

THE STATIC HEADSPACE – INFLUENCE OF SOIL PROPERTIES

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Abstract

As high amount of area in the Czech Republic has been contaminated by VOC, soil remediation and determination of pollutant concentration on soils are topics of a great importance. Common method for soil sample preparation techniques is the extraction with solvents, which are not environmental friendly techniques and therefore new-solvent free techniques are being developed. One of them is static headspace technique, which application is limited due to the soil matrix and its characteristics. With several hypotheses mathematical distributive model was developed and applied on pseudoreal samples of soils contaminated by tetrachloethylene, samples differed by organic carbon content and water content. The influence of water content was observed. Amount of tetrachloroethylene in gas phase was measured and by comparison with calculated data, the correction coefficient was obtained and mathematical distributive model was improved. The experiments proved that real amount of contaminant in soil can be predicted only using other determined soil characteristics. The amount of contaminant in gas phase depends on contaminant and its properties.

Introduction

Czech Republic is one of the countries where environmental problems were missed out for a long time. Efficient strategies for soil remediation have been developing, considering environmental rehabilitation at the lowest possible costs. Before the remediation project a detailed study has to be done including the pre-monitoring of area to be treated in order to evaluate the pollutants that must be extracted to reach-up goals. The determination of pollutant concentration on soils and sediments is one of the most important tasks, since soil and sediments seem to be the most troublesome environmental samples for chemical quantification. As for soil sample preparation techniques the extraction with solvents is the most used one. Nevertheless, as those solvents are not "friendly" environmental compounds, new solvent-free separation techniques are being developed. One of them is static headspace technique.

Methods

Static headspace technique (SHS) is based on an exactly defined time period of sampling container's standstill to reach the equilibrium. Gas phase was sampled and analyzed by GC-FID. The application of SHS is limited due to the soil matrix and its characteristics (1). Therefore the equilibrium behavior of VOC has been predicted using simple mathematical model specifically constructed for the soil system. The sorption on organic matter was considered as a main sorption mechanism.

The mathematical distributive model was developed with several hypotheses. For equilibrium conditions the contaminant in the sample container is distributed according to the following equation:

$$X_S + X_W + X_A = 1 \quad (1)$$

where X_S , X_W and X_A are the equilibrium mass fractions of contaminant, respectively, in the solid, water and gas phases. If water overlays the whole surface of soil particles, which is possible although small amounts of water content is present (2), (3) the equilibria water-gas and soil-water should be considered. The latter is described according to the following equation:

$$K_{SW} = \frac{C_S}{C_W} = \frac{\frac{X_S \cdot M^c_{total}}{M_S}}{\frac{X_W \cdot M^c_{total}}{M_W}} = \frac{X_S}{X_W} \cdot \frac{M_W}{M_S} \quad (2)$$

where K_{SW} is the distribution coefficient solid – water [$\text{ml} \cdot \text{g}^{-1}$] or [$\text{g}_{\text{water}} \cdot \text{g}_{\text{soil}}^{-1}$], C_S is the equilibrium concentration of contaminant in the solid phase [$\text{mg} \cdot \text{g}^{-1}$], C_W is the equilibrium concentration of contaminant in the water phase [$\text{mg} \cdot \text{g}^{-1}$] and M^c_{total} , M_W and M_S are, respectively, the total amount of contaminant, the amount of water, and the amount of dry soil in the sample container [g]. According to the influence of organic carbon content of the soil on sorption, the distribution coefficient solid – water is:

$$K_{SW} = K_{OC} \cdot f_{OC} \quad (3)$$

where K_{OC} is sorption coefficient at the organic carbon, K_{SW} is distributive coefficient solid phase – water and f_{OC} is content of organic carbon in the soil. For low concentration of contaminant, the Henry's law describes the gas - water equilibrium according to the following equation:

$$H' = \frac{c_A}{c_w} \quad (4)$$

where H' is the Henry's constant, c_A and c_w are the equilibrium concentrations of contaminant, respectively, in the gas and water phases [$\text{mg} \cdot \text{m}^{-3}$]. As H' is referred to the phase volumes, the Henry's constant referred to phase masses (H'') was obtained according to the following equation:

$$H'' = H' \cdot \frac{r_W}{r_G} = \frac{C_G}{C_W} \quad (5)$$

where ρ_G and ρ_W are the densities, respectively, of gas and water [$\text{g} \cdot \text{cm}^{-3}$], C_G and C_W are the equilibrium concentrations of contaminant, respectively, in the air and water phases [$\text{mg} \cdot \text{g}^{-1}$]. The mass fractions of contaminants in each phase were obtain

$$X_G = \frac{H'' \cdot X_W \cdot M_G}{M_W} \quad (6)$$

$$X_W = \frac{X_G \cdot M_W}{H'' \cdot M_G} \quad (7)$$

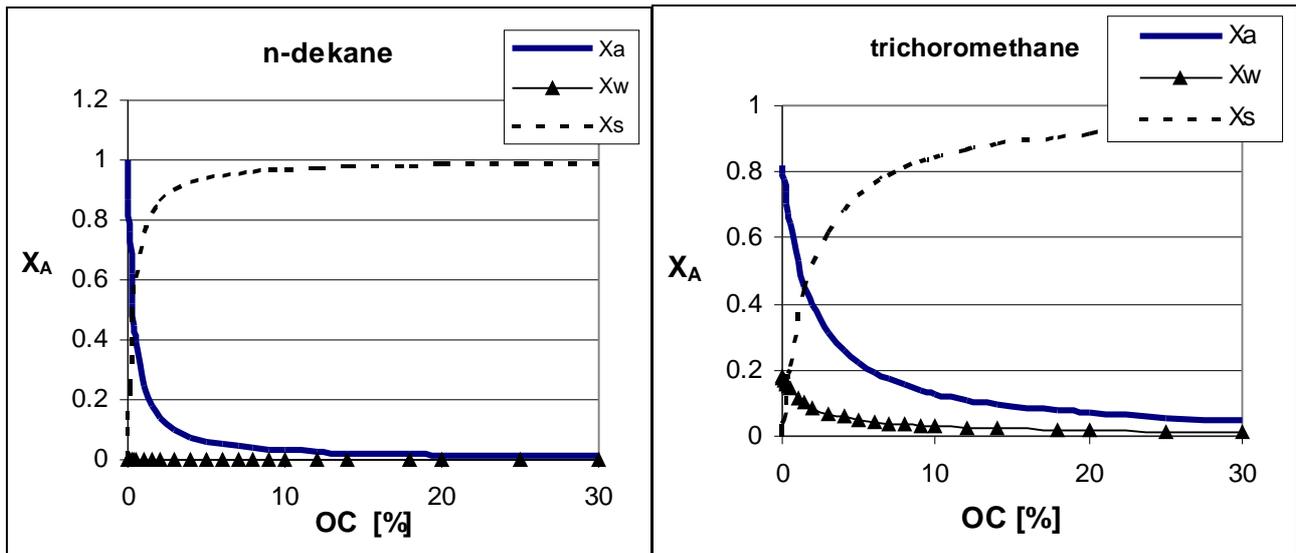
$$X_S = \frac{X_W \cdot M_S \cdot K_{OC} \cdot f_{OC}}{M_W} \quad (8)$$

Applying equations (1), (6), (7), and (8) the final equation for calculation of the mass fraction of contaminant in the headspace (X_A) was obtained:

$$X_A = \frac{1}{\left[1 + \left(\frac{M_W}{H'' \cdot M_G} \right) + \left(\frac{K_{OC} \cdot f_{OC} \cdot M_S}{H'' \cdot M_G} \right) \right]} \quad (9)$$

Using the model equilibrium, the concentration of contaminants (n-dekane, trichloromethane) could be predicted (Fig.1).

Fig. 1: Equilibrium distribution of contaminants between soil (X_s), water (X_w) and air (X_a) – influence of organic carbon content (1000 ml sampling container, 200 g soil sample, water content 15%)

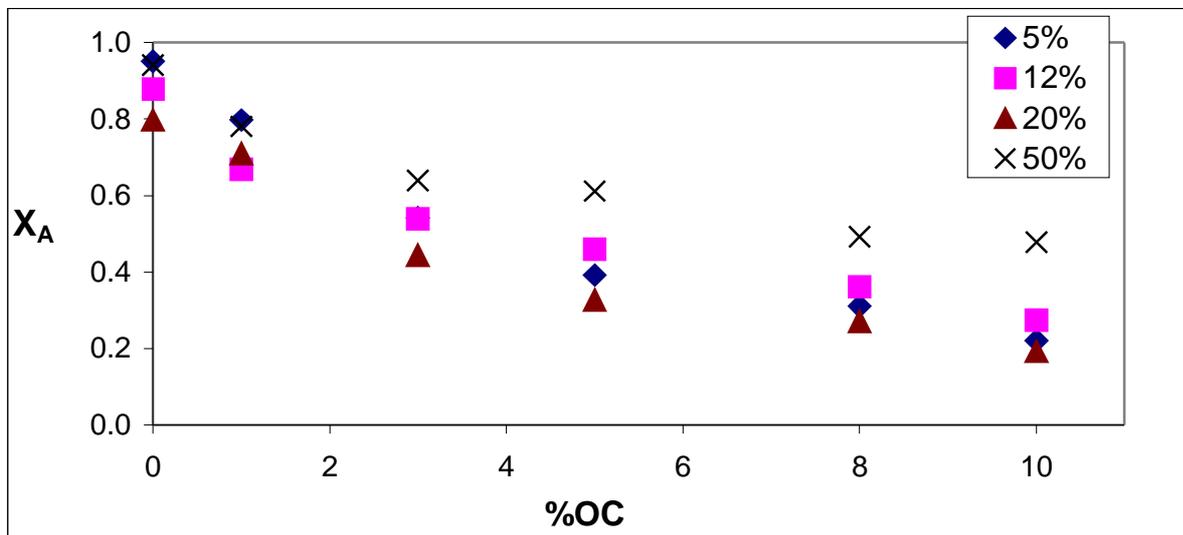


The experiments were performed in simple sampling containers specifically constructed for our need. 20 grams pseudo-real soil sample consisting of well defined sand particles, water and oxihumolite (organic matter source were prepared and placed in 500 ml headspace flasks, being homogenized for 5 minutes with an ultrasonic bath. Different organic matter contents (0, 5, 15, 20, 25, 30 and 50 % w/w) and different water contents (5, 12, 20, 50 % w/w) were induced. Each sample was then spiked with 25 μ l of a tetrachlorethylene as a typical representative of chlorinated VOC.

Results

The equilibrium behavior of contaminants in three-phase system was studied depending on soil properties. The measured concentration is shown on following graph (Fig. 2).

Fig. 2: Relative concentration of PCE in air (X_A) - dependence on organic carbon matter, different water content (5,12, 20,50%)



Measured sorption on organic carbon was compared to calculated ones and the difference was expressed using k , which is the correction coefficient. Therefore the equation (9) was improved into following:

$$X_A = \frac{1}{\left[1 + \left(\frac{M_w}{H'' \cdot M_G} \right) + \left(\frac{k \cdot K_{OC} \cdot f_{OC} \cdot M_s}{H'' \cdot M_G} \right) \right]} \quad (10)$$

As shown at graph (Fig. 2), the concentration of tetrachloroethylene in air was different with different water content. It is easily seen that with higher water content the amount of PCE in air increases.

Table 1: The correction coefficients

correction coefficient k	water content [%]
2,49	5
2,44	12
2,14	50

The relation between correction coefficient and water content (Table 1) is linear and it is expressed as:

$$k = -0,008 \cdot j + 2,53 \quad (11)$$

where φ is the water content [%].

Discussion

The distributive mathematical model includes the sorption on organic matter as the only sorption mechanism. But other sorption mechanisms, which decrease the amount of contaminant in gaseous phase, could be accomplished. These mechanisms could be caused by influence of water content or by the influence of surface sorption. These mechanisms also include the losses of tetrachloroethylene caused by sorption on glass surface of sampling containers, and other parameters such as influence of inorganic carbon and soil porosity.

The soil water content influences the extent of sorption of contaminants. Direct impact of water content, e.g. dissolving of contaminants in water, should be included in the original distributive mathematical model. Or the sorption on surface of soil or the fault of laboratory technician (when adding water wrong volume caused that not enough water was presented to dissolve tetrachloroethylene so the amount in gaseous phase increased) could take place. Due to low solubility of contaminant and high mistake of water volume the latter possibility is not very probable.

The water influence on sorption mechanisms is expressed by the slope in equation 25 and is indirect. Other effects, which cause higher soil sorption like particle surface adsorption, soil chemisorptions, glass surface sorptions are included as constant (intercept) in equation 25.

Conclusion

As the soil is very complicated matrix, the analysis of mere soil air does not quantify the amount of contaminant in soil. The real amount of contaminant in soil can be predicted only using other determined soil characteristics (soil particles distribution, porosity water content, etc.). Organic

carbon content and water content are parameters of great importance. The amount of contaminant in gas phase depends on contaminant and its properties (solubility, polarity, volatility).

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