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Comparison of perchloroethylene extraction techniques in soil gas survey quantification

Invited Paper

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Abstract: Subsurface pollution by volatile organic compounds has emerged as a widespread problem in industrialized countries. This study compares static headspace technique and methanol extraction/purge-and-trap analysis followed by thermal desorption/gas chromatography in attempts for quantification of gas survey results in the determination of these chemicals in soil. Several soils were contaminated with aqueous solution of perchloroethylene (PCE) (140 mg L^{-1}) using a vapor treatment method. Soil spiking took place up to 24 h in desiccator by exposing individual soil samples contained in open 40 mL glass vials to PCE evaporated from the solution. After exposure the samples were stored and analyzed within 2 days. The achieved results strongly suggest that gas extraction can provide quantitative results, regarding PCE concentration in soils, which are not significantly different from liquid based extraction analysis.

Keywords: *Soil • PCE • VOCs • Extraction • Gas survey • Vapor contamination*

1. Introduction

A particularly significant group of soil pollutants consists of volatile organic compounds (VOCs). This group of chemicals (around 150 compounds) occur in the subsurface at numerous contaminated sites and can act as long-term sources of both gaseous-phase and groundwater contamination in developed countries. The mobility and persistence of VOCs through soil depends largely on the property of the chemicals. Depending on the vapor pressure, water solubility (or Henry's law constant), the degree of water saturation and sorption behavior, VOC may be present in the soil either in the liquid or gaseous phase as well as dissolved in soil water, adsorbed on (organic and inorganic) solid soil particles or enclosed in capillary cavities [1,2].

In the unsaturated zone, particularly in dry soils, adsorption onto the soil mineral and organic component surfaces plays an important role in mobility and retardation of VOCs during gaseous transport [2,3]. Therefore, an accurate description and understanding of the sorption mechanisms and behavior of organic contaminants are of great importance.

The present study focuses on the equilibrium vapor-phase adsorption of perchloroethylene (PCE) on four dry soil types with different physical/chemical properties. The experimental data (equilibrium isotherms) were correlated by well-known vapor phase models including Langmuir and Brunauer, Emmett, and Teller (BET) models [4]. Direct proportions between the soil's specific surface area, clay content and amount of adsorbate adsorbed per unit mass of soil were observed. Clear non-direct proportion was found in the relationship between soil bulk density and concentration of PCE in head space.

This work also compares static headspace technique and methanol extraction/purge-and-trap analysis for the determination of PCE in soils. Our findings strongly suggest that gas extraction can provide rapid results that will consistently identify the PCE concentration in soils and which are not significantly different from the results achieved by slower more expensive, liquid based extraction analysis.

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2. Experimental Procedures

2.1 Sample preparation

Generally, the preparation of VOCs contaminated soil samples is performed by injecting the neat compounds below the soil surface or by vapor fortification procedure allowing soil to adsorb vapors in a closed system. Vapor equilibration offers a means of contamination that overcomes many of the shortfalls of liquid spiking method. In the first case the degree of soil contamination strongly depends on initial fortification level, while in the second method, the fortification level is dependent on soil and contaminant properties, time of exposure as well as relative concentrations of the VOCs [5,6]. Soil samples were air-dried at 25°C. Approximately 20 ± 0.001 g of dried soils (0.1 up to 4.2% water content) were placed into 40 mL clear glass EPA vials (28 × 95 mm) *via* a glass funnel. Some relevant physical properties of the soils used are given in Table 1. The values were determined by means of following experimental techniques:

- Sieve analysis for soil texture classification;
- Organic carbon – from the differences between the total organic content measured by LIQUI TOC II ELEMENTAR and inorganic carbon removal by phosphoric acid;
- Water content – determination of loss in mass at 105°C for 4 h.
- Bulk density - cylinder method;
- Particle density – pycnometry determination;
- Surface area - Coulter SA 3100 surface and pore size analyzer.

Six vials filled with one of the four soil types were placed in a modified desiccator with open Petri dish, containing around 50 mL of an aqueous solution of perchloroethylene (PCE) (140 mg L^{-1}). The vials were allocated on the bottom of the apparatus below the Petri dish, due to the high relative vapor density (5.8) of the chemical, allowing vapors to be adsorbed in a closed system. The illustrative picture of the equipment used is presented on Fig. 1. The basic physical properties of the contaminant used are: M.W.: 165.8 [g mol^{-1}], B.P.: 121.1 [^{0}C], W.S. at 20^{0}C: 150 [mg L^{-1}], V.P. at 20^{0}C: 1.9 [kPa], H^I: 0.665, K_{oc}.: 265 [L kg^{-1}]. PCE was selected to be used in this study due to the fact that it is one of the main representatives of chlorinated volatile organic compounds. They are widely used solvents and degreasing agents in numerous industries and therefore are potential threat for subsurface contamination.

Figure 1. Modified desiccator for soil contamination by vapor treatment method: Petri dish with aqueous solution of PCE, glass vials filled with soil and desiccator cover.

Vapor fortification treatment was carried out for periods of 1, 2, 3, 4 and 24 h. After removal from the desiccator, the vials were aspirated for 1 min in order to relieve the PCE vapors from the vial head space and then quickly sealed. 24 mm Screw Caps with 22 mm polytetrafluoroethylene (PTFE-Teflon)/Silicone septa were used to prevent volatilization losses.

2.2 Static headspace

Gas extractions were performed 24 h after fortification was ended in order to achieve thermodynamic equilibrium between the gas phase and the sample. HAMILTON CO., Reno, Nevada – USA 1000 and 5000 µL gastight syringes were used for these purposes. The PCE vapors taken from the space above the soil were then consequently injected into standard stainless-steel, 90 mm × 6.3 mm o.d., 5.0 mm i.d. thermal desorption tubes packed with 200 mg of Tenax GR (mixture of 70% Poly 2,6-diphenyl-p-phenylen oxide and 30% graphitized carbon) in a flow of N_2, using a self constructed equipment, where all flow lines used were Tygon based (see Fig. 2).

Table 1. Physical characteristics of the soil samples.

Soil type	Sand, %	Clay, %	Organic carbon, %	Water content, %	Bulk density, g mL^{-1}	Particle density, g mL^{-1}	Surface area, m^2 g^{-1}
soil 1	74.0	6.0	3.2	4.2	0.93	2.11	17.768
soil 2	77.8	2.2	0.2	0.1	1.29	2.53	0.675
soil 3	74.0	6.0	1.5	0.3	1.33	2.43	1.014
soil 4	0.0	78.0	0.4	1.0	0.88	2.35	21.522

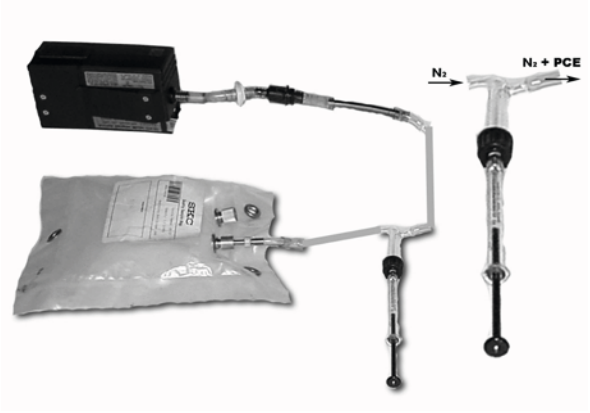

Figure 2. Equipment for vapor preconcentration on sorption tubes: gas sample bag, T-shape glass-tube for vapor injection through the use of gastight syringe, stainless-steel thermal desorption tube, pumping device with adjustable flow holder and constant pressure controller.

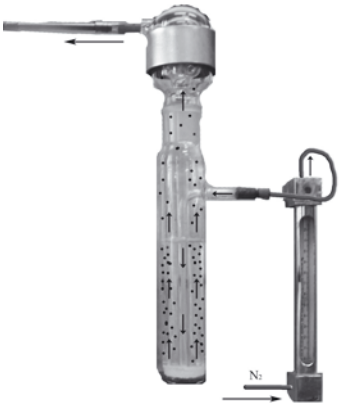

Figure 3. Purge-and-trap laboratory equipment: nitrogen flow meter and controller, stripping column, drops separator and trap with sorption tube.

The vapors injected *via* Teflon/Silicone septa 12 mm in a T-shape two channels glass tube were mixed with nitrogen, held in 1 L SKC Quality Sample Bag 231. The flow rate of 100 mL min^{-1} was maintained by AIRCHEK 52 SKC Air Sampling Pump driving the mixture to the tube. The time of preconcentration was selected to be 1 min, which was enough for full adsorption of the target compound on the adsorbent.

2.3 Methanol conservation

20 mL of methanol (99,8%, Penta) were injected into each head space vials *via* Teflon/Silicone septa in order to extract the PCE from soil. Plastic 10 mL Chirana syringe equipped with needle was used. Methanol/soil mixtures were shaken for 20 min. in ultrasonic compact cleaner bath UCC Teson 1 to desorb PCE from soil pores and particle surface. After sitting for 24 h at ambient temperatures, the vials were opened. Methanol aliquots (200 and 500 µL) were analyzed for PCE using purge and trap equipment. HAMILTON CO., Reno, Nevada – USA microliter syringe (500 µL) was used for the injection. Self constructed stripping apparatus is presented in Fig. 3.

The main parts of the device are: 170 mL stripping column, containing 100 mL distilled water, drops separator, inert gas (nitrogen) flow meter and sorbent trap. The methanol sample containing PCE been extracted from the soil was injected under the water. The nitrogen flow at 100 mL min^{-1} was directed to the bottom of the column through the sintered glass, and the purged analyte is trapped on thermal desorption tube. The stripping time is selected to be 20 min (on base on previously conducted repetitive experiments for wide range of VOCs) for desorption of PCE.

2.4 Thermal desorption/ gas chromatography

Unity two stages Thermal Desorber 1 combined with Ultra 100 Position Thermal Desorption Autosampler 1 from Markes International were used for sample analyses. The temperature regime used in the desorption was: purge time 1 min, primary (tube) desorption up to 300^{0}C for 25 min, secondary (focusing trap) desorption from -8^{0}C at heating rate of 40^{0}C s^{-1} up to 300^{0}C per 3 min. Desorbed analyte was transferred via transfer line to GC-17 A gas chromatograph (Shimadzu) and quantitatively determined. SPB-624 (Sigma Aldrich Co.) middle polar capillary column (30 m × 0.53 mm i.d., film thickness 3 µm, stationary phase: 6% cyanopropyl-phenyl and 94% dimethylpolysiloxane) connected to Flame Ionization (FID) and Electron Capture (ECD) detectors was used. The SPB-624 column is a key column for separating VOCs extracted from different matrixes. The temperature program used in the separation was 50^{0}C, 5 min, 5^{0}C min^{-1} up to 150^{0}C, 0 min, 20^{0}C min^{-1} up to 220^{0}C per 10 min. The temperatures of injector and detectors were 280^{0}C and 250^{0}C (FID), 300^{0}C (ECD), respectively. Under the conditions used, the SPB-624 column provides the highest column efficiency and a unique opportunity for simultaneous determination of various VOCs, including petroleum hydrocarbons, BTEX, halogenated VOCs, *etc*.

2.5 Soil gas data modeling

Methods based on soil gas monitoring have been successfully used to indicate the extent of subsurface contamination and to estimate the volatile organic compounds (VOCs) concentration in soil environment. The simplest model providing capacity for calculation of

contaminants total content in soil depending on soil gas concentration is based on the equilibrium distribution of VOCs between air-soil, water and soil solids phases. The total soil concentration C_T can be estimated from gas concentration by:

$$C_T = C_G \left[\frac{\left(\Theta_G + \frac{\Theta_W}{H^I} + \frac{K_{OC}\, f_{OC}\, \rho_S (1-\Theta_T)}{H^I} \right)}{\rho_S (1-\Theta_T)} \right] \quad (1)$$

where C_T denotes the VOC concentration per unit weight of dry soil [mg kg^{-1}], C_G the soil gas phase concentration [mg m^{-3}], Θ_G is the soil air-filled porosity [m^3 m^{-3}], Θ_W is the soil water-filled porosity [m^3 m^{-3}], Θ_T is the soil total porosity [m^3 m^{-3}], H^I is Henry's law constant [dimensionless], K_{OC} is the organic carbon distribution coefficient [m^3 kg^{-1}], f_{OC} - fraction of organic carbon [g g^{-1}] and ρ_S denotes the density of the solids [kg m^{-3}].

3. Results and Discussion

In order to develop an adequate treatment of volatile compounds and to predict their fate and behavior in the unsaturated zone it is necessary to investigate vapor-phase sorption processes taking place. In this study the effect of exposure time in the vapor-phase sorption processes for different soils was examined. Dry soils were fortified with PCE for different times before analysis. Another aim was to define the equilibrium time at which the soil samples can be contaminated. The fortification times before analysis were selected to be 1, 2, 3, 4, 5 and 24 hours.

Equilibrium concentrations of PCE in the headspace phase obtained during fortification are presented in Table 2.

Detection limits of PCE varied in the range of 0.0035 - 0.07 mg L^{-1}, depending on the soil type. Relative standard deviations (RSD) within individual soils ranged from 7.8 to 10.7% with an average value of 9.1%.

Data show that PCE amounts in the headspace increase by increasing the duration of the contamination period, reaching maximum values at the end of the fortification. Bulk density or soil pore volume also plays an important role in this respect. It is obvious that bigger pore volume contributes to higher equilibrium concentration of PCE in headspace phase.

Fig. 4 shows the kinetic of sorption and uptake of PCE, measured in methanol extracts, for four different soil types at six different fortification times.

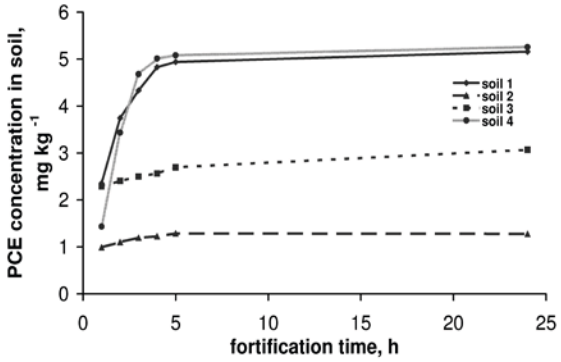

Figure 4. Sorption kinetic and PCE uptake for different soils.

Soil detected concentrations varied slightly at each fortification treatment period, ranging from 0.99 to 5.26 mg kg^{-1} dry soil. Detection limits for PCE in the soils used were found to be in the interval of 0.023 - 0.07 mg kg^{-1}. The overall RSD for the methanol extraction technique was calculated to be 7.65%.

To correlate our experimental PCE adsorption data, the Langmuir extended equation (2) was used.

$$C_{soil} = \frac{1}{a + b\tau^{(c-1)}} \quad (2)$$

where C_{soil} is the concentration of PCE in soil matrix, τ is fortification time and, a, b and c experimentally defined sorption kinetic parameters.

Table 3 shows the Langmuir isotherm parameters a, b, c, standard error S as well as correlation coefficient r in the system PCE vapors/soil

Table 2. Gas extraction data.

Fortification time, h	PCE concentration in headspace, mg L^{-1}			
	Soil 1	Soil 2	Soil 3	Soil 4
1	0.070	0.159	0.044	0.080
2	0.134	0.168	0.056	0.146
3	0.146	0.174	0.065	0.262
4	0.156	0.176	0.071	0.301
5	0.166	0.180	0.077	0.287
24	0.229	0.187	0.129	0.366

Table 3. Langmuir model parameters for different soil types.

Soil type	Sorption temperature, °C	Model coefficients			Errors	
		a	b	c	S	r
soil 1	25.7	0.19	0.24	-0.73	0.11	0.99
soil 2	25.5	0.76	0.26	-0.16	0.03	0.97
soil 3	23.5	0.05	0.39	0.89	0.04	0.99
soil 4	24.4	0.19	0.55	-1.58	0.14	0.99

Four parts in the isotherm can be distinguished. In the first phase (lag phase), diffusion of PCE vapors from the Petri dish to the soil sorption centers is predominant. It takes place within very short period of time so it can not be recognized at the graph. PCE uptake may increase during this time, but practically no changes are observed mainly due to the low detection limits. Lag phase is followed by log phase during which PCE vapor adsorption occurs. This phase is called logarithmic or exponential because the rate of increase in PCE concentration in the system with time follows a multiplicative function. The next stage is the retardation, where due to the combination of internal and external factor the rate at which PCE concentration increase is slowing down. Stationary phase is the last part of the isotherm, where a steady-state equilibrium between PCE concentration in gas and solid phase of the soil is achieved.

The optimal fortification time for equilibrium to be reached in the vapor-phase sorption process was considered to be lower (6, 5, 13 and 5 hours for soil types 1, 2, 3 and 4 respectively) than maximum contamination time (24 h). Values are based on achievement of 95% PCE uptake in soils, indicating no significant differences (5% RSD in methanol extraction determination procedure) in the consequent data. Basically the contamination period for different soil types could be reduced to 5 hours with the exception of soil 3. In this case logarithmic phase is prolonged over the retardation stage and equilibrium is achieved a little bit later mainly due to the influence of some lurking factors.

A general trend shown in Fig. 4 was that PCE concentration in soil increased when the content of organic matter and available surface area in the dry samples, increased. This linear regression between organic carbon content and PCE adsorbed is clearly seen comparing results for soil 1, soil 2 and soil 3. Soil 4 has been excluded from the comparison due to the expansion role of mineral surface area. Clay content was also found to increase the PCE uptake as it can be seen in soil 2, 3 and 4. The combined role of organic matter is evident comparing soil 1 and soil 3. At the same clay percentage but different organic carbon content, 68% more PCE uptake is registered by soil 1.

It has been presented in the literature that for dry soils, the role of mineral matter predominates over organic matter in vapor-phase adsorption processes. This fact is confirmed by the present results. For example, even though soil 1 has a 3.2% organic carbon content and soil 4 only a 0.4% organic carbon content, the latter adsorbs more than the former.

Soil moisture content also plays an important role in adsorption process as is confirmed by Chiou and Shoup [7]. In case of soil 1, the PCE vapors are in competition with more water molecules for soil adsorption sites in comparison to soil 4, therefore less amount of PCE is adsorbed. A positive correlation between the specific surface area and soil sorption capacity (mg PCE kg^{-1} dry soil) was also observed.

From the experimental data soil-vapor partition coefficient K_d^i (L kg^{-1}) can be determined.

$$K_d^i = \frac{C_{soil}}{C_{HS}} \quad (3),$$

L kg^{-1},where C_{soil} is methanol defined PCE concentration in soil, mg kg^{-1} dry mass and C_{HS} is vapor concentration measured in vials, mg L^{-1}. The concept of this coefficient is analogous to an aqueous sorption partition coefficient K_d. Plot of C_{soil} versus C_{HS} for PCE is shown in Fig. 5 and represents equilibrium isotherms. The slope of the curve provides K_d^i values.

The PCE data show clear Type II BET isotherm behavior in the case of soil 1, soil 3 and soil 4. This BET isotherm is typical for multimolecular layer adsorption on nonporous or macroporous (pore width >50 nm) soils. Soil 2 shows weak interaction between non porous mineral surface and adsorbat molecules (Type III isotherm). The relative similarity in the adsorption isotherms suggests that the sorption of PCE vapors on dry soils is primarily a function of available organic and mineral surface area.

Fig. 6 shows the correlation between the results obtained by the methanol extraction method and the modeled values for total concentration of PCE in fortified soils based on gas extraction head space technique. Headspace concentration was converted to soil gas concentration, taking into consideration that equilibrium PCE amount in soil pores has been diluted in the headspace volume in the vials.

Comparing the analytical data between the methanol and gas survey quantification model, no significant differences between the results were observed. For soils 1, 2 and 3 the average PCE concentration differences between these two methods were 23, 22 and 17% respectively. In case of soil 4, the concentration differences were higher on the average by 200%. It is due to the fact that in equilibrium eq. (1) for contaminant distribution in soil system only sorption on organic matter is taken into consideration. The regression between PCE data in soils 1 and 3 shows that the majority of points in gas survey quantification model are above the methanol extraction method data, another means of demonstrating that the headspace modeling analysis

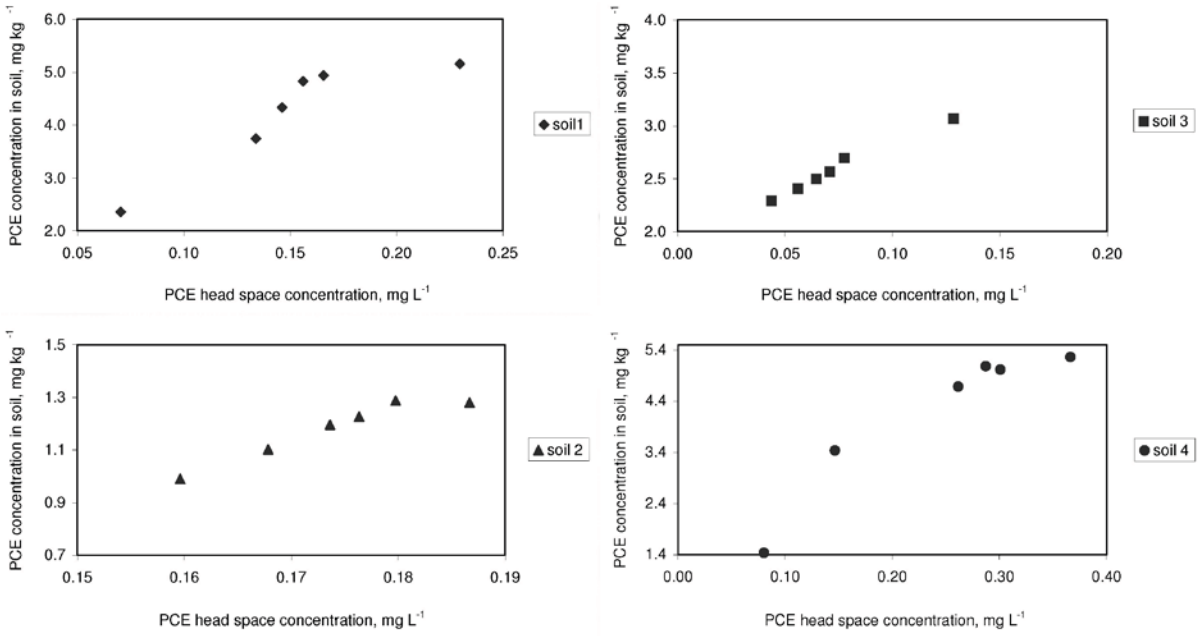

Figure 5. Adsorption isotherm data for different soil types.

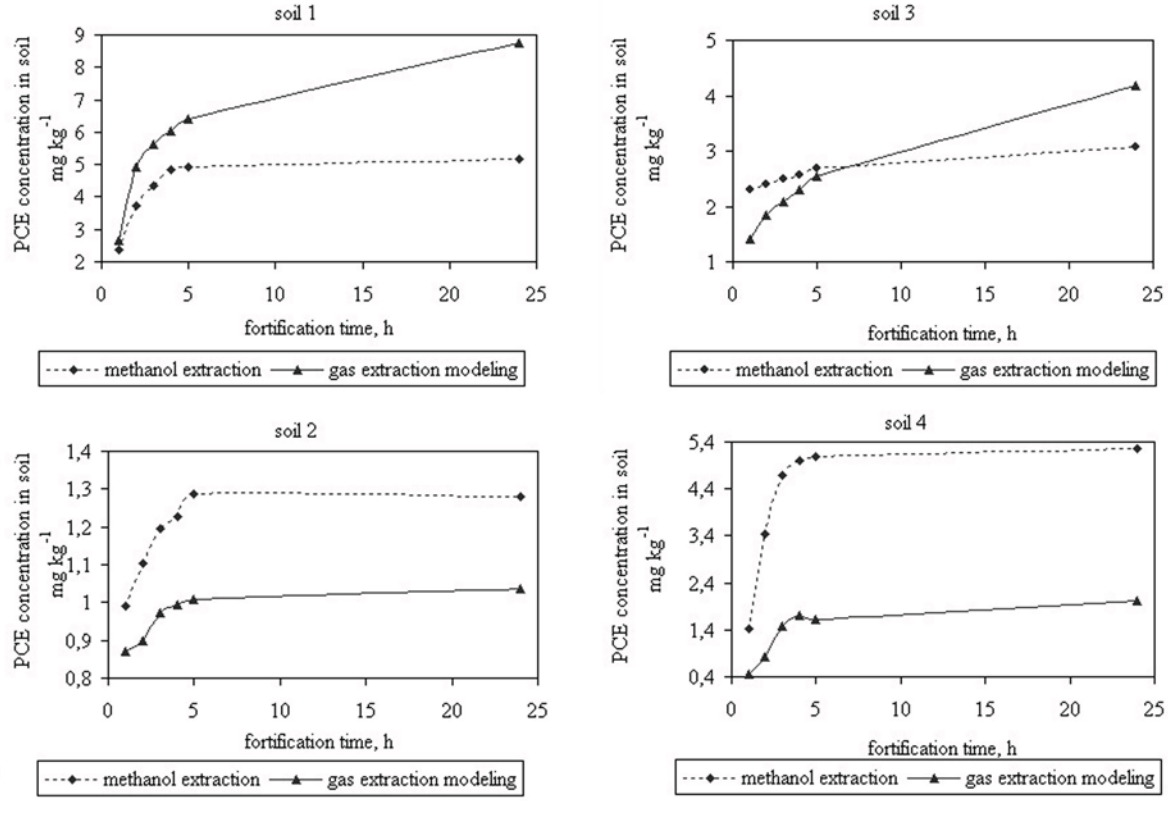

Figure 6. Correlation between methanol and soil gas survey quantification model results.

generally quantified greater soil volatile contaminant concentrations due to the higher theoretical sorption on organic matter. In soils 2 due to the low organic matter content and small mineral surface area methanol-preserved samples, had much higher concentrations. The proposed gas survey quantification model should be carefully applied and extended to the sorption on mineral surface.

4. Conclusions

On the basis of the investigation made and data obtained for the adsorption of perchloroethylene (PCE) on four dry soils the following conclusions could be made:

In the unsaturated zone, particularly in dry soils, gas-phase adsorption is key factor governing the mobility and distribution of volatile organic chemicals (VOCs). This study has confirmed that vapor fortification treatment provides a precise mean of soil contamination, where analyte concentrations are soil-specific and stable during preparation and analysis.

- The times required to reach equilibrium during contamination of soil samples were smaller than was expected 6, 5, 13 and 5 hours for soil types 1, 2, 3 and 4 respectively. Differences in PCE uptake for the four soils can be explained on the basis of organic matter content, available mineral surface area as well as water content.
- The experimental data were correlated by well-known Brunauer, Emmett, and Teller (BET) sorption isotherms model. The sorption results confirmed Type II (soil 1, 3, 4) and Type III (soil 2) isotherm. A direct proportion between the soil's specific organic and mineral surface area was identified.
- Comparing the analytical results between the methanol and gas extraction, quantification model no significant differences were observed. The proposed gas survey quantification model should be carefully applied and extended to the sorption on mineral surface. The overall conclusion from this work is that direct headspace analysis can provide easier and less expensive quantitative results, regarding PCE concentration in soils, which are not significantly different from liquid based extraction technique.
- More detailed experimental work on wide variety of soils with different physical characteristics and their simultaneous contamination with various VOCs is required to quantitatively validate, improve and optimize the model presented in this study.

Acknowledgments

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