Doctoral Thesis Summary

Occurrence, Sources and Degradation of Diuron, Irgarol 1051 and Fenitrothion in Water, Sediments, Plankton and Fishes of Coastal Sea and River Waters, Japan

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General summary (English)

In this study Diuron (3-[3,4-dichlorophenyl]-1,1-dimethylurea) , Irgarol 1051 (2-[tert-butylamino]-4-[cyclopropylamino]-6-[methylthio]-1,3,5-triazine) and Fenitrothion (O,O-Dimethyl O-(3-methyl-4-nitrophenyl)phosphorothioate) were monitored in Kurose River water to assess the contribution of agriculture and urban activities to river pollution. Diuron, Irgarol 1051 and Fenitrothion were also analysed in marine samples (water, sediments, plankton and fishes) so as to assess the distribution pattern of these pesticides in Seto Inland Sea. Lastly, biodegradation and photodegradation of these pesticides was done. Using data in this study and literature information, the mass distributions of the pesticides in Seto Inland Sea were modelled.

Chapter 1 presents a general overview of pesticide use, contamination and some of the studies that have been done in Japan. This study mainly aimed at assessing contamination of pesticides in river water and the marine environment. The use of pesticides in agriculture and the urban environment leads to contamination of surface water bodies like rivers. The rivers in turn end up contaminating larger surface water bodies. Therefore in this study water samples were first collected from Kurose River which drains into Seto Inland Sea and Diuron, Irgarol 1051 and Fenitrothion were analysed. Next seawater, sediments, plankton and fishes were analysed to identify the distribution pattern in marine samples. The persistence of these pesticides was assessed through biodegradation and photodegradation before using modelling to predict the distribution pattern of the pesticides.

Chapter 2 presents a study that was conducted on the pesticides Diuron, Irgarol 1051 and Fenitrothion in Kurose River water from January to December, 2013 at six sites (Namitakiji, Tokumasa, Izumi, Ochiai, Hinotsume and Kurose Bunka Centre) in Higashi Hiroshima City, Japan for a period of one year to assess the contribution of agriculture and urban activities to pesticide pollution of the river. The maximum pesticide concentrations were; 4620 ngL^{-1}, 50 ngL^{-1} and 370 ngL^{-1} for Diuron, Irgarol 1051 and Fenitrothion, respectively. While Diuron and Fenitrothion were detected at all sites, Irgarol 1051 was only present at Izumi, a high density urban and industrial area which also registered the highest concentrations of the pesticides. The pattern showed by Diuron and Fenitrothion was linked to farming activities. Also, Diuron and Fenitrothion concentration correlated with pesticide utilization data for Hiroshima Prefecture. Irgarol 1051 showed a different pattern to that of Diuron and Fenitrothion and its source was attributed to paint. It was noted that 78% and 42% of water samples at Izumi sampling site exceeded the European Union (EU) guidelines for Diuron and Fenitrothion, respectively.

Chapter 3 presents a study that was conducted in Seto Inland Sea, Japan (2012 to 2013), to assess the distribution of Diuron, Irgarol 1051 and Fenitrothion among water, sediments and aquatic organisms (plankton, fish and selected marine animals). The maximum concentrations for Diuron, Irgarol 1051 and Fenitrothion were 2180 ngL^{-1}, 1070 ngL^{-1} and 50 ngL^{-l} in surface waters, respectively; 60 ngL^{-1}, 90 ngL^{-1} and 40 ngL^{-1} in bottom waters, respectively; 75 ngg^{-1} dry weight (dw), 69 ngg^{-1} dw and 51 ngg^{-1} dw in sediments, respectively; 2830 ngg^{-1} dw, 2040 ngg^{-1} dw and 460 ngg^{-1} dw in plankton, respectively;

4120 ngg^{-1} dw, 3140 ngg^{-1} dw and 480 ngg^{-1} dw in fish and selected marine animals, respectively. The highest concentrations of Diuron and Irgarol 1051 were found close to a port and ship building industries, whilst maximum concentrations of Fenitrothion were detected near river estuaries. The general trend was that of decreasing pesticide concentrations away from the mouth of rivers flowing into the Seto Inland Sea. Our calculated bioconcentration factors (BCFs) indicate that plankton, whole fish and selected marine animals samples bio-accumulate antifoulants and pesticides. The accumulation gradient in fish organs was viscera > liver > gills > fillet. Measured concentrations of both the antifoulant booster biocide Irgarol 1051 and the insecticide Fenitrothion in both whole fish and marine animals sampled exceeded the Japanese Maximum Residual Limits (MRLs) as did 21% of foods sampled for Diuron under dry weight conditions.

Chapter 4 presents research done on the biodegradation and photodegradation of Diuron, Irgarol 1051 and Fenitrothion in river water and seawater samples. The section also gives data on further research on the pesticides in river water (Kurose River) and marine samples (water, sediment, plankton and fishes) from Seto Inland Sea, Japan from 2012 to 2014. Data generated in this study and further information from literature were used to model the distribution pattern of the pesticides in Seto Inland Sea. The rate of biodegradation was slower than that of photodegradation. For example in river water, the photodegradation half- lives in days were 2.9, 3.5 and 1.9 for Diuron, Irgarol 1051 and Fenitrothion, respectively. On the other hand in the same river water the biodegradation half -lives in days were 1424.8, 1703.1 and 1174.8 for Diuron, Irgarol 1051 and

Fenitrothion, respectively. The pesticides also degraded faster in river water than seawater. The seawater photodegradation half-lives in days were 43.6, 57.3 and 37.9 for Diuron, Irgarol 1051 and Fenitrothion, respectively. On the other hand the seawater biodegradation half-lives in days were 2000.4, 2394.3 and 1650.2 for Diuron, Irgarol 1051 and Fenitrothion, respectively. The main input for Diuron and Irgarol 1051 to Seto Inland Sea is ship bottom paint while Fenitrothion is mainly from rivers. The pesticides are mainly lost to sediments but the open ocean was found to be an equally important sink.

Chapter 5 gives a general discussion and summary of the results in this study. Agriculture and urban activities are contributing to the contamination of Kurose River which is also the case with most rivers worldwide that pass through high population density areas. The pesticides end up in Seto Inland Sea and are distributed among water, sediments, plankton and marine organisms. The highest concentrations of these pesticides were in marine organisms which was an indication of bioconcentration in agreement with information found in literature. The amounts remaining in water are biodegraded, photodegraded or lost to the open ocean. The major sinks for the pesticides were found to be sediments and the open ocean.