

# Monitoring Lead in Soil Water System Using Complex Permittivity

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**Abstract.** The complex permittivity was investigated to detect lead contamination in soil. The system used consists of an Automatic Network Analyzer (ANA), a sample holder, coaxial cables and a personal computer for data processing. Five samples of Halton Till soil were prepared and mixed with five different concentrations of hybrid blends of lead salts ( $\text{PbSO}_4$ ,  $\text{PbCl}_2$  and  $\text{Pb}(\text{NO}_3)_2$ ). The objective was to investigate the capability of complex permittivity to detect lead, when introduced to the soil in hybrid blend salts. Chemical analysis was conducted on the pore water of the six soil samples to investigate lead transport and the potential risk of lead in groundwater sources. The results show that the complex permittivity is sensitive to the change in lead concentration in soil as the real part decreases and the imaginary part increases with the increase of lead concentration. The real part decreased from 23 to 17 when the concentration of the lead increased from 0 to 1800 ppm. The imaginary part increased from 16 to 24 as the lead concentration in soil increased from 0 to 1800 ppm. The chemical analysis of the pore water showed that the electrolytes increased as lead concentrations increased in soil. The results displayed that the complex permittivity could be used as a non-destructive tool to monitor lead contamination in soil.

## 1. Introduction

Heavy metals (lead, mercury, cadmium and arsenic) are toxic and can cause contamination in the environment. The release of heavy metals to the environment affects human health, wildlife and the ecosystems. Many hazardous substances and heavy metals such as Pb, As, Ba and Cd are released to the subsurface as a result of industrial activities. Improper disposal of these substances has a significant adverse impact on the environment [1].

Many industries all over the world, and especially in the developed countries, generate wastewater daily which contains high levels of metals. In the past, at the start of the industrial revolution, any damage that heavy metals could have caused to the environment was not known. Many industries discharged their wastewaters directly to rivers and lakes causing pollution of water systems. Eventually, the contamination is transferred to humans, wildlife and vegetation. The environmental problem has become an important issue in the world. Strict environmental regulations have been established in order to protect the environment from pollution.

Lead in soil usually results from leaded gasoline, pulverized lead in paint, and from waste disposal. The lead emitted to the atmosphere from various sources accumulates in the soil. Its accumulation depends on the rate of its disposal from the atmosphere and the magnitude of lead released to the environment. Inorganic forms of lead such as lead oxide and lead chloride are the most widely released forms of lead to soil. The concentration of lead in natural soils is usually less than 50 ppm [2].



Lead in soil in populated areas has resulted in an increase of lead levels in the blood of both children and adults. Lead in soil causes severe health problems to children engaged in hand to mouth lead transfer. Therefore, soil should be addressed as a potential lead pathway to people. People should be aware of its danger and the hazard that it represents, so that they can take the required precautions. Regulators and the public health community should acknowledge this as a very serious matter, so that strict regulations can be issued to protect people, animals and the environment from lead contamination [3].

The vast industrial revolution of the last century brought environmental contamination issues to the forefront of mankind attention, which raised environmental awareness. In the last decade environmental contamination became one of the most important global concerns. More recently, soil contamination problems have attracted a lot of research endeavours and resulted in a wealth of pertinent published literature. In particular, it has been recognized that more efficient methods to study and monitor soil contamination process need to be developed.

The conventional monitoring methods involve soil and water sampling and a chemical laboratory analysis. Drawbacks of these methods are that they are expensive and time consuming. It is of great importance to find an alternative, in-situ, fast and non-destructive method, that is able to delineate soil contamination. The study of the interaction between the soil-water system and the incident electromagnetic waves is known as microwave aquametry [4]. Using electromagnetic waves to characterize soil properties and to identify soil contamination is one of the alternative methods used to monitor soil contamination.

The response of the soil-water system to electromagnetic waves can be characterized in terms of conduction and polarization. Polarization represents the ability of material to store electrical energy, while conduction is the energy loss due to polarization and ionic conduction. Both terms are combined in one term known as the soil complex permittivity ( $\epsilon^*$ ). Theoretical and experimental studies have been carried out and results have been reported in the literature on the investigation of soil water complex permittivity [5]-[7]. It has been found that the complex permittivity reflects the physical and chemical properties of a soil-water system, making it feasible to study changes in soil contamination.

In the course of the current research, the soil complex permittivity method is investigated and evaluated for detecting lead contamination in soil. If the soil complex permittivity measurement is found to be sensitive to the chemical change in the soil pore fluid, the complex permittivity method will be a promising tool in lead site assessment. The system used to measure the soil complex permittivity is the transmission line technique, where the soil sample is placed in a coaxial holder to measure its complex permittivity. Because several researchers have had success when using the coaxial holder to characterize soil properties [8], [9]. More details about the used system can be found elsewhere [10].

This paper presents results of complex permittivity measurements in lead contaminated soils. Hybrid blends of three lead salts ( $\text{PbCl}_2$ ,  $\text{PbSO}_4$ ,  $\text{Pb}(\text{NO}_3)_2$ ) at different concentrations were mixed with soil. The lead concentrations are selected based on Ontario Ministry of Environment and Energy (MOEE, 1996) for soil (200 ppm – 1000ppm).

The objective in this chapter is to investigate the relationship between soil complex permittivity and lead concentrations in hybrid lead salts, which could be used as an indicator to detect soil contamination with lead. The main objectives of the current research work can be summarized as follows:

- Study the relationships between lead concentrations in soil contaminated by lead and the complex permittivity.
- Investigate the capability of complex permittivity to detect lead in soil. This was done by measuring the complex permittivity of soils mixed with artificial solutions of three lead salts ( $\text{PbSO}_4$ ,  $\text{PbCl}_2$  and  $\text{Pb}(\text{NO}_3)_2$ ).
- Investigate lead transport and the potential risk of lead in groundwater sources.

## 2. Preparation of Soil Samples Contaminated with Lead Solutions

The soil used in this investigation is Halton Till. The clay minerals in this soil are identified as illite, chlorite and smectite (trace), and the non-clay minerals are quartz, feldspar and carbonates including calcite (12.7%) and dolomite (3.5%) [11]. Multiple salt solutions were prepared using three lead salts (i.e. lead nitrate ( $\text{Pb}(\text{NO}_3)_2$ ), lead chloride ( $\text{PbCl}_2$ ), and lead sulfate ( $\text{PbSO}_4$ )) to study the possibility of tracing lead contamination in complex forms. The lead concentrations used in the investigation were based on Ontario Ministry of Environment (MOE). The lowest concentration were chosen according to the MOE Guideline (MOE 1996) for residential areas, while the highest concentration were based on the allowable lead concentration for industrial areas. Table 1 summarizes the solutions used to prepare soil specimens.

**Table 1.** The solutions used to prepare soil specimens

Chemical	Sample #	Contaminant Concentration in Soil (ppm)		
		$\text{Pb}(\text{NO}_3)_2$	$\text{PbCl}_2$	$\text{PbSO}_4$
	HT1	0	0	0
$\text{Pb}(\text{NO}_3)_2$	HT2	48.76	44.6	51
+	HT3	97.5	89.3	102
$\text{Pb Cl}_2$	HT4	274	251	287
+	HT5	487	447	511
$\text{Pb} (\text{NO}_3)_2$	HT6	867	795	907

Since lead chloride and lead sulfate have low solubility in water, they are sieved through a sieve #200. The lead that passed through this sieve was weighed and mixed with water. After oven drying the soil in the oven, the lead salt solutions were mixed with the soil; the soil was put in bags, sealed and left overnight for the soil moisture to reach equilibrium. The soil mixed with the lead solutions was then compacted in an apparatus designed by Scholte [9]. The soil samples were then mixed with the lead salt solutions and left overnight to reach equilibrium. The pore water was obtained by squeezing the soil sample using a Pneumatic Pore Water Squeezer (Serial No. GRC-3) which generated a maximum stress of 25 MPa on the soil samples. The time needed to squeeze each sample was about six hours.

### 3. Chemical Properties of Soil Pore Water

The concentrations of the major anions and cations were measured from the soil pore fluid. This was done to detect the chemical composition change in the pore fluid due to lead contamination. The pH and electrical conductivity of the pore fluid were measured using pH and conductivity meters. The anion concentrations (chloride, sulfate, nitrate) in the pore water were measured using High Liquid Performance Chromatography (515 HLSPC), which was capable of measuring the three anions at the same time. Cations, such as  $\text{Pb}^{+2}$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$  were measured using a Philips Atomic Absorption Spectrometer PU9100X. The pH of the squeezed liquid was measured using an ORION Ag/AgCl SURE-FLOWTM Electrode (Model No. 9165BN).

Table 2 shows the chemical analyses for all soil samples mixed with lead solutions with different concentrations. As shown in the table, there was no trace of lead in the pore fluid of all five-soil specimens. The concentrations of calcium, magnesium, potassium, chloride, sulfate and nitrate increased when the concentration of lead in the soil increased (Table 2). Sodium and potassium did not show any significant increase. The pH of the pore fluids was remained in a very narrow range with an average of 7.4. This pH value is close to the value reported by Xei [12], which could be attributed to the carbonate in the soil that controlled the pH for all soil samples mixed with lead nitrate.

The analysis of the pore water shows significant amounts of hydrocarbonate ( $\text{HCO}_3^-$ ). Because of the high carbonate content, the pore water remains alkaline. Therefore, the precipitated lead carbonate remains insoluble due the high carbonate, which explains why lead is absent in pore waters of the soil samples tested. It is concluded that the alkaline pH of the soil plays an important role in the attenuation of lead. As indicated by Harter [13]), the presence of calcium (Ca) in soil plays an effective role in the absorption of lead. Because of the exchange reaction between calcium and lead,

calcium desorbs while Pb adsorbs to the clayey soil [14]. Since calcium is situated at the edges of clay particles, it is easily exchanged with lead [15]. Moreover, the maximum cationic exchange occurs when soil pH is higher than seven [16]. It can be seen the increase in sulfate concentration with higher lead concentration introduced into the soil. It can also be attributed to the exchange reaction between sulfate and lead, sulfate desorbs while Pb adsorbs to the clayey soil.

**Table 2.** Summary of pore water analysis

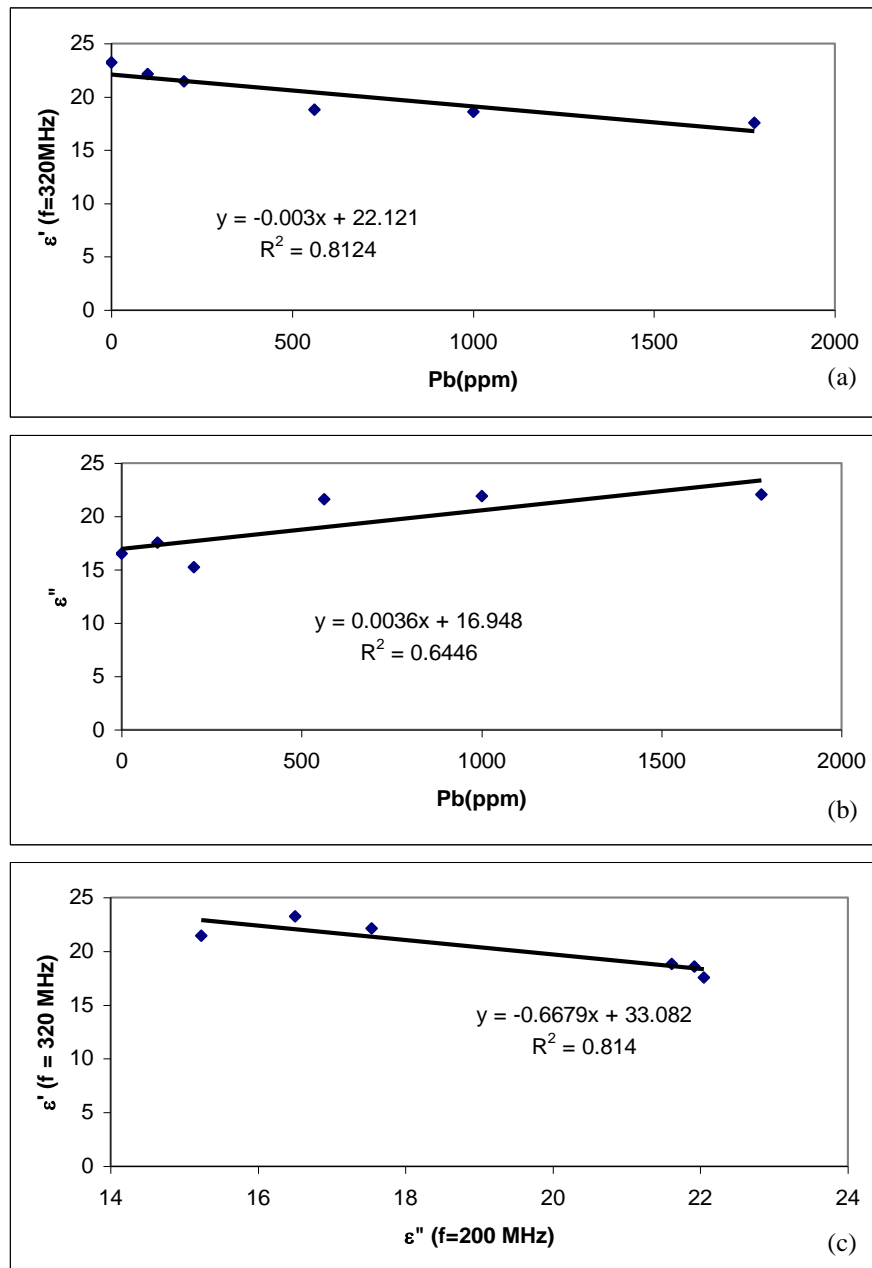
Chemical	P SO <sub>4</sub> + Pb Cl <sub>2</sub> + Pb (NO <sub>3</sub> ) <sub>2</sub>					
Sample	HT1	HT2	HT3	HT4	HT5	HT6
Conductivity (mS/cm)	2.3	2.45	2.62	3.83	4.65	6.12
Pb <sup>2+</sup> (mg/L)	ND*	ND*	ND*	ND*	ND*	ND*
Na <sup>+</sup> (mg/L)	245	230	185	215	205	245
Mg <sup>2+</sup> (mg/L)	130	160	156	226	250	310
Ca <sup>2+</sup> (mg/L)	760	860	906	1348	1784	2380
K <sup>+</sup> (mg/L)	12	13.5	7	5.5	4.75	8.75
Cl <sup>-</sup> (mg/L)	179	87	54	260	470	766
SO <sub>4</sub> <sup>2-</sup> (mg/L)	1800	1087	1820	1800	1820	2030
NO <sub>3</sub> <sup>-</sup> (mg/L)	165	213	200	1530	1700	2500
HCO <sub>3</sub> <sup>-</sup> (mg/L)	114	175	135	279.6	180	371

\*ND: Non detectable

#### 4. Complex permittivity for soil mixed with Pb(NO<sub>3</sub>)<sub>2</sub>+PbCl<sub>2</sub>+PbSO<sub>4</sub> solutions

Figure 1a presents the relationship between lead concentration and the real relative permittivity at the dispersion frequency (320MHz). The real relative permittivities decreases when salt concentrations increase. The relationship is linear with  $R^2 = 0.812$ . Figure 1b presents the relationship between the imaginary part and lead concentrations at frequency 200MHz. They are also linearly related. The imaginary part increases with lead salt increase with  $R^2 = 0.64$ . Figure 1c shows the relationship between the imaginary and relative real permittivity. Which are linearly related with  $R^2 = 0.814$ .

After investigating the feasibility of measuring the complex permittivity to detect lead in soil when lead presents in the seven abovementioned forms, it is concluded that the complex permittivity is sensitive to the changes in lead concentrations in the soil.



**Figure 1.** Halton Till mixed with lead chloride, lead nitrate and lead sulfate  $\text{PbCl}_2 + \text{Pb}(\text{NO}_3)_2 + \text{PbSO}_4$  complex permittivity relationships

- (a)  $\epsilon'$  at dielectric dispersion (f=320 MHz) versus concentration
- (b)  $\epsilon''$  at (f=200 MHz) versus concentration
- (c)  $\epsilon'$  at dielectric dispersion (f=320 MHz) versus  $\epsilon''$  at (f=200 MHz)

##### 5. Complex permittivity of pore water for soil mixed with lead chloride, lead nitrate and lead sulfate

Figure 2a presents the relationship between lead concentration and the real relative permittivity along with the deionized distilled water at 2GHz. This figure shows that the real relative permittivities decrease when salt concentrations increase.

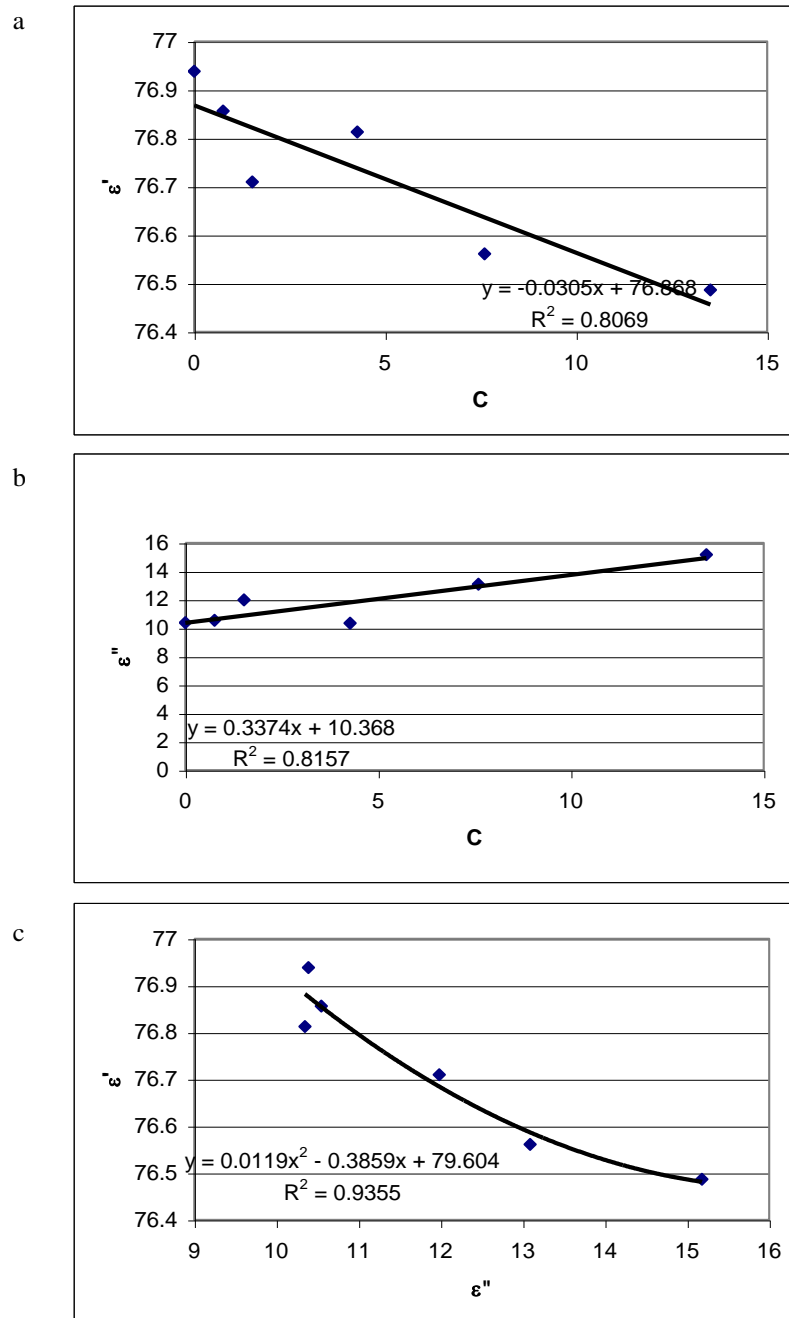


Figure 2. Complex permittivity of pore water squeezed from Halton Till soil mixed with hybrid lead salts (lead chloride, lead nitrate and lead sulfate) at  $f=2$  GHz.

- $\epsilon'$  versus concentration
- $\epsilon''$  versus concentration
- $\epsilon'$  versus  $\epsilon''$

The relationship is linear with  $R^2 = 0.8$ . Figure 2b presents the linearly relationship between the imaginary part and lead concentrations at 2GHz. The imaginary part increases when lead salt increases with  $R^2=0.8152$ . The changes of the complex permittivities of the pore fluids are due to changes in static conductivities and ion concentrations of the soil pore fluids when soil samples are mixed with lead nitrate solutions. This indicates that complex permittivity measurements of pore fluid are sensitive to changes in lead nitrate and lead chloride and lead sulfate concentrations in soil. Figure 2c shows the second order relationship between the imaginary and relative real permittivity with  $R^2=0.93$ .

## 6. Conclusions

The complex permittivity system was investigated to detect lead in soil. Six soil samples were prepared with six different concentrations of ternary blends of lead salts ( $\text{PbSO}_4$ ,  $\text{PbCl}_2$  and  $\text{Pb}(\text{NO}_3)_2$ ). The soil samples were squeezed and the chemicals and complex permittivity of the pore water were measured. The following conclusions can be drawn:

- The complex permittivity of soil is sensitive to changes in lead concentration, the real part decreases and the imaginary part increases as lead concentration increases. The real part decreased from 23 to 17 when the concentration of the lead increased from 0 to 1800 ppm. The imaginary part increased from 16 to 24 as the lead concentration in soil increased from 0 to 1800 ppm.
- The chemical analysis showed that there is no lead in all pore water samples and lead was retained on soil.
- The results showed that the complex permittivity method can be used to detect lead in soil from a contaminated site where the form of lead and its concentrations are not known.

## 7. References

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