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Evaluation of lead concentration by one-box type multimedia model in the Biwako-Yodogawa basin of Japan

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Abstract - A One box multimedia model for lead to assess the environmental risk was developed, and applied to Biwako-Yodogawa basin in Japan. The model includes four media of the atmosphere, the soil, the water body and the sediment. The amount of lead emissions from industrial activities was estimated with reference to PRTR report. The emission from leaded gasoline in the past was also estimated to consider the effect of historical accumulation of lead. The calculated concentration was compared with the measured data. The period of the calculation was 51 years from 1957 to 2007. It was found out that the model could predict lead concentration in the soil and the water body. The concentration in the atmosphere was underestimated. The reason was attributed to the underestimation of the amount of lead emission from incinerator.

***Keywords*:** Multimedia Model, One Box Model, Metal Compounds, lead

1. Introduction

Recently, various hazardous chemicals have been emitted to environmental media along with our industrial activities. The risk assessment to the human health and the ecosystem are requested to regulate the usage of hazardous chemicals. The multimedia model can explain the correlation between the emission amount and environmental concentration of hazardous chemicals. Mackay (1985) and Mackay and Paterson (1991) developed a multimedia model, level Ⅲ fugacity model and applied to organic chemicals. Kawashima (2007) also developed the multimedia model based on mass balance equilibrium in place of fugacity equilibrium. Compared with many reports of model application to an organic matter, there are few reports of model application to metal. As one of a few of the examples, Meent applied a multimedia model, level Ⅲ fugacity model to lead (1990).

The concentration level of lead, which is registered as one of the first target chemicals in the PRTR (Pollutant Release and Transfer Register) system, exceeds environmental standard in many places in Japan. The anxiety to the health risk by lead is high in the environment because the use was completely prohibited by voting on RoHS in Europe in 2003 (web-1).

Lead has been used from B.C. Since the melting point is low and processing is easy, it has been widely used for industries such as solder, types, and lead pipes. The storage battery for the car and the chemical are the main usages now. The influence on human health due to the hazardous property of lead had historically occurred. The hazardous property of lead to the human is anemia, the encephalopathy, arthritis, and the muscular depression, etc. In 1923, because a baby licked his mother's cosmetic that contained the white lead and died by the acute lead encephalopathy, the use of the powder including the white lead was prohibited in Japan in 1935 (Sakurai et al 1979).

In the 20th century, a large amount of lead particles were emitted into atmospheric from the exhaust gas of vehicles, since lead was added into the gasoline. This situation caused an accident called "Lead poisoning accident at Yanagimachi Ushigome". By this accident, the use of the leaded gasoline was restricted immediately. Now the encephalopathy and anemia by acute exposure of the high concentration becomes rare by improving the working environment. As the result, our concern has been shifted to the influence on the human health by chronic exposure of the low concentration.

In this study, One-box type multimedia model based on mass balance equivalent of lead was developed and applied to Biwako-Yodogawa basin to estimate the concentration of lead in the environmental media. The calculated concentrations were compared with the measured data, and the validity of the model was evaluated.

2. Calculated domain

Biwako-Yodogawa basin is located in the Kinki district of Japan (Fig.1). Biwako is the largest lake in Japan and the area is 630.77km^2. Biwako-Yodogawa basin contains a part of the second largest industrial areas and much harmful chemical materials are emitted.

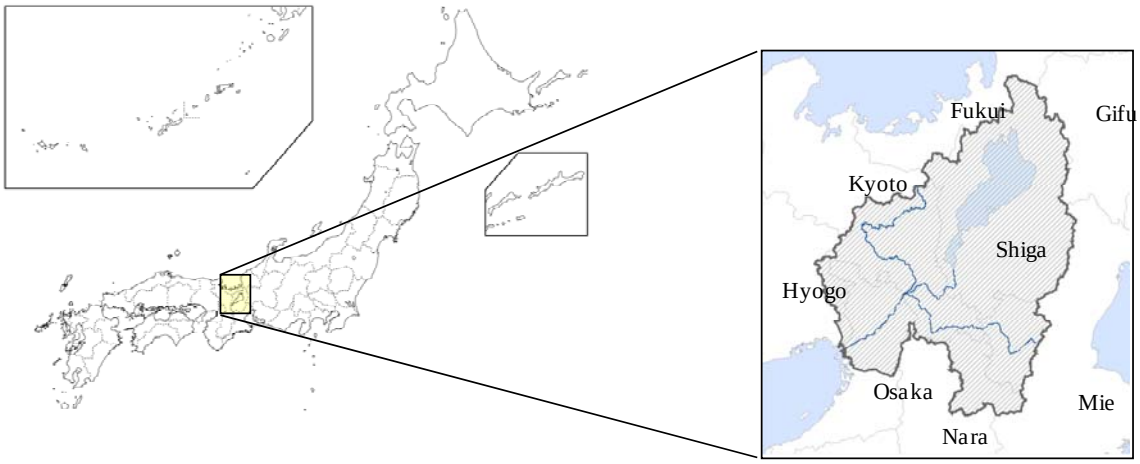

Fig.1 Biwako-Yodogawa basin

3. One-box type multimedia model

3.1. Model

One-box type multimedia model, which can calculate the concentration of lead, consists of the atmosphere, the soil, the water body and the sediment as shown in Fig.2. The following physical processes were considered in the model developed.

(1) The atmosphere consists of two layer; upper layer (higher then mixing height) and lower layer (lower then mixing height). The layer height varies during a day. The water body consists of liquid phase and suspended solid (SS). Lead exists as free ions in liquid phase, and both solid and exchangeable ions in SS. Also the soil and the sediment consist of liquid phase and solid phase. The lead's existence from is the same as in water body.

(2) The chemical transport by the advection in the atmosphere is considered.

(3) The emission amounts described in the section 4 are emitted to each media.

(4) The dry deposition and the wet deposition of the particulate lead in the atmosphere to the water body and the soil are considered. The sedimentation of SS to the sediment is considered.

(5) The inflow of the soil particle to the river accompanied by the inflow of rainwater is considered.

(6) The exchange equilibrium between liquid phase and exchangeable ion in the soil, water body, and the sediment is assumed.

(7) The transfer of free ions between the water body and the liquid phase in the sediment due to the molecular diffusion is considered.

Considering the above 7 physical processes, the mass balance equations for seven variables were constructed. Seven variable were ①gross mass of particle phase in the atmospheric, ②gross mass of particle phase in the soil, ③gross mass of liquid phase and of exchangeable cation in the soil, ④gross mass of particle phase in the water body, ⑤gross mass of liquid phase and of exchangeable cation in the water body, ⑥gross mass of particle phase in the sediment, ⑦gross mass of liquid phase and of exchangeable cation in the sediment.

The primitive equation of the mass balance was expressed by the equation (1). The primitive equation consists of the mass transfer flux by the equilibration between media, the emission flux, the advection flux, and the deposition/sedimentation flux.

$$\frac{dM_i}{dt} = \sum_{j=1}^{MN} f_{eq\_ij} + f_{emi\_i} + f_{fl\_i} + \sum_{j=1}^{MN} f_{dprs\_ij} \qquad (1)$$

i, j Media

MN Number of media

M_i Gross mass of lead in media *i* (mol)
f_{eq} Mass transfer flux by equilibration(mol/s)
f_{emi} Emission flux(mol/s)
f_{fl} Advection flux(mol/s)
f_{dprs} Deposition/sedimentation flux(mol/s)

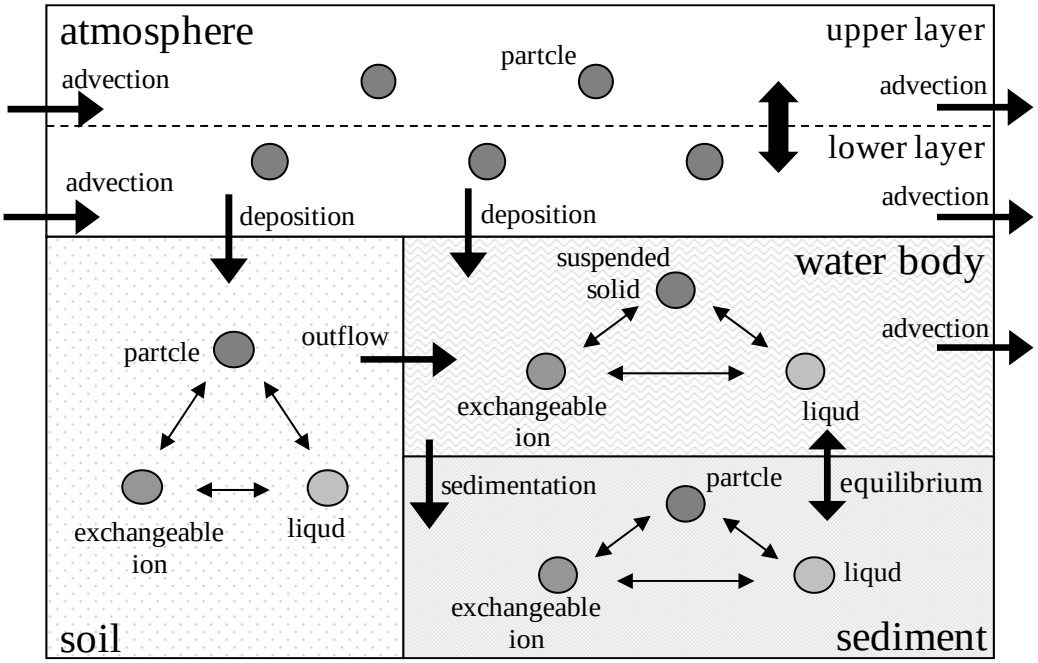

Fig.2 The concept of one-box type multimedia model

3.2. Change in ion concentration

3.3.1. Dissolution rate

In the soil, the water body, and the sediment, lead compound dissolves to liquid phase. The dissolution flux of one particle of lead compound with the diameter of δ can be expressed by

$$J = 2\pi\delta D(C_{water} - C_L) \tag{2}$$

δ Diameter of the particle ($=1.0\times10^{-5}$ [m])
D Molecule diffusion factor ($=1.0\times10^{-9}$[m^2/s])
C_{water} Saturating concentration of the lead compound to water [mol/m^3]
C_L Lead concentration in the liquid phase [mol/m^3]

The number of particles including in gross mass of *M* [mol] can be expressed by

$$N = \frac{6\times10^{-3}mM}{\delta^3\rho} \tag{3}$$

M Gross mass of lead in gross particle [mol]
m Molar weight [g/mol]
ρ Particle density [kg/m^3]

From Eq. (2) and Eq. (3) the dissolution rate of lead compound is induced.

$$K = JN = \frac{12\times10^{-3}mMD(C_{wtsat} - C_L)}{\delta^2\rho} \tag{4}$$

3.3.2. Exchange equilibrium

In the soil, the water body, and the sediment, a part of the lead ion in the liquid phase is adsorbed by the surface of the clay mineral by the exchange equilibrium. The representative of the ion that existed voluminously in the environment was made calcium ion (Ca^{2+}). Assuming the ratio of calcium

ion concentration in liquid phase, $Ca_{,L}$[mol/kg], and abundance in particle, $Ca_{,s}$[mol/kg], is constant, The amount of adsorption of lead ion to calcium ion C_S [mol/kg] is evaluated.

$$C_S = S_{Pb,Ca} C_L \frac{Ca_{,s}}{Ca_{,L}} \tag{5}$$

$S_{Pb,Ca}$ selectivilty to calcium to lead (=2.5 (Bittel and Miller 1974))

4. Estimation of lead emissions

The current main emission of lead in Biwako-Yodogawa basin from industrial activities such as incinerator, landfill, coal-fired power plant and paint (Nakanishi et al 2006), was estimated from PRTR report. In addition, the emission in the atmosphere from leaded gasoline was estimated from 1957 to 1974. After 1975, leaded gasoline was shifted to unleaded gasoline.

4.1. Industrial activities in PRTR report

PRTR is "Chemical release distance written report system". In PRTR report, the emission amounts emitted in the environment and transported to another place by industrial activities were reported for various materials with the hazardous property. The PRTR report has two types of data, the registered emission amounts and the unregistered emission amounts (Web-2).

The registered emission amounts are the amount from point sources. The address of the each point source can be easily converted into the latitude-longitude coordinates on GIS (Geographic Information System) by using CSV address match service (Web-3). The locations lead sources in Biwako-Yodogawa basin are shown in Fig.3. The emission amounts of various industrial activities are shown in Table1.

The unregistered emission amounts, which are divided into the emission amounts to the atmosphere, landfill, and the soil and water body, are totalled by the prefecture level. The emission amounts to landfill and soil are assumed to be negligible. The emission amounts in Biwako-Yodogawa basin were estimated by the population ratio of inside and outside of the basin. The unregistered emission amounts to the atmosphere and to the soil are summarized in Table 2.

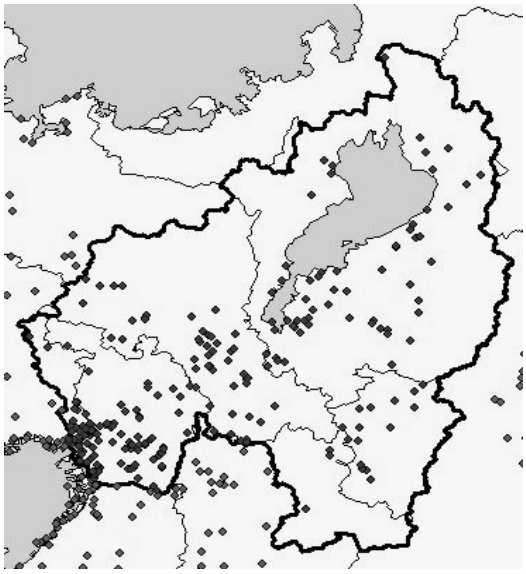

Fig.3. The locations emitted lead in Biwako-Yodogawa basin

4.2. Incinerator

Most lead particles emitted from incinerator are trapped as burned ash and finally buried. However, a part of lead particle is emitted to the atmosphere though the stack. It may not be figured out by PRTR report. Therefore the emissions from incinerator were estimated here. The emissions to atmosphere from incinerator from 1976 to 2005 were calculated from the installation rate of bag filter and electric-static precipitator and their collection efficiency. Since there was not enough data about the installation of dust collectors, the emission from 1957 to 1975 was assumed to be the same

emissions in 1976. The annual variation of emissions from incinerator is shown in Fig.4. The reason of the rapid decrease in the 1990's was the exchange of the most electric-static precipitators to bag filter. The collection efficiency of electric dust collector, bag filter and multi-cyclone is 99.5%, 99.9%, 80%, respectively (Kida et al 2003). The dust collector shifted from the electric dust collector and multi-cyclone to bag filter.

Table1. Emissions of lead from various industrial activities

Industrial activity	Emission of lead to each media (kg/year)			
	Atomos.	Water	Soil	Sewer
Pulp, paper, and fabricating paper	0.0	0.0	0.0	0.0
Publication, print, and related this industry	0.0	0.0	0.0	0.0
Chemical	13.0	4.2	0.0	0.0
Petroleum or coal product	0.0	0.0	0.0	0.0
Plastic product	0.0	0.0	0.0	0.0
Ceramic industry	48.0	0.5	0.0	16.0
Iron and steel industry	18.0	0.0	0.0	0.0
Nonferrous metal	111.0	2.2	0.0	2.0
Metallic product manufacturing	101.0	0.0	0.0	7.0
General machine apparatus	0.0	0.0	0.0	0.0
Electromechanical apparatus	108.0	12.0	0.0	21.0
Electron device	0.0	0.0	0.0	0.0
Transportation machine apparatus	0.0	0.0	0.0	0.0
Ship and related this industry	0.0	0.0	0.0	0.0
Precision machinery and appliances	0.0	0.0	0.0	0.0
Other manufacture	0.0	0.0	0.0	0.0
Sewage line	0.0	1995.0	0.0	0.0
Domestic waste site	0.0	2.3	0.0	0.0
Industrial waste site	0.0	0.1	0.0	0.0
Total	399.0	2016.3	0.0	46.0

Table2. The unregistered emission amounts in Biwa Lake and Yodo river basin

Emissions of lead to each media (kg/year)			
Atmos.	Water	Soil	Sewer
930.0	3.0	0.0	0.0

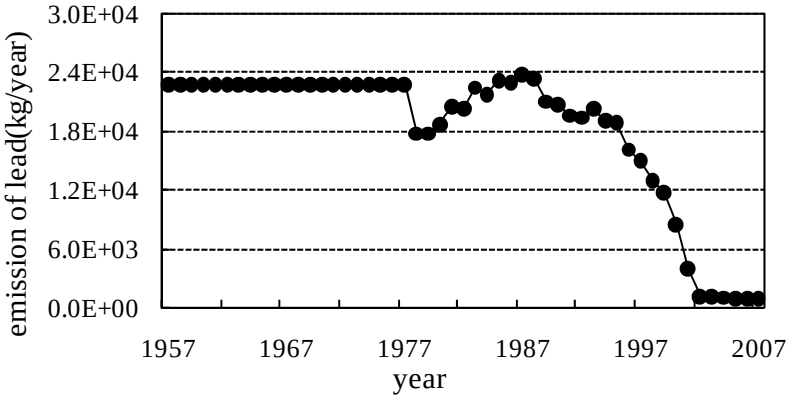

Fig.4. The annual variation of emissions from incinerator

4.3. Other emission sources

We estimated the emission from the follow three sources as other sources, elution from landfills, from the coal-fired power plant, and paints. The result of the estimation is shown in Table3.

Table3. Emission from other sources

emission source	emission of lead to each media (kg/year)			
	atmos.	water(SS)	water(ion)	soil
landfill	0	0	24	0
coal-fired power plant	60	20	0	0
paint	0	4000	0	4000

4.4. Leaded gasoline

Lead particles contained in leaded gasoline were enormously emitted to the atmosphere until 1974 when the use of leaded gasoline was prohibited. All lead added in gasoline was assumed to be emitted to the atmosphere by the combustion. Emissions were estimated from the content rate of lead to gasoline (Kondo 2007) and gasoline consumption (Web-4). The annual variation of emissions from leaded gasoline is shown in Fig.5.

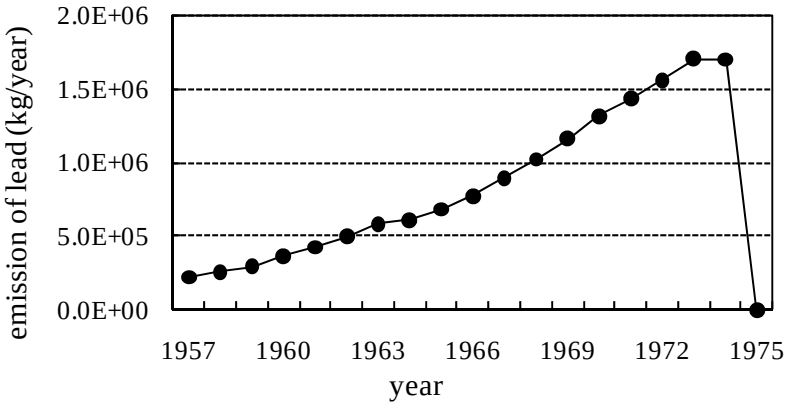

Fig.5. The annual variation of emissions from leaded gasoline

5. Results

The concentration of lead in each media in Biwako-Yodogawa basin was calculated by using the one-box type multimedia model. The calculated concentration was compared with the measured data. The comparison for the atmosphere, the soil, the water body, and the sediment is shown in Fig.4. The calculated concentration in the atmosphere was obviously lower than the measured data. On the other hand, the calculated concentration in the sediment, the soil, and the water body was generally agreed with the measured data.

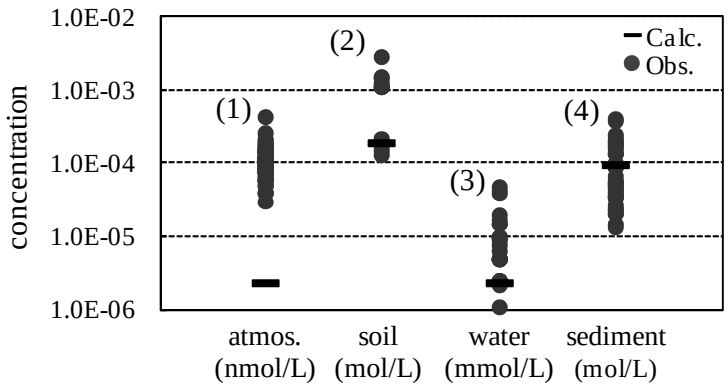

Fig.6. Comparison between the calculated concentration and the measured data
(1) Web-5 (2) Nakanishi et al 2006 (3) Web-6 (4) Web-7

Moreover, the annual variation of the concentration of lead in each media is shown in Fig.7. The concentration in the atmosphere showed a rapid reduction twice until now. The first decrease in 1975 was due to the prohibition of leaded gasoline. The second decrease in 1990's was due to the strengthening of the effluent control. The concentration in the water body had increased until 1975, but rapidly decreased once in 1975 due to the sudden decrease of the deposition from the atmosphere. The concentration in the sediment and in the soil has been kept slight increasing tendency. The calculated concentration in the atmosphere was compared with the measured data in 1975 (Nakanishi et al 2006) across the country as shown in Fig.8. This result suggested that the estimated emissions from leaded gasoline were reasonable.

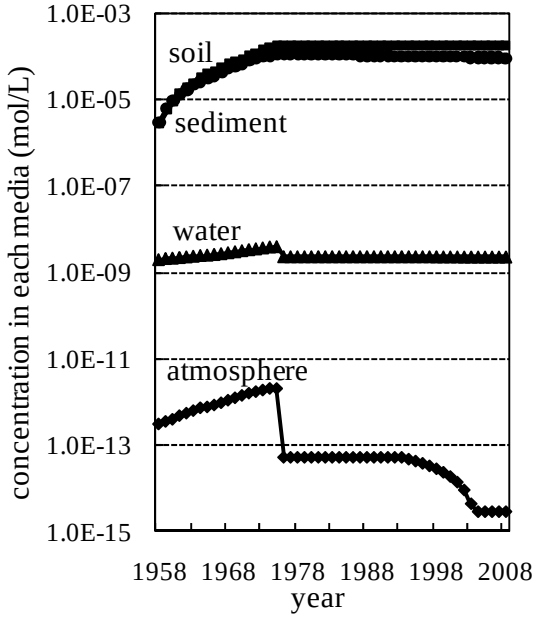

Fig.7. Annual variation of lead concentration

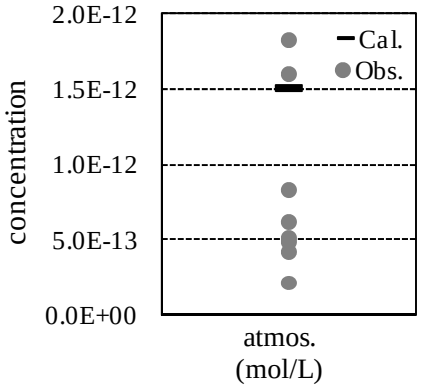

Fig.8. Concentration in the atmosphere in1975

It was guessed that the cause that the calculated concentration was lower than the measured data was the shortage of the emission to the atmosphere. Then the emission from incinerator (see section 4.4) was re-estimated. The collection efficiency of filter was assumed to be 99.9%. Assuming that the collection efficiency decreased year by year, the collection efficiency of filter was set to 98%. Fig.9. shows the calculated concentration. The concentration in the atmosphere rose about 10 times and was very close to the measured data.

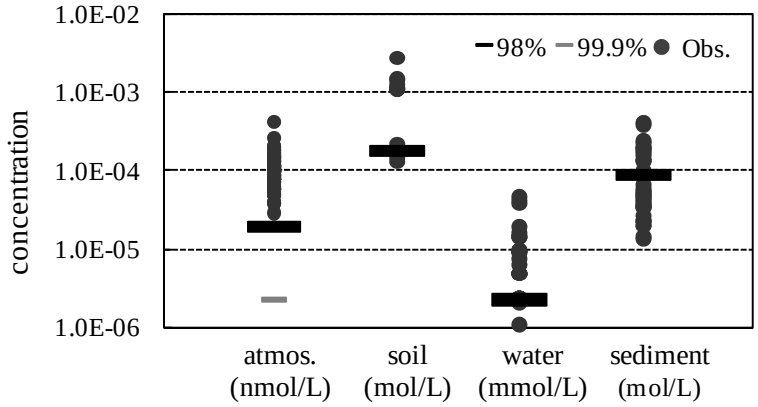

Fig.9. Comparison between the calculated concentration and the measured data with the collection efficiency of 98%

6. Conclusions

It is necessary to predict the concentration of the hazardous chemicals emitted by the industrial activities. In this study, one-box type multimedia model was developed for lead which was concerned to the human health. In the model, the real environment was divided into four media of the atmosphere, the soil, the water body, and the sediment. The validity of model was evaluated by applying the model to Biwako-Yodogawa basin and by comparing with the measured data. The amount of lead emissions was estimated from PRTR report, incinerator, landfill, coal-fired power plant, paint and leaded gasoline until 1974. The period of the calculation was 50 years from 1958 to 2008. The calculated concentration in the soil, the water body, and the sediment was generally agreed with the measured data.

References

Committee on Biologic Effects of Atmospheric Pollutants, National Research Council (1979), Lead in the atmosphere, Tokyodojin (in Japanese)

Kawashima M., Tobe T., Kaga A., Kondo A., Inoue Y., Tatsuwaki K. (2007), Screening level environmental risk evaluation of PRTR chemicals in Lake Biwa and the Yodogawa Basin Aria, Journal of Society of Environmental Science, 20, 119-132

Kida A., Sakai S., Shibakawa S., Matsumoto A. (2003), Heavy Metals Emission from Municipal Solid Waste Incineration System Retrofitted for Dioxins Control, Journal of Environmental Chemistry, 13, 51-67

Kondo A., Hamonangan E., Soda S., Kaga A., Inoue Y., Eguchi M., Yasaka Y., Impact of Conversion from Leaded to Unleaded Gasoline to Ambient Lead Concentration in Jakarta Metropolitan Area, Journal of Environmental Sciences, 19, 5, 694-698

Meent Dik van de (1990), Modelling intercompartment transfer of pollutants: the case of lead, The Science of Total Environment, 90, 41-54

Mackay D., Paterson S. (1991), Evaluating the Multimedia Fate of Organic Chemicals: A Level Ⅲ Fugacity Model, Environ. Sci. Technol., 25, 3, 427-436

Mackay D., Paterson S., Cheung B., Neely W.B. (1985), Evaluating the environmental behaviour of chemicals with a level Ⅲ fugacity model, Chemosphere, 14, 335-374

Nakanishi J., Kobayashi N., Naito W. (2006), Detailed risk evaluation series 9 lead

Web Sites:

Web-1: http://ec.europa.eu/environment/waste/rohs_eee/index_en.htm consulted 23 Mar. 2011.

Web-2: http://www.env.go.jp/chemi/prtr/risk0.html consulted 15 Mar. 2011

Web-3: http://newspat.csis.u-tokyo.ac.jp/geocode/ consulted 12 Mar. 2011

Web-4: http://shouwashi.com/transition-gasoline.html consulted 20 Mar. 2011

Web-5: http://www.epcc.pref.osaka.jp/center_etc/spm/h17/pdf/3_1.pdf consulted 20 Mar. 2011

Web-6: http://www.epcc.pref.osaka.jp/center_etc/water/dokuji/H19/H19_yodo.xls consulted 20 Mar. 2011

Web-7: http://www.epcc.pref.osaka.jp/center_etc/water/dokuji/H19/H19_sediment_river.xls consulted 20 Mar. 2011