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Analysis of the distribution of lead concentration under steady state conditions in urban multimedia environment

Wonjin Jeon*, Chee Burm Shin*,†, Jong Ho Kim, Byoung Kyu Kwak**, Jongheop Yi**, Jun Hee Lee***, Woon Gi Lee***, Sun Woo Lee****, and Hyeon Soo Park******

*Division of Energy Systems Research, Ajou University, Suwon 443-749, Korea
**School of Chemical and Biological Engineering, Seoul National University, Seoul 151-742, Korea
***Korea Testing and Research Institute, Seoul 150-038, Korea
****TO21 Inc., Seoul 156-012, Korea
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Abstract−The environmental contamination problems caused by accelerated industrialization are becoming increasingly important issues. It is necessary to estimate the distributions of the contaminants and to recognize the risks to our environment. The behavior of volatile organic compounds (VOC) can be analyzed with the concept of fugacity. However, it is difficult to simulate the fate of heavy metals with this concept, because their vapor pressure is extremely small or unknown. Therefore, the aquivalence (from "equivalent aqueous") theory, which was derived from the fugacity theory, is utilized to establish a mathematical model and to analyze the fate of heavy metals in an urban multimedia system. The target heavy metal is lead and the target region is around Jungrang stream in Seoul. The multimedia is composed of air, water, sediment, soil and vegetation. To verify the proposed mathematical model, the modeling results were compared with the measurement data obtained from the Korea Testing and Research Institute.

Key words: Equivalence Approach, Heavy Metal Distribution, Environmental Modeling, Lead Concentration

INTRODUCTION

A great deal of attention has been directed toward the problem of environmental contamination caused by rapid industrialization. The pollution is not limited to a specific location, but rather diffuses and is dispersed into the surrounding regions or even other countries. This behavior is caused by the fact that the contaminants are essentially composed of extremely fine particles which can be transported between different media by physical and chemical adsorption [1]. For instance, in the case of pollutants originating from the smokestack of a factory, the contaminants will be dispersed into the surrounding regions. Therefore, further studies of these complex and multiple phenomena are required to analyze the fate of the pollutants. As well as quantitative studies on the sources of the contaminants, qualitative analysis of their behavior can be a crucial factor to obtain proper solutions to the problem of pollution-control. Research into the fate of various contaminants has been briskly progressing since Mackay [2] constituted the theoretical foundation in the 1980s. He and his coworkers developed many effective models which could be applied to volatile organic compounds (VOCs) and metals based on thermodynamic theories. In the case of VOCs, they tried to analyze these thermodynamic phenomena with the concept of fugacity [1,2,5,7,8,10,11]. However, in the case of metals, many researchers used the concept of aquivalence [2,3,10,11] derived from fugacity and in this way were able to establish qualitative and quantitative models for the fate of nonvolatile materials. In further research, more advanced models have been established which can be applied to various compounds, such as mercury, and various media conditions [3,6,9,12,13].

In the simulations performed in this study, lead was selected as the target material and the model employed followed the concept of the aquivalence approach, due to the characteristics of lead as a metal. There are several existing models of the aquivalence approach, which have been applied to various regions of Canada and the U.S. [3,10], such as bay areas or water reservoirs. The main purpose of the present study is to analyze the performance of the existing models in differently characterized regions such as industrial regions or urban areas. Therefore, the target region of the environmental simulation was Seoul, the representative urban area in Korea. To simulate the aquivalence approach model, various information on the modeling conditions were obtained by TO21 Inc. and the Korea Testing and Research Institute (KTR). TO21 Inc. estimated the emission rates of lead and the KTR experimentally measured the lead concentrations at the target locations. To verify the validity of this simulation, the modeling results were compared with the experimental data measured by the KTR.

THEORY

To analyze the fate of volatile contaminants, the concept of fugacity has been applied to mathematical models for multimedia systems [1,8]. The models established by the theory are able to express the behavior of VOCs in simple ways and the results derived from them have shown considerable reliability in several published papers [3]. By using the concept of fugacity, it is possible to establish an equilibrium criterion proper for volatile chemicals which have measur-

†To whom correspondence should be addressed.
E-mail: cbshin@ajou.ac.kr
‡This paper is dedicated to Professor Chang Kyun Choi to celebrate his retirement from the school of chemical and biological engineering of Seoul National University.

able concentrations in the vapor phase [2]. However, in the case of lead, this criterion is unsuitable, because of its extremely low vapor pressure [15] and chemical transformation. In other words, lead cannot maintain available concentrations under specific conditions of temperature and vapor pressure and, thus, the criterion does not work very well.

Table 1 shows the magnitude of the vapor pressure for lead. These data show that lead is hardly vaporized at all in any environmental system. Therefore, some researchers, including Mackay, modified the existing theory and applied this modified version to their models [2,7]. To support the new concept, the term "aquivalent concentration" was introduced. The word "aquivalent" originated from "equivalent aqueous" which means that the basis of the equilibrium criterion is in the water phase rather than in the vapor phase [2]. Instead of the vaporization of metals, a novel mechanism based on water phase flows such as rain was presented by these researchers. Through the modified approach, a more efficient analysis can be achieved for the transport phenomena of non-volatile contaminants like lead.

Table 1. Vapor pressure of lead (Pb)

Temperature in ºC for the indicated pressure					
1 Pa	10 Pa	100 Pa	1 kPa	10 kPa	100 kPa
705	815	956	1139	1387	1754

Table 2. Area distribution of five media

Site	Compartment area [m^2]				
	Air	Water	Soil	Sediment	Vegetation
1	1007473	69515.64	109814.6	29515.64	1007.5
2	528242	50182.99	73425.64	50182.99	528.24
3	576321	49563.61	20171.24	49563.61	576.3
4	778312	13231.3	289532.1	13231.3	778.31
5	226055	16275.96	34134.31	16275.96	226.06
6	1500000	249000	144000	249000	124500
7	956969	31579.98	139717.5	31579.98	15311.5
8	736359	142117.3	131071.9	142117.3	107508.4
9	961451	463419.4	139410.4	463419.4	961.45

1. Description of the Target Sites

Table 2 shows the area distribution of each compartment of the sites. The distribution was obtained by using the Transverse Mercator (TM) coordinates in Fig. 1. Table 3 shows the vertical length such as the thickness or height and other informative properties of each compartment. The values of the depth of the water compartment and water flow rate in the Jungrang stream were calculated

Table 3. Profiles of each compartment

Parameter name	Value	Reference
Water depth [m]	0.6	4
Active sediment depth [m]	0.005	2
Average Vegetation height [m]	0.5	estimated
Air compartment height [m]	1000	3
Water flow rate [m^3/h]	2.17×10^4	4
Rain rate [m/h]	1.48×10^{-4}	4
Volume fraction of aerosol [-]	2×10^{-11}	2
Volume fraction of water particles [-]	2.08×10^{-7}	2
Volume fraction of solids in sediment [-]	0.15	2
Density of water and sediment particles [g/cm^3]	2.4	2
Density of aerosol [g/cm^3]	1.5	2

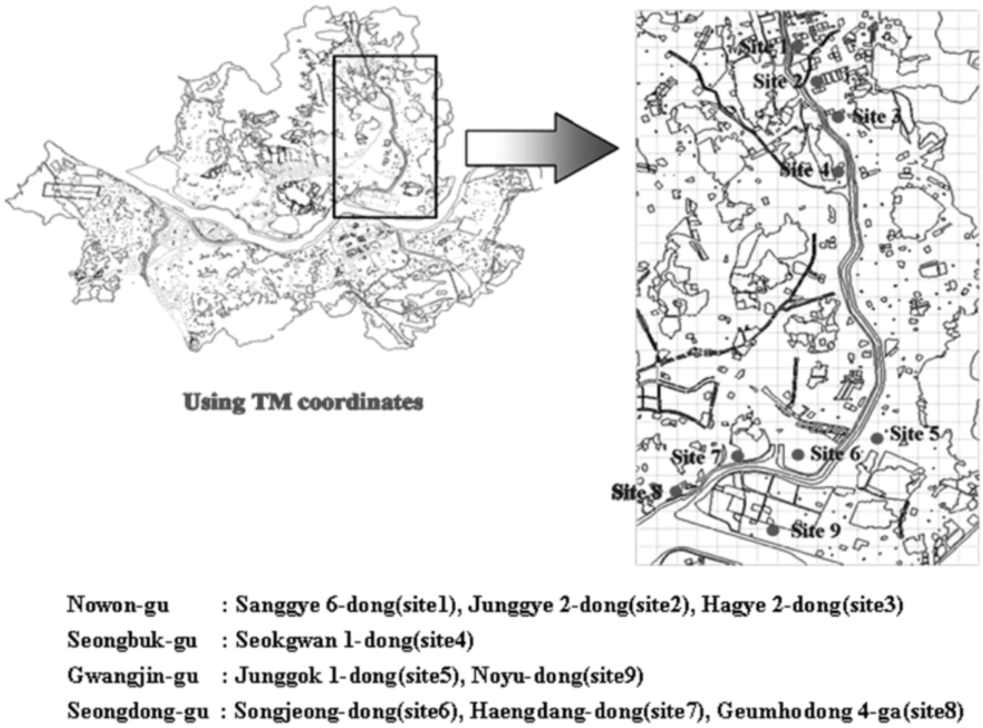


Fig. 1. Description of the target sites on the map.

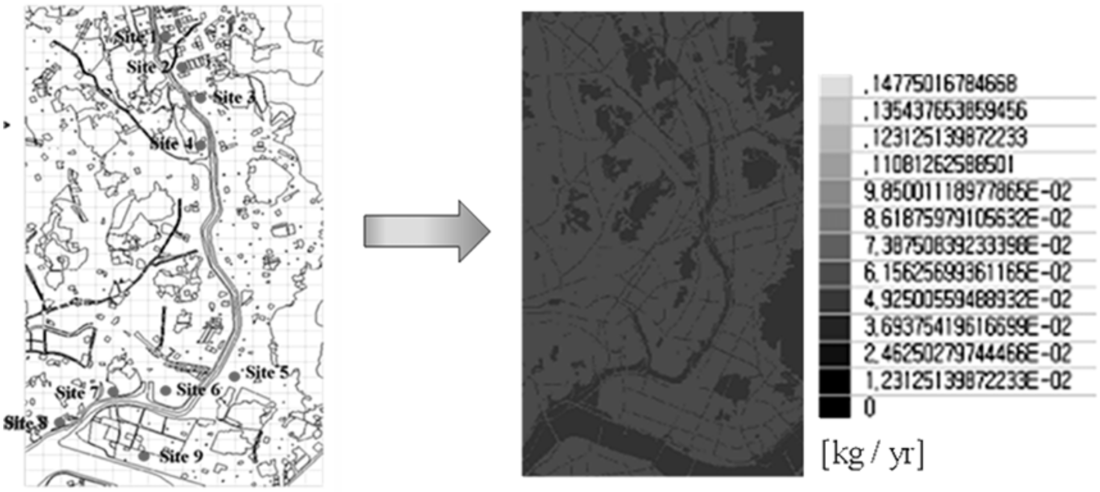


Fig. 2. Distribution of the emission rate of lead and its compounds into the air compartment on the map.

by averaging the measured data of the Korea Water Resources Corporation for the twelve months in 2007. The height of the vegetation compartment was intuitively estimated due to the lack of accurate measured data on the specific target region.

Fig. 2 shows the direct emission rates of lead at each site around the Jungrang stream. As shown in the figure, the distributions of the emission rates in all of the target sites are almost the same. The direct emission data were obtained from the statistical information of emissions which originated from individuals, markets and industrial factories, etc. The emission rates were estimated by research-

Table 4. Z values of environmental media

Compartment	Symbol	Z value [-]	Reference
Air	Z_A	0	2
Water	Z_W	1	2
Sediment	Z_X	302000	12
Soil	Z_S	38000	12
Vegetation	Z_V	10000	estimated
Aerosols	Z_Q	10^8	2
Water particles	Z_P	1600000	2

Table 5. Definitions of transport parameters

Parameter name	Explanation	Value	Reference
G_{Rain}	Raining rate [m/h]	1.48×10^{-4}	1
G_{DD}	Dry deposition velocity [m/h]	10	1
G_I	Water inflow rate [m^3/h]	21718.05	4
G_V	Evaporation rate [m/h]	7.44×10^{-5}	2
G_{SD}	Sediment deposition rate [m/h]	4.6×10^{-8}	1
G_{RS}	Sediment resuspension rate [m/h]	1.1×10^{-8}	1
G_{SB}	Sediment burial rate [m/h]	3.4×10^{-8}	1
G_{RU}	Vegetation water uptake velocity [m/h]	0.0008	5
G_{LS}	Leaching rate(soil to ground water)[m/h]	3.9×10^{-5}	1
G_{WW}	Water runoff rate from soil [m/h]	3.9×10^{-5}	1
G_{SW}	Soil runoff rate from soil [m/h]	2.3×10^{-8}	1
G_{ST}	Diffusion rate to stratosphere [m/h]	0.01	3
k_{LF}	Litter fall rate [1/s]	1.74×10^{-4}	5
k_{AW}	Air side MTC over water [-]	3	1
k_{WA}	Water side MTC [-]	0.03	1
k_{AS}	Air side MTC over soil [-]	1	1
k_{SA}	Soil side MTC [-]	0.02	3
k_{AV}	Air side MTC over vegetation [-]	10	3
k_{VA}	Vegetation side MTC [-]	0.000005	3
k_T	Sediment-water diffusion MTC [m/h]	4×10^{-4}	2
Q	Scavenging ratio [-]	200000	1
V_Q	Volume fraction of aerosols [-]	15×10^{-12}	1
V_P	Volume fraction of water particles [-]	2.08×10^{-7}	2

ers of TO21 Inc. and Seoul National University with their developed estimation method.

2. Z Values

The utilization of fugacity as an equilibrium criterion is not suitable for some metals, organometals and ionic compounds [2]. In an analysis of the fate of alkylbenzenesulfonates in rivers, more satisfactory results were obtained when the equilibrium criterion was based on the water phase rather than on the air phase [16]. Therefore, the Z value based on the water phase is first defined as 1 and then the Z value of the air phase is calculated as being almost zero. The calculating processes of these values are achieved by some mathematical transformations [2]. In the aquivalence approach model, the most influential and dominant property is the aquivalent capacity (Z), which is dimensionless. The magnitude of the Z value is dependent on the partitioning-coefficients and concentration ratios [1,3], and the Z values are linearly proportional to the D values related to the transport of the lead contaminants. Thus, the flows of contaminants between media become more active as the Z values become larger. The aquivalent capacities of five environmental media are introduced in Table 4. The Z value of air medium means that the lead contaminants cannot be transported from one compartment to another compartment by vaporizing. The value of Z_W is 1 because the concept of aquivalence is based on the aquatic phase.

3. D Values

The D-values mean the driving forces of the pollutant transfer and have a unit of volumetric flow, cubic meters per one second. Therefore the quantity of contaminants transferring between the multimedia becomes larger as the D values increase. The D-values are proportional to the aquivalent capacity and are composed of various parameters based on transport phenomena. Table 5 shows the parameters influencing the magnitude of D-values. In general, the larger magnitude of parameter forms the higher D value. For example, as the magnitude of the rain rate is large, the amount of lead contaminant moving into other media is also large with dissolving in the rain water. These values are dependent on the specific environmental conditions such as the characteristics of the media. In this model, most of the values were cited from published papers [2,3] and a reference book [1]. All of the D values used in this simulation are introduced in Table 6. As shown in the table, the D values are calculated from simple multiplications of the transport parameters.

4. Mass Balance Equations

Table 7 lists the five mass balance equations for steady state conditions. It was difficult to solve the mass balance equations for an unsteady state due to insufficient information about initial conditions. In other words, all of the initial contaminant concentrations in five media were not measured at the same initial moment. The solutions were obtained by solving the five simultaneous mass balance equations. The symbol A_i indicates the aquivalent concentrations for the 'ith' compartment, and has units of kilograms per cubic meter. The subscripts A, W, X, S and V are the air, water, sediment, soil and vegetation compartments, respectively. A_I is the concentration of the inlet water flows into the locations. The mathematical software 'MATHEMATICA' was used to solve these equations.

Table 6. Definitions of D-values

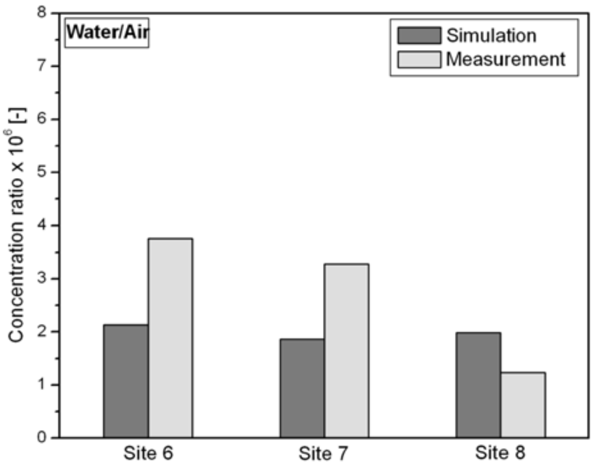
Process	D value [m^3/h]	Reference
Rain resolution	$D_{RD}=G_{Rain}Z_wAR_i$	1
Wet deposition	$D_{WD}=G_{Rain}Qv_QZ_QAR_i$	1
Dry deposition	$D_{DD}=G_{DD}v_QZ_QAR_i$	1
Water inflow	$D_I=G_IZ_W$	2
Water outflow	$D_O=G_I+AR_WG_{Rain}-AR_WG_V$	2
Water particle inflow	$D_{PI}=D_Iv_P$	2
Water particle outflow	$D_{PO}=D_Ov_P$	2
Sediment deposition	$D_{SD}=G_{SD}AR_XZ_P$	1
Sediment resuspension	$D_{RS}=G_{RS}AR_XZ_X$	1
Sediment burial	$D_{SB}=G_{SB}AR_XZ_X$	1
Diffusion (water↔sediment)	$D_{WS}=k_TAR_SZ_W$	2
Root uptake	$D_{RU}=G_{RU}AR_VZ_V$	5
Litter fall	$D_{LF}=k_{LF}V_VZ_V$	5
Leaching in soil	$D_{LS}=G_{LS}AR_SZ_W$	1
Mass transfer between six media	$D_{ii}=k_{ii}AR_iZ_i$	1, 2
Soil water runoff	$D_{WW}=G_{WW}AR_SZ_W$	1
Soil solids runoff	$D_{SW}=G_{SW}AR_SZ_S$	1
Wash out rate (imp.surface→soil)	$D_{WO}=G_{Rain}f_{WO}AR_OZ_W$	1
Diffusion to stratosphere	$D_{ST}=G_{ST}AR_AZ_A$	3
Emission rate to i compartment	E_i	2

RESULTS AND DISCUSSION

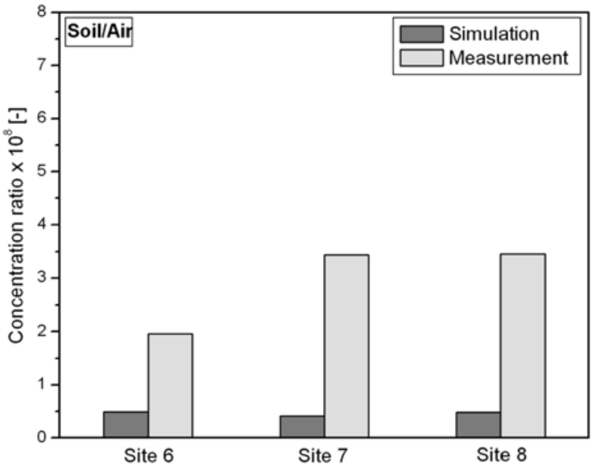
Fig. 3 presents a comparison of the results obtained by the experiment and modeling. The sites 6, 7 and 8 were selected as modeling sites due to more balanced area distributions of the five media than other sites. In other sites, the area of the vegetation compartment is too small, almost a zero percentage; thus, it was regarded as unsuitable for the five multimedia modeling. The inflow of lead contaminants into the urban multimedia system is considered to mostly originate from the air compartment. With well established waste disposal systems, the amount of emission flowing in the air compartment is dominant over the other media. Therefore, in Table

Table 7. Mass balance equations for each compartment in the steady state

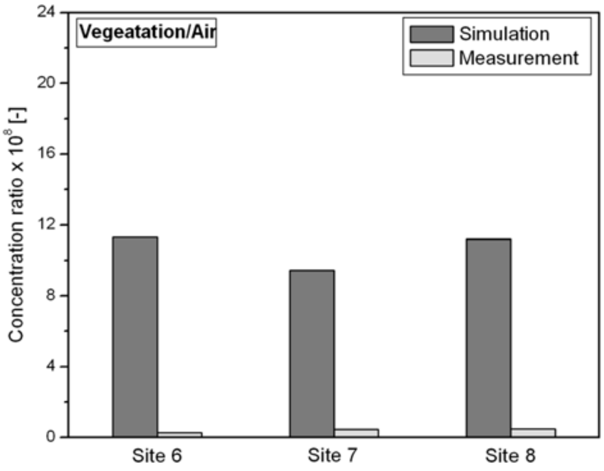
Media	Mass balance equation
Air	$A_A=(E_A)/[(D_{RD}+D_{WD}+D_{DD})_W+(D_{RD}+D_{WD}+D_{DD})_S+(D_{RD}+D_{WD}+D_{DD})_V+D_{AW}+D_{AS}+D_{AV}+D_{ST}]$
Water	$A_W=[E_W+A_I(D_{PI}+D_I)+A_A(D_{RD}+D_{WD}+D_{DD})_W+A_X(D_{RS}+D_{WS})+A_S(D_{WW}+D_{SW})+D_{AW}]/(D_O+D_{PO}+D_{SD}+D_{WS})$
Sediment	$A_X=(A_WD_{SD}+A_WD_{WS})/(D_{SB}+D_{RS}+D_{WS})$
Soil	$A_S=[E_S+A_V(D_{WV}+D_{LF})+A_A(D_{RD}+D_{WD}+D_{DD})_S+A_AD_{AS}]/(D_{WW}+D_{SW}+D_{RU}+D_{LS})$
Vegetation	$A_V=[E_V+A_SD_{RU}+A_A(D_{RD}+D_{WD}+D_{DD})_V+A_AD_{AV}]/(D_{WV}+D_{LF})$



(a) Water/Air concentration ratio

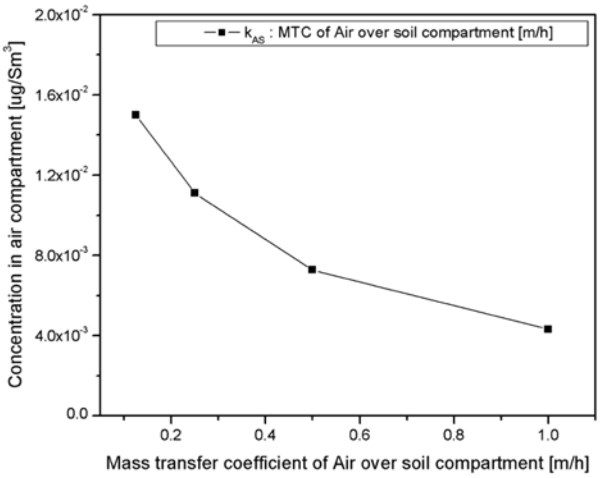


(b) Soil/Air concentration ratio

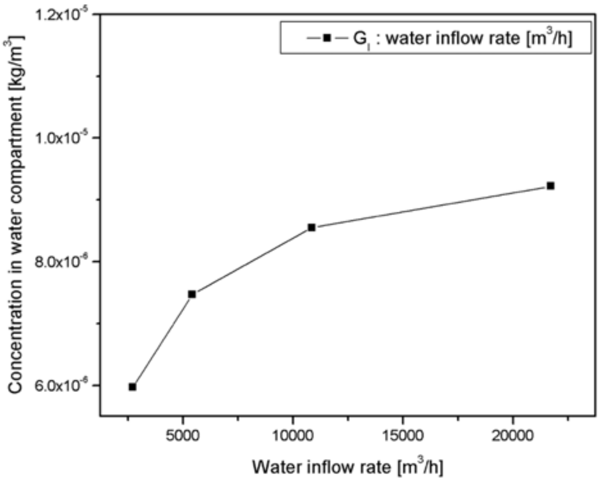


(c) Vegetation/Air concentration ratio

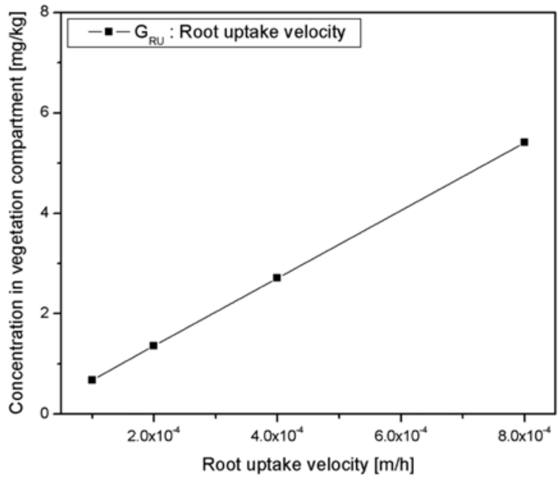
Fig. 3. Comparison between results of simulation and measurement based on the concentration of the air compartment.



(a) Concentration change of air compartment



(b) Concentration change of water compartment



(c) Concentration change of vegetation compartment

Fig. 4. Analysis of the parameter sensitivity.

7, the proportion of the sum of E_W, E_S and E_V in the total amount is less than 10%. The values for the sediment medium were excluded from the results of the analysis, because the experiments and measurements were not performed by the KTR. As shown in the figure, three kinds of graphs are used to verify the availability of the model application based on the concentration of the air compartment. Due to the use of general parameters in this simulation, a number of differences were observed in the comparison. Despite the utilization of these parameters, the results do not indicate a large variation of more than 10 times except in graph (c). The existing parameters from the references were experimentally obtained by researchers. Those parameters are dependent on the environmental surrounding conditions and they may have diverse values on other regions which have different geological characteristics. If the specific parameters in the region of the Jungrang stream were experimentally obtained, more satisfactory results would be expected. The results of the analysis of the parameter sensitivity are introduced in Fig. 4. As shown in graph (a), as the mass transfer coefficient of air over the soil compartment, k_{AS}, becomes larger, the concentration of the air compartment decreases, due to active mass transfer from the air medium to the soil medium. Graph (b) shows the increasing tendency of the concentration of the water medium as the water inflow grows, which means that the water flow takes the lead contaminants from the sediment compartment with powerful hydraulic motions. In graph (c), the concentration of the vegetation compartment varies linearly with the root uptake velocity, which is a very reasonable tendency.

CONCLUSION

It is necessary to analyze the distribution of contaminants in environmental systems to support the environmental policy making process. However, the establishment of mathematical models is difficult because environmental phenomena are very complex and random. The introduced parameters related to the transport of contaminants are key factors in this proposed model. Those parameters can quantitatively illustrate the complicated transfer phenomena of lead contaminants in the five urban compartments. Therefore, first of all, studies of more suitable parameters for specific regions are required to obtain more satisfactory results. In the field, it is very hard to find all of the parameters for every target site and, therefore, parameter tuning for the measured concentration data of contaminants can be another method of reversely finding the proper parameters by using the established model. This simulation was designed by considering the multimedia as a one box system. The application of the fundamental one box model to further advanced models such as the multi-box model composed of elementary boxes can be valuable to obtain a more systematic analysis of the fate of metal contaminants and be expected to produce more reliable and useful results for policy makers, researchers and students interested in environmental contamination.

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