Doctoral Thesis

Distribution, Sources and Mass Balance of Polycyclic Aromatic Hydrocarbons in the Seto Inland Sea and Surrounding Area, Japan

（瀬戸内海周辺域における多環芳香族炭化水素の分布、発生源、物質収支）

(Summary)

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In this study, the concentration of polycyclic aromatic hydrocarbons (PAHs) in marine sediments as well as in the river water and atmosphere of the Seto Inland Sea and its surrounding area was determined in order to evaluate environmental pollution and dynamics, elucidate distribution, possible sources and pathways and fluxes of PAHs, and to calculate their mass balance within the study area.

Chapter 1 describes the background of environmental dynamics analysis of trace chemical substances, which is the focus of this study, the concept of trace chemical substances specifically PAHs in the environment, the geography and natural environment of the Seto Inland Sea, and the purpose of this research. PAHs are trace harmful chemical substances that are distributed in the environment such as air, water and soil, and show carcinogenicity, mutagenicity and teratogenicity. The chemical structure of PAHs is composed of two or more benzene rings containing carbons and hydrogens. PAHs are produced in the environment mainly by fossil fuel combustion and biomass burning. In particular, when PAHs flow into the ocean, they tend to migrate and accumulate in seafloor sediments due to their hydrophobicity, high persistence, and high affinity with organic matters. Therefore, in the marine environment, PAHs are more abundant in seafloor sediments than in overlying seawater. The Seto Inland Sea, which is the target area of this study, is a semi-enclosed sea that is in contact with the open ocean only through the narrow Kanmon Straits, Bungo Channel and Kii Channel. Thus, the exchange rate of seawater in the Seto Inland Sea and the open ocean is slower than that of Tokyo Bay and Ise Bay, and pollutants are not rapidly diluted and diffused into the

open ocean. Therefore, pollutants can easily accumulate in the Seto Inland Sea.

Chapter 2 describes a study on the distribution and source estimation of PAHs in the coastal sediments in the Seto Inland Sea. The concentrations of 17 PAHs in marine surface sediments and sediment cores collected in Osaka Bay in June 2015 and in Aki-Nada, Harima-Nada, Osaka Bay and Kii Channel within the Seto Inland Sea in July 2016 were measured. Sediment core samples from the estuary in Osaka Bay were dated by measuring ^{210}Pb concentration to determine the historical changes of PAHs concentration discharged into the marine environment. The total concentration of 17 PAHs (Σ17PAH) in the surface sediments collected in 2015 and 2016 was 108 ~ 1,590 ng g^{-1}dry weight (dw) (average = 615 ng g^{-1}dw) and 65.8 ~ 604 ng g^{-1}dw (average = 245 ng g^{-1}dw), respectively. In Aki-Nada and Osaka Bay, a decreasing PAHs concentration trend towards the offshore was observed. From the historical changes of PAHs concentration in the estuary of Osaka Bay from 1965 to 2010, the highest PAHs concentration (2,810 ng g^{-1}dw) was detected around 1978, and then their concentration decreased and remain unchanged until around 2010. PAHs diagnostic ratios and principal component analysis of PAHs sources revealed the possible sources of PAHs in surface sediments and sediment cores collected in 2015 and 2016 to be industrial and traffic activities, and biomass burning.

Chapter 3 describes a study on PAHs concentration in sediments, river water and atmosphere in the Seto Inland Sea and its surrounding area, the relationship between PAHs and organic carbon contents and grain size of sediments, and the risk assessment

of PAHs in sediments. Also, based on the measured values obtained in this study and the literature, the transport fluxes in the Seto Inland Sea and its surrounding area were estimated, and the mass balance of PAHs was calculated. 17 PAHs in surface sediments collected from Suo-Nada, Beppu Bay, Bungo Channel, Hiroshima Bay, Iyo-Nada, Hiuchi-Nada, Osaka Bay and Kii Channel in the Seto Inland Sea in December 2018, February–March 2019 and July 2019 were analyzed. Likewise, 17 PAHs in river water samples collected from the Kurose River and Yodo River in November 2019 were also analyzed. In addition, 17 PAHs in rainwater samples collected in Higashi-Hiroshima in December 2020. Furthermore, 12 particulate PAHs in atmospheric samples were collected once a month for 24 h at 4 or 5 air pollution monitoring stations in Osaka city for a total of 4 years from April 2011 to March 2014 and from April 2017 to March 2018. Σ17PAH in the surface sediment was 14.6 ~ 1,160 ng g^{-1}dw (average = 198 ng g^{-1}dw), which was the highest in Beppu Bay and the lowest in Bungo Channel. Σ17PAH in suspended river water averaged 176 ng g^{-1}dw in the Kurose River and 42.1 ng g^{-1}dw in the Yodo River. The particulate Σ12PAH in the atmosphere of Osaka city was 0.38 ~ 7.4 ng m^{-3} (average = 2.3 ng m^{-3}). Atmospheric particulate PAHs showed seasonal variations wherein concentration is high in winter and low in summer. From the measurement of organic carbon in sediments and grain size distribution of sediments, the PAHs showed high concentrations in sediments when the organic carbon ranged between 2 ~ 5 % wet weight (ww), silt content 85 ~ 90 %, clay content 10 ~ 15 %, and gravel + sand content is < 5 %. From the PAHs risk assessment in sediments, only fluorene concentration in

Beppu Bay exceeded the ERL (concentration at which a biological adverse effect occurs with 10 % probability) set by the sediment quality guidelines, but was still below the ERM value (biological adverse effect is 50 % or less); all PAHs concentrations were below the ERL at all sites except Beppu Bay. From the mass balance calculation in the Seto Inland Sea regions, the flux of PAHs flowing into the Seto Inland Sea through rivers was 2.3 ± 0.3 ton yr^{-1}, and the flux of PAHs deposited from the atmosphere into the Seto Inland Sea was 13 ± 1 ton yr^{-1}, and the flux of PAHs deposited on the bottom sediments of the Seto Inland Sea was 5.5 ± 3.3 ton yr^{-1}. The difference between the total flux of PAHs input into the Seto Inland Sea and the flux of PAHs deposited on the seafloor (2.3 + 13 – 5.5 = 9.8 ton yr^{-1}) is considered as the flux that disappears due to discharge to the open ocean, uptake by marine organisms, photodegradation and/or biodegradation, etc. It was estimated that the outflow flux through the uptake by bivalves and microbial degradation were 0.17 and 4.4 ton yr^{-1}, respectively, but other outflow fluxes are unclarified.

Chapter 4 describes the general discussion, summary, conclusions and suggestions for future work.