A FIELD STUDY ON SITE INVESTIGATION AND REMEDIATION METHODS FOR VOCs CONTAMINATED GROUND

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ABSTRACT: The site investigation and remediation methods for volatile organic compounds (VOCs) contaminated ground are studied. The basic principles on partitioning of VOCs between soil air, soil moisture and soil solid phases, and the theories of contaminants transport in ground are briefly reviewed. The applications of the theories in predicting the VOCs movement in ground and remedying the contaminated ground are discussed. Field studies are made at a tetrachloroethylene (PCE) contaminated site in Saga area. Field gas-survey and soil sample analysis results are presented with the discussion on the efficiency of the methods. The vapor extraction system was tested at the site also. It has been demonstrated that vapor extraction system is an effective and economic remediation method for VOCs contaminated ground.

INTRODUCTION

The contamination of soil and ground water by volatile organic compounds (VOCs), including a variety of synthetic solvents, becomes a worldwide environmental problem. The main reason for this is the wide spread use of VOCs in manufacture of pesticides, plastics, paints, pharmaceutical, and as solvents. Among the VOCs, tetrachloroethylene (PCE) and trichloroethylene (TCE) are most commonly used types. In Japan, the reported environmental problem caused by PCE and TCE increased rapidly in past few years. Recently, a site, where the concentration of PCE in ground water was 16,000 times of Japanese environmental standard (0.01 ppm) was reported in Nagoya, Japan. In Saga area, several sites, where the surface soil and ground water have been contaminated by PCE and TCE. PCE, TCE as well as chromium (Cr+6) are main contaminants in Saga area. Therefore, the interest in behavior of VOCs in subsurface and remediation methods for VOCs contaminated ground increased recently.

To treat the VOCs contamination problems, the research and technical developments are progressed in following three aspects, namely, (1) basic understandings on the behavior of VOCs in solid, liquid, and vapor phases of subsoil, (2) techniques for identifying the source of contaminants and the extent of the contaminated area, and the methods for predicting the transport of the VOCs in ground (vadose zone and ground water), and (3) remediation techniques to clean-up VOCs from soil.

In this paper, the basic characteristics of VOCs in ground, and the theories for analyzing the contaminants transport in ground are reviewed. Then, a site (Site A) contaminated by PCE in Saga area has been studied on the effective ways of site investigation and remediation measures. The field conditions and field remediation test results are described in detail. Suggestions are made on selecting the field investigation and remediation methods for VOCs contaminated ground.
PARTITION BETWEEN GAS, LIQUID AND SOLID PHASES OF VOCs IN SOIL

There are three forms of VOCs in ground, namely, (a) vapor (gas) in soil air, (b) dissolved in ground water (or soil moisture), and (b) adsorbed on the surface of soil particles and organic matter. The relationship between these three forms is the basic knowledge for treating VOCs contaminated ground. The degree of partitioning between these 3 forms depends on the volatility and water solubility of the VOCs, the soil moisture content, and the type of soil mineral and organic matter.

Partitioning of VOC between Soil Gas and Soil Moisture Phases. For a given temperature, at equilibrium, the ratio between the concentration of VOCs in soil gas ($C_g^v$) and the concentration of VOCs in water phase ($C_L$) is a constant and is called Henry's law constant $K_H$ ($K_H = C_g^v/C_L$). $K_H$ is a function of the VOC vapor pressure ($p$), concentration in liquid phase ($C_L$), and temperature (T, in kelvin) (Thibodeaux, 1979).

$$K_H = \frac{16.04pM}{T C_L}$$

(1)

where M is the gram molecular weight of the VOC. Henry's law is the basic theory for vapor extraction remediation method. With a constant $K_H$ value, reducing vapor pressure, $p$, by suction will result in reduction of VOC concentration in liquid phase also. A higher $K_H$ value means that the VOCs can easily volatilize from liquid phase into vapor phase. Some reported values of solubility, vapor pressure, as well as calculated Henry's law constant for PCE and TCE (Silka and Jordan, 1993) are listed in Table 1.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Solubility in Water (ppm)</th>
<th>Environmental Objective in Japan (ppm)</th>
<th>Vapor Pressure (mm Hg)</th>
<th>$K_H$</th>
<th>$K_{ow}$ (for $f_{oc}$=0.01)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCE</td>
<td>140</td>
<td>0.01</td>
<td>18.6</td>
<td>1.2</td>
<td>2.88</td>
</tr>
<tr>
<td>TCE</td>
<td>1100</td>
<td>0.03</td>
<td>74</td>
<td>0.49</td>
<td>2.29</td>
</tr>
</tbody>
</table>

Partitioning of VOCs between Dissolved and Adsorbed Phases. When the moisture content of soil is above a critical value, at which the soil particles will be coated by a layer of water. Then, a part of VOCs in water phase will be adsorbed onto the surface of soil particles and organic matters. At equilibrium, the partition coefficient ($K_d$) between the VOC adsorbed per unit dry mass of soil ($S$) and the concentration of VOC in moisture ($C_L$) is a function of the soil organic carbon content, $f_{oc}$, and octanol:water partition coefficient, $K_{ow}$, of VOC (Karickhoff et al., 1979).

$$K_d = \frac{S}{C_L} = 0.63K_{ow} f_{oc}$$

(2)

From above equation, it can be seen that the amount of carbonaceous matter in the soil is a dominant factor controlling the extent of adsorption of organic chemicals. The typical values of $K_d$ and $K_{ow}$ for PCE and TCE are also given in Table 1.

TRANSPORT OF VOCs IN GROUND

Transport of VOC Vapor in Soil Gas. Although the transport of VOC vapor through unsaturated soil can be caused by density gradients, thermal gradients, and pressure gradients (barometric variations), the primary transport mechanism is by diffusion through the soil gas.
under concentration gradients. The distribution of VOC concentration in the soil gas can be modeled by Fick's second law. The one-dimensional (1-D) form is as follows:

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2}
\]  

(3)

where \( C \) is concentration, \( t \) is time, \( z \) is depth, and \( D \) is diffusion coefficient.

The estimated diffusion coefficient for intermediate molecular weight VOC vapor in air is 0.43 m²/day (Jury et al., 1983). However, the diffusion coefficient in soil gas will be reduced due to tortuosity of flow path in soil. The tortuosity factor is expressed by Millington-Quirk tortuosity formula:

\[
D_g = \frac{D_a 10^{1/3}}{n^2}
\]  

(4)

where \( D_g \) is the diffusion coefficient of soil gas, \( a \) is the volumetric air content of the soil, and \( n \) is the total soil porosity. The transport of VOC vapor in soil will be influenced by partitioning between gas, liquid, and solid phases. An effective diffusion coefficient (\( D_e \)) in soil gas can be expressed as (Kury et al., 1983):

\[
D_e = \frac{D_g \rho_d K_d}{K_h + w/K_h + 1}
\]  

(5)

where \( \rho_d \) is the bulk dry density of the soil, and \( w \) is the volumetric soil moisture content. Other parameters are defined previously. Substitute \( C \) by \( C_g \) and \( D \) by \( D_e \) into Eq. 3, the 1-D VOC vapor transport in soil can be predicted.

**Transport of VOC in Soil Water.** Two conditions need to be considered, (1) unsaturated and (2) saturated. For unsaturated case with connected water phase, the main transport mechanism is diffusion due to concentration gradient and can be expressed by Fick's second law (Eq. 3) with corresponding diffusion coefficient. For saturated case, there are three mechanisms controlling the transport of contaminants, namely, (a) diffusion due to concentration gradient, (b) mechanical dispersion due to heterogeneities in the flow field, and (c) advection due to hydraulic gradient. For 1-D case, the distribution of contaminants in ground water is modelled by advection-dispersion-reaction equation.

\[
\frac{\partial C}{\partial t} = \frac{D_h \partial^2 C}{R_d \partial z^2} - \frac{v_s \partial C}{R_d \partial z} - \lambda C
\]  

(6)

where \( R_d \) is the retardation factor, \( v_s \) is seepage velocity, \( \lambda \) is decay constant, which is related to half-life \( t_{50} \) of the radioactive or bio-degrading contaminants by \( \lambda = 0.693/t_{50} \), and \( D_h \) is the coefficient of hydrodynamic dispersion, which is the combination of diffusion coefficient (\( D \)) and dispersion coefficient (\( D_m \)). For the case of a linear adsorption isotherm, \( R_d \) is a function of partition coefficient \( K_d \) and simply written as:

\[
R_d = 1 + \frac{\rho_d}{n} K_d
\]  

(7)

At 25°C, the free-solution diffusion coefficient (\( D \)) of PCE is \( 8.4 \times 10^{-10} \) m²/s and \( 9.89 \times 10^{-10} \) m²/s for TCE (Acar and Haider, 1990). The effective diffusion coefficient, \( D^* \) is expressed as:

\[
D^* = D \cdot \tau
\]  

(8)

where \( \tau \) is tortuosity factor. For fine grained soil, \( \tau \) is 0.1 to 0.4, and <0.84 for sandy soil (Shackelford and Daniel, 1991). The Dispersion coefficient (\( D_m \)) is related to the seepage velocity (\( v_s \)) as follows:
\[ D_m = \alpha_L v_s \]  

where \( \alpha_L \) is scale related, and is empirically related to transport distance \( L \). For fine grained soil, the actual seepage velocity in the ground is low, and therefore the mechanical dispersion does not appear to be significant (Rowe, 1987). The effective hydrodynamic dispersion coefficient, \( D_{h^*} \) is the sum of \( D^* \) and \( D_m \).

**DESCRIPTION OF A VOCI'S CONTAMINATED SITE IN SAGA AREA**

A site close to Karatsu, Saga Prefecture (Site A) was contaminated by VOCs (mainly PCE). The contamination of groundwater was first recognized in 1988. At that time, monitoring the groundwater quality has been required by law in Japan. The site investigation as well as possible remediation measures have been carried out in 1997. The ground is mainly consists of sandy soils. A typical soil profile is shown in Fig. 1. The matrix of top 0.8 m surface soil is sandy clay underlain the sand deposits. At the time of investigation, the groundwater level is 3.2 m deep. At present, the grain size distribution, organic content of the deposits are not available, which will be reported later on.

**SITE INVESTIGATION OF SITE A**

Fig. 1 A typical soil profile

To treat the ground contamination problem, first step is to identify the source and extent of contaminated area. Then, the remediation methods can be evaluated and actions can be planned. Both soil-gas survey and boring were made for investigating the field situation.

*Soil-Gas Survey.* PCE is a volatile organic liquid, which can easily become vapor form and exists in soil air. Gas survey as a preliminary site investigation tool can provide the data on the location and extent of contamination and aid in the design of more detailed studies, such as boring. In this study, the concentration of PCE in soil gas was measured by photoionization detector gas chromatograph (PID-GC). For easy access, the test points were mainly located along the brinks of roads and inside the open farm land. Totally, 85 points were examined. The procedure of conducting a test is as: (a) drive a 850 mm in length and 15 mm in diameter steel rod into ground, (b) withdraw the rod, and suck the soil gas into the gas detector through the hole made by the rod, (c) measuring the gas content by PID-GC method.

The gas survey results are shown in Fig. 2. From the results, the two possible PCE source locations are (1) at the upper corner of building 1 (B1) and (2) near the well point No. 2. At this site, the PCE was used in a dry cleaner shop. By inquiring the local residents that at upper corner of B1, the old laundering machines were dumped there. It is suspected that some amount of PCE was left in the machine and gradually leached out and precipitated into the ground. In interpreting the gas survey results, one thing needs to be mentioned is that the distribution of gas contamination may not represent the distribution of groundwater contamination due to different transport mechanism of contaminants in gas and groundwater.

*Borehole Investigation.* Based on the results of gas survey, a borehole of 5 m depth was made near the highest PCE concentration (gas) location. The borehole profile is already given in Fig. 1. The PCE concentration in soil has been analyzed by PID-GC method. The results are
listed in Table 2. Except the point at 0.5 m depth, the PCE concentration is gradually reduced with depth, which indicates that the source was at ground surface. The lower concentration of PCE at 0.5 depth might be due to the evaporation of PCE vapor into free air. Assuming that (1) in the zone above groundwater, the PCE mainly exists in vapor form and below groundwater in dissolved form, (2) the void ratio of the soil is 1.0, and (3) the specific gravity of the soil particles is 2.6, the PCE concentration in soil (by total weight of soil) can be converted to concentration in soil gas (by volume) for above water table zone and the concentration in groundwater in below water table. The calculated data are also indicated in Table 2. At 0.5 m depth, the converted concentration is 427 ppm by volume, which is close to gas survey results (the gas was extracted from 0 to 0.85 m depth). The highest value of PCE concentration is about 3000 ppm at 0.95 m depth. As shown in Table 1, at 25 °C, the vapor pressure of PCE is 18.6 mm Hg, it means that the saturated PCE vapor concentration can be as high as 24,470 ppm. This indicates that the 3000 ppm PCE concentration in gas is possible. The calculated maximum PCE concentration in water was about 2 ppm, which is much larger than the environment objective of 0.01 ppm in Japan. Due to lower solubility of PCE, the concentration in water is relatively lower than in soil air. By referring to Table 1, the solubility of PCE in water is 140 ppm (at 25 °C).

![Fig. 2 PCE gas survey results](image)

### Table 2 Soil contamination analysis results (PID-GC)

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>PCE in Soil (ppm)</th>
<th>PCE in Air (ppm)</th>
<th>PCE in Water (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1.14</td>
<td>427.5</td>
<td></td>
</tr>
<tr>
<td>0.95</td>
<td>7.76</td>
<td>2920.9</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>3.48</td>
<td>1309.2</td>
<td></td>
</tr>
<tr>
<td>1.95</td>
<td>4.13</td>
<td>1552.7</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>2.60</td>
<td>979.2</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.6</td>
<td>0.54</td>
<td>1.94</td>
<td></td>
</tr>
<tr>
<td>3.95</td>
<td>0.21</td>
<td>0.76</td>
<td></td>
</tr>
<tr>
<td>4.2</td>
<td>0.01</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>4.95</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
</tbody>
</table>

*Unit of PCE concentration: ppm

*Calculated.

Diffusion of PCE in Soil Gas. By assuming (1) the total porosity of the soil is 0.5 (\(\varepsilon=1.0\)), zero water content, and (2) \(K_d=0\), from Eq. 5, the effective vapor diffusion coefficient \(D_e\) of 0.17 m²/day can be estimated. Then under the condition that (1) the concentration at the bottom of surface soil is a constant \(C_0\), and (2) \(C(\infty,t)=0\), (t is time), the solution for Eq. 3 becomes Ogata-Banks solution (Ogata and Banks 1961), and the gas concentration isophene in ground (above groundwater and below surface soil) can be predicted as shown in Fig. 3. It can be seen that the field data is close to the isophene of 10 days. This calculation just quantitatively
shows how fast the PCE vapor can diffuse in soil air.

*Modelling PCE Transport in Groundwater.* It is possibly that the PCE spread on the ground surface has been periodically transported into groundwater by rainfall. In this case, the distribution of concentration in groundwater will vary periodically also. To illustrate this, an assumed case as indicated in Fig. 4 is analyzed under 1-D condition by using Booker-Rowe's solution for Eq. 6 for the limited mass of contaminants case (Booker and Rowe, 1993). In addition, it is assumed: (1) the width (in flow direction) of initially contaminated area is 5 m with a concentration of 100 mg/L, and (2) the partition coefficient, $K_d=0$, and the decay constant, $\lambda=0$. The concentration variations with time at points A, B, and C are shown in Fig. 5. It can be seen that the location of the maximum concentration varies. After about 8 months, the maximum concentration occurs at point B instead of point A (the source). This indicates that it should be caution to directly use the one time measured data on groundwater contamination to identify the source location. In actually case, due to biodegradation and three-dimensional effect, the peak value of concentration at a point away from source may reduce faster than what is indicated in Fig. 5.

![Fig. 3 Diffusion of PCE gas in ground](image)

![Fig. 4 Assumed ground conditions for the analysis](image)

![Fig. 5 Concentration variation with time at point A, B, and C](image)
REMEDIATION TEST BY VAPOR EXTRACTION METHOD

Vapor extraction system (VES) is an effective and relatively cheaper method for remedying the VOCs contaminated land. The operation principles for VES are straightforward. Drawn off the vapor from soil gas promotes the volatilization and mass reduction of VOC contaminants in subsurface. With a vacuum extraction well, the contaminated soil is flushed with fresh air and the VOCs are extracted. As the concentration of VOCs in soil gas is reduced, more VOCs will evaporated into vapor phase from groundwater (Henry's law), and are again drawn off by the vacuum. As a result, the VOC contaminants can be removed (or partially removed) from the ground.

At site A, a test vapor extraction was conducted. The bore hole had a depth of 3.0 m and a diameter of 86 mm. The test period was about 1 month, from February 26, to March 24, 1997. The vapor flow rate was 70 to 80 m³/hr, and the pumping time was about 9 hr/day. The rate of contaminants being extracted (W) is calculated as follows.

$$W = \frac{x_p M_w Q}{RT}$$  (10)

where x is the concentration of corresponding component by volume (or mole fraction), $M_w$ is the molecular weight of component (g/mol), R is gas constant (8.134 J mol⁻¹K⁻¹), T is absolute temperature (K), $p_i$ is total vapor pressure, and Q is vapor flow rate. The variations of PCE concentration and extracted amount of PCE with time are shown in Figs. 6 to 7, respectively. It can be seen that after 15 days, the concentration reaches an equilibrium condition for the case tested. The equilibrium means that the vapor being extracted will be continually being replenished by VOCs vapor from surrounding area as well as the vapor volatilized from soil water and desorbed from soil solids. Unfortunately, the radius of influence is not measured from this test, which is an important design factors for VES.

Fig. 6 The variations of PCE concentration in extracted vapor
Fig. 7 The total amount of extracted PCE
SUMMARIES

Treating the volatile organic compounds (VOCs) contaminated ground becomes one of the important tasks of geoenvironment engineering. The basic principles of VOCs transport in ground are reviewed and their applications to site investigation and remediation methods are discussed.

The effectiveness of gas survey on identifying the potential contaminant source and the extension of contaminated area is illustrated by the field study on a PCE contaminated site in Saga area. The higher PCE concentration zone (in gas) coincide with the suspected source location based on the information of inquiring to local residents.

Vapor extraction system (VES) is an effective and economic method for remediying the VOC contaminated ground. The results of a field test on vapor extraction system (VES) are reported.

ACKNOWLEDGMENTS

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REFERENCES


