Assessment of concentration in contaminated soil by potentially toxic elements using electrical properties

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Abstract Soils contaminated by potentially toxic elements (PTEs) which affect human health, such as zinc, lead, mercury, cadmium, and arsenic, were applied. The aims of this study are to judge contamination of soil and also to evaluate concentration of contaminated soil using electrical properties such as electrical resistivity and permittivity. The frequency was applied in the experiment ranged from 100 Hz to 10 MHz. As a result, the values of electrical resistivity and permittivity of each soil contaminated by PTEs could be presented as a function related to frequency and could determine whether the soil was contaminated. Also, results indicated that electrical properties give a reliable estimation of concentrations of PTEs contamination in soil.

Keywords Soil contamination **·** Electrical resistivity **·** Permittivity **·** Concentration **·** Potentially toxic elements

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Introduction

Environmental contamination has had many unexpected consequences, causing serious damage in all the aspects of our lives. Especially, soil contaminated by potentially toxic elements (PTEs) may not damage the crop but can accumulate in different organs or tissues, hence posing a threat to human health if consumed. Soil contamination has an adverse effect on soil properties and is one of the immediate causes of both underground water and surface water contamination. Water and air pollution can be restored relatively rapidly by natural diffusion or dilution; due to soil's lack of mobility, it becomes contaminated slowly, and restoration is a long process (Nriagu and Pacyn[a](#page-10-0) [1988\)](#page-10-0). Contamination remains a perplexing problem because of the high cost and difficulty of removing hazardous materials properly from the soil (Harrison and Willso[n](#page-9-0) [1985\)](#page-9-0). Soil contamination has become a matter of great importance to mankind due to the fast pace of industrialization. In particular, PTEs are major contaminants, accumulating in the soil over a long period of time. Their toxicities are hazardous to the human body (Nriag[u](#page-10-0) [1988;](#page-10-0) Nriagu and Pacyn[a](#page-10-0) [1988](#page-10-0); Thornto[n](#page-10-0) [1993\)](#page-10-0). When evaluating soil contaminated with PTEs, it is crucial to determine which method of evaluation should be adopted and how to analyze the acquired data. Analysis of total PTE concentrations, sequential chemical extraction, and

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isotopic analysis are used to evaluate soil contaminated with PTEs (Wong and L[i](#page-10-0) [2003](#page-10-0)). Analysis of total PTE concentrations is the most frequently used method to date. It includes neutron activation analysis (NAA), X-ray fluorescence spectroscopy (XRFS), inductively coupled plasma, and atomic absorption spectrometry. A method is chosen according to factors such as sample type, target elements, and laboratory conditions (Wong and L[i](#page-10-0) [2003\)](#page-10-0). Since NAA requires a nuclear reactor or other neutron source to analyze data, it has not been widely used (Helmk[e](#page-9-0) [1996](#page-9-0)). XRFS is known as a rapid, reliable, and nondestructive method that draws a faster result than traditional chemical analysis methods (Karathanasis and Hajek [1996](#page-9-0)). Sequential chemical extraction has been used to examine chemical conditions of PTEs contained in soil, and Tessier's method is the most commonly used of the methods suggested so far (Tessier et al[.](#page-10-0) [1979\)](#page-10-0). Isotopic analysis enables us to judge what kind of PTEs has contaminated the soil. It has been used in numerous studies of PTEs in the environment and has been applied in many previous studies of Lead (Pb) (Farmer and Eade[s](#page-9-0) [1996;](#page-9-0) Gelinas and Schmi[t](#page-9-0) [1997;](#page-9-0) Marcantonio et al[.](#page-9-0) [1999;](#page-9-0) Munksgaard et al[.](#page-10-0) [1998;](#page-10-0) Hansmann and Koppe[l](#page-9-0) [2000;](#page-9-0) Zhu et al[.](#page-10-0) [2001\)](#page-10-0). All the methods mentioned above require special equipment, expert knowledge and time, thus incurring high expenses. In order to overcome this problem, electrical properties of soil were applied.

There are three routes in soil through which an electrical current flows: a route by both soild and pore fluid, by the soil particle alone, and by the pore fluid alone (Smith and Arulananda[n](#page-10-0) [1981;](#page-10-0) Mitchel[l](#page-9-0) [1993](#page-9-0)). In soil with wet conditions, electric currents are conducted through connected the pore fluid which has a high conductivity and is defined to be a main route of electrical currents generated in soil (Yoon et al[.](#page-10-0) [2002\)](#page-10-0). It is also known that electrical resistivity in soil is subject to the influence of factors such as porosity, the electrical resistivity of the pore fluid, characteristics of the solids, degree of saturation, particle shape and orientation, and pore structure (Keller and Frischknecht [1966](#page-9-0); Parkhomenko [1967;](#page-10-0) Arulanandan and Muraleetharan [1988;](#page-9-0) Ward [1990](#page-10-0); Thevanayagam [1993](#page-10-0); Yoon and Park

[2001\)](#page-10-0). The ratio of the real permittivity of the material to the permittivity of free space is called the relative permittivity or dielectric constant and presen[t](#page-9-0)ed as *K'* (Keller and Frischknecht [1966\)](#page-9-0). When subsurface contamination is measured in a soil–fluid system, measuring permittivity in addition to electric resisitivity has been suggested, in order to eliminate factors that could influence electric resistivity (Kaya et al[.](#page-9-0) [1994;](#page-9-0) Thevanayaga[m](#page-10-0) [1995\)](#page-10-0). This is because chemical composition or particle shape rarely influences permittivity in soil, and the value is considerably lower than in most liquids. While water has comparatively high permittivity, most soil has low permittivity (Selig and Mansukhan[i](#page-10-0) [1975](#page-10-0)).

PTEs such as zinc, lead, mercury, cadmium, and arsenic are toxic to humans and cause more serious problems when soil is contaminated by them. Nevertheless, PTEs have been widely used in industry for a long time. Since their properties are colorless and odorless, it is difficult to judge visually contamination of soil and even harder to detect the presence of PTEs. Due to these difficulties, contamination tends to be detected after a long while, serious damage occurred frequently. Therefore, detection of contamination by PTEs as early as possible and evaluation of its concentration are very important in the treatment of soil contamination as a first step. This research suggests an effective method for judging soil contamination by PTEs and for assessment its concentration using electrical properties.

Materials and testing methods

Materials

Three different soils were collected in Hwaseong, Gyeonggi Province, South Korea and were labeled as H-1, H-2, and H-3 according to the sampling location. All of the soils were classified as silty sand by Unified Soil Classification System, and their physical properties are summarized in Table [1.](#page-2-0)

PTEs used in the research were Zinc (Zn), Pb, Mercury (Hg), Cadmium (Cd), and Arsenic (As) as standard solutions in concentration of

1,000 μg/mL (Kanto Chemical Co. Inc., Japan). Fifteen percent of the gravimetric water content was equally applied to all specimens and compacted to the designed dry unit weight $(=12.6 \text{ kN/m}^3)$. Testing data for all specimens with different contaminant types and concentrations were estimated at the same volumetric water content $(=0.19)$ since it was the most practical criterion assessing the electrical properties of unsaturated soil. Distilled water was used in order to avoid the influence of ion in pore water. Diluted solutions of PTEs with distilled water in concentration of 5, 20, 30 mg/L were applied.

Testing methods

Prior to mixing with soils, electrical properties of PTEs solutions were observed. Value variation of each PTE was observed according to frequency ranges and concentration. Electrical resistivity (ρ) was calculated as

$$
\rho = K \frac{V}{I} \frac{A}{d} \tag{1}
$$

where $K =$ calibration factor; $V =$ voltage; $I =$ current; $A =$ the area of the electrodes; and $d =$ distance between the electrodes.

The permittivity (K') were calculated as (Agilent Technolog[y](#page-9-0) [2000\)](#page-9-0)

$$
K' = \frac{C_s}{C_0} = \frac{C_m - C_e}{\varepsilon_0 \times (A/d)}
$$
(2)

where C_s = capacitance of the specimen; C_0 = capacitance of the free space; ε_0 = permittivity of the free space (=8.85 × 10⁻¹² \hat{F}/m); C_m = measured capacitance; and C_e = edge capacitance.

The edge capacitance (C_e) in the dimension of pF was calculated by

$$
C_e = (0.0019K' - 0.00252 \ln d + 0.0068) \pi (2r + d)
$$
\n(3)

where $r =$ radius of circular electrode(mm); and $d =$ thickness of the specimen (mm) (AST[M](#page-9-0) [1994;](#page-9-0) Oh et al[.](#page-10-0) [2007\)](#page-10-0).

The specimen was placed between two brass electrodes that were 70 mm in diameter and 20 mm apart in the acrylic mold. A compaction rod having the same dimension with the mold was used to fill the soil in the mold. For the consistent test condition, the same amount of soil poured into the mold was compacted to the height of 15 cm. A two-electrode method was employed to minimize the effect of non-homogeneity and the disturbance in the specimen (McCarter [1984;](#page-9-0) Rinaldi and Cuestas [2002](#page-10-0)). The electrical properties were measured using HP4285A Precision LCR meter (Hewlett–Packard, USA) at the range of 100 kHz to 10 MHz and Agilent 4263B LCR meter (Agilent Technologies Japan, Ltd.) at the range of 100 Hz to 100 kHz. Also, the electrical properties were measured at 18 ∼ 20◦C to minimize the effect of temperature variation.

For observing polarization and to determine the lower limit of frequency, permittivity of distilled water, tap water, and 1.8 and 3.7 mM KCl solutions were measured. While the permittivity of distilled water was the constant over the frequencies, those of tap water and KCl solutions increased with decreasing frequency at below 100 kHz. From results, 100 kHz (0.1 MHz) was determined as the lower limit of frequency. In order to avoid or minimize polarization, several methods were suggested in previous studies (Scott et al. [1967;](#page-10-0) Hill et al. [1969](#page-9-0); Gross and McGehee [1988\)](#page-9-0). However, Santamarina claims that these methods are ineffective and unreliable (Santamarina et al[.](#page-10-0) [2001](#page-10-0)). Effective quantification of polarization, to date, is difficult and no method can eliminate polarization. Based on these estimations, the permittivity analysis was performed only for the data measured above 100 kHz also to minimize.

Results and discussion

Electrical properties of PTE solutions

Electrical resistivity and permittivity of PTEs solutions diluted with distilled water by 5, 20, 30 mg/L were tested. The results are shown in Table 2.

Fig. 1 Relationship between electrical resistivity (*ER*), permittivity (*PE*), and Frequency for soils mixed with different concentration of Zn solution: **a** ER of H-1; **b** PE of H-1; **c** ER of H-2; **d** PE of H-2; **e** ER of H-3; **f** PE of H-3

Fig. 1 (continued)

While electrical resistivity and permittivity values tended to decrease as concentration got higher, the value of variation was not remarkable in spite of the change of frequency. In arsenic, the electrical resistivity was comparatively higher than others, and it could not measure at 10 MHz. Arsenic also had the constant permittivity value of 82 \sim 83 regardless of various concentrations and frequencies except for 10 MHz.

Electrical properties of contaminated soils by PTEs

Regressive equations were derived from the values of electric resistivity and permittivity in each concentration and frequency. The results of contaminated specimens by Zn are shown in Fig. [1,](#page-4-0) and the regressive equations are presented in Table 3.

As shown in Fig. [1,](#page-4-0) the electrical resistivity decreased with the frequency and the concentration. This is because the high concentration was due to more frequent electric conduction generated by ionic mobility. The permittivity value also had a tendency to decrease as the frequency increased, which is a different result from PTEs solutions. As the concentration got higher, the permittivity value increased, which was particularly remarkable at the considerably low frequency of

The values of electrical resistivity and permittivity could be expressed as functions of log and involution related to frequency, as:

$$
\rho = \alpha \cdot Ln(f) + \beta \tag{4}
$$

$$
K' = \gamma \cdot f^{\delta} \tag{5}
$$

where α , β , γ , δ = constants in dimensionless; and $f =$ Frequency (MHz).

Experiments of contaminated specimens by Pb, Hg, Cd, and As were conducted using the same methods. Equations in Figs. 1–4 of ESM were specified according to the results. Results were very similar to Zn case, which are shown in Figs. 1–4 of ESM, respectively. That is, in all specimens, electrical resistivity and permittivity tended to decrease as the frequency increased. Electrical resistivities of contaminated specimens were lower than those of non-contaminated (original) specimens. Especially, when As solution was mixed soil, electrical resistivity was not much different from other contaminated specimens.

Table 3 Regressive equations of electrical properties vs. frequency for soils mixed with different concentration of Zinc solution

Evaluation of concentration in contaminated soils by PTEs

To evaluate the concentration of contaminated soil, the ratios of electrical properties were found by comparing PTEs solutions to contaminated specimens by PTEs. The ratios were specified as *I*ER and *I*PERM and each of them always has larger value than zero. $I_{\rm ER}$ and $I_{\rm PERM}$ can be obtained by Eqs. 6 and 7.

$$
I_{\rm ER} = \frac{\rho_{\rm mixed}}{\rho_{\rm solution}}\tag{6}
$$

$$
I_{\text{PERM}} = \frac{K'_{\text{mixed}}}{K'_{\text{solution}}}
$$
 (7)

Table 5 Regressive equations of I_{ER} and concentration against all frequency

Heavy metals	Concentration $(mg/L) = A \cdot I_{\text{ER}}^B$ $(A,B;$ constants in dimensionless)	R^2			
			Zinc	$3.54 \cdot I_{\rm FR}^{0.92}$	0.9419
			Lead	$4.19 \cdot I_{\rm ER}^{0.87}$	0.9497
			Mercury	$4.88 \cdot I_{\rm ER}^{0.82}$	0.9331
Cadmium	$3.47 \cdot I_{\rm ER}^{0.95}$	0.9576			
Arsenic	44.80 $\cdot I_{\rm FR}^{1.20}$	0.9284			

where ρ_{solution} , K'_{solution} = Electrical resisitivity and permittivity values of PTEs solution and ρ_{mixed} , $K'_{\text{mixed}} =$ Electrical resisitivity and permittivity values of contaminated soil.

The values of *I*_{ER} and *I*_{PERM} which are average of all specimens obtained by the Eqs. [6](#page-7-0) and [7](#page-7-0) are presented in Table [4.](#page-7-0)

As shown in Table [4,](#page-7-0) I_{ER} and I_{PERM} had a tendency to increase as the concentration of contamination increased. *I*_{ER} values of Arsenic were very low due to its considerably higher value in solution. This result was enough to distinguish it from other PTEs, unlike in the previous experiment**,** in which electrical resistivity of contaminated specimen by arsenic was not distinctive enough from those of contaminated specimens other PTEs.

Since the variation of the values was small according to the frequency at each concentration, the electrical resistivity could be expressed in one equation in the frequency range of 100 Hz \sim 10 MHz, as summarized in Table 5. However, the permittivity was divided into the range based on frequency and concentration because the variation of the permittivity was bigger than the electrical resistivity, as summarized in Table 6.

The concentration of contamination could be found and presented as Eqs. [8](#page-9-0) and [9](#page-9-0) by applying values of both electric resisitivity and permittivity. By applying the Eq. [8,](#page-9-0) the concentration can be

found using I_{ER} . When the Eq. 9 is applied, a more accurate concentration of contaminated soil can be found according to various frequencies and concentrations using I_{PERM} ,

Concentration $\left(\frac{mg}{L}\right) = A \cdot I_{ER}^B$ (8)

Concentration $\left(\text{mg } / L\right) = C \cdot e^{D \cdot I_{\text{PERM}}}$ (9)

Where $A, B, C, D =$ constants in dimensionless.

That is, the concentration of contamination could be simply and quickly evaluated using electrical resistivities, since it is calculated by one equation, while equations of permittivity were divided into the range based on frequency and concentration in order to determine the accurate concentration. Also, these equations are very useful for verifying the concentration of contamination obtained by electrical resistivity.

Summary and conclusions

Electrical properties of PTEs solutions and contaminated specimens by PTEs were estimated both to evaluate the concentration of contamination and to decide whether or not soil was contaminated. Zn, Pb, Hg, Cd, and As were used for this research. The following results were found:

- 1. Permittivity of arsenic solution was almost constant as though concentration and frequency were changed. However, when arsenic solution was mixed with soil, the trend of permittivity was followed the other PTEs.
- 2. In contaminated soils, electrical resistivity and permittivity are related to the function of frequency in different concentrations, which is helpful for judging contamination of PTEs.
- 3. Concentration of PTEs contamination in soil was simply and quickly estimated by one equation was found using electrical resistivity.
- 4. To estimate the concentration of contamination and to verify the results of electrical resistivity in soil, permittivity was very useful. Electrical resistivity and permittivity could be employed as alternative methods for determining PTEs contamination in soils.

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