SIMULATION OF THE EFFECTS OF SALTING-OUT IN THE MERIDIONAL TRANSPORTATION OF PESTICIDES AND POPS BY A NEW FUGACITY-BASED MULTIMEDIA ENVIRONMENTAL FATE MODEL

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Introduction

Global-scale environmental contamination that, e.g. persistent organic pollutants (POPs) are detected in the Arctic, is currently focused on the world environmental problems. It is quite difficult to operate dense and frequent measurements of various chemicals, so mathematical modelling for the estimation of long-range transportation and environmental persistency of chemicals has been playing important roles. Eulerian-type box models for the fate of chemicals are quite effective and there are many examples as the EQC[1], the CoZMo-POP/CoZMO-POP2[2] and the Globo-POP[3], and the CHEMRANGE[4] and the CliMoChem[5]. These models have important ideas and unique characteristics, respectively, but the models all made in Europe or North America where the agricultural land is mostly used as upland fields. It is, therefore, questionable to apply the Asian region where paddy fields are occupied as a large part for agriculture and pesticides have been also emitted mainly to the paddy field. It is necessary for realistic estimation for the environmental fate of chemicals to obtain the actual value and geographical distribution of chemical usages. Lagrangian-type high-resolution atmospheric chemistry transport models have also been developed, but such models have disadvantages that require very high-resolution input data on emissions and other environmental parameters[6].

Effect of salting-out on solubility in seawater[7] was also not well considered in the previous models above described. One aim of this article is to implement the salting-out effect in multicompartmental environmental fate model. One simple method was that the fugacity capacity of seawater was evenly decreased in the fugacity-based model experiment[8], but the physicochemical properties of various chemicals, e.g. water solubility, was expected to be quite different in dependence on the properties of the chemicals, especially on octanol/water partition coefficient (log K_{OW}). Here, a new global-to-regional scale multimedia environmental fate model for pesticides and POPs (National Institute for Agro-Environmental Sciences' Multi-Media environmental fate Model: NIAES-MMM) is currently developed. This model is fugacity-based and possible to apply both Levels III (steady-state) and IV (unsteady-state or dynamic) conditions that could reflect trends of pesticides emissions from the Asian region. In this article, we have investigated the salting-out effect of POPs and pesticides by using the new model and have estimated the differentiations of accumulation of chemicals in correspondence with the differences of water solubility and fugacity capacity in seawater and freshwater.

Materials and Methods

The NIAES-MMM model has the virtual modelling environment, totally consisting of nine compartments

representing two (upper and lower) atmospheric layers, forest and forest (or non-agricultural) soils, two different type of agricultural (upland and paddy) fields, terrestrial water and terrestrial sediment, and the surface-to-deep ocean (Figure 1).

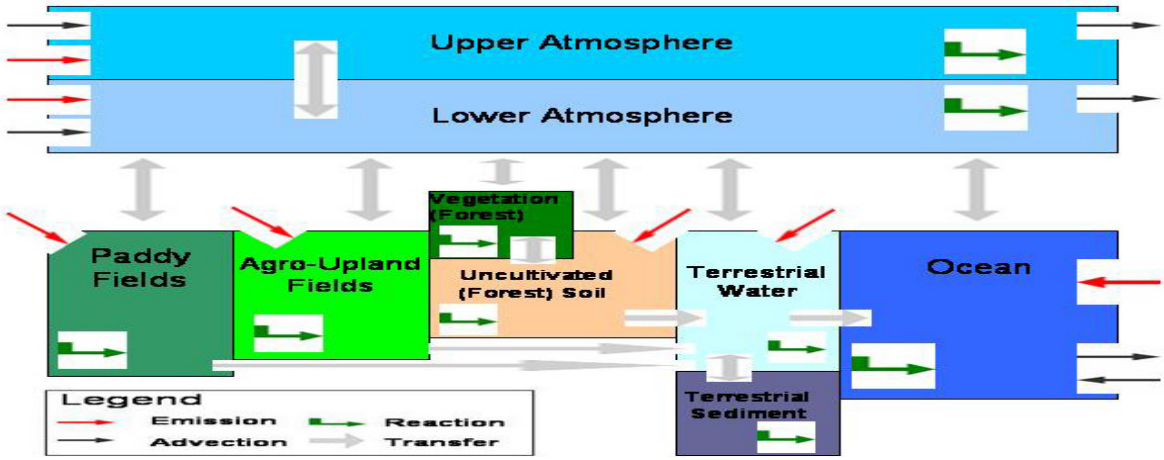

Figure 1: Schematic illustration of the NIAES-MMM.

The model has had two evaluation steps, one was a single-grid model similar to the CoZMo-POP[2] (the Model version 1) and the other was a region including above nine components was connected with other regions meridionally through the interface transfer of chemicals in the atmosphere and ocean compartments from the Antarctic to the Arctic, similar to the Globo-POP[3] (the Model version 2). Currently, forest and agricultural soils was different only in the parameter of water evaporation loss from soil surface and the depth of soils 0.1m for forest and 0.2m for agricultural soils. Further more, biomass of agricultural crop was not considered actually in the model. The model has been possible to both Levels III and IV situations, but in this article the model was driven in Level III because we had to investigate the sensitivity of the salting-out effect under various environmental conditions such as seasonal temperature change.

The salting-out effect of seawater on solubility of chemicals were deduced by the statistical relationships between log K_{OW} of chemicals and the ratio of solubility in fresh water to in seawater, and it was incorporated into in this model. Two chemicals, hexachlorocyclohexanes (HCHs) and polychlorobiphenyls (PCBs) were simulated by the model, the HCHs had relative higher water solubility and the PCBs had the large log K_{OW}. The emissions were assumed to be spatially distributed according to human population, HCHs were emitted to environment with the ratio of 0.175, 0.8, and 0.025 to lower air, agro-land and terrestrial water compartments, respectively and PCBs were emitted only to lower air compartment[3].

Results and Discussions

Figure 2 shows the relationships between log K_{OW} and ratio of solubility in salting water (seawater) to that in pure water (freshwater) obtained from the various literatures associated with POPs and pesticides with the wide range of the log K_{OW}. The water solubility ratio of seawater to that of freshwater (S_0) has been decreased since the log K_{OW} increased. Here, we set three experiments using our new model that treats the water solubility (S)

and the fugacity capacity (Z) in the ocean compartment. In the Experiment-1, S in seawater was set as same as S_0, in the Experiment-2, Z in the ocean compartment (Zwc) was got to decrease to the value with multiple 0.8 to that in terrestrial freshwater (Zw)[8] and in the Experiment-3, S was calculated by the equation in Figure 2.

The results from above three simulations using the NIAES-MMM Ver.1 including the effect of salting-out (Figure 2) and their comparison with no considering to the effect indicates that, for semi-realistic emission scenario of *a*-HCH and PCB-153, the salting-out effect was the most intensive in the Experiment-3. That is, the accumulated ratio of the ocean compartment was the smallest in the Experiment-3, in contrast that the ratio of the agro-upland (lower-air) compartment on *a*-HCH (PCB-52) was the smallest in the experiment-1 (Figure 3). Any results in Experiment-2 were moderate. This feature shows that the salting-out effect was not simulated well in previous Deviller's method[8] (Experiment-2) and that the solubility of seawater have to be accurately estimated used in the relationships to log K_{OW} like Figure 2.

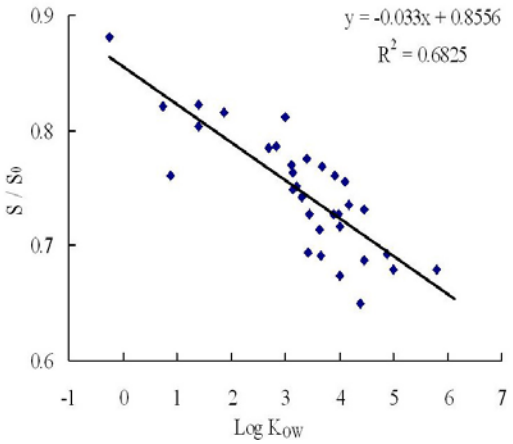

Figure 2: Relationships between logarithmic octanol/water partition coefficient (log Kow) and the ratio of solubility in salting water (S) to that in pure water (S_0).

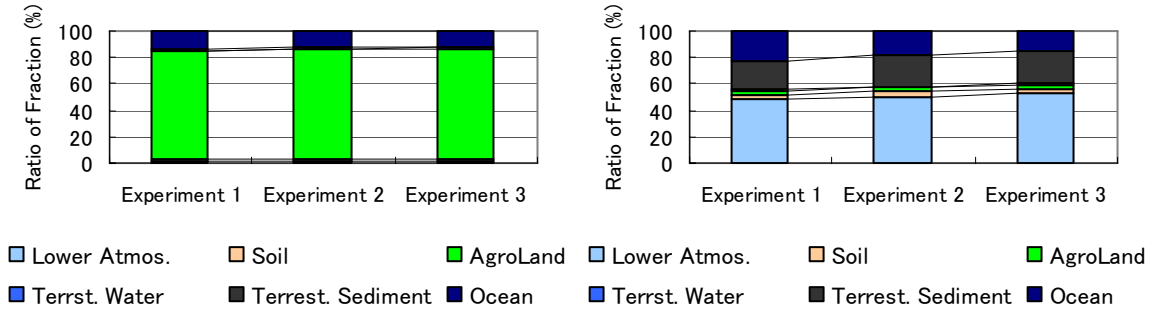

Figure 3: Change of the fraction ratios of (left) *a*-HCH and (right) PCB-52 deduced by three experiments considered the effect of salting-out of coastal sea water by using the NIAES-MMM Ver.1

In the NIAES-MMM Ver.2 simulations, the largest emission was evaluated in the Northern Subtropical zone on *a*-HCH and in the Northern Temperate zone on PCB-153. Figure 4 indicates the calculated zonal distributions of PCB-153. The most remarkable feature was that the higher mass fraction of PCB-153 in the ocean compartment was recorded in the Northern Polar zone which was far northward from the main usage areas. This shows the intense cold condensation in the Northern Polar zone and the evidence of long-range northward transportation of PCB-153. The higher deposition rate of POPs in the northern polar ocean was actually detected in previous researches[9]. In addition, such the accumulation of the Northern Polar zone was relatively smaller with incorporating the salting-out effect (Experiment-3) than that without the effect (Experiment-1). This feature shows that the salting-out effect is more important in hydrophobic (with large log K_{OW}) chemicals like PCBs in

considering to the global distribution of chemicals, especially on the transportation to the Arctic.

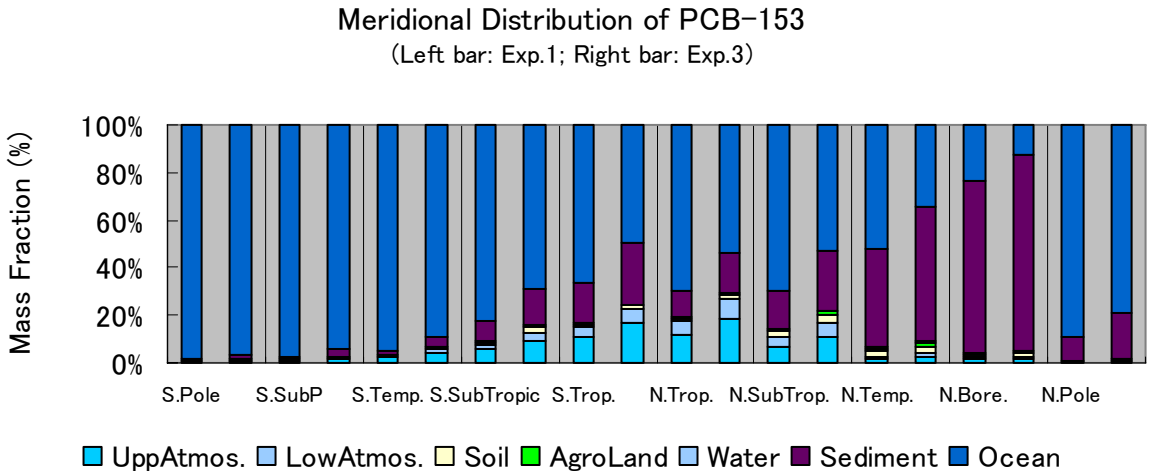

Figure 4: Meridional mass fraction distribution of PCB-153 in the each seven compartments in Experiment- 1 (left bar of each zone: without salting-out effect) and Experiment-3 (right bar of each zone: with salting-out effect) applying the NIAES-MMM Ver.2.

This model has been further improved to be applicable to realistic dynamic emissions and to reflect the seasonal change of vegetation in paddy field, agro-upland and forest components.

Acknowledgment

We would like to specially thank to Prof. D. Mackay of the University of Trent, Canada, Prof. F. Wania of the University of Toronto at Scarborough, Canada and Prof. M. Scheringer of the Swiss Federal Institute of Technology for their useful discussions in beginning with this research. This work was supported in part by a Grant-in-aid (Hazardous Chemicals) from the Ministry of Agriculture, Forestry, and Fisheries of Japan (HC-06-2151-1).

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