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A predictive method for volatile organic compounds emission from soil: Evaporation and diffusion behavior investigation of a representative component of crude oil

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HIGHLIGHTS

- A headspace SPME method was developed to determine VOC from crude oil spills.
- BET analysis has been used for VOC isotherm parameter prediction.
- Experimental VOC diffusion flux through soil amounted to 74% of the forecasted value.

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ABSTRACT

Pipelines are convenient, economical and widely used mode of transportation of crude oil. However, the inevitable or otherwise accidents during such transport of crude oil lead to large scale oil spills, which consequently result in both soil and air pollution. When such pollution occurs, crude oil VOC concentrations in air, soil pollution evaluation and VOC propagation in soil provide important evidence for airborne detection of oils spills. Therefore, several issues, including determination method for VOC, isotherm parameters of VOC sorption on soil surfaces, and VOC diffusion flux simulation, are significant. In our previous study, n-butane and n-pentane were proved to be the maximum VOCs in studied crude oils. Therefore, a predictive method using n-pentane as a representative component is proposed in this paper. Firstly, a headspace solid phase microextraction (SPME) method was developed for determination of n-pentane in non-equilibrium mass transfer conditions. Secondly, Brunauer–Emmett–Teller (BET) analysis with liquid nitrogen was carried out to predict isotherm parameters for n-pentane. Finally, two models were used to predict the emission process. Probably influenced by gas vapor density below and above the soil layer, the experimental data amounted to 74% of the deduced value from the simplified analytical model. However, the free diffusion model fitted well with the experimental results.

1. Introduction

When oil spill occurs, typical crude oil can lose up to 45% of its initial volume within several days (Fingas, 2013), with volatile organic compound (VOC) constituting the bulk of the components lost. Several efforts have therefore been made to detect crude oil components after such accidents (Fingas and Brown, 2013). Crude oil pipes are economical and widely used means of transportation. They are usually buried underground. In cases of accidental burst of the oil pipe, VOCs diffuse through the pore space of the soil into the atmosphere and cause both soil and air pollution. Research on soil pollution was proposed for identification of the hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) after pollution (Lebkowska et al., 2011; Sun et al., 2013; Yu et al., 2012). Besides, during the pollution process, the amount of VOCs adsorbed to soil and the rate of diffusion from soil into the atmosphere present an interesting subject, which may provide scientific evidence for remote detection of oil spills using adapted light detection and ranging (LIDAR) systems (Fix et al., 2004).

To detect VOCs, the developments of sensitive determination methods are requisite. Arthur and Pawliszyn (1990) developed the solid phase microextraction (SPME) to minimize matrix influences. Extracting analytes from the headspace above the sample can minimize matrix interferences in environmental samples (such as water, sand, clay, and sludge) and besides being simple, rapid, inexpensive, it is

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completely solvent-free and easily automated (Zhang and Pawliszyn, 1993). Since its development, the headspace SPME method has been widely used for environmental VOC analysis (Higashikawa et al., 2013; Lasekan et al., 2013; Spietelun et al., 2013; Tian et al., 2013). Subsequently, Ai (1997, 1998) proposed a method to address the situation of the non-steady-state mass transfer for the headspace SPME, which was popularly employed later (Psillakis et al., 2012a, 2012b).

VOCs from crude oil in accidents are mainly light hydrocarbons or PAHs, which are less polar. A higher adsorption of polar than of aliphatic and aromatic compounds to soil was found (Ruiz et al., 1998), which may be caused by the relative polar soil surfaces and indicates that crude oil VOCs may not settle on soil surface, especially on soil with less organics. Trichloroethylene and trichloroethane desorption behavior was proved to be independent from the number of adsorption layers on soil and the monolayer desorption of chlorobenzene was the rate-controlling step of the overall desorption process (Yeo et al., 1997), which somehow accounts for the influence of polarity on isotherms of different compounds. Similarities in the adsorption isotherms of various non-polar VOCs on dry soils and clay minerals were observed and an empirical predictive method was developed to estimate the isotherm parameters (Campagnolo and Akgerman, 1996). Afterwards, soil modification was studied to assess the influence of soil surface on adsorption and desorption of VOCs (Park et al., 2008; Ryu and Yeo, 2010a, 2010b).

Crude oil spill studies have been performed frequently over the sea or above the ground (Fingas, 2004; Stiver and Mackay, 1984), whereas the cases of underground oil spill are least understood. Air emissions from exposed, contaminated sediments and dredged materials were mathematically modeled (Ravikrishna et al., 1998; Valsaraj et al., 1997). Analytical and semi-analytical solutions to the diffusive transport equations to predict emission rates from contaminated soils and sediments that have their moisture content changing with time were developed (Choy et al., 2001). In mixtures (such as hexane/toluene, methanol/toluene and methanol/chlorobenzene), component uptake by soil was influenced by other co-adsorbates (Guo et al., 1998).

In this paper, we aimed to develop a headspace SPME method for determination of VOC (n-pentane) in non-equilibrium mass transfer conditions to evaluate its differing concentrations in the environment. To obtain the isotherm parameters of n-pentane in soil, Brunauer–Emmett–Teller (BET) analysis with liquid nitrogen was carried out to predict the adsorption surface area and the monolayer adsorption amount for n-pentane, which could help to foresee the soil–air equilibrium partition coefficient. Finally, with additional experimental data, we could predict the diffusion flux of n-pentane from soil with the adapted model, and a comparison between the model predicted and experimental flux value was done. We tried to present a determinative and predictive method for VOC adsorption and diffusion through soil.

2. Theory

2.1. SPME non-equilibrium determination

Ai (1997, 1998) proposed a model for SPME, dealing with non-steady-state mass transfer in headspace (Eq. (1)) and an improvement was made later to better conform to the real situation (Eq. (2)).

$$n = n^{\infty}[1-\exp(-a_h t)] \tag{1}$$

$$n = \alpha[1-\exp(-\mathrm{b}t)] + \beta[1-\exp(-dt)]. \tag{2}$$

2.2. Free diffusion

Stiver and Mackay (1984) came up with a model for liquid evaporation, which is spilled over an area of a. This theory was described by Eqs. (3)–(5). When the expression $\mathrm{ka}Pv/V_0RT$ in Eq. (3) is denoted as K_e, the evaporation equation can be written as Eq. (6), which describes the evaporated volume fraction changes with time t.

$$N = \mathrm{ka}P/(RT) \tag{3}$$

$$dF_v/dt = \mathrm{kaPv}/(\mathrm{V_0RT}) \tag{4}$$

$$dF_v = [Pv/(RT)](\mathrm{k\,a}\,dt/\mathrm{V_0}) \tag{5}$$

$$F_v = K_e \cdot t. \tag{6}$$

2.3. Isotherm parameter prediction

Campagnolo and Akgerman (1996) presented the similarities of adsorption isotherms of various non-polar VOCs on dry soils and clay minerals. An empirical predictive method was developed to estimate the isotherm parameters of the BET model, which is given by Eqs. (7)–(10).

$$\alpha_m = 1.091\left(\frac{M}{N_0\rho}\right)^{2/3} \tag{7}$$

$$S_m = \left(\frac{W_m N_0}{M}\right)\alpha_m \tag{8}$$

$$W_{m,voc} = \frac{0.70MS_{m,N_2}}{\alpha_{m,voc}N_0} \tag{9}$$

$$W_{voc} = W_{N_2}\left(\frac{W_{m,voc}}{W_{m,N_2}}\right). \tag{10}$$

2.4. Evaporation flux through soil layers

Choy et al. (2001) developed analytical solutions to the diffusive transport equations to predict emission rates from contaminated soils and sediments that have their moisture content changing with time. In our case, the model is simplified as shown in Eq. (11). $K_{d,dry}$ is calculated with the data from n-pentane isotherm prediction part (Eq. (12)). $D_{A(eff)}$ is approximated by the model of Millington and Quirk (1961) (Eq. (13)).

$$J_A(t) = D_{A(eff)}C_{A0}\left\{\frac{1}{L} + \frac{2L(\varepsilon+\rho_b K_d)}{\pi^2 D_{A(eff)}t}\exp\left[\left(\frac{\pi}{L}\right)^2\frac{-D_{A(eff)}t}{\varepsilon+\rho_b K_d}\right]\right\} \tag{11}$$

$$K_{d,dry} = \frac{W_{mA}}{P_A^{sat}}\exp\left(\frac{\Delta H_{cond}-\Delta H_{ads}}{RT}\right) \tag{12}$$

$$D_{A(eff)} = D_A\frac{\varepsilon_{air}^{10/3}}{(\varepsilon_{air}+\varepsilon_{water})^2}. \tag{13}$$

3. Materials and methods

3.1. Materials

N-pentane (99%) was purchased from Baker Analyzed. The soil used in the experiments was sand (before used, it was dried at 105 °C for 24 h), with porosity of 0.33 and 0.41% organic matter. The sampling location was near Lieberose, Brandenburg, north-east Germany (51° 55′ 49″ N, 14° 22′ 22″ E). All samples were used as received.