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Author(s)	Ariyadasa, Bangamu Hewa Appu Arachchige Kasun Tharaka
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ASSESSMENT OF POTENTIALLY HAZARDOUS PRTR CHEMICALS IN LAKE BIWA-YODO RIVER BASIN OF JAPAN BY USING MULTIMEDIA MODELS

BANGAMU HEWA APPU ARACHCHIGE
KASUN THARAKA ARIYADASA

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Graduate School of Engineering,
Osaka University

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INTRODUCTION

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Chemicals have coexisted harmoniously with the living beings in our environment from the pre historic era. But at present, natural and synthetic chemicals are accumulating in our environments due to the increased consumption of these chemicals for various anthropogenic activities such as industrial, agricultural, transportation, and residential. Anthropogenic activities are consuming various chemicals so much, that now we are unable to quit consuming these chemicals. After the industrial revolution consumption of chemicals increased and this has grown to such a severe level that all of our environmental media namely the atmosphere, hydrosphere, lithosphere, and even the biosphere are now polluted with these chemical pollutants. After considerable damages to the environment were done, many pollutants were identified for their environmental risks, and health risks.

Scientists are researching for less harmful chemicals to substitute the hazardous chemicals that we use in our industries. But the continuation of environmental pollution is assured unless we monitor all the environmental media for the occurrences of chemical pollutants and take proper restorations, remediation, and mitigation measures to avoid the emissions of chemical pollutants to our environments. Individuals, research institutes, and various other organizations from the grass root levels to governments are attempting to fight this problem by various means while promoting science related to environment pollution studies.

Environmental monitoring programs are performed all over the world by the authorities in their capacity to study the status of pollution as one of the pollution management process. Developed countries have taken the lead in these missions by inventing new technologies to evaluate the environmental concentration of these chemicals in all sorts of environmental media. So far the focus of the environmental monitoring has been given to the chemicals which affected the human health and degraded our natural environments. For example heavy metals with health risks such as arsenic (As), lead (Pb), and mercury (Hg), can be shown among many other harmful chemicals. Since the natural water and air directly involved with the human health, environmental monitoring had given their attention to the natural water sources and atmosphere. Therefore the surveys were carried out in these environmental media and they have provided important data on the occurrences of various chemicals in our environments thus the related authorities were able to take mitigative measures to prevent the pollution condition getting worse. Systematic methods were formulated to record these chemical occurrences in the environment and the developments in the information technologies also facilitated these improvements. Flowingly environmental standards were introduced to control environmental concentrations of these pollutants and authorities legitimized the mitigative measures that would help preventing environmental pollution.

Then the scientists realized wide spread nature of the pollution and only the immediate adverse effects of these pollutants are localized. Regardless the pollution sources are point or non-point sources, pollution disperse through our environment via various chemical pathways. Agricultural chemicals and waste water released to the ground, tend to leach into the soil and then to aquifers while polluting the ground water. Aquatic sources such as rivers and lakes transport these pollutants throughout their regions and finally reach to the oceans where a considerable portion accumulates in oceanic aquatic organisms. Chemicals released into the atmosphere are carried out with the wind currents and create trans-boundary pollution. Existence of persistent organic pollutants (POPs) in the Polar Regions is one of the extreme occasions of this process. Also these chemicals may convert into various other chemical species and also will trigger surprisingly diverse health effects and currently, toxicologists are facing a difficult time to figure out the causes of many illnesses.

This brings us to a point where the practicality of environmental monitoring is questioned. Without knowing exactly which chemical pollutants to focus on, without knowing which geographic areas to focus on, environmental monitoring programs are becoming relatively impractical. Considering the geographic scale of the environments, it is impractical to perform field environmental monitoring programs over large geographic regions. Technological requirements, scientific expertise, and financial insufficiencies are some of the other reasons for the hindrances of the practicality.

1.2 Purpose of the research

It is important to identify the behavior, trends, and the fate of the chemical pollutants in the environment and to predict their future proactively, rather than relying only on the environmental monitoring process to provide us better insight information of environmental pollution conditions. Therefore it was considered to use the available environmental chemical data such as monitoring data, emission data, and consumption data, combined with mathematical and computational modeling to study the behaviors, trends, and fate of these chemicals in our environments.

Therefore in this study, two computational models namely one-box multimedia model (OBMM) and distributed multimedia model (DMM) were used to perform computer simulations based on the annual emission amounts of the pollutants and then to evaluate the environmental concentrations of the pollutants in different environmental media. It was necessity to screen a large group of chemical pollutants to identify the chemical pollutants which possess potential health risks based on their environmental concentration levels and the temporal trends of the concentrations. Identified chemicals were then required to study in details for their spatial distribution.

Based on the findings, environmental monitoring process can be provided with required information of which chemicals need to be monitored for and also which geographic regions appear to be more vulnerable for the environmental pollution.

Thus the findings can be experimentally validated and if requires the proper control measures can be taken so that the environmental pollution can be proactively mitigated. This is the main purpose of this study but it doesn't limit to that.

Rather than just using computational modeling to evaluate environmental condition, it was necessary to exploit its possibilities as an informative and managerial tool to prevent environmental pollution. Also various chemical species (mainly divide into metallic and non-metallic) were studied in this research and it enhanced the opportunity to use these environmental models as screening tools. Various chemical parameters were considered in these model calculations and they are required to be properly evaluated through experiments for the computational models to provide reliable simulation results. These models can be improved and then can be applied in various parts of the world to facilitate more practical environmental monitoring processes and thus control the global environmental pollution.

1.3 Literature review

In scientific literature there are many studies related to environmental pollution, environmental monitoring studies related to various chemicals, studies on chemical behavior and fate in the environment. Since the development of information and computer sciences, researchers have tried to use computational models to simulate these natural and anthropogenic chemical phenomena in order to understand them better and to predict the trends of those phenomena. In this section of the introduction chapter, it is required to discuss the researches carried out in closer scientific fields in order to properly comprehend the importance of this work.

History of the metal usage runs back to 6000 BC and gold (Au), copper (Cu), lead (Pb), and mercury (Hg), are some of the metals known to mankind in prehistoric era. Even in the 21st century scientists still discover new metals (*Reardon, 2011*). According to Yeh and Lim, in mid-nineteenth century was the beginning of synthetic chemicals due to the developments in organic chemistry and today we have lot of synthetic substances around us in our environment (*Yeh and Lim, 2007*). As well as the consumption of these chemical substances increased, our environment was exposed to these chemicals gradually and thus started the chemical pollution of our environment. In the recent time, the focuses of environmental pollution studies have been shifting to materials such as heavy metals, asbestos, and persistent organic pollutants (POPs). Pollution conditions got worse due to the uncontrollability of non-point source pollution and trans-boundary pollution (*Makra and Brimblecombe, 2004, and USEPA, 2013(1)*).

Thus scientists have tried to understand the behavior of the pollutants as well as to evaluate the pollution conditions using different methods. Computational modeling of the behavior of chemicals and their transport mechanisms is one of these methods. United States Environmental Protection Authority (USEPA) reports using atmospheric models such as: Community Multi-scale Air Quality Model (CMAQ), Air Quality Model Evaluation International Initiative (AQMEII), and Community Modeling and Analysis Systems (CMAS), to evaluate the concentration of air pollutants in a given area under almost any imaginable emissions or climate scenario (*USEPA, 2014(2)).* In 1983, Hansen published his work related to long-range climate studies in which he focused on various atmospheric factors such atmospheric gases, aerosols, cloud particles, cloud cover, vertical distribution, and many others, while solving simultaneous equations for mass conservation, energy, and momentum (*Hansen et al., 1983*). Atmospheric dispersion of mercury was modeled by Khandakar in 2012 using the two nearest hypothetical point sources (*Khandakar et al., 2012*).

In their review on hydrological modeling of basin-scale climate change and urban development impacts, Praskievicz and Chang summarizes the various hydrological models such as Parallel Climate Model (PCM), Soil and Water Assessment Tool (SWAT), and Precipitation-Runoff Modeling System (PRMS), among many other hydrological models used to evaluate different hydrological scenario (*Praskievicz and Chang, 2009*).

But many of these modeling studies have been performed only for certain environmental medium. A level III fugacity model was used by Mackay in 1985 to evaluate the environmental behavior of 14 chemicals while considering six environmental compartments: air, soil, water, bottom, suspended sediments, and fish. He combined several environmental media in his model without limiting it to single environmental medium (*Mackay et al., 1985*). He also published his work in 1991, on the multimedia fate of organic chemicals using a level III fugacity model, where he incorporated several chemical phenomena: emissions, advections, degradations, and interphase transportation of the chemicals (*Mackay and Paterson., 1991*).

To mathematically interpret the chemical behaviors, the information of chemical parameters are very important. Researchers have reported the relationships of these chemical parameters to the chemical behaviors in different environmental media. Studies published by Brigham reports his studies on cycling of mercury in stream ecosystems (*Brigham et al., 2009*). The distribution of particulate and reactive mercury in surface waters of Swedish forest lakes was evaluated by using an empirically based predictive model by Lindstrom in 2001 (*Lindstrom M., 2001*). In 1996, Lee reported his research work on predicting soil-water partition coefficient for cadmium (*Lee et al., 1996*) and Allison reported the research work by USEPA on evaluating the coefficients for metals in surface waters (*Allison et al., 2005*). Also the exchanges processes of the heavy metals in sediment water systems were studied by Ramamoorthy (*Ramamoorthy and Rust., 1978*) and kinetic studies of adsorption-desorption of mercury was done by Yin in 1997 (*Yin et al., 1997*).

In this study we combined all four environmental media namely the atmosphere, water, soil, and sediment, into a computer model which is based on the mass balance and model simulations were carried out for a relatively larger study area of Lake Biwa-Yodo River Basin (LBYRB) to evaluate environmental concentrations of two well-known metallic pollutants of Pb and Hg. Nine chemical parameters of emission, degradation, advection, atmospheric mixing, dry deposition, wet deposition, sedimentation, re-suspension, and particles and ion exchanges, were considered in the model calculations to evaluate the environmental concentration of Pb and Hg. The study span was 45 years and available emission data were used as the input data for these calculation, thus by this study a large amount of important information on the environmental condition of chemical pollutants were revealed. To improve the model sensitivity, the water-sediment partition coefficient of Hg ($\mathbf{K_{d(Hg)}}$) was experimentally determined for different soil/sediment samples and generalized $\mathbf{K_{d(Hg)}}$ for LBYRB was incorporated in the model calculations. At later stage, LBYRB was evaluated for the environmental concentration of Hg at a micro scale of 1 km x 1 km grid which provided more sensitive spatial data of the distribution of Hg concentration in LBYRB.

Finally the model was tested for its utilization to identify potentially hazardous pollutants from a relatively large group of non-metallic chemicals. Due to these characteristics, this research study would strongly stand out from the researches carried out in the similar field of study.

1.4 Objectives

The main objectives of this study were set to evaluate the behaviors, trends, and fate of hazardous chemical pollutants in LBYRB by using the available emission data and computational modeling. To achieve this main objective the study was divided in to sub objectives:

- To evaluate the temporal environmental concentration of Pb and Hg by OBMM simulations.
- To experimentally determine the chemical parameter ($\mathbf{K_{d(Hg)}}$) used in OBMM calculation.
- To analyze the sensitivity of the OBMM performance on $\mathbf{K_{d(Hg)}}$.
- To evaluate the spatial distribution of Hg concentration by using DMM simulations.
- To screen the potentially hazardous non-metallic PRTR* chemical pollutants by using OBMM as an environmental management tool.

(Pollutant Release and Transfer Registry – section 1.7)*

1.5 Study design and methodology

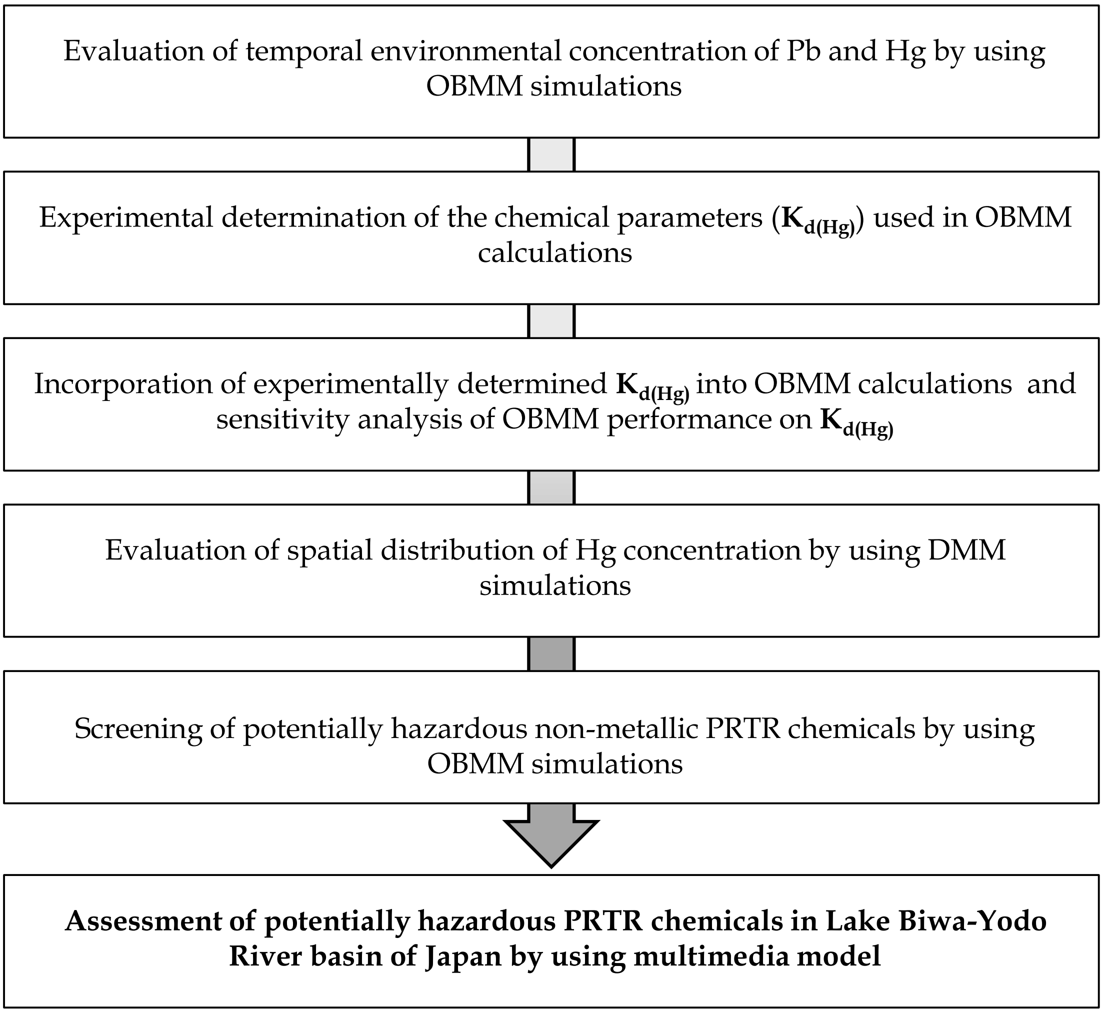

Fig. 1.1 Diagram of the study design.

This study on Evaluation of behaviors, trends and fate of hazardous chemical pollutants in Lake Biwa-Yodo River basin of Japan by using computational modeling was carried out in five main sections and the overall design of the study which was followed to achieve the main objectives is given in the **Fig 1.1.** These five main sections were:

1) Evaluation of temporal environmental concentration of Pb and Hg by using OBMM simulations.

Pb and Hg were selected as representative metallic pollutants and simulations were performed to evaluate environmental concentration in all four environmental media of the atmosphere, water, soil, and sediments in LBYRB for a span of 45 years.

2) Experimental determination of the chemical parameters (**$K_{d(Hg)}$**) in OBMM.

   Water-sediment partition coefficient (**$K_{d(Hg)}$**) is an important chemical parameter used for OBMM calculations. Therefore lab scale shaking-batch experiments were carried out for different soil/sediment samples to determine the **$K_{d(Hg)}$**.

3) Sensitivity analysis of OBMM on experimentally determined **$K_{d(Hg)}$**.

   Experimentally determined **$K_{d(Hg)}$** was incorporated in OBMM model calculations and environmental concentration of Hg was calculated. Calculated concentrations of environmental Hg based on the experimentally determined different partition coefficient values representing different soil/sediment types were then compared with the observed data to analyze the sensitivity of the OBMM on water-sediment partition coefficient.

4) Evaluation of spatial distribution of Hg concentration by DMM simulations.

   Mercury was selected as the representative chemical pollutant and spatial distribution of Hg concentration was evaluated by using DMM simulations.

5) Screening of potentially hazardous non-metallic PRTR chemicals by using OBMM as an environmental management tool.

   Simulations were performed for a span of 11 years for 200 non-metallic compounds selected from PRTR chemicals. Based on their calculated concentrations, the concentration trends were analyzed and the screening of risk possessing chemicals was carried out by prioritizing the chemicals for non-decreasing concentration trends, highest concentration levels, and media of occurrences.

1.6 Lake Biwa-Yodo River basin

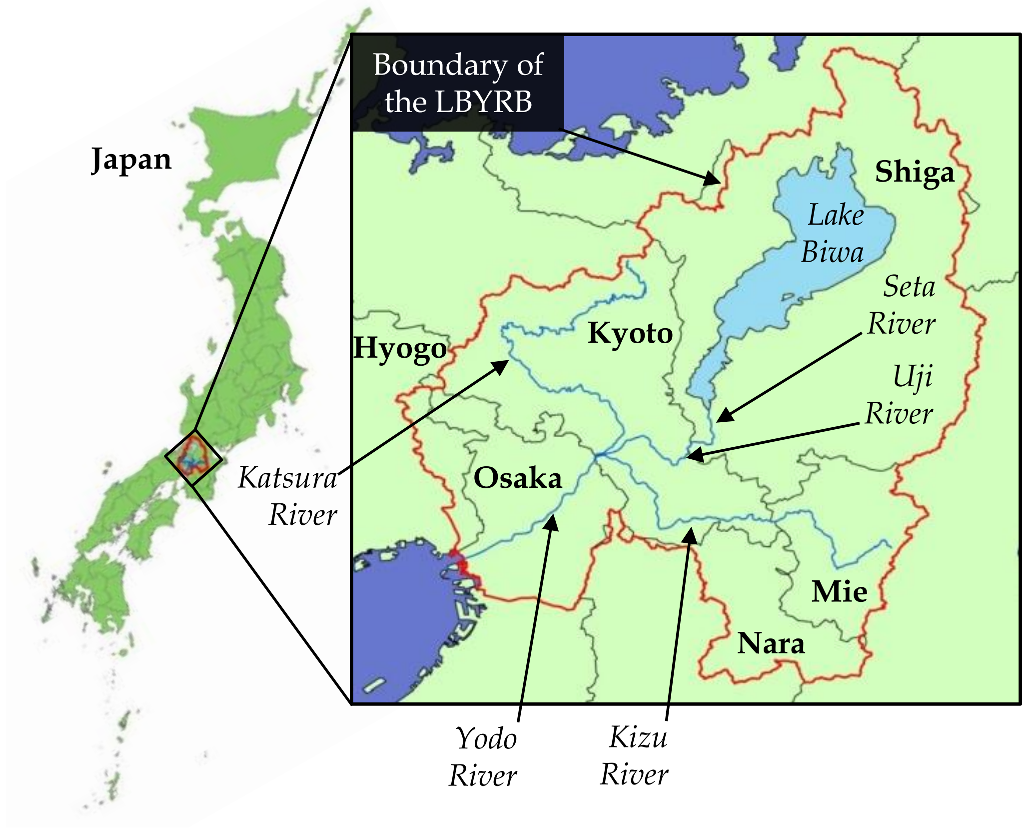

Fig. 1.2 Lake Biwa-Yodo River basin and its major aquatic system.

Lake Biwa-Yodo River basin (LBYRB) 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 Shiga. This study area lies between the latitudes 34.65~35.69 °N and the longitudes 136.15~136.51 °E, while Lake Biwa, the largest natural water body in Japan, is located in the middle of this study area, covering 630.77 km^2. 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. 1.2** (*Sudo et al., 2002*).

1.7 PRTR and other data sources

Chemical emission data required for this study were obtained from PRTR, chemical consumption data, and other scientific literature. Since the PRTR data were the major data source a brief description of PRTR is given by this section.

This system was established in Japan under the supervision of Japanese Ministry of Environment in 1997. In total 562 chemicals are listed under the PRTR based on their degree of hazard and the possibility of exposure. Here the hazard is defined on the destruction of human health, habitat and growth of plants and animals, and/or the ozone layer. These chemicals are divided into 2 categories as class I and class II mainly based on the following conditions of hazard:

- Chemical substances that may be hazardous to human health and/or may adversely affect the ecosystem.
- Chemical substances that may easily form hazardous chemical substances through a naturally-occurring chemical transformation.
- Chemical substances that deplete the ozone layer.

Chemicals which meet the above conditions of hazard and which are identified to be persistent in the environment over a substantial area are categorized under class I. By March 2014, there are 462 chemicals listed in class I category and the annual amounts of handling for these chemicals are set to 1 ton. Among these 462 chemicals, 15 chemicals have been designated as specific class I designated chemical substances based on their carcinogenetic properties and their annual amounts of handling are set to 0.5 ton. Chemicals which meet the above conditions of hazard but expected to occur less frequently in the environment are categorized in class II and by March 2014 there are 100 chemicals listed under this category.

Operational business and the industrial facilities have to calculate the details of their annual amount of chemicals released to the atmosphere, to public water bodies, to the land (on-site) and to the landfill disposals (on-site) or transferred to sewage or to off-sites for further processing and then submit to the authorities to be recorded under the "Notified Release" or called as "Registered PRTR Data"in this study. There are 24 types of businesses which required reporting these emissions. Japanese Ministry of Environment estimates the released amounts of chemicals from the non-point sources such as the businesses that are small in size or handling amount (ex. not meeting the reporting requirements), non-listed industries, household and mobile sources, and records them under "Estimated Releases Outside Notification"or called as "Non-registered PRTR data"in this study. These data of what chemicals, source, and released amounts, are available for public as Registered PRTR data and Non-registered PRTR data via the website of PRTR information plaza, Japan (*PRTR Information Plaza,2014*).

1.8 Chapter organization

The chapters in this thesis are organized in the following manner. Chapter 1 provides an introduction of this research which is divided into sections to provide background, literature review, purpose of this study, objectives, study design, study site, and major data sources used in this study. In chapter 2, both computational models of OBMM and DMM are described including the chemical phenomena, model parameters, and the chemical parameters considered in the model calculations. Chapter 3 to 6 describes the main experimental sections of evaluation of Pb and Hg concentrations in LBYRB by OBMM simulations, evaluation of $\mathbf{K_{d(Hg)}}$ and sensitivity analysis of OBMM, evaluation of spatial distribution of Hg concentration by DMM simulations, and screening of potentially hazardous non-metallic PRTR chemicals in LBYRB by using OBMM as an environmental management tool, respectively. All these sections include the introductions, objectives, methodologies, results, discussions, and conclusions separately for each section. Chapter 7 summarizes the important conclusions obtained from this study and also describe the limitations occurred in the study together with the recommendations for future developments of this research.

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MODEL DESCRIPTIONS

2

2.1 One-box multimedia model
  2.1.1 Chemical phenomena
  2.1.2 Model variables, equations, & chemical parameters
2.2 Distributed multimedia model

One-box multimedia model (OBMM) is a mathematical model which was developed to interpret the behavior and fate of different chemicals in four different environmental media of the atmosphere, soil, water, and the sediment. In the OBMM, the study site (LBYRB) was considered as a three-dimensional, concealed compartment and the **Fig. 2.1** diagrammatically explains OBMM, chemical behaviors considered in the model and the environmental media considered in this study. The model was constructed with the conditions of:

- The chemicals concerned in the calculations observe the mass conservation principles.
- The chemicals concerned in the calculations are in perfect mixing within the environmental media and between the environmental media they are in non-equilibrium state.

Chemical phenomena explained in the section 2.1.1 are mathematically interpreted using a computer code in FORTRAN and therefore when the input data of annual emission data and the values for the chemical parameters of a particular chemical pollutant, fed in to the OBMM together with the values of model parameters, it can calculate the concentrations of the particular chemical pollutant in any of the above mentioned environmental media at a given time.

2.1.1 Chemical phenomena

There are various chemical phenomena occurring in the environmental media of atmosphere, water, soil, and sediment. These phenomena are mathematically interpreted in OBMM and following is a brief description of them.

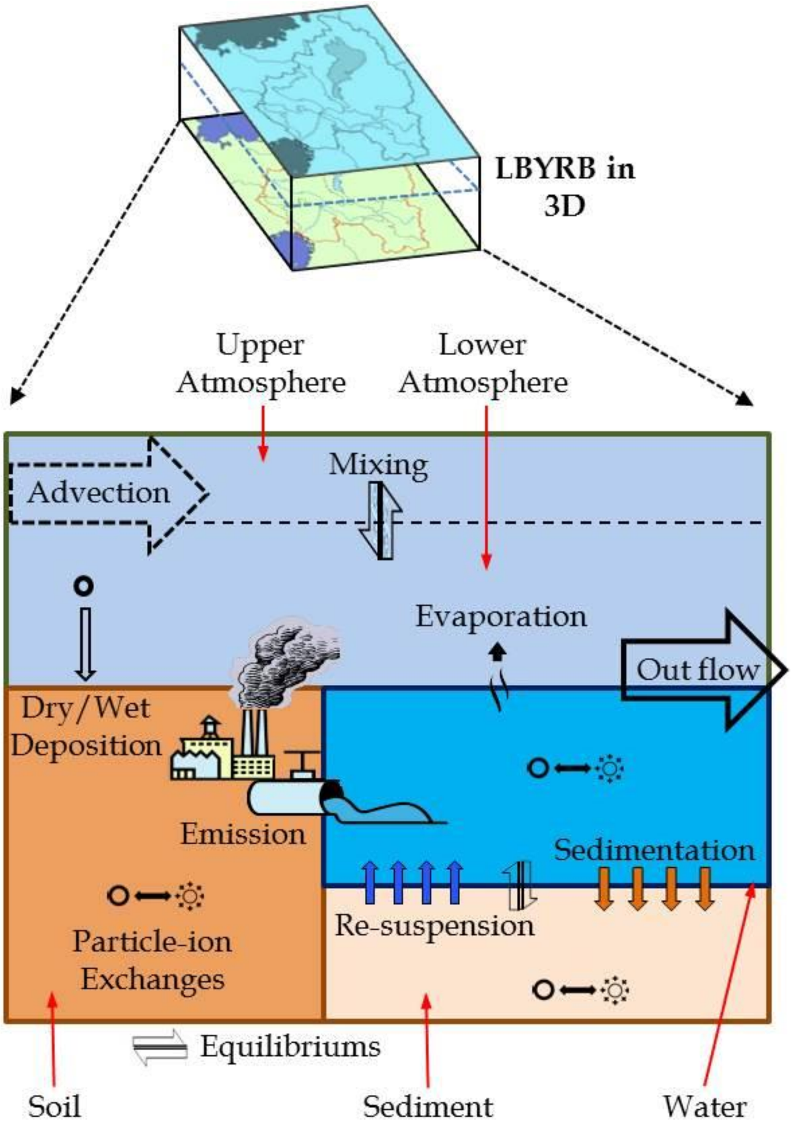


Fig. 2.1 Diagrammatic explanation of OBMM, environmental media and the chemical phenomena considered in the model calculations.

- **Emission**

  This phenomenon represents the entering of various chemicals into the environmental media of the atmosphere, soil, and the water of the three dimensional compartment considered in the OBMM calculation. This phenomenon is mainly affected by anthropogenic activities.

  In certain cases, natural emission and inflow of chemicals by natural processes such as soil erosion and natural transformation into other chemical compounds also can occur *(Seinfeld J.H. and Pandis S.N., 2006)*.

- **Degradation**

  This is the processes of natural decaying, accumulated into living organisms via their consumption and conversion of chemicals into various other chemical compounds in the environment *(Seinfeld J.H. and Pandis S.N., 2006).* Conversion or breaking down into another chemical compounds also is an entering process (emission) of a certain chemicals to the OBMM but mainly degradation is the process that removes chemicals from OBMM.

- **Advection**

  This mechanism refers to the transport of chemicals from one region to another due to the bulk movement of the fluid. In the atmosphere, chemicals move from one region to another due to the wind currents and in the aquatic systems due to water flow *(Seinfeld J.H. and Pandis S.N., 2006)*. In atmosphere, advection can occur in vertically and horizontally but in the OBMM the vertical advection is considered as atmospheric mixing.

- **Atmospheric mixing**

  This process represents the mixing of chemicals between vertical layers of the atmosphere. Atmosphere was divided into two layers of upper mixing layer and lower mixing layer by using the atmospheric mixing height. Upper atmosphere is the atmospheric layer higher than the atmospheric mixing height and this height changes from 200 m to 1000 m from the sea level diurnally. Exchange of various chemicals between these two layers is a natural process that occurs within the atmosphere *(Kondo et al., 2013)*.

- **Dry deposition**

  This is the process by which both the gases and particulate chemicals in the atmosphere collect or deposit themselves on soil or on water body without the aid of precipitation. This may occurs due to gravitation, interception, impaction, diffusion, and turbulence *(Seinfeld J.H. and Pandis S.N., 2006)*.

- **Wet deposition**

  Wet deposition transfers airborne chemical species in gases or particulate phase to the Earth`s surface in an aqueous form such as rain, snow or fog via any kind of processes of precipitation, gravitation, interception and such. In this process, atmospheric hydrometeors such as rain or snow scavenge the chemicals in the atmosphere and deposit on soil or water body. Dissolution of gases phase chemicals into rain, snow, or fog, and removal of atmospheric particles while they serve as nuclei for cloud formation can also occur *(Seinfeld J.H. and Pandis S.N., 2006)*.

- **Sedimentation**

  Sedimentation mainly occurs in water. Suspended solids (SS) in the water settle down on the bottom of the water body due to gravitation and these SS can serve as an adsorbent for the various chemicals and then facilitate the transportation of them to the soil at the bottom of the water body *(Seinfeld J.H. and Pandis S.N., 2006)*.

- **Re-suspension**

  This is the reverse process where the chemicals are released into the water body from the suspended solids *(Seinfeld J.H. and Pandis S.N., 2006)*.

- **Particles and charge (or ion) exchange**

  This is the exchange between the particle phase and charged (or ionic) phase of chemicals. This process can occur within the same environmental media (Intra media exchanges) or between different environmental media (Inter media exchanges).

Inter media exchanges

As an example for inter media exchanges, deposition of chemical particles in the atmosphere on the soil or on the surface water can be shown. Adsorption of chemical particles in the water body, to the suspended solids and also the deposition of chemical particles on the bottom soil of water body, can represent inter media exchanges.

Intra media exchanges

When the exchanges of chemical particles or charged (or ions) occur within the same media, it can be shown as intra media exchanges. For an example, this phenomenon occurs in the atmospheres between the upper mixing and the lower mixing layer. This mechanism allows the gases or particle phase atmospheric chemicals to be exchanged between these two layers but within the same environmental medium of atmosphere.

Another example is the chemical exchanges between suspended solids (SS) and water. Suspended solids are covered with a thin layer of water adjacent to it. Chemical exchanges happen through this thin aqueous layer between water and suspended solids due to molecular diffusions and charge attraction where these exchanges occur within the same environmental medium.

In the soil and sediment, similar exchanges occur and they were mathematically interpreted in the OBMM.

2.1.2 Model variables, equations, and chemical parameters

Based on the chemical phenomena explained in the section 2.1.1, several variables were considered in developing the main equation of the OBMM and they are listed below:

(I) Emission of chemicals to the atmosphere, soil, and water environments.

(II) Degradation of chemicals in all four environmental media.

(III) Transport of chemicals by advection in atmosphere.

(IV) Dry and wet deposition of chemicals in atmosphere.

(V) Sedimentation and re-suspension of chemicals in water.

(VI) Exchanges of particle phase/ charged phase/ ionic phase of chemicals in/ between environmental media.

The main equation of OBMM interprets that the concentration of a particular chemical at a particular environmental media at a particular time can be calculated by the summation of the emission flux, degradation flux, advection flux, sedimentation/deposition flux, and the mass transfer flux between different environmental media at equilibrium. Equation 2.1 expresses the main equation of the mass balance for a particular chemical pollutant (Ex. Chemical name = "**A**").

$$dM_{(\mathbf{A})_i} / dt = \sum_{j=1}^{MN} f_{eq\_i,j} + f_{emi\_i} + f_{ad\_i} + \sum_{j=1}^{MN} f_{dprs\_i,j} + \sum_{j=1}^{MN} f_{deg\_i,j} \quad (2.1)$$

Where ***i, j*** is the environmental media, ***MN*** the number of media, $M_{(a)i}$ the gross mass of **A** in media ***i*** (mol), f_{eq_ij} the mass transfer flux of **A** at equilibrium (mol s^{-1}), f_{emi} the emission flux of **A** (mol s^{-1}), f_{ad} the advection flux of **A** (mol s^{-1}), f_{dprs} is the deposition flux of A while f_{deg} is the degradation flux of **A**. In formulating the OBMM, it was necessary to set the variables. In these expressions, the gross mass of a particular chemical pollutant (e.g., chemical pollutant "**A**") in each media was defined in M (mol), and the following eight variable numbers were set:

- **a)** Mptu (mol): gross mass of **A** **(Particle Phase)** in the upper atmosphere
- **b)** Mptd (mol): gross mass of **A** **(Particle Phase)** in the lower atmosphere
- **c)** Mslpt (mol): gross mass of **A** **(Particle Phase)** in soil
- **d)** Msllq (mol): gross mass of **A** **(Charged/Ionic Phase)** in soil
- **e)** Mwtpt (mol): gross mass of **A** **(Particle Phase)** in water
- **f)** Mwtlq (mol): gross mass of **A** **(Charged/Ionic Phase)** in water
- **g)** Msdpt (mol): gross mass of **A** **(Particle Phase)** in sediment
- **h)** Msdlq (mol): gross mass of **A** **(Charged/Ionic Phase)** in sediment

a) Mptu (mol): gross mass of A $_{\text{(Particle Phase)}}$ in the upper atmosphere

The following three chemical phenomena occur in the upper atmospheric layer: advection, wet deposition on soil and wet deposition on water.

$$dMptu/dt = +Qar(Cptin - Cptu) - Cptu * Vptwd * Ssl - Cptu * Vptwd * Swt \tag{2.2}$$

b) Mptu (mol): gross mass of A $_{\text{(Particle Phase)}}$ in lower atmosphere

The following four chemical phenomena occur in the lower atmospheric layer: advection, emission, dry and wet deposition on soil, and dry and wet deposition on water.

$$\begin{aligned} dMptd/dt = {} & +Qar(Cptin - Cptd) + Gar - Cptd * (Vptdd + Vptwd) * Ssl \\ & - Cptd * (Vptdd + Vptwd) * Swt \end{aligned} \tag{2.3}$$

c) Mslpt (mol): gross mass of A $_{\text{(Particle Phase)}}$ in soil

The following five chemical phenomena occur in soil: dry deposition from the upper atmosphere, dry and wet deposition from the lower atmosphere, emission, elution into liquids in soil and erosion.

$$\begin{aligned} dMslpt/dt = {} & Cptu * Vptdd + Cptd * (Vptdd + Vptwt) * Ssl + Gsl \\ & - Ksl * Mslpt * (Cwtsat - Csllq/Sitsl) - Mslpt * Rosl * ((1 - Esl) * Hsl) \end{aligned} \tag{2.4}$$

d) Msllq (mol): gross mass of A $_{\text{(Charged/Ionic Phase)}}$ in soil

The following three chemical phenomena occur in soil: elution from the particle phase into the soil, diffusion of charged /ionic phase chemicals in unconfined aquifers, and leaching of adsorbed charged / ionic phase chemicals onto soil particles.

$$\begin{aligned} dMsllq/dt = {} & Ksl * Mslpt * (Cslst - Csllq/Sitsl) - CsllqD * (Rof + Rosl * Sitsl/1 - Esl) * Ssl \\ & - Sca * CsllqD * Casl/Casllq * Rosl * Rsl * Ssl \end{aligned} \tag{2.5}$$

Mwtpt (mol): gross mass of A (Particle Phase) in water

The following seven chemical phenomena occur in water: dry deposition from the upper atmosphere, dry and wet deposition from the lower atmosphere, erosion, emission, outflow from the river mouth, elution into the water, and sedimentation. However, deposition from the atmosphere to Lake Biwa is excluded.

$$\begin{aligned} {dMwtpt}/{dt} &= Cptu*Vptdd + Cptd*(Vptdd+Vptwd)*Srv + Msl*Rsl*((1-Esl)*Hsl) \\ &\quad + Gss - Qwt*Css - Kss*Mss*(Cwtsat - Cwt) - Vssdep*{Mss}/{Hwt} \end{aligned} \tag{2.6}$$

e) Mwtlq (mol): gross mass of A (Charged/Ionic Phase) in water

The following eight chemical phenomena occur in water: diffusion of charged/ionic phase chemicals in unconfined aquifer, adsorption of charged/ionic phase chemical onto soil, elution of charged/ionic phase chemical from the liquid to the particle phase in water, emission, outflow from the river mouth, sedimentation of charged/ionic phase chemical in water, diffusion of charged/ionic phase chemical into the sediment, inflow of charged/ionic phase chemical to the ground from surface water (river & lake).

$$\begin{aligned} {dMwtlq}/{dt} &= CsllqD*(Rof + Rosl*{Sitsl}/{1-Esl})*Ssl \\ &\quad + (Sca*CsllqD*{Casl}/{Casllq}*Rosl*Rsl*Ssl)*Rss \\ &\quad + Kss*Mss*(Cwtsat - Cwt) + Gwtlq - Qwt*Cwtlq \\ &\quad - Vssdep*CwtD*Sca*{Cass}/{Cawt}*scss*Rsl*Srv \\ &\quad - Kwtsd*(CwtD - CsdlqD)*Srv - CwtD*DHsd*Sitsd*Srv \end{aligned} \tag{2.7}$$

f) Msdpt (mol): gross mass of A (Particle Phase) in sediment

The following two chemical phenomena occur in sediment: sedimentation of chemical pollutants with suspended solids, elution of chemical pollutants into the liquid phase in the sediment.

$${dMsdpt}/{dt} = Vssdep*{Mss}/{Hwt} - Ksd*Msdpt*(Cwtsat - Csdlq) \tag{2.8}$$

g) Msdlq (mol): gross mass of A (Charged/ Ionic Phase) in sediment

The following three chemical phenomena occurred in sediment: sedimentation of charged/ ionic phase chemicals in surface water (river & lake), diffusion of charged/ ionic phase chemicals from the water, inflow of charged/ ionic phase chemical to the ground from surface water (river & lake).

$$\begin{aligned} dMsdlq/dt &= Vssdep * CwtD * Sca * Cass/Cawt * scss * Rsl * Srv + Kwtsd\,(CwtD - CsdlqD) * Srv \\ &+ Cwt * DHsd * Sitsd * Srv + Ksd * Msdpt * (Cwtsat - Csdlq) \end{aligned} \tag{2.9}$$

Parameters and the abbreviations used in these equations are provided in the **Appendix 01.** For these OBMM calculations several chemical parameters per respective chemicals were required and the **Table 2.1** summarizes those parameters.

Table 2.1 Chemical properties required for the OBMM calculations.

Chemical Property	**Units**
Molecular Weight	Da
Henry`s Coefficient	atm m^3 mol^{-1}
Vapor Pressure	atm
Distribution Coefficient	log (POW)
Dissolution Coefficient	g L^{-1}
Diffusion Coefficient (Atmosphere)	m^2 s^{-1}
Diffusion Coefficient (Water)	m^2 s^{-1}
Half-life (Atmosphere)	hours
Half-life (Soil)	hours
Half-life (Water)	hours
Half-life (Sediment)	hours

2.2 Distributed multimedia model

Distributed multimedia model (DMM) is a mathematical model which was developed to interpret the spatial distribution of different chemicals in four different environmental media of the atmosphere, soil, water, and the sediment. In the DMM, the study site (LBYRB) was study site was divided into a grid of 1 km x 1 km as shown in the **Fig. 2.2** and each of these grids were considered as a three-dimensional compartments which interact with the adjacent compartments as explained in the **Fig. 2.2.** These compartments are composed of environmental media of the atmosphere, water, soil, and sediments and chemical phenomena previously explained under the

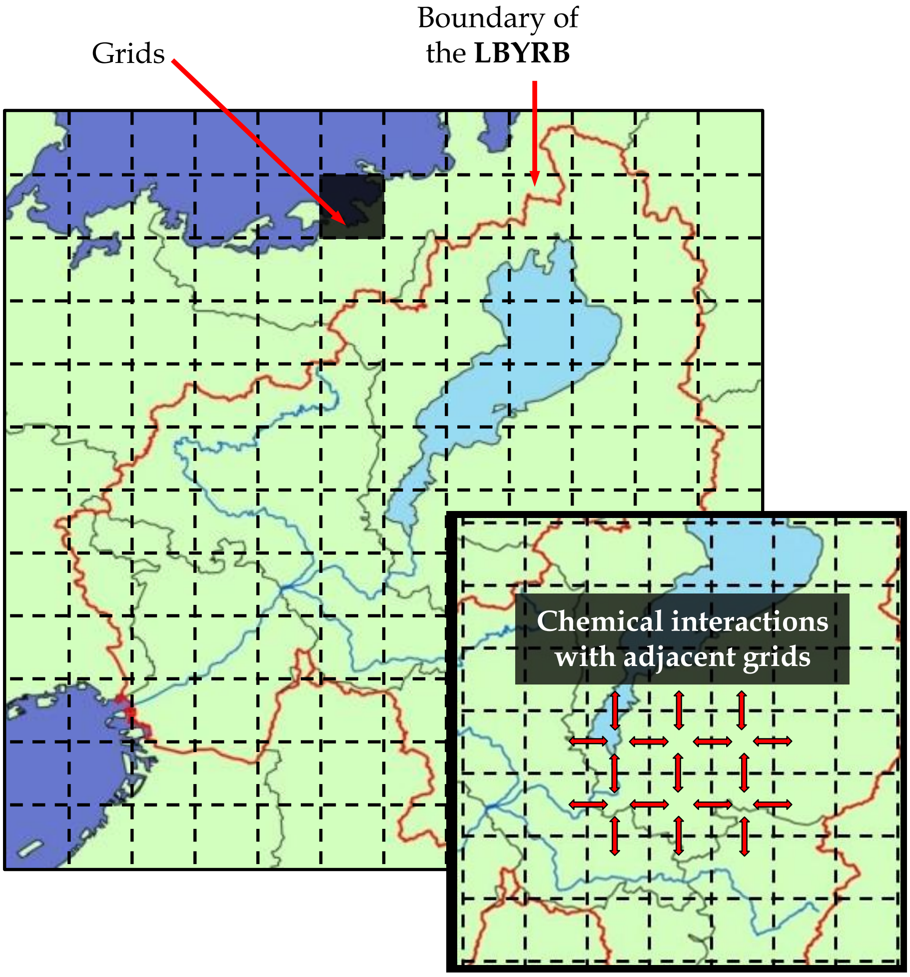


Fig. 2.2 Diagram of the grid arrangement in the LBYRB for DMM and the chemical interactions between adjacent grids.

section 2.1.1, are occurring in each of the compartment with the addition of transport of chemicals into the compartments and they move out from one compartment to the other. This is represented in the **Fig. 2.3** as inflow and outflow together with the diagrammatic explanation of the grid arrangement, environmental media, and the chemical phenomena considered in the DMM.

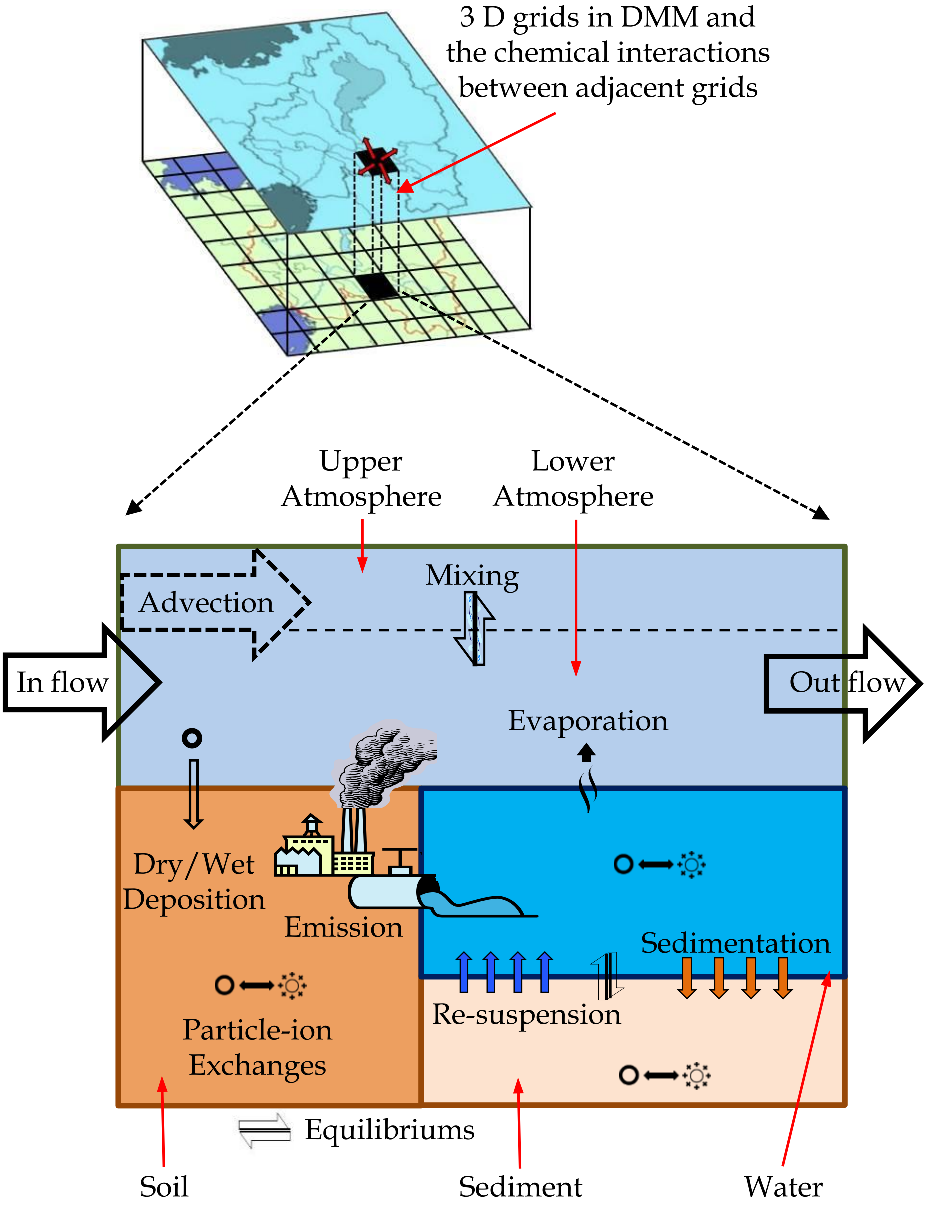


Fig. 2.3 Diagrammatic explanation of DMM with the grid arrangement, environmental media, and the chemical phenomena considered in DMM.

Chemical phenomena explained in the section 2.1.1 including the inflows and out flows of chemicals in/between the compartments are mathematically interpreted using a computer code in FORTRAN and DMM was constructed with the conditions of:

- The chemicals concerned in the calculations observe the mass conservation principles.
- The chemicals concerned in the calculations are in perfect mixing within the environmental media and between the environmental media they are in non-equilibrium state.
- Chemical transfer fluxes are considered between the adjacent compartments.

When the input data of annual emission data related to each of these compartments and the values for the chemical parameters of a particular chemical pollutant, are fed into the DMM together with the values for model parameters, it can calculate the concentrations of the particular chemical pollutant in any of the above mentioned environmental media at a given time for each of the grids. Thus the spatial distribution and the concentration levels of a certain chemical can be obtained by DMM simulations.

Chemical phenomena and the equations related to DMM are similar to that of OBMM; therefore the details can be referred from the previous section 2.1.1.

References

1 Seinfeld J.H. and Pandis S.N., 2006. Atmospheric Chemistry and Physics: From Air Pollution to Climate Change. John Wiley & Sons, Inc., New Jersey.

2 Kondo A., Yamamoto M., Inoue Y., and Ariyadasa B.H.A.K.T., 2013. Evaluation of lead concentration by one-box type multimedia model in Lake Biwa-Yodo River basin of Japan. *Chemosphere,* 92, 497-50.

EVALUATION OF LEAD & MERCURY CONCENTRATION BY ONE-BOX MULTIMEDIA MODEL

3

3.1 Introduction
3.2 Objectives
3.3 Methodology
  3.3.1 Emission data calculation
  3.3.2 OBMM simulation
3.4 Results and Discussion
3.5 Conclusions

Lead (Pb) and Mercury (Hg) are two of the metallic pollutants that have been emitted to the environment along with many anthropogenic activities. Both these metallic pollutants are well known for their adverse effects on the environment and on human health. Therefore they have obtained enough attention from the environmentalist, scientists, and authorities that have even led to the legislation of various mitigations processes to limit their emissions.

Due to its physical properties such as low melting point and easy processbility, Pb has been one of the first metals mankind ever used. At present, Pb is widely used for industries such as soldering and production of 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 *(International Lead and Zinc Study Group Report, 2014)*. In developing countries, recycling of electronic waste has been reported as another main contamination source of lead into the environment *(Guo et al., 2009 and Nguyen et al., 2009)*. Lead poisoning due to its hazardous properties has historically been reported such as the cases of anemia, the encephalopathy, arthritis, and muscular depression *(Aung et al.,2004)*. Based on these health hazards the consumption of lead was completely prohibited by Restriction of the Use of certain Hazardous Substances in Electrical and Electronic Equipment (RoHS) in Europe in 2003 *(European Commission Environmental Report, 2008)*. 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 and after the incident, use of leaded gasoline was restricted immediately. At present, the encephalopathy and anemia by acute exposure of the high concentration becomes rare due to the improved working environments and as the result, recent focus has shifted to the influence on the human health by chronic exposure to the low concentration of Pb. Japanese emission standards for Pb from industrial chimneys are set to be 10-30 mg Nm^{-3} *(Center of Chiba Pharmaceutical Association, 2008)*, while the air quality standards set by USEPA is less than 0.15 μg m^{-3} (*USEPA website, 2013*). According to the Japanese Ministry of Environment, the environmental quality standard for lead is 0.01 mg L^{-1} in water body, ground water, and soil *(Japanese Ministry of Environment, 1994)*. Average lead concentrations in Japan were reported as 2.1 x 10^{-7} mg m^{-3} in atmosphere, 13.2 mg kg^{-1} in soil, 5.0 x 10^{-3} mg L^{-1} in water bodies, and 3.5 mg kg^{-1} in sediments *(Yamamoto et al., 2011)*. Lead was registered as one of the first target chemicals in the PRTR system. Even though the averaged lead concentrations in Japan seem to be lower than the environmental standards, the risk still stand that in certain cases its concentration in the environment exceeds Japanese environmental standards *(Aung et al., 2004).*

Similarly, Hg has been used in various industries, as catalysts, fertilizers, pharmaceuticals (inorganic chemicals), machinery, batteries, medical supplies (amalgam), explosives (gun powder), and paints *(Kida, 2012 and Takahashi et al., 2008)*. Serious environmental and health damage had caused in Japan by Hg in the past. In 1956, a disease caused by methyl mercury poisoning was discovered in the Minamata city, which is located in the southwest region of Japan's Kyushu Island; this disease was later named Minamata disease *(Harada, 1995)*. More over Hg is responsible for the adverse health effects such as carcinogenicity, child developmental defects, and toxic effects on nervous, digestive, and immune systems *(Mercury and health, 2013).* Consumption and release of Hg has been legally controlled in Japan since 1973 *(Lessons from Minamata Disease and mercury Management in Japan, 2011)*, but still, many industries consume Hg in their production processes; thus, Hg appears in the environmental analysis data *(Sakata and Marumoto, 2005)*. The Japanese Ministry of Environment has set the environmental standards for the Hg concentration in water and soil to be less than 0.5 μg L^{-1} and for the alkyl mercury limit to be less than the detection limits (*Ministry of the Environment, Japan, 2014)*. In June 2013, a global treaty of The Minamata Convention on mercury was established and acknowledged by 96 countries (by February 2014) to protect human health and the environment from the adverse effects of Hg *(Minamata convention on mercury, 2013)*.

Therefore considering the environmental and health risk of these metallic pollutants possess, it was essential to study about their behavior and fate to have a better knowledge how to manage the pollution that might happen due to these metallic pollutants of Pb and Hg. Environmental monitoring is performed to fulfil this necessity but considering the long range dispersion of these metallic pollutants through various environmental transport mechanisms and large scale of the geographic regions, environmental monitoring is not a very practical process to be perform by any governmental authority. To avoid this impracticality, information and prediction of the occurrences of these pollutants and their concentration trends are important.

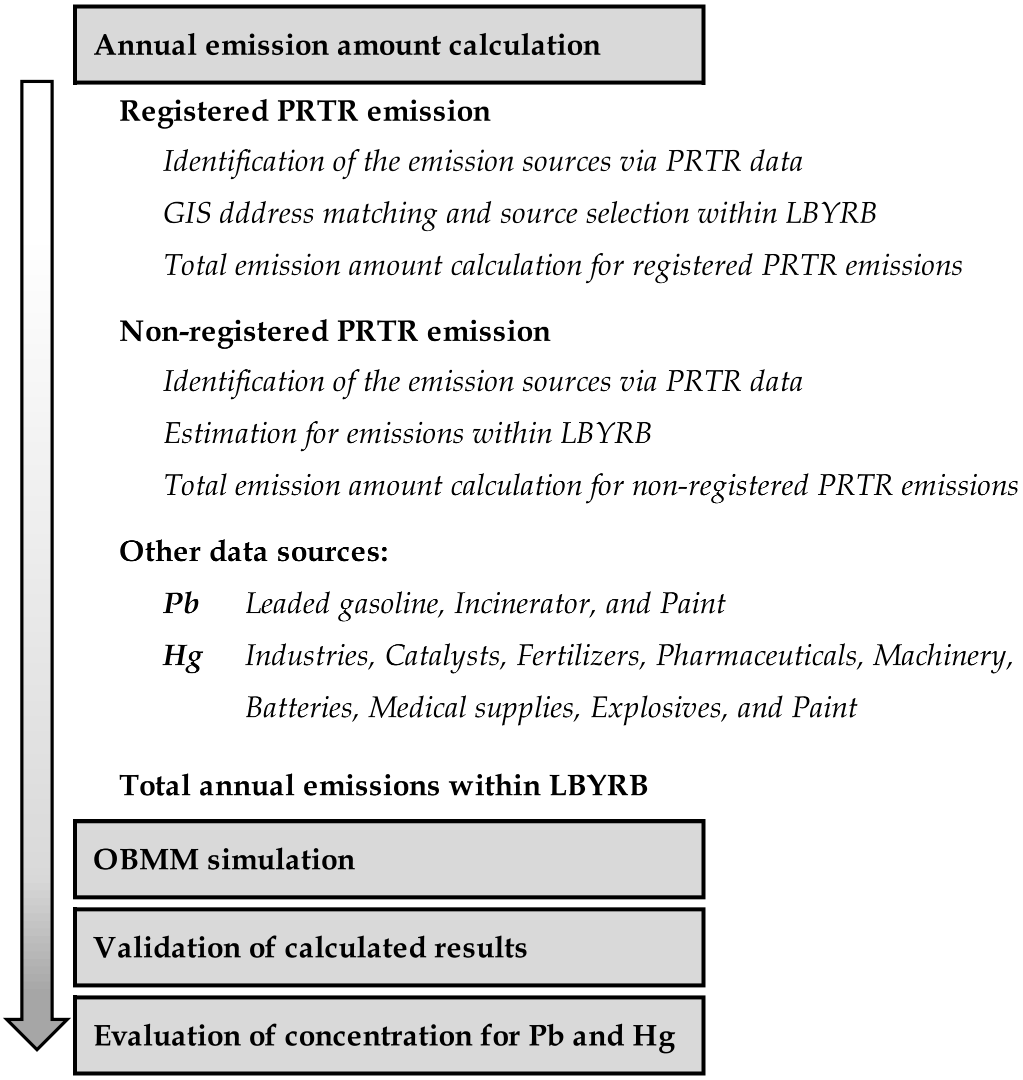
There are published studies of using computer models to simulate and predict certain chemical behaviors. Macay used a level Ⅲ multimedia model which based on fugacity was developed and applied to organic chemicals to evaluate their environmental behavior *(Mackay et al., 1985; Mackay and Paterson, 1991)*. In 1990, Meent used a level Ⅲ fugacity multimedia model, to evaluate lead transfers *(Meent, 1990)* and multimedia model based on mass balance equilibrium replacing the fugacity equilibrium, was developed by Kawashima to evaluate the concentrations of dioxins *(Kawashima et al., 2007)*. There are modeling studies ranging from modeling of macro-scale environmental issues such as global climate change to modeling of localized micro-scale environmental modeling assessments in the scientific literature. In 1983, Hansen published a study on efficient three-dimensional global models for climate studies: Models I and II provide the proof of the geographical macro-scale of these studies proving that atmospheric transportations can be mathematically modelled *(Hansen et al., 1983)*. In his review on the community multiscale air quality (CMAQ) modeling system, Byun describes the different components of chemical behaviors considered in air quality models *(Byun and Schere, 2006)*. However compared with many reported model applications to study the environmental risk by the organic compounds, there is few reported model application on metallic compounds or on metals. Even though the studies on metallic pollutants were few, these studies showed the possibility of simulating the environmental behavior and fate of the metallic pollutants. Our research group published the research work in which a computational model of OBMM, which can combine all of the environmental media of the atmosphere, water, soil, and sediment, was developed and the available consumption and emission data of Pb were used to simulate their concentrations in the LBYRB *(Kondo et al., 2013)*. In this section of the thesis, the evaluation of concentrations of both Pb and Hg is reported.

3.2 Objectives

The main objective of this section in the thesis study was to evaluate the concentrations of the metallic pollutants of Pb and Hg in the LBYRB using OBMM simulations.

3.3 Methodology

Concentrations of Pb and Hg in the atmosphere, water, soil, and sediments in the LBYRB were calculated using an OBMM for a span of 45 years from 1960 to 2005. Estimated annual emissions of Pb and Hg within the LBYRB were separately used as the input data for separate OBMM simulations. The accuracy of the OBMM calculations was evaluated by comparing the calculated concentrations with the observed data of both Pb and Hg separately. Validated calculated concentrations were then analyzed for their concentration trends and environmental concentrations of Pb and Hg were evaluated according to the experimental flow described in **Fig. 3.1**. The study site of LBYRB and the major data sources; PRTR are described in the sections of 1.6 and 1.7 of this thesis and the details of the OBMM are explained in the section 2.1.



Annual emission amount calculation

Registered PRTR emission

Identification of the emission sources via PRTR data

GIS dddress matching and source selection within LBYRB

Total emission amount calculation for registered PRTR emissions

Non-registered PRTR emission

Identification of the emission sources via PRTR data

Estimation for emissions within LBYRB

Total emission amount calculation for non-registered PRTR emissions

Other data sources:

Pb *Leaded gasoline, Incinerator, and Paint*

Hg *Industries, Catalysts, Fertilizers, Pharmaceuticals, Machinery, Batteries, Medical supplies, Explosives, and Paint*

Total annual emissions within LBYRB

OBMM simulation

Validation of calculated results

Evaluation of concentration for Pb and Hg

Fig. 3.1 Summary of the methodology for evaluation of Pb and Hg concentration by OBMM.

3.3.1 Emission data calculation

3.3.1.1 Calculation of Pb emissions

The main emission of Pb into LBYRB was calculated for a span of 45 years from 1960 to 2005, based on five main data sources listed below.

1) Registered PRTR emissions
2) Non-registered PRTR emissions
3) Leaded gasoline
4) Incinerator
5) Landfills

1) Registered PRTR emissions

As described in the section 1.7 under the PRTR data, the reported amounts of Pb emitted to the environment and transported to other locations by the operational businesses or industries facilities are reported under the registered PRTR data *(PRTR Information Plaza, 2007)*. These data provide the locations of the emissions and address matching facility provided by the Center for Spatial Sciences of Tokyo University by using Geographic Information Systems (GIS) was used to locate the emissions within the LBYRB boundary *(Center for Spatial Information Science, Tokyo University, 2012)*. Emissions from the identified locations within the study site were summed to obtained total emission amounts of Pb from registered PRTR data.

2) Non-registered PRTR emissions

The non-registered emission amounts for Pb, which are divided into the emission amounts to the atmosphere, to the landfill, to the soil and to the water body, are summed together on prefecture base *(PRTR Information Plaza, 2007)*. The emission of Pb to landfills and soil were negligible. The emission amounts in LBYRB were estimated based on the population ratio of inside the study area to the total population of Hyogo, Osaka, Kyoto, Nara, Mie and Shiga prefectures.

3) Leaded gasoline

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. Emissions were estimated from the content rate of lead to gasoline and gasoline consumption (*Itagaki, 2007*).

4) Incinerator

Most lead particles emitted from incinerators are trapped as burned ash and finally buried. However, a portion of lead particles are emitted to the atmosphere though the stack which may not be mentioned in PRTR data. Therefore the emissions from incinerator were estimated in this study. 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 were not enough data about the installation of dust collectors, the emission from 1960 to 1975, it was assumed to be the same emissions as in 1976.

5) Paint

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. These emissions were included in the calculation of annual lead emissions.

Emissions of Pb from the above five sources were summed up and Total annual Pb emissions were estimated.

3.3.1.2 *Calculation of Hg emissions*

Annual emissions of Hg from 1960 to 2005 were calculated for the LBYRB based on the records of Hg consumption and PRTR data. These emission amounts calculations were performed for the three time periods depending on the data availability. From 1960 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 *(Kida, 2012 and Takahashi et al., 2008)*. From 1990 to 2000 there was no record of Hg emissions. From 2001, emissions of Hg were recorded in PRTR and therefore the Hg emissions from 2001 to 2005 were calculated based on the PRTR data *(PRTR Information Plaza, 2007)*. The averaged emissions from 2001 to 2005 were used to represent the Hg emissions from 1990 to 2000.

3.3.2 OBMM simulations

The calculated annual emission amounts for Pb and Hg from 1960 to 2005 were used as input data and computer simulations were carried out using OBMM to evaluate environmental concentrations of these two metals in all four environmental media separately. These calculations were performed based on the conditions of:

- The chemicals concerned in the calculations observe the mass conservation principles.
- The chemicals concerned in the calculations are in perfect mixing within the environmental media and between the environmental media they are in non-equilibrium state.

Time steps for these calculations were set to 6 minutes, and a series of differential equations (major equations are provided in the section 2.1.2) was solved using the Runge-Kutta technique by a computer program coded in FORTRAN. The calculated Pb and Hg concentrations were validated using the published observed data for the occurrence of Pb and Hg in the environment to evaluate the reliability of the OBMM calculations.

3.4 Results and Discussion

3.4.1 Evaluation of Pb

3.4.1.1 Emissions data calculation for Pb

Calculated annual emission amounts of Pb based on registered and non-registered PRTR emissions for the year 2005 are summarized in **Table 3.1** and according to these calculations nearly 3394 kg of Pb emissions were recorded for the year 2005. Calculated Pb emissions and the annual variation of the emissions by leaded gasoline from 1960 to 1990 are shown in **Fig. 3.2** where a distinctive decrease of Pb emission is visible after 1975 due to the changing of leaded gasoline to unleaded gasoline.

Table 3.1 Calculated Pb emissions.

Registered & Non-registered Pb emission in PRTR to each media (kg y^{-1})				
Industrial Activity	**Atms.**	**Water**	**Soil**	**Sedim.**
Registered lead emission in PRTR				
Nonferrous metal	111.0	2.2	-	2.0
Electromechanical apparatus	108.0	12.0	-	21.0
Metallic product manufacturing	101.0	-	-	7.0
Ceramic industry	48.0	0.5	-	16.0
Iron and steel industry	18.0	-	-	-
Chemical	13.0	4.2	-	-
Sewage line	-	1995.0	-	-
Domestic waste site	-	2.3	-	-
Industrial waste site	-	0.1	-	-
Registered lead emission in PRTR (Total)	**399.0**	**2016.3**	-	**46.0**
Non-registered lead emission in PRTR (Total)	**930.0**	**3.0**	-	-
Total lead emission	**1329.0**	**2019.3**	-	**46.0**

After 1987 the Pb emissions from gasoline become zero because all the gasoline consumption became unleaded in Japan. The variation of annual Pb emissions by incinerators from 1960 to 2005 is shown in **Fig. 3.3.** Since there were not enough data on emissions by incinerators from 1960 to 1975, the emissions were estimated to be equal to the emission in 1976. Installation of bag filters and electric-static precipitators to the incinerators is the reason for the decrease of Pb emissions after 1987. Emissions from paint from 1960 to 2005 are shown in **Fig 3.4** and the emission amounts increased throughout the time due to the increased consumption of paints used for construction work, structures, and road markings.

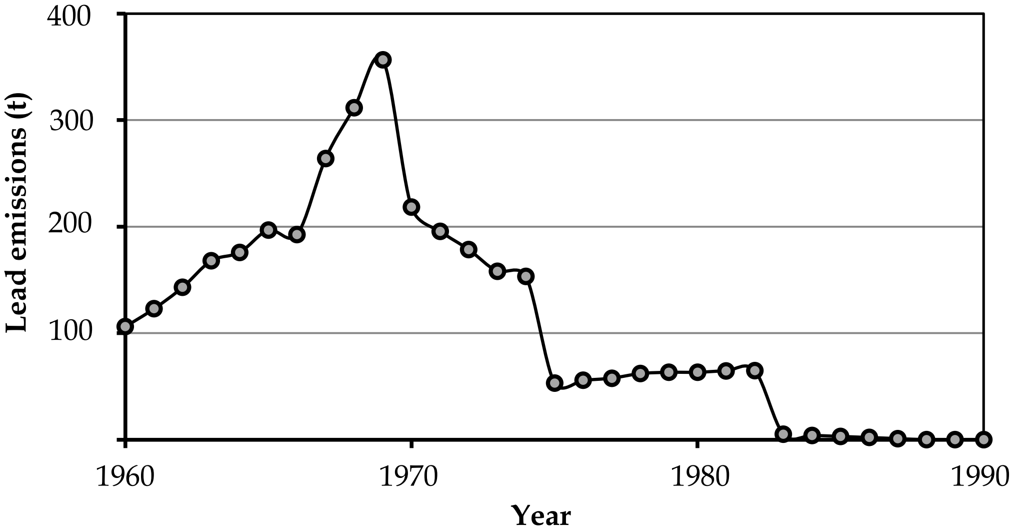


Fig. 3.2 Annual variation of Pb emissions to the environment by leaded gasoline from 1960 to 1990.

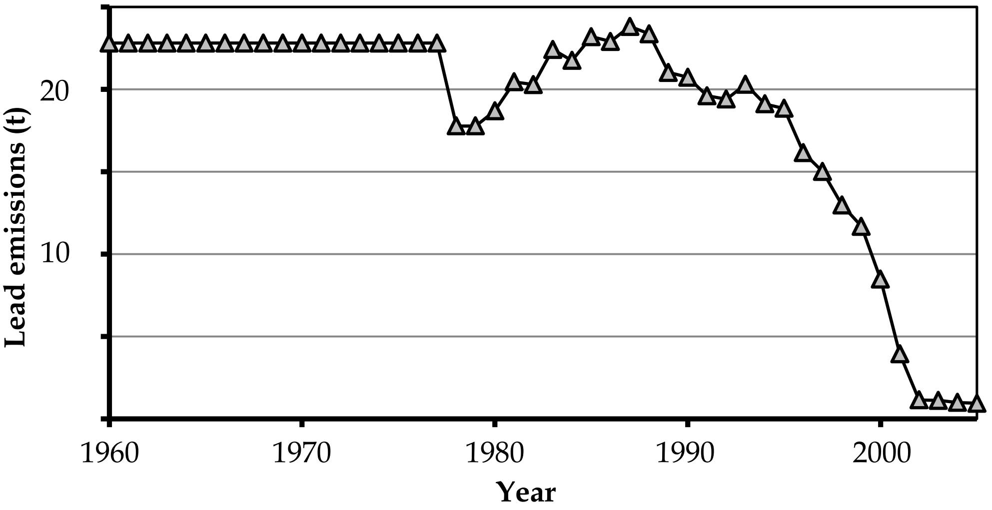


Fig. 3.3 Annual variation of Pb emissions to the environment by incinerators from 1960 to 2005.

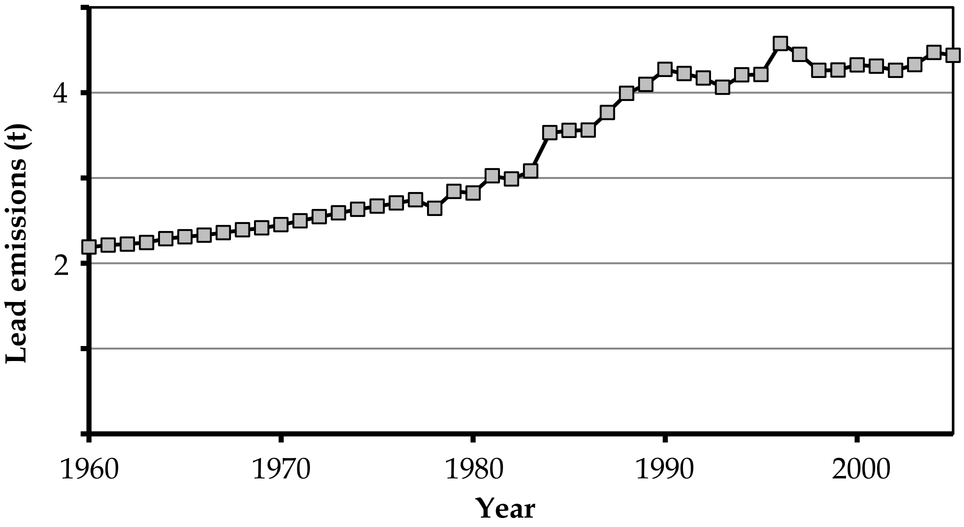


Fig. 3.4 Annual variation of Pb emissions to the environment by paints from 1960 to 2005.

3.4.1.2 OBMM simulations on Pb

The concentration of Pb in each media in LBYRB was calculated by using the OBMM. The annual variation of the concentration of Pb in each media from 1960 to 2005 is shown in **Fig. 3.5.** During this study span of 45 years, the atmospheric Pb concentrations varied from $2.9\text{x}10^{-6}$ to $2.0\text{x}10^{-3}$ μmol m^{-3}, while in water it varied from 2.1 to 3.8 μmol m^{-3}. In sediment and soil, the calculated Pb concentrations ranged from 4.0 to $5.1\text{x}10^{1}$ μmol kg^{-1} and 4.1 to $7.9\text{x}10^{1}$ μmol kg^{-1}, respectively. The concentration in the atmosphere showed two reductions during the study span. 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 emission control by the exchanging most of the electric-static precipitators used in incinerators to bag filter which performed better in capturing Pb from the exhausts. The concentrations in the water body had increased until 1975, but decreased once in 1975 due to the sudden decrease of the deposition from the atmosphere. The concentration in the sediment and in the soil showed slightly increasing tendency.

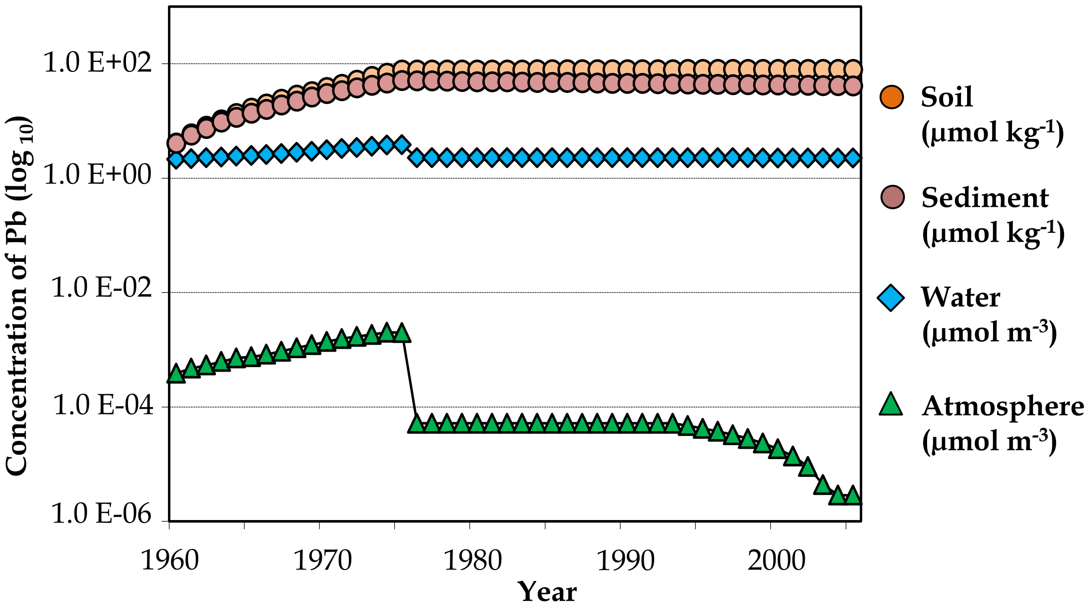


Fig. 3.5 Annual variation of calculated Pb concentration in each environmental media from 1960 to 2005.

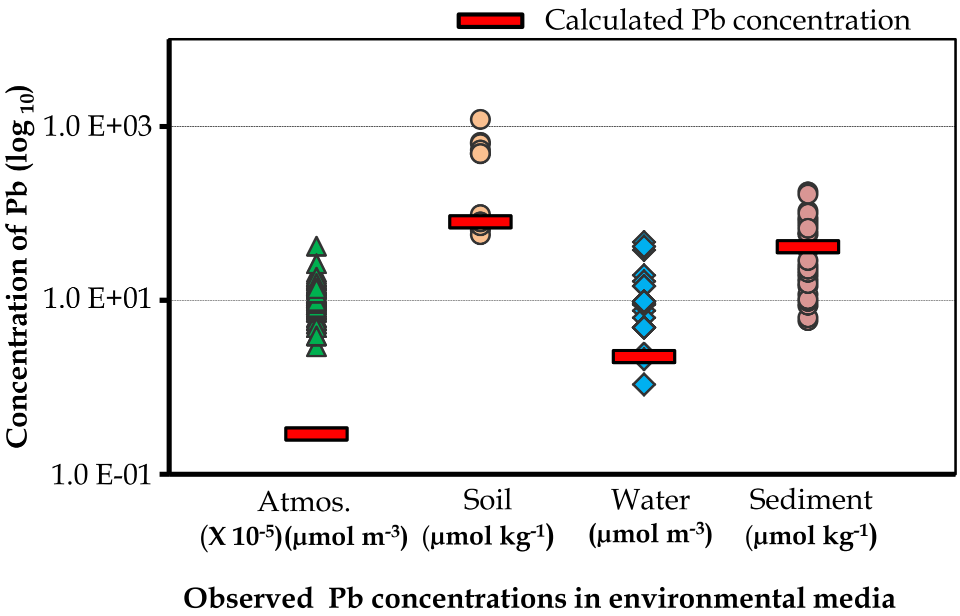


Fig. 3.6 Comparison of calculated Pb concentrations in all four environmental media with observed Pb concentrations for 2005.

The calculated concentrations by OBMM simulations were compared with the observed data published by the Osaka prefectural government research institute of environment, agriculture and fisheries *(Osaka Prefecture Government Research Institute of Environment, 2005)*. The comparison of calculated data and observed data for the year 2005 in the atmosphere, soil, water, and the sediment is shown in **Fig. 3.6**. The observed atmospheric Pb concentration was varying from $2.9\text{x}10^{-5}$ to $4.15\text{x}10^{-4}$ µmol m^{-3} while the calculated Pb concentration for 2005 was $2.9\text{x}10^{-6}$ µmol m^{-3}. The calculated concentration in the atmosphere was comparatively lower than the measured data for 2005. It was suggested that the cause for calculated atmospheric Pb concentration to be lower than the measured concentrations was the shortage of the emission calculations to the atmosphere. Also the observation stations are usually placed at the locations where the atmospheric Pb concentration is possible to be higher and thus the observed concentration might result a higher value. Calculated Pb concentration in the water for 2005 was 2.2 µmol m^{-3} where the observed Pb concentrations ranged from 1.0 to 46.5 µmol m^{-3}. In the soil, the observed Pb concentration for 2005 varied from 56.5 to 1200 µmol kg^{-1} while the calculated concentration was 79 µmol kg^{-1} and in sediment the calculated concentration was 41 µmol kg^{-1} which was within the observed concentration range of 5.8 to 176 µmol kg^{-1}. Therefore it was observed the calculated concentration in the sediment, the soil, and the water bodies closely agreed with the measured concentrations.

3.4.2 Evaluation of Hg

3.4.2.1 Emissions data calculation for Hg

Total emissions of Hg to the environment from 1960 to 2005 are shown in **Fig. 3.7.** Emissions of Hg have been controlled since 1973 and it explains the decreasing of Hg emissions after 1973. From 1990 to 2000 there was no record of Hg emissions. From 2001, emissions of Hg were recorded in PRTR and the Hg emissions under the registered PRTR emissions were zero from 2001. However, there are comparatively smaller Hg emissions recorded in the non-registered PRTR emissions category from industries having less than 20 employees and with less than 1 ton per year annual Hg consumptions from 2001 to 2005 *(PRTR Information Plaza, 2007)*. Thus, the average Hg emissions from 2001 to 2005 were used to represent the Hg emission from 1991 to 2000, as shown in **Fig. 3.7**

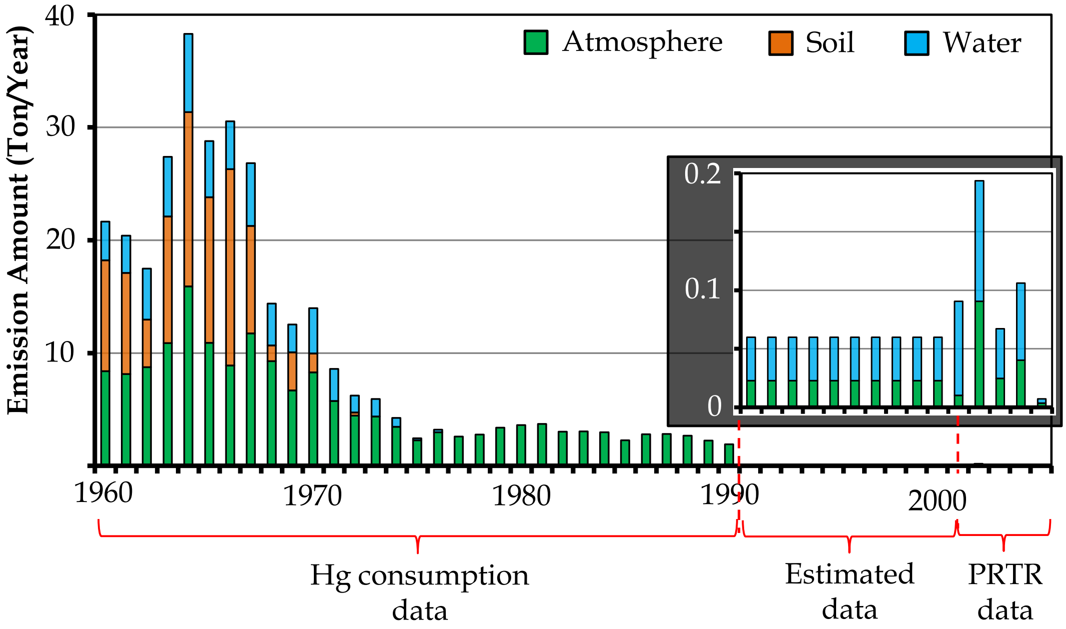


Fig. 3.7 Total emission of Hg to the environment from 1960 to 2005.

3.4.2.2 *OBMM simulations on Hg*

The concentration of Hg in each media in LBYRB was calculated by using the OBMM. The annual variation of the concentration of Hg in each media from 1960 to 2005 is shown in **Fig. 3.8.** During this study span of 45 years, the atmospheric Hg concentrations vary from 2.54×10^{-6} to 1.20×10^{-5} µmol m^{-3}, while in water it vary from 8.41×10^{-2} to 8.59×10^{-1} µmol m^{-3}. In sediment and soil, the calculated Hg concentrations range from 2.97×10^{-1} to 4.20 µmol kg^{-1} and 5.78×10^{-2} to 6.96×10^{-1} µmol kg^{-1}, respectively. According to the temporal concentration trends of Hg shown by the calculated results in **Fig. 3.8,** accumulation of Hg in the water, soil, and sediments can be seen until the 1970s; after that time, the concentrations became slightly decreasing due to the controlled Hg emissions. In the last 30 years of the study, the Hg concentrations in water showed a slight decrease and becoming 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 to the ocean. The slightly higher Hg concentration showed by the sediments proves this scenario. It was observed that with controlled Hg emissions, the concentrations of Hg in the water and soil are becoming constant. The atmospheric Hg concentration showed relatively small variations during the time span of this study.

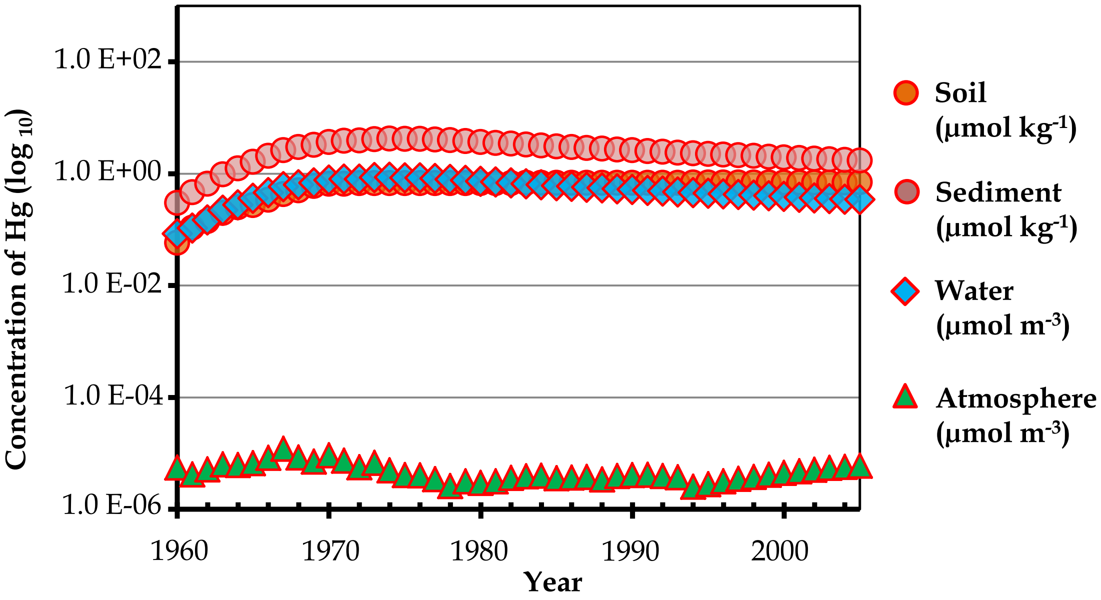


Fig. 3.8 Annual variation of calculated Hg concentration in each environmental media from 1960 to 2005.

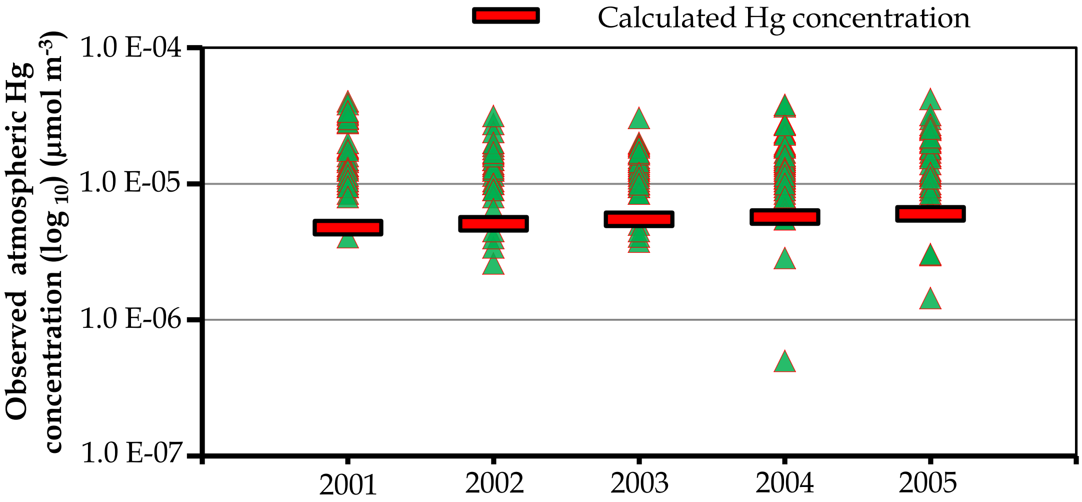


Fig. 3.9 Comparison of calculated Hg concentrations and observed atmospheric Hg concentrations from 2001 to 2005.

Henry`s coefficient is one of the vital chemical parameter in these calculations to represent the chemical transfer between atmosphere and water. Due to the higher complexity of Hg compounds and their reaction in atmosphere this coefficient was set similar to the value of Pb as representative values are given in the appendix 01 (*Lin and Pehkonen, 1998 and Schroeder and Munthe, 1998)*.

The lower accuracy of the estimation methods in the non-registered PRTR data and the long-range atmospheric transport of Hg from the Asian continent might have caused these variations (*Jaffe et al., 2005*) and the incensement of the atmospheric Hg concentration observed in the last five years can be due to the atmospheric influx from the East Asian region (*Shimizu et al., 2010*).

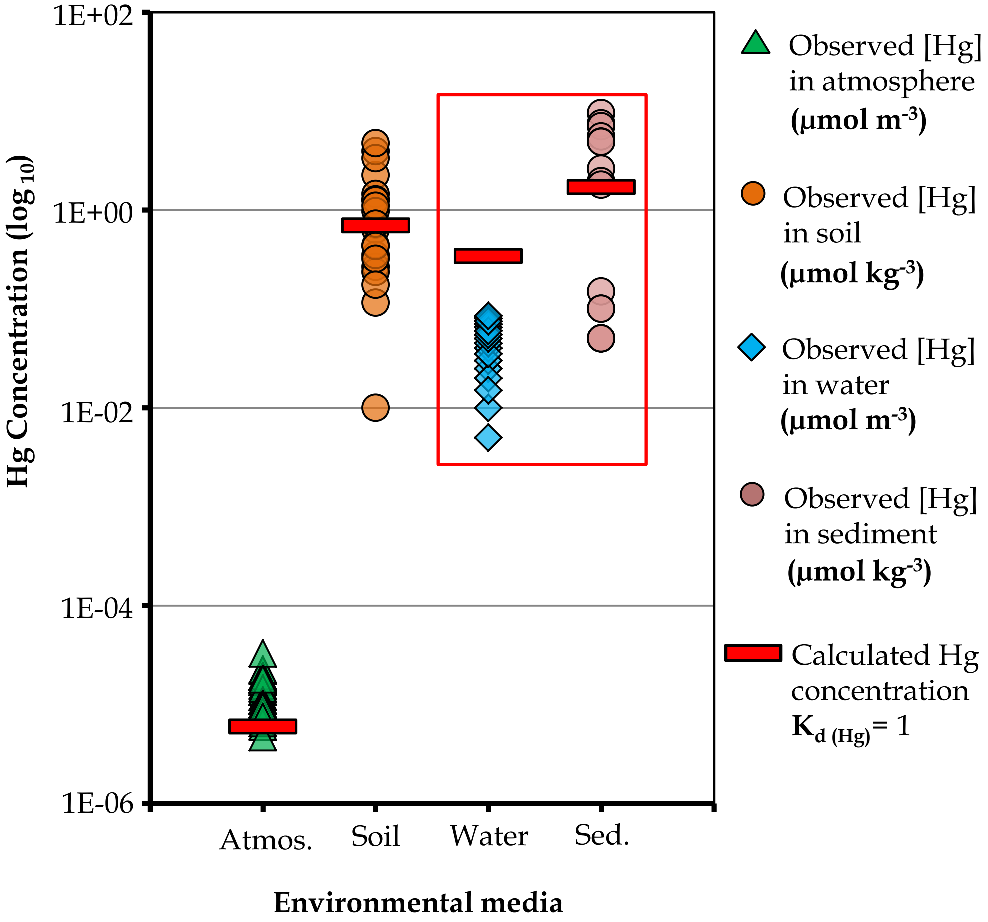


Fig. 3.10 Comparison of calculated Hg concentrations in all four environmental media with observed Hg concentrations for 2005.

Due to the strict management practices applied to the consumption and emission of Hg from the 1970s, a distinctive increase in the Hg concentrations in the environmental media is not visible except for relatively small variations in the atmospheric Hg concentrations. These calculated results were compared with the observed data for the environmental Hg concentrations as shown in **Fig. 3.9 and 3.10**. Calculated Hg concentrations from 2001 to 2005 are compared with the observed Hg concentrations in Osaka Prefecture in the **Fig 3.9** *(Osaka Prefectural Government, 2005)*. Calculated atmospheric Hg concentrations from 2001 to 2005 were within the observed atmospheric Hg concentrations for the Osaka area proving the OBMM calculations were reliable.

The comparison of the calculated Hg concentrations by the OBMM simulations for 2005 with the observed Hg concentrations in all four environmental media is shown by the **Fig. 3.10.** Calculated Hg concentrations in the atmosphere, soil, and sediments were within the range of observed Hg concentrations but the calculated Hg concentration for water was higher than the observed Hg concentration. Even the calculated Hg concentration for sediments was noted to be at the lower end of the observed Hg concentration range. This suggested the calculations of chemical transfers between water and sediments need to be improved and further studied are required to increase the reliability of the OBMM calculations.

Among the various chemical parameters involved in these OBMM calculations, water-sediment partition coefficient of these metals directly relates to the chemical transfers between water and sediment ($\mathbf{K_d}$) *(Ramamoorthy and Rust., 1978, Louis., 1979 and Yin et al., 1997)*. In these calculations, $\mathbf{K_d}$ value was set to one ($\mathbf{K_d=1}$)**.** Therefore it was suggested to experimentally evaluate the water-sediment partition coefficient of Hg (as the representative chemical) and section 4 of this thesis describes the experiments and the effect of the experimentally evaluated partition coefficient on the OBMM calculations.

3.5 Conclusions

The necessity of evaluating the concentrations of hazardous metallic pollutants in LBYRB was identified and Pb and Hg were selected as representative metallic pollutants. Nine chemical phenomena of these chemicals were considered to occur in four environmental media of the atmosphere, water, soil, and sediments and they were mathematically interpreted into an OBMM model. Using PRTR data and the other published emission data, the annual emission amounts of these two representative metals were calculated from 1960 to 2005. Calculated annual emission amounts were then used for separate OBMM simulations for a span of 45 years to evaluate the concentrations of Pb and Hg in all four environmental media. Calculated concentrations of Pb and Hg were studied for their concentration trends after validating the reliability of the calculated concentrations by comparing them with the observed Pb and Hg concentrations for the LBYRB. Calculated atmospheric concentrations for Pb showed a distinctive decrease after 1975 and by 2005 it reached to 2.9×10^{-6} µmol m^{-3} and Hg showed variations of the atmospheric Hg concentration from 2.54×10^{-6} to 1.20×10^{-5} µmol m^{-3} throughout the study span of 45 years. Accumulations of both these metals were observed in soil and sediments and their concentration in water were observed to be effected by the deposition of atmosphere. Except for the atmosphere, the calculated concentrations of both Pb and Hg were becoming constant for the last 25 years of the study span because of the controlled emissions. Among several chemical parameters that affect the chemical behavior of these metallic pollutants, water-sediment partition coefficient was suggested to be determined experimentally and to incorporate the experimentally evaluated values in OBMM in order to improve the reliability of the OBMM calculations to evaluate environmental concentrations of metallic pollutants.

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EXPERIMENTAL DETERMINATION OF CHEMICAL PARAMETERS IN OBMM AND SENSITIVITY ANALYSIS ON CHEMICAL PARAMETERS

4

4.1 Introduction

4.2 Objectives
4.3 Methodology
4.4 Results and Discussion
4.5 Conclusions

In the previous chapter of this thesis, evaluation of metallic pollutant concentrations in the atmosphere, water, soil, and the sediments by using OBMM simulations was discussed. Several chemical parameters related to the metallic pollutants' behavior, such as partition coefficient, dissolution coefficient, and diffusion coefficients, are important to interpret the behavior and fate of the metallic compounds *(Kondo et al., 2013, Khandakar et al., 2012, Brigham et al., 2009, and Lindstrom M., 2001)*. Hence, it was considered to experimentally determine of the values for possible chemical parameters and incorporate the values in the OBMM calculations in order to improve the sensitivity of the model.

Considering the adverse health effects posed by Hg such as carcinogenicity, child developmental defects, and toxic effects on nervous, digestive, and immune systems *(Mercury and health, 2013)* as well as Japanese history related to the Minamata disease caused by environmental Hg *(Harada, 1995)*, Hg was considered as a deserving pollutant for further studies of its behavior and fate in the environment. Results in the section 3.4.2.2 showed the tendency of Hg to accumulate in the soil and sediment, thus it is important to experimentally determine the water–sediment partition coefficient for Hg ($\mathbf{K_{d\ (Hg)}}$) and to evaluate the sensitivity of the OBMM on the experimentally determined $\mathbf{K_{d\ (Hg)}}$ value.

There are published research works on evaluating the partition coefficients of chemicals and Lee published his work on predicting soil-water coefficient for cadmium

(Lee et al., 1996) and United States Environmental Protection Agency published their work on partition coefficients for metals in surface water, soil, and waste in 2005 *(Allison and Allison, 2005)*. Since the $\mathbf{K_{d\ (Hg)}}$ value is greatly affected by the composition of the soil and sediments in the environment *(Yin et al., 1997)*, it was required to carry out experiments to evaluate the $\mathbf{K_{d\ (Hg)}}$ values for the soil and sediment samples collected from the study site of LBYRB. Referring to the scientific literature it was decided to carry out laboratory-scale batch-shaking experiments to determine the $\mathbf{K_{d\ (Hg)}}$ values, using soil samples collected from the LBYRB *(Ramamoorthy and Rust, 1978 and* Yin *et al., 1997)*. The experimentally determined $\mathbf{K_{d\ (Hg)}}$ value was incorporated into the OBMM calculations and simulations were performed for a time span of 45 years from 1960 to 2005 to evaluate Hg concentrations in the environment. The sensitivity of the OBMM calculations to the $\mathbf{K_{d\ (Hg)}}$ value was evaluated by comparing the observed data for Hg concentrations in water and sediments with the calculated concentrations based on the experimentally determined $\mathbf{K_{d\ (Hg)}}$ values obtained from other samples such as sediment and sand.

4.2 Objectives

The main objectives of this section in the thesis study was to experimentally determine the $\mathbf{K_{d\ (Hg)}}$ by using soil/sediment samples collected from the LBYRB and then to evaluate the sensitivity of OBMM simulations on $\mathbf{K_{d\ (Hg)}}$ when evaluating the environmental Hg concentration in the LBYRB.

4.3 Methodology

This section of the thesis study was carried out in two main parts. To determine the $\mathbf{K_{d\ (Hg)}}$ value, laboratory-scale batch experiments were carried out with soil/sediment samples collected from different geographic areas within the study site of LBYRB. Upon determining the $\mathbf{K_{d\ (Hg)}}$ with experiments, the values were incorporated into OBMM calculations and model simulations were performed to evaluate environmental Hg concentrations in the LBYRB. The model calculations were validated using published observed data for environmental Hg. Calculated environmental Hg concentrations based on representative $\mathbf{K_{d\ (Hg)}}$ values were compared with the observed data in order to evaluate the sensitivity of the OBMM on $K_{d\ (Hg)}$ value. Section 1.6 and 1.7 of the introduction of this thesis describe about the study site of LBYRB and the OBMM model used for the experiments.

4.3.1 Experimental determination of $K_{d\ (Hg)}$

4.3.1.1 Materials and equipment

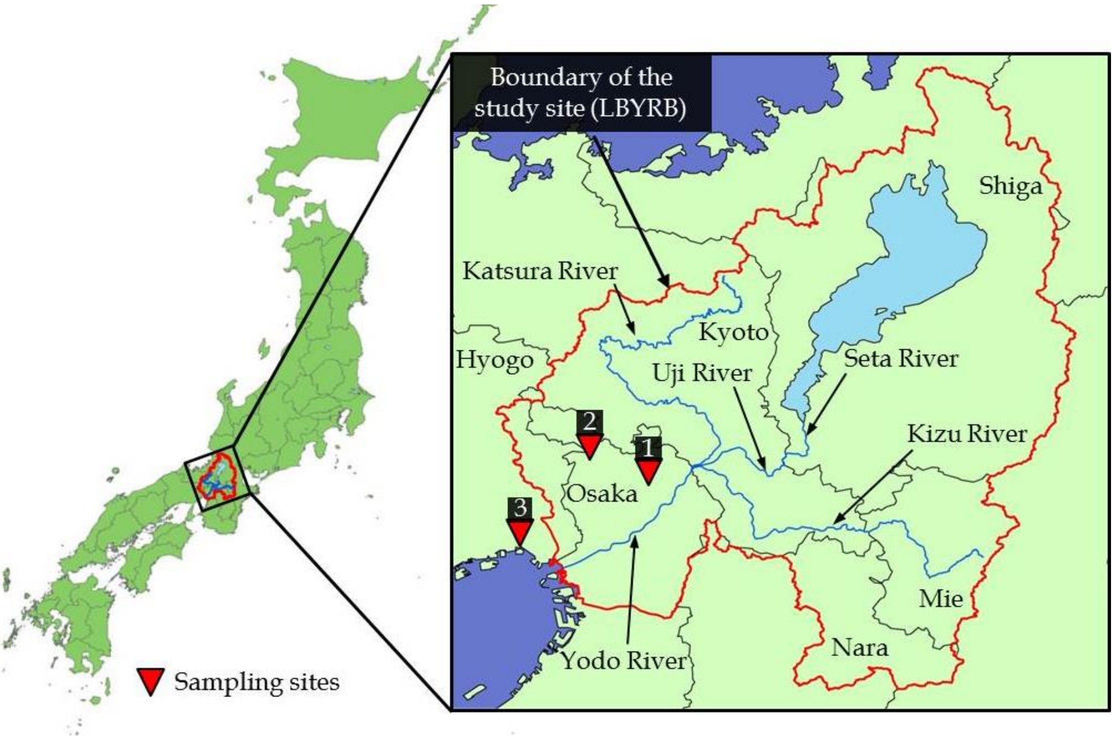

Fig. 4.1 Locations of the sampling sites in LBYRB.

A soil sample was collected from sample point 1, as shown in **Fig. 4.1**, for the experiments to determine the $K_{d\ (Hg)}$. Additionally sediment and sand samples were collected from sampling points 2 and 3 to study the $K_{d\ (Hg)}$ levels in different types of representative landmasses in the study area. The details of sampling and properties of the samples are given in **Table 4.1.**

Teflon containers were used to collect the samples, and 500 mL volume glass bottles were used for the shaking experiments. The temperature and pH of the collected samples were measured at the sampling points using a portable pH meter (SK-631PH Model by Sato Keiryoki MFG. Co., Ltd.). A Yamato DX302 drying oven

Table 4.1 Details of the sampling sites and the sample properties.

Sample properties		Sampling point 1	Sampling point 2	Sampling point 3
Location		Osaka University Suita City	Ina River Ikeda City	Ashiya Beach Ashiya City
Cordinates	N	34° 49.299'	34° 51.538'	34° 42.454'
	E	135° 31.364'	135° 24.066'	135° 18.613'
Samples collected		Ground soil (10 cm below surface)	River sediments (1 m from shore line)	Sea sediments (1 m from shore line)
		-	River water	Saline water
Sample Temperature (°C)		20 *26	26	23
pH		7.2 *7.1	7.8	8.2
Sample texture		Loam soil	Silt/ Clay	Fine sand

* Secondary evaluation

was used for drying the samples. Shaking experiments were performed with an Eyela NTS 4000 thermostat shaker. Chemical analysis of the concentration of Hg was performed at a certified chemical analysis facility (Teijin Eco Science Ltd., Japan) using Atomic Absorption Spectroscopy (AAS) with a Mercury Analyzer (RA-2A by Nippon Instruments Corporation) following Japanese industrial standards (*Japanese Industrial Standard, 2011 and Suzuki, 2004*). Vessels were cleaned before they were used for the sampling and shaking experiments using tap water and 0.1 mol L^{-1} hydrochloric acid (HCl) (purchased from Wako Pure Chemical Industries Ltd., Japan) and then with *Milli-Q* water (Millipore) to remove impurities. *Milli-Q* water was used in the control experiments, and a standard mercury solution ($HgCl_2$ in 0.1 mol L^{-1} .HNO_3 (Hg: 100 mg L^{-1})), purchased from Wako Pure Chemical Industries Ltd., Japan, was used for spiking.

4.3.1.2 Experimental setup

The experimental flow and the conditions applied in the determination of the $K_{d\,(Hg)}$ are shown in **Fig. 4.2**. A soil sample was collected and dried using a drying oven until the sample reached a constant dry weight. Then, it was sieved with a 2 mm x 2 mm mesh to remove larger debris. In the preliminary step, five sub-samples were prepared by adding 200 mL of *Milli-Q* water to 100 g of the soil in 500 mL glass bottles. Sub-samples were pretreated by shaking them on the shaker at 40 rpm for 1 hr at 25 °C temperature. After the pretreatment step, samples were spiked with 50, 100, 150, and 200 µL of standard Hg solution, as described in **Fig. 4.2**; the control sample was not spiked with Hg. The shaking experiment was carried out for 3 days continuously as a batch. Then, the sub-samples were removed from the shaker and transferred to Teijin Eco Science Ltd. for the chemical analysis of Hg in both aqueous and solid phases, following the Japanese Industrial Standard (JIS) Hg analysis methods *(Japanese Industrial Standard, 2011 and Suzuki, 2004)*.

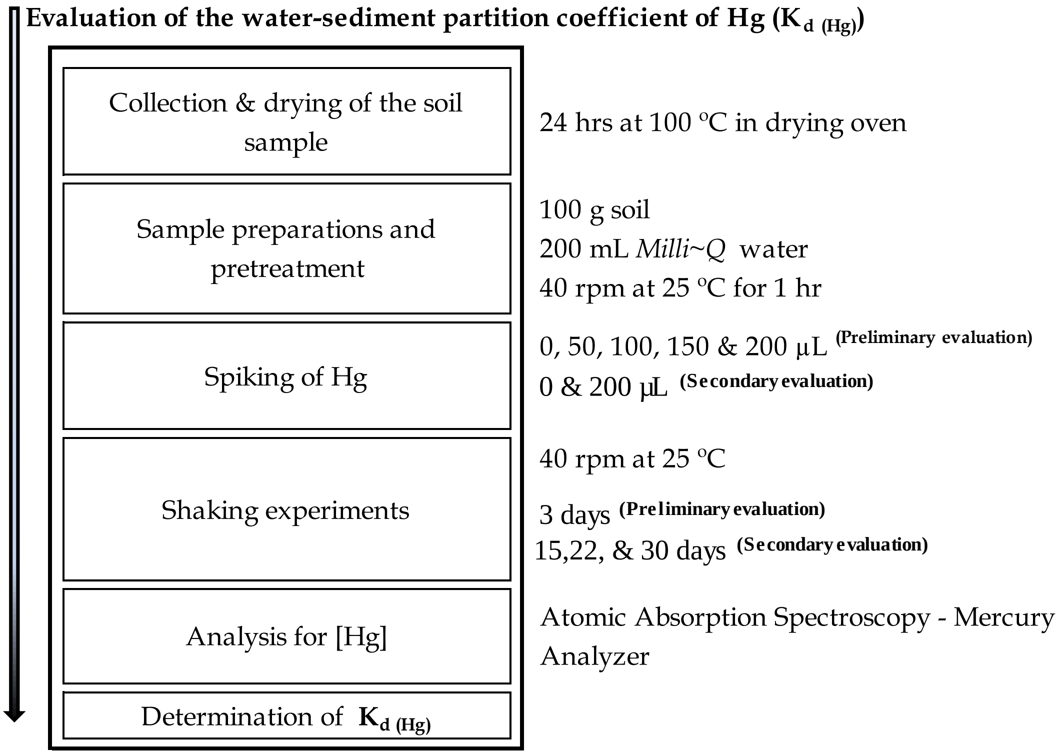

Fig. 4.2 Summary and the flow diagram of the experiment to determine $K_{d(Hg)}$.

$$\mathbf{Hg}_{\mathbf{(Water)}} \rightleftharpoons \mathbf{Hg}_{\mathbf{(Sediment)}}$$

$$\text{Water-sediment partition coefficient} \quad \mathbf{K_{d\,(Hg)}} = \frac{\text{Concentration of Hg in Sediment } \mathbf{[Hg]_{(Sediment)}}}{\text{Concentration of Hg in Water } \mathbf{[Hg]_{(Water)}}} \qquad (4.1)$$

Partition coefficients were calculated for each sub-sample, as shown in **equation 4.1**. The calculated $\mathbf{K_{d\,(Hg)}}$ values were plotted against the spiked Hg volume. After the preliminary evaluation, a secondary step was performed to confirm the results of the preliminary evaluation for longer shaking periods of 15, 22, and 30 days. A similar experimental procedure was performed when pretreating the four soil samples. The Hg spiked samples were added to the shaker in descending order of their shaking period. The control sample was added to the shaker without any spiking of Hg together with the 30-day sample, which was spiked with 200 μL of the standard Hg solution. Then, the shaking experiments for the secondary evaluation commenced. The experimental conditions were similar to the preliminary evaluation step. On the 8th day after starting the shaking experiment, the 22-day sample was added to the shaker after pretreatment followed by Hg spiking. Similarly the 15-day sample was added on the 15th day of shaking. After 30 days of shaking, the samples were collected and transferred to Teijin Eco Science Ltd. for the chemical analysis of Hg concentrations in both the aqueous and solid phases, following JIS Hg analysis methods *(Japanese Industrial Standard, 2011 and Suzuki, 2004)*. The partition coefficients **(**$\mathbf{K_{d\,(1)}}$ = 15 days of shaking, $\mathbf{K_{d\,(2)}}$ = 22 days of shaking, and $\mathbf{K_{d\,(3)}}$ = 30 days of shaking) were calculated using **eq. 4.1**, and the $\mathbf{K_{d\,(Hg)}}$ value to be incorporated in the OBMM calculations was decided.

To observe the variations in the $\mathbf{K_{d\,(Hg)}}$ in other environments with different soil types, samples were collected from sampling points 2 and 3, which represent sediment and sand. Experimental procedures similar to the preliminary evaluation were performed, and the representative $\mathbf{K_{d\,(Hg)}}$ values were calculated. These $\mathbf{K_{d\,(Hg)}}$ values were applied to the OBMM calculations at a later stage to evaluate the sensitivity of the OBMM to different $\mathbf{K_{d\,(Hg)}}$ values. Total organic carbon (TOC) was measured in all of the control samples according to the general rules for chemical analysis stated by the Japanese Industrial Standard Committee *(Japanese Industrial Standard, 2011)*.

4.3.1.3 Analysis of Hg concentration

Chemical analysis for Hg was carried out for the aqueous phase and solid phase separately. From the aqueous phase of the sub-samples, 50 mL was collected in conical flasks and 0.5 mL of 50% H_2SO_4 (aq), 60% HNO_3 (aq), 5% $KMnO_4$ (aq), and 5% $K_2S_2O_8$ (aq) was added. Then, the samples were heated to 95-100 °C on a hot plate for 2 hrs. After the samples cooled down, additional $KMnO_4$ (aq) was removed by adding $NH_2OH.HCl$ (aq) until the reddish-violet color faded, and the sample volumes were readjusted to 50 mL with distilled water. Then, 20 mL of the pretreated samples was combined with 1 mL of 50% H_2SO_4 (aq) and 10% $SnCl_2$ (aq). The concentrations of Hg were analyzed with the Hg Analyzer using the AAS technique.

For the solid phases (soil, sediment, and sand), 10 g of wet samples was measured in conical flasks, and 50 mL of distilled water was added to each sample, followed by 10 mL of 50% H_2SO_4 (aq), 60% HNO_3 (aq), and 0.5 mL of 5% $K_2S_2O_8$ (aq). Sufficient amounts of 5% $KMnO_4$ (aq) were added until the samples became a reddish-violet color. Samples were then heated to 95-100 °C for 2 hrs using a hot plate. After they cooled down, the additional $KMnO_4$ (aq) in the samples was removed by adding 5 mL of 10% CH_4N_2O (aq) and 20% $NH_2OH.HCl$ (aq) until the reddish-violet color faded. After filtering the samples with glass fiber filters, the volumes of the filtrates were adjusted to 100 mL with distilled water. Then, 20 mL of the filtrates was combined with 1 mL of 50% H_2SO_4 (aq) and 10% $SnCl_2$ (aq), and the concentrations of Hg were analyzed with the Hg Analyzer using the AAS technique. The air circulation was maintained at a 0.7 L min^{-1} flow rate, and the absorption wavelength was 253.7 nm for the analysis. Measured values were used to calculate the Hg concentrations in 200 mL of the aqueous phase and 100 g of the solid phase of the samples.

4.3.2 OBMM simulations and sensitivity analysis

For the OBMM simulation, calculation of annual emission amounts of Hg was required. As described in the previous section 3.4.2.1 of this thesis, annual emission amounts of Hg within LBYRB was calculated for a time span of 45 years from 1960 to 2005. The calculated annual emissions of Hg were then entered into the OBMM, and the calculations were performed to evaluate the concentration of Hg in all four environmental media. These calculations were performed based on the conditions that the Hg observes the mass conservation law in the environmental systems, and are in perfect mixing within the environmental media and between the environmental media they are in non-equilibrium state. Time steps for these calculations were set to 6 minutes, and a series of differential equations was solved using the Runge-Kutta technique by a computer program coded in FORTRAN. Calculations were carried out with the experimentally determined $\mathbf{K_{d\,(Hg)}}$ value for a time span of 45 years from 1960 to 2005. The calculated Hg concentrations were validated using the published observed data for the occurrence of Hg in the environment to evaluate the reliability of the OBMM calculations. Additional OBMM calculations were performed for the $\mathbf{K_{d\,(Hg)}}$ values obtained for the different samples of sediment and soil. The calculated concentrations based on different $\mathbf{K_{d\,(Hg)}}$ values were then compared with the observed data to study the sensitivity of the OBMM calculations to the $\mathbf{K_{d\,(Hg)}}$ values.

4.4 Results and Discussion

4.4.1 Determination of $\mathbf{K_{d(Hg)}}$

The initial pH and temperature measured at the sampling sites are given in **Table 4.1**. During the shaking experiments, the temperature was maintained at 25 °C to avoid temperature changes affecting the chemical behavior of Hg. Measurements of the TOC were taken in the control samples after the shaking experiments to investigate the amount of organic materials present in the samples because the adsorption-desorption processes of metals are affected by the presence of organic matter (*Ramamoorthy and Rust, 1978*). Among the three different samples studied, the soil-*Milli-Q* water (control) sample had the highest TOC measurement of 370 mg L^{-1}, sediment-*Milli-Q* water (control) sample had 23 mg L^{-1}, and the sand-*Milli-Q* water (control) sample had 9.9 mg L^{-1}.

Calculations of the $\mathbf{K_{d\,(Hg)}}$ between the aqueous and solid phases were interpreted by **eq. 4.1** *(Ramamoorthy and Rust, 1978 and Louis, 1979)*. These evaluations were carried out with the assumption that Hg will acquire equilibrium between the aqueous and solid phases of the sample after the shaking experiments and the evaporation of Hg into the air inside the glass bottles is negligible because of the low volume of air in the glass bottles and the low concentrations of Hg spiked. When deciding the range of the spiking dose for the preliminary evaluation, the following facts had to be considered. If the concentration in the sample is too low, then the forward reaction (adsorption) becomes slower, resulting in a prolonged shaking time for the system to reach equilibrium; the chemical analysis of Hg also becomes more difficult at lower concentrations (*Louis, 1979*). If the spiking dose is higher, then the solid phases of the samples might become saturated with Hg. Therefore, considering the reported occurrences of Hg in soil ranging from 2-900 $\mu g\ kg^{-1}$ (*Nakagawa, 2008*)**;** the range of the Hg spiking was set at 250-1000 $\mu L\ L^{-1}$ in the preliminary evaluation.

Figure 4.3 summarizes the results obtained from the shaking-batch experiments to evaluate the $\mathbf{K_{d\,(Hg)}}$. The concentrations of Hg in the aqueous and solid phases of the samples were used to calculate the $\mathbf{K_{d\,(Hg)}}$ values for each sub-sample. The calculated

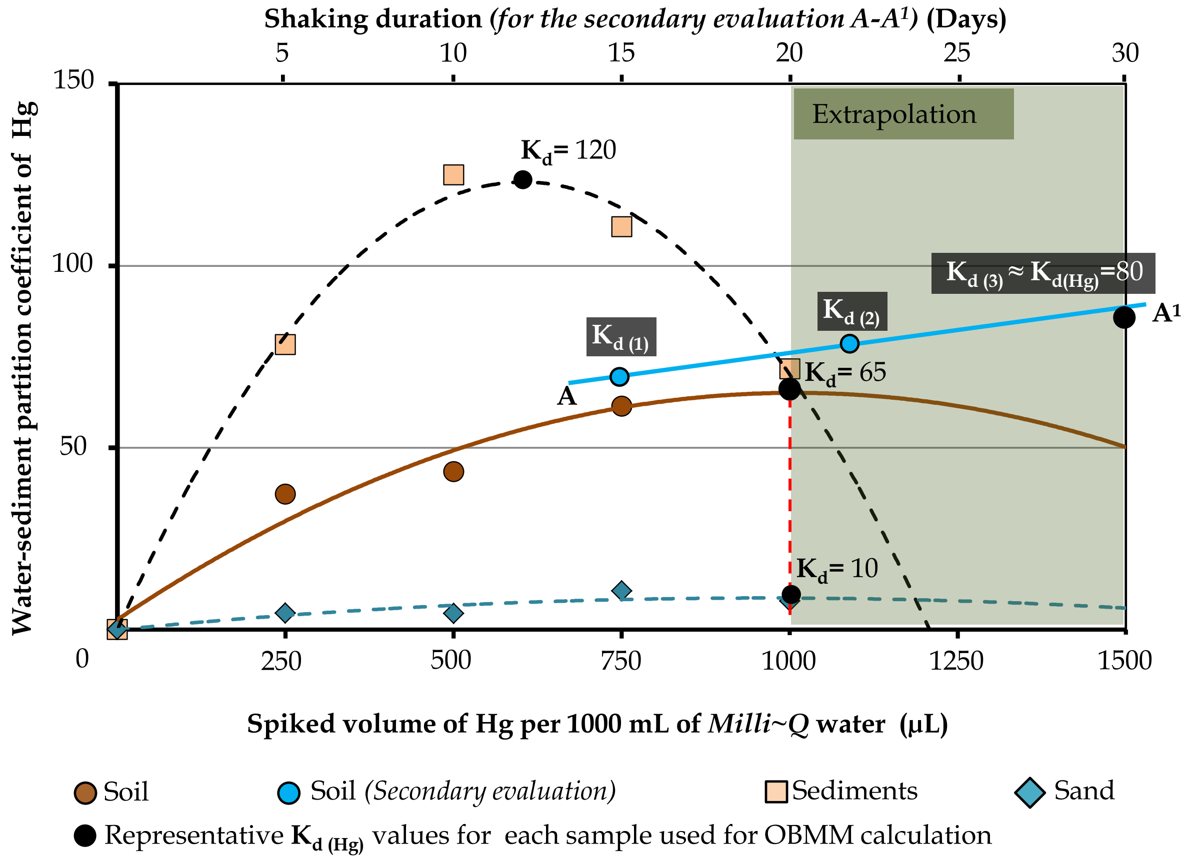

Fig. 4.3 Variation of the $\mathbf{K_{d\,(Hg)}}$ against the spiking dose of Hg to soil, sediment, and sand in the *Milli-Q* water systems. The variation of the $\mathbf{K_{d\,(1,\,2\,\&\,3)}}$ over the shaking duration for a 1000 $\mu L\ L^{-1}$ spiking dose.

$\mathbf{K_{d\,(Hg)}}$ values for the soil sample were plotted against the spiked volumes of Hg per 1 L of *Milli-Q* water, as shown in **Fig. 4.3**. Variations in the $\mathbf{K_{d\,(Hg)}}$ values were extrapolated with the best fitted second-order polynomial curve to observe the trend of the $\mathbf{K_{d\,(Hg)}}$ at higher spiking doses than 1000 μL L^{-1}. Similar trends have been reported in other publications on kinetics of Hg (Yin Y. et al., 1997).

Because the greatest portion of the LBYRB is composed of land, the soil sample was selected as the representative sample. After 3 days of shaking at 40 rpm, 36 μg kg^{-1} of Hg was detected in the control sample for soil, but the amount of Hg released to the *Milli-Q* water media from the soil was more than 250 times smaller, showing that the Hg already existing in the sample was hardly involved in the adsorption-desorption reaction. The loam texture of the soil and the presence of higher organic content results in the lower desorption of Hg from the soil (Yin Y. et al., 1997). At the 1000 μL L^{-1} spiking dose, the soil sample showed a maximum $\mathbf{K_{d\,(Hg)}}$ value of 65.8. Considering this result and the kinetics of the adsorption-desorption reactions, 1000 μL L^{-1} was chosen as the spiking dose to reduce the elongated time for Hg to reach equilibrium and to avoid saturating the solid phase (Yin Y. et al., 1997). Confirmative experiments were performed for shaking periods of 15, 22, and 30 days to evaluate the $\mathbf{K_{d\,(Hg)}}$ values for prolonged shaking periods. The experimental conditions applied in this step are shown in **Fig. 4.2** and the $\mathbf{K_{d\,(1\text{-}3)}}$ values were calculated from the Hg concentrations obtained from the chemical analysis of the soil and *Milli-Q* water samples. Line **A-A^1** of **Fig. 4.3** shows the variation in the $\mathbf{K_d}$ values versus the shaking periods of 15, 22, and 30 days, where $\mathbf{K_{d\,(1)}}$= 68.4, $\mathbf{K_{d\,(2)}}$= 77.1 and $\mathbf{K_{d\,(3)}}$= 84.1 represent the $\mathbf{K_{d\,(Hg)}}$ values for the samples with shaking durations of 15, 22, and 30 days, respectively. From the $\mathbf{K_{d\,(1\text{-}3)}}$ values, the rounded $\mathbf{K_{d\,(3)}}$ value (=80) was used in the OBMM simulations to evaluate the Hg concentration in the LBYRB, assuming that the Hg is in equilibrium within the aqueous and solid phases of the sample after 30 days of shaking.

It was important to study samples collected from other representative geographic locations in the LBYRB area with different soil textures to observe their variations in the $\mathbf{K_{d\,(Hg)}}$ values and to evaluate the sensitivity of the OBMM to the $\mathbf{K_{d\,(Hg)}}$ values obtained from those samples. The properties of these samples are shown in **Table 4.1**. The preliminary evaluation of their $\mathbf{K_{d\,(Hg)}}$ values was performed with the experimental conditions given in **Fig. 4.2**. After 3 days of shaking, in both the control samples of the sediment and sand, the release of Hg into the *Milli-Q* water media was not detectable. In the sub-samples of the sediment, the maximum $\mathbf{K_{d\ (Hg)}}$ value was 125 at the Hg spiking dose of 500 µL L^{-1}; then, the $\mathbf{K_{d\ (Hg)}}$ value started to decrease. The reasons for this behavior are either that the sediment samples became saturated at the higher spiking doses of Hg over 500 µL L^{-1}, so the adsorption process of Hg was stopped, or the desorption of Hg from the sediment, releasing it to the aqueous phase. Sub-samples of the sand reached a maximum $\mathbf{K_{d\ (Hg)}}$ value of 10.6 at the Hg spiking dose of 750 µL L^{-1}. Therefore, the $\mathbf{K_{d\ (Hg)}}$ values of 10, 65, and 120 were selected to represent the samples of sand, soil, and sediment, respectively. The OBMM calculations for these $\mathbf{K_{d\ (Hg)}}$ values were compared with the OBMM calculation carried out with $\mathbf{K_{d\ (Hg)}}$ of 80.

The accuracy of these results could be improved by evaluating the $\mathbf{K_{d\ (Hg)}}$ between the aqueous and solid phases of samples collected for different geographic areas in the study site. In this study, the number of replicates was one; therefore, increasing the number of replicates for the sub-samples would have increased the accuracy of the $\mathbf{K_{d\ (Hg)}}$ evaluation. Saturation levels of the solid phase samples have to be studied in detail to confirm the occurrence of the desorption process. Additionally, further studies about the composition of the solid phase samples would have given more detailed explanations of the behavior of Hg between these two phases.

4.4.2 OBMM simulation and model sensitivity

One-box multimedia model simulations were carried out for a 45-year span to evaluate the Hg concentrations in all of the environmental media in the LBYRB from 1960 to 2005. In **Fig. 4.4**, the calculated Hg concentrations by the OBMM with the experimentally evaluated $\mathbf{K_{d\ (Hg)}}$ value (=80) for the atmosphere, water, soil, and sediments are shown in $\log_{10}$ scale for a 45-year span. Atmospheric Hg concentrations were reported from 2.54×10^{-6} to 1.20×10^{-5} µmol m^{-3}, while concentrations in water ranged from 1.33×10^{-2} to 6.66×10^{-2} µmol m^{-3}. In the soil, the Hg concentration varied from 5.78×10^{-2} to 6.96×10^{-1} µmol kg^{-1}, and in the sediments, the Hg concentration varied from 3.03×10^{-1} to 5.57 µmol kg^{-1}. According to the temporal concentration trends shown by the results in **Fig. 4.4**, accumulation of Hg in the soil and sediments can be seen until the 1970s; after that time, the concentrations became constant due to the controlled Hg emissions. In the last 30 years of the study, the 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 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.

Henry`s coefficient is one of the vital chemical parameter in these calculations to represent the chemical transfer between atmosphere and water. Due to the higher complexity of Hg compounds and their reaction in atmosphere this coefficient was set similar to the value of Pb as representative values are given in the appendix 01 (*Lin and Pehkonen, 1998 and Schroeder and Munthe, 1998)*.

The lower accuracy of the estimation methods in the non-registered PRTR data and the long-range atmospheric transport of Hg from the Asian continent might have caused these variations *(Jaffe et al., 2005 and Shimizu et al., 2010)*. Due to the strict management practices applied to the consumption and emission of Hg from the 1970s, a distinctive increase in the Hg concentrations in the environmental media is not visible except for relatively small variations in the atmospheric Hg concentrations.

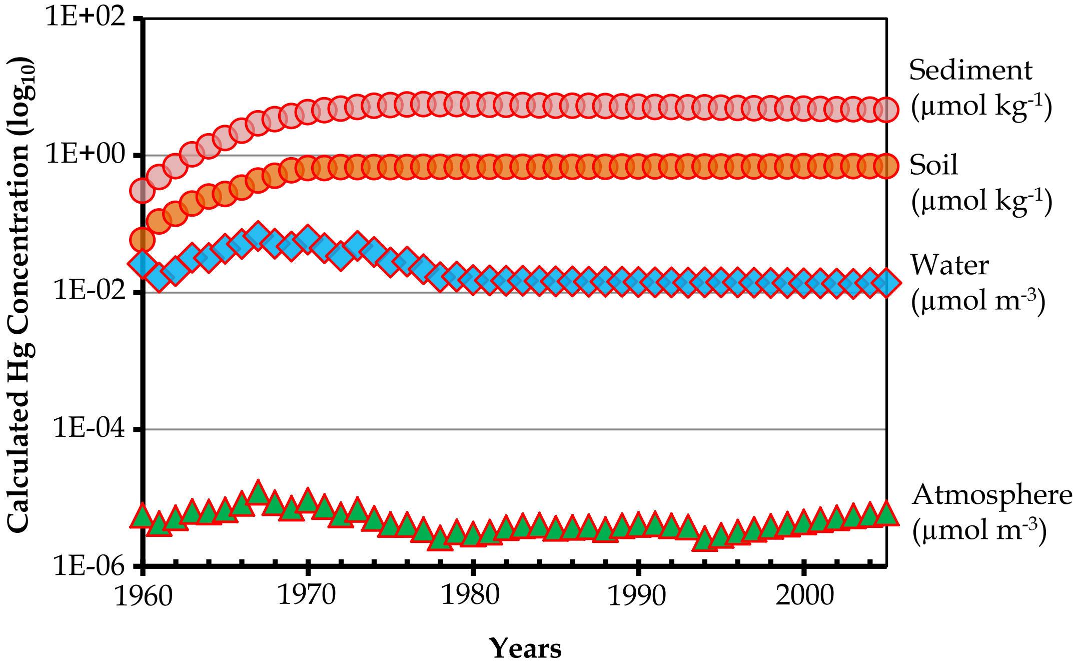

Fig. 4.4 Calculated concentrations for Hg from 1960 to 2005 in the atmosphere, water, soil, and sediments using the OBMM with $K_{d\,(Hg)}$ =80.

These calculated results were validated by comparing them with the observed data for the environmental Hg concentrations. The observed Hg concentrations in the atmosphere in Osaka Prefecture from 2001 to 2005 and the calculated Hg concentrations by the OBMM simulations for the respective years are shown in the **Fig. 4.5** *(Osaka Prefectural Government, 2011)*. The observed data were monitored at suspected locations for the occurrences of higher Hg concentrations, but the OBMM calculations seem to produce a general value for the whole study area; therefore, the calculated Hg concentrations represent the lower range of the observed Hg concentrations in the atmosphere. Calculated Hg concentrations (with $\mathbf{K_{d\ (Hg)}}$ =80) for all of the environmental media for the year 2005 were compared with the observed data for all of the environmental media for the same year, as shown in the **Fig. 4.6** *(Osaka Prefectural Government, 2011 and Japan Meteorological Agency, 2013)*. The calculated Hg concentrations fall within the range of the observed Hg concentrations, validating the reliability of the calculated results. To observe the effect of the $\mathbf{K_{d\ (Hg)}}$ value on the OBMM calculations, simulations were carried out with different $\mathbf{K_{d\ (Hg)}}$ values obtained from the $\mathbf{K_{d\ (Hg)}}$ evaluation experiments ($\mathbf{K_{d\ (Hg)}}$ = 10, 65, 80, and 120) for the year 2005. The results were compared with the observed Hg concentrations in water and sediment, as shown in **Fig. 4.6** together with the calculated concentration obtained in the section 3.4.2.2 of this thesis with $\mathbf{K_{d(Hg)}}$ = 1 condition for the year 2005. The observed Hg concentrations in water varied from 4.99x10^{-3} to 8.47x10^{-2} µmol m^{-3}, with an average of 4.49x10^{-2} µmol m^{-3}.

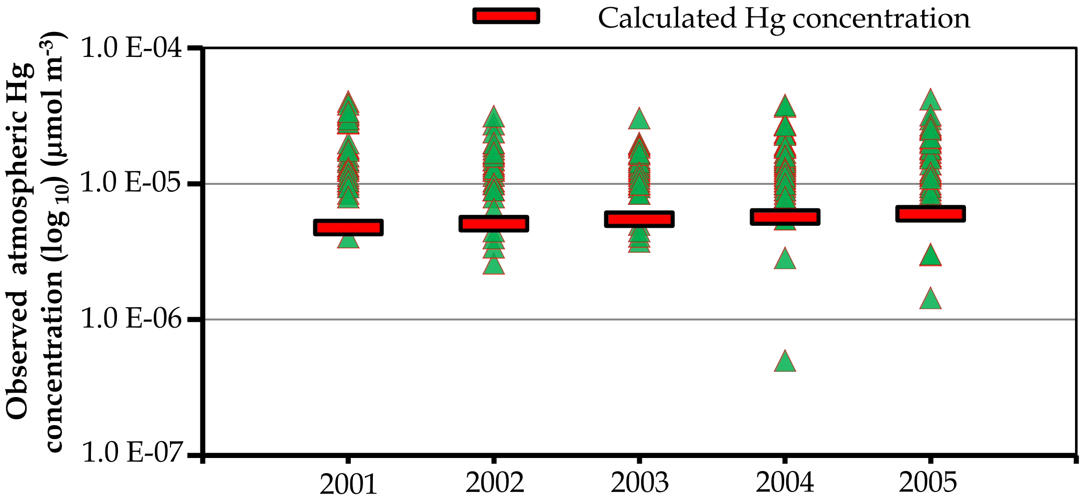

Fig. 4.5 Comparison of calculated Hg concentrations and observed atmospheric Hg concentrations from 2001 to 2005.

The calculated Hg concentrations with $\mathbf{K_{d\ (Hg)}}$ = 1 and $\mathbf{K_{d\ (Hg)}}$ = 10 conditions provided higher concentrations than this range, while the calculated Hg concentrations with $\mathbf{K_{d\ (Hg)}}$ = 65 and $\mathbf{K_{d\ (Hg)}}$ = 80 provided results closer to the average observed Hg concentration in water. In the case of $\mathbf{K_{d\ (Hg)}}$ = 120, the calculated Hg concentration resulted in the lowest from the average observed concentration as shown in **Fig. 4.6.**

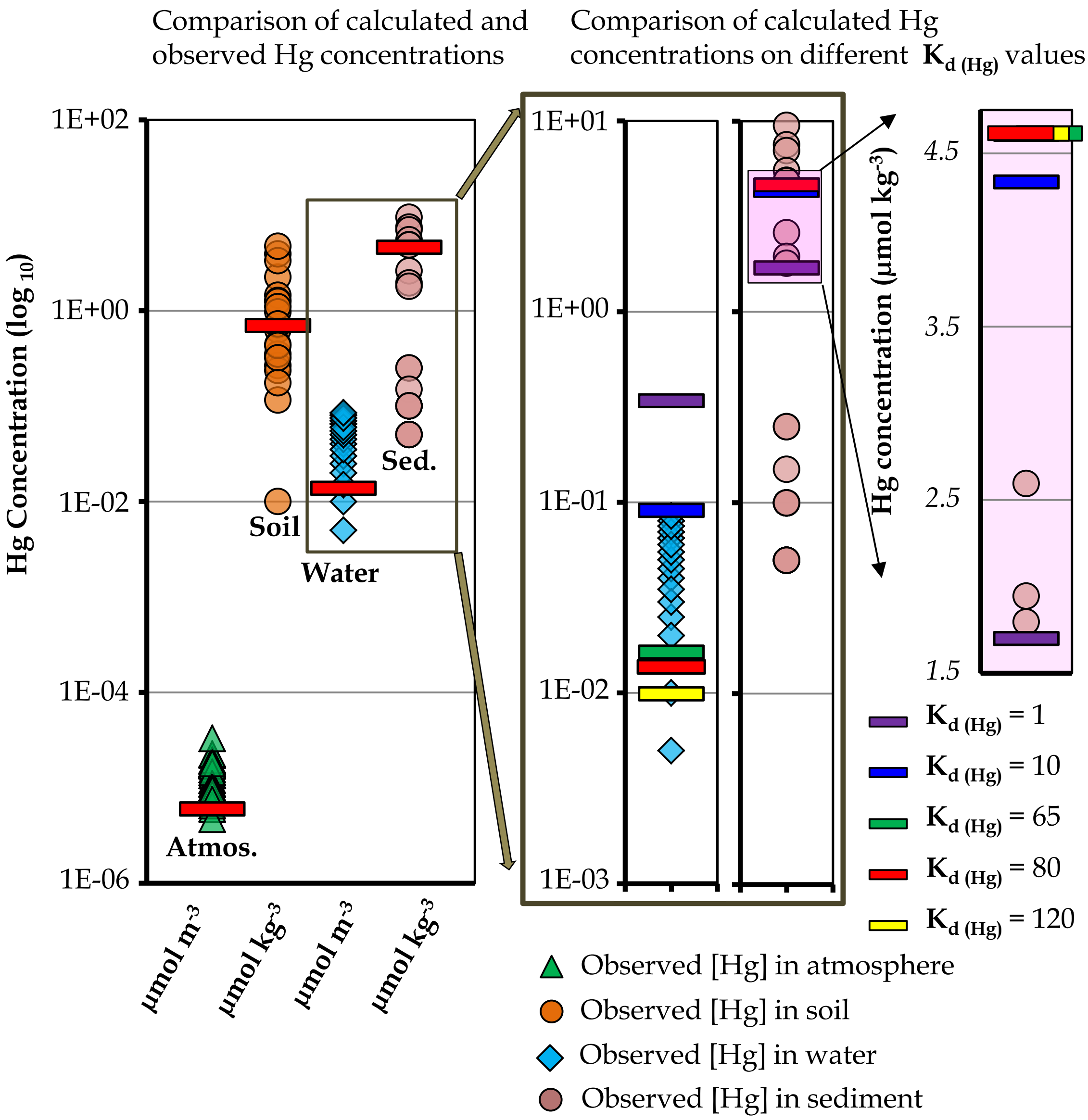

Fig. 4.6 Observed and calculated concentrations of Hg in each environmental media in the LBYRB for 2005 and the comparison of the effect of the $\mathbf{K_{d\ (Hg)}}$ value on the OBMM calculations.

In sediment, the observed Hg concentrations varied from 9.97x10^{-2} to 9.47 µmol kg^{-1} with an average of 1.96 µmol kg^{-1}. The calculated Hg concentrations in sediment with all **K$_d$** (Hg) values were between the range of the observed Hg concentration. As described with the magnification in **Fig. 4.6**, calculated Hg concentrations for the conditions of K$_{d\ \mathbf{(Hg)}}$ = 1 resulted in 1.70 µmol kg^{-1} while **K$_{d\ (Hg)}$** = 10 resulted in 4.33 µmol kg^{-1}. In the case of **K$_{d\ (Hg)}$** = 65, 80, and 120, the calculated concentration of Hg in sediments was 4.61 µmol kg^{-1}, showing that the calculated concentrations of Hg in the sediments were not affected by higher **K$_{d\ (Hg)}$** (≥65) values but were affected by lower **K$_{d\ (Hg)}$** (1≤65) values. It was apparent that the calculated Hg concentrations in water were affected by the **K$_{d\ (Hg)}$** value, which was clearly affected by the soil types. Each respective **K$_{d\ (Hg)}$** value obtained from samples with different geographic characteristics provided a different calculated Hg concentration, and **K$_{d\ (Hg)}$** = 80 provided a generalized calculated Hg concentration in water for the whole LBYRB area. Taking these results into consideration and the calculated Hg concentrations with **K$_{d(Hg)}$** = 1 condition, it showed that incorporating the experimentally evaluated **K$_{d\ (Hg)}$** into the OBMM calculation provided calculated Hg concentrations in water and sediments that were much closer values to the average observed Hg concentration, thereby proving that the OBMM calculations have improved.

Many chemical coefficients other than the **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 into the OBMM calculations. The 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 the OBMM calculations and the validation of the calculated results of the model.

4.5 Conclusions

Laboratory-scale experiments were carried out to evaluate the **K$_{d\ (Hg)}$** between the aqueous and solid phases of the environment, and an experimentally determined **K$_{d\ (Hg)}$** value (=80) was incorporated into the OBMM. Annual emissions of Hg for LBYRB were calculated using the literature on Hg consumption and PRTR data for a 45-year span. The concentrations of Hg in four environmental media, namely the atmosphere, water, soil, and sediments, of the LBYRB were evaluated using the calculated annual Hg emission data and OBMM simulations. The calculated Hg concentrations were compared with the observed Hg concentrations in the study area to validate the accuracy of the OBMM calculations. Variations were observed in the calculated atmospheric Hg concentrations while in the sediment and soil, accumulation of Hg was observed. Except for the atmosphere, the calculated Hg concentrations in the soil, water, and sediment became constant over the last three decades of the study span, due to the controlled consumption of Hg. The sensitivity of the OBMM calculations to 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. The results showed that the experimentally evaluated $\mathbf{K_{d\ (Hg)}}$ value (=80) improved the accuracy of the OBMM calculations by providing a generalized $\mathbf{K_{d\ (Hg)}}$ value representing the whole study area. Therefore, the objective of this study was successfully achieved.

Furthermore, this study can be used to formulate detailed studies to investigate the occurrences of environmental Hg. This study will provide sufficient details about Hg in the environment to the interested parties, such as authorities responsible for environmental monitoring and management, so that they can proceed with better environmental management practices to mitigate environmental pollution by Hg. This makes the environmental monitoring process more successful and eventually protects the environment.

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EVALUATION OF SPATIAL DISTRIBUTION OF MERCURY BY USING DISTRIBUTED MULTIMEDIA MODEL

5

5.1 Introduction

5.2 Objectives
5.3 Methodology
  5.3.1 Emission data calculation
  5.3.2 OBMM simulation
5.4 Results and Discussion
5.5 Conclusions

Due to the environmental and health damages such as Minamata disease *(Harada, 1995)*, as a carcinogen, due to child development defects, and due to the toxic effects on nervous, digestive, and immune systems, *(Mercury and health, 2013)* consumption and release of Mercury (Hg) has been legally controlled in Japan since 1973 *(Lessons from Minamata Disease and mercury Management in Japan, 2011)*, but still, many industries consume Hg in their production processes; thus, Hg appears in the environmental analysis data *(Sakata and Marumoto, 2005)*. The Japanese Ministry of Environment has set the environmental standards for the Hg concentration in water and soil to be less than 0.5 $\mu g\ L^{-1}$ and for the alkyl mercury limit to be less than the detection limits (*Ministry of the Environment, Japan, 2014)*. In June 2013, a global treaty of The Minamata Convention on mercury was established and acknowledged by 96 countries (by February 2014) to protect human health and the environment from the adverse effects of Hg *(Minamata convention on mercury, 2013)*.

In the previous sections of this thesis (Chapter 3 & 4), evaluation of temporal variations of Hg concentrations in the study site of LBYRB was discussed. For that purpose, one-box multimedia model were provided with the calculated annual emission amounts of Hg and the simulations were performed. Computational calculations were improved by incorporating the experimentally determined model parameters such as $\mathbf{K}_{\mathbf{d\ (Hg)}}$ to obtain more accurate calculations of the Hg concentrations in the environment. Results from those previous sections showed the tendency to accumulate Hg in water, soil, and sediments while in the atmosphere the concentration levels were varying through the study span (*Ariyadasa et al., 2014*).

However to have a complete understanding of the environmental occurrences of Hg in LBYRB, not only the temporal variations of Hg concentration but also the information of the spatial distribution of Hg concentration is required. For this purpose Distributed Multimedia Model (DMM) was used to simulate the spatial distribution of Hg concentration in LBYRB.

Annual emission data were calculated for a span of 45 years from 1960 to 2005 from the consumption data gathered from various industries, as catalysts, fertilizers, pharmaceuticals (inorganic chemicals), machinery, batteries, medical supplies (amalgam), explosives (gun powder), and paints *(Kida, 2012 and Takahashi et al., 2008)*. Study area of LBYRB was divided into 1 km x 1 km grid and DMM simulations were performed. Calculated Hg concentrations were validated using the published monitoring data and the spatial distribution of Hg concentration was evaluated. In this section of the thesis the findings of the evaluation of the Hg concentration by DMM is discussed.

5.2 Objectives

The main objective of this section in the thesis study was to evaluate the spatial distribution of the Hg concentrations in the LBYRB using DMM simulations.

5.3 Methodology

Concentrations of Hg in the atmosphere, water, soil, and sediments in the LBYRB were calculated using a DMM for a span of 45 years from 1960 to 2005. Estimated annual emissions of Hg within the LBYRB were used as the input data for DMM simulations. The accuracy of the DMM calculations was evaluated by comparing the calculated concentrations with the observed data for Hg. Validated calculated concentrations were then analyzed for their spatial distributions within the study site. The experimental flow described in **Fig. 5.1**. The study site of LBYRB and the major data sources; PRTR are described in the sections of 1.6 and 1.7 of this thesis while the details of the DMM are explained in the section 2.2.

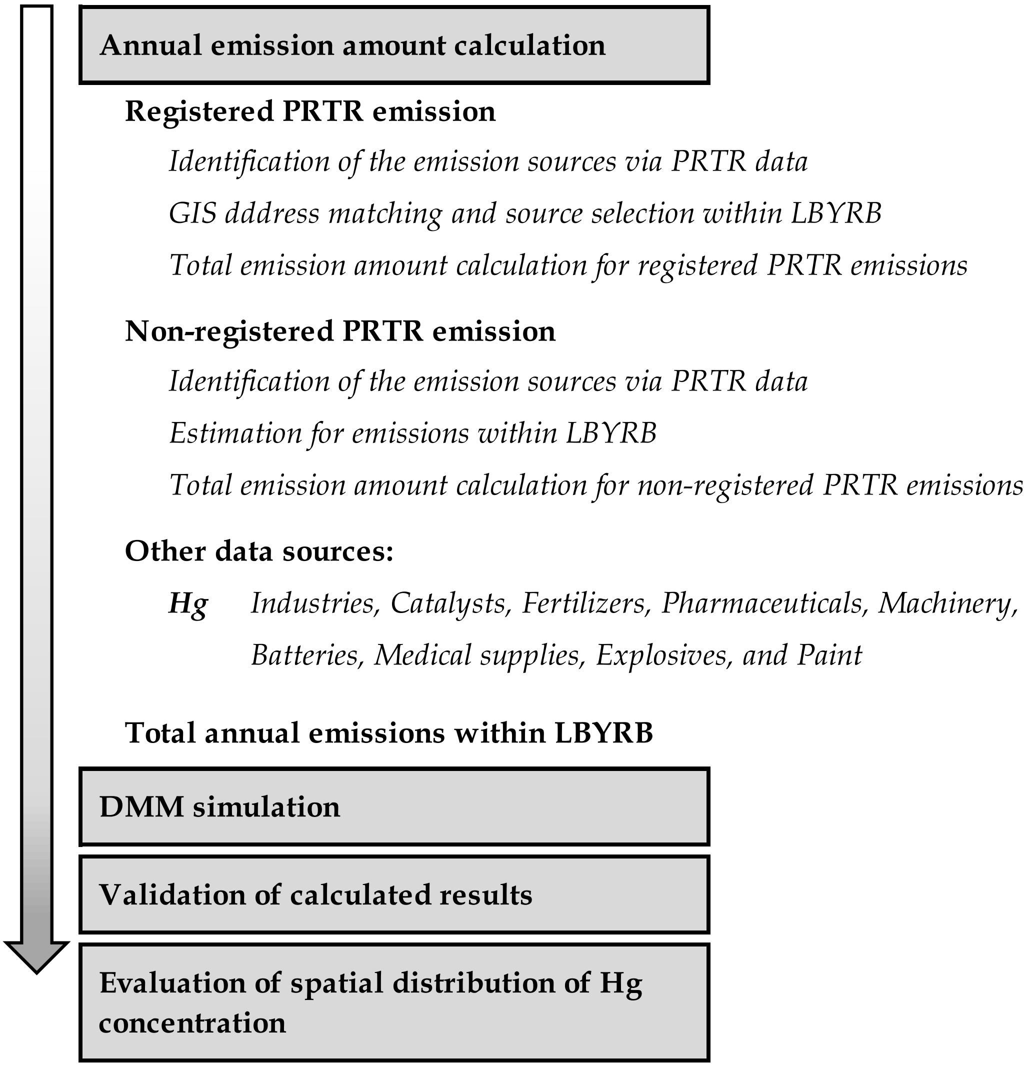

Fig. 5.1 Summary of the methodology for the evaluation of spatial distribution of Hg concentration by DMM.

5.3.1 Emission data calculation of Hg

Annual emissions of Hg from 1960 to 2005 were calculated for the LBYRB based on the records of available Hg consumption and PRTR data. From 1960 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 *(Kida, 2012 and Takahashi et al., 2008)*. From 1990 to 2000 there was no record of Hg emissions. From 2001, emissions of Hg were recorded in PRTR and therefore the Hg emissions from 2001 to 2005 were calculated based on the PRTR data *(PRTR Information Plaza, 2007)*. The averaged emissions from 2001 to 2005 were used to represent the Hg emissions from 1990 to 2000. Emissions in each grid were calculated in two separate processes for the registered PRTR data and the other data (non-registered PRTR and consumption data).

Registered PRTR data provide the emissions and quantities of chemicals transferred per year by compound, area, and industry. The locations of the emission sources were provided as addresses in the PRTR system. The emissions and transfer data for Hg were collected for the six prefectures from which the LBYRB is composed of. The geocoding service developed by the Center for Spatial Information Science, Tokyo University was used to select the emission sources of Hg within LBYRB (*Center for Spatial Information Science, Tokyo University, Japan*). Based on the emission source locations, the emissions were allocated to the respective girds used in DMM calculation and the Hg emissions to air, water, and soil, were calculated per each grid.

Non-registered PRTR data provide the diffuse or non-point-source emissions estimated for businesses that are smaller in size or product volume, non-listed industries, households, and mobile sources (*PRTR Information Plaza, 2007*). Both consumption data and the non-registered PRTR data are provided by region (Kinki region), thus estimation of emissions per each gird was required. The population ratio of the region to the respective DMM grids was assumed to be representative to the ratio of emissions between region and to that of the each respective DMM grid. Emissions of Hg to each DMM grid were estimated based on the above assumption. Finally the emissions from registered PRTR data, non-registered PRTR data, and consumption data, to each DMM grid were summed to obtain the Hg emissions for each DMM grid.

5.3.2 DMM simulations

The calculated annual emission amounts for Hg from 1960 to 2005 were used as input data and computer simulations were carried out using DMM to evaluate environmental concentrations of Hg in all four environmental media separately. These calculations were performed based on the conditions of:

- Hg observes the mass conservation principles in the environmental systems.
- Hg mixes perfectly within the environmental media and between the environmental media Hg are in non-equilibrium state.
- Transfer fluxes of Hg are considered between the adjacent compartments.

Time steps for these calculations were set to 6 minutes, and a series of differential equations (major equations are provided in the section 2.1.2) was solved using the Runge-Kutta technique by a computer program coded in FORTRAN. The calculated Hg concentrations were validated using the published observed data for the occurrence of Hg in the environment to evaluate the reliability of the OBMM calculations. Calculated concentrations from DMM were then plotted in the area maps using Geographic Information Systems (GIS) techniques to evaluate the spatial distribution of the Hg concentrations.

5.4 Results and Discussion

5.4.1 Emission data of Hg

Calculated total emission amounts of Hg to the LBYRB from 1960 to 2005 are shown in the **Fig. 3.7** from the chapter 3. Emissions of Hg have been controlled since 1973 and it explains the decreasing of Hg emissions after 1973. From 1990 to 2000 there was no record of Hg emissions. From 2001, emissions of Hg were recorded in PRTR and the Hg emissions under the registered PRTR emissions were zero from 2001. However, there are comparatively smaller Hg emissions recorded in the non-registered PRTR emissions category from industries having less than 20 employees and with less than 1 ton per year annual Hg consumptions from 2001 to 2005 *(PRTR Information Plaza, 2007)*. Thus, the average Hg emissions from 2001 to 2005 were used to represent the Hg emission from 1991 to 2000, as shown in **Fig. 3.7**. Hg emissions to the atmosphere, soil, and water in LBYRB for the years of 1960 and 1970 with their allocations to the DMM grids are shown in the **Fig. 5.2**.

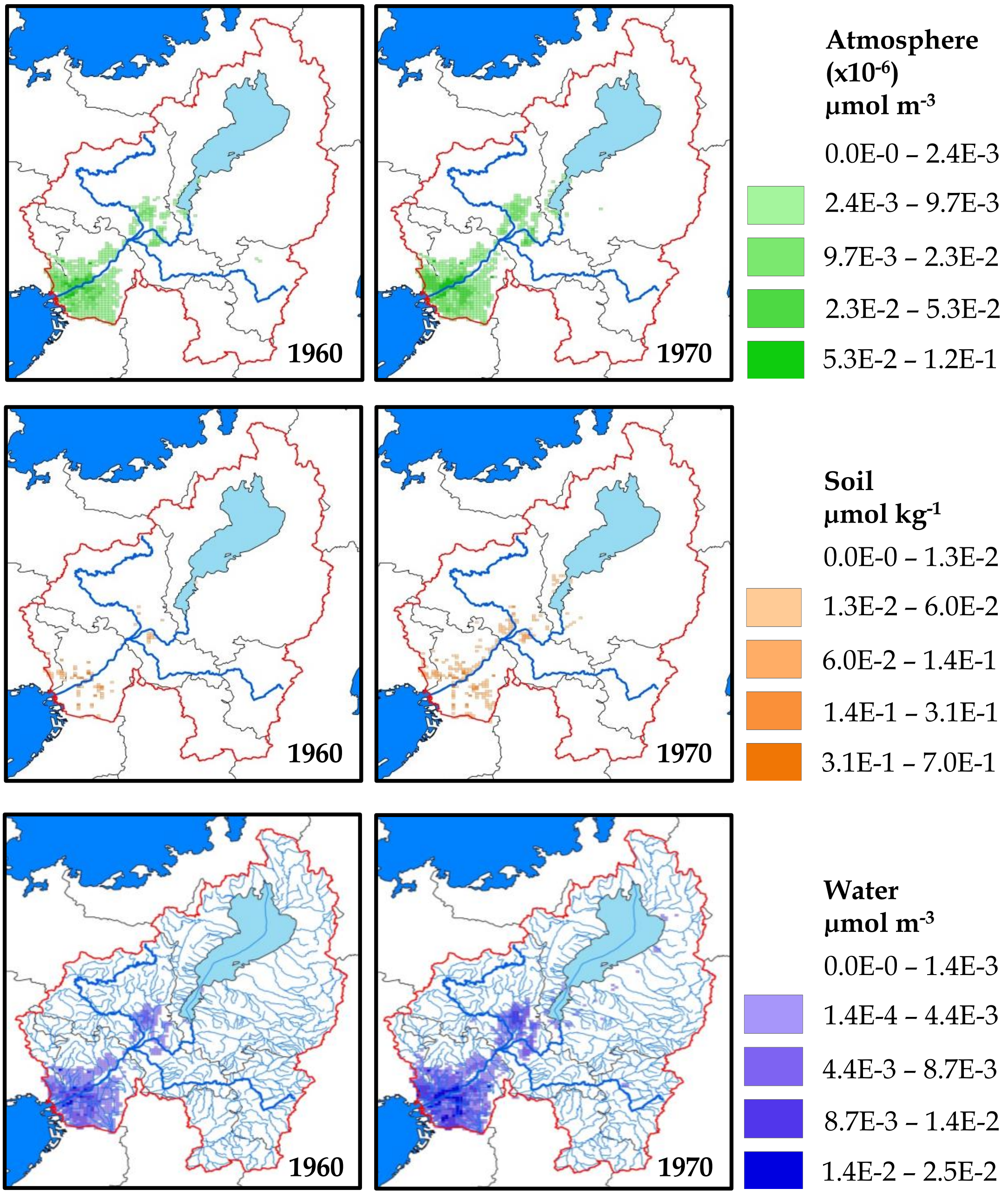

Fig. 5.2 Spatial distribution (on DMM grids) of the Hg emissions to the atmosphere, soil, and water in LBYRB for the 1960 and 1970.

5.4.2 Spatial distribution of Hg

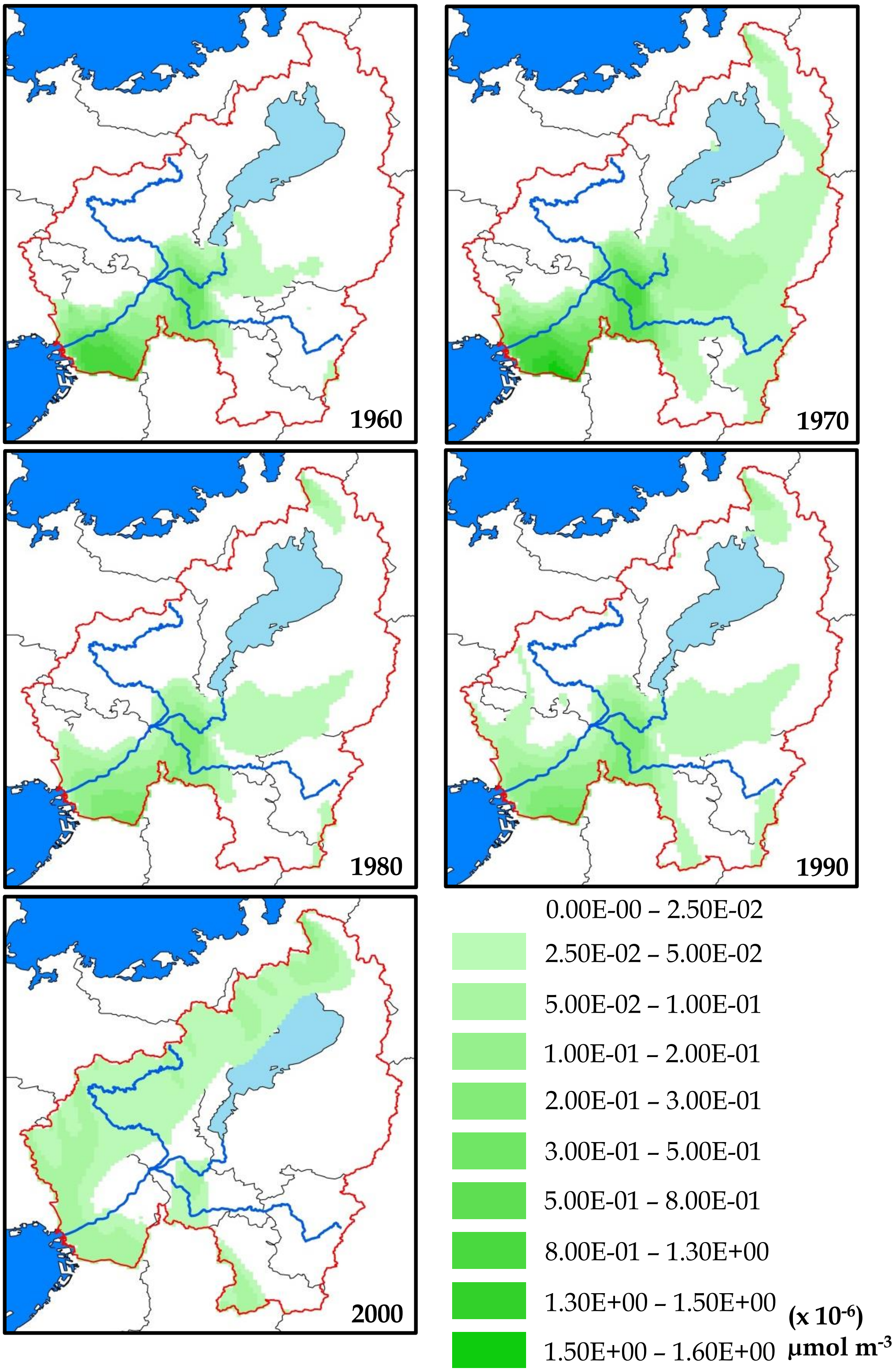

Fig. 5.3 Spatial distribution of the Hg concentration in the atmosphere of LBYRB from 1960 to 2000.

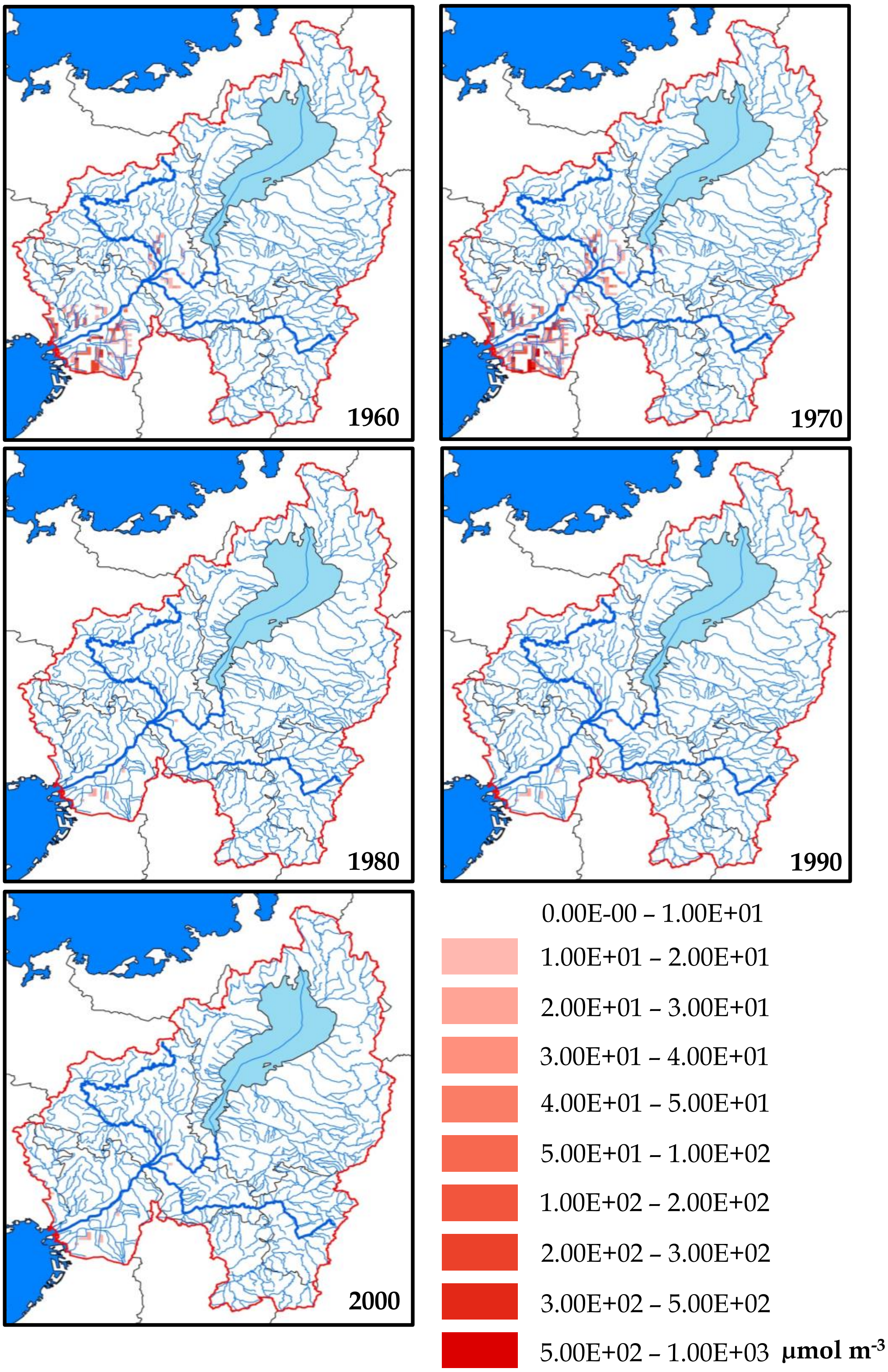

Fig. 5.4 Spatial distribution of the Hg concentration in the water of LBYRB from 1960 to 2000.

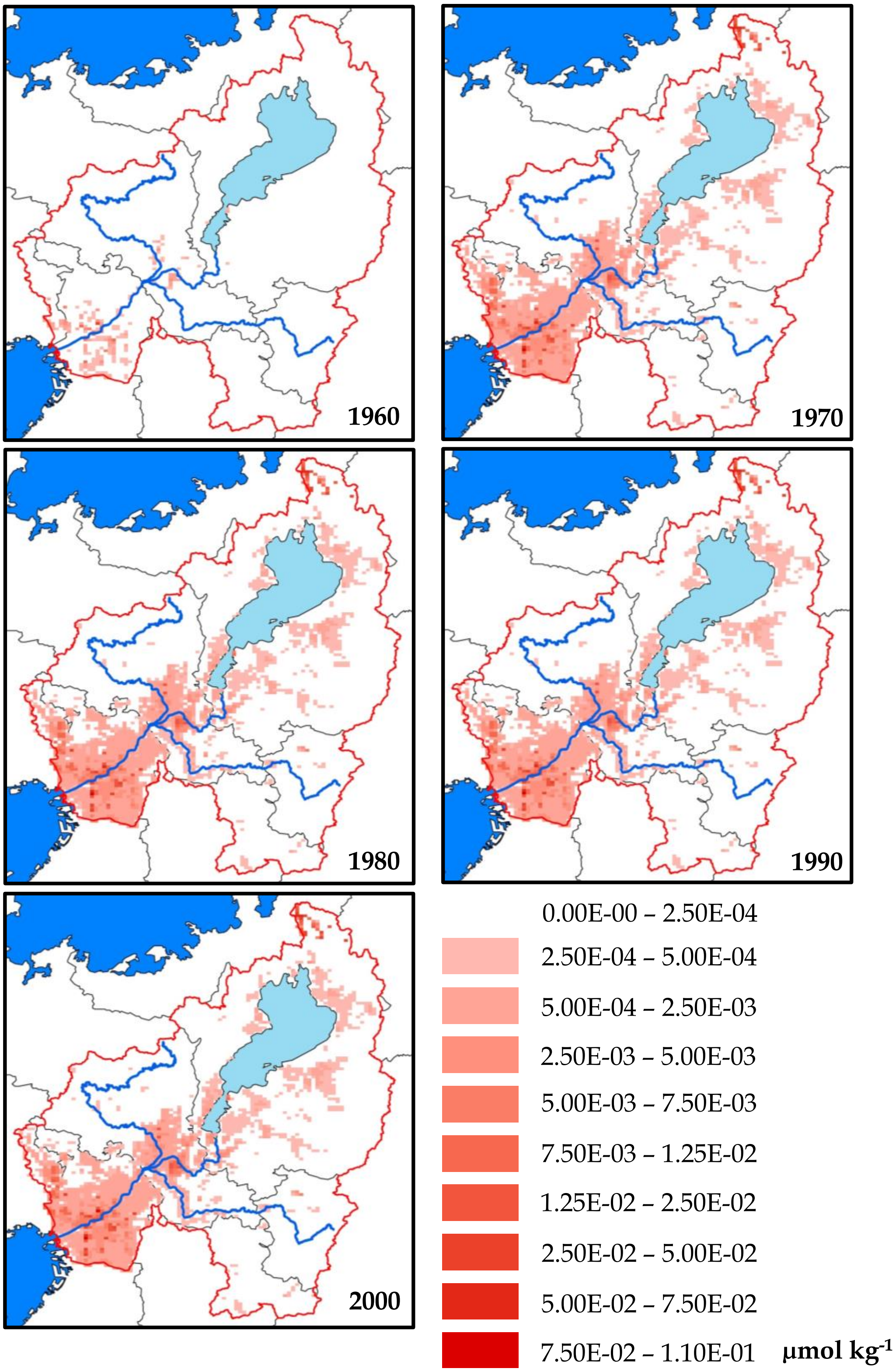

Fig. 5.5 Spatial distribution of the Hg concentration in the soil of LBYRB from 1960 to 2000.

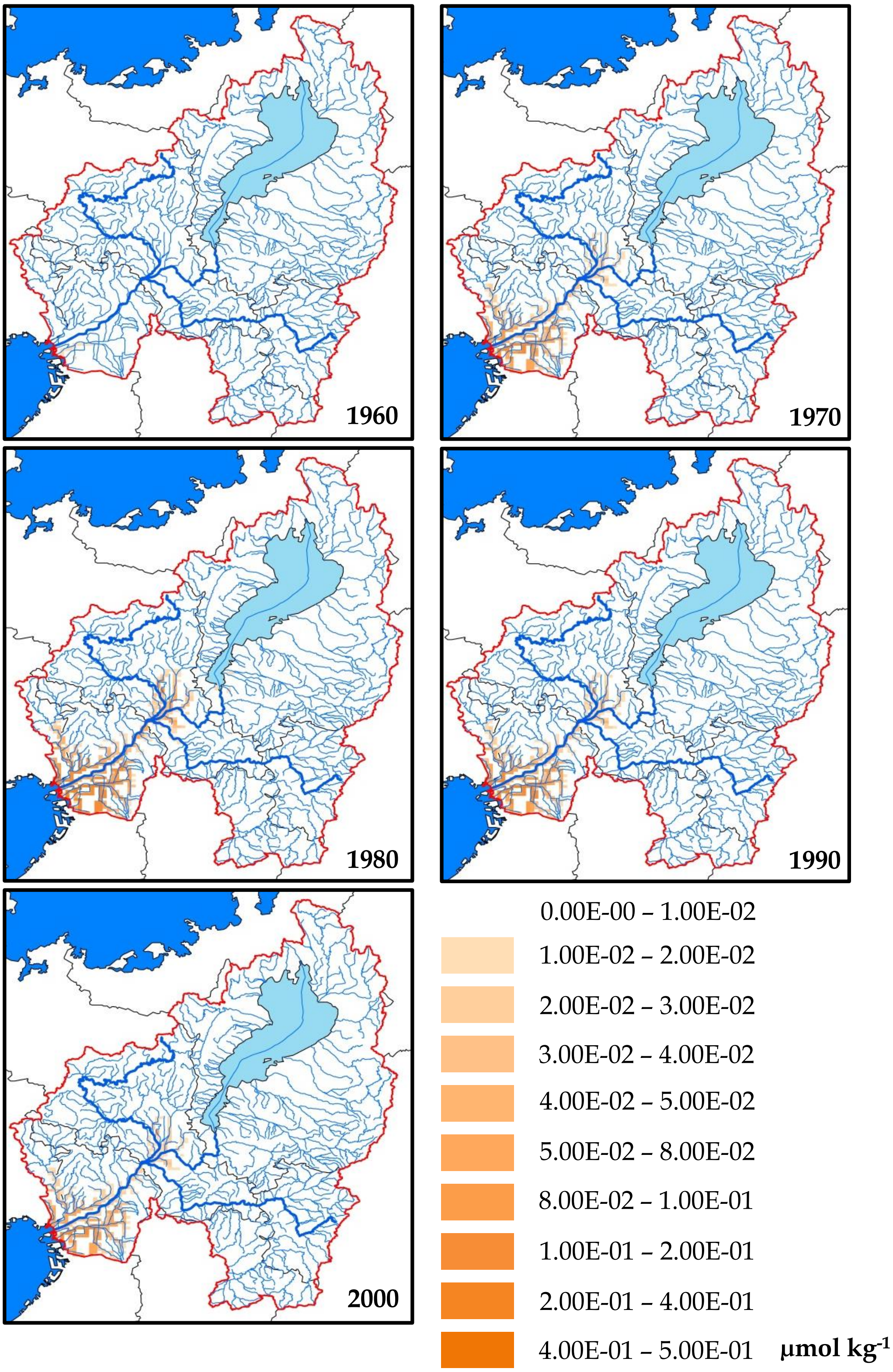

Fig. 5.6 Spatial distribution of the Hg concentration in the sediment of LBYRB from 1960 to 2000.

The spatial distribution of the Hg concentrations in each environmental media of LBYRB was simulated by using the DMM and the **Fig. 5.3 to Fig. 5.6** show the spatial distribution of Hg concentrations in the atmosphere, water, soil, and sediment for every 10 years from 1960 to 2000.

The atmospheric Hg concentration showed relatively small variations from zero to 1.6x10^{-6} µmol m^{-3} during the time span of this study as shown in the **Fig. 5.3.** 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 (> 5.0x10^{-7} µmol m^{-3}) were not observed but the occurrences in lower atmospheric concentrations (< 5.0x10^{-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 (J*affe et al., 2005 and Shimizu et al., 2010*).

The concentration of Hg in the water varied from zero to 1x10^{3} µmol m^{-3} and from 1960 to 1970 the concentrations were observed to increase in the southwestern areas close to Osaka bay as shown in the **Fig. 5.4.** Adsorption of a certain portion of Hg into the sediments and transportation of Hg 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. To the latter years of the study span few localized areas were observed by the DMM simulations for the occurrences of relatively higher Hg concentration in the water.

As shown in the **Fig. 5.5**, the concentration of Hg in soil varied from zero to 1.1x10^{-1} µmol kg^{-1} and from 1960 the Hg concentrations were observed to increase in the study area dispersedly. Considering the latter years of the study span, an accumulation of Hg were observed specially in the southwestern areas close to Osaka Bay as shown in the **Fig. 5.5.** After 1980, spots for relatively higher Hg concentrations were observed to decrease.

In the sediments, the Hg concentrations were increasing towards the southwestern areas of the study site closer to Osaka Bay ranging from zero to 5.0x10^{-1} µmol kg^{-1}as shown in the **Fig. 5.6.** With the controlled emissions of Hg in 1970s, Hg concentration in sediments decreased while accumulating in the downstream areas of the main rivers in the study site.

To validate the calculated concentrations from the DMM simulations for their reliability, the calculated concentrations were compared with the observed Hg concentrations in atmosphere, soil, and water based on their locations of observed *(Osaka Prefectural Government)*. This comparison is shown in the **Fig. 5.7**. For the atmospheric Hg concentrations, DMM calculations provided relatively lower calculated concentrations but within the range of x10^1 deviation. The observed data were monitored at suspected locations for the occurrences of higher Hg concentrations, but the DMM would provide a general value for 1 km x 1 km grid. Hence with a much

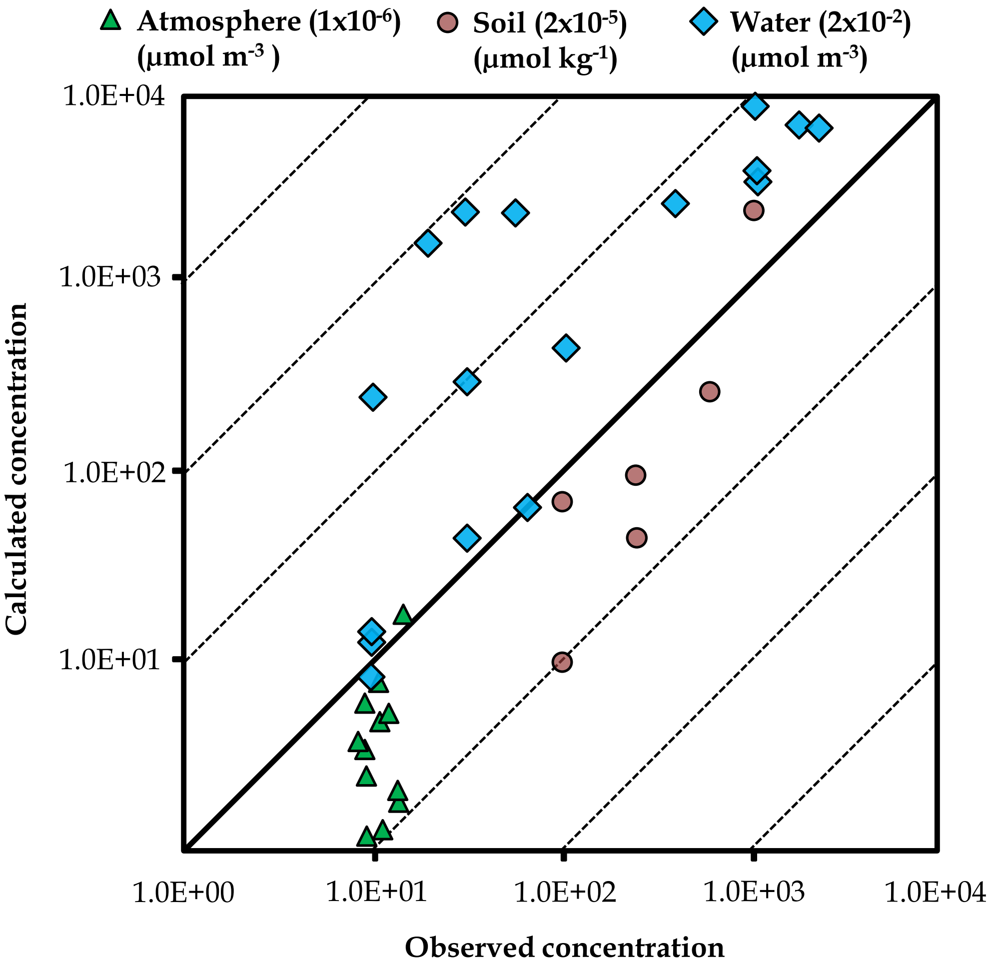

Fig. 5.7 Comparison between the calculated Hg concentrations and the observed Hg concentrations in air, water, and soil.

smaller gird size DMM would be able to provide more accurate results. Calculated concentrations of Hg in water by DMM were relatively higher than the observed Hg concentrations in the water but the deviations were within the range of x10^2. In the soil, the calculated Hg concentrations were relatively lower than the observed Hg concentrations yet the deviations were within the range of x10^1. This suggest that more Hg should be transferred to soil from the water and further experimental determinations of the chemical parameters such as water-sediment partition coefficients of Hg would provide the valuable information to improve the sensitivity of the DMM. Overall, the calculated concentrations were within the acceptable range of deviations from the observed Hg concentrations to validate the reliability of the DMM. Due to the lack of monitoring data on sediments, the comparison of calculated Hg concentrations with the observed Hg concentrations in sediment was not possible.

5.5 Conclusions

The necessity of evaluating the spatial distribution of Hg concentrations in LBYRB was required to complete the understanding of environmental occurrences of Hg. Therefore the study site was divided into 1 km x 1 km grid and DMM simulations were performed to evaluate the spatial distribution of Hg in the atmosphere, water, soil, and sediments. Emission data of Hg were calculated from 1960 to 2000 and used as input data. Calculated Hg concentrations by DMM were compared with the published data for observed Hg concentrations within the study site and the reliability of the DMM was validated. Then the simulation results were plotted into spatial graphs using GIS techniques for the years of 1960, 1970, 1980, 1990, and 2000, to evaluate spatial distributions of Hg in all environmental media. Increments of the Hg concentrations were observed until 1980s and in the latter period of the study span, the accumulations of the Hg in soil and sediments were observed towards the Southwestern part of the LBYRB especially towards the Yodo River mouth and the Osaka Bay. Atmospheric Hg concentrations were observed to decrease in LBYRB, but at the same time the occurrences of atmospheric Hg in relatively lower concentrations were observed to the Western and Northwestern parts of the LBYRB. This provided valuable spatial information of the occurrences of environmental Hg while achieving the objectives of this section of the thesis.

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6

SCREENING OF POTENTIALLY HAZARDOUS PRTR CHEMICALS BY ONE-BOX MULTIMEDIA MODEL

6.1 Introduction

6.2 Objectives
6.3 Methodology
  6.3.1 Emission data calculation
  6.3.2 OBMM simulation
  6.3.3 Screening scenarios for the risk possessing chemicals
6.4 Results and Discussion
6.5 Conclusions

Invisible invasion of our environment by chemical pollutants is a much known fact. When chemical pollution in the environment reaches a threshold level, these chemicals begin to damage the environment and the health of humans, plants, and animals. In most cases, we become aware of these adverse effects by these chemicals after the damage became apparent. Situations such as the Minamata disease caused by methyl-mercury poisoning in Kumamoto, Japan *(Harada, 1995)*, and the Itai Itai disease due to cadmium poisoning in Toyoma prefecture, Japan *(Inaba et al., 2005)* are profound examples.

In most countries, various controlling measures are carried out to maintain a lower environmental pollution condition and environmental monitoring is one of the major processes among those measures. It enables better management practices by elucidating the status of these chemicals in the environment. But environmental monitoring is challenging when the pollutants with the potential to do damage to the environment and the living beings are unknown. Thus, alternative data sources and mathematical and computational modeling may be used to produce environmental-modeling tools to increase the efficiency of environmental monitoring and environmental management, ultimately helping to protect the environment.

There are published studies on using computer models to evaluate environmental chemicals. In 1991, Mackay used a level-III multimedia model based on fugacity to evaluate the fate of organic chemicals (*Mackay and Paterson, 1991*). In 2001, a multicompartmental, multi-basin fugacity model was used to describe the fate of polychlorinated biphenyls in the Baltic Sea (*Wania et al., 2001*). These studies including many others are a good example for utilizing computational models for the assessing the environment.

But, most of these environmental-modeling studies focus on a particular chemical or on smaller chemical groups and on a particular environmental medium. Usually, the studies describe the fate of these chemicals but the extended applications of environmental modeling as a tool to mitigation of environmental pollution was absent.

6.2 Objectives

The main objective of this chapter of the thesis was to identify the non-metallic chemicals posing a environment and health risk based on the emission data provided in the PRTR data in the Lake Biwa-Yodo River basin using a one-box multimedia model. For that reason, we studied the behavior and the fate of a much wider chemical group to provide better insight of the status of these pollutants and to prevent environmental pollution proactively.

6.3 Methodology

The methodology used in this section is consisting of three main steps of annual emission amount calculation, OBMM simulations (*described in section 2.1 of this thesis*), and scenario development for the screening of potentially hazardous chemicals. PRTR chemicals and their emission data (*described in section 1.7 of this thesis*) were used as the data sources and OBMM was used for the simulations to evaluate the environmental concentrations of 200 non-metallic PRTR chemicals in the study site of LBYRB (*described in section 1.6 of this thesis*).

6.3.1 Emissions data calculation

Annual emissions for 200 non-metallic PRTR chemicals were calculated using PRTR data for the years of 1997, 2002, and 2008 covering an 11 years span. These calculations were carried out as two separate processes because the emissions and quantities of chemicals transferred are available as registered PRTR data and non-registered PRTR data.

a) Registered PRTR data

The registered PRTR data provide the emissions and quantities of chemicals transferred per year by compound, area, and industry. The locations of the emission sources were provided as addresses in the PRTR system. The emissions and transfer data for the 200 non-metallic chemicals were collected for the six prefectures. Then, the geocoding service developed by the Center for Spatial Information Science, Tokyo University was used to select the emission sources of these chemicals within each study site, and their emissions were summed to calculate the emission of each pollutant from the registered PRTR data (*Center for Spatial Information Science, Tokyo University, Japan*).

b) Non-registered PRTR data

The non-registered PRTR data include the diffuse or non-point-source emissions estimated for businesses that are smaller in size or product volume, non-listed industries, households, and mobile sources. These data are delimited by emissions to the atmosphere, water, landfills and soil. Emissions to landfills and soil were negligible and thus were not considered in the calculation of non-registered emissions in this study. As these data were provided by region, estimation was required to calculate the total emissions in the LBYRB. The population ratio of the LBYRB to the Kinki region was assumed to be representative to the ratio of emissions between LBYRB and to that of Kinki region. Total emissions from non-registered PRTR emissions into the LBYRB were estimated based on the above assumption for the respective 200 non-metallic PRTR chemicals.

After the total emissions from both registered PRTR data and non-registered PRTR data for LBYRB were calculated, they were summed to obtain the total annual emissions of the 200 non-metallic PRTR chemicals in the study site for the years of 1997, 2002, and 2008 (*PRTR Information Plaza, 2007*).

6.3.2 OBMM simulations

Details of the OBMM are provided in the section 2.1 of this thesis. Calculated annual emissions were input to the OBMM together with the other required chemical properties to calculate the concentrations of the chemicals in the atmosphere, soil, water, and sediment. Simulations were carried out separately for 1997, 2002, and 2008 in a similar manner. These calculations were performed based on the conditions of:

- These chemicals observe the mass conservation law in the environmental systems.
- These chemicals are mixing perfectly within the environmental media and between the environmental media they are in non-equilibrium state.

Time steps for these calculations were set to 6 minutes, and a series of differential equations was solved using the Runge-Kutta technique by a computer program coded in FORTRAN. The calculated concentrations for the non-metallic PRTR chemicals were validated using available published observed data for their occurrence in the environment.

6.3.3 Development of screening scenarios

Calculated concentrations (or results) from the OBMM were analyzed for trends in concentration in each of the environmental media from 1997 to 2008. Chemicals were screened using the following criteria to identify the environment and health risk possessing PRTR chemicals as shown in the **Fig. 6.1** and then the screened PRTR chemicals were qualitatively analyzed for health risks they pose by using the health-risk categories set by the United States Department of Labor (*United States Department of Labor, 2013*) to confirm their potential risk on the environment and health.

- For possessing non-declining concentration trends over the time span of the study.
- For possessing the highest calculated concentration in each environmental media (upper 10% of the 200 chemicals, listed descendingly on their averaged calculated concentrations).
- For the occurrences in all four environmental media.

6.4 Results and Discussion

From the PRTR chemicals, 200 non-metallic chemicals were selected for this study and the list of the chemicals studied are given in the **Appendix 02.** Annual emission amounts for these 200 non-metallic chemicals to the air, soil, and water were calculated using registered and non-registered PRTR data. These emission amounts for the years of 1997, 2002, and 2008 are listed in the **Appendix 03.**

Calculated concentrations of the 200 non-metallic PRTR chemicals in all four environmental media for each year were plotted against their representative PRTR number as shown in the **Fig. 6.2** and **Fig. 6.3.** These concentrations are given in log $_{10}$ scale and in all environmental media, the range of the concentrations of as a group decreased from 1997 to 2008.

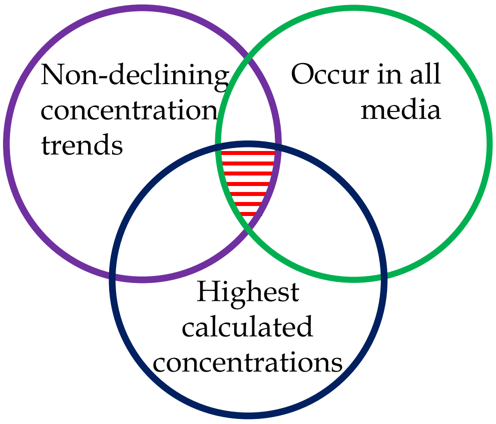

Fig.6.1 Scenario used for screening the environmental and health risk possessing chemicals.

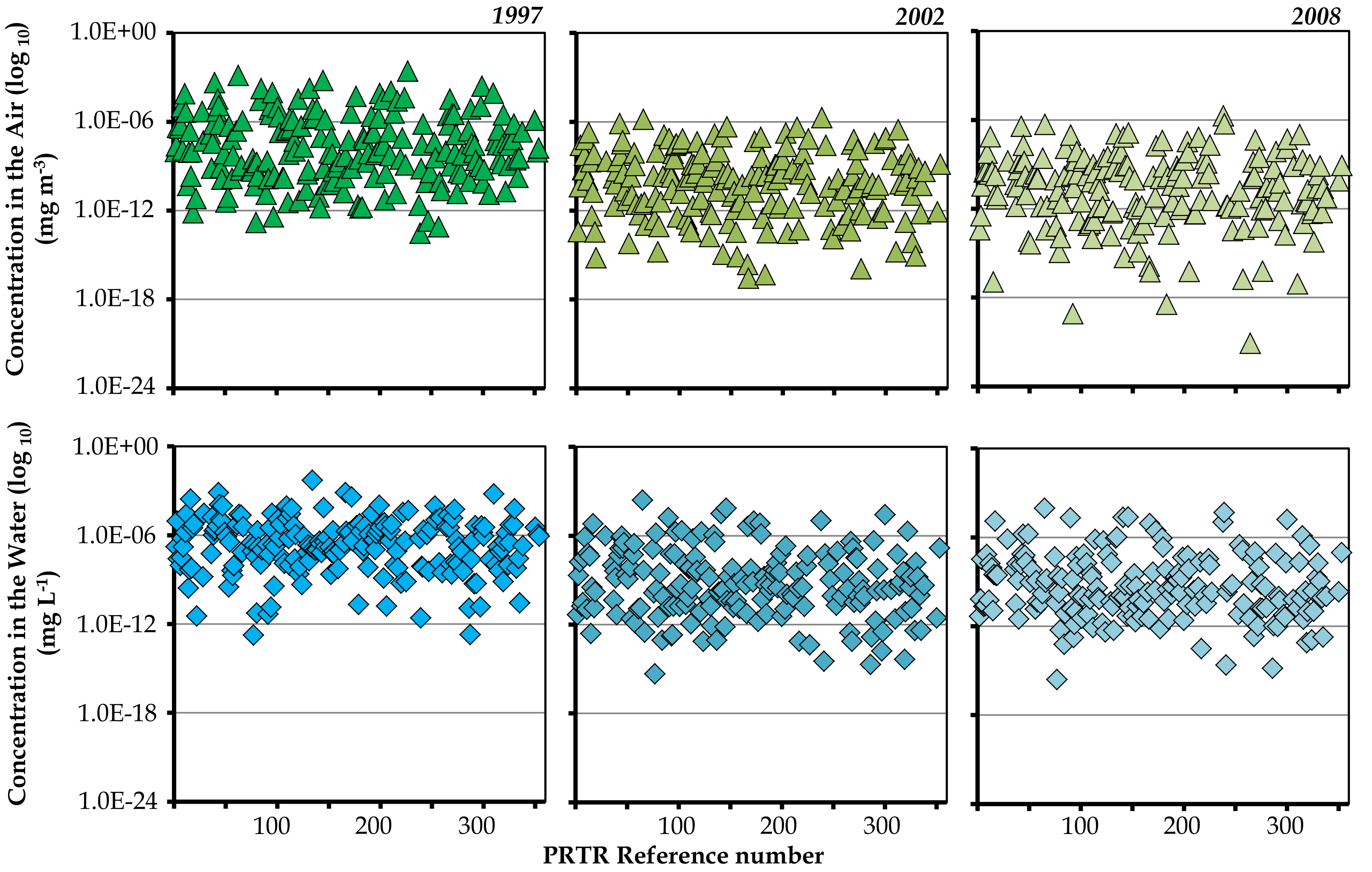

Fig. 6.2 Calculated concentrations of the 200 non-metallic PRTR chemicals in air and water for 1997, 2022, and 2008 against their PRTR number.

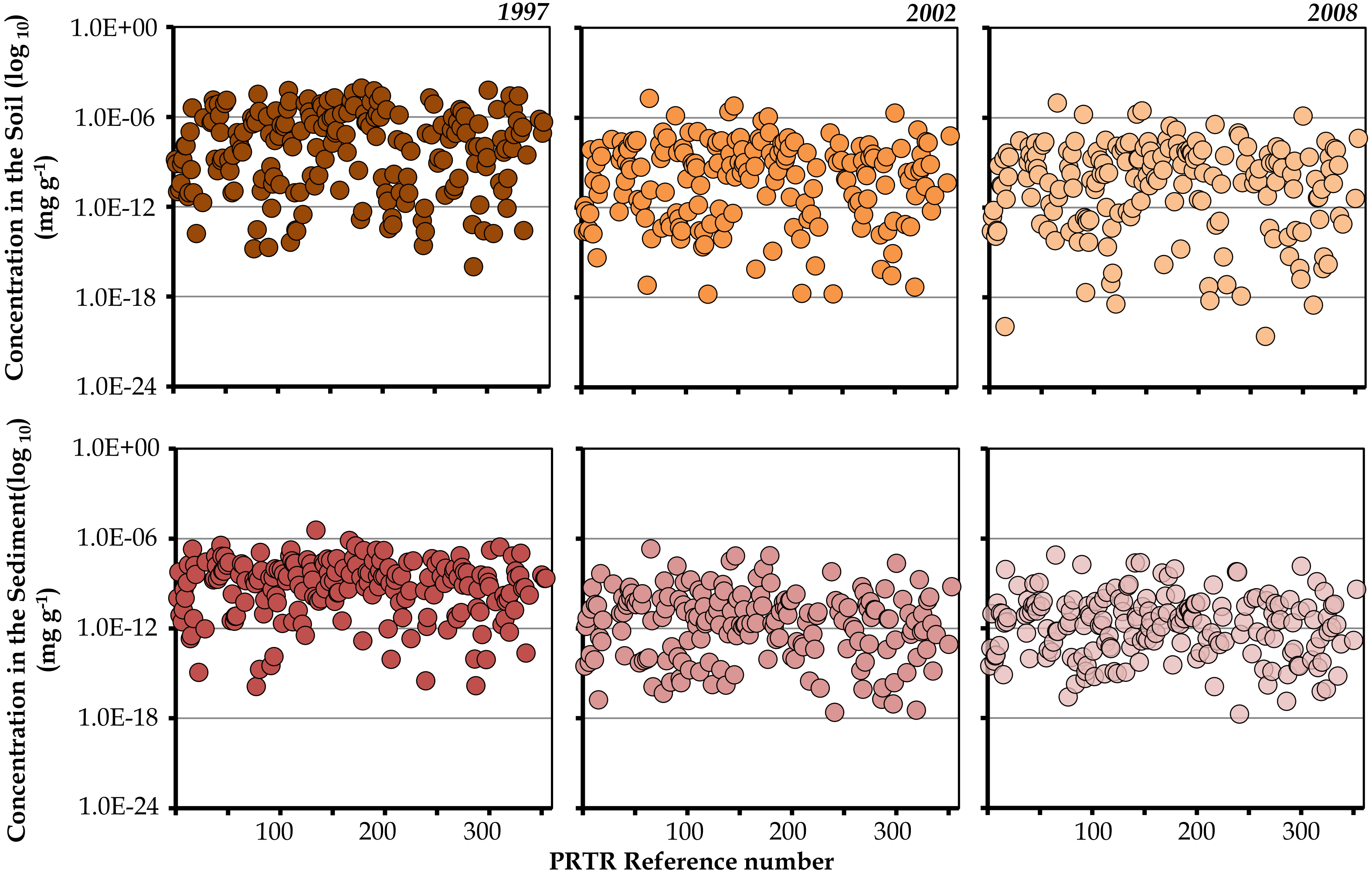

Fig. 6.3 Calculated concentrations of the 200 non-metallic PRTR chemicals in soil and sediment for 1997, 2022, and 2008 against their PRTR number.

The calculated results were compared with the available published data to validate the accuracy and reliability of the OBMM simulation. For example, glyoxal (PRTR No. 65) was calculated in the atmosphere at 5.49x10^{-10}, 1.46x10^{-06} and 4.93x10^{-07} mg m^{-3} in 1997, 2002 and 2008, respectively. The observed glyoxal concentration in the atmosphere around Tokyo was 5.86x10^{-07} mg m^{-3} (*Ortiz et al., 2007*). Atrazine (PRTR No. 75) is an antifouling compound and a herbicide which was observed 58.8 ng L^{-1} in water at a fishery harbor in Kobe, Japan (*Liu et al., 1999*) and the calculated concentration of atrazine in water in 1997 was 2.98x10^{-1} ng L^{-1}. Calculated concentrations by OBMM were close to the observed concentration of the chemicals of which the published monitoring data were available and thus the reliability of the OBMM was validated.

To confirm this overall decreasing concentration trends observed in **Fig. 6.2 & 6.3**, each of these chemicals was analyzed individually for their trends in concentration. While majority of these chemicals showed the decreasing concentration trends from 1997 to 2008, some chemicals exhibited differed concentration trends as shown in the **Fig 6.4.** Of the 200 non-metallic PRTR chemicals, 53 chemicals in the atmosphere, 69 in water, 65 in soil, and 63 in sediment exhibited the non-decreasing concentration trends from 1997, 2002 to 2008.

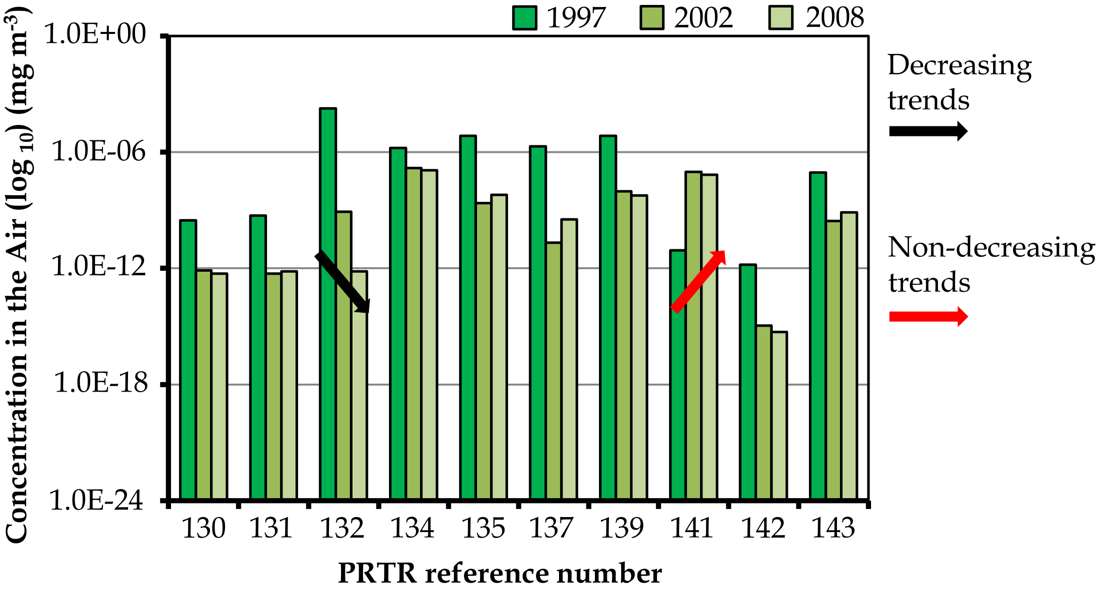

Fig. 6.4 Temporal trends in calculated atmospheric concentrations for PRTR chemicals (PRTR No. 130 to PRTR No. 143).

The average calculated concentrations for the three OBMM simulations were obtained for these 200 chemical compounds in each of the environmental media. They were arranged in descending order; the chemicals with the highest 10% average calculated concentrations were selected, and their relationships to the non-decreasing chemicals were observed. **Figure 6.5** shows the chemicals that showed these properties in each environmental media. In total, 35 of the 200 non-metallic chemicals had both the highest calculated concentrations and exhibited non-declining concentration trends over time. In the atmosphere 17 chemicals showed both these properties while in water, soil and sediments 25, 11, and 19 chemicals showed them respectively. Occurrences in multiple environmental media of these chemicals were observed at this point and that explains the total number of chemicals showing both highest calculated concentrations and non-declining concentration trends became 35 instead of 72 which is the total number of chemicals in all four environmental media showing both properties of non-declining concentration trends and highest calculated concentrations.

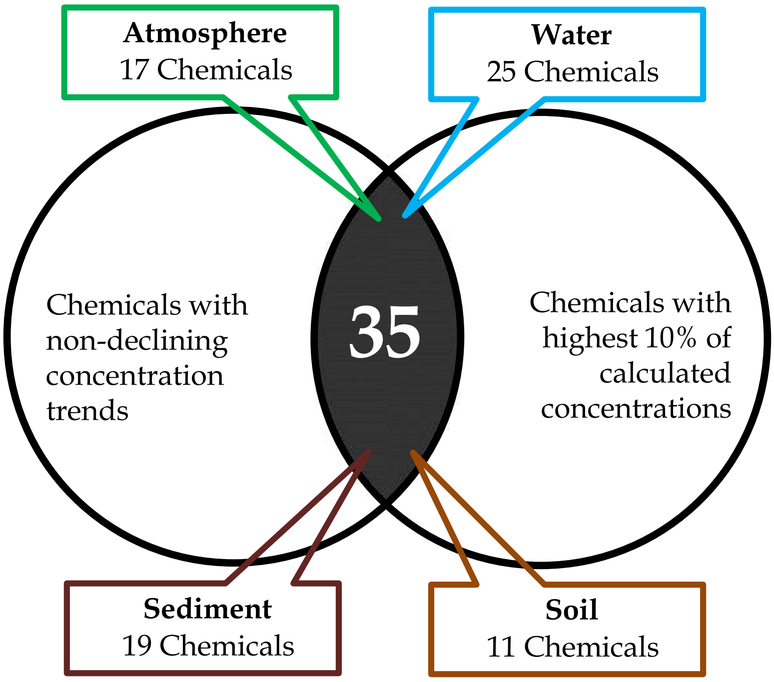

Fig. 6.5 Number of chemicals possessing both non-declining concentration trends and the highest 10% of calculated concentrations.

Table 6.1 Potentially hazardous chemical pollutants occurring in all four environmental media.

PRTR No	Chemical Name (IUPAC name)*	Cas No
65	Glyoxal (ethanedial)*	107-22-2
90	Shimazine (6-chloro-N-N-diethyl-1,3,5-triazine-2,4-diamine)*	122-34-9
146	Dithianon (5,10-dihydro-5,10-dioxonaphtho[2,3-b]-1,4-dithiine-2,3-dicarbonitrile)*	3347-22-6
179	Dioxins	
238	N-nitrosodiphenylamine (N,N-di(phenyl)nitrous amide)*	86-30-6
239	p-Nitrophenol (4-Nitrophenol)*	100-02-7
300	1,2,4-Benzenetricarboxylic 1,2-anhydride (1,3-dioxo-2-benzofuran-5-carboxylic acid)*	552-30-7

Therefore the third selection criteria of occurrence in all environmental media was introduce to the screening process, because the chemicals those occur in all four environmental media with non-declining concentration trends and occur within the highest 10% of the avg. calculated concentrations, possess a higher potential to damage the environment.

Seven of these 35 chemicals listed in the **Table 6.1** were identified to occur in all four environmental media. As these seven chemicals possess non-declining concentration trends and present in relatively high concentrations, their health-risk potential was qualitatively studied using the Health Hazard Criteria of the Occupational Safety and Health Administration, United State Department of Labor (*United States Department of Labor, 2013*). The health risk and the adverse effects of the chemical substances are categorized into following ten main categories:

- Acute toxicity
- Aspiration hazard

- Carcinogenicity
- Germ-cell mutagenicity
- Reproductive toxicity
- Skin corrosion/irritation
- Respiratory or skin irritation
- Serious eye damage/eye irritation
- Specific target-organ toxicity (single exposure)
- Specific target-organ toxicity (repeated/prolonged exposure)

A diagrammatical explanation of the relationships among these seven chemicals, their calculated concentrations in the atmosphere, water, and soil, together with their adverse health effects are shown in **Fig. 6.6.** As the potential of sediments to directly affect human health is comparatively negligible, sediment is not shown in **Fig. 6.6.** Three axes show the average calculated concentrations of the seven chemicals from **Table 6.1** for atmosphere, water, and soil. In water, dioxins were present at the minimum average calculated concentration ($2.62x10^{-6}$ mg L^{-1}), while glyoxal was present at the highest averaged calculated concentration ($1.22x10^{-4}$ mg L^{-1}). In the atmosphere, the calculated concentrations of these chemicals varied from $4.33x10^{-8}$ to $9.41x10^{-7}$ mg m^{-3}, while in soil, it varied from $2.03x10^{-8}$ to $9.79x10^{-6}$ mg g^{-1}.

The qualitative health risks posed by these seven chemicals are shown in **Fig. 6.6.** Dioxins pose five categories of health risks: carcinogenicity, skin corrosion/ irritation, respiratory or skin sensation, serious eye damage/eye irritation, and specific target- organ toxicity (*Bertazzi et al., 2000 and Kogevinas M., 2011*). Simazine poses risks of carcinogenicity, germ-cell mutagenicity, reproductive toxicity, and specific target-organ toxicity (*IARC Monographs on the Evaluation of Carcinogenic Risk to Humans, 1999 and Zorrilla et al., 2010*). Glyoxal (*Kielhorn et al., 2004*), Dithianon (*Paolini M. et al., 1997 and Toxicology Data Network*) and p-Nitrophenol **(***Edwards F. L. and Tchounwou P. B., 2005*) pose three categories of health risks as shown in the **Fig. 6.6**. These results support the findings of this section of the thesis and the seven chemicals given in the Table 6.1 were identified as potentially hazardous chemicals among the 200 non-metallic PRTR chemicals that were initially considered in this study.

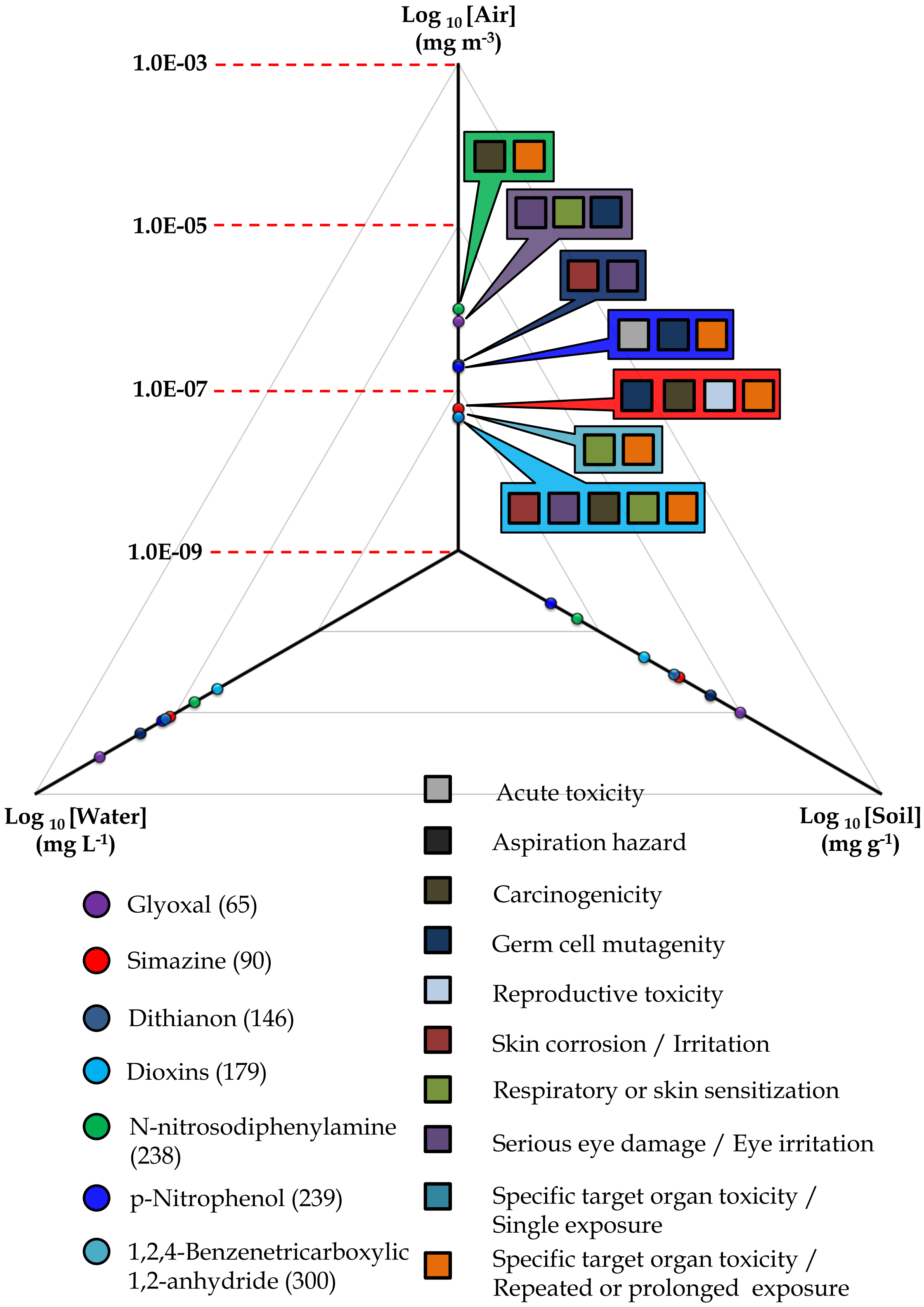

Fig. 6.6 Summary of the calculated concentrations and qualitative health risks of the potentially hazardous PRTR chemicals.

6.5 Conclusions

The one-box multimedia model was used to identify the potentially hazardous chemicals to the environment and health in LBYRB. Initially, 200 non-metallic chemicals were selected from the PRTR chemicals, and their emissions were estimated for 1997, 2002, and 2008 using PRTR data. These data were input to the OBMM to calculate chemical concentrations in the atmosphere, soil, water, and sediment. The calculated results were validated using the published monitoring data. Trends in the calculated concentrations over time were analyzed from 1997-2008. From the 200 non-metallic chemicals initially considered, 35 chemicals were identified for their non-declining calculated concentration trends and occurrence with higher concentrations. Seven of these 36 chemicals (Glyoxal, Simazine, Dithianon, N-nitrosodiphenylamine, Dioxins, p-Nitrophenol and 1,2,4-Benzenetricarboxylic anhydride) occur in all four environmental media and were identified as potentially hazardous PRTR chemicals. Therefore the objective of this section of the thesis to use OBMM as a tool to improve environmental management practices was achieved. The associated risks should be thoroughly studied in the future. The lack of monitoring data was a weakness in validating the concentrations calculated from the OBMM. More monitoring data would allow us to increase the accuracy, reliability, and adaptability of this model to diverse study sites.

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Conclusions

7

As described in the **chapter 1**, our environment has been polluted by the various natural and man-made chemical pollutants. Various management practices are carried out to control and prevent the environmental pollution. Monitoring these pollutants for their occurrences provides us valuable information that is used to mitigate environmental pollution. In most cases these target chemicals are identified after their adverse effects on the environment and the living beings are observed. But the prevention measures for environmental pollution have to be proactive and thus we need to recognize the chemicals those are potentially hazardous. Therefore it was suggested to use the available emission and monitoring data of these chemicals together with computational modeling to simulate the behavior, fate and trends of the chemical pollutants in our environment. Lake Biwa-Yodo River basin (LBYRB) was selected as the suitable study site due to its importance based on the complex geography, multiple land use patterns including the natural water source for the Kinki region of Japan. Emission amounts of the chemical pollutants were calculated based on the data of their consumptions and the data from the Pollutant Release and Transfer Registry (PRTR). The main objectives of this study were set to

- To evaluate the behavior, fate, temporal concentration trends and spatial distribution of the chemical pollutants in LBYRB by using mathematical and computational modeling.
- To experimentally determine the chemical parameters used in the computer models and to improve the model sensitivity.
- To evaluate potentially hazardous chemical pollutants by using the simulation results.

Chapter 2 provides the details about the two computer models; One-Box Multimedia Model (OBMM) and Distributed Multimedia Model (DMM) used in this study to evaluate the behavior, fate, temporal concentration trends, and spatial distribution of the chemical pollutants in LBYRB. Study area was divided into four environmental media namely; the atmosphere, water, soil, and sediments and chemical phenomena used to interpret the fate and the behavior of the chemical pollutants such as emission, degradation, advection, atmospheric mixing, dry/wet deposition, sedimentation, re-suspension, and particle and ion exchanges, are described in this chapter including the model variables and chemical parameters considered in the model calculations.

Chapter 3 describes the evaluation of metallic pollutant concentration in LBYRB by using OBMM simulations. Lead (Pb) and mercury (Hg) were selected as representative metallic pollutants because of their effects to the environment and human health. Annual emissions of Pb and Hg in LBYRB were calculated from 1960 to 2005 using PRTR data and the other published emission data. Calculated annual emission amounts were then used for separate OBMM simulations for a span of 45 years to evaluate the concentrations of Pb and Hg in all four environmental media. Calculated concentrations of Pb and Hg were studied for their concentration trends after validating the reliability of the calculated concentrations by comparing them with the observed Pb and Hg concentrations for the LBYRB.

Calculated atmospheric concentrations for Pb showed a distinctive decrease after 1975 and by 2005 it reached to 2.9×10^{-6} μmol m^{-3} and Hg showed variations of the atmospheric Hg concentration from 2.54×10^{-6} to 1.20×10^{-5} μmol m^{-3} throughout the study span of 45 years. Accumulations of both these metals were observed in soil and sediments and their concentration in water were observed to be effected by the deposition of atmosphere. Except for the atmosphere, the calculated concentrations of both Pb and Hg were becoming constant for the last 25 years of the study span because of the controlled emissions.

Results obtained from the research work described in the chapter 3 suggested the necessity of experimental determination of chemical parameters such as water-sediment partition coefficient **(K_d)** and incorporate the experimentally determined chemical parameter values in the model calculation, in order to improve the OBMM performances. The study carried out for this purpose is described in the **chapter 4**. Mercury was selected as the representative chemical pollutant and laboratory-scale experiments were carried out to evaluate the water-sediment partition coefficient of Hg **($K_{d\ (Hg)}$)** between the aqueous and solid phases of the environment, and an experimentally determined **$K_{d\ (Hg)}$** value (=80) was incorporated into the OBMM. The concentrations of Hg in the atmosphere, water, soil, and sediments, of the LBYRB were evaluated from 1960 to 2005 using the calculated annual Hg emission data and OBMM simulations.

Variations were observed in the calculated atmospheric Hg concentrations while in the sediment and soil, accumulation of Hg was observed. Except for the atmosphere, the calculated Hg concentrations in the soil, water, and sediment became constant over the last 25 years of the study span, due to the controlled consumption of Hg. The sensitivity of the OBMM calculations to the **$K_{d\ (Hg)}$** value was studied by comparing the calculated Hg concentrations on different **$K_{d\ (Hg)}$** values representing different soil types. The results showed that the experimentally evaluated **$K_{d\ (Hg)}$** value (=80) improved the accuracy of the OBMM calculations by providing a generalized **$K_{d\ (Hg)}$** value representing the whole study area.

To completely understand the environmental status of Hg concentration, the evaluation of spatial distribution of Hg was required. In **chapter 5**, the research work related to the evaluation of spatial distribution of Hg concentration in LBYRB by DMM is described. The study site was divided into 1 km x 1 km grid and DMM simulations were performed to evaluate the spatial distribution of Hg in the atmosphere, water, soil, and sediments. Emission data of Hg were calculated from 1960 to 2000 and used as input data. After validating the simulation results by comparing them with the reported observed data, they were plotted into spatial graphs using GIS techniques for the years of 1960, 1970, 1980, 1990, and 2000.

Increments of the Hg concentrations were observed until 1980s and in the latter period of the study span, the accumulations of the Hg in soil and sediments were observed towards the Southwestern part of the LBYRB especially towards the Yodo River mouth and the Osaka Bay. Atmospheric Hg concentrations were observed to decrease in LBYRB, but at the same time the occurrences of atmospheric Hg in relatively lower concentrations were observed to the Western and Northwestern parts of the LBYRB.

Chapter 6 describes the use of OBMM to identify the potentially hazardous non-metallic chemicals in LBYRB. Initially, 200 non-metallic chemicals were selected from the PRTR chemicals, and their emissions were estimated for 1997, 2002, and 2008 using PRTR data. These data were used in OBMM simulations to evaluate the chemical concentrations in the atmosphere, soil, water, and sediment. Trends in the calculated concentrations over time were analyzed from 1997-2008.

From the 200 non-metallic chemicals initially considered, 35 chemicals were identified for their non-declining calculated concentration trends and occurrence with higher concentrations. Seven of these 36 chemicals (Glyoxal, Simazine, Dithianon, N-nitrosodiphenylamine, Dioxins, p-Nitrophenol and 1,2,4-Benzenetricarboxylic anhydride) were identified to occur in all four environmental media. After confirming their health risks with the qualitative health risk analysis, these seven chemicals were identified as potentially hazardous PRTR chemicals while proving the use of OBMM as an environmental assessing tool can improve environmental management practices.

Recommendations

- Both the models used in this study required environmental information such as: meteorological and hydrological data, geochemical data, and chemical management data, for more advance studies. Since these are separate study areas, the collaborations between the scientists in these fields are required for the progress of environmental modeling studies.
- These models have to be tested in other different geographical areas to observe the model performances, and the improvements of the models are required so that the models can be applied in any part of the world to evaluate the chemical concentration levels.
- Actual values for the coefficients of chemical parameters play an important role when the chemical behaviors are interpreted into mathematical and computational models. Since, these chemical parameters depends of various

conditions of the environment, the actual values for these chemical parameters have to be experimentally evaluated and the actual values have to be incorporated in the model calculations used in this study. More accurate simulation results will be able to obtain through this process.

- Thorough studies are required in experimentally evaluating the chemical parameters considered in the model calculations. Increasing the number of replicates in these experiments would provide more reliable experimental data.
- Emission data calculations were a quite complex part of this study. But having a proper systematic system (or a method) to track the total amount of the chemical consumption would facilitate the function of PRTR system to overview the chemical loading to the environment. Also this would support the researchers and the authorities to have enough information for their research and managerial processes to protect the environment.
- Environmental monitoring data were very important in validating the model calculations. Because of the practical difficulties in environmental monitoring process, many of the chemicals lack environmental monitoring data and this lack of information is a drawback in validating the calculated results, which has to be address in order to improve the model reliability.
- Adverse effects of the chemicals are vital information. But the risk and toxicology studies are very complex, so that the important findings for different chemicals are difficult to compare. Much simpler systems are required to compare the adverse (health and environmental) effect of the chemical pollutants, so that it becomes easier to evaluate the chemicals which would become potentially hazardous.

PUBLICATIONS

Certain sections of this thesis have been taken from the following publications:

PEER –REVIEWED JOURNAL ARTICLES

1. **Ariyadasa B.H.A.K.T.**, Kondo A., Shimadera H., Ochi H., Inoue Y., 2014. Evaluation of mercury concentration in the Lake Biwa-Yodo River basin by a one-box multimedia model and model sensitivity on the experimentally determined water-sediment partition coefficient. *Journal of Environmental Engineering and Ecological Science*, 3:3.

2. **Ariyadasa B.H.A.K.T.**, Kondo A., Inoue Y., 2014. Temporal screening for hazardous PRTR chemicals in the Lake Biwa-Yodo River Basin of Japan using a one-box multimedia model. Environmental Science and Pollution Research, (Submitted -25th January 2014. Under review by 2nd May 2014).

3. Kondo A., Yamamoto M., Inoue Y., **Ariyadasa B.H.A.K.T.**, 2013. Evaluation of lead concentration by one-box type multimedia model in Lake Biwa-Yodo River basin of Japan. *Chemosphere*, Vol. 93 pp 497-503.

PEER –REVIEWED INTERNATIONAL CONFERENCE PRESENTATION

1. **Ariyadasa T**., Kondo A., Inoue Y., 2013. Evaluation of risk possessing chemicals in Lake Biwa-Yodo River basin using computational modeling. *The 6th Korea-China-Japan Graduate Student Forum, Daejeon, Korea.* ***(Best Presentation Award).***
2. **Ariyadasa T.**, Kondo A., Inoue Y., 2013. Temporal screening of risk possessing PRTR chemicals in Lake Biwa-Yodo River Basin using one-box multimedia model. *2nd International Conference on Environmental Pollution, Restoration, and Management, Hanoi, Vietnam.* (***Best Presentation Award***).
3. Kondo A., **Ariyadasa B.H.A.K.T.**, Shimadera H., Ochi H., Inoue Y., 2014. Temporal evaluation of mercury concentration in Lake Biwa-Yodo River basin by one-box multimedia model. *Proceeding of the 4th International Conference on Environmental Pollution and Remediation, Prague, Czech Republic.*

LOCAL CONFERENCE PRESENTATION

1. **Ariyadasa T.**, Kondo A., Inoue Y., 2012. Screening of risk processing PRTR chemicals in Lake Biwa-Yodo River Basin using one-box multimedia mode*l. Conference of Environmental Chemistry, Yokohama, Japan.*

OTHER RESEARCH PRESENTATIONS

1. **Ariyadasa T**., Kondo A., Inoue Y., 2012. Evaluation of health risk and fate of PRTR chemicals in Lake Biwa – Yodo River basin (Japan) using distributed Multimedia Model. *Summer School of the HeKKSaGOn Consortium Heidelberg, Germany.* ***(Best Presentation Award-3rd Place)***

MASTER'S THESIS

Ariyadasa B.H.A.K.T., 2011. Study on processes of coagulation and adsorption to remove perfluorooctane sulfonate (PFOS) and perfluorooctanic acid (PFOA) from domestic and industrial wastewater. *Master's Thesis.* Graduate School of Global Environmental Studies, Kyoto University, Japan.

APPENDIX

In the appendix of this thesis the additional details are provided relates to the following:

Appendix 01	**P**arameters and the abbreviations used in the model equations.
Appendix 02	List of 200 non-metallic PRTR chemicals studied in chapter 6.
Appendix 03	Emission amounts of the 200 non-metallic PRTR chemicals to the atmosphere, water, and soil for the years of 1997, 2002, and 2008.

Appendix 01

Abbreviations	**Model Parameters**		**Values**	
			Pb	**Hg**
	Molecular weight	**(Da)**	**207.19**	**200.59**
	Henry`s coefficient	**(atm m^3 mol^{-1})**	**$1.35x10^4$**	**$1.35x10^4$**
	Vapor pressure	**(atm)**	**$1.45x10^{-4}$**	**$2.00x10^{-6}$**
	Water-sediemt partition coefficient	**(log(POW))**	**1**	**80**
Gar	Emission to atmosphere (PP)		–	
Gsl	Emission to soil (PP)		–	
Gss	Emission to water (suspended solids)		–	
Gwtlq	Emission to water (CP)		–	
Cptu	Calculated conc. in upper atmosphere (PP)		–	
Cptd	Calculated conc. in lower atmosphere (PP)		–	
Cptin	Calculated conc. in inflow atmosphere (PP)		–	
Csllq	Calculated conc. in soil (CP)		–	
CsllqD	Calculated conc. in soil per water volume (CP)		–	
Css	Calculated conc. in suspended solids		–	
Cwt	Calculated conc.in water (PP)		–	
Cwtlq	Calculated conc. in water (CP)		–	
CwtD	Calculated conc. in water per water volume (CP)		–	
Cwtsat	Set value for conc. of saturated solution (LP)		–	
Csdlq	Calculated conc. in sediment (CP)		–	
Ssl	Set value for soil area	**(m^2)**	**$7.35x10^{-9}$**	
Swt	Set value for water area	**(m^2)**	**$8.63x10^{-8}$**	
Srv	Set value for river area	**(m^2)**	**$2.08x10^{-6}$**	
Hsl	Set value for soil depth	**(m)**	**$5.00x10^{-2}$**	
Hwt	Set value for river depth	**(m)**	**3**	
DHsd	Sediment depth variation		–	
Rsl	Set value for soil particle density		**$2.30x10^{-3}$**	

PP**-Particle Phase* *__CP__-Charged Phase* *__LP__-Liquid Phase* ***Contd;

Abbreviations	Model Parameters		Values	
			Pb	Hg
Esl	Set value for soil voidage		**5.00×10^{-1}**	
Sitsl	Set value for soil moisture content		**2.50×10^{-1}**	
Sitsd	Sediment moisture content		**1.40×10^{-1}**	
Qar	Air inflow		–	
Qwt	Set value for water inflow	**(m^3 s^{-1})**	**298**	
Rosl	Set value for outflow rate of soil particle	**(m s^{-1})**	**8.7**	
Rof	Set value for outflow water volum	**(m^3 s^{-1})**	**4.2**	
Vptwd	Wet deposition rate		–	
Vptdd	Dry deposition rate	**(m s^{-1})**	**1.00×10^{-2}**	
Vssdep	Sedimentaiton rate of suspended particle	**(m s^{-1})**	**7.13×10^{-6}**	
Ksl	Solution rate to the liquid phase in soil		–	
Kss	Solution rate to the liquid phase in water		–	
Ksd	Solution rate to the liquid phase in sediment		–	
Kwtsd	Diffusion rate from water body to sediment		–	
scss	Suspended particle conc.		–	
Ksl	Solution rate to the liquid phase in soil		–	
Kss	Solution rate to the liquid phase in water		–	
Ksd	Solution rate to the liquid phase in sediment		–	
Kwtsd	Diffusion rate from water body to sediment		–	
scss	Suspended particule concentaration		–	
Casl	Exchangeable ion content in soil		–	
Casllq	Exchangeable ion conc. in soil liquid phase		–	
Cass	Exchangeable ion content in suspended particulate		–	
Cawt	Exchangeable ion conc. in water body		–	
Casd	Exchangeable ion content in sediment		–	
Casdlq	Exchangeable ion conc. in sediment liquid phase		–	
Sca	Selectivity coefficient of substitute ions		–	

Appendix 02

PRTR No	Chemical Name	Cas No
2	Acrylamide	79-06-1
3	Acrylic acid	79-10-7
4	Ethyl acrylate	140-88-5
6	Methyl acrylate	96-33-3
7	Acrylonitrile	107-13-1
8	Acrolein	107-02-8
9	bis(2-Ehtylhexyl) adipate	103-23-1
11	Acetaldehyde	75-07-0
12	Acetonitrile	75-05-8
14	o-Anisidine	90-04-0
15	Aniline	62-53-3
16	2-Aminoethanol	141-43-5
17	N-(2-aminoethyl)-1,2-ethanediamine; diethylenetriamine	111-40-0
18	5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-3-cyano-4-[(trifluoromethyl)sulfinyl]pyrazole; fipronil	120068-37-3
19	3-Amino-1H-1,2,4-triazole; amitrole	61-82-5
22	Allyl alcohol	107-18-6
28	Isoprene	78-79-5
29	4,4'-Isopropylidenediphenol; bisphenol A	80-05-7
36	O-Ethyl O-(6-nitro-m-tolyl)sec-butylphosphoramidothioate; butamifos	36335-67-8

PRTR No	Chemical Name	Cas No
38	N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine; pendimethalin	40487-42-1
39	S-ethyl hexahydro-1H-azepine-1-carbothioate; molinate	2212-67-1
40	Ethylbenzene	100-41-4
42	Ethylene oxide	75-21-8
43	Ethylene glycol	107-21-1
44	Ethylene glycol monoethyl ether	110-80-5
45	Ethylene glycol monomethyl ether	109-86-4
46	Ethylenediamine	107-15-3
47	Ethylenediaminetetraacetic acid	60-00-4
49	Manganese N,N'-ethylenebis(dithiocarbamate); maneb	12427-38-2
51	1,1'-Ethylene-2,2'-bipyridinium dibromide; diquat dibromide	85-00-7
53	5-Ethoxy-3-trichloromethyl-1,2,4-thiadiazole; echlomezol	2593-15-9
54	Epichlorohydrin	106-89-8
56	1,2-Epoxypropane; propylene oxide	75-56-9
57	2,3-Epoxypropyl phenyl ether	122-60-1
58	1-Octanol	111-87-5
61	Epsilon-caprolactam	105-60-2
63	Xylene	1330-20-7
65	Glyoxal	107-22-2
66	Glutaraldehyde	111-30-8

PRTR No	Chemical Name	Cas No
67	Cresol	1319-77-3
75	2-Chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine; atrazine	1912-24-9
76	2-Chloro-2'-ethyl-N-(2-methoxy-1-methylethyl)-6'-methylacetanilide; metolachlor	51218-45-2
77	Chloroethylene; vinyl chloride	75-01-4
78	3-Chloro-N-(3-chloro-5-trifluoromethyl-2-pyridyl)-alpha,alpha,alpha-trifluoro-2,6-dinitro-ptoluidine; fluazinam	79622-59-6
79	1-({2-[2-Chloro-4-(4-chlorophenoxy)phenyl]-4-methyl-1,3-dioxolan-2-yl}methyl)-1H-1,2,4-triazole; difenoconazole	119446-68-3
80	Chloroacetic acid	79-11-8
81	2-Chloro-2',6'-diethyl-N-(2-propoxyethyl)acetanilide; pretilachlor	51218-49-6
82	2-Chloro-2',6'-diethyl-N-(methoxymethyl)acetanilide; alachlor	15972-60-8
84	1-Chloro-1,1-difluoroethane; HCFC-142b	75-68-3
85	Chlorodifluoromethane; HCFC-22	75-45-6
90	2-Chloro-4,6-bis(ethylamino)-1,3,5-triazine; shimazine; CAT	122-34-9
91	3-Chloropropene; allyl chloride	107-05-1
92	4-Chlorobenzyl N-(2,4-dichlorophenyl)-2-(1H-1,2,4-triazol-1-yl)thioacetimidate; imibenconazole	86598-92-7
93	Chlorobenzene	108-90-7
94	Chloropentafluoroethane; CFC-115	76-15-3
95	Chloroform	67-66-3

PRTR No	Chemical Name	Cas No
96	Chloromethane; methyl chloride	74-87-3
97	(4-Chloro-2-methylphenoxy)acetic acid; MCP; MCPA	94-74-6
98	2-Chloro-N-(3-methoxy-2-thienyl)-2',6'-dimethylacetanilide; thenylchlor	96491-05-3
101	2-Ethoxyethyl acetate; ethylene glycol monoethyl ether acetate	111-15-9
102	Vinyl acetate	108-05-4
103	2-Methoxyethyl acetate; ethylene glycol monomethyl ether acetate	110-49-6
106	(S)-α-Cyano-3-phenoxybenzyl (S)-2-(4-chlorophenyl)-3-methylbutyrate; esfenvalerate	51630-58-1
107	α-Cyano-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylate; cypermethrin	52315-07-8
109	2-(Diethylamino)ethanol	100-37-8
110	(S)-4-Chlorobenzyl N,N-diethylthiocarbamate; thiobencarb	28249-77-6
111	N,N-Diethyl-3-(2,4,6-trimethylphenylsulfonyl)-1H-1,2,4-triazole-1-carboxamide; cafenstrole	125306-83-4
112	Tetrachloromethane	56-23-5
113	1,4-Dioxane	123-91-1
114	Cyclohexylamine	108-91-8
116	1,2-Dichloroethane	107-06-2
117	1,1-Dichloroethylene; vinylydene dichloride	75-35-4
118	cis-1,2-Dichloroethylene	156-59-2
121	Dichlorodifluoromethane; CFC-12	75-71-8
122	3,5-Dichloro-N-(1,1-dimethyl-2-propynyl)benzamide; propyzamide	23950-58-5

PRTR No	Chemical Name	Cas No
124	2,2-Dichloro-1,1,1-trifluoroethane; HCFC-123	306-83-2
126	2-[4-(2,4-Dichloro-m-toluoyl)-1,3-dimethyl-5-pyrazolyloxy]-4-methylacetophenone	82692-44-2
129	3-(3,4-Dichlorophenyl)-1,1-dimethylurea; diuron; DCMU	330-54-1
130	3-(3,4-Dichlorophenyl)-1-methoxy-1-methylurea; linuron	330-55-2
131	2,4-Dichlorophenoxyacetic acid; 2,4-D; 2,4-PA	94-75-7
132	1,1-Dichloro-1-fluoroethane; HCFC-141b	1717-00-6
134	1,3-Dichloro-2-propanol	96-23-1
135	1,2-Dichloropropane	78-87-5
137	1,3-Dichloropropene; D-D	542-75-6
139	Dichlorobenzene	95-50-1/ 106-46-7
141	2-[4-(2,4-Dichlorobenzoyl)-1,3-dimethyl-5-pyrazolyloxy]acetophenone; pyrazoxyfen	71561-11-0
142	4-(2,4-Dichlorobenzoyl)-1,3-dimethyl-5-pyrazolyl 4-toluenesulfonate; pyrazolynate	58011-68-0
143	2,6-Dichlorobenzonitrile; dichlobenil; DBN	1194-65-6
145	Dichloromethane; methylene dichloride	75-09-2
146	2,3-Dicyano-1,4-dithiaanthraquinone; dithianon	3347-22-6
147	Diisopropyl 1,3-dithiolan-2-ylidenemalonate; isoprothiolane	50512-35-1
148	o-Ethyl S S diphenyl phosphorodithioate; edifenphos; EDDP	17109-49-8
151	O,O-Diethyl S-2-(ethylthio)ethyl phosphorodithioate; ethylthiometon; disulfoton	298-04-4
152	O,O-Diethyl S-(6-chloro-2,3-dihydro-2-oxobenzoxazolinyl)methyl phosphorodithioate;	2310-17-0
153	O-2,4-Dichlorophenyl O-ethyl S-propyl phosphorodithioate; prothiofos	34643-46-4

PRTR No	Chemical Name	Cas No
154	S-(2,3-Dihydro-5-methoxy-2-oxo-1,3,4-thiadiazol-3-yl)methyl O,Odimethylphosphorodithioate; methidathion; DMTP	950-37-8
155	O,O-Dimethyl S-1,2-bis(ethoxycarbonyl)ethyl phosphorodithioate; malathon;malathion	121-75-5
156	O,O-Dimethyl S-(N-methylcarbamoyl)methyl phosphorodithioate; dimethoate	60-51-5
159	Diphenylamine	122-39-4
161	2,3-Dihydro-2,2-dimethyl-7-benzo[b]furyl N-(dibutylamino)thio-N-methylcarbamate;	55285-14-8
165	S-4-Phenoxybutyl N,N-dimethylthiocarbamate; phenothiocarb	62850-32-2
166	N,N-Dimethyldodecylamine N-oxide	1643-20-5
167	Dimethyl 2,2,2-trichloro-1-hydroxyethylphosphonate; trichlorfon; DEP	52-68-6
170	S-Benzyl N-(1,2-dimethylpropyl)-N-ethylthiocarbamate; esprocarb	85785-20-2
172	N,N-Dimethylformamide	68-12-2
173	Ethyl 2-[(dimethoxyphosphinothioyl)thio]-2-phenylacetate; phenthoate; PAP	2597-03-7
177	Styrene	100-42-5
179	Dioxins	
180	2-Thioxo-3,5-dimethyltetrahydro-2H-1,3,5-thiadiazine; dazomet	533-74-4
181	Thiourea	62-56-6
183	O-1-(4-Chlorophenyl)-4-pyrazolyl O-ethyl S-propyl phosphorothioate; pyraclofos	77458-01-6
184	O-4-Cyanophenyl O,O-dimethyl phosphorothioate; cyanophos; CYAP	2636-26-2
185	O,O-Diethyl O-2-isopropyl-6-methyl-4-pyrimidinyl phosphorothioate; diazinon	333-41-5
188	O,O-Diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate; chlorpyrifos	2921-88-2

PRTR No	Chemical Name	Cas No
189	O,O-Diethyl O-5-phenyl-3-isoxazolyl phosphorothioate; isoxathion	18854-01-8
192	O,O-Dimethyl O-3-methyl-4-nitrophenyl phosphorothioate; fenitrothion; MEP	122-14-5
193	O,O-Dimethyl O-3-methyl-4-(methylthio)phenyl phosphorothioate; fenthion; MPP	55-38-9
194	O-3,5,6-Trichloro-2-pyridyl O,O-dimethyl phosphorothioate; chlorpyrifos-methyl	5598-13-0
195	O-4-Bromo-2-chlorophenyl O-ethyl S-propyl phosphorothioate; profenofos	41198-08-7
196	S-Benzyl O,O-diisopropyl phosphorothioate; iprobenfos; IBP	26087-47-8
198	1,3,5,7-Tetraazatricyclo[3.3.1.13.7]decane; hexamethylenetetramine	100-97-0
199	Tetrachloroisophthalonitrile; chlorothalonil; TPN	1897-45-6
200	Tetrachloroethylene	127-18-4
203	Tetrafluoroethylene	116-14-3
204	Tetramethylthiuram disulfide; thiram	137-26-8
205	Terephthalic acid	100-21-0
206	Dimethyl terephthalate	120-61-6
209	1,1,1-Trichloroethane	71-55-6
210	1,1,2-Trichloroethane	79-00-5
211	Trichloroethylene	79-01-6
214	Trichloronitromethane; chloropicrin	76-06-2
216	(3,5,6-Trichloro-2-pyridyl)oxyacetic acid; triclopyr	55335-06-3
217	Trichlorofluoromethane; CFC-11	75-69-4
220	α,α,α-Trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine; trifluralin	1582-09-8

PRTR No	Chemical Name	Cas No
222	Tribromomethane; bromoform	75-25-2
224	1,3,5-Trimethylbenzene	108-67-8
225	Toluidine	95-53-4/ 106-49-0
227	Toluene	108-88-3
238	N-Nitrosodiphenylamine	86-30-6
239	p-Nitrophenol	100-02-7
240	Nitrobenzene	98-95-3
241	Carbon disulfide	75-15-0
242	Nonylphenol	25154-52-3
245	2,4-bis(Ethylamino)-6-methylthio-1,3,5-triazine; simetryn	1014-70-6
247	3,6-bis(2-Chlorophenyl)-1,2,4,5-tetrazine; clofentezine	74115-24-5
249	Zinc bis(N,N-dimethyldithiocarbamate); ziram	137-30-4
253	Hydrazine	302-01-2
254	Hydroquinone	123-31-9
257	1-(4-Biphenylyloxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-butanol; bitertano	55179-31-2
258	Piperazine	110-85-0
260	Pyrocatechol	120-80-9
264	Phenylenediamine	108-45-2/ 108-45-2
266	Phenol	108-95-2
267	3-Phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate; permethrin	52645-53-1

PRTR No	Chemical Name	Cas No
268	1,3-Butadiene	106-99-0
269	di-n-Octyl phthalate	117-84-0
270	di-n-Butyl phthalate	84-74-2
272	bis(2-Ethylhexyl) phthalate	117-81-7
273	n-Butyl benzyl phthalate	85-68-7
274	2-Tert-butylimino-3-isopropyl-5-phenyltetrahydro-4H-1,3,5-thiadiazin-4-one; buprofezin	69327-76-0
275	N-Tert-butyl-N'-(4-ethylbenzoyl)-3,5-dimethylbenzohydrazide; tebufenozide	112410-23-8
276	Methyl N-[1-(N-n-butylcarbamoyl)-1H-2-benzimidazolyl]carbamate; benomyl	17804-35-2
279	2-(4-Tert-butylphenoxy)cyclohexyl 2-propynyl sulfite; propargite; BPPS	2312-35-8
280	2-Tert-butyl-5-(4-tert-butylbenzylthio)-4-chloro-3(2H)-pyridazinone; pyridaben	96489-71-3
286	Bromotrifluoromethane; halone-1301	75-63-8
287	2-Bromopropane	75-26-3
288	Bromomethane; methyl bromide	74-83-9
289	hexakis(2-Methyl-2-phenylpropyl)distannoxane; fenbutatin oxide	13356-08-6
291	6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepine 3-oxide; endosulfan	115-29-7
292	Hexamethylenediamine	124-09-4
293	Hexamethylene diisocyanate	822-06-0
297	Benzyl chloride	100-44-7
298	Benzaldehyde	100-52-7

PRTR No	Chemical Name	Cas No
299	Benzene	71-43-2
300	1,2,4-Benzenetricarboxylic 1,2-anhydride	552-30-7
301	2-(2-Benzothiazolyloxy)-N-methylacetanilide; mefenacet	73250-68-7
306	Polychlorinated biphenyls; PCBs	1336-36-3
310	Formaldehyde	50-00-0
312	Phthalic anhydride	85-44-9
313	Maleic anhydride	108-31-6
314	Methacrylic acid	79-41-4
315	2-Ethylhexyl methacrylate	688-84-6
316	2,3-Epoxypropyl methacrylate	106-91-2
318	2-(Dimethylamino)ethyl methacrylate	2867-47-2
319	n-Butyl methacrylate	97-88-1
320	Methyl methacrylate	80-62-6
322	(Z)-2'-Methylacetophenone 4,6-dimethyl-2-pyrimidinylhydrazone; ferimzone	89269-64-7
324	Methyl isothiocyanate	556-61-6
325	2-Isopropylphenyl N-methylcarbamate; isoprocarb; MIPC	2631-40-5
326	2-Isopropoxyphenyl N-methylcarbamate; propoxur; PHC	114-26-1
329	1-Naphthyl N-methylcarbamate; carbaryl; NAC	63-25-2
330	2-Sec-butylphenyl N-methylcarbamate; fenobucarb; BPMC	3766-81-2
332	3-Methyl-1,5-di(2,4-xylyl)-1,3,5-triazapenta-1,4-diene; amitraz	33089-61-1

PRTR No	Chemical Name	Cas No
334	6-Methyl-1,3-dithiolo[4,5-b]quinoxalin-2-one	2439-01-2
335	α-Methylstyrene	98-83-9
338	Tolylene diisocyanate	26471-62-5
350	Dimethyl 2,2-dichlorovinyl phosphate; dichlorvos; DDVP	62-73-7
353	Tris(dimethylphenyl) phosphate	25155-23-1
354	Tri-n-butyl phosphate	126-73-8

Appendix 03

No.	PRTR No	Total emission amounts (kg $year^{-1}$)								
		1997			**2002**			**2008**		
		Air	Soil	Water	Air	Soil	Water	Air	Soil	Water
1	2	2.6E+05	0.0E+00	1.0E+01	2.9E+02	0.0E+00	6.7E+01	2.3E+00	3.0E+00	2.5E+00
2	3	1.6E+05	0.0E+00	3.2E+05	1.6E+05	0.0E+00	7.2E+02	4.7E+01	8.6E+01	1.5E+03
3	4	2.8E+06	0.0E+00	9.3E+02	3.7E+03	0.0E+00	3.0E-01	1.9E+03	0.0E+00	7.0E-01
4	6	2.2E+06	0.0E+00	1.0E+02	2.6E+03	0.0E+00	4.5E-02	2.3E+03	0.0E+00	0.0E+00
5	7	2.7E+06	0.0E+00	0.0E+00	3.1E+04	0.0E+00	6.1E+02	2.1E+03	0.0E+00	7.0E-02
6	8	5.8E+07	0.0E+00	0.0E+00	4.3E+05	0.0E+00	0.0E+00	3.8E+04	0.0E+00	0.0E+00
7	9	8.6E+04	0.0E+00	0.0E+00	7.3E+02	0.0E+00	2.3E+00	1.2E+01	1.3E+03	1.2E+01
8	11	4.9E+08	0.0E+00	1.9E+05	7.9E+05	0.0E+00	3.1E+02	3.1E+05	0.0E+00	0.0E+00
9	12	1.8E+07	2.8E+05	4.0E+05	2.7E+04	7.2E+02	3.7E+02	3.4E+03	1.9E+03	7.6E+01
10	14	7.0E+02	0.0E+00	0.0E+00	8.6E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	1.1E+00
11	15	1.7E+05	0.0E+00	0.0E+00	3.8E+02	0.0E+00	0.0E+00	1.7E+02	5.6E-03	2.8E+02
12	16	4.7E+06	0.0E+00	2.6E+07	3.0E+04	0.0E+00	6.8E+04	2.8E+02	1.5E+03	1.3E+05
13	17	1.0E+03	0.0E+00	0.0E+00	6.0E-01	8.0E+00	0.0E+00	7.6E+01	0.0E+00	1.3E+01
14	18	1.5E+05	8.4E+05	0.0E+00	0.0E+00	1.4E+03	0.0E+00	1.6E+02	1.2E+03	0.0E+00
15	19	1.4E+01	0.0E+00	6.1E+04	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00
16	22	4.3E+01	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00
17	28	7.0E+07	0.0E+00	0.0E+00	7.1E+04	0.0E+00	0.0E+00	5.6E+04	0.0E+00	1.1E+02

No.	**PRTR No**	**Total emission amounts (kg year^{-1})**								
		1997			2002			2008		
		Air	Soil	Water	Air	Soil	Water	Air	Soil	Water
18	29	1.7E+06	0.0E+00	8.3E+04	7.0E+02	0.0E+00	1.1E+02	4.3E+01	1.7E+02	7.4E+01
19	36	1.1E+04	7.4E+05	0.0E+00	0.0E+00	1.5E+03	0.0E+00	0.0E+00	1.1E+03	0.0E+00
20	37	0.0E+00	5.5E+05	2.0E+05	0.0E+00	2.2E+03	2.6E+01	0.0E+00	1.1E+03	1.7E+02
21	38	0.0E+00	1.2E+06	0.0E+00	2.8E+00	3.0E+03	0.0E+00	0.0E+00	2.7E+03	0.0E+00
22	39	0.0E+00	4.3E+06	0.0E+00	0.0E+00	9.9E+03	0.0E+00	0.0E+00	6.4E+03	0.0E+00
23	40	2.1E+09	7.3E+05	1.6E+05	3.3E+06	2.2E+03	6.0E+02	1.4E+06	1.9E+05	5.5E+01
24	42	2.2E+07	0.0E+00	1.2E+05	3.9E+04	0.0E+00	2.3E+03	8.5E+03	2.8E+03	3.0E+03
25	43	2.4E+08	2.8E+06	1.1E+07	1.8E+05	2.1E+04	2.8E+04	1.0E+05	6.4E+04	6.7E+04
26	44	7.1E+07	0.0E+00	2.4E+06	3.0E+05	0.0E+00	2.1E+03	8.7E+03	1.0E+04	3.8E+02
27	45	3.8E+06	0.0E+00	2.2E+04	8.5E+03	0.0E+00	2.3E+02	4.0E+03	7.0E+02	4.1E+01
28	46	2.1E+04	0.0E+00	9.1E+04	2.1E+02	0.0E+00	3.7E+03	9.6E+01	2.6E+00	2.0E+02
29	47	1.2E+03	0.0E+00	1.0E+06	0.0E+00	0.0E+00	6.3E+03	0.0E+00	0.0E+00	1.8E+04
30	49	4.7E+04	1.7E+06	0.0E+00	0.0E+00	4.6E+03	0.0E+00	0.0E+00	6.2E+03	0.0E+00
31	51	0.0E+00	3.0E+06	0.0E+00	0.0E+00	7.7E+03	0.0E+00	0.0E+00	0.0E+00	0.0E+00
32	53	0.0E+00	3.2E+02	0.0E+00	0.0E+00	6.0E+01	0.0E+00	1.0E+03	0.0E+00	0.0E+00
33	54	2.1E+06	0.0E+00	4.5E+03	3.4E+04	0.0E+00	1.5E+03	4.6E+02	0.0E+00	0.0E+00
34	56	2.9E+05	0.0E+00	0.0E+00	5.0E+03	0.0E+00	3.0E+03	4.5E+02	6.0E+00	0.0E+00

No.	PRTR No	Total emission amounts (kg year^{-1})								
		1997			2002			2008		
		Air	Soil	Water	Air	Soil	Water	Air	Soil	Water
35	57	8.3E+00	1.3E+03	0.0E+00	2.1E-01	1.2E+01	0.0E+00	2.6E+01	3.9E-01	4.0E-01
36	58	2.1E+04	0.0E+00	7.4E+01	1.0E+01	0.0E+00	2.5E-02	1.4E+04	0.0E+00	1.1E+01
37	61	4.4E+06	0.0E+00	4.6E+03	1.4E+01	0.0E+00	1.0E+00	4.4E+06	7.0E+05	1.1E+05
38	63	7.1E+09	2.2E+07	1.6E+06	1.3E+07	5.6E+04	9.5E+04	0.0E+00	1.3E+00	9.5E+00
39	65	4.9E+03	0.0E+00	2.4E+05	2.0E+01	0.0E+00	4.6E+01	8.8E+00	5.5E+01	8.5E+01
40	66	6.2E+03	0.0E+00	0.0E+00	8.0E-01	0.0E+00	0.0E+00	3.7E+03	3.8E+00	7.5E+00
41	67	8.9E+06	3.1E+03	1.7E+04	9.5E+03	0.0E+00	5.7E+01	0.0E+00	1.2E+02	0.0E+00
42	75	2.1E+04	1.1E+05	0.0E+00	0.0E+00	4.3E+02	0.0E+00	0.0E+00	1.7E+02	0.0E+00
43	76	3.2E+03	7.4E+04	0.0E+00	0.0E+00	3.1E+02	0.0E+00	1.3E+02	0.0E+00	0.0E+00
44	77	1.2E+05	0.0E+00	0.0E+00	7.4E+04	0.0E+00	7.8E+02	0.0E+00	8.2E+02	0.0E+00
45	78	8.7E+03	1.8E+05	0.0E+00	0.0E+00	1.2E+03	0.0E+00	0.0E+00	2.6E+02	0.0E+00
46	79	7.9E+02	9.5E+04	0.0E+00	6.0E-01	1.4E+02	4.6E-03	0.0E+00	0.0E+00	0.0E+00
47	80	1.2E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	5.9E+03	0.0E+00
48	81	2.8E+01	7.4E+06	6.2E+02	0.0E+00	9.8E+03	0.0E+00	0.0E+00	6.3E+02	0.0E+00
49	82	0.0E+00	5.3E+05	0.0E+00	0.0E+00	9.0E+02	0.0E+00	5.1E+04	0.0E+00	0.0E+00
50	84	1.2E+08	0.0E+00	0.0E+00	5.3E+05	0.0E+00	0.0E+00	1.1E+06	0.0E+00	0.0E+00
51	85	7.5E+08	0.0E+00	0.0E+00	8.9E+05	0.0E+00	0.0E+00	0.0E+00	7.9E+02	2.0E+00

No.	PRTR No	Total emission amounts (kg year^{-1})								
		1997			2002			2008		
		Air	Soil	Water	Air	Soil	Water	Air	Soil	Water
52	90	0.0E+00	2.3E+05	1.8E+03	0.0E+00	1.6E+03	2.0E+00	0.0E+00	0.0E+00	1.5E+01
53	91	9.4E+03	0.0E+00	0.0E+00	3.1E+03	0.0E+00	0.0E+00	0.0E+00	1.2E+02	0.0E+00
54	92	2.4E+03	1.6E+04	0.0E+00	0.0E+00	1.1E+02	0.0E+00	8.2E+03	1.2E+03	7.0E+01
55	93	2.9E+07	2.9E+05	1.3E+05	3.1E+04	4.9E+02	9.1E+00	7.9E+03	0.0E+00	0.0E+00
56	94	1.4E+07	0.0E+00	0.0E+00	1.3E+04	0.0E+00	0.0E+00	2.5E+04	5.7E+02	7.3E+03
57	95	5.2E+07	0.0E+00	1.4E+06	1.0E+05	0.0E+00	8.6E+03	2.8E+03	0.0E+00	0.0E+00
58	96	4.0E+08	0.0E+00	0.0E+00	3.9E+05	0.0E+00	0.0E+00	0.0E+00	4.3E+02	0.0E+00
59	97	0.0E+00	3.6E+05	0.0E+00	0.0E+00	9.8E+02	0.0E+00	0.0E+00	1.7E+02	0.0E+00
60	98	0.0E+00	5.8E+05	0.0E+00	0.0E+00	8.4E+02	0.0E+00	3.5E+03	1.1E+04	3.7E+00
61	101	5.7E+07	0.0E+00	6.0E+04	3.1E+05	0.0E+00	6.9E+00	1.2E+04	6.2E+02	4.4E+00
62	102	1.8E+07	0.0E+00	2.9E+04	3.5E+05	0.0E+00	1.6E+03	1.2E+03	0.0E+00	0.0E+00
63	103	9.2E+05	0.0E+00	0.0E+00	7.7E+02	0.0E+00	0.0E+00	0.0E+00	4.0E+01	0.0E+00
64	106	1.1E+03	4.9E+04	0.0E+00	0.0E+00	1.5E+02	0.0E+00	0.0E+00	1.9E+02	0.0E+00
65	107	0.0E+00	7.9E+04	0.0E+00	0.0E+00	2.0E+02	0.0E+00	3.5E+02	0.0E+00	1.6E+01
66	109	2.3E+06	0.0E+00	5.2E+05	9.6E+02	0.0E+00	0.0E+00	0.0E+00	7.1E+03	5.3E+00
67	110	0.0E+00	1.4E+07	1.7E+04	0.0E+00	2.7E+04	1.9E+00	0.0E+00	4.1E+03	0.0E+00
68	111	0.0E+00	2.5E+06	0.0E+00	0.0E+00	5.7E+03	0.0E+00	8.0E-01	0.0E+00	1.7E+00

No.	PRTR No	Total emission amounts (kg year^{-1})								
		1997			2002			2008		
		Air	Soil	Water	Air	Soil	Water	Air	Soil	Water
69	112	2.5E+04	0.0E+00	2.4E+03	9.8E+00	0.0E+00	3.0E+00	3.0E+03	3.7E+02	8.2E+03
70	113	7.9E+06	0.0E+00	2.8E+05	1.4E+04	0.0E+00	6.9E+03	0.0E+00	0.0E+00	9.7E+00
71	114	4.6E+06	0.0E+00	7.1E+05	9.7E+02	0.0E+00	8.8E+02	0.0E+00	2.4E+02	2.5E+01
72	116	5.4E+06	0.0E+00	1.1E+05	2.1E+05	0.0E+00	8.9E+02	7.8E+01	0.0E+00	3.5E+00
73	117	2.3E+05	0.0E+00	6.9E+03	6.3E+03	0.0E+00	2.4E+02	0.0E+00	0.0E+00	5.8E+00
74	118	0.0E+00	0.0E+00	5.9E+04	0.0E+00	0.0E+00	2.5E+01	5.1E+04	0.0E+00	0.0E+00
75	121	1.4E+08	0.0E+00	0.0E+00	1.6E+05	0.0E+00	0.0E+00	0.0E+00	1.9E+03	0.0E+00
76	122	0.0E+00	9.4E+04	0.0E+00	0.0E+00	3.5E+02	0.0E+00	1.6E+04	0.0E+00	0.0E+00
77	124	2.1E+06	0.0E+00	0.0E+00	1.1E+03	0.0E+00	0.0E+00	0.0E+00	2.9E+03	0.0E+00
78	126	0.0E+00	1.9E+06	0.0E+00	0.0E+00	3.5E+03	0.0E+00	0.0E+00	8.3E+03	2.1E+02
79	129	0.0E+00	4.6E+06	0.0E+00	0.0E+00	1.2E+04	0.0E+00	0.0E+00	2.2E+03	0.0E+00
80	130	5.2E+03	1.1E+06	1.3E+02	0.0E+00	1.7E+03	0.0E+00	0.0E+00	2.3E+03	0.0E+00
81	131	0.0E+00	1.7E+06	0.0E+00	0.0E+00	3.6E+03	0.0E+00	5.1E+05	0.0E+00	0.0E+00
82	132	7.8E+08	0.0E+00	0.0E+00	6.6E+05	0.0E+00	0.0E+00	0.0E+00	1.8E+02	3.8E+04
83	134	7.3E+06	0.0E+00	5.5E+07	3.5E+02	0.0E+00	1.4E+04	6.3E+02	1.0E+03	5.6E+00
84	135	3.1E+07	0.0E+00	2.6E+03	5.1E+04	0.0E+00	1.0E+02	0.0E+00	2.5E+04	1.7E+00
85	137	2.4E+04	9.9E+06	5.6E+03	1.2E+02	4.0E+04	1.7E+00	1.1E+06	0.0E+00	0.0E+00

No.	PRTR No	Total emission amounts (kg year^{-1})								
		1997			2002			2008		
		Air	Soil	Water	Air	Soil	Water	Air	Soil	Water
86	139	3.0E+07	1.6E+04	1.1E+03	1.8E+04	1.9E-01	1.1E+00	0.0E+00	4.0E+02	0.0E+00
87	141	0.0E+00	1.7E+06	0.0E+00	0.0E+00	8.7E+02	0.0E+00	0.0E+00	3.7E+03	0.0E+00
88	142	0.0E+00	1.2E+06	0.0E+00	0.0E+00	1.4E+03	0.0E+00	1.3E+06	2.3E+05	5.9E+02
89	143	0.0E+00	4.3E+05	0.0E+00	0.0E+00	5.5E+02	0.0E+00	0.0E+00	6.2E+02	0.0E+00
90	145	2.6E+09	0.0E+00	3.8E+06	4.1E+06	2.7E+00	2.4E+03	0.0E+00	2.2E+03	0.0E+00
91	146	1.2E+04	4.5E+05	0.0E+00	0.0E+00	1.5E+03	0.0E+00	0.0E+00	6.4E+02	0.0E+00
92	147	0.0E+00	5.8E+06	0.0E+00	0.0E+00	7.0E+03	0.0E+00	0.0E+00	6.2E+03	0.0E+00
93	148	0.0E+00	2.8E+06	0.0E+00	0.0E+00	4.8E+03	0.0E+00	0.0E+00	1.8E+01	0.0E+00
94	151	1.1E+03	4.0E+06	2.5E+03	0.0E+00	1.1E+04	0.0E+00	0.0E+00	1.3E+03	0.0E+00
95	152	0.0E+00	4.1E+03	0.0E+00	3.2E+00	1.2E+02	0.0E+00	0.0E+00	6.4E+03	0.0E+00
96	153	0.0E+00	5.8E+05	0.0E+00	0.0E+00	1.6E+03	0.0E+00	0.0E+00	3.9E+03	0.0E+00
97	154	2.6E+04	4.2E+06	0.0E+00	0.0E+00	9.9E+03	0.0E+00	0.0E+00	3.3E+02	0.0E+00
98	155	7.2E+03	1.1E+06	0.0E+00	0.0E+00	2.5E+03	0.0E+00	0.0E+00	1.5E+01	3.5E-01
99	156	4.2E+03	3.1E+05	0.0E+00	0.0E+00	8.7E+02	0.0E+00	0.0E+00	5.7E+02	0.0E+00
100	159	2.1E+04	0.0E+00	7.2E+01	2.7E+02	0.0E+00	2.2E+00	0.0E+00	7.0E+01	0.0E+00
101	161	0.0E+00	3.7E+05	0.0E+00	0.0E+00	1.4E+03	0.0E+00	0.0E+00	0.0E+00	1.7E+05
102	165	2.3E+01	1.5E+04	3.2E+03	0.0E+00	1.3E+02	0.0E+00	4.0E+01	8.6E+03	0.0E+00

No.	PRTR No	Total emission amounts (kg year^{-1})								
		1997			2002			2008		
		Air	Soil	Water	Air	Soil	Water	Air	Soil	Water
103	166	2.8E+03	0.0E+00	4.0E+07	0.0E+00	0.0E+00	8.0E+04	0.0E+00	2.3E+03	0.0E+00
104	167	8.1E+04	3.8E+06	1.7E+04	2.4E+02	9.6E+03	0.0E+00	1.4E+05	1.4E+04	9.4E+02
105	170	2.2E+04	2.9E+06	0.0E+00	0.0E+00	6.9E+03	0.0E+00	0.0E+00	1.2E+03	0.0E+00
106	172	2.2E+08	2.3E+06	1.6E+07	4.0E+05	4.9E+03	2.5E+04	4.0E+05	8.7E+02	2.1E+00
107	173	3.7E+03	1.3E+06	0.0E+00	0.0E+00	2.9E+03	0.0E+00	1.1E+04	0.0E+00	3.0E+01
108	177	5.7E+08	0.0E+00	1.7E+05	9.8E+05	1.1E+00	5.6E+02	0.0E+00	5.6E+04	0.0E+00
109	179	2.2E+01	0.0E+00	2.2E-01	6.5E+04	0.0E+00	5.1E+02	0.0E+00	3.7E-04	7.0E+01
110	180	3.8E+04	1.9E+07	0.0E+00	0.0E+00	5.5E+04	0.0E+00	0.0E+00	7.9E+02	0.0E+00
111	181	2.2E+01	0.0E+00	7.3E+04	8.0E-04	0.0E+00	1.9E+01	0.0E+00	4.7E+02	0.0E+00
112	183	0.0E+00	3.8E+05	0.0E+00	0.0E+00	1.3E+03	0.0E+00	5.2E+01	1.1E+04	0.0E+00
113	184	8.6E+03	4.7E+05	0.0E+00	0.0E+00	7.9E+02	0.0E+00	0.0E+00	9.4E+02	0.0E+00
114	185	1.2E+06	6.1E+06	0.0E+00	1.2E+03	1.5E+04	0.0E+00	0.0E+00	2.3E+03	0.0E+00
115	188	6.4E+03	4.3E+05	0.0E+00	0.0E+00	9.5E+02	0.0E+00	9.0E+02	1.8E+03	0.0E+00
116	189	1.1E+03	2.3E+06	0.0E+00	0.0E+00	6.3E+03	0.0E+00	2.4E+02	0.0E+00	0.0E+00
117	192	5.1E+06	1.8E+07	2.0E+04	5.1E+03	3.4E+04	0.0E+00	0.0E+00	3.8E+02	0.0E+00
118	193	7.5E+05	4.3E+06	5.1E+03	9.6E+02	9.5E+03	0.0E+00	0.0E+00	5.9E+03	0.0E+00
119	194	7.7E+05	1.2E+04	0.0E+00	8.9E+02	6.4E+01	0.0E+00	7.9E+01	5.4E+02	4.7E+02

No.	PRTR No	Total emission amounts (kg year^{-1})								
		1997			2002			2008		
		Air	Soil	Water	Air	Soil	Water	Air	Soil	Water
120	195	0.0E+00	3.9E+05	0.0E+00	0.0E+00	6.2E+02	0.0E+00	0.0E+00	8.2E+03	0.0E+00
121	196	0.0E+00	2.6E+06	0.0E+00	0.0E+00	1.0E+04	0.0E+00	1.2E+05	4.1E+04	2.3E+02
122	198	9.5E+04	1.9E+05	6.7E+02	2.2E+01	1.8E+03	6.1E+02	3.4E+04	0.0E+00	0.0E+00
123	199	3.8E+06	4.8E+06	1.0E+06	0.0E+00	1.2E+04	0.0E+00	0.0E+00	2.7E+03	3.0E+02
124	200	3.4E+08	0.0E+00	5.3E+05	8.1E+05	0.0E+00	3.7E+01	0.0E+00	0.0E+00	0.0E+00
125	203	1.5E+08	0.0E+00	0.0E+00	1.2E+05	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00
126	204	2.8E+04	2.1E+06	3.5E+05	4.9E-01	2.1E+03	4.4E+00	0.0E+00	0.0E+00	4.7E+00
127	205	9.2E+01	0.0E+00	1.7E+05	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	2.3E+00
128	206	1.4E+03	0.0E+00	0.0E+00	1.4E+00	0.0E+00	1.0E-01	2.3E+05	7.0E+04	2.4E+01
129	209	8.5E+05	0.0E+00	7.2E+04	2.9E+03	0.0E+00	1.8E+00	0.0E+00	5.2E+02	0.0E+00
130	210	6.9E+03	0.0E+00	3.8E+04	0.0E+00	0.0E+00	7.3E+00	4.6E+04	0.0E+00	0.0E+00
131	211	5.2E+08	0.0E+00	5.2E+05	1.8E+06	1.9E+01	2.4E+02	0.0E+00	5.4E+03	0.0E+00
132	214	2.7E+05	1.7E+07	0.0E+00	0.0E+00	6.1E+04	0.0E+00	0.0E+00	0.0E+00	2.8E+03
133	216	0.0E+00	3.1E+05	0.0E+00	0.0E+00	1.3E+03	0.0E+00	5.4E+00	0.0E+00	1.6E+01
134	217	1.1E+08	0.0E+00	0.0E+00	1.4E+05	0.0E+00	0.0E+00	9.5E+06	1.1E+06	3.3E+03
135	220	1.6E+04	1.3E+06	0.0E+00	7.5E+00	2.6E+03	0.0E+00	0.0E+00	0.0E+00	0.0E+00
136	222	1.8E+05	0.0E+00	5.5E+05	0.0E+00	0.0E+00	7.1E+02	6.7E+00	0.0E+00	0.0E+00

No.	PRTR No	Total emission amounts (kg year^{-1})								
		1997			2002			2008		
		Air	Soil	Water	Air	Soil	Water	Air	Soil	Water
137	224	4.4E+08	0.0E+00	2.3E+04	1.2E+06	0.0E+00	1.3E+02	0.0E+00	1.8E+01	2.2E+00
138	225	2.0E+04	0.0E+00	0.0E+00	0.0E+00	7.0E+01	0.0E+00	1.9E+01	2.1E+02	8.4E-01
139	227	1.3E+10	3.0E+04	3.2E+06	2.2E+07	4.4E+01	1.0E+04	0.0E+00	2.5E+03	0.0E+00
140	238	2.2E+01	0.0E+00	9.9E+03	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00
141	239	5.2E-01	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	5.4E+02	0.0E+00
142	240	8.8E+03	0.0E+00	9.2E+01	9.2E+00	0.0E+00	0.0E+00	3.3E+02	2.0E+03	1.5E+04
143	241	1.2E+05	0.0E+00	1.3E+03	1.1E+05	2.0E+00	2.7E+00	0.0E+00	1.3E+01	1.4E+03
144	242	3.1E+06	0.0E+00	5.1E+03	6.6E+02	0.0E+00	2.8E+00	0.0E+00	8.8E+01	0.0E+00
145	245	0.0E+00	4.2E+06	0.0E+00	0.0E+00	4.2E+03	0.0E+00	0.0E+00	0.0E+00	0.0E+00
146	247	0.0E+00	1.4E+04	0.0E+00	0.0E+00	8.0E+01	0.0E+00	0.0E+00	0.0E+00	6.0E-02
147	249	5.3E+03	1.6E+06	2.2E+04	2.3E+01	1.1E+03	0.0E+00	6.1E+03	7.1E+02	3.2E+02
148	253	5.4E+05	0.0E+00	3.8E+06	2.9E+03	0.0E+00	3.7E+03	1.2E+03	3.8E+02	1.3E-01
149	254	7.9E+04	0.0E+00	5.0E+05	1.7E+01	0.0E+00	9.8E+02	2.4E+05	0.0E+00	1.6E+01
150	257	0.0E+00	6.1E+04	0.0E+00	0.0E+00	2.1E+02	0.0E+00	8.5E+03	4.6E+03	1.2E+02
151	258	8.5E+02	0.0E+00	1.6E+05	0.0E+00	0.0E+00	0.0E+00	4.0E-01	0.0E+00	0.0E+00
152	260	2.6E+02	0.0E+00	7.4E+01	2.4E+01	0.0E+00	1.2E+00	1.6E+01	2.1E+01	0.0E+00
153	264	4.7E+05	0.0E+00	0.0E+00	0.0E+00	2.3E+01	0.0E+00	0.0E+00	2.6E+03	0.0E+00

No.	PRTR No	Total emission amounts (kg year^{-1})								
		1997			2002			2008		
		Air	Soil	Water	Air	Soil	Water	Air	Soil	Water
154	266	1.9E+07	0.0E+00	2.5E+05	1.4E+05	0.0E+00	2.6E+03	0.0E+00	2.8E+02	0.0E+00
155	267	2.7E+06	1.7E+05	0.0E+00	2.0E+03	4.0E+02	0.0E+00	0.0E+00	1.6E+03	0.0E+00
156	268	3.7E+08	0.0E+00	0.0E+00	3.3E+05	0.0E+00	1.0E+00	0.0E+00	2.2E+02	0.0E+00
157	269	5.7E+03	0.0E+00	0.0E+00	7.0E+01	0.0E+00	0.0E+00	0.0E+00	1.3E+02	0.0E+00
158	270	1.7E+07	0.0E+00	1.7E+05	9.8E+03	1.5E+00	1.5E+02	2.2E+03	0.0E+00	0.0E+00
159	272	2.1E+07	0.0E+00	7.4E+01	1.5E+02	0.0E+00	0.0E+00	1.7E+03	3.5E+04	0.0E+00
160	273	4.0E+04	0.0E+00	0.0E+00	0.0E+00	3.5E+03	0.0E+00	0.0E+00	2.8E+02	0.0E+00
161	274	9.5E+03	1.3E+06	0.0E+00	0.0E+00	5.5E+02	0.0E+00	0.0E+00	2.9E+02	0.0E+00
162	275	0.0E+00	4.5E+04	0.0E+00	0.0E+00	8.5E+02	0.0E+00	2.3E+02	0.0E+00	4.6E-01
163	276	3.9E+04	5.8E+05	0.0E+00	0.0E+00	9.9E+02	0.0E+00	1.5E+01	0.0E+00	1.9E-01
164	279	1.1E+03	2.4E+05	0.0E+00	0.0E+00	1.8E+02	0.0E+00	1.0E-01	0.0E+00	4.5E-02
165	280	2.1E+03	4.1E+04	0.0E+00	3.0E+02	0.0E+00	0.0E+00	5.2E+04	1.6E-01	1.5E+03
166	286	1.1E+06	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	8.3E+05	1.0E+04	5.0E+01
167	287	4.0E+02	0.0E+00	0.0E+00	1.3E+04	1.7E+05	0.0E+00	0.0E+00	0.0E+00	0.0E+00
168	288	3.8E+06	2.7E+07	0.0E+00	0.0E+00	5.0E+02	0.0E+00	0.0E+00	3.7E+03	0.0E+00
169	289	5.3E+03	1.6E+05	0.0E+00	0.0E+00	5.4E+02	0.0E+00	0.0E+00	0.0E+00	7.0E-01
170	291	0.0E+00	1.6E+05	0.0E+00	2.2E+02	0.0E+00	6.4E+01	7.4E+05	7.2E+03	2.3E+04

No.	PRTR No	Total emission amounts (kg year^{-1})								
		1997			2002			2008		
		Air	Soil	Water	Air	Soil	Water	Air	Soil	Water
171	292	2.3E+05	0.0E+00	5.6E+01	5.0E+00	0.0E+00	0.0E+00	2.2E+02	5.7E-01	7.8E+02
172	293	1.1E+04	0.0E+00	0.0E+00	5.0E+00	0.0E+00	0.0E+00	2.1E+01	7.6E-01	2.4E+00
173	297	4.4E+03	0.0E+00	0.0E+00	2.9E+05	0.0E+00	0.0E+00	1.0E+02	2.1E+02	2.2E+04
174	298	6.5E+07	0.0E+00	0.0E+00	1.3E+06	1.6E-01	8.0E+01	5.0E-01	0.0E+00	0.0E+00
175	299	1.1E+09	1.3E+01	5.6E+04	0.0E+00	0.0E+00	0.0E+00	2.0E+01	0.0E+00	3.0E-03
176	300	1.2E+03	0.0E+00	8.8E+03	0.0E+00	1.4E+04	0.0E+00	1.2E+01	0.0E+00	0.0E+00
177	301	6.4E+03	1.4E+07	0.0E+00	0.0E+00	1.0E+00	1.0E-01	1.8E+02	0.0E+00	1.9E-01
178	306	9.2E-01	0.0E+00	3.0E+02	2.1E+06	0.0E+00	2.0E+04	1.5E+04	5.2E+02	4.3E+01
179	310	1.1E+09	0.0E+00	1.5E+05	7.7E+01	0.0E+00	1.0E+00	0.0E+00	2.7E+03	0.0E+00
180	312	3.9E+05	0.0E+00	0.0E+00	6.3E+02	0.0E+00	2.0E+00	2.1E+00	0.0E+00	0.0E+00
181	313	6.3E+04	0.0E+00	6.9E+02	5.2E+03	0.0E+00	1.2E+01	0.0E+00	5.3E+02	0.0E+00
182	314	2.7E+05	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	1.3E+03	0.0E+00
183	315	1.2E+06	0.0E+00	0.0E+00	3.2E+02	0.0E+00	0.0E+00	4.9E+02	0.0E+00	0.0E+00
184	316	1.4E+04	0.0E+00	0.0E+00	7.0E-01	0.0E+00	0.0E+00	1.2E+03	1.8E+03	0.0E+00
185	318	8.7E+03	0.0E+00	1.0E+02	2.1E+02	7.1E+02	1.0E-01	2.3E+03	2.5E+03	0.0E+00
186	319	1.2E+05	0.0E+00	0.0E+00	1.0E+05	0.0E+00	4.4E+00	0.0E+00	1.5E+02	0.0E+00
187	320	2.7E+07	0.0E+00	6.7E+03	0.0E+00	6.1E+03	0.0E+00	0.0E+00	1.0E+02	0.0E+00

No.	PRTR No	Total emission amounts (kg year^{-1})								
		1997			2002			2008		
		Air	Soil	Water	Air	Soil	Water	Air	Soil	Water
188	322	0.0E+00	5.8E+06	0.0E+00	7.5E+01	7.9E+02	0.0E+00	2.4E+01	0.0E+00	1.1E+00
189	324	0.0E+00	1.7E+05	0.0E+00	6.2E+02	1.8E+02	0.0E+00	5.8E+03	7.7E+03	0.0E+00
190	325	0.0E+00	7.0E+05	0.0E+00	0.0E+00	7.9E+01	0.0E+00	2.2E+01	3.7E-02	0.0E+00
191	326	5.9E+05	6.8E+04	0.0E+00	8.1E+02	5.6E+03	0.0E+00	0.0E+00	3.9E-01	0.0E+00
192	329	1.2E+06	1.3E+06	0.0E+00	0.0E+00	1.7E+02	0.0E+00	0.0E+00	1.7E+02	0.0E+00
193	330	4.2E+06	4.8E+06	0.0E+00	0.0E+00	2.2E+02	0.0E+00	0.0E+00	2.2E+02	0.0E+00
194	332	0.0E+00	3.0E+04	0.0E+00	1.9E+03	0.0E+00	3.0E-01	1.9E+03	0.0E+00	3.0E-01
195	334	0.0E+00	4.7E+04	0.0E+00	1.0E+04	0.0E+00	0.0E+00	1.0E+04	0.0E+00	0.0E+00
196	335	1.5E+04	0.0E+00	0.0E+00	0.0E+00	2.5E+02	0.0E+00	0.0E+00	2.5E+02	0.0E+00
197	338	8.8E+05	0.0E+00	0.0E+00	0.0E+00	2.5E+02	0.0E+00	0.0E+00	2.5E+02	0.0E+00
198	350	1.0E+07	3.6E+06	8.9E+02	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00
199	353	6.6E+04	0.0E+00	1.3E+03	6.6E+04	0.0E+00	1.3E+03	6.6E+04	0.0E+00	1.3E+03
200	354	8.9E+04	9.0E+04	0.0E+00	8.9E+04	9.0E+04	0.0E+00	8.9E+04	9.0E+04	0.0E+00