

Significant Parameters for Assessing Soil Contaminant-Leaching to Groundwater and Determining Soil Sample Size in Field Survey

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Abstract

For a given soil-contaminated site, a level of soil contamination is characterized and decisions on risk may be made from the risk assessment. The study evaluated critical design factors for the determination of sample size in the sampling design plan and the assessment of soil contaminant-leaching to groundwater. Two variables, the minimum relative detectable difference (T) and coefficient of variation (CV) were evaluated for the sample size determination. The minimum number of samples can be appropriately determined by CV under a T value greater than or equal to 0.2. Soil-contaminant leaching to groundwater was evaluated by using the Soil Screening Level equation of U.S. Environmental Protection Agency and the Risk Based Screening Level equation of American Society for Testing and Materials, with the same input parameters. The groundwater concentrations estimated from soil contaminant concentrations were significantly affected by the Darcy velocity of groundwater and the organic content of soil.

Keywords: Site characterization, Soil contamination, Risk assessment, Exposure concentration, Groundwater contamination, Exposure pathway

1. Introduction

The number of hazardous sites contaminated by inorganic or organic compounds are increasing in several industrial countries. In the United States, a total of 1499 sites has been known as contaminated sites and most of the sites are still remediated by several trials.¹⁾ European countries have also found a huge number of contaminated sites and spent much efforts to remediate them.²⁾ Once a possible contaminated site was discovered, an investigation-procedure-line would be applied for site characterization and evaluation; preliminary survey, preliminary investigation, main site investigation, implementation of remediation activities.³⁾

Contaminated sites pose a unique challenge for risk assessment and remediation because contaminants present in a site may be exposed to humans and ecological receptors.⁴⁾ Risk assessment is normally conducted to characterize the potential threat to human health and the environment that may be posed by contaminants at a contaminated-site. The first step to risk assessment of contaminated site is to characterize a level of contamination and determine an exposure concentration of the area.

Natural field soils have quite heterogeneous properties, both in the horizontal and vertical directions. A sample set of measurements of soil contaminant concentrations might vary significantly in space or in time. Soil data obtained from field may include three types of errors; sampling error, sample preparation and analysis errors.⁵⁾ It is known that sampling and sampling preparation errors are similar to errors occurred from the chemical analysis.⁶⁾ Accumulation of all types of errors made during soil investigation could substantially affect environmental decision-making. A statistical test is thus performed to make a correct decision about whether a site is contaminated.

In a statistical test, the decision being made is whether to accept or reject the null hypothesis. Four possible outcomes of a test can be obtained as shown in Table 1.⁷⁾ If the null hypothesis was incorrectly rejected, that would be called Type I error. If the null hypothesis was incorrectly accepted, that would be called Type II error. The possibility making Type I error, α , is conventionally set at 0.05,⁸⁾ while there is no traditional value for the possibility making Type II error, β . U.S. Environmental Protection Agency (USEPA) admits these errors in soil data and suggests specifying limits on the decision error rates.⁵⁾ It suggests that the probability of Type I error is normally set at 5 percent ($\alpha = 0.05$) and the probability of Type II error is set at 20 percent ($\beta = 0.20$). Therefore, the sampling design plan from

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the beginning of the site investigation should be prepared based on the decision error rates for later making a reasonable decision. This study investigated important factors influencing on determining the number of samples that would be compliant to the decision error rates.

Exposure concentrations of the chemicals of potential concern in different environmental media are so important in the risk assessment to calculate intakes in the exposure assessment. Exposure concentration of contaminant in soil is normally determined at the 95 percent upper confidence limit on the arithmetic mean chemical concentration. However, considerable effort and expense can be required for groundwater data collection, due to the installation and development of monitoring wells. Risk assessors may be recommended to use simple, screening level analytical models for estimating exposure concentrations of contaminants in groundwater. There are two analytical models for estimating groundwater concentration from soil contaminant concentration; equations for obtaining Risk-Based Screening Level (RBSL) of American Society for Testing and Materials (ASTM) and Soil Screening Level (SSL) of USEPA. This study evaluated the difference between two analytical equations and sensitivity of input parameters.

The purposes of the study were to suggest appropriate parameter values for determining a practical and efficient sample size in soil sampling planning and to find parameters influencing on determining groundwater concentration from soil concentration through analytical models.

2. Determination of Sample Size

The number of samples required to meet statistical acceptance is suggested by the following equation⁹⁾;

$$n \geq \left(\frac{Z_{1-\alpha} + Z_{1-\beta}}{D} \right)^2 + 0.5Z_{1-\alpha}^2 \quad (1)$$

where n is the number of samples required to achieve a specified precision and confidence level, $Z_{1-\alpha}$ and $Z_{1-\beta}$ are the critical values for the normal distribution with probabilities of $1-\alpha$ and $1-\beta$, D is T / CV , T is the minimum detectable relative difference, and CV is the coefficient of variation. As described, the equation is governed by several parameters. Determination of the number of samples should be considered with respect to the cost and time to fulfil investigation. This study evaluated sensitivity of each parameters of the equation to select appropriate parameters for practical use.

3. Estimation of Groundwater Concentration

Table 1. A definitive explanation of types of errors in statistical testing

Decision	True	
	H_0	H_A
Accept H_0	Correct (certainty = $1-\alpha$)	Type II error (probability = β)
Accept H_A	Type I error (probability = α)	Correct (power = $1-\beta$)

H_0 : null hypothesis; H_A : alternative hypothesis

There are three analytical models for estimating groundwater concentration from soil contaminant concentration. ASTM presents an equation relating soil contaminant concentration to groundwater concentration.¹⁰⁾ Concentrations of chemicals in two media are related by the leaching factor. The equation of ASTM was rearranged to well express the relation between soil concentration and groundwater concentration (Eq. 2). USEPA suggested the soil-water partition equation for migration to groundwater pathway for users to estimate groundwater concentrations from calculation of a dilution factor that relates the concentration of contaminant in soil to the soil leachate concentration.⁵⁾ Equation (3) was also rearranged to express the relation between two media concentrations. Therefore, Equations (2) and (3) were rearranged from equations for obtaining RBSL of ASTM and SSL of USEPA, respectively. The RBSL equation of ASTM shown in equation (2) includes both soil leachate generation and dilution due to groundwater mixing, while the SSL equation of USEPA in Equation (3) separates the two processes. Definitions of symbols used in Equations (2) and (3) can be found in Tables 2 and 3.

$$RBSL_w \left[\frac{mg}{L-H_2O} \right] = RBSL_s \left[\frac{mg}{kg-soil} \right] \times \frac{\rho_b}{(\theta_w + K_d \rho_b + H' \theta_a) \left(1 + \frac{U_{gw} \delta_{gw}}{IW} \right)} \quad (2)$$

$$C_w (mg/L) = \frac{SSL (mg/kg)}{\left(K_d + \frac{(\theta_w + \theta_a H')}{\rho_b} \right) \left(1 + \frac{Kid}{IL} \right)} \quad (3)$$

The third equation available for estimating groundwater concentration from soil contaminant concentration is an equation suggested by the National Institute of Public Health and the Environment (RIVM). An equilibrium concentration in pore water is calculated from soil contaminant concentration and the contaminant concentration in groundwater is then determined by dividing the pore water concentration by a constant dilution factor of 10.¹¹⁾

This study evaluated Equations (2) and (3) with same input parameters. Table 2 shows the input parameters used for comparison of the groundwater equations. The soil and groundwater properties used for comparison were same, except for the groundwater mixing zone depth. The groundwater mixing zone depth of RBSL was identified as a default value of 200 cm, while that of SSL was calculated according to an equation shown in the foot note of Table 2. Table 3 shows chemical parameters of organic contaminants used for comparison of the two equations. Table 4 shows chemical parameters of inorganic contaminants used for comparison.

Table 2. Input parameters used for comparison of the soil contaminant-leaching to groundwater equations

	RBSL	SSL
Soil bulk density	1.7 kg/L	⇒ ^a
Porosity	0.38	⇒
Volumetric water content (θ_w)	0.12	⇒
Volumetric air content (θ_a)	0.26	⇒
Fraction of organic carbon in soil (f_{oc})	0.01	⇒
Infiltration rate of water through soil	30 cm/yr	⇒ (0.3 m/yr)
Source dimension	1,500 cm (width)	⇒ (15 m, length)
Darcy groundwater velocity	2500 cm/yr	⇒ (25 m/yr)
Groundwater mixing zone depth	200 cm	1.76 m ^b
Aquifer thickness (d_a)	-	5 m

^asame to value of RBSL

$$d = \sqrt{0.0112L^2 + d_a} \left(1 - \exp\left(\frac{-Ll}{K_d d_a}\right) \right)$$

^bcalculated from

Table 3. Chemical parameters of organic contaminants used for estimation of groundwater concentration

	Benzene	Toluene	Ethyl benzene	Mixed xylenes ¹⁰⁾
Soil organic carbon-water partition coefficient (K_{oc} , L/kg) ^a	58.9	182	363	239.8833
Dimensionless Henry's law constant (H') ⁵⁾	0.228	0.272	0.323	0.29
Soil contaminant concentration (mg/kg)	20	20	20	20
$RBSL_w$ (mg/L) calculated by Eq. 2 using the parameters above	2.378	0.855	0.440	0.657
C_w (mg/L) calculated by Eq. 3 using the parameter above	2.666	0.958	0.494	0.737

^a K_{oc} used for $K_d = K_{oc} f_{oc}$ ⁵⁾

Table 4. Chemical parameters of inorganic contaminants used for estimation of groundwater concentration^a

	Soil-water partition coefficient (K_d)	Dimensionless Henry's law constant (H')
Hg	52	182
Cd	75	
As (III)	29	
Pb	2457 ^b	
Cr (VI)	19	
Ni	65	

^a at pH = 6.8⁵⁾

^b at pH = 6.8¹³⁾

4. Results and Discussion

4.1. Sensitivity of Input Parameters in Determination of Sample Size

Two variables, T and CV in Equation (1) were evaluated in this study. Figs. 1(a) and 1(b) show variations in the sample number required to satisfy the decision errors that were set at $\alpha = 0.05$ and $\beta = 0.20$. The number of samples decreased with increasing T (Fig. 1(a)), while that increased as CV increased (Fig. 1(b)).

In the region of T greater than 0.5, the lines of Fig. 1(a) showed convergence in the number of samples. The convergence implies that T may play an insensitive role in determining the number of samples under a certain condition. However, Fig. 1(a) also reveals that n is so sensitive to T values in the region less than 0.3. As T became small, there was a substantial increase in

n because soil contamination would not be easily discriminated from background levels. Fig. 1(b) shows variations of n with changing CV at four T values (0.1, 0.2, 0.3 and 0.4). Four T values were selected in the sensitive region shown in Fig. 1(a).

Change in n was greatly dependent on T rather than CV under T values of 0.1 and 0.2, while that was relatively insensitive to T at two values of 0.3 and 0.4 (Fig. 1(b)). Generally, n would be dependent to CV rather than T, except for T values less than 0.2. The minimum number of samples, n, may be appropriately determined by CV under a T value greater than or equal to 0.2. Therefore, CV should be approximately determined through the reference⁹⁾ or preliminary study. It is known that the CV values of heavy metals obtained from contaminated sites were normally larger than those of organic contaminants.¹²⁾ As the CV value increases, the number of samples is then increased.

4.2. Important Field Parameters in Estimation of Groundwater Concentration

Equations (2) and (3) relating soil and groundwater contaminations were evaluated with the same input parameters. The most frequently detected contaminants in the oil spill area, benzene, toluene, ethyl benzene, and xylenes, were selected for comparison. As shown in Table 3, all contaminant concentrations in soil were assumed at 20 mg/kg. RBSL_w and C_w of Table 3 show comparative results of the groundwater concentrations estimated by Equations (2) and (3). Little difference was observed in the groundwater concentration between two equations.

This study evaluated influencing factors on the determination of groundwater concentration from Equations (2) and (3). Four

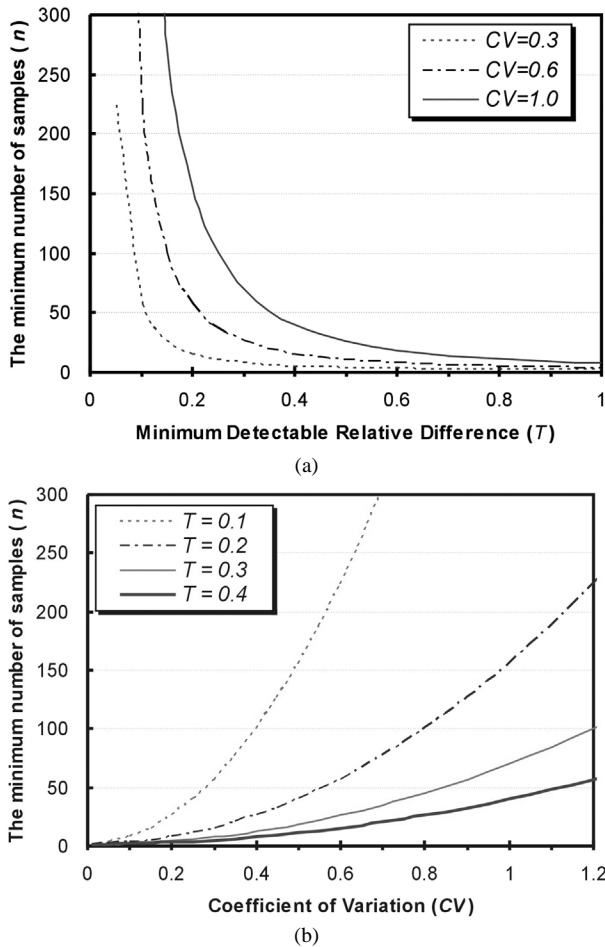


Fig. 1. Variations in the sample number required to satisfy the decision errors that were set at $\alpha=0.05$ and $\beta=0.20$, under conditions of CV and T .

parameters, soil contaminant source dimension, water and air content in soil, organic content in soil, and Darcy's velocity were selected for analysis, and the parameter sensitivity to groundwater concentration was then evaluated by varying each parameter value.

The target contaminant for sensitivity analysis was benzene, and the values already shown in Tables 2 and 3 were used as input parameters. Fig. 2(a) shows the sensitivity of the groundwater benzene concentration to the benzene contaminant source dimension in soil for SSL and RBSL equations. As already shown in Equations (2) and (3), the RBSL equation and the SSL equation used width and length for the contaminant source dimension, respectively. Groundwater concentrations obtained by Equation (3) (the SSL equation) were little higher than those of Equation (2) (the RBSL equation). Generally, groundwater concentrations are linearly related to soil contaminant source dimension.

Fig. 2(b) presents variations in the groundwater concentration for soil contaminant source dimension. The result also showed that groundwater concentrations of the example contaminants linearly increased with increasing the soil contaminant source dimension. The estimated groundwater concentration of Cr(VI) was found to be highly dependent on the length of soil contaminant source.

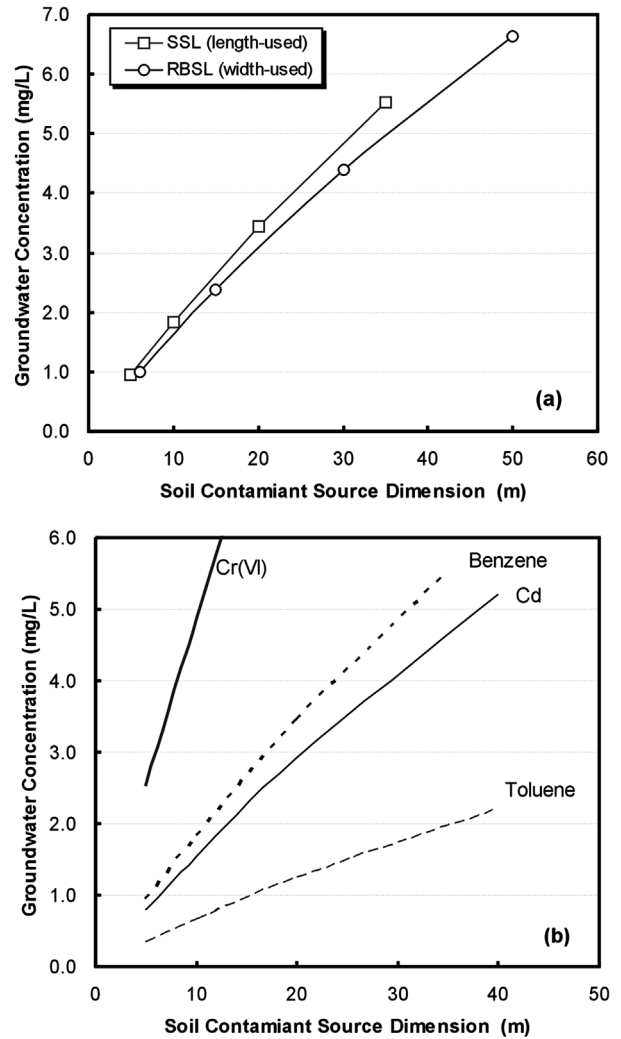


Fig. 2. (a) Sensitivity of the groundwater benzene concentration to the benzene source dimension in soil for SSL (Soil Screening Level) and RBSL (Risk-Based Screening Level) equations; (b) variations in the contaminant concentration in groundwater for soil contaminant source dimension.

nant source.

The effect of the organic content in soil on the groundwater concentration was evaluated by using Equation (3) (Fig. 3). Groundwater concentration significantly increased in a region of the organic fraction in soil less than 0.02 (2%), implying its dependency on the organic fraction in soil. However, groundwater concentrations were found to be relatively independent of the organic content in soil greater than 0.02. Therefore, the results indicate that organic content should be carefully determined for estimation of groundwater concentration. Table 5 lists several default values of organic content in soil. Various default values for the organic content in soil are used. The SSL equation uses a small value of 0.002 (0.2%) for organic content while RBSL uses 0.01 (1%). According to Fig. 3, users of SSL and RBSL equation would be recommended to accurately measure an organic content in the contaminated site-soil.

Fig. 4 shows the sensitivity of water and air contents in soil to determination of groundwater concentration. The analysis

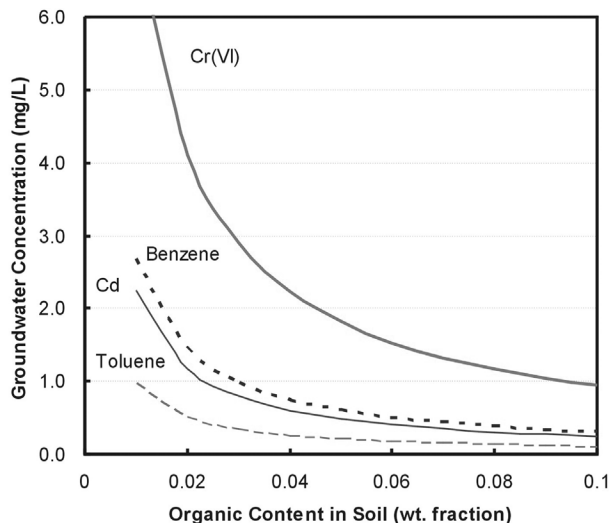


Fig. 3. Effect of the organic content in soil on the ground water concentration estimated through Equation 3.

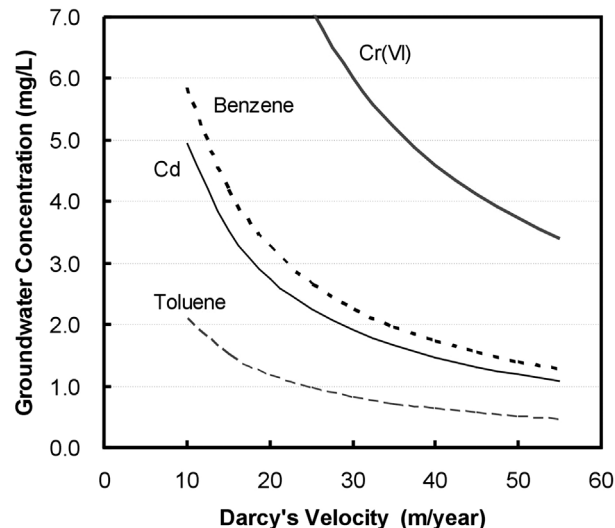


Fig. 5. Effect of Darcy velocity on the groundwater concentration estimated from Equation 3.

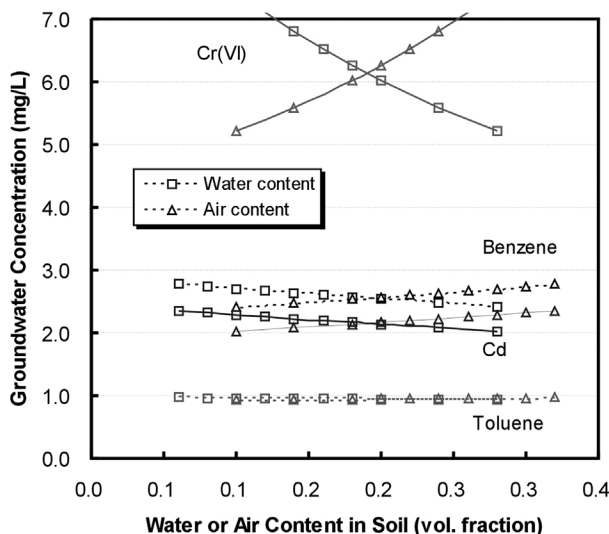


Fig. 4. Sensitivity of the groundwater concentration to the water and air contents in soil.

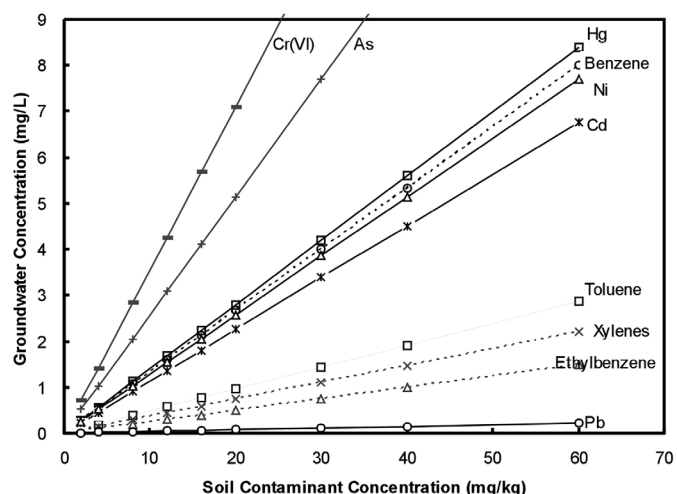


Fig. 6. Comparison of the soil contaminant concentration to the groundwater concentration estimated through a soil contaminant-leaching to groundwater equation.

Models	f_{oc}	
RBSL ¹⁰⁾	0.01	
SSL ⁵⁾	Inhalation pathway	0.006
	Groundwater pathway	0.002
Cal-Tox ^a	Upper soil zone	0.0156
	Vadose zone	0.00306
	Aquifer zone	0.00306
CLEA ¹⁴⁾	0.025 or 0.050	
CSOIL ¹¹⁾	0.058	

^a California residential site¹⁵⁾

revealed little difference in the most groundwater concentrations. The estimated groundwater concentrations were found to be relatively independent to the water and air content in soil, except for Cr(VI).

Fig. 5 shows the effect of Darcy velocity on the groundwater

concentration estimated from SSL equation. The groundwater concentration would increase with decreasing Darcy's velocity. The groundwater concentrations estimated from soil contaminant concentrations were normally dependent on the Darcy velocity. Therefore, risk assessors would be recommended to obtain a site-specific Darcy velocity for better prediction of groundwater concentration.

The relationship between soil contaminant concentrations and groundwater concentrations estimated through the soil-leaching to groundwater equation (Eq. 3) was displayed in Fig. 6. Contaminants in soil were leached into the groundwater zone and the leached contaminants would be mixed with groundwater, resulting in groundwater contamination. The SSL modified equation (Eq. 3) relates the concentration of contaminant in soil to the groundwater concentration. The study estimated groundwater concentrations from soil contaminant concentrations by using Equation (2). Chromium (Cr (VI)) present in soil was much leached to the groundwater while lead present in soil was little lea-

ched to the groundwater. As shown in Table 4, the soil-water partitioning coefficient (K_d) of Cr (VI) is lower than those of other metals. Lower K_d implies less adsorption to soil. Generally, inorganic contaminants in soil would be more leached to the groundwater than organic contaminants in soil. For this reason, soil-water partitioning coefficient appears to be a key factor for understanding the leaching of soil contaminants to the groundwater. In the risk assessment for soil contamination, if a site is contaminated by inorganic contaminants, much attention should be made to groundwater pathway of exposure assessment. A relationship between soil contaminants and groundwater contamination as like Fig. 6 can be appropriately used for screening exposure pathway and estimating a level of groundwater contamination.

5. Conclusions

This study evaluated factors of the USEPA formula influencing on determination of sample size. The formula was so sensitive to T values in the region less than 0.3. Evaluation of two parameters showed that the sample size was dependent to CV rather than T. Therefore, the minimum number of samples would be appropriately determined by CV under a T value greater than or equal to 0.2.

Two analytical equations of ASTM and USEPA for soil-contaminant leaching to groundwater were evaluated with the same input parameters. Although the SSL equation of USEPA showed higher groundwater concentrations than the RBSL equation of ASTM, little difference was observed. Generally, groundwater concentration is linearly related to soil contaminant source dimension. Groundwater concentration was significantly increased in a region of the organic fraction in soil less than 0.02 (2%). However, groundwater concentrations were found to be relatively independent of the organic content in soil greater than 0.02. The estimated groundwater concentrations were found to be relatively independent of the water and air content in soil. The groundwater concentration would increase with decreasing Darcy's velocity. The groundwater concentrations estimated from soil contaminant concentrations were normally dependent on the Darcy velocity. Therefore, risk assessors would be recommended to obtain a site-specific Darcy velocity and an organic content for better prediction of groundwater concentration.

The results of soil contaminant-leaching to groundwater showed that chromium (Cr(VI)) present in soil was much leached to the groundwater while lead present in soil was little leached to the groundwater. Sites contaminated by chemicals having low soil-water partitioning coefficients should be carefully assessed for groundwater pathway in the risk assessment.

Acknowledgement

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References

1. USEPA, Treatment Technologies for Site Cleanup: Annual Status Report (Eleventh Edition), EPA/542/R-3/009, Office of Solid Waste and Emergency Response, Washington DC, (2004).
2. Vik, E. A., and Bardos, P., Remediation of Contaminated Land Technology Implementation in Europe, Contaminated Land Rehabilitation Network for Environmental Technologies (CLARINET), Austria (2002).
3. LaGrega, M. D., Buckingham, P. L., Evans, J. C., and Environmental Resources Management, Hazardous Waste Management, 2nd Ed., McGraw Hill Inc, New York (2001).
4. USEPA, Risk Assessment Guidance for Superfund Volume I, EPA/540/1-89/002, Office of Emergency and Remedial Response, Washington DC (1989).
5. USEPA, Soil Screening Guidance: Technical Background Document, EPA/540/R-95/128, Office of Solid Waste and Emergency Response, Washington DC (1996).
6. Wagner, G., Mohra, U., Sprengarta, J., Desalesb, A., Muntauc, H., Theocharopoulos, S., and Quevauvillere, P., "Objectives, concept and design of the CEEM soil project." *Sci. Total Environ.*, **264**(1), 3-15 (2001).
7. McBean, E. A., and Rovers, F. A., Statistical Procedures for Analysis of Environmental Monitoring Data & Risk Assessment, 1st Ed., Prentice Hall Inc, New Jersey (1998).
8. Underwood, A. J., and Chapman, M. G., "Power, precaution, Type II error and sampling design in assessment of environmental impacts," *Jour. Experi. Marine Biol. Ecol.*, **296**, 49-70 (2003).
9. Barth, D. S., Mason, B. J., Starks, T. H., and Brown, K. W., Soil Sampling Quality Assurance User's Guide, EPA/600/8089/046, USEPA, Nevada (1989).
10. ASTM, Standard Guide for Risk Based Corrective Action Applied at Petroleum Release Sites E 1739-95, ASTM International, Pennsylvania (2002).
11. Rikken, M. G., Lijzen, J. P., and Corneles, A. A., Evaluation of Model Concepts on Human Exposure; Proposals for Updating the Most Relevant Exposure Routes of CSOIL, Report Number 711701, RIVM, Netherlands (2001).
12. USEPA, Guidance for Data Usability in Risk Assessment (Part A), EPA/540/R92/003, Office of Research and Development, Washington DC (1991).
13. USEPA, Understanding Variation in Partition Coefficient K_d Values Vol II, EPA/402/R99/004B, Office of Air and Radiation, Washington DC (1999).
14. Earl, N., Macklin, Y., and Abedo, T., CLEA UK Handbook (Draft): Support Document for the CLEA UK Software Beta Version 1.0, Environment Agency, Bristol, UK (2005).
15. McKone, T. E., and Enoch, K. G., Cal-Tox A Multimedia Total Exposure Model Spreadsheet User's Guide Version 4.0 (Beta), LBNL-47399, Lawrence Berkley National Laboratory, California (2002).