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Temporal Evaluation of Mercury Concentration in Lake Biwa-Yodo River Basin by One-box Multimedia Model

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Abstract -Mercury has a well-known history in Japan as pollutant which caused severe damage to the environment and to human health, even leads to the world treaty of The Minamata convention on mercury in order to prevent its environmental damages. Therefore it is important to evaluate the mercury concentration in environmental media of: the atmosphere, the water, the soil, and the sediment. Lake Biwa-Yodo River basin of Japan was selected as the study site due to its multiple land use patterns. Recorded consumption and emission data of mercury were used to calculate the total annual emission amounts from 1959 to 2009 and used for one-box multimedia model simulations to calculate the concentrations of mercury in all four environmental media. Experimentally evaluated water-sediment partition coefficient was incorporated in the model calculations to improve the sensitivity of the calculations and the calculated results were validated using the available monitoring data. From 1959 to 1970 mercury concentration increased in all four environmental media and after that constant concentration of mercury in soil and sediment was observed for the last four decades due to the accumulation. Atmospheric mercury concentrations showed variation throughout the study span and in water the concentration decreased until 1980 and then became constant. Comparison of the calculated concentrations on different partition coefficients with the observed mercury concentrations proved the improvements of the model performances. Thus, it was conclude the one-box multimedia model could reliably calculate the temporal mercury concentrations based on the emission data and the sensitivity of the model was improved by using the experimentally evaluated partition coefficient value of mercury. Experimental evaluation of the other parameters used in the model calculations would be used for further improvements of the model in future.

***Keywords*:** Lake Biwa-Yodo River basin, Mercury, One-box multimedia model, Partition coefficient.

1. Introduction

Mercury (Hg) has a well-known history in Japan because of the damage it caused to the environment and to the human health. A disease caused by methylmercury poisoning was discovered in south west region of the Kyushu Island, Japan in 1956 which was later named as the Minamata disease (Harada, 1995). Many other adverse health effects of Hg such as its carcinogenicity, child developmental defects, toxic effects on nervous, and on digestive and immune systems are reported in the Mercury and health report by the world health organization (Web-1). Even though the consumption and release of Hg is legally controlled in Japan since 1973 (Web-2), many industries still consume Hg in their production processes and due to this reason Hg appears in environmental monitoring data (Sakata and Marumoto, 2005). Japanese environmental standards require the Hg concentration for water and soil should be less than 0.5 $\mu g\ L^{-1}$ and for the alkyl mercury the limit should be less than the detection limits (Web-3). To protect human health and the environment from the adverse effects of Hg, a global treaty of The Minamata convention on mercury was established in June 2013, acknowledged by 96 countries (Web-4).

Monitoring environmental Hg in a larger geographical region is practically a difficult task. Long range environmental transport of Hg is one of the reasons for this. Considering the practical difficulty in monitoring the whole land mass for Hg occurrences and the effects of Hg, it was considered to evaluate the concentration of Hg by using environmental modeling. There are published research works proving the feasibility of using environmental modeling for this purpose. Khandakar et al. (2012) and Lindstrom (2001) published their modeling studies on atmospheric transport and aquatic-soil systems of Hg. In his review on community multiscale air quality (CMAQ) modeling system, Byun et al. (2006) described the different components of chemical behaviors considered in air quality models. In another study by our research group, we published the use of One-Box multimedia Model (OBMM) which can combine all environmental media of the atmosphere, the water, the soil, and the sediment for evaluating environmental concentrations of metallic pollutants and evaluated the lead concentration on Lake Biwa-Yodo River basin (LBYRB) in Japan (Kondo et al., 2013).

For this evaluation of Hg concentrations in four environmental media, the chemical behaviors and the transport mechanisms of Hg in all four environmental media were mathematically interpreted into a OBMM. Since the water–sediment partition coefficient of Hg ($\mathbf{K_{d\,(Hg)}}$) is an important chemical behavior of Hg (Khandakar et al., 2012, Lindstrom, 2001 and Stein et al., 1996), $\mathbf{K_{d\,(Hg)}}$ was experimentally evaluated and incorporated in OBMM calculations. Because of the important and multiple land use patterns of the LBYRB, it was selected as the study site for this evaluation. Annual emission amounts of Hg were calculated for a 50 years span from 1959 to 2009 based on the available consumption and emission data from various data sources and used for OBMM calculations to evaluate the temporal Hg concentrations in the environment. The validity and the sensitivity of the OBMM calculations were evaluated by comparing the calculated concentrations with observed environmental concentrations of Hg.

The main objective of this study was carried to evaluate the temporal concentrations of Hg in LBYRB by using a OBMM and to evaluate the sensitivity of the model by comparing the calculated data with the observed Hg concentration.

2. Methodology

One-box multimedia model simulations were carried out to calculate the Hg concentrations in the atmosphere, the water, the soil, and the sediments in LBYRB for a 50 years span from 1959 to 2009. Estimated annual emissions of Hg in LBYRB were used as the input data. Water-sediment partition coefficient of Hg ($\mathbf{K_{d\,(Hg)}}$) was experimentally evaluated by a laboratory scale batch-shaking experiments and the $\mathbf{K_{d\,(Hg)}}$ value was incorporated in the OBMM calculations. Accuracy of the OBMM calculations was evaluated by comparing the calculated Hg concentrations with the observed data for the year 2009. The sensitivity of the model was evaluated by comparing the calculated Hg concentrations with different $\mathbf{K_{d\,(Hg)}}$ values with the observed Hg concentrations. The study site and the model are described in this section followed by the processes of annual emission amounts calculation and OBMM simulation.

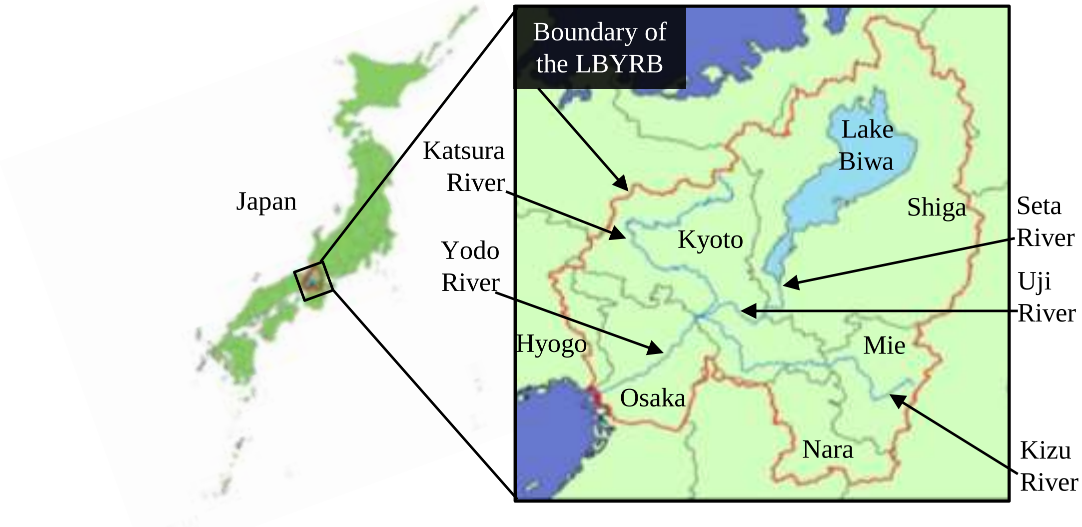

Fig. 1. Lake Biwa-Yodo River Basin.

2. 1. Lake Biwa-Yodo River Basin

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 $km^{2.}$ This study area has a dense rivers and tributaries system mainly composed of the Seta River which starts from the southern tip of Lake Biwa and turns into the Uji River and then joins with the Kizu River and Katsura River to become the Yodo River which finally flows to Osaka bay (Sudo et al., 2002). This lake-river system also provides the natural drinking water source for a population of nearly 13 million in the region. Also this is an important geographical area with multiple land use patterns of residential, agricultural, and industrial in Japan’s Main Island. It covers the parts of six prefectures: Hyogo, Kyoto, Mie, Nara, Osaka, and Shiga which collectively refers as Kinki region. Thus, LBYRB was selected as the study site for this study and Fig. 1 diagrammatically represents the study area.

2. 2. One-box Multimedia Model

The study site, composed of four environmental media of the atmosphere, the water, the soil, and the sediments was considered as a three-dimensional, closed entity in this model as shown in the Fig. 2. Nine chemical phenomena considered in the model calculations: emission, degradation, advection, sedimentation, re-suspension, dry/wet deposition, atmospheric mixing, and particle-ion exchange. Model calculations were carried out with the conditions of observing mass conservation and the chemical equilibriums are at steady state to calculate the Hg concentration in any of the four media at a given time. The main equation of the calculations is given by the equation (1) and the main variables considered in these calculations are (**a**) Emission of Hg into the atmosphere, soil, and water (**b**) Degradation of Hg in all four environmental media (This variable was set to zero for Hg) (**c**) Exchange of Hg^{+2}-$Hg_{(S)}$ in/between environmental media (**d**) Transport of Hg by advection in the atmosphere (**e**) Dry and wet deposition of Hg from the atmosphere (**f**) Sedimentation and re-suspension of Hg in water. More details of the OBMM were published in Kondo et al.,(2013).

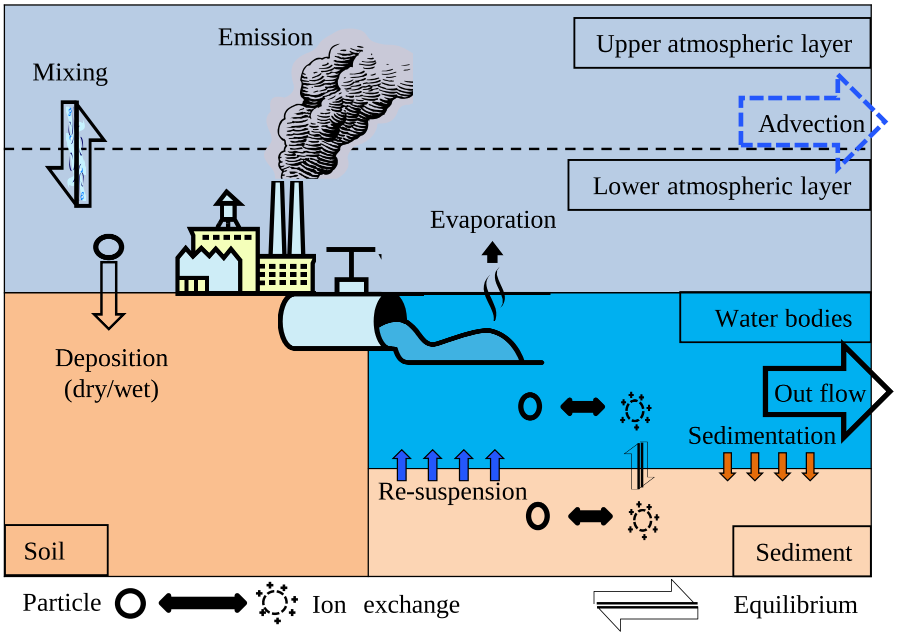

Fig. 2. Diagrammatic explanation of the OBMM and the chemical phenomena.

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

Where *i,j* is the environmental medium; *MN* is the number of media; M_i is the gross mass of Hg in media *i* (mol); $f_{eq\_i,j}$ is the mass-transfer flux of Hg at equilibrium (mol s^{-1}); f_{emi} is the emission flux of Hg (mol s^{-1}); f_{ad} is the advection flux of Hg (mol s^{-1}); f_{dprs} is the deposition flux of Hg (mol s^{-1}); and f_{deg} is the degradation flux of Hg (mol s^{-1}).

2. 3. Annual Emission Amount Calculation

Annual emissions of Hg from 1959 to 2009 were calculated for the LBYRB based on the records of Hg consumption and data from the Pollutant Release and Transfer Registry (PRTR-which is maintained by Japanese Ministry of Environment). 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., 2007 and Web-5). Total emissions to the atmosphere, the water, and the soil from 1959 to 2009 are shown in Fig. 3. Emissions of Hg were controlled since 1973 and from 1990 to 2000 there was no record of Hg emissions until the PRTR started recording the emissions in 2001. In PRTR the emissions are recorded under two categories; registered PRTR emissions and non-registered PRTR emissions. From 2001 to 2009 the Hg emissions recorded in the registered PRTR category were considered to be none. However, in non-registered PRTR emissions category, comparatively smaller emission amounts from the industries; having less than 20 employees, and with less than 1 ton per year annual Hg consumptions were recorded from 2001 to 2009 (Web-6). Thus the average of Hg emissions from 2001 to 2009 was used to represent the Hg emission from 1991 to 2000.

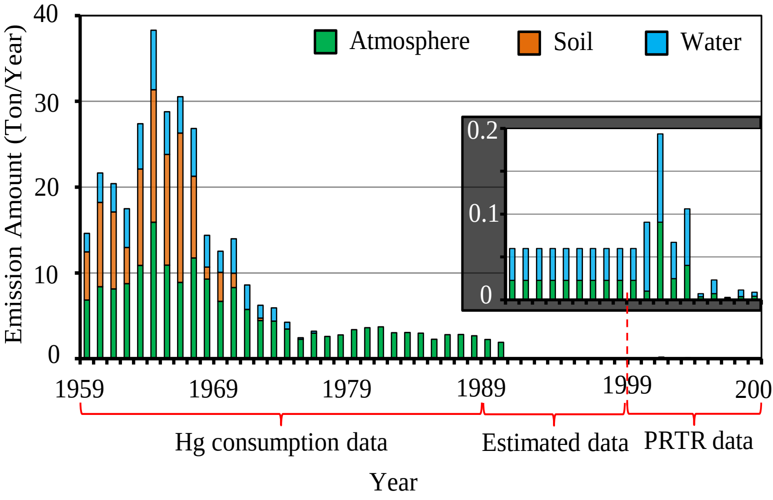

Fig. 3. Total Hg emissions to the atmosphere, soil, and water from 1959 to 2009.

2. 4. OBMM Simulations

Calculated annual emission amounts of Hg were fed to the OBMM and the calculations were carried out to evaluate the temporal concentration of Hg in all four environmental media. These calculations were carried out with the conditions of Hg is in chemical equilibrium between the environmental media and also it observes the mass conservation law in the environmental systems. Experimentally evaluated $\mathbf{K_{d\,(Hg)}}$ value (=80) was used in the calculations for a 50 years span of time from 1959 to 2009 and the time steps were set to 6 minutes. A series of differential equations were solved using the Runge-Kutta technique by a computer program coded in FORTRAN. Calculated Hg concentrations were validated by using the published observed data for the occurrences of Hg in the environment in order to evaluate the reliability of the OBMM calculations. Additional OBMM calculations were carried out for different $\mathbf{K_{d\ (Hg)}}$ values (= 10, 65 and 120 which were experimentally evaluated for representing soil types of sand, ground soil, and sediments in the study area) and the calculated concentrations based on these different $\mathbf{K_{d\ (Hg)}}$ values were then compared with the observed data in order to study the sensitivity of the OBMM calculations to $\mathbf{K_{d\ (Hg)}}$ values.

3. Results and Discussion

One-box multimedia model simulations were carried out for 50 years span to evaluate the Hg concentrations in all environmental media in LBYRB from 1959 to 2009. Figure 4 shows the calculated Hg concentrations by OBMM with the experimentally evaluated $\mathbf{K_{d\ (Hg)}}$ value (=80) for the atmosphere, the water, the soil, and the sediments in log $_{10}$ scale. In the sediment, the Hg concentration varied from $3.03\text{x}10^{-1}$ to 5.57 µmol kg^{-1} while in soil it varied from $1.27\text{x}10^{-2}$ to $6.66\text{x}10^{-2}$ µmol kg^{-1}. Calculated Hg concentration was varying from $5.78\text{x}10^{-2}$ to $6.96\text{x}10^{-2}$ µmol m^{-3} in the water and the atmospheric Hg concentrations were ranging from $2.54\text{x}10^{-6}$ to $1.20\text{x}10^{-5}$ µmol m^{-3}. According to the temporal concentration trends shown by the results in Fig. 4, concentration of Hg in the sediment, soil, and water increased. For the next 10 years only the concentration in water decreased and for the last 30 years of the temporal span, the calculated Hg concentrations became constant due to the controlled Hg emissions.

This decrease of Hg concentration in water is due to the adsorption of certain portion of Hg on to the sediments and also because of the transportation of Hg to the ocean through the river flow. Atmospheric Hg concentration showed relatively small variations during the temporal span of this study. Increased atmospheric Hg concentrations at the first decade are due to the higher consumptions of Hg. The lower accuracy of the estimation methods in non-registered PRTR data and the long range atmospheric transport of Hg from the Asian continent might have caused these variations in the last three decades (Jaffe et al., 2005). Except for relatively small variations in the atmospheric Hg concentrations a distinctive increase of Hg concentrations in the environmental media is not visible due to the strict management practices applied on the consumptions and emissions of Hg from 1970's.

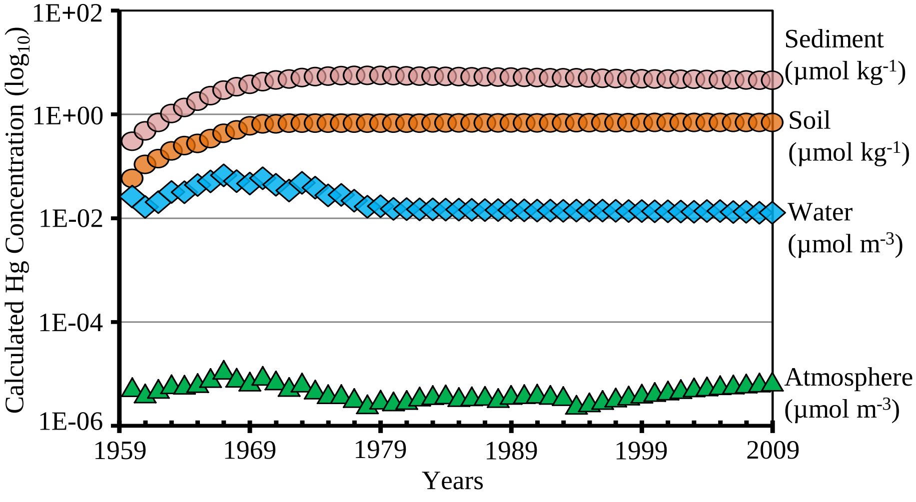

Fig. 4. Calculated concentrations for Hg from 1959 to 2009 in the atmosphere, the water, the soil, and the sediments by OBMM with the $\mathbf{K_{d\ (Hg)}}$ =80.

These calculated results were validated by comparing them with the observed atmospheric Hg concentrations in Osaka Prefecture from 2001 to 2009 (Web-7) and the calculated Hg concentrations by OBMM simulations for the respective years. Calculated atmospheric Hg concentrations were within the range of observed Hg concentrations. Calculated Hg concentrations (with $\mathbf{K_{d\ (Hg)}}$=80) for all environmental media for the year 2009 were compared with the observed data for all environmental media for the same year as shown in the Fig. 5 (Nakagawa, (2008), Web-7, 8, & 9) and the calculated Hg concentrations fall within the range of the observed Hg concentrations, validating the reliability of the calculated results.

In order to observe the effect of $\mathbf{K_{d\ (Hg)}}$ value on OBMM calculations, simulations were carried out with different $\mathbf{K_{d\ (Hg)}}$ values obtained for representative soil types in LBYRB. For the Sand-*Milli~Q* water, $\mathbf{K_{d\ (Hg)}}$ value was evaluated to be 10 and for the ground soil-*Milli~Q* water it was 65. In river sediment-*Milli~Q* water, the $\mathbf{K_{d\ (Hg)}}$ value was 120. Calculated concentrations of Hg in water and sediments for these different $\mathbf{K_{d\ (Hg)}}$ values were plotted together with the observed Hg concentrations in the water and the sediments for 2009 as shown in the Fig. 5. Observed Hg concentrations in water varied from 4.99x10^{-3} to 8.47 x10^{-2} μmol m^{-3} with an average of 4.49 x10^{-2} μmol m^{-3}. Calculated Hg concentration with $\mathbf{K_{d\ (Hg)}}$ =10 provided higher concentrations than this range, while the calculated Hg concentrations with $\mathbf{K_{d\ (Hg)}}$ = 65 and $\mathbf{K_{d\ (Hg)}}$ = 80 provided the results closer to the average observed Hg concentration. In the case of $\mathbf{K_{d\ (Hg)}}$ = 120, the calculated Hg concentration resulted with the lowest from the average observed concentration as shown in the Fig. 5.

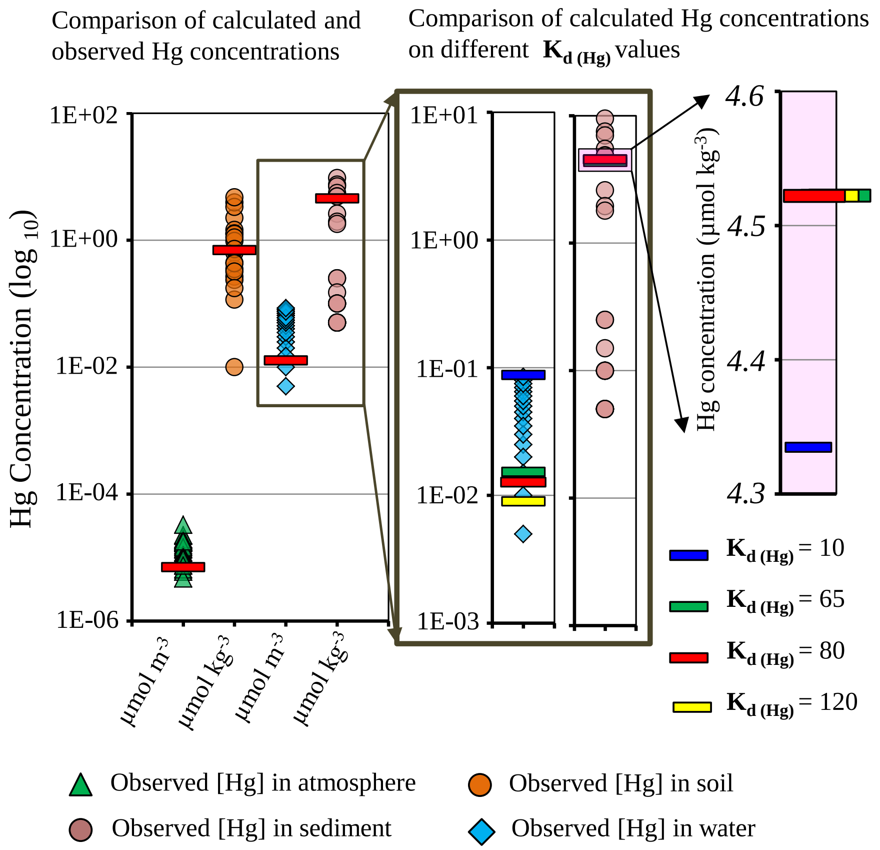

Fig. 5 Observed & calculated concentration of Hg in each environmental media in LBYRB for 2009 and the comparison of the effect of $K_{d\ (Hg)}$ value on OBMM calculations.

In sediment, the observed Hg concentrations varied from 9.97×10^{-2} to 9.47 µmol kg^{-1} with an average of 1.96 µmol kg^{-1}. Calculated Hg concentration in sediment with all $\mathbf{K_{d\,(Hg)}}$ values were between the range of the observed Hg concentration. As described with the magnification in Fig. 5, $\mathbf{K_{d\,(Hg)}}$ = 10 resulted with 4.33 µmol kg^{-1}. In the case of $\mathbf{K_{d\,(Hg)}}$ = 65, 80, and 120 the calculated concentration of Hg in sediments were 4.52 µmol kg^{-1} showing the calculated concentrations of Hg in sediments were not affected by the higher $\mathbf{K_{d\,(Hg)}}$ (≥65) values but affected in lower $\mathbf{K_{d\,(Hg)}}$ (10≤65) values. It was visible the calculated Hg concentrations in water was effected by the $\mathbf{K_{d\,(Hg)}}$ value. Each respective $\mathbf{K_{d\,(Hg)\,values}}$ obtained from the different samples with different geographic characters provided the calculated Hg concentration relatively to their geographic characters, and $\mathbf{K_{d\,(Hg)}}$ = 80 provided a generalized calculated Hg concentration in water for whole LBYRB area. With these results it became clear that, by incorporating the experimentally evaluated $\mathbf{K_{d\,(Hg)}}$ into the OBMM calculation, the calculated Hg concentrations in water and sediments showed much closer values to the average observed Hg concentration, thus proving the OBMM calculations have improved.

4. Conclusion

Concentration of Hg in four environmental media of the atmosphere, the water, the soil, and the sediments of LBYRB was evaluated by using a OBMM. Annual emission amounts of Hg were calculated by using the literature on Hg consumption and PRTR data, for a 50 years span. Experimentally evaluated $\mathbf{K_{d\,(Hg)}}$ value (=80) was incorporated in OBMM and concentrations of environmental Hg were calculated using the annual emission amounts. Calculated Hg concentrations were compared with the observed Hg concentrations in the study area in order to validate the accuracy of the OBMM calculations. Variations were observed in calculated atmospheric Hg concentrations throughout the temporal span. Sediments and soil, showed the accumulation of Hg in it. Except for the atmosphere the calculated Hg concentrations in soil, water, and sediment were became constant for the last three decades of the temporal span. The sensitivity of the OBMM calculations for the $\mathbf{K_{d\,(Hg)}}$ value, was studied by comparing the calculated Hg concentrations on different $\mathbf{K_{d\,(Hg)}}$ values representing different soil types and it was able to identify the experimentally evaluated $\mathbf{K_{d\,(Hg)}}$ value (=80) improved the accuracy of OBMM calculations by providing a generalized $\mathbf{K_{d\,(Hg)}}$ value representing the whole study area.

Thus the objective of this study was successfully achieved. Many chemical coefficients other than $\mathbf{K_{d\,(Hg)}}$, affect the chemical behavior of Hg in the environment so the OBMM surely can be improved by experimentally evaluating and incorporating those experimentally evaluated coefficients in OBMM calculations. Availability of the emission data and observed data for the occurrences of Hg in different environmental media is really important to improve the accuracy of OBMM calculations and also for the validation of the calculated results of the model. This study can be used to formulate detailed studies to investigate the occurrences of environmental Hg not only temporally but also spatially. Also this study will provide sufficient details of the environmental condition related with Hg to the interested parties such as authorities responsible for environmental monitoring and management, thus they can proceed with better environmental management practices to mitigate environmental pollution. Also by modifying the model, the environmental condition of other pollutants can be evaluated while making the environmental monitoring process more successful and eventually protecting the environment.

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