of the HPLC (within a single analysis run). An additional source of variability caused by the different analysis runs, was estimated with

standards. Graphs or experiments that compared points from a single analytical run, had an error that could be estimated from the replicate hypovials, whereas experiments that compared measurements from several runs had an error estimated from the standards. The details of the error calculation are given in Appendix A.

For measurements that take place through time, two choices are available: destructive or repeated sampling. In destructive sampling, the hypovials are sampled only once and discarded; different hypovials are sampled at each time. In repeated sampling, each hypovial is sampled at each time. Repeated sampling has the advantage of requiring fewer vials, and of giving "smoother " time curves. The "smoother" curves are due to the fact that there is less variability within a single hypovial than between several hypovials. The difficulty with repeated sampling is that the time behaviour is confounded with the hypovial behaviour. A special hypovial will produce a special time behaviour (for all times) instead of appearing as an abberation at one time as in the case of destructive sampling. Destructive sampling is also easier to analyze statistically.

In these experiments, destructive sampling was used because it would be difficult to maintain septum integrity and to keep track of the mass balance if samples were repeatedly taken from the same hypovial. For a given experiment, all hypovials were prepared at the beginning of the experiment, and two or three hypovials were selected at random for each time measurement. In this way, the measurements at each time are independent of one another instead of being correlated in the case of repeated sampling, due to the fact that they would come from the same hypovial. The hypovials were prepared in random order and were also chosen for sampling in random order. The randomization was simply done by preparing the hypovials in no predefined order and by choosing them for sampling with no predefined order.

4.2 Batch tests

4.2.1 Methods

Laboratory batch tests were used to evaluate the removal of PCP from water in the presence of metallic iron. The tests were performed using 60 mL glass hypovials, in which the PCP concentration was monitored over time. Three types of sample hypovials were prepared :

- *Blank:* PCP in water (organic solution)
- *Control:* metallic iron + organic free water
- *Reactive:* metallic iron + organic solution

The Control and Reactive vials contained 20 g of metallic iron with an iron to solution ratio of 0.35g/ mL for all the tests, except for the iron to solution ratio and for the adsorption experiments, where the amount of iron varied from 1 g to 50 g. Quantities of solutions and iron were all determined by weight. The batch experiments were conducted in duplicates or triplicates using the procedure described below. First, the Blank hypovials were filled in random order with the organic solution leaving no head space. They were immediately sealed with teflon® septa. The Control hypovials were also randomly filled with organic free water. The Reactive hypovials were then filled randomly with the same organic solution as the Blank hypovials. The hypovials containing metallic iron (Reactive and Control), were first half filled with the appropriate solution and gently agitated for few seconds to remove air from the iron. They were then completely filled. In this procedure there was no randomization between the Blank, Control, and Reactive hypovials. The Blank hypovials were always filled first followed by the Control hypovials and the Reactive hypovials. This order of solution filling was chosen because in the blank hypovials no treatment was applied so the PCP concentration would remain constant. The Control hypovials were utilized simply for verifying the change in water chemistry caused by the iron, and the Reactive hypovials

that had the treatment were filled at last because the process was relatively rapid. Since the three types of hypovials will be considered separately, the lack of randomization between the types of hypovial will not affect the results. Water solution samples were taken in triplicates before and after filling the Reactive and the Blank hypovials to certify that no volatilization occurred during filling. These six samples were utilized to determine the initial PCP and Cl^- concentrations; and the initial pH and Eh values.

All the hypovials were then placed on a vertical rotating disc turning at 3 revolutions per minute in the dark and at room temperature (23°C). This rotating apparatus allowed mixing without agitation.

At each sampling time, duplicate or triplicate Blank, Control and Reactive hypovials were selected at random from the rotating disc. Water samples were collected with glass syringes through teflon® septa and filtered with 0.22 µm Millex-GV_{13} filters for the organic and Cl^- analyses. For the organic samples, the syringe was rinsed with 1 mL of sample and another 1 mL was then withdrawn from which 0.5 mL was filtered and discarded and the remaining 0.5 mL was filtered and introduced in equal amount (0.15 mL) in two HPLC vials. For the chloride samples, fifteen to twenty mL of solution were sampled and filtered. Between sampling bottles, the syringe was cleaned with ethanol and organic free water and the filter was changed. pH and Eh readings were taken directly from the hypovials. The experiments were generally carried over a period of one week. The experimental design diagram for the batch test is given in Appendix B.

4.2.2 Results and discussion

In total, four batch tests were performed with different initial concentrations and test durations. The results for all tests are tabulated and plotted in Appendix C. The results of a typical batch test are presented in Figure 1a. In this test, the initial concentration of PCP

was 23 mg/L and the iron to solution ratio was 0.35g/mL. The results are presented as the concentration of PCP relative to the initial concentration of PCP as a function of time in hours. The results are shown for the Blank, Control and Reactive hypovials. The concentration of PCP in the Blank hypovials did not decrease over time. This suggests that PCP did not degrade, was not sorbed on the glass or the septum, and was not volatilized in the hypovials that did not contain metallic iron. In the Control hypovials, no PCP was detected during the experiment indicating that no PCP was released from the glassware or the iron. For the Reactive hypovials, PCP removal was up to 80 % of the initial concentration after 7 hours and up to 90% after 192 hours. The rate of PCP removal was very rapid for the first 7 hours, moderate between 7 and 20 hours, and after 20 hours, no additional PCP removal was observed. At the conclusion of the experiment (T= 192 hours), the PCP concentration was 2 mg/L. Results for the other batch tests were similar, with little additional removal after 200 hours. The calculations of the 95% confidence intervals of the PCP concentrations are presented in Appendix A. They varied from ± 0.19 to ± 0.54 mg/L depending on the concentration and are given on Figure 1a. The concentration at T=192 hours was still significantly different than zero (Ho: C = 0; P=0.005) (See details in Appendix A).

Figure 1b shows the pH measurements for the three types of hypovial as a function of time. The Blank hypovials showed little change in pH for the complete duration of the experiment, while the Reactive and the Control hypovials showed a similar rapid and significant increase in pH. The pH increased from 7 at the beginning of the test to near 10.9 at the end of the test. The increase in pH was very rapid for the first 7 hours. After that time the pH was fairly stable. The increase in pH can be attributed to the presence of metallic iron rather than PCP, because it was observed in the PCP-free vials (Controls). Furthermore, the period of time when pH increases correspond with the period when the PCP concentration decreases. The calculations of the 95% confidence intervals of the pH are presented in Appendix D. These intervals varied from ± 0.07 to ± 0.22 pH unit.

As shown in Figure 1c, the Eh of the solution in the Blank hypovials stayed relatively constant for the entire duration of the test, at +100 to +250 mV. This indicates that moderately oxidizing conditions were maintained in the Blank hypovials for the entire duration of the experiment. For the Reactive and Control hypovials, the Eh of the solution rapidly decreased from +250 mV to -100 mV after 7 hours and then progressively decreased to -300 mV by the end of the test. The Eh decline was very rapid for the first 7 hours and was moderate to low for the rest of the test. This indicates that the redox conditions changed very rapidly to reducing conditions in the hypovials containing metallic iron. The calculations of the 95% confidence intervals of the Eh measurements are included in Appendix D.

The results were similar when the experiment was carried out for 700 hours (28 days) (Figure 2a). The initial PCP concentration in this experiment was 22 mg/L and the iron to solution ratio was 0.17g/mL. During the first 24 hours, 80 % of the initial PCP concentration was removed in the Reactive hypovials and no more PCP removal was observed after that time. Thus, the process involved in the removal of PCP acts mainly within the first 24 hours of contact between the metallic iron and the PCP. In the Blank hypovials, the PCP concentration remained constant at 22 mg/L except for a slight increase at late times that can be attributed to the variability of the HPLC (as shown by the 95% confidence intervals presented in Appendix A. Meanwhile, the pH readings of the Reactive and the Control hypovials increased to 10.2 at early times (0 to 7 hours) and remained constant thereafter (Figure 2b). For the Blank hypovials, the pH measurements stayed constant at 6.9 for the duration of the test.

Degradation products expected to be found during the experiment (tetra-, tri-, di- and mono-chlorophenols and phenols) were monitored through time in the water solution. None of these compounds were detected by the HPLC (detection limit = 0.5 mg/L) at any time during the tests. The open characterization for volatile and semi-volatile compounds, conducted on a

water solution sample collected after 7 days, did not show any by-products at concentrations in the µg/L range (see Appendix E). The absence of by-products was not anticipated considering that up to 90% of the PCP was removed from solution and that sorption onto the hypovial material or volatilization could not account for the lost. This is counter to other studies using chlorinated aliphatics in contact with metallic iron (O'Hannesin and Gillham, 1992), where concentrations of by-products were detected, suggesting dechlorination of the organic compounds.

Chloride concentrations as a function of time are presented in Figure 3. Figure 3a presents the Cl^- results of the first batch experiment containing 24 mg/L PCP, 0.17g/mL iron and 40 mg/L $CaCO_3$ in solution, and Figure 3b for one with 22 mg/L PCP, 0.35g/mL iron and no $CaCO_3$ in solution. $CaCO_3$ was added to the solution in the initial experiments to simulate groundwater chemistry. After the first evidence of PCP removal during the treatment, addition of $CaCO_3$ was dropped from the laboratory procedures to avoid complex formation of potential by-products in the solution. Chloride was analyzed by a commercial laboratory, Bondar-Clegg Ltd, using standard ion chromatography procedures. These graphs were the two best cases (results are tabulated in Appendix F).

In Figure 3a, chloride increased early in the experiment in the Reactive hypovials and stabilized after 7 hours, except at t= 150 hours. The Cl^- concentration was higher in the Reactive hypovials than in the Control hypovials, suggesting a partial dechlorination of PCP (Ho: Cl^- Reactive = Cl^- Control, H_A: Cl^- Reactive > Cl^- Control; P=0.04). The expected chloride concentration in solution assuming complete dechlorination of PCP is also shown on the graph; it was calculated by subtracting the final PCP concentration in the Reactive hypovials from the initial PCP concentration at each time. The expected Cl^- concentration thus represents the Cl^- concentration if there was complete dechlorination (1 mg/L of PCP corresponds to 0.67 mg/L of Cl^-). For the first 4 hours the measured and expected Cl^- concentrations were the same but as the time increased concentrations diverged. This

divergence may be caused by reactions involving Cl^- in solution, perhaps complexation or precipitation.

In Figure 3b, the results in the absence of $CaCO_3$ indicate that the chloride concentration in the Reactive hypovials was not significantly different than the Control hypovials with an average Cl^- concentration of 2.5 mg/L. In this case it is difficult to suggest that chloride came from the partial dechlorination of PCP in the Reactive hypovials, because the Control hypovials showed the same Cl^- level. For the Blank hypovials, the Cl^- concentration was very low (0.15 mg/L) which corresponds to the detection limit (0.10 mg/L).

Comparing Figures 3a and 3b, it is apparent that the chloride concentrations are higher when $CaCO_3$ was present than when it was not. Some of the Cl^- could have been introduced by the impurities in the $CaCO_3$ salt used in the experiment. However, the concentration resulting from these impurities should have been very small (0.001% x 40 mg/L $CaCO_3$ = 4 x 10^{-4} mg/L Cl^-). In addition, the high variability in the Cl^- concentrations is not due to the analytical variability which was evaluated at 1% (Appendix F). The high concentration of Cl^- in the presence of $CaCO_3$ could not be explained.

The natural log of C/C_o for PCP in the batch test presented in Figure 1 was plotted against time in Figure 4 to evaluate if a first-order kinetic model could explain the rate of PCP removal. Exponential decay models typically explain several chemical, biological and radiological processes. The first order kinetic model can be described by the equation:

$$C = C_0 \ e^{-kt} \qquad (2)$$

where C is the concentration in solution at time t, C_0 is the initial concentration of the organic solution, k is the first order rate constant, and t is time.

By rearranging and taking the natural log, equation 1 becomes:

$$\ln (C/C_0) = -kt \qquad (3)$$

In Figure 4, the natural log of C/C_0 is represented by a non linear decline instead of a straight line, as would be predicted by the model. Consequently, this model is not appropriate to explain the behaviour of PCP removal by metallic iron. All batch tests conducted in the study showed a similar behaviour as Figure 4. This differs from the study of O'Hannesin (1993), where the first order kinetic model was applied to the degradation curves of several aliphatic compounds with good coefficients of correlation (r^2). The observed behaviour of PCP removal over time could have important practical implications on the use of the in situ reactive wall technology. Estimation of the time required to completely remove PCP would be underestimated by the first order model. As a result, PCP concentrations above the cleanup objectives could exit the reactive wall designed using this model.

The gas in the headspace that developed in the reactive hypovials was analyzed by gas chromatography and was quantified against four known standards: nitrogen, oxygen, methane and carbon dioxide. From the analyses performed, only nitrogen could be detected. However, hydrogen could not be detected using the available equipment. These results are comparable to those of O'Hannesin (1993) and do not exclude the possibility of hydrogen being present due to hydrolysis (Appendix G).

The hydrogen gas formation in a system containing iron and water with limited amount of oxygen is a possible thermodynamic reaction, explained by the following reactions:

cathodic reactions: $H^+ + e^- \rightarrow H$

$H + H \rightarrow H_2$

anodic reaction : $Fe \rightarrow Fe^{2+} + e^-$

The anodic reaction can continue until the water, in which OH^- is now in excess, H^+ is removed, becomes supersaturated with respect of solid $Fe(OH)_2$, ferrous hydroxide (Evans, 1981).

4.3 Extraction tests

4.3.1 Methods

This extraction test was executed following the 0.35g/mL iron/solution ratio experiment on PCP removal. It was conducted to evaluate if any PCP was sorbed onto the metallic iron during the batch tests. After predetermined times of contact between the iron and the PCP solution (2, 7, 21, 48, 81, 126, and 192 hours), the water remaining in the Reactive hypovials was decanted and discarded, while retaining the iron particles in the hypovial. Three Reactive hypovials were decanted at each contact time (triplicate). Ten mL of methanol were then added to the metallic iron in each hypovial and agitated on the rotating disc for 24 hours. The methanol was then sampled in duplicate from each hypovial and analyzed for PCP with the HPLC (A schematic of the experimental design is given in Appendix B). Following this first extraction, all the methanol was decanted from the hypovials, without removing the iron particles, and 10 mL of fresh methanol were added for a second extraction.

The extraction of PCP was also conducted by a commercial laboratory (Paracel Ltd) on one Reactive hypovial after one week of contact time (170 hrs). The contact time of one week was chosen to ensure that a significant amount of PCP was removed from solution and therefore to increase the chances of finding PCP sorbed onto the iron. The procedure was the same as explained above except that 15 mL of water (acidified to pH of <2) and 10 mL of dichloromethane were added to 20g of iron in a 40 mL VOA hypovial. After 24 hours of horizontal shaking, a 1 mL aliquot of the extract was derivatized (chemically changed) with diazomethane, solvent exchanged, and diluted to a final volume of 10 mL with iso-octane

before injection in the GC (Gas Chromatograph).

4.3.2 Results and discussion

Figure 5 compares the mass of PCP recovered from the iron filings by extraction with the total mass of PCP removed from the solution as a function of time. Each point of the mass-recovered curve is the average of the triplicate hypovials. The mass of PCP recovered from the extraction of iron increased with time from 0 to a maximum of 0.4 mg with some fluctuations. The maximum extracted PCP was found at time 192 hours and corresponded to 37 % of the total PCP removed from the solution. The second extraction (not shown) accounted only for 2% of the total PCP lost for each time. Thus the first extraction with methanol recovered approximately 98% of the recoverable PCP from the iron, while the second extraction accounted for only 2%.

The extraction performed by the commercial laboratory with acidified water and dichloromethane showed that 32% of the removed PCP was extractable from the iron (Appendix E). This is similar to the results obtained for the methanol extraction. The two extraction methods showed that a maximum of 32-37% of the removed PCP could be extracted from the iron. Because PCP removal is not fully explained by sorption onto iron, other processes such as chemical reactions, may be responsible for the removal of PCP.

4.4 Iron loading test

4.4.1 Method

The objective of this test was to evaluate if the metallic iron would become saturated with PCP after successive contacts with fresh PCP solutions. The rationale being that if the process by which PCP is removed from solution is degradation catalyzed by the iron, then

the efficiency with which PCP is removed from solution should not decline appreciably with successive contacts. On the other hand, if the removal of PCP is the result of a reaction at the surface of the iron (sorption, complexation) then the surface of the iron should become "loaded" with PCP with successive contacts, and therefore the efficiency with which PCP is removed would decline with successive contacts.

Three Reactive hypovials were filled with 20 g of iron and a 22 mg/L PCP solution. After 24 hours of vertical rotation, the hypovials were sampled for PCP and readings for pH and Eh were taken. Each hypovial was then emptied of the PCP solution and refilled with fresh PCP solution at the same concentration. After another 24 hours, sampling and pH and Eh readings were repeated. The iron was put in contact with PCP in this manner a total of four times. For the last refill sampling was performed after 43 hours instead of 24 hours.

4.4.2 Results and discussion

The results for the iron loading test are presented in Figure 6a as the relative concentration of PCP left in solution after equilibration as a function of the number of refills. For the first refill, an average of 84% of the PCP was removed after 24 hours. After the second refill and another 24 hours, an average of 42 % was removed, half the amount removed after refill #1. For refill #3, an average of 16% of the PCP was removed, and for refill #4, only 12 % of the PCP was removed. As the number of refill increased, the effectiveness of iron decreased and the extent of PCP removal seemed to level off. In Figure 6b, the averaged mass of PCP removed relative to the mass of PCP introduced in the hypovial is plotted against the number of refills. After one refill, 84 % of the introduced mass of PCP was removed from the solution. After two and three refills, 62% and 47% of the introduced mass of PCP was removed respectively. However, an average of only 38% of the mass introduced was removed after four refills. The behaviour of pH and Eh is presented in Figure 6c. pH increased to a maximum value of 10.8. Eh decreased to a minimum of -286 mV after the

third refill. The error on the Eh measurements was extremely high in this experiment (25% <cv< 72%) and therefore trends in the Eh behaviour can not be declared significant. Without considering the minor fluctuations, the pH became basic and the Eh became reducing after the first refill and these conditions were reproduced after each refill.

The results of this experiment suggest that the iron surface may become loaded with PCP, or perhaps with its degradation products, resulting in a reduced effectiveness of the PCP removal process. The results also suggest that the PCP removal process is not one of a reaction catalyzed by the iron unless the catalyzed reaction becomes fouled in some way. This may have important implications in a dynamic flow system such as groundwater flow through a reactive wall, where the iron would be constantly in contact with fresh solution. According to these results, the effectiveness of the iron removal method could decrease very rapidly. However, the iron would also be in contact with groundwater at a constant lower pH, which may increase the efficiency of PCP removal. It would therefore be important for future work to examine the effect of pH on this process and also to examine the process under dynamic conditions.

4.5 Iron to solution ratio test

4.5.1 Method

This experiment was conducted to evaluate if the rate and the extent of removal of PCP was influenced by the iron to solution ratio. This was done to verify if the process was related to the amount of iron particles (or surface) in the hypovial. The tests were conducted along the same procedures as for the batch tests described above, but at two iron to solution ratios (0.35 g / mL and 0.17 g / mL) and in duplicates. Each hypovial was analyzed twice. The schematic of the experimental design is given in Appendix B.

4.5.2 Results and discussion

Figure 7a shows the concentration of PCP versus time for two iron to solution ratios (0.17 and 0.35 g/mL) and for two Blanks (0g/mL iron). From Figure 6a, it is apparent that as the mass of iron (or iron surface) increases, the rate of PCP removal increases at early times. This is consistent with previous studies (Gillham and O'Hannesin, 1992; O'Hannesin, 1993; Gillham and O'Hannesin, 1994) showing the rate of degradation increasing with the mass of iron. At the end of the test, 73% of the initial PCP concentration was removed for the 0.17g/mL ratio (1.5 mg of removed PCP per g of iron), while 90% of the initial PCP concentration was removed for the 0.35g/mL ratio (0.99 mg of removed PCP per g of iron). The final PCP concentrations in solution were 7.8 mg/L and 2.1 mg/L for the 0.17g/mL ratio and the 0.35g/mL ratio respectively.

Figure 7b shows the variations in pH for this experiment. The initial pH for both experiments was close to 7 and increased to 10.1 for the 0.17g/mL ratio experiment and to 10.8 for the 0.35g/mL experiment. These values are moderately different (Ho: $pH_{0.17g/mL} = pH_{0.35g/mL}$; P=0.25). The rate of increase is identical for both experiments. In both cases, the pH rose quickly then persisted at a relatively constant value for the duration of the test. Hence, with the exception of the first few hours, the pH appears to depend upon the amount of iron present rather than the time of contact. Furthermore, the break in the PCP removal curve of both tests happens after the pH has reached 10. This is consistent with the study of Gillham and O'Hannesin (1994) that concluded that the reaction rate appears to be strongly reduced by pH values higher than 9-9.5. Eh measurements are not available for the iron/solution ratio test, because of a defective Eh electrode.

The results of this experiment support the hypothesis of a surface-controlled process for the removal of PCP. They also show that the rate of reaction does not appear to depend strongly on the iron to solution ratio, and that most of the removal of PCP occurs in the first 24 hours

of contact.

4.6 Sorption isotherm experiments

4.6.1 Method

This experiment was conducted to investigate if the removal of PCP from solution was consistent with sorption models published in the literature. Two types of sorption tests were completed, both in duplicates and at room temperature (22°C +/- 2°C). In the first test, the mass of iron was varied (1, 2.5, 5, 7.5, 10, 20, 30, and 50 g) in the hypovials without changing the initial PCP concentration (23 mg/L). After an equilibration time of 44 hours, determined from the batch tests, the solution was sampled from all hypovials and was analyzed in duplicates by HPLC. The pH and Eh were also measured. In the second test, the mass of iron was constant (10 g), but the initial concentration of PCP solution varied (5, 10, 15, 20, and 25 mg/L). After 44 hours, HPLC analysis and pH and Eh measurements were repeated as in the first test. A schematic of the experimental design is given in Appendix B.

For both tests, removal of PCP from the solution was assumed to be caused by sorption only. Based on this assumption, the mass balance equation for PCP is:

$$C_o V - C V = S M_s \qquad (4)$$

where C_o is the initial solution concentration, V is the volume of liquid in the hypovial, C is the measured aqueous phase concentration at equilibrium, S is the solid phase concentration (mass of PCP/mass iron), and M_s is the mass of iron in the hypovial. Rearranging gives the solid phase concentration:

$$S = (C_o - C)V/M_s \qquad (5)$$

A plot of S as a function of C will be referred to as a sorption isotherm even though the mechanism for PCP removal is unknown.

4.6.2 Results and discussion

Figure 8a, is a sorption isotherm for the first sorption test, where the initial concentration of PCP was constant in the solution and the mass of iron varied between 1g and 50g. The minimum detection limit on S and the 95% confidence intervals S are also shown on the graph (detailed calculations are presented in Appendix H). The minimum detection limit on S represents the smallest value of S that can be detected at the 95% confidence level, given the errors on Co, C, V, and M_s in equation 5. As shown by the high detection limits and variability on S, the last three points on the isotherm are not significant. These three points correspond to C values larger than 15 μg/mL approximately. The remaining points on the figure show that as the equilibrium concentration (C) increases the sorbed concentration increases to approximately 75 μg/mL at C = 6 μg/mL and remains constant up to C = 15 μg/mL.

The pH and Eh measurements for this experiment are presented in Figure 8b. The pH increased from 10.0 when 1 g of iron was used to 11.0 when 50 g of iron were used. Based on a linear regression, this trend was significant (Ho: slope of pH = 0; P=0.02). This is consistent with previous studies (Gillham and O'Hannesin, 1994) that showed a slight increase in pH when the mass of iron is increased. The Eh values decreased with a slope significantly different than zero (Ho: slope of Eh = 0; P=0.02). The Eh and the pH therefore appear to be influenced by the iron to solution ratio.

Figure 9a is the sorption isotherm for the second sorption test, where the mass of iron remained constant at 10 g and the concentration of PCP varied from 5 mg /L to 25 mg/L. The minimum detection limit and the 95% confidence intervals on S are also shown on the

graph. Calculations are presented in Appendix H. In this graph, all the data points except the first one are significant. When the initial PCP concentration was relatively low (C_0 = 5mg/L), the equilibrium PCP concentration C was less than the detection limit of the HPLC and therefore the first point is not significant. As the initial PCP concentration increased up to 25 mg/L, both the equilibrium PCP concentration C and the solid concentration S increased. This sorption curve appears to follow the general aspect of common isotherms found in the literature (Domenico and Schwartz, 1990).

The pH and Eh results are presented in Figure 9b. The pH had an average value of 10.7 for all the equilibrium concentrations. The slope of a straight line fitted to the data was not significantly different than zero (Ho: slope of pH = 0; P=0.01). The consistency in pH values suggested that the presence of PCP had no measurable effect on pH. The Eh values were always negative ranging between -150 mV and - 300 mV with no significant linear trend (Ho: slope of Eh = 0; P=0.01). This supports an observation made earlier that Eh and pH appeared to be controlled by the iron to solution ratio.

Figure 10 is a composite isotherm produced from all equilibrium estimates of S vs C, from the previous experiments of this study. Specifically, Figure 10 includes:

- data from the iron/solution ratio experiment at large times (>24 hrs)
  - batch test 10g iron
  - batch test 20 g iron;
- data from the batch tests at large times (>24 hrs)
  - batch test (24-700hrs);
- data from the iron loading experiment in which case the cumulative PCP removed in the four refills was plotted against equilibrium concentration of the last refill;
- significant data from the two isotherms presented above.

The use of the above data to produce an isotherm permitted to have a better control of the error by averaging the replicates of each experiment while providing a wider range of C values. The resulting isotherm was compared to two commonly-used sorption isotherms:

$$S = K \cdot C^n \qquad \text{Freundlich} \qquad (6)$$

$$S = Q_o\, KC/\,(1+KC) \qquad \text{Langmuir} \qquad (7)$$

where S is the concentration associated with the solid phase [M/M], C is the concentration in the solution phase, K is the distribution coefficient of the solute [L^3/M], n is a constant ranging between 0.7-1.2, and Q_o is the maximum sorptive capacity for the surface (Karickhoff et al., 1979). These relations describe linear, concave and convex isotherms that exist when an organic solute partitions instantaneously between the liquid and the solid phases, without any other phenomena participating in the removal of an organic solute (degradation, chemical transformation, or intra particle diffusion).

The details of the curve fitting procedure are presented in Appendix I. Using the least-squared fitted parameters the isotherms were described by:

$$S = 42\ C^{0.29} \qquad (8)$$

and

$$S = 109*0.36*C\ /\ (1+0.36C). \qquad (9)$$

Both sorption models fitted the data with significant regressions (Appendix I). Sorption isotherm of PCP on metallic iron can be compared to isotherms of PCP on soil. In the study of Banerji et al (1986), adsorption experiments were done at a slightly acidic pH (5.7-6.7) with PCP concentrations ranging from 0.01 mg/L to 10 mg /L on a Missouri soil containing between 5 to 15% organic matter. Their adsorption isotherms fitted the Freunlich model with

good regression coefficient (R^2 = 0.99) and the adsorption was found to be reversible to a maximum of 84%. Other experiments on PCP adsorption reached the same conclusions, namely that adsorption was reversible (Choi and Aomine, 1974).

Although the data could be represented very well with sorption models, sorption can not completely explain the removal of PCP in this study because of the irreversibility of the process (as shown by the extraction experiment). Also, the modelling of sorption systems using isotherms is an empirical approach that is not often physically realistic (Domenico and Schwartz, 1990). Other physical and chemical processes can also be described by such models. This study, therefore provides evidence that the process involved in the removal of PCP using metallic iron appears to be a surface phenomenon but its physical and/or chemical origin remains unknown.

5. SUMMARY AND CONCLUSIONS

The treatment of PCP-contaminated water with metallic iron in batch tests resulted in the removal of a maximum of 90% of the initial mass of PCP in a relatively short time. The presence of iron in the water caused the pH to increase to values between 10 and 11 and the Eh to decrease to reducing conditions. These pH and Eh changes were very rapid upon contact between the iron and the water and were attributed primarily to the presence of iron rather than PCP in water.

Degradation products such as chlorinated phenols were not detected during the removal of PCP using two completely different analytical procedures. Another degradation by-product, chloride, was found in highly variable concentrations that were generally lower than what would be expected for a complete dechlorination of PCP. The time behaviour of the PCP removal was not compatible with a first order kinetic model that is often used to explain biological and/or chemical decay.

The extraction of PCP from iron that had been in contact with PCP using methanol could only account for a maximum of 37% of the PCP that was removed from solution. The effectiveness of iron in removing PCP decreased with the number of contact with fresh PCP solutions.

The PCP removal behaviour could be described well by commonly used sorption models (Langmuir and Freunlich) despite the lack of reversibility (desorption of PCP from the iron).

The process involved in the PCP removal remains uncertain. Degradation of some sort could explain partially the PCP removal, but the lack of organic degradation products and the low concentration of Cl^- can not fully support this hypothesis. Adsorption can explain the behaviour of PCP removal to some extent in light of the good fit of the experimental

isotherms to well known adsorption models. However, the lack of reversibility in the sorption process as shown by the extraction experiment and the fact that other chemical or physical processes could contribute to the PCP removal do not support adsorption as the sole process involved in PCP removal.

The results of this study are partly compatible with those found by O'Hannesin (1993), where chlorinated aliphatics in water were dehalogenated in contact with iron. The results compatible with those found in the study of O'Hannesin are: the rapid PCP removal from solution in contact with iron. the rapid change in pH and Eh conditions, the formation of an headspace in hypovials and the release of chloride in solution. The results that are different from those found in the study of O'Hannesin are: the time behaviour of PCP removal not supporting the first order kinetic model, the sorption of a fraction of PCP onto the iron, the non-detection of organic degradation by-products and the decline of iron effectiveness in repeated batch tests using the same iron.

The results of the present study still support the potential use of metallic iron to remediate groundwater contamination plumes containing PCP. However, the processes involved in the removal of PCP have to be better understood to evaluate all the implications of this technology. Some future studies could concentrate in the search of degradation by-products (in water solution and on the iron) by the use of adequate analytical techniques at early times in the experiment (within the first 8 hours). A good way would be the use of radioactive PCP. This is important in determining if PCP degrades completely or produces more harmful products or if PCP simply transfers from the aqueous phase to the solid phase. After these questions are answered, there will be a need to try the experiment in column to evaluate the effect of dynamic conditions and the presence of continuous fresh PCP solution at neutral pH on the long term effectiveness of the iron. Finally, the inorganic geochemical processes that may influence the PCP removal need to be studied to understand its role in the degradation process and then to improve the system.

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TABLE

Table 1: Chemical and physical properties of Pentachlorophenol

Pentachlorophenol (PCP)	C_6Cl_5OH	
Molecular weight	266.34 g/mol	
Solubility in water	15 mg/L at 25 °C and at pH=5,1	(a)
Acidity constant	pKa : 4.74	(b)
Henry's law constant	2.8×10^{-7} - 3.4×10^{-6} atm·m^3/mol	(b)
Vapour pressure	1.7×10^{-5} mmHg at 20-25 °C	(b)
Octanol/water partition coefficient	log Kow : 5.01-5.24	(c)

(a) Bailey et al. (1965)
(b) Montgomery et al. (1990)
(c) Schellenberg et al. (1984)

FIGURES

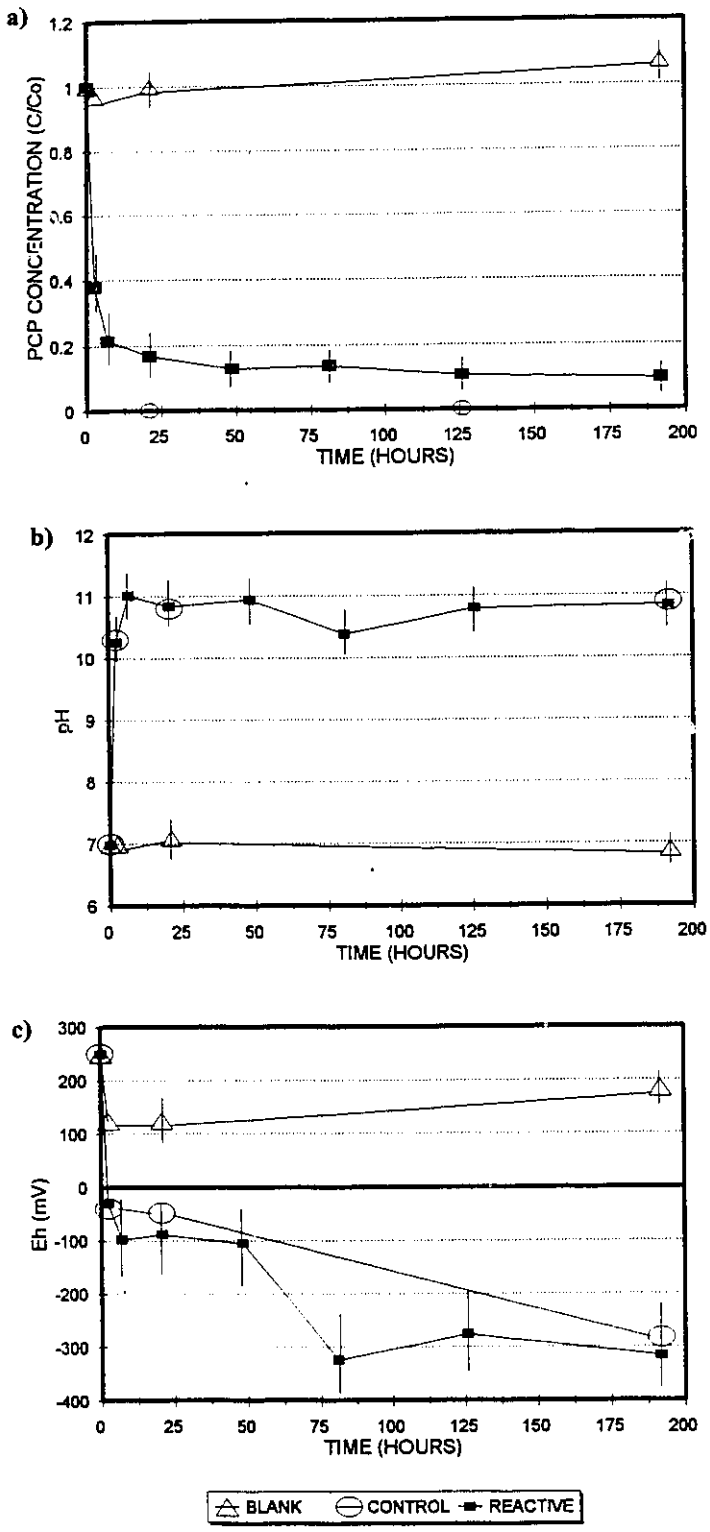
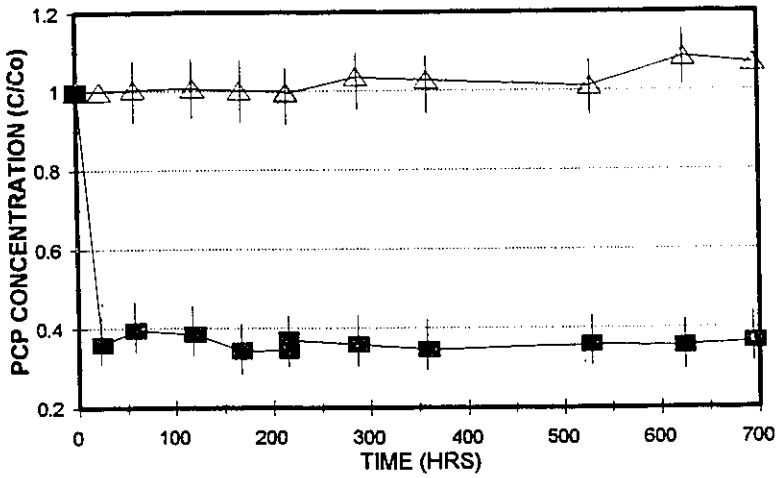


Figure 1 : Typical batch test results for PCP
a) PCP concentration versus time, b) pH versus time
c) Eh versus time
Note: vertical lines on all graphs indicate 95% confidence intervals

a)



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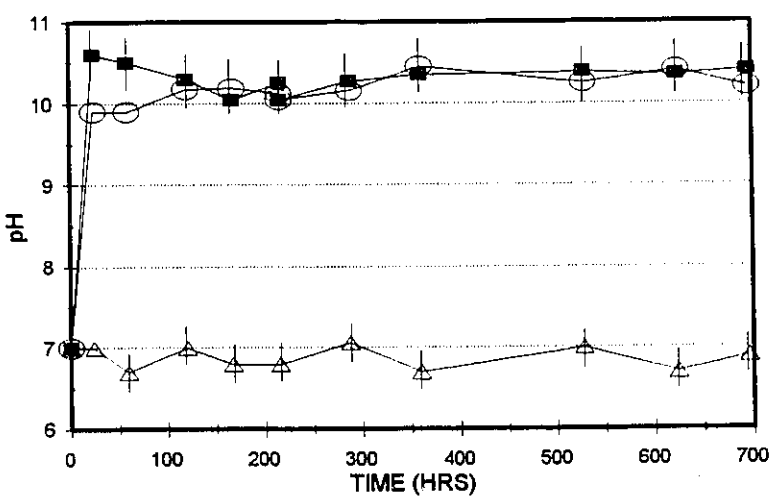


Figure 2 : Batch test results for PCP during long term experiment
a) PCP removal versus time
b) pH versus time

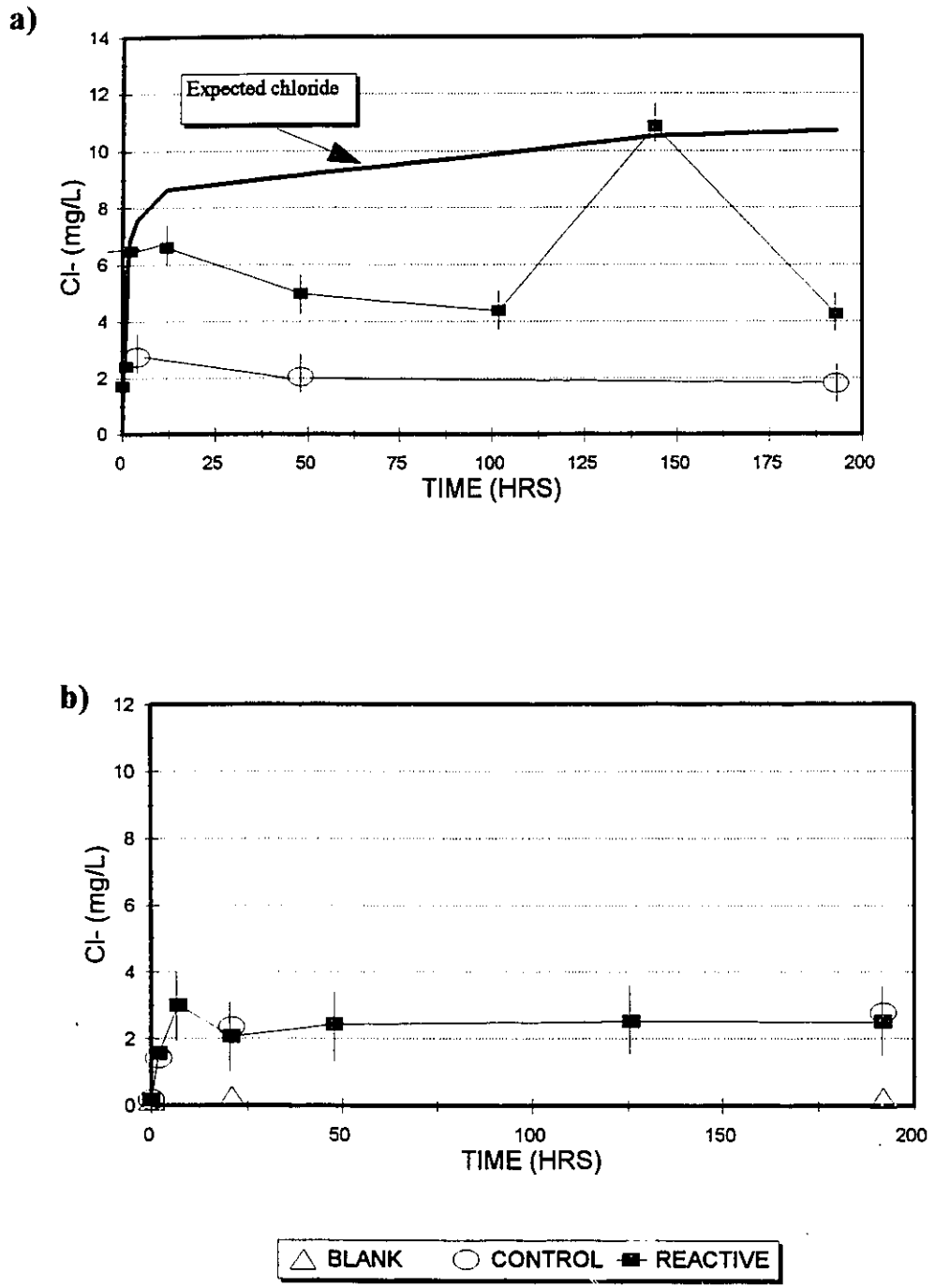


Figure 3 : Chloride concentration versus time from batch tests
a) PCP solution with CaCO3, b) PCP solution without CaCO3

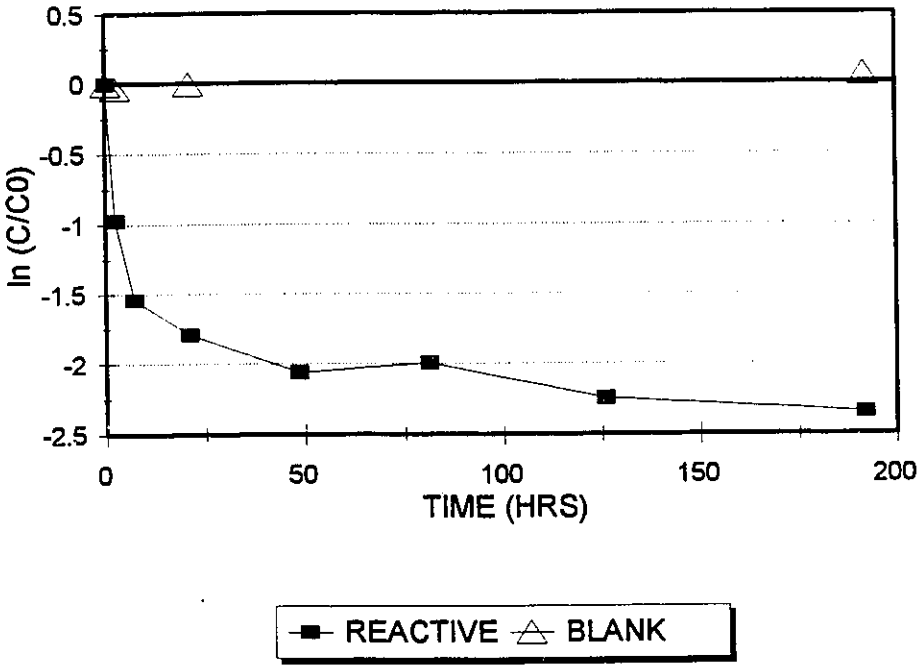


Figure 4 : Semilogarithmic plot of PCP removal from batch test results

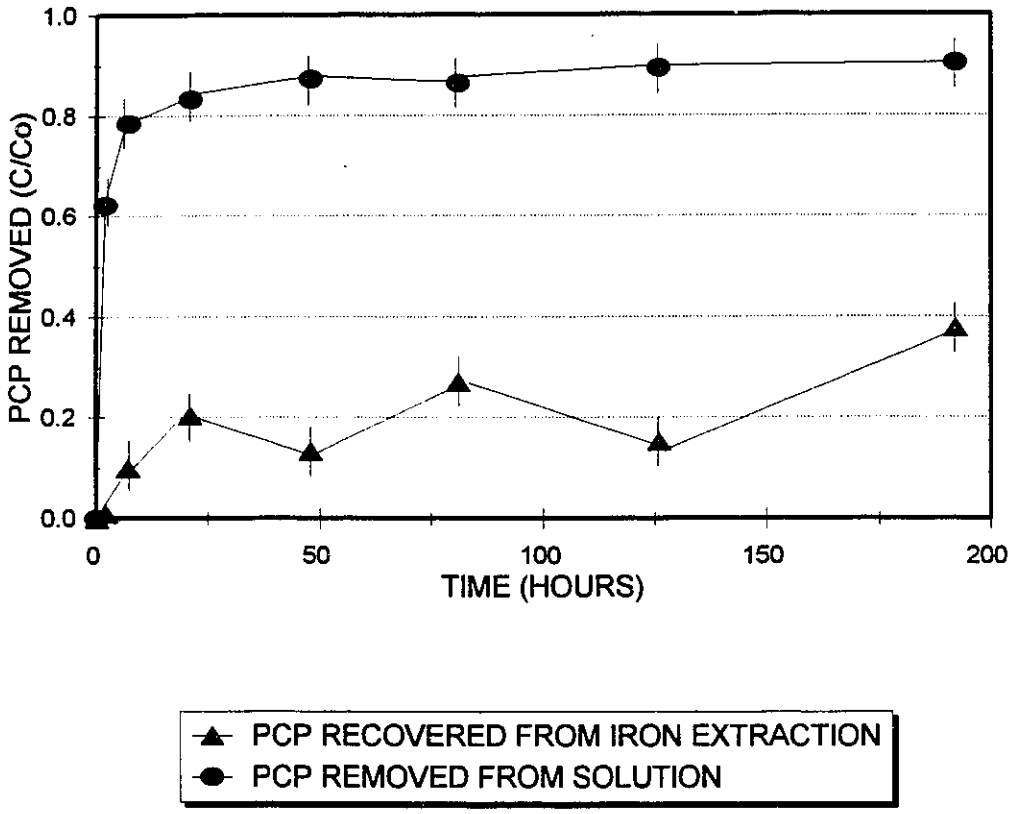
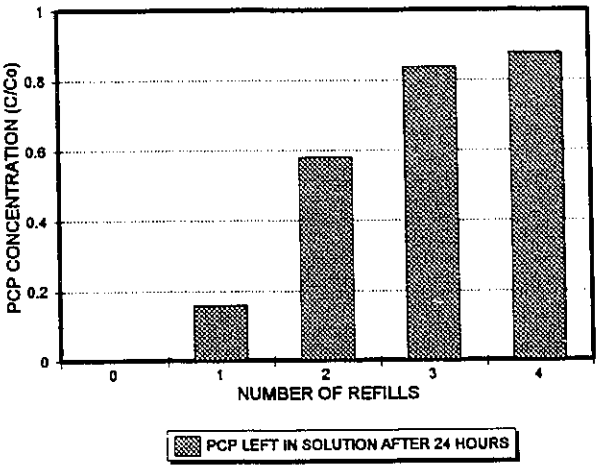


Figure 5 : Extraction test results: PCP removed from solution and recovered from iron by extraction with methanol

a)



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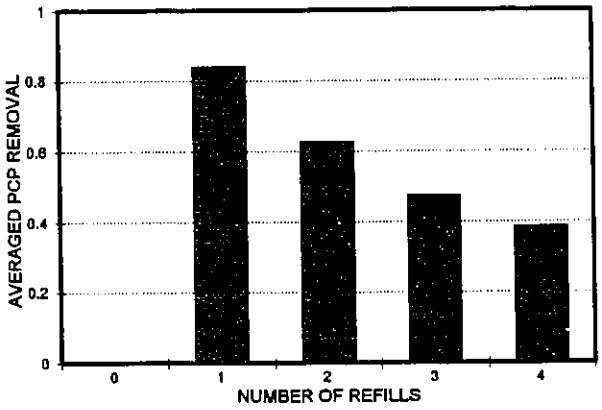

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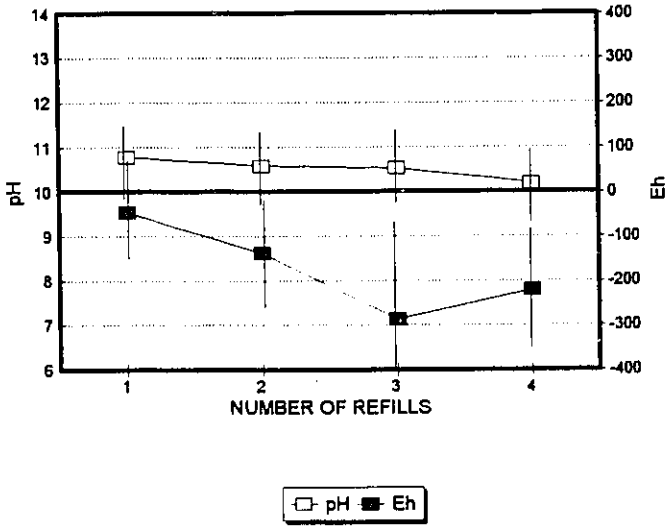
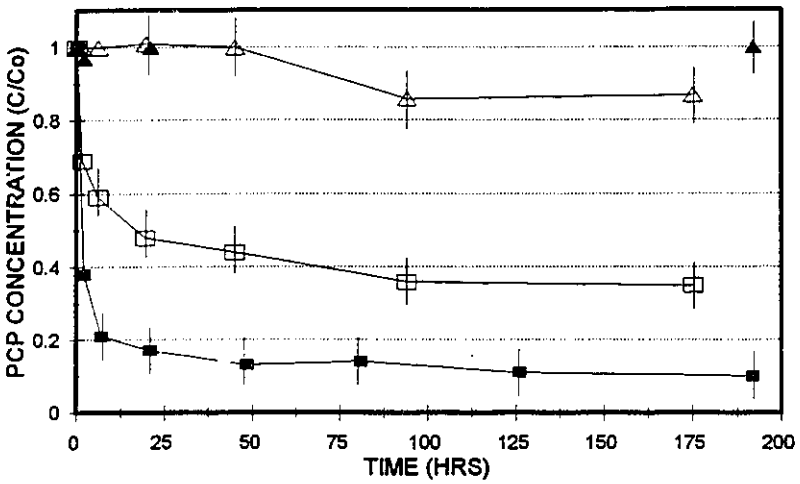


Figure 6 :. Iron loading test
a) Equilibrium PCP concentration after 24 hrs, left in solution
b) Averaged PCP removal c) pH of solution after 24 hrs

a)



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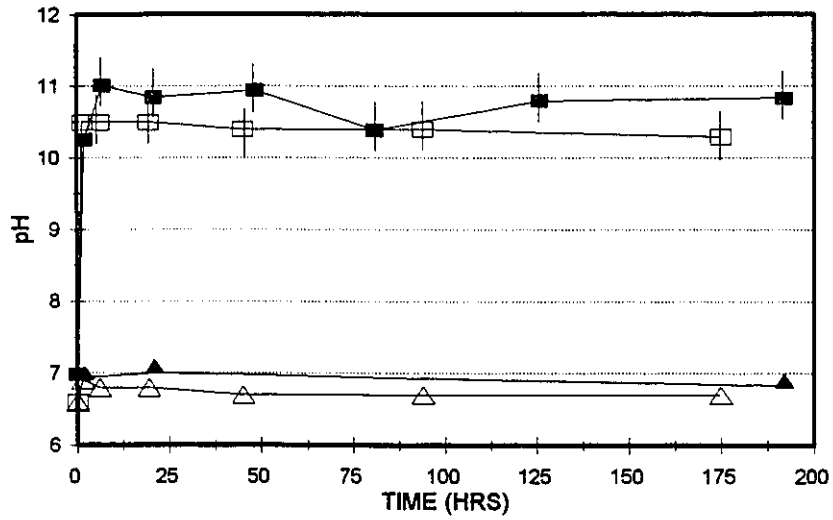
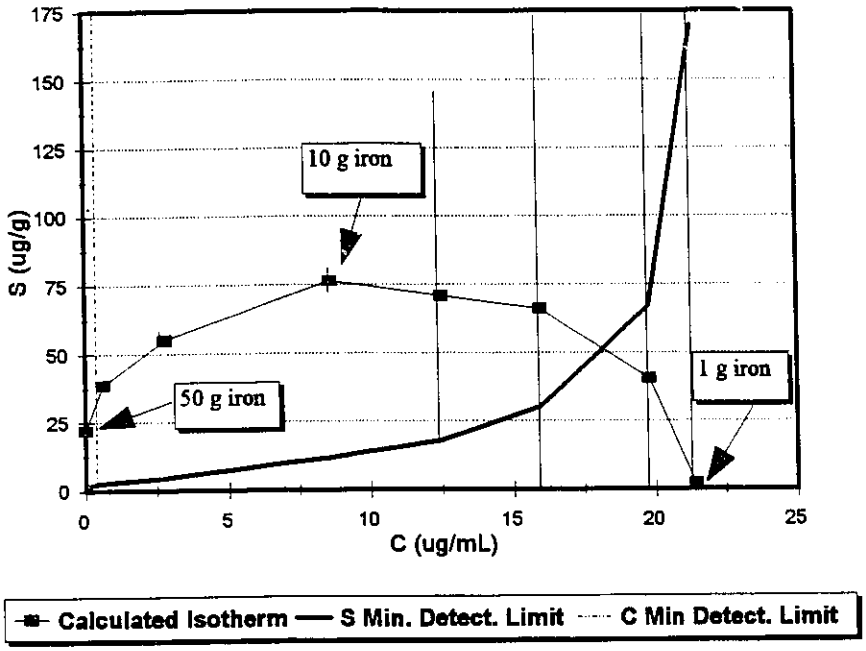


Figure 7 : Iron to solution ratio test
a) PCP removal for two iron/solution ratios (0.17g/mL and 0.35g/mL)
b) pH of solutions (0.17 g/mL and 0.35 g/mL)

a)



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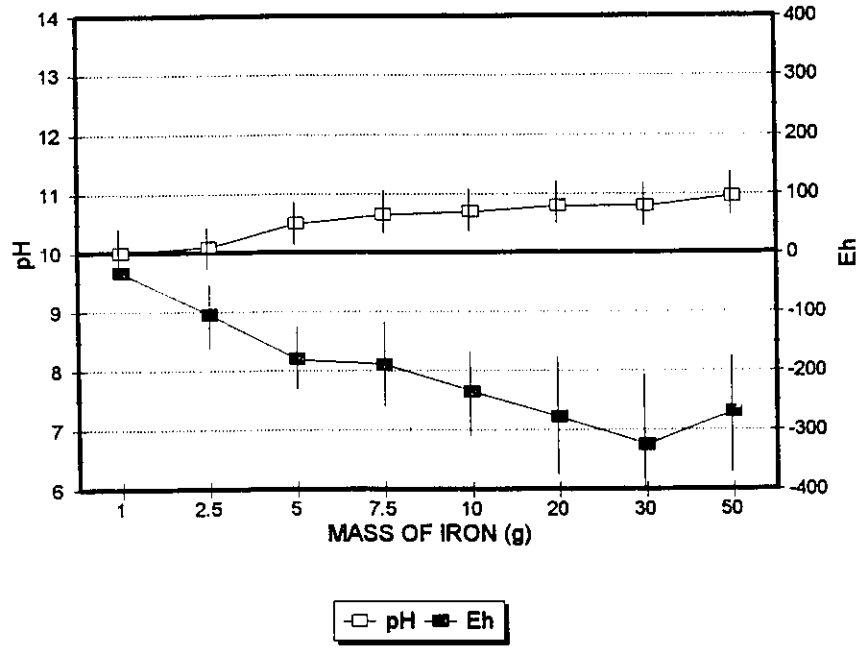
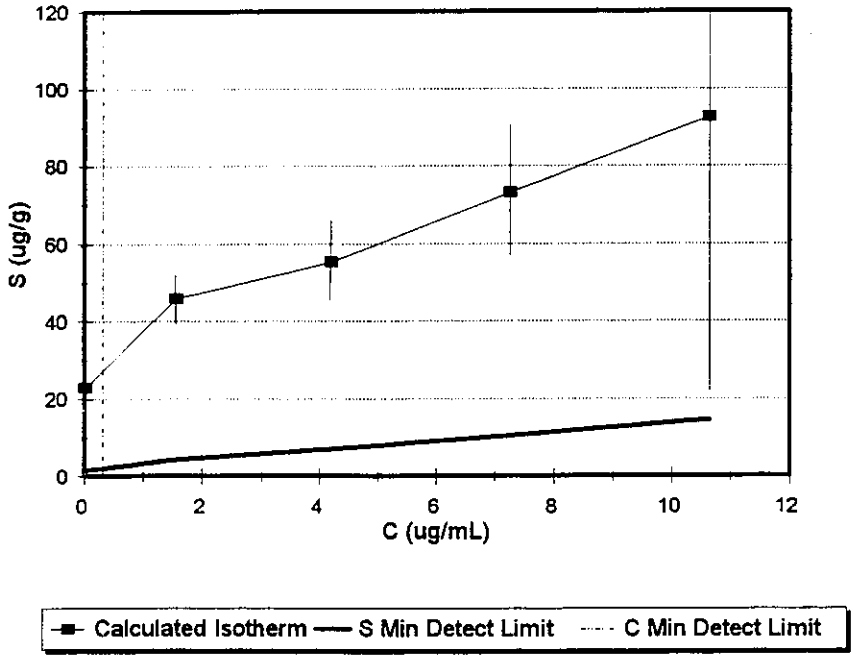


Figure 8 : PCP isotherm using variable iron mass
a) Isotherm , where the three last data are not significant
b) pH and Eh of solution

a)



b)

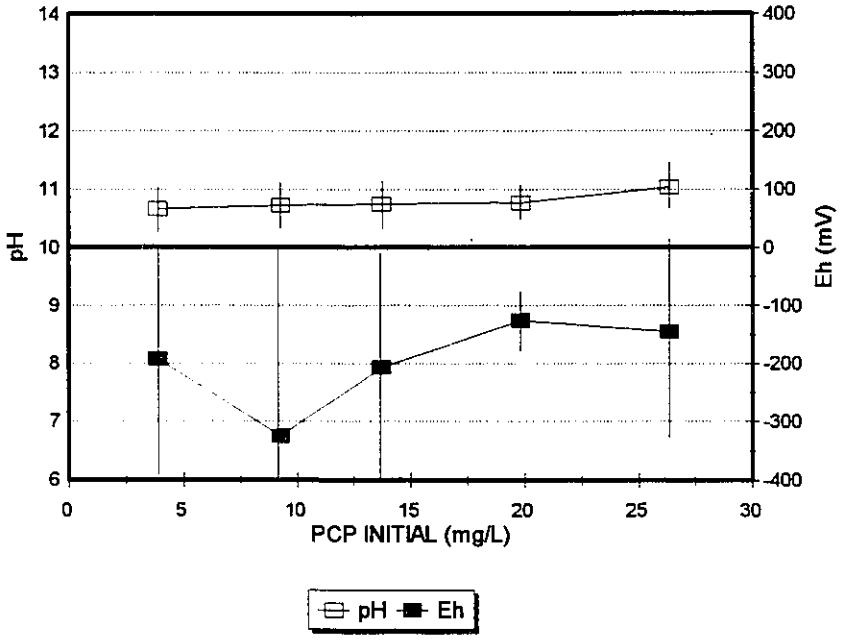


Figure 9 : PCP isotherm using variable initial PCP concentration
a) isotherm, where all data are significant
b) pH and Eh of solution

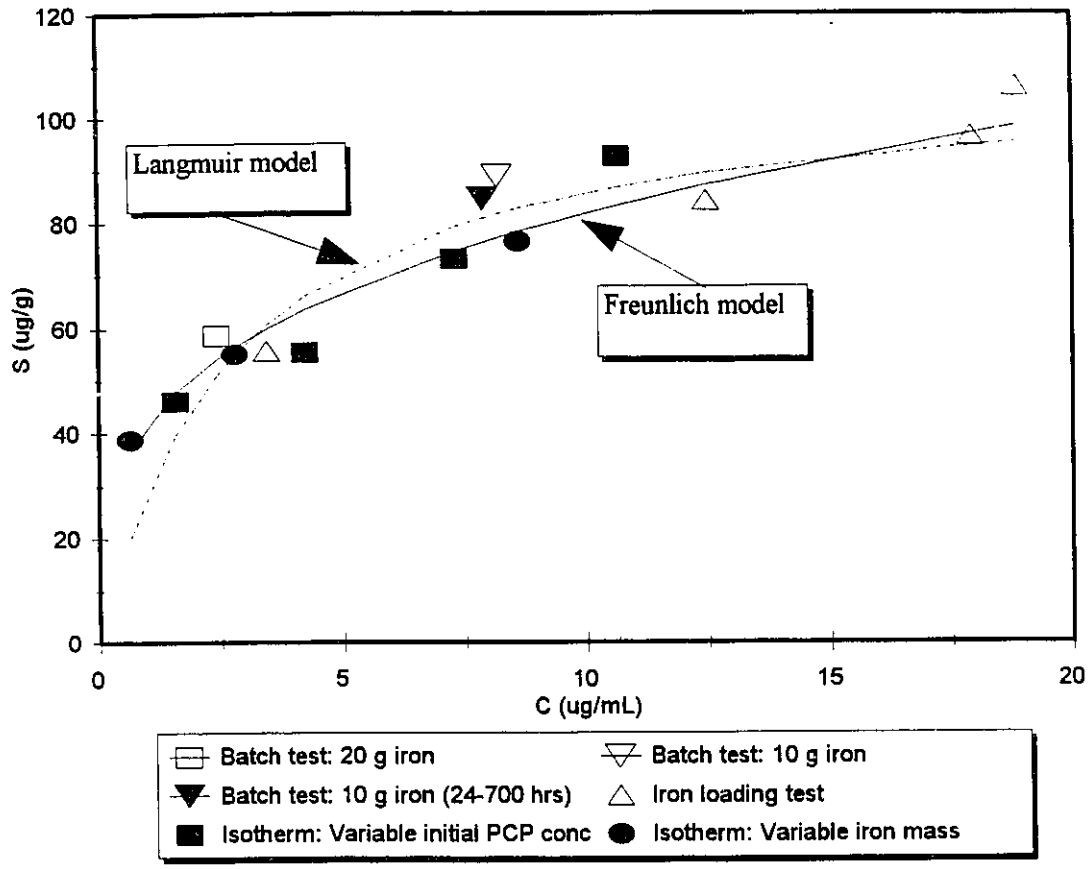


Figure 10 : Combined isotherm
PCP concentrations at equilibrium from six tests
Adsorption model fitting (Langmuir and Freunlich)

APPENDIX A

CALCULATION OF THE ERRORS BETWEEN ANALYTICAL HPLC RUNS AND BETWEEN REPLICATE HYPOVIALS ANALYSIS OF VARIANCE

Analytical error on HPLC

The error produced by the HPLC was estimated with standards. For each analysis run, PCP standards of concentration 1, 5, 10, and 20 mg/L were analyzed. The measured concentration obtained for the standards were compared to the known concentration of the standard. The difference was used to calculate the standard deviation and the 95% confidence intervals. The standard deviation was estimated as the root mean squared deviation between a measured and a known concentration.

The deviations between the measured standard concentration and the known value are called residuals and are plotted on graph APX-1. From the graph, the deviations appeared to be randomly distributed about the known values except at low concentrations (1 mg/L). The coefficients of variability (cv), defined as the ratio of the standard deviation to the mean, varied between 8.2 % at 20 mg/L and 14.3 % at 10 mg/L. Because of the random distribution of the residuals and the consistency of cv, no systematic adjustment was made to the data prior to additional statistical calculations.

Analysis of variance (ANOVA) was also performed on PCP concentration results for all experiments to determine factors affecting the variability. Hierarchal ANOVA were performed on four PCP concentration groups namely, 5 mg/L, 10 mg/L, 15 mg/L and 20 mg/L (see ANOVA tables). Factors affecting the variability of PCP concentrations were the analysis duplicates, bottle replicates, number of samples and HPLC runs. Results showed that for three PCP concentration groups (10-15-20 mg/L), the HPLC runs and the number of samples were the most important factors affecting the variability of the PCP concentration. Analysis duplicates contributed the least to the overall variability.

From this analysis, it is clear that the analysis run produces a major source of error. The quality of data measured on HPLC could therefore be improved by insuring that numbers that are to be compared are analyzed in the same run.

For experiments where samples were analyzed over several analysis runs, the error at each concentration was estimated using the variability between all the standards of that concentration measured over the course of this study. For experiments, where samples were analyzed all in one analysis run, the error was estimated from replicate hypovials. The detailed calculations are given in the following tables.

Calculation of significance

Throughout the text in the thesis statements concerning the significance of a relationship are followed by a parenthesis containing the null hypothesis and critical level of the test. To do the test, the mean is compared to a number or compared to another mean, according to the

hypothesis to test. Then, the statistic is calculated and compared to the statistic found in the student's distribution (details on the theory are presented in Scherrer, 1984).

For example, in the case where we want to verify if the concentration of PCP after 192 hours is significantly different than zero, a null hypothesis is made; Ho: concentration of PCP (C) = 0. The statistical test allows us to reject the null hypothesis with a probability P of committing an error in doing so. In this case, the calculation of the statistic (t) permitted to state that the concentration of PCP is different than zero with 99.5% confidence meaning that there is 0.5% probability (P=0.005) of falsely rejecting Ho. Thus the statement would read: " The concentration at T = 192 hours was significantly different than zero (Ho : C = 0; P = 0.005)". The contents of the parenthesis should be interpreted as " there is a probability P (= 0.005) of incorrectly rejecting Ho (C = 0).

CALCULATION OF THE ERROR CAUSED BY THE HPLC RUNS
USING MEASURED PCP STANDARDS ALL STANDARDS MEASUREMENTS REPORTED

1 ppm

STANDARDS	MEASURED STANDARDS	(xi-X)^2
1	0.57	0.1849
1	0.42	0.3364
1	0.48	0.2704
1	0.36	0.4096
1	0.55	0.2025
1	0.53	0.2209
1	0.55	0.2025
1	0.52	0.2304
1	0.59	0.1681
1	0.32	0.4624
1	0.48	0.2704
1	0.23	0.5929
1	0.1	0.81
13		
sum (xi-X)^2		4.361
sum (xi-X)^2/n		0.335
std dev		0.579
95% int		**0.286**
CV (%)		57.92

5 ppm

STANDARD	MEASURED STANDARD	(xi-X)^2
5	4.40	0.36
5	4.25	0.5625
5	4.37	0.3969
5	4.23	0.5929
5	3.77	1.5129
5	4.60	0.16
5	4.93	0.0049
5	4.97	0.0009
5	5.53	0.2809
5	4.95	0.0025
5	4.80	0.04
5	4.79	0.0441
5	5.80	0.64
5	4.80	0.04
5	4.81	0.0361
5	4.77	0.0529
5	4.17	0.6889
5	3.99	1.0201
5	4.73	0.0729
5	4.14	0.7396
5	3.86	1.2996
5	5.57	0.3249
5	5.50	0.25
5	6.21	1.4641
5	5.42	0.1764
5	4.71	0.0841
5	4.64	0.1296
5	5.12	0.0144
5	4.22	0.6084
5	5.07	0.0049
30		
sum (xi-X)^2		11.605
sum (xi-X)^2/n		0.387
std dev		0.622
95% int		**0.193**
CV (%)		12.439

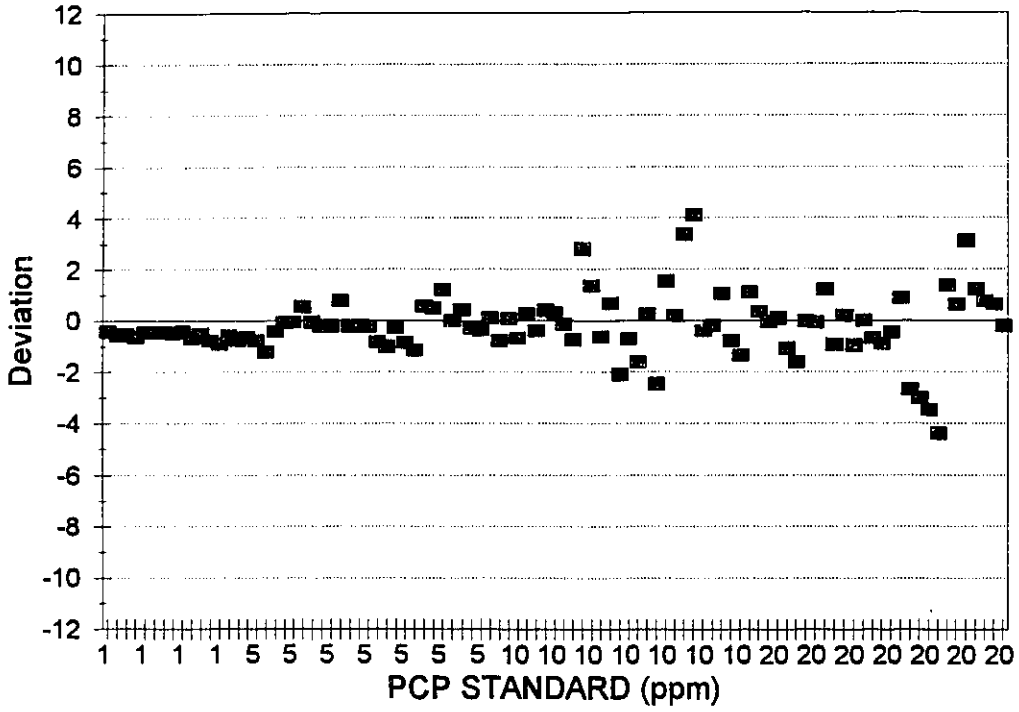
10 ppm

STANDARD	MEASURED STANDARDS	(xi-X)^2
10	9.31	0.4761
10	10.27	0.0729
10	9.62	0.1444
10	10.41	0.1681
10	10.29	0.0841
10	9.85	0.0225
10	9.25	0.5625
10	12.80	7.84
10	11.36	1.8496
10	9.37	0.3969
10	10.66	0.4356
10	7.90	4.41
10	9.30	0.49
10	8.39	2.5921
10	10.24	0.0576
10	7.53	6.1009
10	11.53	2.3409
10	10.21	0.0441
10	14.11	16.8921
10	9.61	0.1521
10	9.82	0.0324
10	11.05	1.1025
10	9.21	0.6241
10	8.64	1.8496
24		
sum (xi-X)^2		48.741
sum (xi-X)^2/n		2.031
std dev		1.425
95% int		**0.498**
CV (%)		14.251

20 ppm

STANDARD	MEASURED STANDARD	(xi-X)^2
20	21.12	1.2544
20	20.36	0.1296
20	19.97	0.0009
20	20.10	0.01
20	18.90	1.21
20	18.38	2.6244
20	19.99	0.0001
20	19.93	0.0049
20	21.22	1.4884
20	19.05	0.9025
20	20.20	0.04
20	19.04	0.9216
20	19.32	0.4624
20	19.09	0.8281
20	19.53	0.2209
20	20.88	0.7744
20	17.32	7.1824
20	16.98	9.1204
20	16.51	12.1801
20	15.62	19.1844
20	21.39	1.9321
20	20.65	0.4225
20	23.11	9.6721
20	21.24	1.5376
20	20.75	0.5625
20	20.64	0.4096
20	19.79	0.0441
27		
sum (xi-X)^2		73.120
sum (xi-X)^2/n		2.708
std dev		1.646
95% int		**0.539**
CV (%)		8.228

The 95 % confidence intervals for the standards were calculated for each concentration level for experiments where the PCP samples were analyzed in more than one HPLC run (batch tests, extraction tests, iron loading tests, iron to solution ratio tests)



Graph APX-1-1 : Deviation from standard for errors between analytical run

Calculation of the errors between analyses and between replicates

The 95 % confidence interval calculated between replicates is attributed to PCP concentrations that were analyzed in one HPLC run (adsorption experiments)

Between analyses

0-2.5 mg/L		PCP (mg/L)	AVG PCP	(xi-X)^2	Sum (xi-X)^2/ n-1	std deviation	CV (%)
rep	a1	2.82	2.81	0.0001	0.0002	0.014142	0.5033
	a2	2.8		1E-04			
	a1	2.94	2.97	0.0009	0.0018	0.042426	1.4285
	a2	3		0.0009			
rep	a1	0.84	0.84	0	0	0	0.0000
	a2	0.84		0			
	a1	0.82	0.82	0	0	0	0.0000
	a2	0.82		0			
rep	a1	2.47	2.45	0.0004	0.0008	0.028284	1.1545
	a2	2.43		0.0004			
	a1	2.28	2.2	0.0064	0.0128	0.113137	5.1426
	a2	2.12		0.0064			
	a1	2.31	2.3	0.0001	0.0002	0.014142	0.6149
	a2	2.29		1E-04			
rep	a1	2.15	2.075	0.005625	0.01125	0.106066	5.1116
	a2	2		0.005625			
	a1	2.04	2.085	0.002025	0.00405	0.06364	3.0523
	a2	2.13		0.002025			
	a1	2.1	2.115	0.000225	0.00045	0.021213	1.0030
	a2	2.13		0.000225			
rep	A1	1.72	1.715	2.5E-05	5E-05	0.007071	0.4123
	A2	1.71		2.5E-05			
	A1	1.48	1.415	0.004225	0.00845	0.091924	6.4964
	A2	1.35		0.004225			
rep	A1	0.04	0.04	0	0	0	0.0000
	A2	0.04		0			
	A1	0	0	0	0	0	0.0000
	A2	0		0			
		28		0.04005			

Between replicates

AVG PCP	(xi-X)^2	Sum (xi-X)^2/ n-1	std deviation	CV (%)
2.89	0.0049	0.0092	0.0959	3.3189
	0.0081			
	0.0025			
	0.0121			
0.83	0.0001	0.0001	0.0115	1.39
	0.0001			
	0.0001			
	0.0001			
2.31667	0.0235111	0.0154	0.1242	5.36
	0.0128444			
	0.0013444			
	0.0386778			
	4.44E-05			
	0.0007111			
2.09167	0.0034028	0.0035	0.0591	2.83
	0.0084028			
	0.0026694			
	0.0014694			
	6.94E-05			
	0.0014694			
1.565	0.024025	0.0328	0.1812	11.58
	0.021025			
	0.007225			
	0.046225			
0.02	0.0004	0.0005	0.0231	115.47
	0.0004			
	0.0004			
	0.0004			

Calculation of the errors between analyses and between replicates

2.5 - 7.5 mg/L		PCP (mg/L)	AVG PCP	(xi-X)^2	Sum (xi-X)^2/ n-1	std deviation	CV (%)	AVG PCP	(xi-X)^2	Sum (xi-X)^2/ n-1	std deviation	CV (%)
rep	a1	4.25	4.245	2.5E-05	5E-05	0.007071	0.1666	4.705	0.2070	0.2200	0.4691	9.9697
	a2	4.24		2.5E-05					0.2162			
	a1	4.61	4.595	0.000225	0.00045	0.021213	0.4617		0.0090			
	a2	4.58		0.000225					0.0156			
	a1	5.24	5.275	0.001225	0.00245	0.049497	0.9383		0.2862			
	a2	5.31		0.001225					0.3660			
rep	a1	3.55	3.525	0.000625	0.00125	0.035355	1.0030	3.56167	0.0001	0.1185	0.3443	9.6666
	a2	3.50		0.000625					0.0038			
	a1	3.92	3.92	0	0	0	0.0000		0.1284			
	a2	3.92		0					0.1284			
	a1	3.49	3.24	0.0625	0.125	0.353553	10.9121		0.0051			
	a2	2.99		0.0625					0.3268			
rep	a1	2.57	2.57	0	0	0	0.0000	2.78333	0.0455	0.0328	0.1812	6.5095
	a2	2.57		0					0.0455			
	a1	2.94	2.97	0.0009	0.0018	0.042426	1.4285		0.0245			
	a2	3		0.0009					0.0469			
	a1	2.82	2.81	0.0001	0.0002	0.014142	0.5033		0.0013			
	a2	2.8		1E-04					0.0003			
rep	a1	3.03	2.925	0.011025	0.02205	0.148492	5.0767	2.975	0.0030	0.0060	0.0771	2.5928
	a2	2.82		0.011025					0.0240			
	a1	3	3	0	0	0	0.0000		0.0006			
	a2	3		0					0.0006			
	a1	2.99	3	1E-04	0.0002	0.014142	0.4714		0.0002			
	a2	3.01		1E-04					0.0012			
rep	a1	2.39	2.385	2.5E-05	5E-05	0.007071	0.2965	3.42667	1.0747	0.7829	0.8848	25.8216
	a2	2.38		2.5E-05					1.0955			
	a1	3.59	3.545	0.002025	0.00405	0.06364	1.7952		0.0267			
	a2	3.5		0.002025					0.0054			
	a1	4.41	4.35	0.0036	0.0072	0.084853	1.9506		0.9669			
	a2	4.29		0.0036					0.7453			
rep	A1	4.25	4.25	0	0	0	0.0000	4.2225	0.0008	0.0070	0.0838	1.9850
	A2	4.25		0					0.0008			
	A1	4.29	4.195	0.009025	0.01805	0.13435	3.2026		0.0046			
	A2	4.1		0.009025					0.0150			
		34		0.1828								

7.5 - 15 mg/L		PCP (mg/L)	AVG PCP	(xi-X)^2	Sum (xi-X)^2/ n-1	std deviation	CV (%)	AVG PCP	(xi-X)^2	Sum (xi-X)^2/ n-1	std deviation	CV (%)
rep	a1	15.94	15.91	0.0009	0.0018	0.042426	0.2667	15.895	0.0020	0.0010	0.0311	0.1956
	a2	15.88		0.0009					0.0002			
	a1	15.89	15.88	0.0001	0.0002	0.014142	0.0891		0.0000			
	a2	15.87		1E-04					0.0006			
rep	a1	13.52	13.475	0.002025	0.00405	0.06364	0.4723	13.575	0.0030	0.0148	0.1218	0.8972
	a2	13.43		0.002025					0.0210			
	a1	13.69	13.675	0.000225	0.00045	0.021213	0.1551		0.0132			
	a2	13.66		0.000225					0.0072			
rep	a1	11.21	11.27	0.0036	0.0072	0.084853	0.7529	11.08	0.0169	0.0506	0.2249	2.0302
	a2	11.33		0.0036					0.0625			
	a1	10.90	10.89	1E-04	0.0002	0.014142	0.1299		0.0324			
	a2	10.88		1E-04					0.0400			
rep	a1	9.85	9.865	0.000225	0.00045	0.021213	0.2150	10.005	0.0240	0.0276	0.1662	1.6615
	a2	9.88		0.000225					0.0156			
	a1	10.19	10.145	0.002025	0.00405	0.06364	0.6273		0.0342			
	a2	10.1		0.002025					0.0090			
rep	a1	8.19	8.19	0	0	0	0.0000	8.3575	0.0281	0.0378	0.1945	2.3271
	a2	8.19		0					0.0281			
	a1	8.55	8.525	0.000625	0.00125	0.035355	0.4147		0.0371			
	a2	8.5		0.000625					0.0203			
rep	a1	8.07	8.13	0.0036	0.0072	0.084853	1.0437	7.9725	0.0095	0.0356	0.1887	2.3675
	a2	8.19		0.0036					0.0473			
	a1	7.8	7.815	0.000225	0.00045	0.021213	0.2714		0.0298			
	a2	7.83		0.000225					0.0203			

rep	a1	8.47	7.885	0.342225	0.68445	0.827315	10.4923	7.90667	0.3173	0.2175	0.4664	5.8991
	a2	7.3		0.342225					0.3680			
	a1	8.31	7.88	0.1849	0.3698	0.608112	7.7172		0.1627			
	a2	7.45		0.1849					0.2085			
	a1	8.07	7.955	0.013225	0.02645	0.162635	2.0444		0.0267			
	a2	7.84		0.013225					0.0044			
rep	a1	10.97	10.84	0.0169	0.0338	0.183848	1.6960	12.47	2.2500	1.7977	1.3408	10.7521
	a2	10.71		0.0169					3.0976			
	a1	12.75	12.79	0.0016	0.0032	0.056569	0.4423		0.0784			
	a2	12.83		0.0016					0.1296			
	a1	13.76	13.78	0.0004	0.0008	0.028284	0.2053		1.6641			
	a2	13.8		0.0004					1.7689			
rep	a1	12.1	12.215	0.013225	0.02645	0.162635	1.3314	12.4725	0.1388	0.0989	0.3145	2.5213
	a2	12.33		0.013225					0.0203			
	a1	12.78	12.73	0.0025	0.005	0.070711	0.5555		0.0946			
	a2	12.68		0.0025					0.0431			
rep	a1	8.55	8.525	0.000625	0.00125	0.035355	0.4147	8.3575	0.0371	0.0378	0.1945	2.3271
	a2	8.5		0.000625					0.0203			
	a1	8.19	8.19	0	0	0	0.0000		0.0281			
	a2	8.19		0					0.0281			
rep	A1	10.89	10.89	0	0	0	0.0000	10.645	0.0600	0.1286	0.3587	3.3692
	A2	10.89		0					0.0600			
	A1	10.67	10.4	0.0729	0.1458	0.381838	3.6715		0.0006			
	A2	10.13		0.0729					0.2652			
rep	A1	7.27	7.27	0	0	0	0.0000	7.28	0.0001	0.0114	0.1068	1.4666
	A2	7.27		0					0.0001			
	A1	7.42	7.29	0.0169	0.0338	0.183848	2.5219		0.0196			
	A2	7.16		0.0169					0.0144			
		52		1.3581								

15 - 25 mg/L		PCP (mg/L)	AVG PCP	(xi-X)^2	Sum (xi-X)^2/ n-1	std deviation	CV (%)	AVG PCP	(xi-X)^2	Sum (xi-X)^2/ n-1	std deviation	CV (%)
rep	a1	23.20	23.235	0.001225	0.00245	0.049497	0.2130	22.99	0.0441	0.1350	0.3674	1.5982
	a2	23.27		0.001225					0.0784			
	a1	22.46	22.745	0.081225	0.16245	0.403051	1.7720		0.2809			
	a2	23.03		0.081225					0.0016			
rep	a1	22.95	22.955	2.5E-05	5E-05	0.007071	0.0308	22.9925	0.0018	0.0025	0.0499	0.2171
	a2	22.96		2.5E-05					0.0011			
	a1	23.06	23.03	0.0009	0.0018	0.042426	0.1842		0.0046			
	a2	23.00		0.0009					0.0001			
rep	a1	23.18	23.1	0.0064	0.0128	0.113137	0.4898	23.16	0.0004	0.0107	0.1036	0.4473
	a2	23.02		0.0064					0.0196			
	a1	23.17	23.22	0.0025	0.005	0.070711	0.3045		0.0001			
	a2	23.27		0.0025					0.0121			
rep	a1	23.08	23.01	0.0049	0.0098	0.098995	0.4302	22.9275	0.0233	0.0264	0.1624	0.7081
	a2	22.94		0.0049					0.0002			
	a1	22.99	22.845	0.021025	0.04205	0.205061	0.8976		0.0039			
	a2	22.7		0.021025					0.0518			
rep	a1	19.81	19.765	0.002025	0.00405	0.06364	0.3220	19.845	0.0012	0.0099	0.0995	0.5014
	a2	19.72		0.002025					0.0156			
	a1	19.92	19.925	2.5E-05	5E-05	0.007071	0.0355		0.0056			
	a2	19.93		2.5E-05					0.0072			
rep	a1	20	19.975	0.000625	0.00125	0.035355	0.1770	19.925	0.0056	0.0038	0.0614	0.3080
	a2	19.95		0.000625					0.0006			
	a1	19.87	19.875	2.5E-05	5E-05	0.007071	0.0356		0.0030			
	a2	19.88		2.5E-05					0.0020			
rep	a1	21.77	21.76	0.0001	0.0002	0.014142	0.0650	21.7767	0.0000	0.0380	0.1949	0.8950
	a2	21.75		1E-04					0.0007			
	a1	21.76	21.605	0.024025	0.04805	0.219203	1.0146		0.0003			
	a2	21.45		0.024025					0.1067			
	a1	22.04	21.965	0.005625	0.01125	0.106066	0.4829		0.0663			
	a2	21.89		0.005625					0.0128			
rep	a1	22.02	21.995	0.000625	0.00125	0.035355	0.1607	21.915	0.0110	0.0327	0.1807	0.8248
	a2	21.97		0.000625					0.0030			
	a1	21.96	21.755	0.042025	0.08405	0.289914	1.3326		0.0020			
	a2	21.55		0.042025					0.1332			
	a1	21.97	21.995	0.000625	0.00125	0.035355	0.1607		0.0030			
	a2	22.02		0.000625					0.0110			

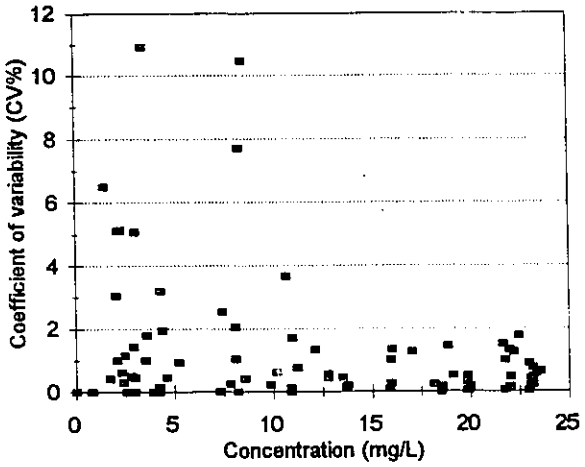
rep	a1	23.57	23.46	0.0121	0.0242	0.155563	0.6631	23.4033	0.0278	0.0217	0.1475	0.6301
	a2	23.35		0.0121					0.0028			
	a1	23.17	23.295	0.015625	0.03125	0.176777	0.7589		0.0544			
	a2	23.42		0.015625					0.0003			
	a1	23.36	23.455	0.009025	0.01805	0.13435	0.5728		0.0019			
	a2	23.55		0.009025					0.0215			
rep	a1	17.02	17.175	0.024025	0.04805	0.219203	1.2763	17.955	0.8742	0.3997	0.6322	3.5210
	a2	17.33		0.024025					0.3906			
	a1	18.14	18.17	0.0009	0.0018	0.042426	0.2335		0.0342			
	a2	18.2		0.0009					0.0600			
	a1	18.54	18.52	0.0004	0.0008	0.028284	0.1527		0.3422			
	a2	18.5		0.0004					0.2970			
rep	a1	18.5	18.5	0	0	0	0.0000	18.845	0.1190	0.0886	0.2977	1.5798
	a2	18.5		0					0.1190			
	a1	18.83	19.025	0.038025	0.07605	0.275772	1.4495		0.0002			
	a2	19.22		0.038025					0.1406			
	a1	19.08	19.01	0.0049	0.0098	0.098995	0.5208		0.0552			
	a2	18.94		0.0049					0.0090			
rep	a1	21.65	21.42	0.0529	0.1058	0.325269	1.5185	21.7075	0.0033	0.1708	0.4133	1.9040
	a2	21.19		0.0529					0.2678			
	a1	22.19	21.995	0.038025	0.07605	0.275772	1.2538		0.2328			
	a2	21.8		0.038025					0.0086			
rep	a1	19.81	19.805	2.5E-05	5E-05	0.007071	0.0357	19.7975	0.0002	0.0034	0.0580	0.2927
	a2	19.8		2.5E-05					0.0000			
	a1	19.86	19.79	0.0049	0.0098	0.098995	0.5002		0.0039			
	a2	19.72		0.0049					0.0060			
rep	a1	16	15.85	0.0225	0.045	0.212132	1.3384	15.9525	0.0023	0.0378	0.1945	1.2192
	a2	15.7		0.0225					0.0638			
	a1	15.94	16.055	0.013225	0.02645	0.162635	1.0130		0.0002			
	a2	16.17		0.013225					0.0473			
		66		0.861								

Between analyses

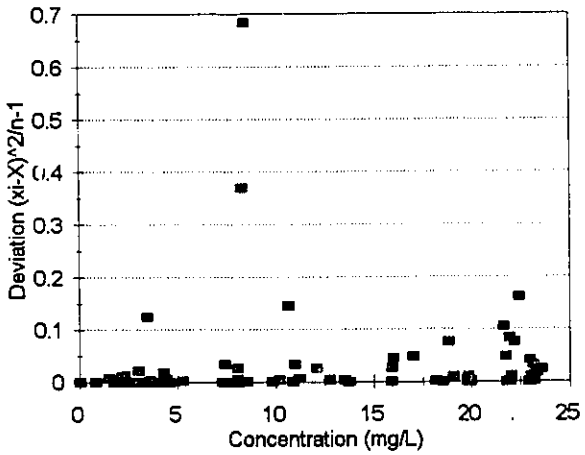
		Sum (xi-X)^2/ n-1	std deviation	CV (%)	95% conf int.
Sum:	Sum total / n classe	0.0271	0.1647	**1.4155**	**0.0344**

Between replicates

	Sum (xi-X)^2/ n-	std deviation	CV (%)	95% conf int.
Sum n-nclass	0.1518	0.3896	**3.3483**	**0.0813**



a)



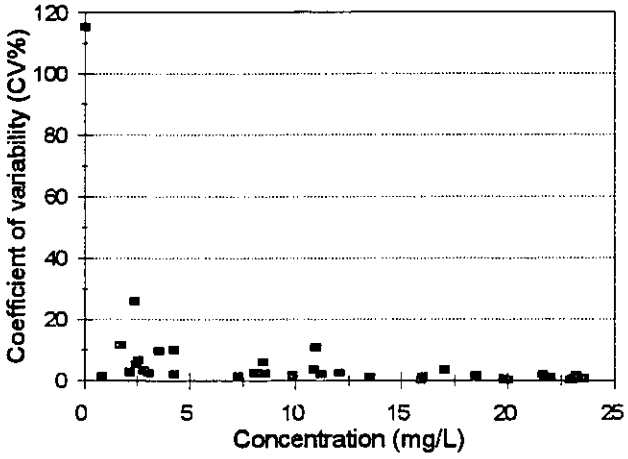
b)

Graph APX-1-2 : Calculation of the PCP concentration errors between analyses

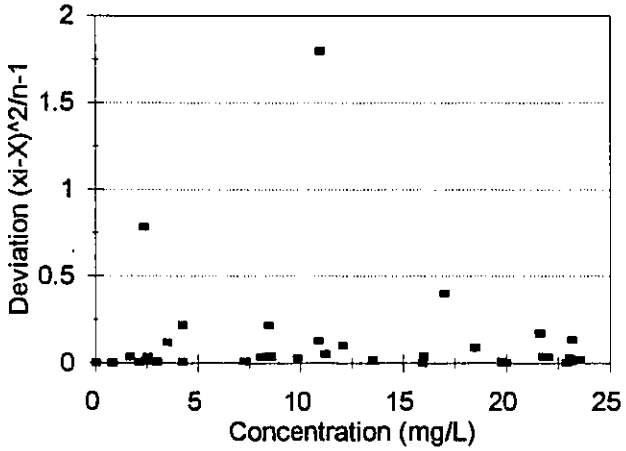
a) CV vs PCP concentration

b) Deviation vs PCP concentration

a)



b)



Graph APX-1-3 Calculation of the PCP concentration errors between replicates
a) CV vs PCP concentration
b) Deviation vs PCP concentration

ANOVA FOR PCP CONCENTRATIONS

Analytical runs	All Concentration		Analyses PCP	Analyses ^2	Replicate	Sample	Run	Total
Run 1	rep 1	a1	4.24	17.9776	36.04005	131.508	247.0865	
		a2	4.25	18.0625				
	rep 2	a1	4.61	21.2521	41.9528			
		a2	4.55	20.7025				
	rep 3	a1	5.24	27.4576	54.4968			
		a2	5.2	27.04				
	rep 1	a1	3.55	12.6025	25.56125	80.44682		
		a2	3.6	12.96				
	rep 2	a1	3.92	15.3664	30.2642			
		a2	3.86	14.8996				
	rep 3	a1	3.49	12.1801	24.7808			
		a2	3.55	12.6025				
	rep 1	a1	2.57	6.6049	12.85245	46.09282		
		a2	2.5	6.25				
	rep 2	a1	2.94	8.6436	17.6418			
		a2	3	9				
	rep 3	a1	2.82	7.9524	15.7922			
		a2	2.8	7.84				
Run 2	rep 1	a1	3.03	9.1809	17.11125	53.22282	53.22282	
		a2	2.82	7.9524				
	rep 2	A1	3	9	18.1202			
		A2	3.02	9.1204				
	rep 3	A1	2.99	8.9401	18			
		A2	3.01	9.0601				
Run 3	rep 1	A1	2.39	5.7121	11.37645	70.45227	70.45227	
		A2	2.38	5.6644				
	rep 2	A1	3.59	12.8881	25.13405			
		A2	3.5	12.25				
	rep 3	a1	4.41	19.4481	37.845			
		a2	4.29	18.4041				
Run 4	rep 1	a1	4.1	16.81	34.445	69.5556	69.5556	
		a2	4.2	17.64				
	rep 2	a1	4.29	18.4041	35.1122			
		a2	4.09	16.7281				

# data:	34	sum x2=	sum =	sum =	sum =	sum =
		456.597	456.5265	451.2783	440.3171	436.33
		sum dl=	sum dl=	sum dl=	sum dl=	sum dl=
		17	11	2	3	33

ANOVA

Sources of variability	Sum of Squares RAW		Correction	Sum of square corrected	Degrees freedom	Mean Square	Expected Mean Square
HPLC RUNS	A =	440.32	-E	3.99	3	1.330	0.000
SAMPLES	B =	451.28	-A	10.96	2	5.480	0.878
REPLICATES	C =	456.53	-B	5.25	11	0.477	0.237
ANALYSIS	D =	456.6	-C	0.07	17	0.004	0.004
TOTAL	E =	436.33	**SUM:**	20.27	33		

Ho : HPLC runs have no effect on PCP concentrations

$$F = \frac{1.33}{5.48} \quad \mathbf{0.242701} \quad < \quad F_{3,2,0.05} \quad \mathbf{19.16}$$

we can not reject Ho Effect of runs is not significant

Ho : Bottle samples have no effect on PCP concentrations

$$F = \frac{5.48}{0.477} \quad \mathbf{11.48847} \quad > \quad F_{2,11,0.05} \quad \mathbf{3.98}$$

we can reject Ho

Ho : Replicates have no effect on PCP concentrations

$$F = \frac{0.477}{0.004} \quad \mathbf{119.25} \quad > \quad F_{11,17,0.05} \quad \mathbf{2.41}$$

we can reject Ho

Sources of error on PCP concentrations in order of importance

1- **SAMPLES**
2- **REPLICATES**
3- **ANALYSES**
4- **RUNS**

Error caused by runs could not be shown to be significant at this concentration level

ANOVA FOR PCP CONCENTRATIONS

Analytical runs	All Concentration		PCP (mg/L)	Analyses ^2	Replicate	Sample	Run	Total
Run1	rep 1	a1	11.21	125.6641	254.0258	491.0656	491.0656	
		a2	11.33	128.3689				
	rep 2	a1	10.9	118.81	237.1842			
		a2	10.88	118.3744				
Run 2	rep 1	a1	10.19	103.8361	205.8421	402.4036	402.4036	
		a2	10.1	102.01				
	rep 2	a1	9.95	99.0025	196.6145			
		a2	9.88	97.6144				
Run 3	rep 1	a1	8.55	73.1025	145.3513	279.3912	533.3378	
		a2	8.5	72.25				
	rep 2	a1	8.19	67.0761	134.1522			
		a2	8.19	67.0761				
	rep 1	a1	8.07	65.1249	132.1938	254.243		
		a2	8.19	67.0761				
	rep 2	a1	7.8	60.84	122.1485			
		a2	7.83	61.3089				
Run 4	rep 1	a1	8.47	71.7409	142.2985	412.5104	412.5104	
		a2	8.4	70.56				
	rep 2	a1	8.31	69.0561	138.7778			
		a2	8.35	69.7225				
	rep 3	A1	8.07	65.1249	131.5442			
		A2	8.15	66.4225				
Run 5	rep 1	A1	10.97	120.3409	235.0112	933.0054	933.0054	
		A2	10.71	114.7041				
	rep 2	A1	12.75	162.5625	327.1682			
		A2	12.83	164.6089				
	rep 3	A1	13.76	189.3376	379.7768			
		A2	13.8	190.44				
Run 6	rep 1	a1	10.89	118.5921	236.7488	452.8384	1068.375	
		a2	10.87	118.1569				
	rep 2	a1	10.67	113.8489	216.32			
		a2	10.13	102.6169				
	rep 1	a1	12.1	146.41	298.4125	622.253		
		a2	12.33	152.0289				
	rep 2	a1	12.68	160.7824	324.1058			
		a2	12.78	163.3284				
		# data:	36	sum x2=	sum =	sum =	sum =	sum =
				3857.92	3857.676	3847.711	3840.698	3426.5
					sum dl=	sum dl=	sum dl=	sum dl=	sum dl=
					18	10	2	5	35

ANOVA

Sources of variability	Sum of Squares RAW		Correction	Sum of squa corrected	Degree freedom	Mean Square	sigma ^2
HPLC RUNS	A =	3840.7	-E	414.25	5	82.850	13.224
SAMPLES	B =	3847.71	-A	7.01	2	3.505	0.557
REPLICATES	C =	3857.68	-B	9.97	10	0.997	0.492
ANALYSIS	D =	3857.92	-C	0.24	18	0.013	0.013
TOTAL	E =	3426.45	**SUM:**	431.47	35		

Ho : HPLC runs have no effect on PCP concentrations

$$F = \frac{82.85}{3.505} \quad \mathbf{23.63766} \quad > \quad F_{5,2,0.05} \quad \mathbf{19.3}$$

we can reject Ho

Ho : Bottle samples have no effect on PCP concentrations

$$F = \frac{3.505}{0.997} \quad \mathbf{3.515547} \quad < \quad F_{2,10,0.0} \quad \mathbf{4.1}$$

we can not reject Ho

Ho : Replicates have no effect on PCP concentrations

$$F = \frac{0.997}{0.013} \quad \mathbf{76.69231} \quad > \quad F_{10,18,0.05} \quad \mathbf{2.41}$$

we can reject Ho

SOURCES OF ERROR ON PCP CONCENTRATIONS IN DECREASING ORDER

1- **RUNS**
2- **SAMPLES**
3- **REPLICATES**
4- **ANALYSES**

ANOVA FOR PCP CONCENTRATIONS

Analytical runs	All Concentration		PCP (mg/L)	Analyses ^2	Replicate	Sample	Run	Total
Run1	rep 1	a1	15.94	254.0836	507.5298	1011.876	1738.141	
		a2	15.92	253.4464				
	rep 2	a1	15.89	252.4921	504.3488			
		a2	15.87	251.8569				
	rep 1	a1	13.52	182.7904	363.1513	737.1225		
		a2	13.43	180.3649				
	rep 2	a1	13.69	187.4161	374.0113			
		a2	13.66	186.5956				
Run 2	rep 1	a1	17.02	289.6804	589.9613	1934.292	1934.292	
		a2	17.33	300.3289				
	rep 2	a1	18.14	329.0596	660.2978			
		a2	18.2	331.24				
	rep 3	a1	18.54	343.7316	685.9808			
		a2	18.5	342.25				
Run 3	rep 1	a1	19.08	364.0464	722.7602	2132.689	2132.689	
		a2	18.94	358.7236				
	rep 2	a1	18.83	354.5689	723.9013			
		a2	19.22	369.4084				
	rep 3	a1	18.5	342.25	686.3513			
		a2	18.55	344.1025				
Run 4	rep 1	A1	16	256	502.445	1017.929	1017.929	
		A2	15.7	246.49				
	rep 2	A1	15.94	254.0836	515.5261			
		A2	16.17	261.4689				
		# data:	24	sum x2=	sum =	sum =	sum =	sum =
				6836.479	6836.265	6833.909	6823.051	6752.9

ANOVA

			dl = 12	dl = 7	dl = 1	dl = 3	sum 23
Sources of variability	Sum of Squares RAW		Correction	Sum of squa corrected	Degree freedom	Mean Square	Expected Mean Square
HPLC RUNS	A =	6823.05	-E	70.11	3	23.370	2.085
SAMPLES	B =	6833.91	-A	10.86	1	10.860	2.192
REPLICATES	C =	6836.27	-B	2.36	7	0.337	0.160
ANALYSIS	D =	6836.48	-C	0.21	12	0.017	0.017
TOTAL	E =	6752.94	**SUM:**	83.54	23		

Ho : HPLC runs have no effect on PCP concentrations

$$F = \frac{23.37}{10.86} \quad \mathbf{2.151934} \quad < \quad F_{3,1,0.05} \quad \mathbf{215.17}$$

we can not reject Ho

Ho : Bottle samples have no effect on PCP concentrations

$$F = \frac{10.86}{0.337} \quad \mathbf{32.22552} \quad > \quad F_{1,7,0.05} \quad \mathbf{5.59}$$

we can reject Ho

Ho : Replicates have no effect on PCP concentrations

$$F = \frac{0.337}{0.017} \quad \mathbf{19.82353} \quad > \quad F_{7,12,0.05} \quad \mathbf{2.91}$$

we can reject Ho

SOURCES OF ERROR ON PCP CONCENTRATIONS BY DECREASING ORDER

1- **SAMPLES**
2- **REPLICATES**
3- **ANALYSES**

ANOVA FOR PCP CONCENTRATIONS

Analytical runs	All Concentration		PCP (mg/L)	Analyses ^2	Replicate	Sample	Run	Total
Run 1	rep 1	a1	22.46	504.4516	1034.67	2114.16	6374.247	
		a2	23.03	530.3809				
	rep 2	a1	23.2	538.24	1079.73			
		a2	23.27	541.4929				
	rep 1	a1	23.17	536.8489	1078.337	2145.542		
		a2	23.27	541.4929				
	rep 2	a1	23.18	537.3124	1067.22			
		a2	23.02	529.9204				
	rep 1	a1	22.95	526.7025	1053.864	2114.62		
		a2	22.96	527.1616				
	rep 2	a1	23.06	531.7636	1060.762			
		a2	23	529				
Run 2	rep 1	a1	23.08	532.6864	1058.92	2102.681	2102.681	
		a2	22.94	526.2436				
	rep 2	a1	22.99	528.5401	1043.788			
		a2	22.7	515.29				
Run 3	rep 1	a1	19.81	392.4361	781.3105	1575.296	3163.306	
		a2	19.72	388.8784				
	rep 2	a1	19.92	396.8064	794.0113			
		a2	19.93	397.2049				
	rep 1	a1	19.87	394.8169	790.0313	1588.023		
		a2	19.88	395.2144				
	rep 2	a1	20	400	798.0013			
		a2	19.95	398.0025				
Run 4	rep 1	a1	22.04	485.7616	978.5888	2743.482	5616.013	
		a2	22.2	492.84				
	rep 2	a1	21.76	473.4976	874.8745			
		a2	20.07	402.8049				
	rep 3	a1	21.77	473.9329	891.6865			
		a2	20.46	418.6116				
	rep 1	a1	21.97	482.6809	959.22	2873.282		
		a2	21.83	476.5489				
	rep 2	a1	21.96	482.2416	946.5601			
		a2	21.55	464.4025				
	rep 3	a1	21.97	482.6809	967.5601			
		a2	22.02	484.8804				
Run 5	rep 1	a1	23.36	545.6896	1100.274	3286.296	3286.296	
		a2	23.55	554.6025				
	rep 2	a1	23.17	536.8489	1085.314			
		a2	23.42	548.4964				
	rep 3	a1	23.57	555.5449	1100.743			
		a2	23.35	545.2225				
Run 6	rep 1	a1	21.65	468.7225	917.6328	1884.862	3445.33	
		a2	21.19	449.0161				
	rep 2	a1	22.19	492.3961	967.5601			
		a2	21.8	475.24				
	rep 1	a1	19.81	392.4361	784.4761	1567.764		
		a2	19.8	392.04				
	rep 2	a1	19.86	394.4196	783.2882			
		a2	19.72	388.8784				

# data:	50	sum x2=	sum =	sum =	sum =	sum =
		24001.32	23998.42	23996.01	23987.87	23910.47
		dl =	dl =	dl =	dl =	sum
		25	14	5	5	49
				70		

ANOVA

Sources of variability	Sum of Squares RAW		Correction	Sum of squa corrected	Degree freedom	Mean Square	Expected Mean Square
HPLC RUNS	A =	23987.87	-E	77.4	5	15.480	1.663
SAMPLES	B =	23996.01	-A	8.14	5	1.628	0.324
REPLICATES	C =	23998.42	-B	2.41	14	0.172	0.028
ANALYSIS	D =	24001.33	-C	2.91	25	0.116	0.116
TOTAL	E =	23910.47	**SUM:**	90.86	49		

Ho : HPLC runs have no effect on PCP concentrations

$$F = \frac{15.48}{1.628} \quad \mathbf{9.5086} \quad > \quad F_{5,5,0.05} \quad \mathbf{5.05}$$

we can reject Ho

Ho : Bottle samples have no effect on PCP concentrations

$$F = \frac{1.628}{0.172} \quad \mathbf{9.465116} \quad > \quad F_{5,14,0.05} \quad \mathbf{2.96}$$

we can reject Ho

Ho : Replicates have no effect on PCP concentrations

$$F = \frac{0.172}{0.116} \quad \mathbf{1.482759} \quad < \quad F_{14,25,0.05} \quad \mathbf{2.09}$$

we can not reject Ho

SOURCES OF ERROR ON PCP CONCENTRATIONS
IN DECREASING ORDER OF IMPORTANCE

1- **RUNS**
2- **SAMPLES**
3- **REPLICATES**
4- **ANALYSES**

APPENDIX B

DIAGRAMS OF EXPERIMENTAL DESIGN

1 - BATCH TESTS: ONE WAY CLASSIFICATION WITH NESTED ANALYSES

PCP	TIME (hrs)							
	T1		T2		...		Tn	
BLANK	Rep. 1	A1	Rep. 1	A1	Rep. 1	A1	Rep. 1	A1
		A2		A2		A2		A2
	Rep. 2	A1	Rep. 2	A1	Rep. 2	A1	Rep. 2	A1
		A2		A2		A2		A2
CONTROL	Rep. 1	A1	Rep. 1	A1	Rep. 1	A1	Rep. 1	A1
		A2		A2		A2		A2
	Rep. 2	A1	Rep. 2	A1	Rep. 1	A1	Rep. 1	A1
		A2		A2		A2		A2
REACTIVE	Rep. 1	A1	Rep. 1	A1	Rep. 1	A1	Rep. 1	A1
		A2		A2		A2		A2
	Rep. 2	A1	Rep. 2	A1	Rep. 2	A1	Rep. 2	A1
		A2		A2		A2		A2

Rep: replicates
A: analyses on HPLC

For PH and Eh, measurements were done for all Reactive hypovials, but for the Control and Blank hypovials, measurements were done at the beginning, middle and at the end of the experiment. Chloride analyses were done twice on two separate batch test experiments for most of the Reactive hypovial (early times to late times) and for few Control and Blank hypovials (beginning and end of experiment).

STATISTICAL MODEL:

$$X_{ijk} = \mu + X_i + X_{j(i)} + X_{k(j(i))}$$

i = Blank, Control, Reactive
j = Rep.1, Rep.2
k = A1, A2

2 - EXTRACTION TESTS: ONE WAY CLASSIFICATION WITH NESTED ANALYSES

FIRST AND SECOND EXTRACTION

PCP (mg/L)	TIME (hrs)							
	T1		T2		...		Tn	
BLANK	n.a.		n.a.		n.a.		n.a.	
	n.a.		n.a.		n.a.		n.a.	
CONTROL	n.a.		n.a.		n.a.		n.a.	
	n.a.		n.a.		n.a.		n.a.	
REACTIVE	Rep.1	A1	Rep. 1	A1	Rep. 1	A1	Rep. 1	A1
		A2		A2		A2		A2
	Rep. 2	A1	Rep. 2	A1	Rep. 2	A1	Rep. 2	A1
		A2		A2		A2		A2
	Rep. 3	A1	Rep. 3	A1	Rep. 3	A1	Rep. 3	A1
		A2		A2		A2		A2

n.a.: not applicable
Rep: replicates
A: analyses on HPLC

The methanol extraction was done on all Reactive hypovials.

STATISTICAL MODEL:

$$X_{ijk} = \mu + X_i + X_{j(i)} + X_{k(j(i))}$$

i = Blank, Control, Reactive
j = Rep.1, Rep.2
k = A1, A2

3- IRON LOADING TEST : MIXED RANDOM BLOCK / REPEATED SAMPLING

PCP		Refill			
		1	2	3	4
Reactive Hypovials	Rep. 1	A1	A1	A1	A1
		A2	A2	A2	A2
	Rep. 2	A1	A1	A1	A1
		A2	A2	A2	A2
	Rep. 3	A1	A1	A1	A1
		A2	A2	A2	A2

Rep: replicates
A: analyses on HPLC

PH and Eh measurements were taken from the three replicates for all refills.

STATISTICAL MODEL:

$$X_{ijl} = \mu + X_i + X_j + (X)_{ij} + X_{k(ij)}$$

i = Replicates (Rep.1, Rep.2, Rep.3)
j = Refills (1-2-3-4)
k = Analyses (A1-A2)

4- IRON TO SOLUTION RATIO TEST: MIXED 3-WAY FACTORIAL/ NESTED ANALYSES

PCP		TIME (hrs)							
		T1		T2		...		Tn	
0.17 g/mL	B	Rep.1	A1	Rep.1	A1	Rep. 1	A1	Rep. 1	A1
			A2		A2		A2		A2
		Rep.2	A1	Rep.2	A1	Rep. 2	A1	Rep. 2	A1
			A2		A2		A2		A2
	C	Rep.1	A1	Rep.1	A1	Rep. 1	A1	Rep. 1	A1
			A2		A2		A2		A2
		Rep.2	A1	Rep.2	A1	Rep. 1	A1	Rep. 1	A1
			A2		A2		A2		A2
	R	Rep.1	A1	Rep.1	A1	Rep. 1	A1	Rep. 1	A1
			A2		A2		A2		A2
		Rep.2	A1	Rep.2	A1	Rep. 2	A1	Rep. 2	A1
			A2		A2		A2		A2
0.35 g/mL	B	Rep. 1	A1	Rep.1	A1	Rep. 1	A1	Rep. 1	A1
			A2		A2		A2		A2
		Rep.2	A1	Rep.2	A1	Rep. 2	A1	Rep. 2	A1
			A2		A2		A2		A2
	C	Rep.1	A1	Rep.1	A1	Rep. 1	A1	Rep. 1	A1
			A2		A2		A2		A2
		Rep.2	A1	Rep.2	A1	Rep. 2	A1	Rep. 2	A1
			A2		A2		A2		A2
	R	Rep.1	A1	Rep.1	A1	Rep. 1	A1	Rep. 1	A1
			A2		A2		A2		A2
		Rep.2	A1	Rep.2	A1	Rep. 2	A1	Rep. 2	A1
			A2		A2		A2		A2

Rep: replicates
A: analyses on HPLC

Same as the batch test where the experiment was done twice with two iron to solution ratios.

Only PH measurements were done on all Reactive hypovials and on some Blank hypovials.

STATISTICAL MODEL

$$X_{ijklm} = \mu_x + X_i + X_j + X_k + (X)_{ij} + (X)_{ik} + (X)_{jk} + X_{l(ijk)} + X_{m(l(ijk))}$$

i = 0.17, 0.35
j = Reactive, Control, Blank
k = T1, T2, T3...Tn
l = Rep1, Rep2
m = A1, A2

5- SORPTION ISOTHERM :ONE WAY CLASSIFICATION WITH NESTED ANALYSES

Variation of iron mass (g)

	Iron mass (g)	After 44 hrs	
REACTIVE HYPOVIALS	1	Rep. 1	A1
			A2
		Rep. 2	A1
			A2
	2.5	Rep. 1	A1
			A2
		Rep. 2	A1
			A2
	5	Rep. 1	A1
			A2
		Rep. 2	A1
			A2
	7.5	Rep. 1	A1
			A2
		Rep. 2	A1
			A2
	10	Rep. 1	A1
			A2
		Rep. 2	A1
			A2
	20	Rep. 1	A1
			A2
		Rep. 2	A1
			A2
	30	Rep. 1	A1
			A2
		Rep. 2	A1
			A2
	50	Rep. 1	A1
			A2
		Rep. 2	A1
			A2

Rep. : Replicates; A1 : HPLC analyses

PH and Eh measurements were taken in all replicate 1 only.

STATISTICAL MODEL:

$$X_{ijk} = \mu + X_i + X_{j(i)} + X_{k(j(i))}$$

i = Blank, Control, Reactive; j = Rep.1, Rep.2; k = A1, A2

6- SORPTION ISOTHERM :ONE WAY CLASSIFICATION WITH NESTED ANALYSES

Variation of PCP concentrations

	PCP (mg/L)	After 44 hrs	
REACTIVE HYPOVIALS	5	Rep. 1	A1
			A2
		Rep. 2	A1
			A2
	10	Rep. 1	A1
			A2
		Rep. 2	A1
			A2
	15	Rep. 1	A1
			A2
		Rep. 2	A1
			A2
	20	Rep. 1	A1
			A2
		Rep. 2	A1
			A2
	25	Rep. 1	A1
			A2
		Rep. 2	A1
			A2

Rep. : Replicates
A1 : HPLC analyses

PH and Eh measurements were taken from all replicates.

STATISTICAL MODEL:

$$X_{ijk} = \mu + X_i + X_{j(i)} + X_{k(j(i))}$$

i = Blank, Control, Reactive
j = Rep.1, Rep.2
k = A1, A2

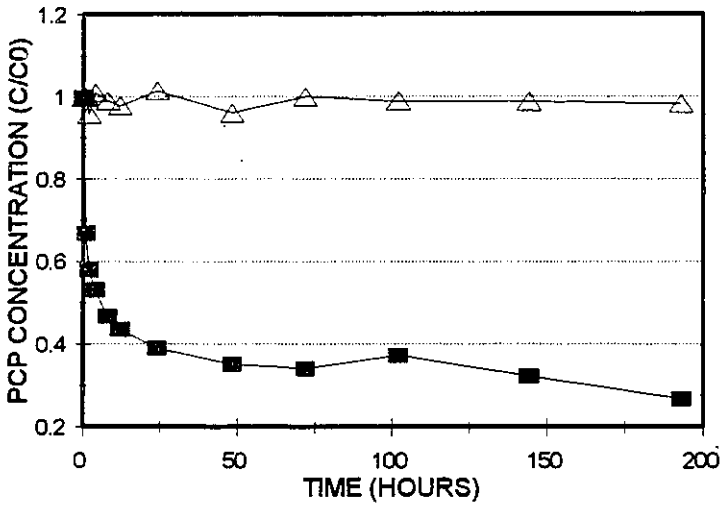
APPENDIX C

BATCH TEST RESULTS AND TABLES

EXPERIMENT # 1	DEGRADATION OF PCP AT 25 mg/l FOR 8 DAYS AT ROOM TEMPERATURE
(08-06-93)	WATER SOLUTION CONTAINED CALCIUM CARBONATE (CaCO3) 40 mg/L

SAMPLE	DESCRIPTION	IRON (g)	WATER (g)	RANK	TIME (HRS)	PCP (mg/l)	C/C0	pH	Cl-	TEMP °C	LN C/C0	PCP REMOVED	Cl - IN WATER
					0	24.38	1.00	7.1	1.7	21	0.0000	0	0.00
9	REACTIVE	9.737	59.199	1	1.00	16.28	0.67	10.0	2.4	22	-0.4038	8.1	5.39
2	"	10.010	58.893	2	2.00	14.13	0.58	10.1	6.48	22	-0.5455	10.25	6.82
6	"	9.934	59.285	3	4.00	12.98	0.53	10.2		23	-0.6304	11.4	7.59
8	"	9.737	59.220	4	8.00	11.41	0.47	9.9		23.5	-0.7593	12.97	8.63
10	"	9.900	59.180	5	12.00	10.62	0.44	10.1	6.6	24	-0.8310	13.76	9.16
5	"	10.209	59.944	6	24.00	9.51	0.39	10.3		24	-0.9414	14.87	9.90
11	"	10.149	57.606	7	48.33	8.57	0.35	10.3	4.98	28	-1.0455	15.81	10.52
1		9.987	57.362	8	71.67	8.31	0.34	10.3		21	-1.0763	16.07	10.70
7	"	9.819	59.183	9	101.92	9.1	0.37	10.1	4.38	21	-0.9855	15.28	10.17
3	"	10.003	57.569	10	144.33	7.85	0.32	10.1	10.86	16	-1.1332	16.53	11.00
4	"	10.214	58.069	11	192.83	6.54	0.27	10.2	4.26	20	-1.3158	17.84	11.87
C-11	IRON+H20	9.941	57.461	1	1.42			9.6		22			
C-9	"	9.948	58.385	2	2.42			9.8		22			
C-2	"	10.063	59.048	3	4.17			10.0	2.76	23			
C-6	"	9.894	58.311	4	8.17			10.0		23.5			
C-4	"	10.056	59.115	5	12.17			10.0		24			
C-10	"	10.125	57.736	6	24.17			10.0		24			
C-1	"	10.200	58.703	7	48.50			9.9	2.04	28			
C-3	"	10.014	57.630	8	72.17	N.D.		10.1		21			
C-7	"	10.201	58.293	9	102.35			9.9		21			
C-8	"	10.077	58.281	10	144.42		1	10.0		20			
C-5	"	9.883	59.126	11	193.25	24.38	1.00	10.0	1.8	16	0.0000		
C1-10	PCP+H20		60.725	1	1.42	23.36	0.96	-		22	-0.0427		
C1-9	"		58.981	2	2.42	24.64	1.01	7.2		22	0.0106		
C1-6	"		60.675	3	4.42	24.15	0.99	7.5		23	-0.0095		
C1-2	"		59.473	4	8.25	23.86	0.98	7.2		23.5	-0.0216		
C1-4	"		58.780	5	12.25	24.76	1.02	7.3		24	0.0155		
C1-8	"		59.737	6	24.25	23.43	0.96	7.3		24	-0.0397		
C1-11	"		60.853	7	48.70	24.4	1.00	7.3		28	0.0008		
C1-3	"		59.176	8	72.07	24.13	0.99	7.2		21	-0.0103		
C1-7	"		60.647	9	102.30	24.1	0.99	7.2		21	-0.0116		
C1-1	"		60.004	10	144.67	23.97	0.98	7.3		20	-0.0120		
C1-5	"		59.632	11	193.15	22.84	0.94	7.3		16	-0.0652		

a)



b)

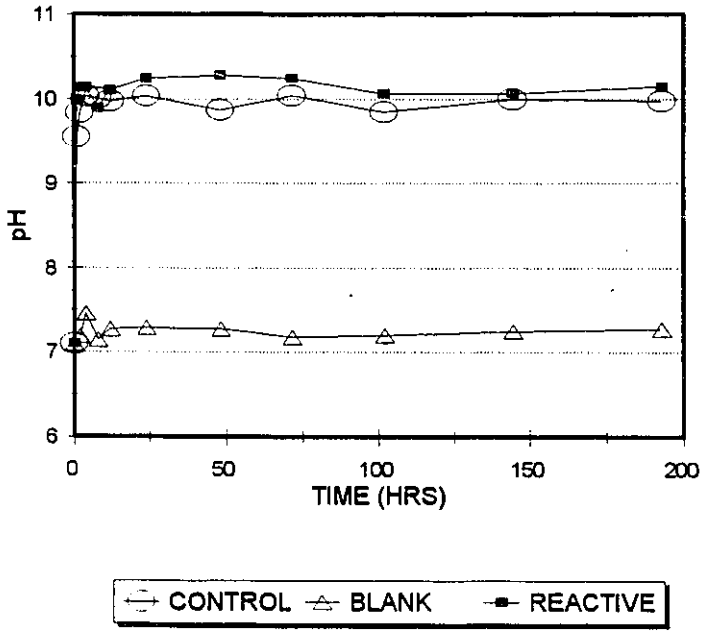


Figure APX-C-1: Batch test # 1: Water solution with CaCO3
a) PCP removal versus time
b) pH versus time

EXPERIMENT # 2 DEGRADATION OF PCP AT 22 mg/l FOR 29 DAYS AT ROOM TEMPERATURE

SAMPLE	DESCRIPTION	IRON (g)	WATER (g)	RANK	TIME (HRS)	PCP (mg/l)	C/CO	pH	LN C/CO	Cl-	TEMP °C
					0	21.73	1.00	7.0	0		22
					24	7.8	0.36	10.6	-1.0246		22
2	REACTIVE	10.040	58.614	1	59.00	8.59	0.40	10.5	-0.9287	5.35	21
4	"	9.899	57.839	2	120.00	8.37	0.38	10.3	-0.9546	4.04	22
10	head space	10.005	56.808	3	168.00	7.46	0.34	10.0	-1.0698	3.19	29
7	"	9.939	58.535	5	216.00	7.49	0.34	10.3	-1.0651	4.88	21
5	REACTIVE	9.036	57.754	4	216.00	8.05	0.37	10.0	-0.993	2.9	21
6	"	10.104	58.337	6	288.00	7.79	0.36	10.3	-1.0259	5.07	22
8	head space	9.925	56.558	7	360.00	7.51	0.35	10.4	-1.0625	3.42	22
1	REACTIVE	10.245	58.853	8	528.00	7.78	0.36	10.4	-1.0278	0.06	22
9	head space	9.934	56.960	9	624.00	7.72	0.36	10.4	-1.0349	3.33	21
3	REACTIVE	10.180	59.445	10	696.00	7.95	0.37	10.4	-1.0062	2.85	21
					0.00		0.00	7.0			
					24.00			9.9			
C-3	IRON+H20	9.928	59.224	1	59.00			9.9		2.95	21
C-5	"	9.982	58.571	2	120.00			10.2		0.28	22
C-10	"	10.040	57.450	3	168.00			10.2		3.73	29
C-6	"	9.948	57.815	4	216.00			10.1		2.27	21
C-7	"	9.949	59.207	5	216.00			10.1			21
C-2	"	10.023	57.729	6	288.00			10.2		2.33	22
C-8	"	10.110	57.371	7	360.00			10.5		3.15	22
C-4	"	9.902	59.004	8	528.00	—		10.3		1.41	22
C-9	"	10.050	55.501	9	624.00			10.4		0.83	21
C-1	"	10.062	58.316	10	696.00	—		10.2		0.1	21
					0.00	21.73	1	7.0	0		
					24.00	21.73	1.00	7.0	0		
K-6	PCP+H20	xxx	60.426	1	59.00	21.84	1.00	6.7	0.0048	0	21
K-2	"	xxx	61.567	2	120.00	21.90	1.01	7.0	0.0076	2.34	22
K-8	head space	xxx	58.670	3	168.00	21.75	1.00	6.8	0.0009		29
K-1	"	xxx	59.195	4	216.00	21.67	1.00	6.8	-0.003		21
K-7	"	xxx	60.679	5	216.00	21.61	0.99	6.8	-0.0055		21
K-5	"	xxx	60.488	6	288.00	22.52	1.04	7.1	0.0357	0	22
K-10	head space	xxx	58.144	7	360.00	22.33	1.03	6.7	0.0272	0	22
K-4	"	xxx	59.891	8	528.00	21.99	1.01	7.0	0.0117	3.64	22
K-9	head space	xxx	59.289	9	624.00	23.59	1.09	6.7	0.0821	0	21
K-3	PCP + H2O	xxx	60.052	10	696.00	23.26	1.07	6.9	0.0578	0	21
	"										

EXPERIMENT #3 DEGRADATION OF PCP AT 23 mg/l FOR 7 DAYS AT ROOM TEMPERATURE
(02 - 08 - 93)

SAMPLE	DESCRIP	IRON (g)	WATER (g)	TIME (hrs)	PCP (mg/l)	AVG PCP	C/C0	AVG C/CO	pH	AVG pH	Eh (mv)	AVG Eh	TEMP °C
INITIAL				0	23.02	23.02	1.00	1.00	6.6	6.6	253	253	23
21	REACTIVE	9.956	59.053	1.5	15.94	15.91	0.69	0.69	10.5	10.5	-5	-25	17
23	"	10.036	59.905	6.0	13.48	13.58	0.59	0.59	10.5	10.5	-30	-49	18
24	"	9.910	57.758	19.5	11.27	11.08	0.49	0.48	10.5	10.5	-75	-63	19
22	"	9.967	59.284	45.0	10.15	10.03	0.44	0.44	10.3	10.4	-160	-122	20
25	"	10.034	58.473	94.0	8.19	8.36	0.36	0.36	10.4	10.4	-160	-175	28
20	"	9.935	58.423	175.0	7.82	7.98	0.34	0.35	10.3	10.3	-353	-340	28
INITIAL	"			0.0	23.02		1.00		6.6		253		23
27	REACTIVE	10.004	58.834	1.5	15.88		0.69		10.5		-45		17
28	"	9.959	57.658	6.0	13.68		0.59		10.5		-68		18
31	"	10.034	58.215	19.5	10.89		0.47		10.5		-50		19
26	"	9.917	57.631	45.0	9.92		0.43		10.4		-83		20
29	"	9.985	59.157	94.0	8.53		0.37		10.4		-190		28
30	"	9.998	59.219	175.0	8.13		0.35		10.3		-327		28
INITIAL				0.0			0.00		7.0	7	210	210	23
C-23	IRON+H20	9.918	57.785	1.5			0.00		10.5	10.4	-48	-39	17
C-20	"	10.000	58.607	6.0			0.00		10.5	10.5	-16	-21	18
C-26	"	9.942	58.488	19.5			0.00		10.5	10.4	-24	-37	19
C-21	"	9.926	59.306	45.0			0.00		10.3	10.3	-118	-129	20
C-25	"	10.052	58.866	94.0			0.00		10.4	10.4	-221	-200	28
C-30	"	10.032	59.064	175.0	—		0.00		10.3	10.3	-360	-363	28
INITIAL	"			0.0			0.00						23
C-28	IRON+H20	10.029	59.011	1.5			0.00		10.4		-30		17
C-24	"	9.996	58.223	6.0			0.00		10.5		-25		18
C-29	"	10.052	58.322	19.5			0.00		10.4		-50		19
C-22	"	9.952	59.544	45.0			0.00		10.3		-140		20
C-27	"	10.036	59.509	94.0			0.00		10.4		-179		28
C-31	"	10.047	58.993	175.0	—		0.00		10.2		-366		28
INITIAL				0.0	23.02	23.02	1.00	1.00	6.6	6.6	253	253	23
K-23	PCP+H20	—	58.910	1.5	23.24	22.99	1.01	1.00	6.9	6.9	130	133	17
K-20	"	—	61.088	6.0	22.96	23.00	1.00	1.00	6.8	6.8	160	147	18
K-24	"	—	60.080	19.5	23.10	23.17	1.00	1.01	6.7	6.8	151	166	19
K-28	"	—	60.316	45.0	22.85	22.99	0.99	1.00	6.7	6.7	220	212	20
K-22	"	—	60.416	94.0	19.93	19.85	0.87	0.86	6.7	6.7	270	233	28
K-25	"	—	61.116	175.0	19.98	19.93	0.87	0.87	6.7	6.7	237	239	28
INITIAL				0.0	23.02		1.00						23
K-31	PCP+H20	—	60.066	1.5	22.75		0.99		6.8		136		17
K-21	"	—	60.646	6.0	23.04		1.00		6.8		133		18
K-29	"	—	59.639	19.5	23.23		1.01		6.8		180		19
K-30	"	—	60.053	45.0	23.14		1.01		6.7		204		20
K-27	"	—	60.744	94.0	19.77		0.86		6.7		196		28
K-26	"	—	60.139	175.0	19.88		0.86		6.7		240		28

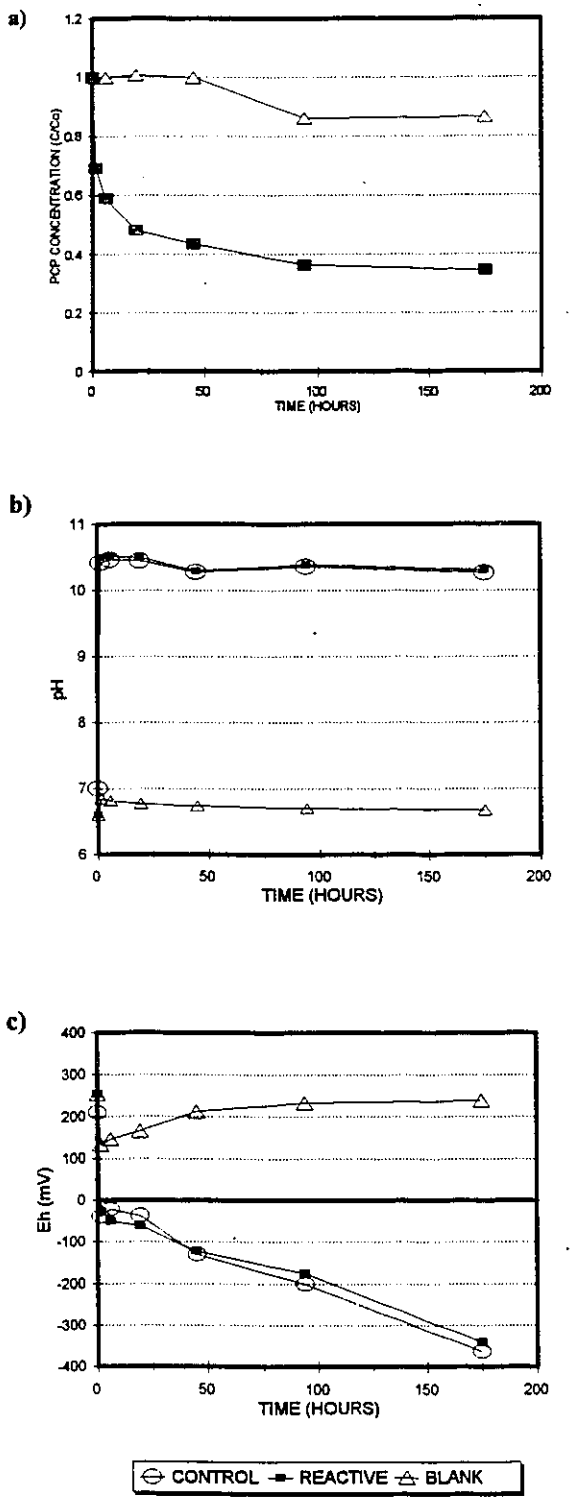


Figure APX-C-3: Batch test # 3 : Water solution with no CaCO3
a) PCP removal versus time b) pH versus time
c) Eh versus time

EXPERIMENT #4 DEGRADATION OF PCP AT 23 mg/l FOR 8 DAYS AT ROOM TEMPERATURE (13-8-93)

SAMPLE	DESCRIPTIO	TIME (hrs)	PCP (mg/l)	AVG PCP	C/C0	AVG C/CO	pH	AVG pH	Eh (mv)	AVG Eh	TEMP °C
INITIAL		0	21.87	21.87	1.00	1.00	7.0	7.0	250	250	25
39		2.0	8.31	8.28	0.38	0.38	10.3	10.3	-40	-30	10
42		2.0	8.07		0.37		10.3		-81		10
33		2.5	8.47		0.39		10.2		30		10
35		7.1	4.25	4.70	0.19	0.21	10.9	11.0	-102	-98	15
37		7.1	4.61		0.21		11.2		-86		15
40		7.4	5.24		0.24		10.9		-106		15
32		21.0	3.55	3.65	0.16	0.17	10.9	10.8	-90	-88	19
34		21.0	3.92		0.18		10.8		-82		19
47		21.0	3.49		0.16		10.9		-92		19
30	REACTIVE	48.5	2.57	2.79	0.12	0.13	11.0	10.9	-135	-106	20
41		48.5	3.00		0.14		10.9		-87		20
43		48.5	2.80		0.13		10.9		-95		20
31		81.0	2.93	2.99	0.13	0.14	10.4	10.4	-315	-324	21
44		81.0	3.02		0.14		10.4		-377		21
45		81.0	3.01		0.14		10.4		-280		21
38		126.0	2.45	2.32	0.11	0.11	10.8	10.8	-268	-276	20
46		126.0	2.20		0.10		10.8		-268		20
49		126.0	2.30		0.11		10.8		-292		20
36		192.0	2.08	2.10	0.10	0.10	10.7	10.8	-445	-316	22
48		192.0	2.09		0.10		11.0		-246		22
50		192.0	2.12		0.10		10.9		-258		22
C-34	control	2.0			0.00	0.00	10.3	10.3	-45	-40	10
C-37		2.0			0.00	0.00	10.2		-50		10
C-31		2.5			0.00	0.00	10.4		-24		10
C-30		21.0			0.00	0.00	10.8	10.8	-48	-48	19
C-33		21.0			0.00	0.00	10.7		-35		21
C-35		21.0			0.00	0.00	11.0		-60		19
C-32		192.0			0.00	0.00	10.8	10.9	-347	-283	22
C-36		192.0			0.00	0.31	10.9		-236		22
C-38		192.0			0.00	0.64	11.0		-266		22
K-36	Blank	2.0	20.07	21.29	0.92	0.97	7.1	7.0	125	124	10
K-38		2.0	21.77		1.00		7.1		128		10
K-30		2.5	22.04		1.01		7.0		120		10
K-31		21.0	21.97	21.85	1.00	1.00	7.0	7.1	125	125	19
K-32		21.0	21.55		0.99		7.0		140		19
K-33		21.0	22.02		1.01		7.2		110		19
K-34		192.0	23.46	23.40	1.07	1.07	6.9	6.9	188	184	22
K-35		192.0	23.30		1.07		6.9		189		22
K-37		192.0	23.46		1.07		6.9		175		22

CALCULATION OF IRON AND WATER (for experiment #4)

AVERAGED IRON:	**19.955**	**95% conf. int.:**	**0.040**
standard deviation: (n-1	0.130	CV % :	0.650
AVERAGED WATER:	**57.683**	**95% conf. int.:**	**0.363**
standard deviation: (n-1	0.659	CV % :	1.143

SAMPLE	BOTTLE	BOTTLE + IRON	BOTTLE +IRON +CAP	BOTTLE + H2O	BOTTLE AT THE END	IRON (g)	WATER (ml)	TIME
39	49.450	69.531	72.389	128.969	128.946	20.081	56.580	2
42	50.796	70.816	72.676	130.299	130.293	20.020	57.623	2
33	50.371	70.163	71.907	129.095	129.077	19.792	57.188	2.5
35	49.471	69.486	71.362	128.704	128.683	20.015	57.342	7
37	51.147	71.017	72.761	129.638	129.622	19.870	56.877	7
40	51.449	71.456	73.244	129.581	129.557	20.007	56.337	7.4
32	50.260	70.113	71.931	129.416	129.398	19.853	57.485	21
34	52.078	72.004	73.777	131.199	131.180	19.926	57.422	21
47	50.137	70.215	72.014	128.864	128.817	20.078	56.850	21
30	50.237	70.129	71.917	129.465	129.431	19.892	57.548	48
41	50.696	70.581	72.403	129.664	129.641	19.885	57.261	48
43	50.427	70.379	72.148	129.341	129.323	19.952	57.193	48
31	49.493	69.394	71.149	128.723	128.693	19.901	57.574	81
44	50.400	70.331	72.135	129.943	129.901	19.931	57.808	81
45	49.749	69.580	71.366	129.357	129.314	19.831	57.991	81
38	49.310	69.486	71.354	129.830	129.791	20.176	58.476	126
46	49.820	69.681	71.529	128.997	128.952	19.861	57.468	126
49	51.792	71.631	73.502	129.808	129.763	19.839	56.306	126
36	49.838	69.819	73.554	129.388	129.307	19.981	55.834	192
48	52.219	72.109	73.899	131.251	131.166	19.890	57.352	192
50	51.242	71.193	72.949	129.771	129.712	19.951	56.822	192
C-30	49.948	70.217	72.050	130.046	130.034	20.269	57.996	
C-31	49.512	69.463	71.231	128.305	128.292	19.951	57.074	
C-32	50.871	70.905	72.720	129.760	129.629	20.034	57.040	
C-33	52.268	72.187	74.052	130.157	130.134	19.919	56.105	
C-34	50.554	70.210	72.024	129.128	129.118	19.656	57.104	
C-35	49.388	69.281	71.052	128.809	128.776	19.893	57.757	
C-36	50.295	70.201	72.065	129.874	129.800	19.906	57.809	
C-37	53.083	73.122	74.892	130.888	130.875	20.039	55.996	
C-38	51.533	71.785	73.573	129.675	129.591	20.252	56.102	
K-30	52.817		54.597	113.703	113.689	0.000	59.106	
K-31	49.536		51.367	111.658	111.619	0.000	60.291	
K-32	50.280		52.142	111.799	111.779	0.000	59.657	
K-33	51.479		53.200	112.699	112.674	0.000	59.499	
K-34	52.126		53.849	112.743	112.702	0.000	58.894	
K-35	49.503		51.310	111.170	111.120	0.000	59.860	
K-36	52.736		54.509	113.295	113.283	0.000	58.787	
K-37	51.641		53.459	113.091	113.058	0.000	59.632	
K-38	51.401		53.240	112.824	112.827	0.000	59.584	

variance 0.016808 0.434573

EXTRACTION OF IRON WITH 10 ml METHANOL TO RECOVER PCP SORBED ONTO IRON

EXTRACTION 1: MEOH:(g/mL): 0.796

SAMPLE	IRON (g)	BOTTLE + IRON (g)	mg/l PCP IN WATER	BOTTL +IRON NO H2O	BOTTL +IRON + MEOH	AFTER 24 HRS	mg/l PCP IN MEOH	H2O (ml) REMAINING	MEOH (g)	MEOH (ml)	mg OF PCP IN REMAIN H2O	mg OF PCP EXTRACTED	EXTRACTED - IN REMAIN H2O	mg OF PCP INITIAL	mg OF PCP REMO IN H2O	mg OF PCP LOST	% extracted	avg % extracted	EXTRACTION 1 + EXTRACTION 2: EXTRACTED - IN REMAIN H2O	EXTRACTION 1 + EXTRACTION 2: avg extracted
													0	INITIAL :		1.26			0	0
initial																				
39	20.081	69.531	8.31	74.437	82.261	82.258	4.18	4.906	7.824	9.829	0.04077	0.06159	0.02082	1.23740	0.42941	0.767225	2.71	-2.31	0.04807	0.00858
42	20.020	70.816	8.07	75.271	83.074	83.074	0.27	4.455	7.803	9.803	0.03595	0.00385	-0.03210	1.26022	0.42907	0.795197	-4.04		-0.00181	
33	19.792	70.163	8.47	75.228	83.079	83.077	0.00	5.065	7.851	9.863	0.04290	0.00000	-0.04290	1.25070	0.44148	0.766319	-5.60		-0.02058	
35	20.015	69.486	4.25	74.275	82.153	82.091	10.35	4.769	7.878	9.897	0.02035	0.15200	0.13165	1.25407	0.22335	1.010366	13.03	8.59	0.13778	0.09743
37	19.870	71.017	4.61	75.243	82.995	82.969	0.86	4.226	7.752	9.739	0.01948	0.01201	-0.00747	1.24390	0.24272	0.981697	-0.76		0.02240	
40	20.007	71.456	5.24	76.050	83.913	83.900	10.40	4.594	7.863	9.878	0.02407	0.15051	0.12644	1.23209	0.27113	0.936884	13.50		0.13212	
32	19.853	70.113	3.55	76.109	84.016	83.991	16.48	5.996	7.907	9.933	0.02129	0.26252	0.24123	1.25720	0.18279	1.053125	22.91	17.20	0.27839	0.21381
34	19.926	72.004	3.92	78.142	85.889	85.845	9.33	6.138	7.747	9.732	0.02406	0.14807	0.12401	1.25582	0.20103	1.030725	12.03		0.15780	
47	20.078	70.215	3.49	76.595	84.481	84.414	12.07	6.38	7.866	9.882	0.02227	0.19628	0.17402	1.24331	0.17614	1.044903	16.65		0.20514	
30	19.892	70.129	2.57	76.406	84.264	84.252	5.96	6.277	7.858	9.872	0.01613	0.09625	0.08012	1.25857	0.13177	1.110676	7.21	8.62	0.15778	0.14588
41	19.885	70.581	3.00	76.948	84.725	84.694	7.29	6.367	7.777	9.770	0.01910	0.11764	0.09854	1.25230	0.15268	1.080515	9.12		0.13783	
43	19.952	70.379	2.80	77.045	84.831	84.811	7.45	6.666	7.786	9.781	0.01866	0.12253	0.10387	1.25081	0.14148	1.090871	9.52		0.14144	
31	19.901	69.394	2.93	75.150	82.992	82.971	12.18	5.756	7.842	9.852	0.01684	0.18979	0.17295	1.25914	0.15157	1.090739	15.86	26.28	0.18482	0.29845
44	19.931	70.331	3.02	76.554	84.396	84.360	21.51	6.223	7.842	9.852	0.01879	0.34577	0.32697	1.26426	0.15579	1.089681	30.01		0.33525	
45	19.831	69.580	3.01	76.489	84.350	84.313	22.69	6.909	7.861	9.876	0.02080	0.38084	0.36005	1.26826	0.15376	1.09371	32.92		0.36928	
38	20.176	69.486	2.45	75.241	83.177	83.158	5.44	5.755	7.936	9.970	0.01410	0.08554	0.07144	1.27887	0.12917	1.135604	6.29	14.66	0.07713	0.17116
46	19.861	69.681	2.20	75.856	83.857	83.818	12.45	6.175	8.001	10.052	0.01358	0.20202	0.18844	1.25883	0.11284	1.130396	16.87		0.19627	
49	19.839	71.631	2.30	77.823	85.599	85.597	15.41	6.192	7.776	9.769	0.01424	0.24596	0.23172	1.23141	0.11528	1.101908	21.03		0.24008	
36	19.981	69.819	2.08	75.951	83.781	83.771	30.60	6.132	7.83	9.837	0.01275	0.48864	0.47589	1.22109	0.10338	1.104955	43.07	37.93	0.47589	0.42485
48	19.890	72.109	2.09	77.762	85.449	85.442	27.70	5.653	7.687	9.657	0.01179	0.42409	0.41230	1.25429	0.10779	1.134709	36.34		0.41230	
50	19.951	71.193	2.12	76.917	84.796	84.785	25.47	5.724	7.879	9.898	0.01213	0.39790	0.38576	1.24270	0.10833	1.122235	34.37		0.38576	

EXTRACTION 2:

SAMPL	IRON (g)	BOTTLE + IRON (g)	PCP IN WATER	BOTTL +IRON NO H2O	BOTTL +IRON + MEOH	AFTER 24 HRS	mg/l PCP IN MEOH	H2O (ml) REMAINING	MEOH (g)	MEOH (ml)	mg OF PCP IN REMAIN H2O	mg OF PCP EXTRACTED	EXTRACTED - IN REMAIN H2O	mg OF PCP INITIAL	mg OF PCP REMO IN H2O	mg OF PCP LOST	% extracted	avg % extracted	
													0			0			
INITIAL			21.87																
39	20.081	69.531	8.31	72.593	80.965	80.838	3.88	3.062	8.372	10.518	0.02545	0.05269	0.02724	1.23740	0.44473	0.767225	3.55	3.42	
42	20.020	70.816	8.07	74.061	82.208	82.071	4.19	3.245	8.147	10.235	0.02619	0.05648	0.03029	1.26022	0.43883	0.795197	3.81		
33	19.792	70.163	8.47	73.233	81.13	80.968	3.72	3.07	7.897	9.921	0.02800	0.04833	0.02232	1.25070	0.45838	0.766319	2.91		
35	20.015	69.486	4.25	72.609	80.488	80.399	1.49	3.123	7.879	9.898	0.01327	0.01940	0.00613	1.25407	0.23043	1.010366	0.61	1.42	
37	19.870	71.017	4.61	74.405	81.996	81.832	3.52	3.388	7.591	9.536	0.01562	0.04549	0.02988	1.24390	0.24858	0.981697	3.04		
40	20.007	71.456	5.24	74.74	82.478	82.354	1.78	3.284	7.738	9.721	0.01721	0.02289	0.00568	1.23209	0.27800	0.936884	0.61		
32	19.853	70.113	3.55	75.089	82.86	82.773	3.72	4.976	7.771	9.763	0.01766	0.05483	0.03716	1.25720	0.18641	1.053125	3.53	3.27	
34	19.926	72.004	3.92	77.064	84.72	84.714	3.66	5.08	7.656	9.618	0.01984	0.05372	0.03389	1.25582	0.20526	1.030725	3.29		
47	20.078	70.215	3.49	75.638	83.25	83.241	3.34	5.423	7.612	9.563	0.01893	0.05005	0.03113	1.24331	0.17948	1.044903	2.98		
30	19.892	70.129	2.57	75.318	83.18	83.002	6.04	5.189	7.862	9.877	0.01334	0.09100	0.07766	1.25857	0.13456	1.110676	6.99	4.69	AVG: 2.05
41	19.885	70.581	3.00	75.638	83.523	83.303	3.64	5.057	7.885	9.906	0.01517	0.05446	0.03929	1.25230	0.15681	1.080515	3.64		
43	19.952	70.379	2.80	75.429	83.307	83.108	3.46	5.05	7.878	9.897	0.01414	0.05172	0.03758	1.25081	0.14600	1.090871	3.45		
31	19.901	69.394	2.93	74.46	82.362	82.279	1.78	5.068	7.902	9.927	0.01482	0.02660	0.01187	1.25914	0.15359	1.090739	1.09	0.90	
44	19.931	70.331	3.02	76.024	83.93	83.821	1.63	5.693	7.906	9.932	0.01719	0.02547	0.00828	1.26426	0.15739	1.089681	0.76		
45	19.331	69.580	3.01	74.928	83.118	83.042	1.62	5.348	8.19	10.289	0.01810	0.02533	0.00923	1.26826	0.15848	1.09371	0.84		
38	20.176	69.486	2.45	74.65	82.406	82.3	1.23	5.164	7.756	9.744	0.01265	0.01834	0.00568	1.27887	0.13081	1.135604	0.50	0.65	
46	19.861	69.681	2.20	74.85	82.746	82.73	1.29	5.269	7.796	9.794	0.01159	0.01943	0.00784	1.25883	0.11484	1.130396	0.69		
49	19.839	71.631	2.30	76.841	84.691	84.68	1.35	5.21	7.85	9.862	0.01198	0.02035	0.00836	1.23141	0.11752	1.101908	0.76		
36	19.981	69.819	2.08	75.137	83.124			5.318	7.927	10.034	0.01106	0.00000	-0.01106	1.22109	0.10507	1.104955	0.00	0.00	
48	19.890	72.109	2.09	77.618	85.691			5.509	8.073	10.142	0.01149	0.00000	-0.01149	1.25429	0.10809	1.134709	0.00		
50	19.951	71.193	2.12	76.896	84.744			5.703	7.848	9.859	0.01209	0.00000	-0.01209	1.24270	0.10837	1.122235	0.00		

APPENDIX D

CALCULATION OF THE ANALYTICAL ERRORS ON pH AND Eh MEASUREMENTS

Calculation of the 95% confidence interval for pH and Eh from batch tests, iron/solution ratio test

Calculations were done as for the analytical error between replicates explained in Appendix A

	pH	AVG PCP	(xi-X)^2	Sum (xi-X)^2 / n-1	std deviation	95 % int	CV (%)	AVG PCP	(xi-X)^2	Sum (xi-X)^2 / n-1	std deviation	95 % int	CV (%)
Reactive	10.3	10.26	0.0040	0.0036	0.060	0.259	0.5877	10.726	0.1646	0.080	0.283	0.132	2.6388
	10.3		0.0000						0.2263				
	10.2		0.0032						0.2764				
	10.9	11.01	0.0069	0.0234	0.153	0.659	1.3899		0.0417				
	11.2		0.0312						0.2156				
	10.9		0.0087						0.0377				
	10.9	10.84	0.0000	0.0049	0.070	0.302	0.6478		0.0154				
	10.8		0.0054						0.0020				
	10.9		0.0044						0.0340				
	11.0	10.94	0.0081	0.0061	0.078	0.336	0.7139		0.0926				
	10.9		0.0025						0.0270				
	10.9		0.0016						0.0304				
	10.4	10.39	0.0009	0.0007	0.026	0.114	0.2546		0.0935				
	10.4		0.0004						0.1265				
	10.4		0.0001						0.1195				
	10.8	10.8	0.0001	0.0001	0.010	0.043	0.0926		0.0041				
	10.8		0.0001						0.0071				
	10.8		0.0000						0.0055				
	10.7	10.84	0.0245	0.0226	0.150	0.647	1.3883		0.0021				
	11.0		0.0205						0.0647				
	10.9		0.0002						0.0154				
control	10.3	10.25	0.0000	0.0110	0.105	0.452	1.0244	10.647	0.1573	0.098	0.313	0.218	2.9411
	10.2		0.0107						0.2467				
	10.4		0.0114						0.0822				
	10.8	10.81	0.0011	0.0177	0.133	0.573	1.2315		0.0178				
	10.7		0.0128						0.0028				
	11.0		0.0215						0.0982				
	10.8	10.87	0.0152	0.0126	0.112	0.484	1.0337		0.0107				
	10.9		0.0007						0.0642				
	11.0		0.0093						0.1045				
Blank	7.1	7.04	0.0001	0.0007	0.026	0.114	0.3758	6.9933	0.0032	0.009	0.096	0.067	1.3678
	7.1		0.0004						0.0044				
	7.0		0.0009						0.0003				
	7.0	7.06	0.0036	0.0063	0.079	0.342	1.1243		0.0000				
	7.0		0.0009						0.0013				
	7.2		0.0081						0.0245				
	6.9	6.88	0.0000	0.0004	0.020	0.086	0.2907		0.0128				
	6.9		0.0004						0.0087				
	6.9		0.0004						0.0178				

Calculation of the 95% confidence interval for pH and Eh from batch tests, iron/solution ratio test

	Eh (mv)	AVG Eh	(xi-X)^2	Sum (xi-X)^2 / n-1	std deviation	95 % int	CV (%)	AVG PCP	(xi-X)^2	Sum (xi-X)^2 / n-1	std deviation	95 % int	CV (%)
Reactive	-40	-30	93	4405.51	66.37	285.6	-218.8	-177	18743	15639	125	57	-71
	-81		8328						9198				
	30		390						42810				
	-102	-98	16	112.00	10.58	45.5	-10.8		5611				
	-86		144						8264				
	-106		64						5027				
	-90	-88	4	28.00	5.29	22.8	-6.0		7552				
	-82		36						9007				
	-92		16						7209				
	-135	-106	860	661.33	25.72	110.7	-24.3		1756				
	-87		348						8083				
	-95		114						6708				
	-315	-324	81	2413.00	49.12	211.4	-15.2		19070				
	-377		2809						40038				
	-280		1936						10629				
	-268	-276	64	192.00	13.86	59.6	-5.0		8298				
	-268		64						8298				
	-292		256						13247				
	-445	-316	16555	12452.33	111.59	480.2	-35.3		71875				
	-246		4947						4774				
	-258		3403						6576				
control	-45	-40	28	190.33	13.80	59.4	-34.8	-123	6154	15243	123	86	-100
	-50		107						5394				
	-24		245						9889				
	-48	-48	0	156.33	12.50	53.8	-26.2		5692				
	-35		160						7822				
	-60		152						4025				
	-347	-283	4096	3297.00	57.42	247.1	-20.3		49977				
	-236		2209						12669				
	-266		289						20322				
Blank	125	124	0.4	16.33	4.04	17.4	3.3	144	378	956	31	21	21
	128		13.4						270				
	120		18.8						598				
	125	125	0.0	225.00	15.00	64.5	12.0		378				
	140		225.0						20				
	110		225.0						1186				
	188	184	16.0	61.00	7.81	33.6	4.2		1897				
	189		25.0						1985				
	175		81.0						934				

Calculation of the 95% confidence interval on pH and Eh from iron loading test

	pH	AVG PCP	(xi-X)^2	Sum (xi-X)^2 / n-	std deviation	95 % int	CV (%)
Refill 1	10.5	10.80	0.090	0.07	0.265	0.657294	2.44977
	11		0.040				
	10.9		0.010				
Refill 2	10.5	10.60	0.010	0.01	0.100	0.248434	0.9434
	10.7		0.010				
	10.6		0.000				
Refill 3	10.9	10.53	0.134	0.10	0.321	0.798603	3.05179
	10.4		0.018				
	10.3		0.054				
Refill 4	10.5	10.20	0.090	0.07	0.265	0.657294	2.59387
	10.1		0.010				
	10		0.040				

	Eh	AVG PCP	(xi-X)^2	Sum (xi-X)^2 / n-	std deviation	95 % int	CV (%)
Refill 1	-40	-45.00	25.000	1075.00	32.787	81.45448	-72.86
	-15		900.000				
	-80		1225.000				
Refill 2	-100	-138.33	1469.444	1258.33	35.473	88.12692	-25.643
	-145		44.444				
	-170		1002.778				
Refill 3	-100	-286.67	34844.444	32533.33	180.370	448.1001	-62.92
	-300		177.778				
	-460		30044.444				
Refill 4	-100	-220.00	14400.000	11200.00	105.830	262.9176	-48.105
	-260		1600.000				
	-300		6400.000				

Calculation of the 95% confidence interval for sorption experiments

	Replicates	pH	Average pH	(xi-X)^2	Sum (xi-X)^2 / n	std deviation	95 % int	CV (%)
1	rep1	11.1	11.05	0.002500	0.005000	0.070711	0.635300	0.639916
	rep2	11.0		0.002500				
2	rep1	10.8	10.77	0.000900	0.001800	0.042426	0.381180	0.393931
	rep2	10.7		0.000900				
3	rep1	10.8	10.8	0.000000	0.000000	0.000000	0.000000	0
	rep2	10.8		0.000000				
4	rep1	10.8	10.725	0.002025	0.004050	0.063640	0.571770	0.593376
	rep2	10.7		0.002025				
5	rep1	10.6	10.66	0.001600	0.003200	0.056569	0.508240	0.530662
	rep2	10.7		0.001600				

	Replicates	Eh	Average Eh	(xi-X)^2	Sum (xi-X)^2 / n	std deviation	95 % int	CV (%)
1	rep1	-129	-144.5	240.3	480.5	21.9	196.9	-15.1698
	rep2	-160		240.3				
2	rep1	-130	-125	25.0	50.0	7.1	63.5	-5.65685
	rep2	-120		25.0				
3	rep1	-170	-206.5	1332.3	2664.5	51.6	463.8	-24.997
	rep2	-243		1332.3				
4	rep1	-275	-325	2500.0	5000.0	70.7	635.3	-21.7571
	rep2	-375		2500.0				
5	rep1	-160	-192.5	1056.3	2112.5	46.0	412.9	-23.8763
	rep2	-225		1056.3				

APPENDIX E

RESULTS OF OPEN CHARACTERIZATION AND IRON EXTRACTION FROM PARACEL LABORATORIES LTD

PARACEL LABORATORIES Ltd.
2319 St. Laurent Blvd. Unit 100
Ottawa, Ontario
K1G 4K6

TEL: (613)-731-9577
FAX: (613)-731-9064

CERTIFICATE OF ANALYSIS

TO: University of Ottawa
161 Louis Pasteur
Ottawa, Ontario K1N 6N5

Attn: Ms. France Beaudet

Date: 10/19/93
Paracel: W3366

Tel: 613-564-4089
Fax:

Customer Order#:
Project: PCP Degradation

Sample Date: 09/27/93
Reference:

The following is a final report of:

1.0 Open-characterization for volatile organic compounds in your submitted sample of:

Sample	Matrix
51	WATER

2.0 Open-characterization for semi-volatile extractable organic compounds in your submitted sample of:

Sample	Matrix
52, 53, 55	WATER

Analyst: _____ **Dale Robertson, B.Sc.**

Scientific Approval: _____ **Mark Charbonneau, Ph.D.**

Methodology: The samples were analyzed, after sample preparation, using gas chromatography with mass spectrometric detection in full scan mode.

The identifications are tentative and are based on the matching of sample mass spectra with those found in the National Bureau of Standards (NBS) Library of Mass Spectra. The column indicating Match is a measure of similarity between the library mass spectra and that of the sample. A perfect match would yield a 100 and a comparison showing no similarity would yield a 0. Compounds indicated by Manual in the Match column indicate the identification has been made based on standard interpretation techniques of mass spectra.

The quantitations reported are referenced according to the response of toluene-d8 for the volatile analysis, and phenanthrene-d10 for the semi-volatile analysis. For this reason, the quantitations are semi-quantitative and denoted by the prefix A.

Instrumentation:

1. Volatile Open Characterization - Finnigan GC/MS 1050
   DB-624, 75m x 0.53mm ID, 3μm film
   Tekmar LSC 2000 Purge & Trap
   Tekmar ALS 2016 Multi-Port Module

2. Semi-Volatile Extractable Open Characterization -
   Hewlett Packard 5971A MSD
   Hewlett Packerd 5890II GC
   DB-5, 30m x 0.25mm ID, 0.2μm film

1. Volatile Open Characterization Results
See figure 1 for total ion chromatogram.

Sample ID	**51**
Paracel ID	**W3366A3W.1**

Entry No.	Retention Time(min)	Identity	Conc. (µg/L)	Library Match
no compounds detected above 10 µg/L				

2.Semi-Volatile Extractable Open Characterization Results
See figure 2 for total ion chromatogram.

Sample ID	**52,53,55**
Paracel ID	**W3366E3W.2**

Entry No.	Retention Time(min)	Identity	Conc. (mg/L)	Library Match
1	22.94	Pentachlorophenol	A-0.25	91

See figure 3 for mass spectrum of entry no. 1 along with probability based matched mass spectrum from NBS43K library.

Figure 1: GC/MS Volatile Total Ion Chromatogram
For: France Beaudet
Sample ID: 51
Paracel ID: W3366.1

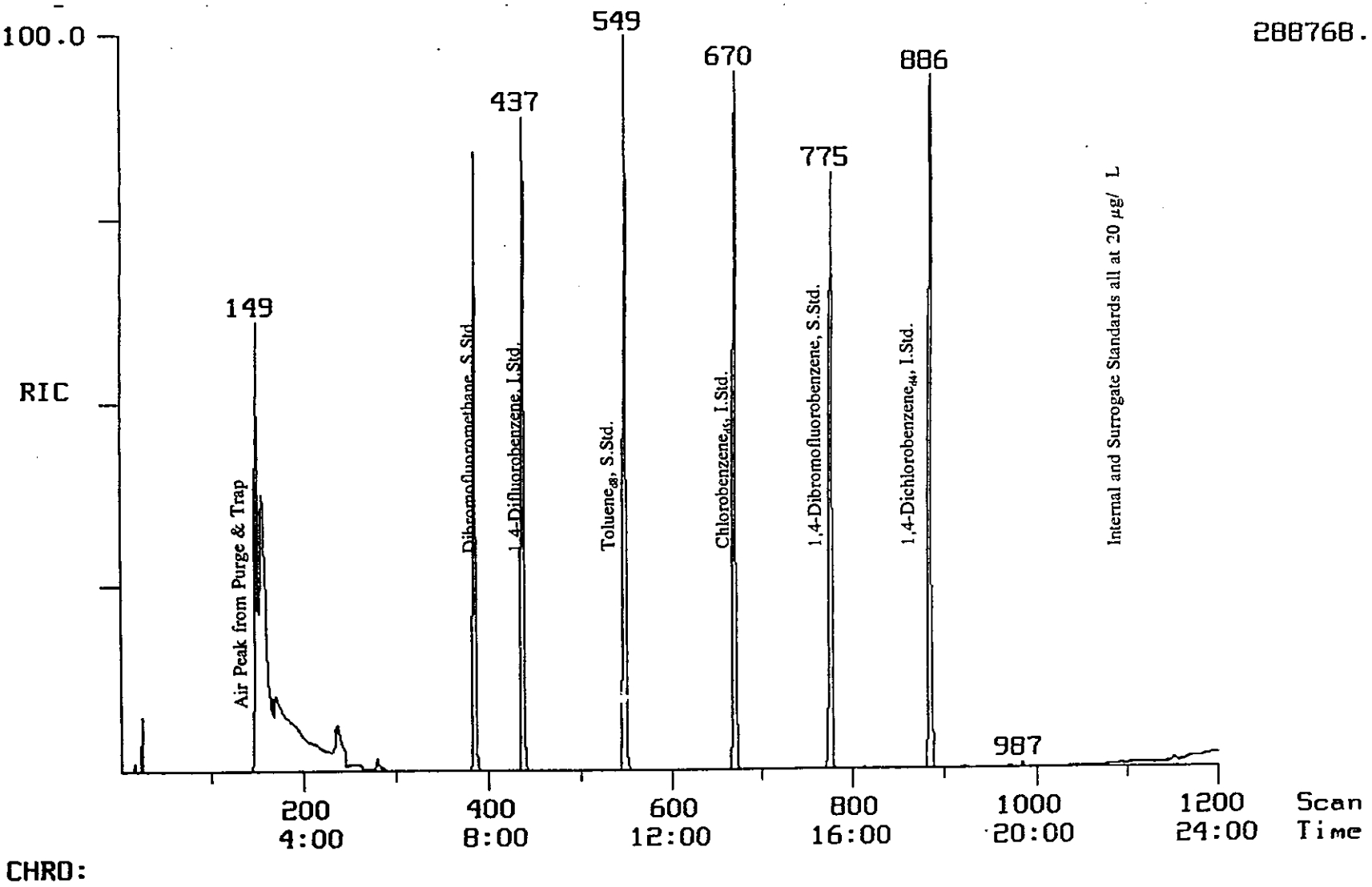


Figure 2: GC/MS Semi-Volatile Extractable Total Ion Chromatogram
For: France Beaudet
Sample ID: 52,53,55
Paracel ID: W3366.2

Pentachlorophenol, Tentative Identification

Phenanthrene$_{d10}$ Internal Standard, 0.15mg/L equivelant

Hydrocarbon, in Blank

Phthalate Ester, in Blank

Hydrocarbon, in Blank

Sample Mass Spectrum

NBS43K Library Mass Spectrum

Figure 3: Mass Spectra from Sample and Library Match
For: France Beaudet
Sample ID: 52,53,55
Paracel ID: W3366.2

PARACEL
LABORATORIES Ltd.
2319 St. Laurent Blvd. Unit 100
Ottawa, Ontario
K1G 4K6

TEL: (613)-731-9577
FAX: (613)-731-9064

CERTIFICATE OF ANALYSIS

TO: University of Ottawa
161 Louis Pasteur
Ottawa, Ontario K1N 6N5

Attn: Ms. France Beaudet

Date: 10/19/93
Paracel: W3366

Tel: 613-564-4089
Fax: 613-564-9916

Customer Order#: 2501050910
Project: PCP Degradation

Sample Date: 09/27/93
Reference:

The following is a final report of:

1.0 Volatiles purge and trap GC/MS results for your submitted samples of:

WATER: 51

VOLATILES ANALYSES OF WATER

Methodology: based upon extended U.S. EPA 624 procedures and
MOE methods: SMPBVOL-E3189A.1
LFPT-POCODO.1

Instrumentation: Finnigan GC/MS 1050
Tekmar LSC 2000 Purge and Trap
Tekmar ALS 2016 Multi-Port Module

VOLATILES IN WATER RESULTS
(results are reported in µg/L)

Date: 10/19/93

Sample ID		**51**
Paracel ID	**MDL**	**W3366AAW.1**
Dilution factor		1
Benzene	0.5	nd
Bromodichloromethane	0.4	nd
Bromoform	0.8	nd
Bromomethane	1.0	nd
Carbon Tetrachloride	0.5	nd
Chlorobenzene	0.4	nd
Chloroethane	1.0	nd
Chloroform	0.6	nd
Chloromethane	3.0	nd
Dibromochloromethane	0.5	nd
1,2-Dibromoethane	1.0	nd
m-Dichlorobenzene	0.4	nd
o-Dichlorobenzene	0.4	nd
p-Dichlorobenzene	0.4	nd
1,1-Dichloroethane	0.5	nd
1,2-Dichloroethane	0.5	nd
1,1-Dichloroethylene	2.0	nd
c-1,2-Dichloroethylene	0.4	nd
t-1,2-Dichloroethylene	1.0	nd
1,2-Dichloropropane	0.7	nd
c-1,3-Dichloropropene	0.4	nd
t-1,3-Dichloropropene	0.5	nd
Ethylbenzene	0.5	nd
Methylene Chloride	5.0	nd
Styrene	0.4	nd
1,1,2,2-Tetrachloroethane	0.6	nd
Tetrachloroethylene	0.5	nd
Toluene	1.0	nd
1,1,1-Trichloroethane	0.4	nd
1,1,2-Trichloroethane	0.6	nd
Trichloroethylene	0.4	nd
Trichlorofluoromethane	1.0	nd
1,3,5-Trimethylbenzene	0.5	nd
Vinyl Chloride	3.0	nd
m/p-Xylene	1.0	nd
o-Xylene	0.5	nd
Surrogate Recovery		
Dibromofluoromethane		65
Toluene-d8		97
1,4-Bromofluorobenzene		109

VOLATILES IN WATER QUALITY CONTROL
(results are reported in µg/L)

Date: 10/19/93

Parameter	MDL	BLANK
Benzene	0.5	nd
Bromodichloromethane	0.4	nd
Bromoform	0.8	nd
Bromomethane	1.0	nd
Carbon Tetrachloride	0.5	nd
Chlorobenzene	0.4	nd
Chloroethane	1.0	nd
Chloroform	0.6	nd
Chloromethane	3.0	nd
Dibromochloromethane	0.5	nd
1,2-Dibromoethane	1.0	nd
m-Dichlorobenzene	0.4	nd
o-Dichlorobenzene	0.4	nd
p-Dichlorobenzene	0.4	nd
1,1-Dichloroethane	0.5	nd
1,2-Dichloroethane	0.5	nd
1,1-Dichloroethylene	2.0	nd
c-1,2-Dichloroethylene	0.4	nd
t-1,2-Dichloroethylene	1.0	nd
1,2-Dichloropropane	0.7	nd
c-1,3-Dichloropropene	0.4	nd
t-1,3-Dichloropropene	0.5	nd
Ethylbenzene	0.5	nd
Methylene Chloride	5.0	nd
Styrene	0.4	nd
1,1,2,2-Tetrachloroethane	0.6	nd
Tetrachloroethylene	0.5	nd
Toluene	1.0	nd
1,1,1-Trichloroethane	0.4	nd
1,1,2-Trichloroethane	0.6	nd
Trichloroethylene	0.4	nd
Trichlorofluoromethane	1.0	nd
1,3,5-Trimethylbenzene	0.5	nd
Vinyl Chloride	3.0	nd
m/p-Xylene	1.0	nd
o-Xylene	0.5	nd

Surrogate Recovery	
Dibromofluoromethane	98
Toluene-d8	98
1,4-Bromofluorobenzene	104

For: 51

VOLATILES IN WATER QUALITY CONTROL
(results are reported in µg/L)

Date: 10/19/93

Parameter	Replicate Avg.	Replicate Diff.
Benzene	nd	nd
Bromodichloromethane	nd	nd
Bromoform	nd	nd
Bromomethane	nd	nd
Carbon Tetrachloride	nd	nd
Chlorobenzene	nd	nd
Chloroethane	nd	nd
Chloroform	**0.9**	**nd**
Chloromethane	nd	nd
Dibromochloromethane	nd	nd
1,2-Dibromoethane	nd	nd
m-Dichlorobenzene	nd	nd
o-Dichlorobenzene	nd	nd
p-Dichlorobenzene	nd	nd
1,1-Dichloroethane	nd	nd
1,2-Dichloroethane	nd	nd
1,1-Dichloroethylene	nd	nd
c-1,2-Dichloroethylene	nd	nd
t-1,2-Dichloroethylene	nd	nd
1,2-Dichloropropane	nd	nd
c-1,3-Dichloropropene	nd	nd
t-1,3-Dichloropropene	nd	nd
Ethylbenzene	nd	nd
Methylene Chloride	nd	nd
Styrene	nd	nd
1,1,2,2-Tetrachloroethane	nd	nd
Tetrachloroethylene	nd	nd
Toluene	nd	nd
1,1,1-Trichloroethane	nd	nd
1,1,2-Trichloroethane	nd	nd
Trichloroethylene	nd	nd
Trichlorofluoromethane	nd	nd
1,3,5-Trimethylbenzene	nd	nd
Vinyl Chloride	nd	nd
m/p-Xylene	nd	nd
o-Xylene	nd	nd

For: 51

VOLATILES IN WATER QUALITY CONTROL
(results are reported in µg/L)

Date: 10/19/93

Parameter	Check Expected	Check Measured
Benzene	40	42
Bromodichloromethane	40	41
Bromoform	40	38
Bromomethane	*	*
Carbon Tetrachloride	40	41
Chlorobenzene	40	40
Chloroethane	*	*
Chloroform	40	42
Chloromethane	*	*
Dibromochloromethane	40	40
1,2-Dibromoethane	40	40
m-Dichlorobenzene	40	38
o-Dichlorobenzene	40	39
p-Dichlorobenzene	40	39
1,1-Dichloroethane	40	43
1,2-Dichloroethane	40	42
1,1-Dichloroethylene	40	38
c-1,2-Dichloroethylene	40	42
t-1,2-Dichloroethylene	40	41
1,2-Dichloropropane	40	41
c-1,3-Dichloropropene	40	40
t-1,3-Dichloropropene	40	40
Ethylbenzene	40	40
Methylene Chloride	40	42
Styrene	40	38
1,1,2,2-Tetrachloroethane	40	40
Tetrachloroethylene	40	40
Toluene	40	41
1,1,1-Trichloroethane	40	41
1,1,2-Trichloroethane	40	40
Trichloroethylene	40	41
Trichlorofluoromethane	*	*
1,3,5-Trimethylbenzene	40	38
Vinyl Chloride	*	*
m/p-Xylene	80	76
o-Xylene	40	38
Surrogate Recovery		
Dibromofluoromethane	100	101
Toluene-d8	100	98
1,4-Bromofluorobenzene	100	95

For: 51

VOLATILES IN WATER QUALITY CONTROL
(results are reported in µg/L)

Date: 10/19/93

Parameter	M/E	LLA	ULA
Benzene	106%	37%	151%
Bromodichloromethane	102%	35%	155%
Bromoform	95%	45%	169%
Bromomethane	*	*	*
Carbon Tetrachloride	101%	70%	140%
Chlorobenzene	100%	37%	160%
Chloroethane	*	*	*
Chloroform	106%	51%	138%
Chloromethane	*	*	*
Dibromochloromethane	101%	53%	149%
1,2-Dibromoethane	100%	50%	150%
m-Dichlorobenzene	95%	59%	156%
o-Dichlorobenzene	97%	18%	190%
p-Dichlorobenzene	97%	18%	190%
1,1-Dichloroethane	107%	59%	155%
1,2-Dichloroethane	105%	49%	155%
1,1-Dichloroethylene	95%	1%	234%
c-1,2-Dichloroethylene	106%	1%	200%
t-1,2-Dichloroethylene	102%	54%	156%
1,2-Dichloropropane	103%	1%	210%
c-1,3-Dichloropropene	99%	1%	227%
t-1,3-Dichloropropene	100%	17%	183%
Ethylbenzene	99%	37%	162%
Methylene Chloride	106%	1%	221%
Styrene	95%	50%	150%
1,1,2,2-Tetrachloroethane	100%	46%	157%
Tetrachloroethylene	100%	64%	148%
Toluene	102%	47%	150%
1,1,1-Trichloroethane	102%	52%	162%
1,1,2-Trichloroethane	101%	52%	150%
Trichloroethylene	102%	71%	157%
Trichlorofluoromethane	*	*	*
1,3,5-Trimethylbenzene	95%	50%	150%
Vinyl Chloride	*	*	*
m/p-Xylene	95%	50%	150%
o-Xylene	95%	50%	150%
Surrogate Recovery			
Dibromofluoromethane	101%	50%	150%
Toluene-d8	98%	50%	150%
1,4-Bromofluorobenzene	95%	50%	150%

For: 51

Glossary

MDL: Normal Method Detection Limit. It is the lowest level of the parameter that can be quantitated with confidence.

SURROGATE RECOVERIES: Surrogate compounds are added to the sample prior to analysis and their recovery is reported in percent.

BLANK: Results from the analysis of a blank sample. Reported results are not corrected for blank values.

REPLICATE: Replicate analysis of a sample in the same run.
Avg.: The average result from a replicate analysis and the actual sample analysis.
Diff.: The difference between the replicate result and the sample result.

CHECK: Check sample analysis.
Measured: Results obtained from the analysis of a matrix blank fortified at the Expected level.

M/E: Measured check sample result divided by the expected result expressed in percent.
LLA: The lowest level acceptable for the M/E percentage.
ULA: The highest level acceptable for the M/E percentage.

nd Not detected or found below the method detection limit.
* Not used in continuing calibration.

Notes

LLA and ULA values are based on published US EPA - Method 624 values.

Certification

Analyst: _____ **Dale Robertson, B.Sc.**

Scientific Approval: W Craig for **Mark Charbonneau, Ph.D.**

QC Authorization: W Craig **W.G. Craig, Ph.D.**

PARACEL LABORATORIES Ltd.
2319 St. Laurent Blvd. Unit 100
Ottawa, Ontario
K1G 4K6

TEL: (613)-731-9577
FAX: (613)-731-9064

CERTIFICATE OF ANALYSIS

TO: University of Ottawa
161 Louis Pasteur
Ottawa, Ontario K1N 6N5

Attn: Ms. France Beaudet

Customer Order#:
Project:

Date: 10/15/93
Paracel: W3366

Tel: 613-564-4089
Fax:

Sample Date: 09/27/93
Reference:

The following is a final report of:

1.0 Chlorophenols GC/ECD results for your submitted samples of:

Sample
Iron Solids

The iron solids sample received was analysed for the listed chlorophenols using gas chromatography with electron capture detection at the amounts tabulated below.

Results are reported in µg/g

Sample ID **Paracel ID**	**Reporting Limit**	**Iron Solids** **W3366CPS.3**
Dilution Factor		2000
2,4,6-trichlorophenol	10	nd
2,4,5-trichlorophenol	10	nd
2,3,5-trichlorophenol	10	nd
2,3,4-trichlorophenol	10	nd
2,3,5,6-tetrachlorophenol	10	nd
2,3,4,6-tetrachlorophenol	10	nd
2,3,4,5-tetrachlorophenol	10	nd
pentachlorophenol	10	22

Note: 20.41 g of solid material from hypo-vial #52 was extracted for this analysis. In a 40 mL VOA vial the 20.41 g of sample, 15 mL of water (acidified to pH of <2) and 10 mL of dichloromethane were shaken on a horizontal shaker for 24 hours. A 1 mL aliquot of the extract was derivatized with diazomethane, solvent exchanged, and diluted to a final volume of 10 mL with iso-octane for injection in the GC.

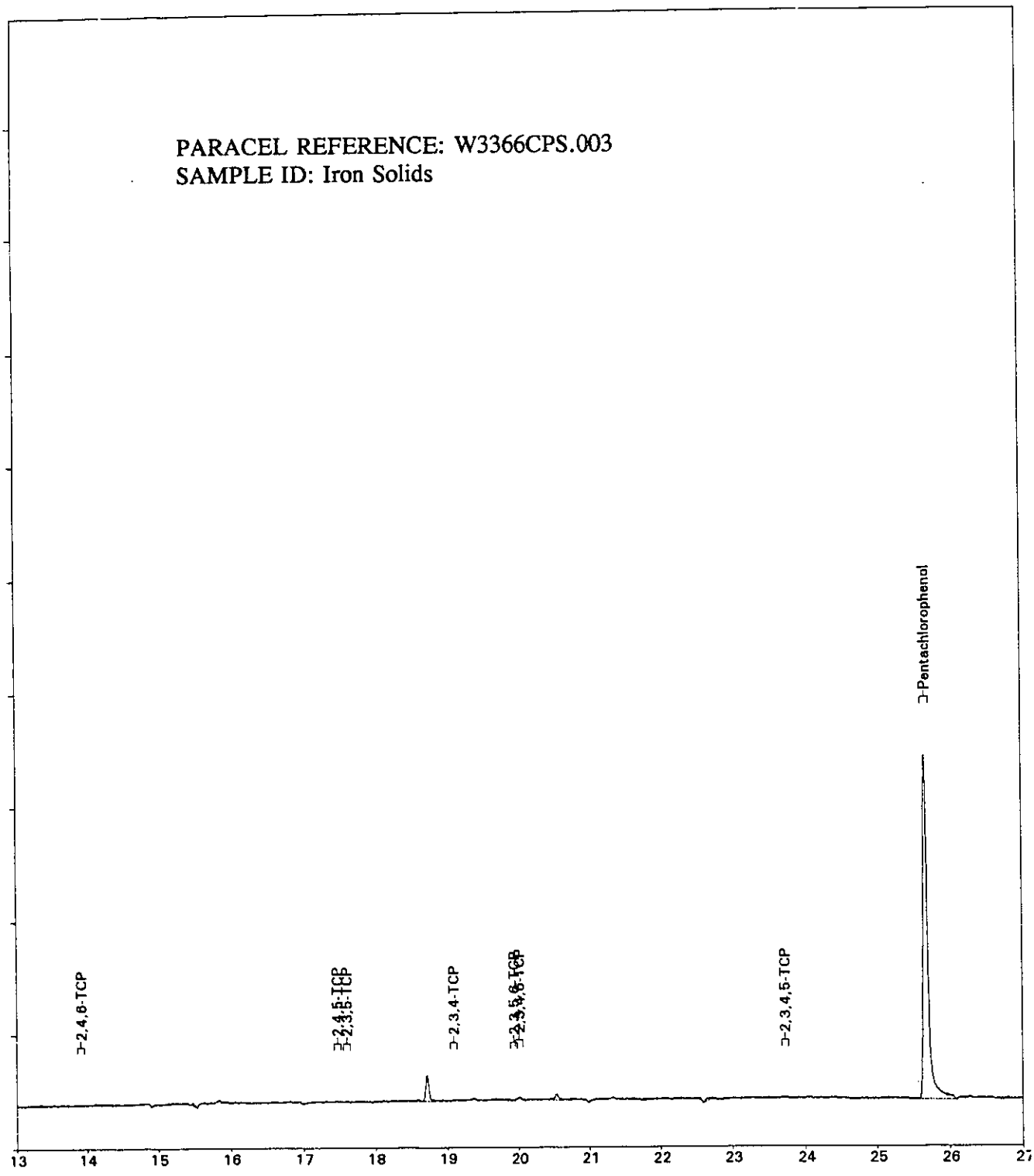
Certification

Analyst: _____ **Robert Walker, cCT**

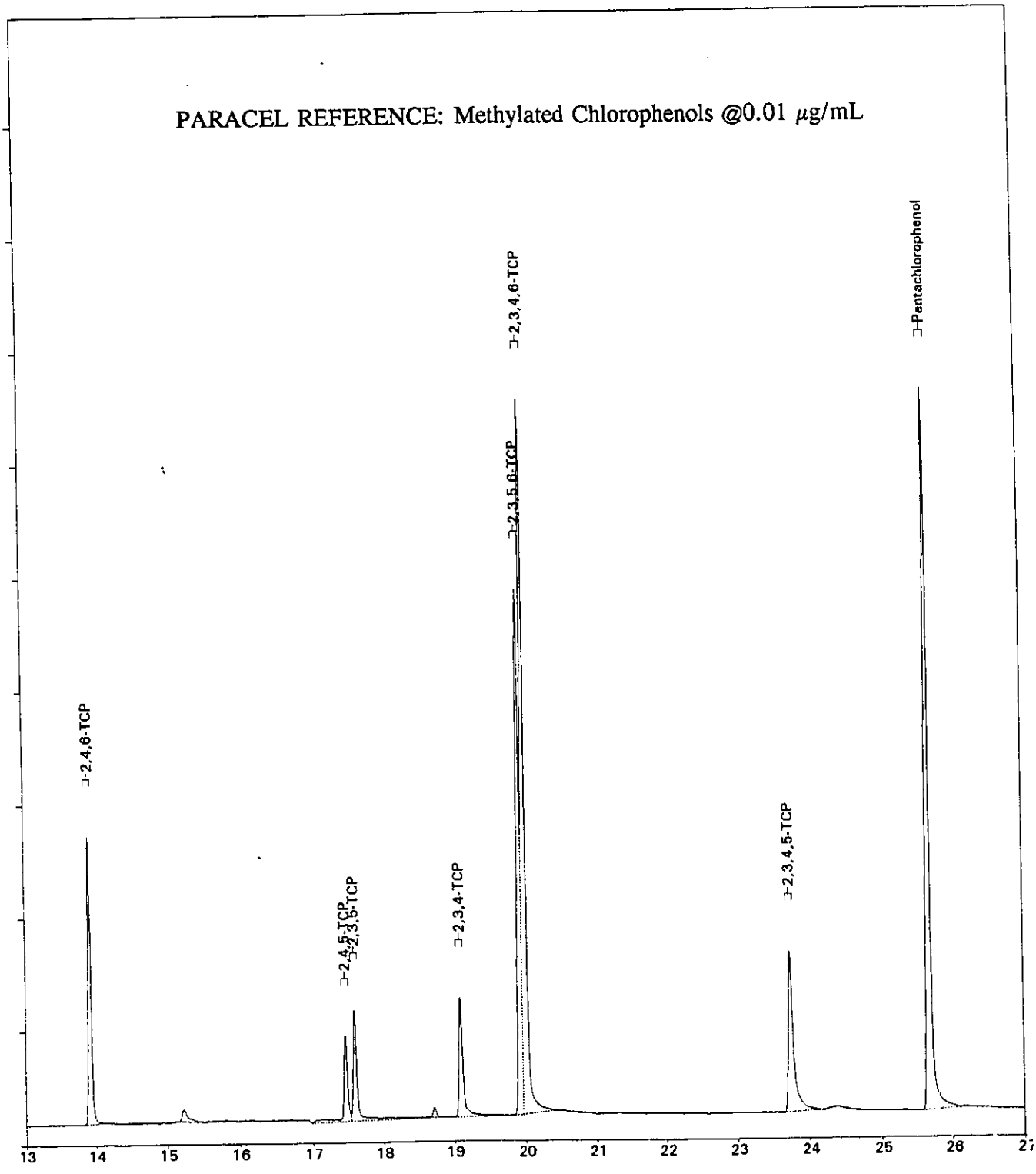
Scientific Approval: W Craig **W. G. Craig, Ph.D.**

File=C:\DIRECT\VARIAN\FDGHTRE.11R Sample name=3366 Iron Solids dil 1:2000 Date printed= 10-18-1993 Time= 11:01:16
13.00 to 27.00 min. Low Y = -10.00000 mv High Y = 500.00003 mv Span = 510.00003 mv

PARACEL REFERENCE: W3366CPS.003
SAMPLE ID: Iron Solids



File=C:\DIRECT\VARIAN\FDGHTRE.12R Sample name=Methylated Chlorophenols @ 0.01 ug/mL Date printed= 10-18-1993 Time= 11:00:04
13.00 to 27.00 min. Low Y = -30.00000 mv High Y = 1500.00012 mv Span = 1530.00012 mv



APPENDIX F

RESULTS OF CHLORIDE FROM BONDAR - CLEGG AND CALCULATION OF THE 95% CONFIDENCE INTERVAL ON ANALYSES AND REPLICATES

BONDAR-CLEGG

Certificate of Analysis

Inchcape Testing Services

DATE PRINTED: 30-AUG-93

REPORT: 093-40971.8 (COMPLETE)

PROJECT: NONE

SAMPLE NUMBER	ELEMENT UNITS	Cl PPM
40		3.00
42		1.56
43		2.43
46		2.53
47		2.07
48-CL		2.45
49		2.53
50-CL		2.57
C01		0.18
C33		2.23
C35		2.44
C36-CL		2.77
C37		1.41
C38-CL		2.76
K32		0.27
K37-CL		0.23

Bondar-Clegg & Company Ltd.
5420 Canotek Road, Ottawa, Ontario, K1J 9G2, Canada
Tel: (613) 749-2220, Fax: (613) 749-7170

Lab Supervisor

BONDAR-CLEGG

Certificate of Analysis

Inchcape Testing Services

DATE PRINTED: 25-JUN-93

REPORT: 093-40682.8 (COMPLETE)

PROJECT: NONE

SAMPLE NUMBER	ELEMENT UNITS	Cl PPM
C2		2.76
C1		2.04
C5		1.80
2		6.48
3		10.86
4		4.26
7		4.38
9		2.40
10		6.60
11		4.98
12		5.82
13		5.76

Bondar-Clegg & Company Ltd.
5420 Canotek Road, Ottawa, Ontario, K1J 9G2, Canada
Tel: (613) 749-2220, Fax: (613) 749-7170

Lab Supervisor

Calculation of the 95% confidence interval on chloride measurements

Experiment with no CaCO3 and 20 g of iron

	sample	time (hrs)	Cl- mg/L	Average	(xi-X)^2	Sum (xi-X)^2/n-1	std deviation	95% interval	CV (%)
	C0	0	0.18						
Reactive	42	2	1.56						
	40	8	3						
	47	21	2.07						
	43	48	2.43						
	46	126	2.53	2.53	0.00	0.00	0.00	0.00	0.00
	49	126	2.53		0.00				
	48	192	2.45	2.51	0.00	0.01	0.08485	0.76	3.38
	50	192	2.57		0.00				
Control	c-37	2	1.41						
	c-33	21	2.23	2.34	0.01	0.02	0.14849	1.33	6.36
	c-35	21	2.44		0.01				
	c-36	192	2.77	2.77	0.00	0.00	0.00707	0.06	0.26
	c-38	192	2.76		0.00				
Blank	k-32	21	0.27						
	k-37	192	0.23						

Calculation of the 95% confidence interval on chloride measurements

Experiment with 40 mg/L CaCO3 and 10 g of iron

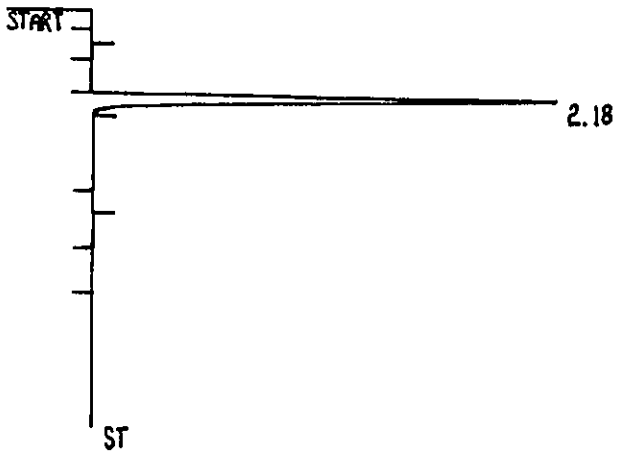
	sample	time (hrs)	Cl- mg/L	Average	(xi-X)^2	Sum (xi-X)^2/n-1	std deviation	95% interval	CV (%)
Reactive	9	1	2.4						
	2	2	6.48						
	10	12	6.6						
	11	48	4.98						
	7	102	4.38						
	3	144	10.86						
	4	193	4.26						
Control	c-2	4	2.76						
	c-1	48	2.04						
	c-5	193	1.8						
Standard	5.75 mg/L		5.82	5.79	0.0009	0.0018	0.042426	0.38118	0.732753
	5.75 mg/L		5.76		0.0009				
			0.030	0.041577					

APPENDIX G

RESULTS OF GAS ANALYSES

Typical gas results for reactive hypovial. The retention time (RT=2.20) of the peak corresponded to nitrogen at 100 %.

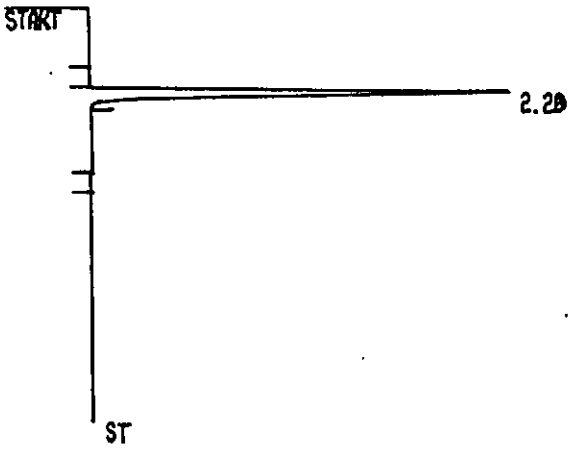
TOTAL AREA= 8731500
MUL FACTOR= 1.0000E+00



RUN # 160 OCT/29/93 00:44:37
WORKFILE ID: B
WORKFILE NAME:

ESTD RT	AREA	TYPE	CAL #	AMOUNT
2.18	8562700	PB	1	0.671

TOTAL AREA= 8562700
MUL FACTOR= 1.0000E+00



RUN # 161 OCT/29/93 00:59:05
WORKFILE ID: B
WORKFILE NAME:

ESTD RT	AREA	TYPE	CAL #	AMOUNT
2.20	7629500	PB	1	0.598

TOTAL AREA= 7629500

APPENDIX H

CALCULATION OF THE MINIMUM DETECTION LIMIT AND THE VARIANCE ON S FOR THE SORPTION ISOTHERMS

Calculation of the minimum detection limit and the error on S for the sorption isotherm experiments

For the sorption experiments the amount of PCP sorbed was calculated from the difference between the initial and the equilibrium concentrations according to:

$$S = (Co - C)\, V / m$$

where:

Co = initial PCP concentration
C = final equilibrium PCP concentration
V = volume of solution in hypovials
m = mass of iron .

Since S is calculated from a combination of variables, each with a different error, the error on S must also be calculated from a combination of the errors on the variables that comprise S. The variances can be combined according to the rules described by Kretz (1985). If, for example, a variable y is a function of three variables, x1, x2, and x3 then the variance of y can be calculated by:

$$var(y) = var(x1)\,(\partial y/\partial x1)^2 + var(x2)\,(\partial y/\partial x2)^2 + var(x3)\,(\partial y/\partial x3)^2$$

Applying these rules to S, with the additional rule that $var(A \pm B) = var(A) + var(B)$, we get:

$$var(S) = (var(Co) + var(C))(V/m)^2 + ((Co-C)/m)^2 var(V) + (Co-C)V/m^4\, var(m)$$

and assuming a constant coefficient of variability (cv) for the concentration measurements, we have

$$var(Co) = (Co*cv)^2 \quad \text{and} \quad var(C) = (C*cv)^2$$

hence:

$$var(S) = (Co^2 + C^2)\, cv^2\, (V/m)^2 + ((Co-C)/m)^2\, var(V) + (Co-C)/m^4\, var(m)$$

The variances of the hypovial volume and of the iron mass are small relative to that of the squared concentrations, and therefore the first term dominates the equation. Based on the first term, it is clear that the variance of S is proportional to the sum of the squared concentrations (assuming a constant cv) and therefore the variance or the error on S increases rapidly with concentration. The 95% confidence intervals given in the Results and Discussion sections were based on the variance of S estimated with var(m)= 0.017,var(v) = 0.43 and cv= 3.35 %.

Since S is based on the difference between two concentrations, these two concentrations have to be significantly different from one another for S to be significantly different than zero. The value of S where, C is significantly different from Co at the 95% confidence level, is significantly different than zero when:

$$Co - C \geq 2(\sigma_{Co} + \sigma_C)$$

or:

$$S = (Co - C)\ V/m \geq 2(\sigma_{Co} + \sigma_C)\ V/m$$

If the coefficient of variability is constant over the range of Co-C, then

$$\sigma_{Co} = cv \cdot Co \quad \text{and} \quad \sigma_C = cv \cdot C$$

and therefore, S is significantly different than zero when

$$S \geq 2\ cv\ (Co + C)\ V/m.$$

The cv, Co and V were more or less constant during the experiments; only m and C varied. It is clear from this formula that when m decreases and/or C increases the detection limit on S increases. In the sorption experiments, when the mass of iron in the hypovials was small, little PCP was sorbed and therefore C remained high and close to Co. The combined effect of the small mass m and the high equilibrium concentration, C, resulted in extremely high detection limits as shown in the following tables and in Figures 8 and 9.

Calculation of the minimum detection limit and the error on S for sorption isotherms

SAMPLE	solution (mL)	solution (L)	IRON (g)	CV	PCP (mg/L)	pH	Eh	S ug/g	C ug/mL	Mass iron	Minimum Det. limit	Error on S variance s	variance iron	variance volume	95 % Conf int
				C	21.48										
A+B 1g	59.680	0.05968	1.011	0.0335	21.45	10.0	-33.0	2.10	21.45	1	169.77	3602.77	0.0003	1.116	7751.351
A+B 2.5g	60.000	0.06000	2.476	0.0335	19.80	10.1	-104.0	40.72	19.80	2.5	67.04	562.78	0.0003	0.286	1210.815
A+B 5g	59.640	0.05964	4.985	0.0335	15.96	10.5	-180.0	66.12	15.96	5	30.01	115.21	0.0006	0.145	247.867
A+B 7.5g	58.678	0.05868	7.459	0.0335	12.48	10.7	-189.0	70.84	12.48	7.5	17.90	42.93	0.0022	0.051	92.356
A+B 10g	58.110	0.05811	10.095	0.0335	8.58	10.7	-235.0	76.47	8.58	10	11.59	20.76	0.0031	0.531	44.675
A+B 20g	57.405	0.05740	19.889	0.0335	2.79	10.8	-278.0	55.09	2.79	20	4.69	4.77	0.0168	0.435	10.263
A+B 30g	55.765	0.05576	30.005	0.0335	0.63	10.8	-325.0	38.76	0.63	30	2.75	1.86	0.0148	0.145	4.002
A+B 50g	51.718	0.05172	50.059	0.0335	0.00	11.0	-270.0	22.19	0.00	50	1.49	0.55	0.0051	0.007	1.192

MEAN:	solution (mL)	solution (L)	IRON (g)	CV	PCP initia (mg/L)	pH	Eh (mV)	S ug/g	C ug/mL	Mass iron	Minimum Det. limit	Error on S variance s	variance iron	variance volume	95 % Conf int
100+101	58.743	0.05874	9.953	0.0335	26.35	11.1	-144.5	92.71	10.65	10	14.63	32.90	0.003136	0.531232	70.774
102+103	58.146	0.05815	9.984	0.0335	19.85	10.8	-125.0	73.21	7.28	10	10.59	17.86	0.003136	0.531232	38.425
104+105	58.460	0.05846	10.036	0.0335	13.74	10.8	-206.5	55.44	4.22	10	7.01	8.35	0.003136	0.531232	17.954
106+107	59.579	0.05958	9.946	0.0335	9.26	10.7	-325.0	46.09	1.57	10	4.34	3.87	0.003136	0.531232	8.327
108+109	58.949	0.05895	10.014	0.0335	3.90	10.7	-192.5	22.83	0.02	10	1.55	0.67	0.003136	0.531232	1.445

Calculation of the 95% confidence interval for sorption experiment

Mass of iron varied

DATA	REPLICATE	PCP mg/L	Average PCP	(xi-X)^2	Sum (xi-X)^2 / n-	std deviation	95 % int	CV (%)
1 g	B1	21.65	21.7075	0.0033	0.1708	0.4133	0.6576	1.904
	B1	21.19		0.2678				
	B2	22.19		0.2328				
	B2	21.8		0.0086				
2.5 g	B1	19.81	19.7975	0.0002	0.0034	0.0580	0.0922	0.2927
	B1	19.8		0.0000				
	B2	19.86		0.0039				
	B2	19.72		0.0060				
5 g	B1	16	15.9525	0.0023	0.0378	0.1945	0.3094	1.2192
	B1	15.7		0.0638				
	B2	15.94		0.0002				
	B2	16.17		0.0473				
7.5	B1	12.1	12.4725	0.1388	0.0989	0.3145	0.5003	2.5213
	B1	12.33		0.0203				
	B2	12.78		0.0946				
	B2	12.68		0.0431				
10 g	B1	8.55	8.3575	0.0371	0.0378	0.1945	0.3094	2.3271
	B1	8.5		0.0203				
	B2	8.19		0.0281				
	B2	8.19		0.0281				
20 g	B1	2.82	2.89	0.0049	0.0092	0.0959	0.1526	3.3189
	B1	2.8		0.0081				
	B2	2.94		0.0025				
	B2	3		0.0121				
30 g	B1	0.84	0.83	0.0001	0.0001	0.0115	0.0184	1.3912
	B1	0.84		0.0001				
	B2	0.82		0.0001				
	B2	0.82		0.0001				
50 g	B1	0	0	0.0000	0.0000	0.0000	0	-
	B1	0		0.0000				
	B2	0		0.0000				
	B2	0		0.0000				

Calculation of the 95% confidence interval for sorption experiment

Concentration varied

Data	Rep	Analyse	PCP (mg/L)	Average PCP	(xi-X)^2	Sum (xi-X)^2 / n-	std deviation	95 % int
1	B1	A1	10.89	10.645	0.0600	0.1286	0.3587	0.57062
1	B1	A2	10.89		0.0600			
1	B2	A1	10.67		0.0006			
1	B2	A2	10.13		0.2652			
2	B1	A1	7.27	7.28	0.0001	0.0114	0.1068	0.169872
2	B1	A2	7.27		0.0001			
2	B2	A1	7.42		0.0196			
2	B2	A2	7.16		0.0144			
3	B1	A1	4.25	4.2225	0.0008	0.0070	0.0838	0.13335
3	B1	A2	4.25		0.0008			
3	B2	A1	4.29		0.0046			
3	B2	A2	4.1		0.0150			
4	B1	A1	1.72	1.565	0.0240	0.0328	0.1812	0.288289
4	B1	A2	1.71		0.0210			
4	B2	A1	1.48		0.0072			
4	B2	A2	1.35		0.0462			
5	B1	A1	0.04	0.02	0.0004	0.0005	0.0231	0.036743
5	B1	A2	0.04		0.0004			
5	B2	A1	0		0.0004			
5	B2	A2	0		0.0004			

APPENDIX I

CURVE FITTING PROCEDURE FOR THE TWO SORPTION MODELS

Interpretation of the isotherm obtained from all data.

The data at equilibrium (T ≥ 24 hours) from several PCP removal experiments conducted in this study were used to generate the composite isotherm of Figure 10. This isotherm was calculated assuming that all the PCP removed from the solution was attributed to sorption on the iron solids. Six groups of data were plotted on the isotherm:

1· Batch test with Co = 22 mg/L, iron mass = 20g, duration : 193 hours
2· Batch test with Co = 23 mg/L, iron mass = 10g, duration : 175 hours
3· Batch test with Co = 22 mg/L, iron mass = 10g, duration : 700 hours
4· Iron loading test with Co = 22 mg/l, iron mass = 20 g
using cumulative PCP removed after 1,2,3 and 4 refills
5· Sorption test, variable iron, Co = 21.5 mg/L
6· Sorption test, variable initial concentration, iron mass = 10 g

Two sorption isotherm models were used to fit the experimental data: the Freunlich and the Langmuir isotherms as described in Dominico and Schwartz (1990).

Freundlich isotherm

This isotherm has the form :

$$S = K C^n \quad (1)$$

where

C : aqueous concentration at equilibrium
S : sorbed concentration at equilibrium
K, n: isotherm constants

The same Freunlich model can be written in a new form such as:

$$\log S = n \log C + \log K \quad (2)$$

By transforming the experimental data in log C and log S, the Freunlich isotherm plots as a linear relationship such as:

$$y = ax + b \quad (3)$$

where

$a = n$
$b = \log K$

A linear regression was performed on the log transformed data assuming a log normal error distribution on S. Constant n was found to equal 0.29 and b to equal 1.6235. By substituting

the constants into equation, the Freunlich isotherm becomes:

$$S = 42\ C^{0.29} \tag{4}$$

Langmuir isotherm

This isotherm has the form :

$$S = Q_0\ KC\ /\ (1 + KC) \tag{5}$$

where

C : aqueous concentration at equilibrium
S : sorbed concentration at equilibrium
Q_0: maximum sorptive capacity
K, n: isotherm constants

The same Langmuir model can be written in a new form such as:

$$C/S = 1/Q_0\ C + 1/(Q_0\ K) \tag{6}$$

By transforming the experimental data in C/S and C, the Langmuir isotherm plots as a linear relationship of the form:

$$y = ax + b \tag{3}$$

where

$a = 1/Q_0$
$b = 1/(Q_0K)$

A linear regression yielded $1/Q_0$ to equal 0.0092 and $1/(Q_0K)$ to equal 0.025. By substituting the constants in Equation (5), the Langmuir becomes:

$$S = 109*0.36*C\ /\ (1+0.36C) \tag{7}$$

The implication of this transformation on the error structure is not known.

The goodness of fit for both isotherm models was estimated from the coefficient of regression given by:

$$r^2 = SS_{regression} / SS_{total}$$

$$SS_{total} = SS_{residual} + SS_{regression}$$

SS_{total} : the sum of the squared deviations between plotted data and the mean of the regression

$SS_{residual}$: the sum of the squared deviations between plotted data and the regression data

$SS_{regression}$: the sum of the squared deviations between the regression data and the mean of the regression

The coefficient of regression is a measure of the amount of variability that is accounted for by the model. The regression was significant for both models:

r^2 Freunlich = 0.85 and r^2 Langmuir = 0.84.

Total isotherm

experiment	volume (L)	iron mass (g)	initial PCP (mg/L)	Final PC (mg/L)	S (ug/g)	C (ug/mL)
1 : batch test	0.06	20	22	2.41	58.77	2.41
2 : batch test	0.06	10	23	8.17	88.98	8.17
3 : batch test	0.06	10	22	7.87	84.78	7.87
4 : iron loading test	0.06	20	21.5	3.43	55.71	3.43
				12.47	84.30	12.47
				17.96	96.54	17.92
				18.85	105.99	18.85
5 : sorption test	PCP vary	10			92.71	10.645
					73.21	7.28
					55.44	4.22
					46.09	1.565
6 : sorption test	iron vary				76.47	8.58
					55.09	2.785
					38.76	0.625

Freundlich

S (measured)	C	S calc S=42C**0.29	c log	s log	SS residual S - Scalc	SS regression Scalc-S mean	SS total	r **2
38.757	0.625	36.648	-0.204	1.588	4.446	1169.218		
46.087	1.565	47.825	0.195	1.664	3.021	529.773		
58.770	2.410	54.204	0.382	1.769	20.845	276.817		
55.087	2.785	56.526	0.445	1.741	2.072	204.952		
55.710	3.430	60.046	0.535	1.746	18.801	116.556		
55.438	4.220	63.766	0.625	1.744	69.357	50.071		
73.207	7.280	74.691	0.862	1.865	2.202	14.812		
84.780	7.870	76.398	0.896	1.928	70.258	30.867		
88.980	8.170	77.231	0.912	1.949	138.031	40.822		
76.470	8.580	78.336	0.933	1.883	3.480	56.155		
92.706	10.645	83.391	1.027	1.967	86.759	157.484		
70.837	12.475	87.317	1.096	1.850	271.603	271.435		
96.540	17.920	96.988	1.253	1.985	0.201	683.596		
105.990	18.850	98.421	1.275	2.025	57.284	760.614		
mean :	7.630357	70.842		sum:	748.3579	4363.171	5111.529	0.8536

Regression Output:

Constant "b"		1.62348
Std Err of Y Est		0.04506
R Squared		0.88969
No. of Observations		14
Degrees of Freedom		12
X Coefficient(s) "n"	0.29082	
Std Err of Coef.	0.02956	

n = 0.29
K = 42

Langmuir

S (measured)	C	c/s	c/s calc 0.0092*C+0.0	S calc	SS residual S - Scalc	SS regression Scalc-S mean	SS total	r **2
38.757	0.625	0.016	0.031	20.259	342.155	2502.279		
46.087	1.565	0.034	0.039	39.663	41.278	937.570		
58.770	2.410	0.041	0.047	51.064	59.390	369.361		
55.087	2.785	0.051	0.051	55.007	0.006	233.345		
55.710	3.430	0.062	0.057	60.668	24.585	92.428		
55.438	4.220	0.076	0.064	66.174	115.257	16.879		
73.207	7.280	0.099	0.092	79.308	37.224	81.467		
84.780	7.870	0.093	0.097	80.970	14.518	114.221		
88.980	8.170	0.092	0.100	81.746	52.335	131.409		
76.470	8.580	0.112	0.104	82.740	39.302	155.186		
92.706	10.645	0.115	0.123	86.821	34.638	273.513		
70.837	12.475	0.176	0.139	89.511	348.730	369.758		
96.540	17.920	0.186	0.189	94.699	3.389	596.177		
105.990	18.850	0.178	0.198	95.323	113.775	627.062		
Mean :	7.630		Mean:	70.282	1226.583	6500.656	7727.240	0.8413

Regression Output:

Constant "1/(QoK)"		0.02513
Std Err of Y Est		0.01443
R Squared		0.93542
No. of Observations		14
Degrees of Freedom		12
X Coefficient(s) "1/Qo	0.00916	
Std Err of Coef.	0.00069	
Qo	109.19845	
K	0.3644656	