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Development of One-Box Type and Distributed Type Multimedia Model for Heavy Metals

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Abstract **-** In this paper, one box multimedia model and distributed multimedia model based on mass balance equilibrium were developed. Both models consist of four environmental media; atmosphere, water, soil, and sediment. The nine chemical and physical phenomena considered in each media are emission, degradation, advection, sedimentation, re-suspension, dry/wet deposition, atmospheric mixing, and particle-ion exchange. Metal species is assumed to be in perfect mixing within the same environmental media and at non-equilibrium state between the different environmental medium. Lead and mercury were applied for one box multimedia model during 1957-2007 and 1959-2009, respectively and mercury was applied for distributed multimedia model. The calculated concentrations of four media were compared with the observed data. Though emissions of lead and mercury after 2001 are relatively accurate because of the use of PRTR, they until 2000 are inaccurate because of the limitation of the available data. Considering these uncertainty, the calculated concentrations well captured the observed data. The uncertainty analysis of lead concentrations was performed by Monte Carlo simulation. It was found that the parameter of sediment depth strongly affected concentrations.

Keywords**:** one box multimedia model, distributed multimedia model, uncertainty analysis, lead, mercury

1. Introduction

Lead (Pb) has been used from very early ages due to its physical properties of low melting point and easy processbility. It has been widely used for industries such as soldering and lead pipes. According to the International Lead and Zinc Study Group report, 80% of current lead consumption is contributed by lead-acid batteries used in vehicles, hospital emergency systems and in computers ect. Lead poisoning due to its hazardous properties has historically been reported such as the cases of anemia, the encephalopathy, arthritis, and the muscular depression, etc. There is a reported incident in Japan, a death of a baby due to acute lead encephalopathy in 1923. It was reported the poisoning occurred through the baby licking his mother's cosmetics which contained white lead and this incident led to the prohibition of use of the powders that contained white lead in 1935 (Lead: airborne lead in perspective, National Academy of Sciences, 1980). The health risk by lead is in the environment was highly concerned and the use was completely prohibited by Restriction of the Use of certain Hazardous Substances in Electrical and Electronic Equipment (RoHS) in Europe in 2003. In the 20th century, a large amount of lead particles were emitted into the atmosphere through the exhaust gases from vehicles due to the addition of lead into the gasoline. "Lead poisoning at Yamaguchi Ushigome" is a well-known incident in Japan due to this addition of lead into gasoline and after the incident, use of leaded gasoline was restricted immediately.

Mercury (Hg) possesses a well-known history in Japan because of the damages it caused to the environment and to the human health. A disease caused by methylmercury poisoning was discovered in southwestern region of the Kyushu Island, Japan in 1956 which was later named as the Minamata disease (Harada, 1995). This incident even led to a global treaty to prevent consumption of Hg called the Minamata Convention, which at the moment signed by 96 countries all over the globe (Web-1). Mercury possesses other adverse health effects such as carcinogenicity, child developmental defects, toxic effects on nervous, and on digestive and immune systems (Web-2). Releasing of Hg to the environment through

various industrial consumptions is the major pathway of Hg to enter into our environment. Industries have been using Hg as catalysts, in fertilizers, pharmaceuticals (inorganic chemicals), machinery, batteries, medical supplies (amalgam), explosives (gun powder), and paints for a long time (Web-3 and Takahashi et al., 2008). Consumption and release of Hg has been legally controlled in Japan since 1973 (Web-4), but still, many industries consume Hg in their production processes; thus, Hg appears in the environmental analysis data (Sakata and Marumoto, 2005).

Regulating the consumption of these metallic pollutants is requested as a result of risk assessments carried out on human health and on ecosystems. Environmental monitoring processes are performed in order to gather information on environmental occurrences of metallic pollutants but when considered a larger geographical region, this is practically a difficult task. Technological requirements, skilled labor, and finance are some of the hindering factors for this impracticality in environmental monitoring process. Long range environmental transport of metallic pollutants is another factor which complicates the environmental occurrence of metallic pollutants. Therefore, considering the practical difficulty in monitoring the whole land mass for metallic pollutants occurrences and the effects of metallic pollutants, necessity of a system that can computationally evaluate the concentration trends and spatial distribution of metallic pollutants was identified. The multimedia model can interpret the correlation between the emission and environmental concentration of hazardous chemicals. Level Ⅲ multimedia model which based on fugacity was developed and applied to organic chemicals by Mackay et al., (1985) and Mackay and Paterson (1991). A multimedia model based on mass balance equilibrium replacing the fugacity equilibrium, was developed by Kawashima et al. (2007). In another case a multimedia model, level Ⅲ fugacity model was used to evaluate lead transfers by Meent (1990). Kondo et al., (2013, 2014) evaluated lead and Hg concentrations on Lake Biwa-Yodo River basin in Japan by using One-Box multimedia Model (OBMM) which can combine all environmental media of the atmosphere, the water, the soil, and the sediment. However compared with many reported model applications to study the

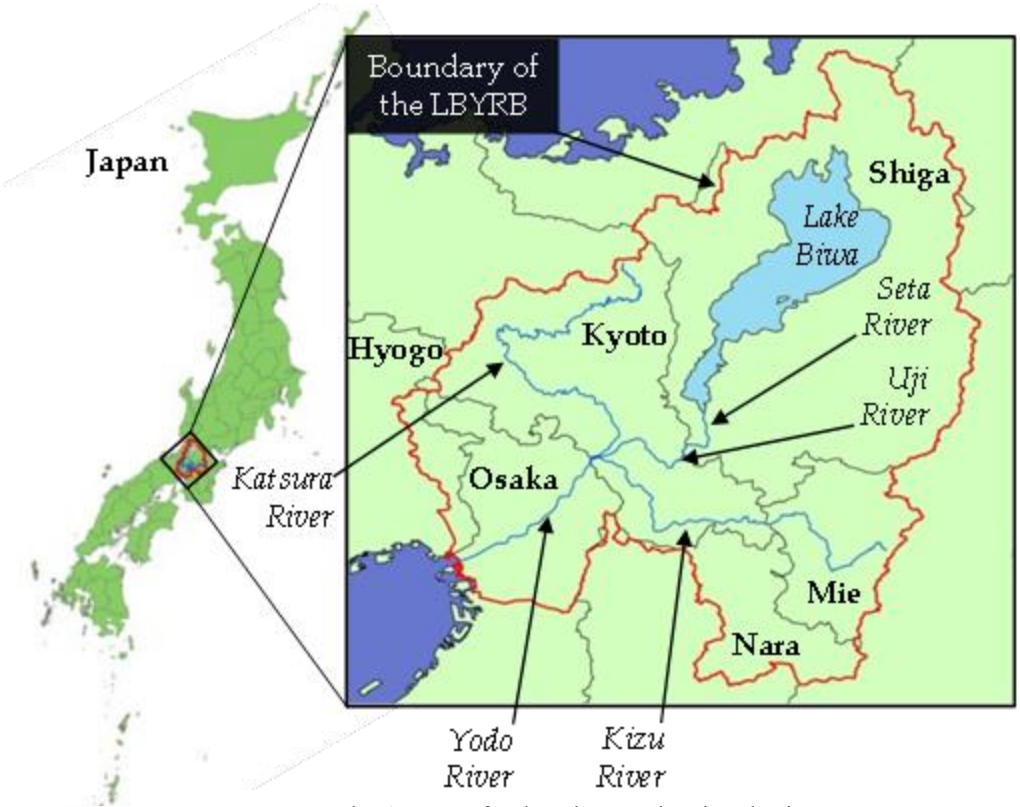

Fig. 1 Map of Lake Biwa-Yodo River basin

environmental risk by the organic compounds, there is few reported model application on metallic compounds or on metals.

In this paper, I introduced the temporal changes of lead and Hg concentrations by using OBMM on Lake Biwa-Yodo River basin and the spatial distribution of Hg concentrations on Lake Biwa-Yodo River basin by using Distributed Multimedia Model (DMM) which can evaluate concentrations on small grid. Moreover I introduced the uncertain analysis of the temporal changes of lead concentrations by using OBMM by Monte-Carlo simulation.

2. Study site and model descriptions

2. 1. Lake Biwa-Yodo River basin

Lake Biwa-Yodo River basin of Japan was selected as the study site because of its importance as a geographical area with multiple land use patterns namely as residential, industrial, and agricultural. Lake Biwa and its river system serves as the drinking water supply for a population of nearly 13 million people living in the Kinki region which is composed of six prefectures: Hyogo, Kyoto, Mie, Nara, Osaka, and

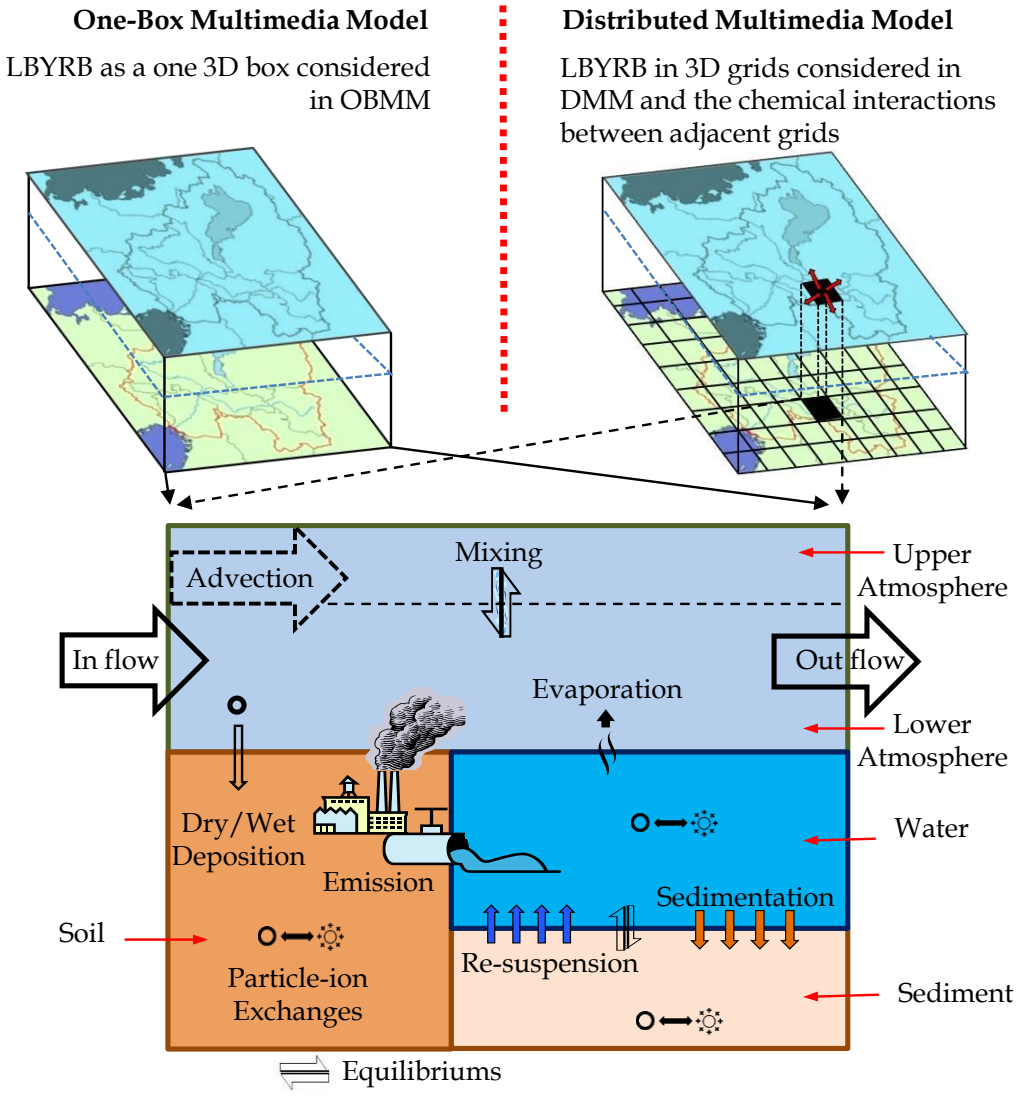

Fig. 2 Diagrammatic explanation of the environmental media, grid configuration, and the chemical transport mechanisms considered in the OBMM and DMM.

Shiga. This study area lies between the latitudes 34.65~35.69 ºN and the longitudes 136.15~136.51 ºE, while Lake Biwa, the largest natural water body in Japan, is located in the middle of this study area, covering 630.77 km2. The Seta River starts from the southern tip of Lake Biwa, turns into the Uji River, and then joins with the Kizu River and Katsura River to become the Yodo River, which flows to Osaka Bay as shown in the Fig. 1 (Sudo et al., 2002).

2. 2. Model description

In OBNN, the study site is composed of four environmental media, which are the atmosphere, water, soil, and sediments. It is considered to be a three-dimensional, closed entity in this model. The nine chemical and physical phenomena considered in the model calculations are emission, degradation, advection, sedimentation, re-suspension, dry/wet deposition, atmospheric mixing, and particle-ion exchange, which are diagrammed in Fig. 2. Metal species of gaseous metal in atmosphere, dissolved metal and ionic metal in water, soil and sediments were considered under these chemical phenomena. These calculations were performed based on the conditions; that metal species is in perfect mixing within the same environmental media, is at non-equilibrium state between the different environmental medium. The mass conservation equation of OBMM is given by

$$\frac{dM_i}{dt} = \sum_{j=1}^{MN} f_{eq\_i,j} + f_{emi\_i} + f_{ad\_i} + \sum_{j=1}^{MN} f_{dprs\_i,j} + \sum_{j=1}^{MN} f_{deg\_i,j} \quad (1)$$

where i, j is the environmental medium; MN is the number of media; M_i is the gross mass of metal in medium i (mol); $f_{eq\_i,j}$ is the mass-transfer flux of metal at equilibrium (mol s^{-1}); f_{emi_i} is the emission flux of metal (mol s^{-1}); f_{ad_i} is the advection flux of metal (mol s^{-1}); $f_{dprs\_i,j}$ is the deposition flux of metal (mol s^{-1}); and $f_{deg\_i,j}$ is the degradation flux of metal (mol s^{-1}). Utilization of an OBMM was previously published, and more details about the model can be found in Kondo, 2013 (Kondo et al., 2013).

In DMN, the study site was divided into a grid size of 1 km x 1 km as shown in the Fig. 2. Similar chemical and physical mechanisms described in the OBMM were considered to occur in each of these grids. Wind velocity data and river discharge data in each grid were given from the simulations (Shimadera et al., 2009 and Shrestha, 2010) by Weather Research Forecasting Model (WRF) and Hydrological Model on Lake Biwa-Yodo River basin, respectively. As the simulation period by WRF and Hydrological Model was one year, these data were repeatedly used during the periods of DMN calculations. The observed atmospheric concentrations of metals were set at the inflow lateral boundary condition.

3. Emission

3. 1. Lead emission

The main emission of lead into Lake Biwa-Yodo River basin is calculated based on five sources; (1) Registered emission in PRTR (Chemical Release and Transport Registry) (large industries and large sewage lines), (2) Unregistered emission in PRTR (small industries, small sewage lines and paint), (3) Leaded gasoline, (4) Incinerator, (5) Paint. Lead emission was estimated from these five sources from 1957 to 2007. Emissions in PRTR, which started recording the emissions in 2001, were divided into the emissions to the atmosphere and to the water. Lead particles contained in leaded gasoline were enormously emitted to the atmosphere. In Japan the regular leaded gasoline was changed into unleaded in 1975 and the high octane gasoline was changed into unleaded in 1983. After 1987, all gasoline consumption became unleaded in Japan. All lead added in the gasoline was assumed to be emitted to the atmosphere by the combustion. Most lead particles emitted from incinerators are trapped as burned ash and finally buried. The emissions from incinerator to

atmosphere from the year 1976 to 2005 were calculated based on the installation rate of bag filters and electric-static precipitators to the incinerators and their collection efficiency. Since there was not enough data about the installation of dust collectors, the emission from 1957 to 1975, it was assumed to be the same emissions as in 1976. Paint used in construction, for structures (ex. bridge), and for road makings is the one of the major pathways of lead been released into the environment. The annual variation of emission from paint from 1957 to 2007 was evaluated. Total emissions to the atmosphere, the water, and the soil from 1957 to 2007 are shown in Fig. 3.

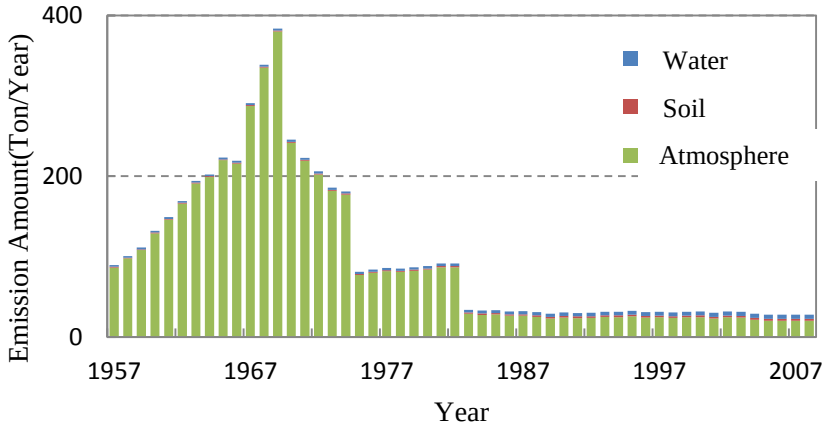

Fig. 3. Total lead emissions to the atmosphere, soil, and water from 1957 to 2007.

3. 2. Mercury emission

Annual emissions of Hg from 1959 to 2009 were calculated for the Lake Biwa-Yodo River basin based on the records of Hg consumption and data from PRTR. These emission amounts calculations were carried out in three time periods depending on the data availability. From 1959 to 1990, the annual emissions of Hg were calculated based on the reported Hg consumptions for industries, catalysts, fertilizers, pharmaceuticals (inorganic chemicals), machinery, batteries, medical supplies (amalgam), explosives (gun powder), and paints (Takahashi et al., 2008). Emissions of Hg were controlled since 1973 and from 1990 to 2000 there was no record of Hg emissions. From 2001 to 2009 the Hg emissions recorded in the registered PRTR category were considered to be none. However, in unregistered PRTR emissions category were recorded from 2001 to 2009 (Web-5). Thus the average of Hg emissions from 2001 to 2009 was used to represent the Hg emission from 1991 to 2000. Total emissions to the atmosphere, the water, and the soil from 1959 to 2009 are shown in Fig. 4.

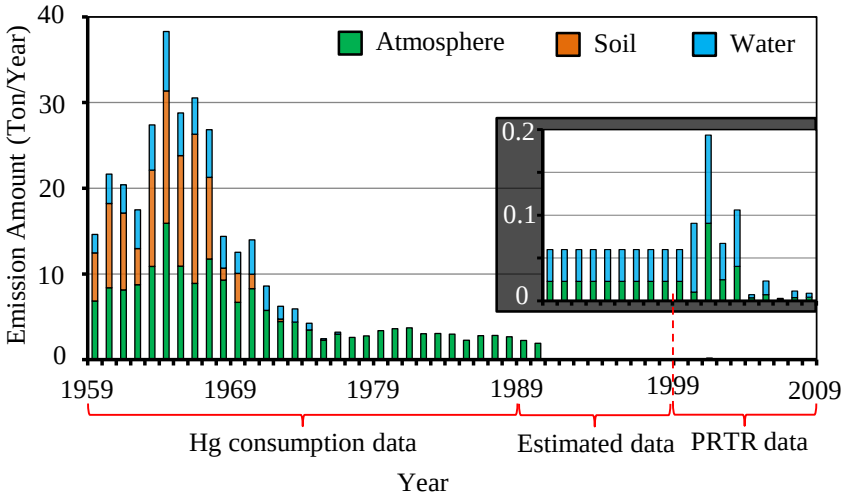

Fig. 4. Total Hg emissions to the atmosphere, soil, and water from 1959 to 2009.

4. Results and Discussions

4. 1. Lead concentration by OBMM

The concentration of lead in each media in Lake Biwa-Yodo River basin was calculated by using the one-box type multimedia model. The calculated concentration was compared with the measured data published by the Osaka prefecture government research institute of environment, agriculture and fisheries and in the detailed risk evaluation series 9 lead (Nakanishi et al., 2006). The comparison of calculated data and measured data in 2006 for the atmosphere, the soil, the water body, and the sediment is shown in Fig. 5(a). The calculated concentrations in all medium were comparatively lower than the measured data.

Moreover, the annual variation of the concentration of lead in each media from 1958 to 2008 is shown in Fig. 5(b). The concentration in the atmosphere showed two rapid reductions 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 sedimentation showed the increase until 1980 and kept the constant after that.

4. 2. Uncertainty analysis of lead concentration

The one-box type multimedia model has many uncertainty parameters. The parameters which has strong influence on concentration were selected by

$$S = \left| \frac{y_{1..1} - y_{0.9}}{0.2 y_{1.0}} \right| \tag{2}$$

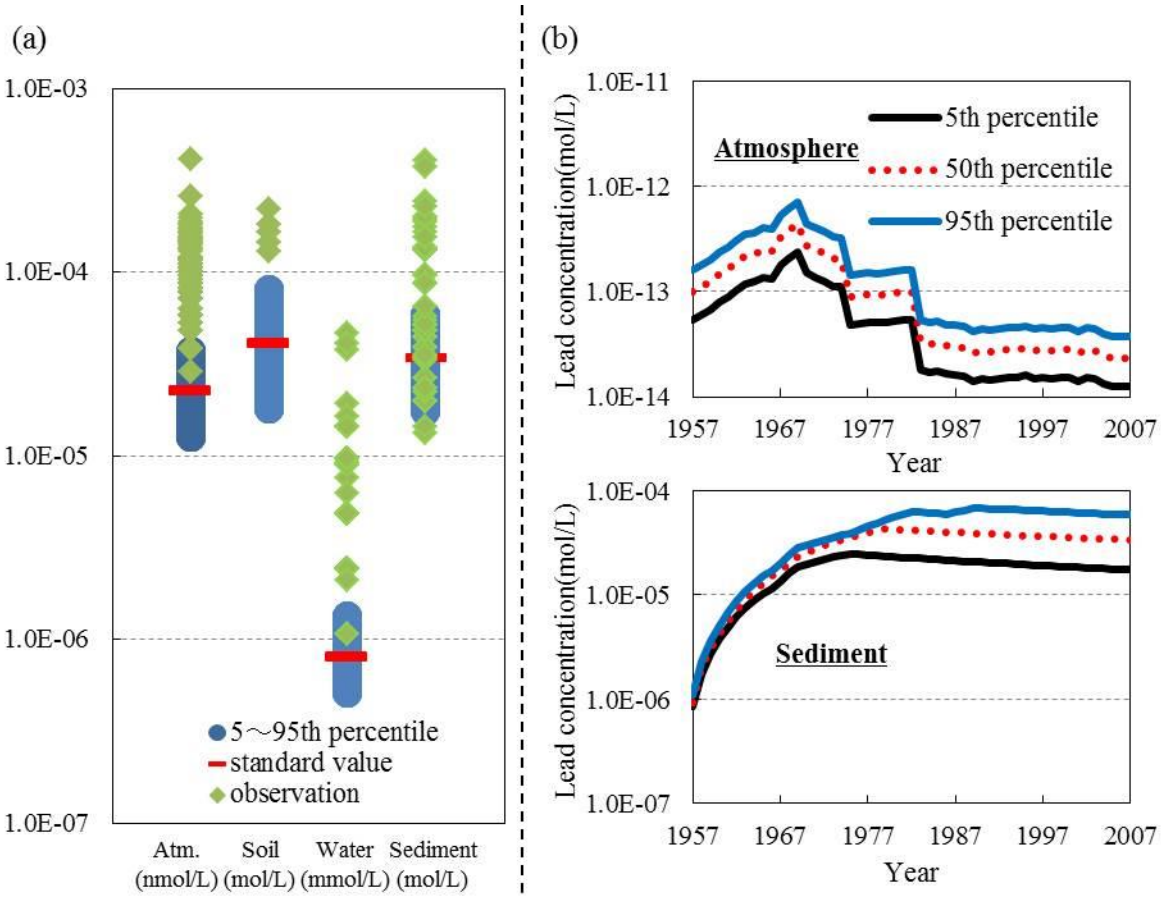

Fig. 5(a) Validation of the calculated lead concentration by observed environmental lead in 2007 and uncertainty analysis output, (b) Calculated lead concentrations by OBMM simulations from 1957 to 2007 in the atmosphere and sediments, and uncertainty analysis output.

where $y_{1.0}$ is concentration by using the standard parameter value, $y_{1.1}$ is concentration by using 1.1 times of the standard parameter value, and $y_{0.9.}$ is concentration by using 0.9 times of the standard parameter value (Cao et al., 2004). Six parameters; soil depth (0.05cm), emission to atmosphere (20.3 t/year), sediment depth (10cm), terminal velocity of SS (7.3μm/s), scavenging rate of rain (1.28×10^{-3}), emission to water (5.2 t/year) were selected from 31 parameters. Assuming the normal distribution with the standard deviation value of 0.2 times of the standard value, the uncertainty analysis was performed by Monte Carlo simulation. The Monte Carlo simulation was repeated 1000 times. Fig. 5 showed the temporal concentration of both 5% tile and 95% tile. The influence on concentration in atmosphere was the constant for each year. On the other hand, the influence on concentration in sediment became strong year by year.

4. 3. Mercury concentration by OBMM

Calculated Hg concentrations in all four environmental media (atmosphere, water, soil, and sediments) by OBMM simulations for 45-year span are shown in the Fig. 6 (a) in log 10 scale and the validation of the calculated Hg concentrations by using observed environmental Hg concentrations are shown in Fig. 6 (b). These calculated results were validated by comparing them with the observed environmental Hg concentrations reported for all environmental media in Osaka Prefecture for 2005 as shown in the Fig. 6 (b) (Web-6 and Web-7). Calculated Hg concentrations fall within the range of the observed Hg concentrations, validating the reliability of the calculated results. According to the temporal concentration trends shown in Fig. 6 (a), accumulation of Hg in the soil and sediments could be observed until the 1970s; after that time, the concentrations became constant due to the controlled Hg emissions. In the last three decades of the study, Hg concentrations in water decreased and have become stable compared to the first 15 years. This decrease is due to the adsorption of a certain portion of Hg into the sediments and transportation of them to the ocean. It was observed that with controlled Hg emissions, the concentrations of Hg in the water became constant. The atmospheric Hg concentration showed relatively small variations during the time span of this study.

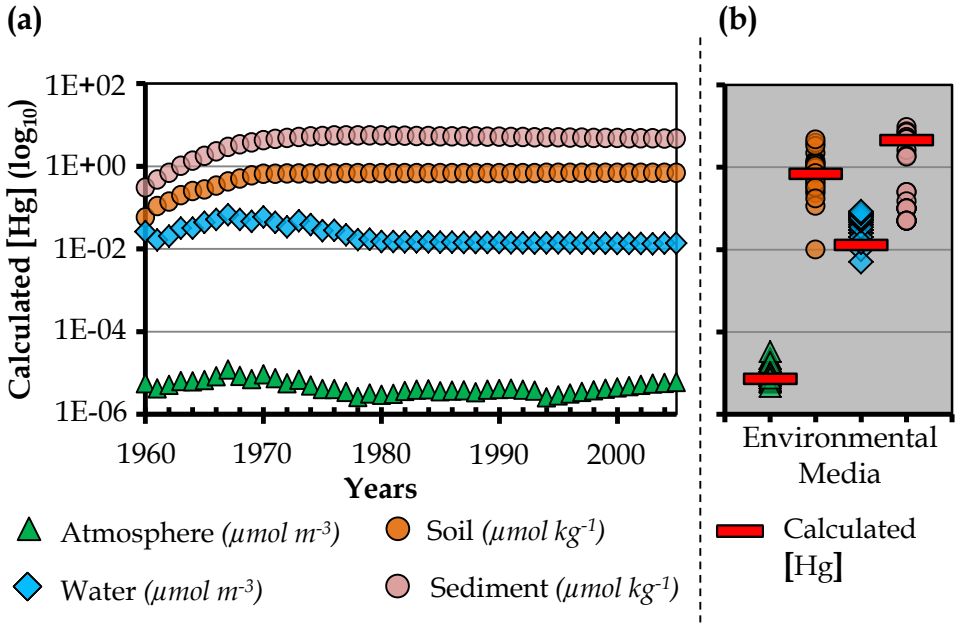

Fig. 6(a) Calculated Hg concentrations by OBMM simulations from 1960 to 2005 in the atmosphere, water, soil, and sediments, (b) Validation of the calculated Hg concentration by observed environmental Hg in 2005.

4. 4. Mercury concentration by DMM

The spatial distribution of Hg concentrations in all four environmental media for 1960, 1970, 1980, and 2000 are shown in Fig. 7. Relatively higher atmospheric concentrations were observed to increase in southwestern part of the LBYRB towards the Osaka Bay from 1960 to 1970 and then the atmospheric Hg concentrations decreased. In the last three decades occurrences of relatively higher atmospheric concentrations (> 5.0×10^{-7} µmol m^{-3}) were not observed but the occurrences in lower atmospheric concentrations (< 5.0×10^{-7} µmol m^{-3}) were observed. To the end of the study span the expansion of lower concentration atmospheric concentrations were observed in the western and northwestern face of the LBYRB which might have caused due to the long-range atmospheric transport of Hg from the Asian continent (Jaffe et al., 2005 and Shimizu et al., 2010). From 1960 to 1970 the calculated Hg concentrations were observed to increase in the southwestern areas close to Osaka bay as shown in the Fig. 7. Adsorption of a certain portion of Hg into the sediments and transportation with the river flow to the ocean explains this situation (Stein et al., 1996). After 1980 the Hg concentrations were decreasing and the controlled Hg emissions from 1973 can be given as the reason for this decrease.

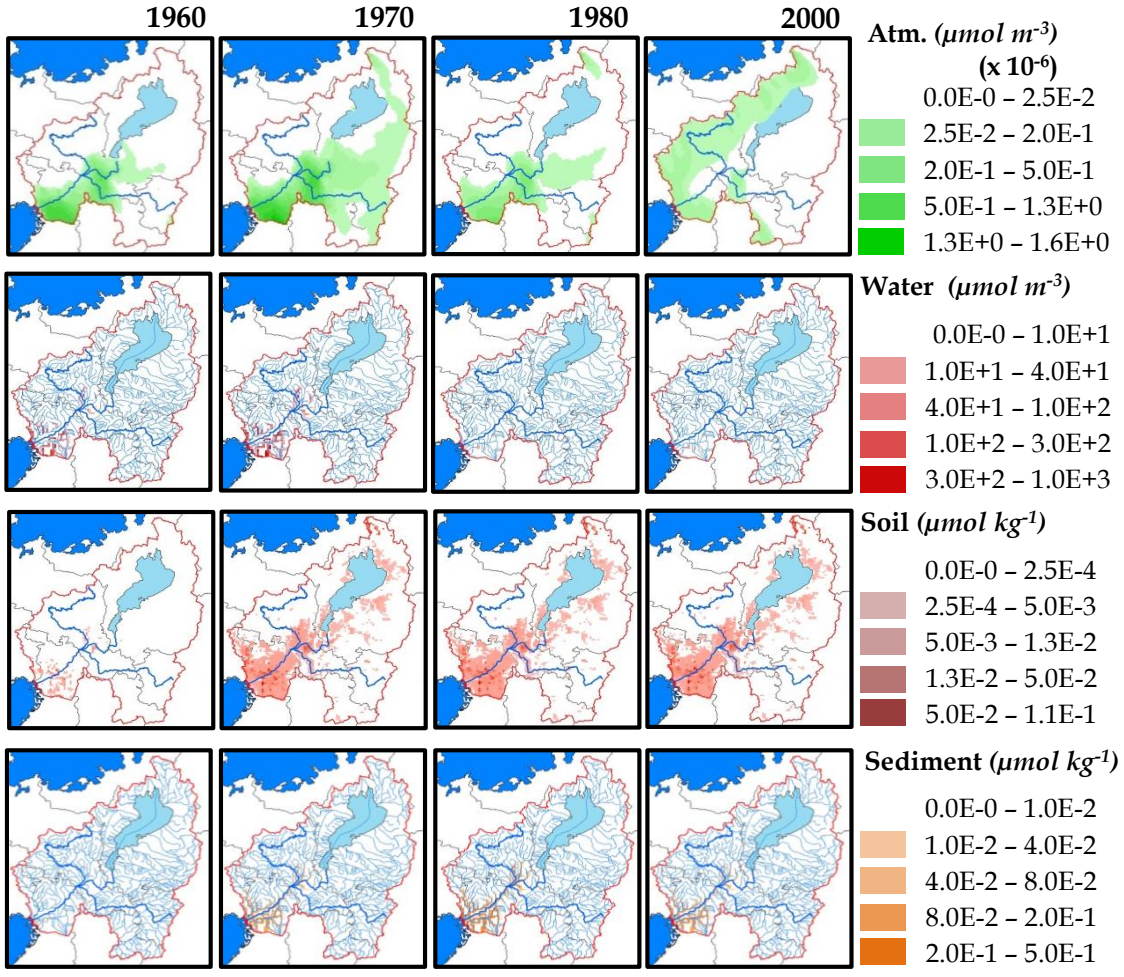

Fig. 7 Changes of spatial distribution of Hg concentration evaluated by DMM simulations for 1960, 1970, 1980 and 2000.

4. Conclusion

In this study, one box multimedia model and distributed multimedia model based on mass balance equilibrium were developed. Both models consist of four environmental media; atmosphere, water, soil, and sediment. The nine chemical and physical phenomena considered in each media are emission, degradation, advection, sedimentation, re-suspension, dry/wet deposition, atmospheric mixing, and particle-ion exchange. Metal species is assumed to be in perfect mixing within the same environmental media and at non-equilibrium state between the different environmental medium. Lead and mercury were applied for one box multimedia model during 1957-2007 and 1959-2009, respectively and mercury was applied for distributed multimedia model. The uncertainty analysis of lead concentrations was performed by Monte Carlo simulation.

The main conclusions obtained from these simulations are following:

1. The lead concentration in the atmosphere dramatically decreased twice during 1957-2007 due to the prohibition of leaded gasoline and the strengthening of effluent control. The calculated concentrations in four media well captured the observed data, though the calculated concentrations were slightly lower than the observed data.
2. Though the mercury emissions exceeded a few tons per year, the mercury emissions of the past decade became less than 100 kg per year due to the prohibition of mercury. The calculated concentrations in four media increased until 1970 and kept the constant value except for atmosphere because of the transboundary pollution. The calculated concentrations in four media well captured the observed data.
3. The sensitive analysis selected 6 parameters that strongly affected lead concentrations. Assuming the normal distribution with the standard deviation value of 0.2 times of the standard value, the uncertainty analysis was performed by Monte Carlo simulation. The influence on concentration in atmosphere was the constant for each year. On the other hand, the influence on concentration in sediment became strong year by year.
4. Using distribution multimedia model, the spatial distribution of lead concentrations in four media was calculated. The spatial distributions in each year were reasonable and temporal variations were also reasonable. The calculated concentrations in four media didn't necessarily capture the observed data.

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