The residual concentration of regular gasoline in unsaturated soil

Junko Nishiwaki[A] , Yoshishige Kawabe [B], Yasuhide Sakamoto[C] and Takeshi Komai[D]

[A]Institute for Geo-Resources and Environment, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan, Email junko-nishiwaki@aist.go.jp
[B]Institute for Geo-Resources and Environment, AIST, Tsukuba, Japan, Email y-kawabe@aist.go.jp
[C]Institute for Geo-Resources and Environment, AIST, Tsukuba, Japan, Email sakamoto-yasuhide@aist.go.jp
[D]Institute for Geo-Resources and Environment, AIST, Tsukuba, Japan, Email takeshi-komai@aist.go.jp

Abstract

Petroleum hydrocarbons and organic solvents are two of the major contaminants in the groundwater and the soil. Risk and exposure assessments for soil and groundwater are very important for both health and environmental protection, as well as making decisions and remedial goals for engineering goals. To understand the risk levels of toxic chemicals, a risk assessment model has been developed. Although parameters related to the fate of hazardous chemical compounds, such as advection, dispersion, volatilization or sorption are important factors in this system, those parameters for mineral oils have not been investigated enough. In this study, we focused on the residual property and residual concentration of gasoline and gasoline components in unsaturated soil. A set of column experiments was carried out. The residual concentration of the gasoline and gasoline components was different at each depth. Additionally, the components that have different carbon numbers show different rates of movement in soil.

Key Words

Mineral oils, gasoline, component, soil contaminant, laboratory experiment.

Introduction

The number of groundwater and soil contamination cases is increasing. In Japan, organic solvents, such as trichloroethylene and tetrachloroethylene, are regulated as specified toxic substances under the Soil Contamination Countermeasures Act established in 2002. However, mineral oils, such as gasoline, light oil and heavy oil, have not been controlled until recently. In 2006, the Ministry of the Environment in Japan published a guideline for treating the contamination of mineral oils. Thus it is becoming important to survey and clean sites that have been contaminated by mineral oils, as well as to assess the risk of mineral oils to human health.

We are developing a Geo-environmental Risk Assessment System (GERAS) that will enable us to estimate the amount of exposure to hazardous chemicals (e.g. organic compounds or heavy metals) and the risk to human health (Kawabe *et al.* 2005; 2003). However, mineral oils are mixtures of more than one hundred different hydrocarbons. As each component has different physical-chemical properties such as volatility and water solubility, it is difficult to predict the fate of mineral oils underground. Furthermore, mineral oils will often change into a different state, e.g. gas, liquid etc. Factors affecting the fate of mineral oils are complex. Furthermore, different components included in mineral oils cause different risks to human health (Edwards *et al.* 1997). Thus, it is important to find out the fate and residual properties of mineral oils and those components in the soil. In this study, the residual concentration of gasoline Total Petroleum Hydrocarbons (TPH) and gasoline components in unsaturated soil were investigated by a set of laboratory experiments. The final goal of this study is to clarify the fate of mineral oils in soil and assess the risk of mineral oils to human health.

Methods

Materials

We used Toyoura sand (d_{50} = 106 μm, the soil particle density is 2.64 Mg/m^3) which is considered to be standard soil in Japan and the physical-chemical properties of it are widely known. The sand was air dried in the laboratory at room temperature for a few weeks prior to use. We chose commercially available regular gasoline (RG) as the mineral oil contaminant. At the time of application, the gasoline contained more than one hundred hydrocarbons, with carbon numbers ranging between C4 and C13.

In this study, RG was added to the clean soil to simulate the contaminated soil.

Experimental Procedure

A stainless steel column, with an inner diameter of 85 mm and a depth of 500 mm, was used to investigate the residual concentration of RG in unsaturated soil (Figure 1). This column is divided into ten 50 mm deep short columns. A stainless steel meshed filter was set at the bottom of the column to prevent soil from running off. An inlet port for RG was set at a depth of 175 mm from the top. We conducted a set of experiments in a room with a constant temperature of 15℃. After the column was filled with Toyoura sand (bulk density was 1.60 Mg/m, soil water content was 0.07), ~ 300 mL RG was injected using a pump (10 mL/min). The top of the column was opened to the air and the column was left for a certain period of time. The column was separated into 10 portions at predetermined times (0, 2, 5, 10, 30 days from the beginning of the experiment) and the concentration of RG remaining in each depth was analyzed by GC-FID. Carbon disulfide (CS_2) was used as the extraction solvent for residual gasoline and gasoline components from soil.

Figure 1. Photo of experimental equipment.

Results

Total Petroleum Hydrocarbon (TPH)

TPH concentration remaining in the whole column had decreased 5 days from the beginning of the experiment, after that the remaining TPH concentration was almost constant. Figure 2 shows the variations of the TPH concentrations remaining at each depth. The horizontal axis indicates the ratio of TPH concentration remaining in the soil ((mg-remaining RG/mg-injected RG)/kg-soil), and the vertical axis indicates the depth. It shows that TPH is decreasing from the upper side of the column and that it remains in the deep portion of the column, especially deeper than 325 mm.

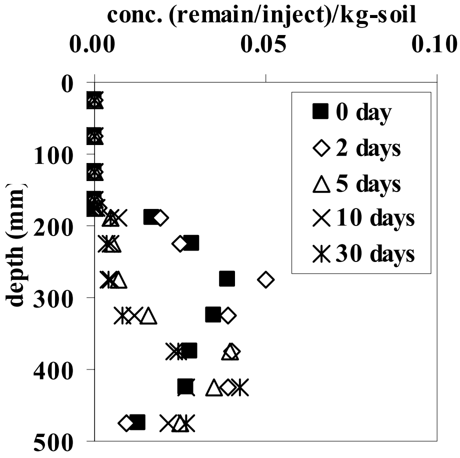

Figure 2. Time-dependent change of residual TPH remaining in each depth.

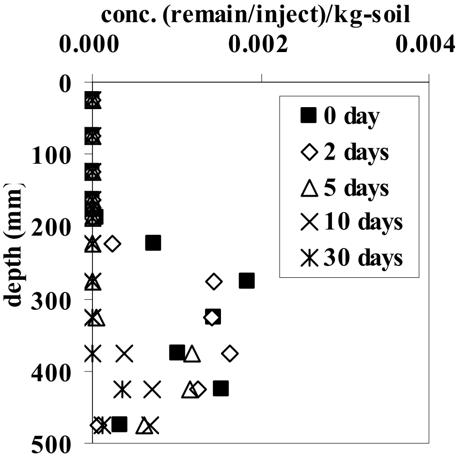

Figure 3. Time-dependent change of residual iC4 remaining in each depth.

Gasoline components

The variations of the concentrations of the RG components remaining at each depth indicated that the hydrocarbons with small carbon numbers were continued to decrease from soil such as Iso-butane (iC4) and iso-pentane (iC5). In contrast, the hydrocarbons with higher carbon numbers, such as benzene (B), ethyle-benzene (EB) and meta-xylene (mX) decreased from the soil early in the experiment and remained in the soil after that. Figures 3 and 4 show the variations of the concentrations of iC4 and EB at each depth, respectively. iC4 continued to decrease from the soil at any depth. EB decreased and almost diminished at depth shallower than 325 mm and remained at depth deeper than 325 mm. Some other components, such as mX or Naphtalene, continued to remain at some deeper depths. The ratios of the components concentration remaining in the soil 30 days after the beginning of the experiment on the value of 0 day, listed in Table 1. It shows that hydrocarbons with small carbon numbers are easily diminished from soil. On the other hand, hydrocarbons with large carbon numbers tend to remain in the soil. The main mechanism for this decrease might be volatilization, due to the initial speed of hydrocarbon depletion followed by a more linear depletion, as show in Figure 5.

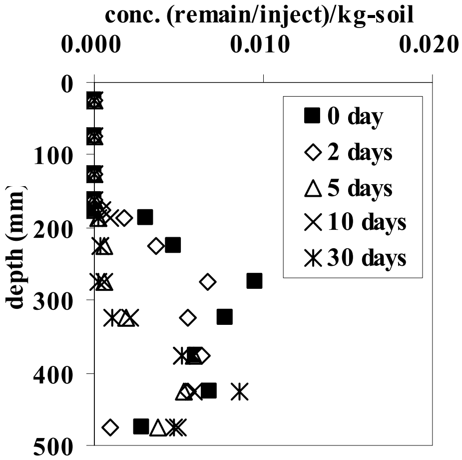

Figure 4. Time-dependent change of residual EB remaining in each depth.

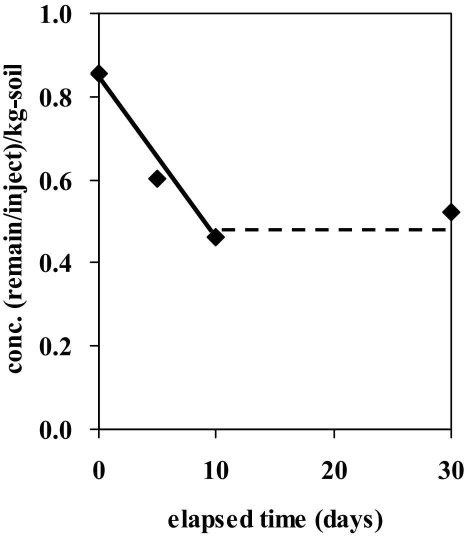

Figure 5. Time-dependent change of residual TPH remaining in a whole column.

Table 1. List of the remaining ratio of each component.

Regular gasoline components	remaining ratio (30 days after/initial value)
iso-butane (iC4)	0.07
iso-pentane (iC4)	0.21
Benzene (B)	0.53
Ethyl Benzene (EB)	0.50
meta-Xylene (mX)	0.50
1methyle3ethyl benzene (1MEB)	0.51
Naphthalene (Naph.)	0.49

Conclusion

In this study, the property of remaining RG in unsaturated soil was examined. RG decreased only at shallower through the soil layers depth in unsaturated soil. Also, the results indicate that different components move in different ways. Especially, the carbon number of these compounds will directly affect their soil level transmission properties. Mineral oil such as gasoline is composed of various components and each component has different risks to human health. It would be possible to protect human health using risk assessment systems. We intend to collect more data about mineral oil soil dispersion, which will enable us to feed this data into risk analysis systems. This will in turn enable us to better focus on the health issues posed to human, in the near future.

References

Edwards DA, Andriot MD, Amoruso MA, Tummey AC, Bevan CJ, Tveit A, Hayes LA, Youngren SH, Nakles DV (1997) Total Petroleum Hydrocarbon Criteria Working Group Series Volume 4, Development of Fraction Specific Reference Doses (RfDs) and Reference Concentration (RfCs) for Total Petroleum

Hydrocarbons (TPH), pp.15-34. (Amherst Scientific Publishers.).

Yoshishige Kawabe, Takeshi Komai and Yasuhide Skamoto (2003) Exposure and Risk Estimation of Inorganic Arsenic in Japan. *Journal of the MMIJ* 119, 489-49

Yoshishige Kawabe, Takeshi Komai and Yasuhide Skamoto (2005) Exposure Estimation of Organic Compounds in Japan –Risk Analysis by Geo-environmental Risk Assessment Model-. *Journal of the MMIJ* 121, 19-27