Journal of Environmental Science International
29(10); 969~979; October 2020

pISSN: 1225-4517 eISSN: 2287-3503
https://doi.org/10.5322/JESI.2020.29.10.969

ORIGINAL ARTICLE

Mass Balance of Perfluorooctane sulfonates in a Semi-enclosed Bay, Korea

Min Ji Heo, Kyong Joon Roh[1)], Dong-Myung Kim[1)*]

Busan Development Institute, Busan 47210, Korea
[1)]Department of Ecological Engineering, Pukyong National University, Busan 48513, Korea

Abstract

A numerical simulation was conducted on perfluorooctane sulfonate (PFOS) in the Gwangyang Bay using a multi-box model to estimate the transport of organic chemicals in the coastal environment. The results of the sensitivity analysis on dissolved PFOS and PFOS in Particulate Organic Carbon (POC) indicate that they were most significantly influenced by the adsorption rate, desorption rate, and sinking velocity coefficients. PFOS in phytoplankton was found to be sensitive to bio-concentration and the excretion rate. The results of the mass balance indicate that the standing stocks of PFOS in water, POC, and phytoplankton are 345.55 g, 63.76 g, and 0.11 g, respectively, in the inner part and 149.90 g, 27.51 g, and 0.05 g, respectively, in the outer part. Considering flux in the inner part, adsorption to POC had the highest value among transition paths. The next highest were desorption, outflow to the outer part, and inflow to the inner part. Outflow into the open sea was found to have the highest value for the outer part.

Key words : PFOS, Multi-box model, Gwangyang Bay, Mass balance

1. Introduction

Pollution by chemicals such as persistent organic pollutants (POPs) and endocrine disrupting chemicals (EDCs) in the marine ecosystem has led to the increasing possibility of irreversible damage to human health and the ecosystem (Kim et al., 2004).

Some compounds found in POPs, such as perfluorinated chemicals (PFCs), exhibit unique properties including high surface activity, thermal resistance, acid resistance, hydrophobicity, and lipophilicity (Kissa, 2001). Thus, they have been found to be very useful in a wide range of applications. PFCs have been used widely as surfactants, lubricants, paper and textile coatings, polishes, and food packaging materials over the past 60 years (Giesy et al., 2006). As an emerging chemicals group of environmentally persistent and bioaccumulative contaminants, PFCs, specifically perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), have been ubiquitously found in the environment. Owing to their wide range of application, they enter the environment through various pathways (Higgins et al., 2005).

Notably, PFOS was categorized as a PFC by the Stockholm Convention on Persistent Organic

Received 19 August, 2020; **Revised** 13 October, 2020;
Accepted 16 October, 2020
[*]**Corresponding author**: Dong-Myung Kim, Department of Ecological Engineering, Pukyong National University, Busan 48513, Korea
Phone : +82-51-629-6545
E-mail : dmkim@pknu.ac.kr

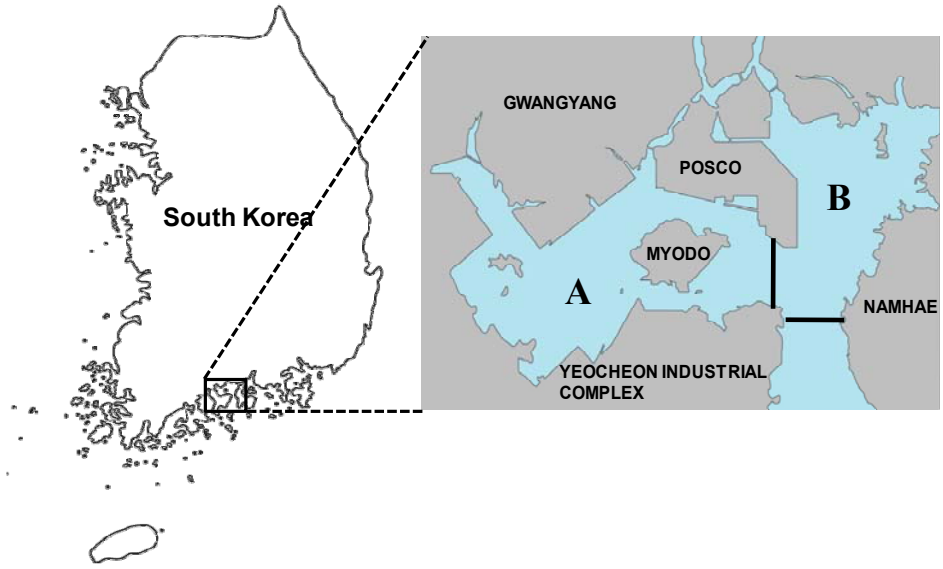

Fig. 1. Map of the study area.

Pollutants in May 2009. PFOS and associated salts are fully fluorinated organic molecules produced synthetically in an electrochemical fluorination process (Grasty et al., 2003). These chemicals are characterized by their persistence, bio-concentration toxicity, and long-range transport capability. Research has revealed that PFOS is an anthropogenically produced chemical found ubiquitously in water, soil, humans, and wildlife.

Studies on PFCs have been conducted primarily to determine their concentration and distribution in the freshwaters (Son et al., 2014; Ahrens et al., 2016; Wu et al., 2020), watersheds (Sun et al., 2018) and coastal environments (Munschy et al., 2013; Paik et al., 2017; Son et al, 2017). Research on the fate and transport of PFCs in the environment is considered critical, but the body of work on this topic remains limited (KFDA, 2006).

Because POPs and PBTs have received increasing attention as pollutants that are detrimental to human health, we conducted a numerical simulation on the PFOS level in the Gwangyang Bay using a multi-box model to predict the fate and transport of organic chemicals in the coastal environment.

2. Materials and Methods

2.1. Study area

Gwangyang Bay is one of the most rapidly developing coastal areas. It is located in on the southern coast of South Korea (hereafter “Korea”) and is characterized by semi-enclosed geographic surroundings. Moreover, it borders one of the most concentrated industrial areas in Korea. Several rivers, including the Seomjin River, enter the bay; seawater is exchanged with the South Sea in the southern part of the bay. Gwangyang and Suncheon are in the vicinity, and a representative industrial complex and a container terminal are located in the northern part of the study area. The Yulchon Industrial Complex and the Yeocheon Petrochemical Complex are situated in the southern part of the study area (Lee et al, 2003).

This water depth in this area is less than 5 m in the

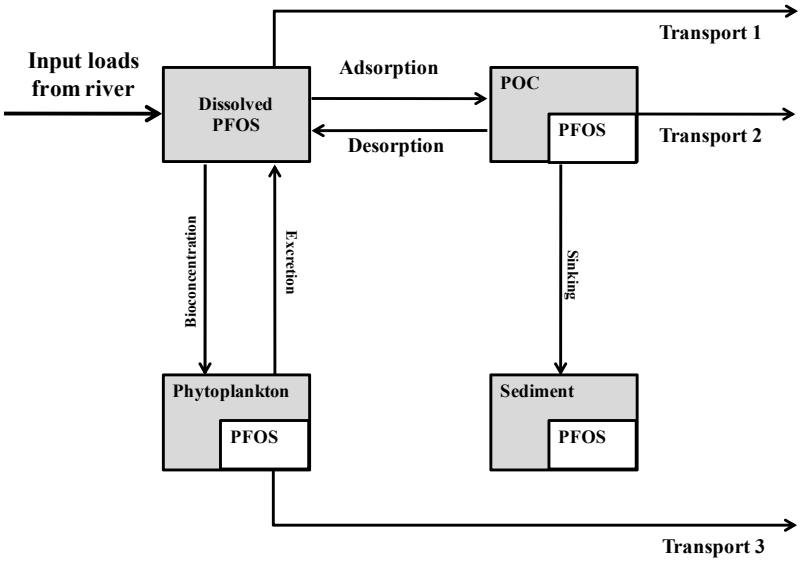

Fig. 2. Schematic diagram of the fate and transport of chemicals in the box model.

western part of the bay and exceeds 20 m near Myodo and in the eastern part of the bay. The Gwangyang Bay Area is at high risk of contamination. The Ministry of Maritime Affairs & Fisheries (MOMAF) was designated a special management area to implement management strategies (KORDI, 2003).

Fig. 1. shows the study area, which is divided into two boxes to designate the inner part (A box) and outer part (B box).

2.2. Model composition

Fig. 2. presents a model schematic diagram. The model comprised two boxes. The loading flux of PFOS from the watersheds is only used in this model. The PFOS flowing into the Gwangyang Bay Area undergoes several chemical and biological processes. Thus, this model was used to examine the tidal outflow of dissolved PFOS into the open sea, adsorption and desorption of Particulate Organic Carbon (POC), bio-concentration and excretion of phytoplankton, and sediment settling. PFOS was exchanged between A box and B box. Each box has state variables consist of dissolved PFOS, PFOS in POC, and PFOS in phytoplankton. Table 1 presents the equations applied in this model.

2.3. Estimated input data

The fate of PFOS was constructed using the presented multi-box model. The input data used are presented in Table 4.

The volume, area, and cross-sectional area for each box were calculated based on water depth in the Gwangyang Bay. The transport values were applied by multiplying the flow rate and cross-sectional area. The Kd values applied a partition coefficient in POC, which was calculated by measuring dissolved PFOS among the POC in a field survey of the study area. Adsorption and desorption rate could be determined when dissolved PFOS and PFOS in POC reached a steady state by applying this partition coefficient to the model.

The input load considered in this model was the dissolved PFOS in the input loads from the

Table 1. Equations used in the model

Dissolved PFOS (t) = Dissolved PFOS (t-dt)
+ (Input loads from river - Adsorption + Desorption – Bio-concentration of phytoplankton
+ Excretion from phytoplankton - Transport1) * dt
PFOS in POC (t) = PFOS in POC (t-dt)
+ (Adsorption - Desorption - settling - Transport) * dt
PFOS in phytoplankton (t) = PFOS in phytoplankton (t-dt)
+ (Bio-concentration of phytoplankton - Excretion from phytoplankton - Transport3) * dt
Adsorption = Adsorption rate * Dissolved PFOS * POC
Desorption = Desorption rate * Dissolved PFOS * POC
Bio-concentration = Bio-concentration rate * Dissolved PFOS * phytoplankton
Excretion = Excretion rate * PFOS * phytoplankton
Settling = Sinking velocity * PFOS in POC
Transport 1 = Transport rate by tide * Dissolved PFOS
Transport 2 = Transport rate by tide * PFOS in POC
Transport 3 = Transport rate by tide * PFOS in phytoplankton
Input loads from river
Transport by tide
Phytoplankton = standing stock of phytoplankton
POC = Standing stock of Particular Organic Carbon
INIT Dissolved PFOS = Initial concentration of Dissolved PFOS
INIT PFOS in POC = Initial concentration of PFOS in POC
INIT POFS in phytoplankton = Initial concentration of PFOS in phytoplankton

Table 2. Average concentration of PFOS in seawater

Station	Minimum concentration	Maximum concentration	Average concentration
Inner part	N.D.	6.4	0.214
Outer part	N.D.	1.5	1.025
mean		0.619	

Table 3. PFOS loads from each stream around the Gwangyang Bay watershed

Station	Discharge (m^3/day)	PFOS (ng/L)	Loading does (g/day)
Inner part	37,197,226.5	355.7	24.35
Outer part	2,897,045.0	111.6	79.26
Total	40,094,271.5	467.3	103.61

watershed. The observed concentrations of PFOS represent the average concentrations measured at each box within the study area. These values were measured once in June 2007. We used the actual values of dissolved PFOS from the watersheds listed in Table 2. These values were calculated by multiplying input loads by flow rate (Cho, 2008). Input load values are presented in Table 3.

Standing stock of phytoplankton, sinking velocity of POC, and BCF were applied at 20.63 mg/m^3, 4.3 × 10^{-1} m/day, 1.0 × 10^3 L/kg, respectively (Lee et al, 2004; Hong et al., 2007; Rayne et al., 2009). Other

Table 4. Parameters used in the model

Definition	Unit	Value		Ref.
		Inner part (A box)	Outer part (B box)	
Volume	m^3	363,720,500	603,171,200	
Average depth	m	4.86	8.92	
Area	m^2	74,730,000	70,490,000	
Cross Sectional area	m^2	43,142	86,625	
Dissolved PFOS				
Input loads from watershed	g/day	24.33	79.29	Cho, 2008
Standing stock of Phytoplankton	mg/m^3	20.63		Lee et al., 2004
Sinking velocity	m/day	4.3×10^{-1}		Hong et al., 2007
Bio-concentration factor	L/kg	1.0×10^{3}		Rayne et al., 2009; Kim, 2011
Uptake rate	L/ (kg day)	1.1×10^{1}		Kim 2007
Excretion rate	1/day	9.5x10-1		Kim, 2007; Kim, 2011
Partition coefficient	L/kg	4.1×10^{5}		Jorgensen et al., 2000; Kim et al. 2004
Adsorption rate	L/ (kg day)	2.9×105		Estimated by calibration
Desorption rate	1/day	7.2×10^{-1}		Kim et al., 2004

parameters such as uptake rate, excretion rate, adsorption rate, and desorption rate were treated as adjustable parameters.

3. Results

3.1. Multi-box model construction

The model used in this study constitutes a method for calculating the flow of a material in a costal environment. Fig. 3 illustrates the model constructed by applying the STELLA computer language. The study area was divided into A box and B box to separately analyze the inner and outer areas of the region. The results were analyzed by identifying the characteristics of the PFOS circulation and the fate of the PFOS pollution within the study area.

State variables consisting of dissolved PFOS, PFOS in POC, and PFOS in phytoplankton. The biological and chemical processes considered were adsorption and desorption from POC, bioaccumulation and excretion by phytoplankton, sediment sinking, and seawater exchange via inflow and outflow. Inflow from the open sea to the outer part (B box) was not considered in this model. Because the concentration value of PFOS was not detected in the open sea.

The multi-box model can yield more accurate results when the study area is divided into more boxes. As a preliminary study of PFOS in the coastal area, this model consisted of two boxes, and the concentration in the Gwangyang Bay was measured once. Modeling an ecosystem, which has a complicated structure, can be simplified by considering only a selection of the responses in the system. This simplified model presents trends and representative values of PFOS in the Gwangyang Bay.

The model results suggest directions for further studies to establish a management counterplan for reducing PFOS levels in the Gwangyang Bay.

3.2. Application of model and sensitivity analysis

The modeling system was applied to the Gwangyang Bay, and results were analyzed. Fig. 4. shows the concentration of PFOS, which was

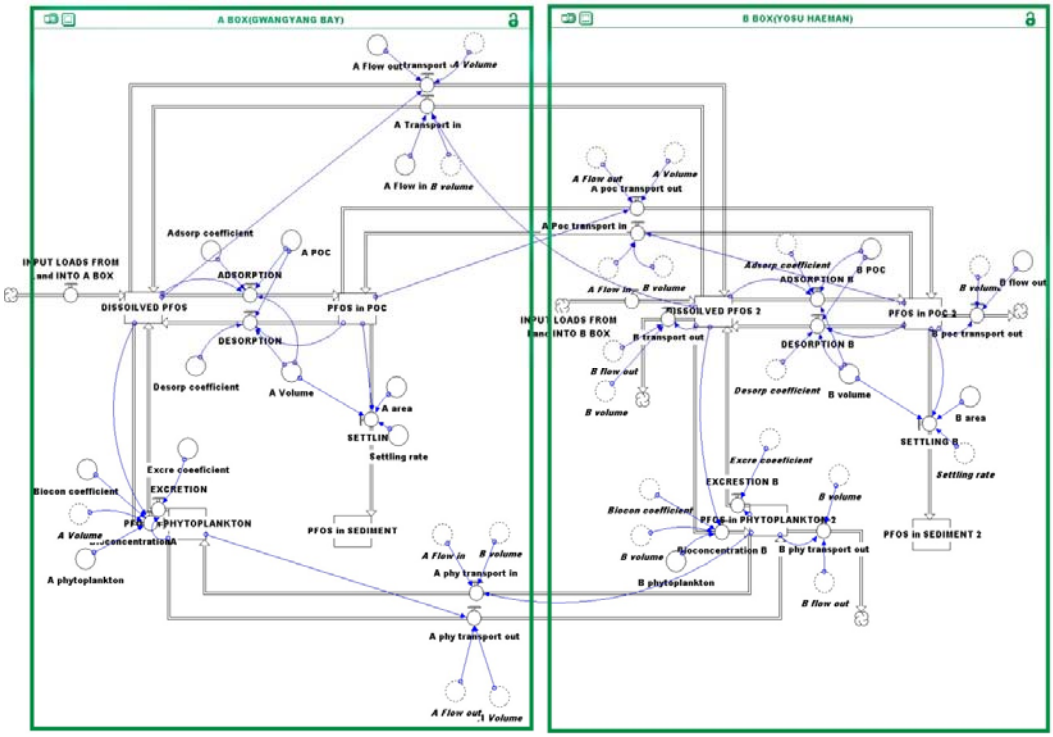

Fig. 3. Diagram of PFOS fate model applied to the Gwangyang Bay.

calculated to examine the applicability of the model. The model was computed using 4th-order Runge -Kutta method until the results reached a steady state. The concentration of dissolved PFOS, PFOS in POC, and PFOS in phytoplankton was stabilized in a relatively short time. The concentration in each box was examined, and Cho's observed concentrations (Cho, 2008) were compared with our findings. The calculated concentration of dissolved PFOS was 0.950 ng/L and the observed concentration was 1.025 ng/L, with a relative error of -7.32% in the inner part (A Box). The calculated concentration of dissolved PFOS was 0.214 ng/L and the observed concentration was 0.249 ng/L, with a relative error of 16.36%, in the outer part (B box). Considering the relative error, the reproducibility of the model was found to be good. The correlation coefficient and coefficient of determination could not apply due to limitations of the monitoring data and box-type model. Application of various statistical analyses would be needed to accurate assessment for the applicability of the model in future research.

Sensitivity analysis was conducted by changing the coefficient by a 200% increase or 50% decrease. Table 5 shows the results of the sensitivity analysis of parameters by changing the state variables. Higher result values are correlated with greater influence on the state variable's concentration. Dissolved PFOS showed great concentration changes of more than 10% as the adsorption and desorption rates increased or decreased. It was observed that the concentration of dissolved PFOS is greatly affected by the adsorption and desorption rates.

Similarly, the concentration of PFOS in POC is also influenced by the adsorption and desorption rates, and the sinking velocity. PFOS in POC showed

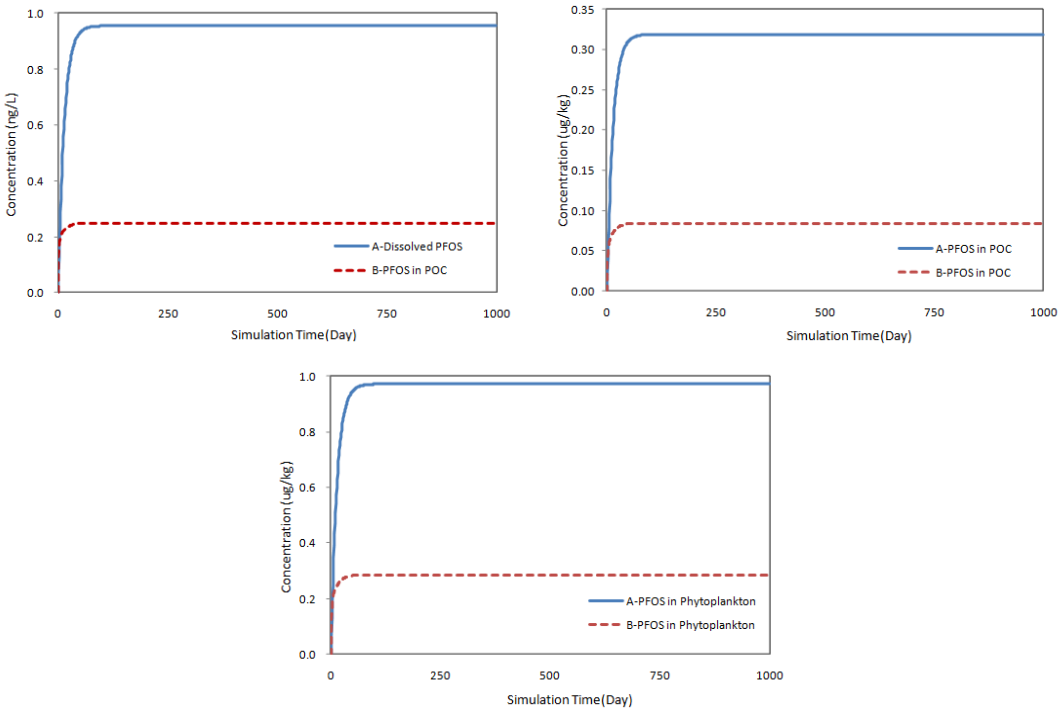

Fig. 4. Simulated PFOS concentration.

Table 5. Sensitivity analysis results of PFOS concentration by change in coefficient values

ITEM	The changes of PFOS (%)		
	In water	in POC	in phytoplankton
Bio-concentration factor × 1/2	0.00	0.00	-49.99
Bio-concentration factor × 2	0.00	0.00	99.93
Excretion rate × 1/2	0.00	0.00	56.43
Excretion rate × 2	0.00	0.00	-27.83
Adsorption rate × 1/2	11.87	-43.70	13.01
Adsorption rate × 2	-16.05	66.19	-17.39
Desorption rate × 1/2	-16.23	15.71	-16.96
Desorption rate × 2	18.74	-9.47	19.74
Sinking velocity × 1/2	5.80	9.55	6.47
Sinking velocity × 1/2	-8.00	-13.15	-8.53

the greatest concentration change of more than 40% as the adsorption rate increased or decreased. The concentration of dissolved PFOS was greatly affected by the adsorption rate. In the case of PFOS in phytoplankton, the concentration changed by more than 10% with the increase or decrease of bio-concentration and the excretion rate, showing that it is sensitive. Further studies are needed to identify the critical influencing factors.

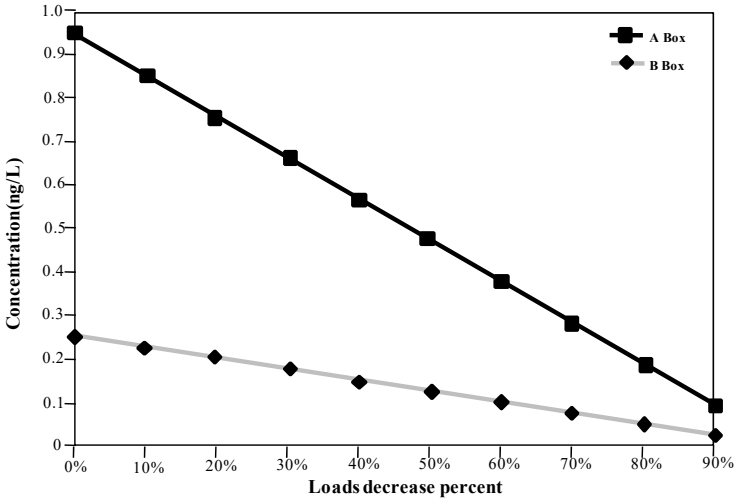

Fig. 5. Scenario analysis results.

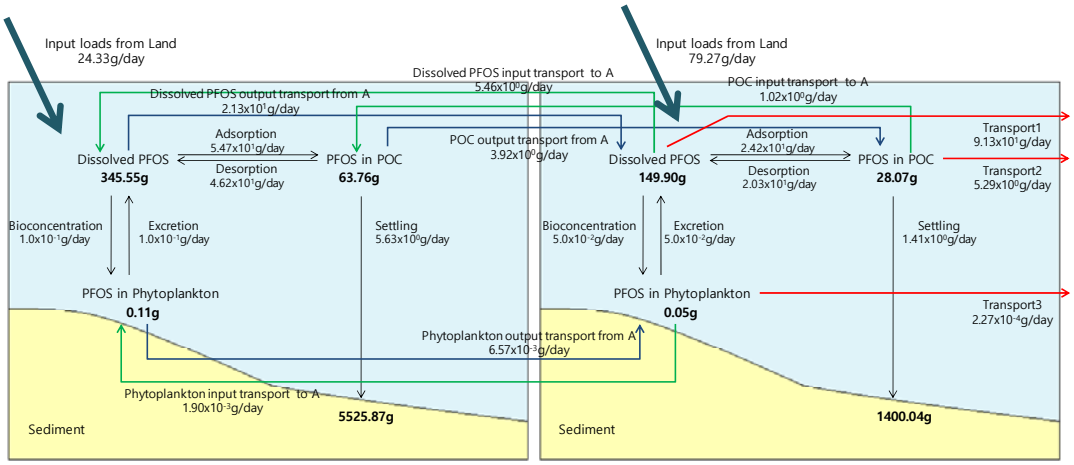

Fig. 6. Mass balance estimation.

3.3. Scenario analysis and mass balance

The scenario analysis consisted of one plan to reduce the input loads from the watershed loads by 10%. The result showed that the concentration of dissolved PFOS concentration was gradually reduced in each box (Fig. 5.).

Fig. 6. shows the mass balance of PFOS in the Gwangyang Bay, which was calculated from the results obtained from the model simulation. The standing stock of PFOS in the inner part (A box) of the Gwangyang Bay is 345.55 g in the water column, 63.76 g in POC, and 0.11 g in phytoplankton. The standing stock of PFOS in the outer part (B box) is 149.90 g in the water column, 27.51 g in POC, and 0.05 g in phytoplankton.

The input loads indicate that 24.33 g/day of dissolved PFOS flowed in from the watershed based loads into the inner part (A box) and 79.27 g/day of

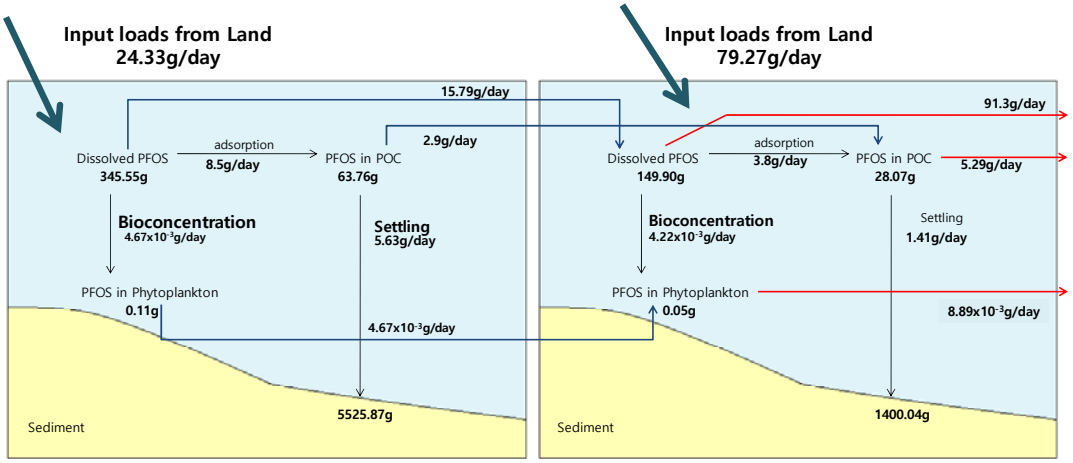

Fig. 7. PFOS flux estimation.

dissolved PFOS flowed into outer part (B box).

In the case of the inner part (A box), with respect to the flux of dissolved PFOS, the highest value of 5.38×10^{1} g/day of dissolved PFOS was adsorbed to POC; the next highest value of 4.53×10^{1} g/day was desorbed to dissolved PFOS, followed by 2.14×10^{1} g/day via outflow from the inner part (A box) to the outer part (B box) and 5.47×10^{1} g/day via inflow from the outer part (B box) to the inner part (A box).

In the case of the outer part (B box), with respect to the flux of dissolved PFOS, the highest value of 9.17×10^{1} g/day of dissolved PFOS was effluent to the open sea, followed by 2.36×10^{1} g/day adsorbed to PFOS in POC, 2.14×10^{1} g/day via inflow from the inner part (A box), and 1.98×10^{1} g/day via desorption.

In the case of outflow from the inner part (A box) to the outer part (B box), the highest value was dissolved PFOS (2.14×10^{1} g/day), and next highest was PFOS in POC (3.88 g/day), followed by PFOS in phytoplankton (6.60×10^{-3} g/day). In the case of inflow from the outer part (B box) to the inner part (A box), dissolved states had the highest value of 5.47 g/day, followed by POC states of 1.00 g/day and phytoplankton states of 1.90×10^{-3} g/day.

In the case of outflow from outer part (B box) to the open sea, the highest value was 9.17×10^{1} g/day of PFOS in the form of dissolved effluent, the second highest value was 5.32 g/day of PFOS distributed to POC, followed by 2.27×10^{-4} g/day of PFOS accumulated in the body of phytoplankton. Fig. 7 presented a mass balance in this model by applying the difference between partitioning coefficients.

4. Conclusion

This study estimated the fate of PFOS in the Gwangyang Bay using a multi-box model. The result of a numerical simulation of the PFOS level indicates that PFOS in seawater had a relative error of -7.32% and 16.36% in the inner and outer boxes, respectively. These relative errors show that the model has good reliability. The dissolved PFOS in the water layer was greatly affected by the adsorption rate, desorption rate, and sinking velocity. These were also found to be the most important coefficients for PFOS in POC. PFOS in phytoplankton was found to be highly sensitive to bio-concentration and the excretion rate.

The result of the scenario analysis indicated that

the concentration of dissolved PFOS concentration was gradually reduced. However, there are no applicable water quality standards. Therefore, setting water quality standards is necessary.

The standing stocks of PFOS were 345.55 g in dissolved PFOS, 63.76 g in POC, and 0.11 g in phytoplankton in the inner part (A box). The standing stocks of PFOS were 149.90 g in dissolved PFOS, 27.51 g in POC, 0.05 g in phytoplankton in the outer part (B box). Thus, the standing stock in the Gwangyang Bay is in the order of dissolved PFOS, PFOS in POC, and PFOS in phytoplankton. In the inner part (A box), adsorption to POC was the transition path with the highest value, followed by desorption, outflow to the outer part (B box), and inflow to the inner part (A box). In the outer part (B box), outflow into the open sea was the transition path with the highest value, followed by adsorption, inflow from the inner part (A box), and desorption from POC.

Outflow from the inner part (A box) to the outer part (B box) and inflow from the outer part (B box) to the inner part (A box) were found to be associated with the highest value of dissolved PFOS, followed by that in POC and in phytoplankton.

The following need to be considered in future research. There should be regarded the application of three-dimensional fine-grid ecotoxicological model, connection with hydrodynamic model, consideration of various processes like resuspension, and monitoring for ecosystem.

Acknowledgements

This work was supported by a Research Grant of Pukyong National University (2019).

REFERENCES

Ahrens, L., Gashaw, H., Sjöholm, M., Gebrehiwot, S. G., Getahun, A., Derbe, E., Bishop, K., Åkerblom, S., 2016, Poly- and perfluoroalkylated substances (PFASs) in water, sediment and fish muscle tissue from Lake Tana, Ethiopia and implications for human exposure, Chemosphere, 165, 352-357.

Cho, C. R., 2008, Residual characteristics of perfluorinated chemicals in main coastal areas and main stream watersheds of Korea, Ph.D. Dissertation, Chonnam National University, Jeollanam-do, Korea.

Giesy, J. P., Mabury, S. A., Martin, J. W., Kannan, K., Jones, P. D., Newsted, J. L., Coady, K., 2006, Perfluorinated compounds in the Great Lakes, Springer, Germany, 391-438.

Grasty, R. C., Grey, B. E., Lau, C. S., Rogers, J. M., 2003, Prenatal window of susceptibility to perfluorooctane -sulfonate-induced neonatal mortality in the Sprague -Dawley rat, Birth Defects Res., Part B, 67, 465-471.

Higgins, C. P., Field, J. A., Criddle, C. S., Luthy, R. G., 2005, Quantitative determination of perfluorochemicals in sediments and domestic sludge, Environ. Sci. Technol., 39, 3946-3956.

Hong, S. J., Lee, J. S., Oh, H. T., Yoon, S. P., Kim, H. C., Kim, D. M., 2007, Ecological modeling for estimation of autochthonous COD in Jinhae Bay, J. Environ. Sci. Int., 16, 959-971.

Jorgensen, L. A., Jorgensen, S. E., Nielsen, S. N., 2000, ECOTOX: ecological modelling and ecotoxicology, Elsevier Science, Amsterdam, Netherlands (CD-ROM).

Kim, D. M., 2007, Numerical simulation of PFOA in Tokyo Bay using EMT-3D, Korean Soc. Mar. Environ. Saf., 13, 173-181.

Kim, D. M., 2011, Numerical simulation for the prediction of PAHs in Jinhae Bay using EMT-3D model, Korean Soc. Mar. Environ. Saf., 17, 7-13.

Kim, D. M., Norihide, N., Toshihiro, H., Hideshige, T., Hiroaki, S., Osami, N., 2004, Numerical simulation of organic chemicals in a marine environment using a coupled 3D hydrodynamic and ecotoxicological model, Mar. Pollut. Bull., 48, 671-678.

Kissa, E., 2001, Fluorinated surfactants and repellents, 2nd edition, Surfactant Science Series, Vol. 97., CRC Press, USA, 640.

Korea Food and Drug Administration (KFDA), 2006, The survey of exposure level for PFOS and PFOA in human, TRKO20020005742, KFDA, Chungcheongbuk-do, Korea.

Korea Ocean Research and Development Institute (KORDI), 2003, A study on the management model for environ -mental pollution of special management area in Namhae (1) Gwangyang Bay study, TRKO200200057423, KORDI, Busan, Korea.

Lee, D. I., Cho, H. S., Cho, C. R., Lee, J. H., Kang, J. H., Choi, M. H., Kim, D. H., Yoon, J. S., 2004, Characteristics of pollutant loads and temporal variations of point sources in Kwangyang Bay watershed, Bull. Fish. Sci. Inst. Chonnam Natl. Univ., 13, 59-68.

Lee, D. I., Park, C. K., Cho, H. S., 2003, Characteristics of pollutant loads and water quality in Kwangyang Bay, Korea, J. Fish. Sci. Technol., 6, 149-154.

Munschy, C., Marchand, P., Venisseau, A., Veyrand, B., Zendong, Z., 2013, Levels and trends of the emerging contaminants HBCDs (hexabromocyclododecanes) and PFCs (perfluorinated compounds) in marine shellfish along French coasts, Chemosphere, 91, 233-240.

Paik, B. C., Kam, S. K., 2017, Detection characteristics of perfluorinated compounds (PFCs) in the southern coastal sediment of South Korea and annual concentration in sea water, J. Korean Soc. Urban Environ., 17, 231-241.

Rayne, S., Forest, K., Friesen, K. J., 2009, Estimated bio-concentration factors (BCFs) for the C4 through C8 perfluorinated alkysulfonic acid (PFSA) and alkylcarboxylic acid (PFCA) congeners, J. Environ. Sci. Health, Part A, 44, 598-604.

Son, H. J., Hwang, Y. D., Yoom, H. S., Choi, J. T., Kwon, K. W., 2013, Detection of perfluorinated compounds (PFCs) in Nakdong River basin, Korean Soc. of Environ. Eng., 35, 84-93.

Son, J. H., Chung, S. Y., Kwon, B. G., 2017, Monitoring of perfluorinated compounds (PFCs) in the seawater of the east and west coast in Korea, J. Korean Geoenviron. Soc., 18, 5-12.

Sun, R., Wu, M., Tang, L., Li, J., Qian, Z., Han, T., Xu, G., 2018, Perfluorinated compounds in surface waters of Shanghai, China: source analysis and risk assessment, Ecotoxicol. Environ. Saf., 149, 88-95.

Wu, J., Junaid, M., Wang, Z., Sun, W., Xu, N., 2020, Spatiotemporal distribution, sources and ecological risks of perfluorinated compounds (PFCs) in the Guanlan River from the rapidly urbanizing areas of Shenzhen, China, Chemosphere, 245, 125637, https://doi.org/10.1016/j.chemosphere.2019.125637.

• Researcher. Min-Ji Heo
Busan Development Institute
raimyou@bdi.re.kr
• Instructor. Kyong-Joon Roh
Department of Ecological Engineering, Pukyong National University
rkjoon@pknu.ac.kr
• Professor. Dong-Myung Kim
Department of Ecological Engineering, Pukyong National University
dmkim@pknu.ac.kr