

Occurrence of Diuron and Irgarol in seawater, sediments and planktons of Seto Inland Sea, Japan

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The concentrations of the herbicide Diuron and algaecide Irgarol in the Seto Inland Sea, Japan, were assessed for October 2008 and October 2009. Overall, 29 seawater, sediment and plankton samples were collected from off-shore areas around the sea. The Diuron levels were 0.01–0.062 $\mu\text{g/L}$, 0.01–0.09 $\mu\text{g/g}$ dry weight (dw) and 0.075–0.45 $\mu\text{g/g}$ dw in seawater, sediments and planktons respectively. Irgarol levels were 0.011–0.055 $\mu\text{g/L}$, 0.011–0.068 $\mu\text{g/g}$ dw and 0.02–0.36 $\mu\text{g/g}$ dw in seawaters, sediments and planktons respectively. This is the first study to report the presence of Diuron and Irgarol in plankton from aquatic environments. The concentrations of Diuron and Irgarol were similar in both years and the highest levels of concentration were found near the coastal area of Osaka bay, second largest metropolitan region in Japan. The distribution of Diuron and Irgarol in seawaters, sediment and plankton would be largely determined by riverine discharge or uses of these pesticides as antifouling agent at harbors and ports and then transport to offshore from coastal waters by water flows.

Keywords: Diuron, Irgarol, Seto Inland Sea, riverine discharge, offshore transport

INTRODUCTION

For many years, pesticides have been used in fresh water systems such as ponds, water pits and reservoirs as well as in orchards, roadsides and paddy fields. The wide use of agrochemical products against parasitic plants has allowed enhancement of agricultural production and a significant improvement in culture yields. Estimation of the impact of agricultural activity on continental water quality requires precise information concerning the origin and transfer of those products from treated parcels to streams and groundwater (Hosokawa *et al.*, 1995). It is well known that once pesticides are applied, they may be transported over considerable distances through soil, groundwater, surface runoff and oceans (Alegria and Shaw, 1999). One transport pathway for pesticides that has not been well studied is offshore transport from estuarine systems to surface waters of the coastal ocean. Zhou *et al.* (1996) stated that the quantitative fluxes and fates of hydrophobic organic micropollutants along the environmental continuum from catchment to rivers, and to estuary and coastal seas have rarely been mass-balanced. This is especially true with regard to currently used pesticides that were designed to break down quickly,

but may have a potential to impact the coastal ocean via surface runoff due to their solubility (Lamoree *et al.*, 2002).

Diuron (3-[3,4-dichlorophenyl]-1,1-dimethylurea) is an herbicide derived from urea that is considered to be a priority hazardous substance by the European commission (Malato *et al.*, 2002). Accordingly, countries including the UK, Sweden, Denmark and France have restricted the use of Diuron in antifouling paints (Konstantinou and Albanis, 2004). In Japan, Diuron has long been used in agricultural and other activities, and a large amount of Diuron discharged into river water has been transported into the Seto Inland Sea with little or no degradation (Sakugawa *et al.*, 2010). Furthermore, extensive quantities of Diuron are used as antifouling paints by the shipping industry and the highest concentration occurred in seawater of Japan was 3.05 $\mu\text{g/L}$ (Okamura *et al.*, 2003). In addition urban areas of Okinawa Island, Japan apply a significant amount of Diuron as a weed control (Kitada *et al.*, 2008).

Irgarol (2-[tert-butylamino]-4-[cyclopropylamino]-6-[methylthio]-1,3,5-triazine) is a protective algaecide widely used in antifouling paints and has a wide range of action against a number of algal organisms. Irgarol belongs to the s-triazine group of compounds, which act as photosystem-II (PSII) inhibitors, with the inhibition of photosynthetic electron capture transport in chloroplasts as their biochemical mode of action (Dahl and Blanck, 1996). Okamura *et al.* (2003) found the highest concen-

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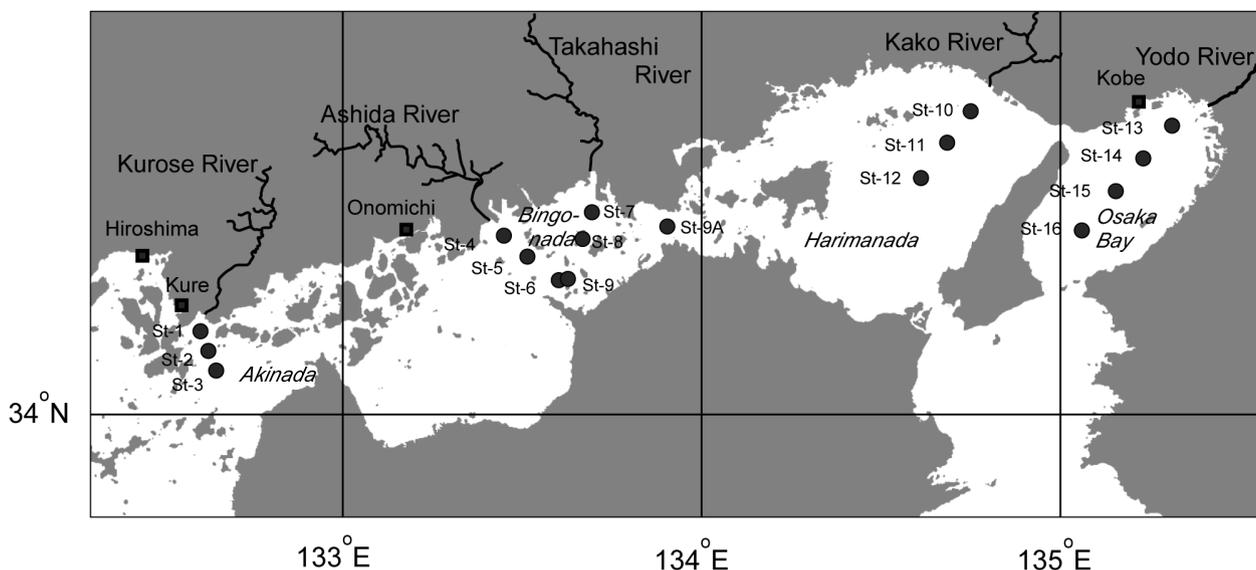


Fig. 1. Map showing the sampling sites at Seto Inland Sea during October 2008 and 2009.

tration of 0.26 $\mu\text{g/L}$ of Irgarol from Hyogo prefecture coastal waters in Seto Inland Sea. Harino *et al.* (2005) investigated the distribution of Irgarol concentration in the coastal waters of Osaka port zone from January 2002 to October 2003. Irgarol is considered to be non-biodegradable and its degradation in seawater and freshwater is slow, with half-life of about 100 and 200 days, respectively (Callow and Willingham, 1996).

The results of these studies suggest that in areas of large-scale utilization, the coastal ocean could be heavily influenced by pesticides and point to the need for further studies regarding the offshore movement of pesticides to coastal waters. In October 2008 and 2009, we conducted a survey of coastal waters of the Seto Inland Sea, Japan to measure levels of pesticides currently used in this region. The goal of this study was to determine the budget of these pesticides in the inner shelf (the subsection of coastal ocean extending from the coast) and to make preliminary estimates of the extent of offshore transport of pesticides from local sources. Large-scale agriculture in the prefectures surrounding the Seto Inland Sea has resulted in the heavy usage of many pesticides in this region (Okamura *et al.*, 2003). This region also has several major rivers which drain agricultural lands and empty into the Seto Inland Sea. Consequently, the coastal sea in this region may be impacted by pesticides. Thus, this region represents an ideal study site for determination of the importance of off shore transport of currently used pesticides from estuaries to the open sea.

MATERIALS AND METHODS

Chemicals

Diuron was obtained from Kanto Chemical Co. Inc. (Tokyo, Japan) and Irgarol was obtained from Sigma-Aldrich Laborchemikalien (Seelze, Germany). HPLC grade acetonitrile (99.8%) and methanol (99.7%) obtained from Nacalai Tesque Inc. (Kyoto, Japan) were used for the HPLC analyses. Dichloromethane (99.5%) was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Sep-pak C18 solid phase extraction cartridges were purchased from Waters Corporation (U.S.A.).

Sample collection

Marine samples such as seawater, sediments and planktons were collected during two cruises to the Seto Inland Sea from 20–24 October 2008 and 05–09 October 2009 on the research vessel Toyoshio-Maru operated by Hiroshima University. Total 16 and 13 stations were sampled in October 2008 and October 2009, respectively. Sampling sites are shown on the map in Fig. 1. In 2008, five coastal sea area were sampled Akinada (St-1: 34 12N, 132 36E, St-2: 34 09N, 132 37E, St-3: 34 06N, 132 38E), Fukuyama (St-4: 34 24N, 133 26E, St-5: 34 22N, 133 30E, St-6: 34 20N, 133 34E), Bingonada (St-7: 34 28N, 133 40E, St-8: 34 25N, 133 38E, St-9: 34 20N, 133 35E, St-9A: 34 26N, 133 55E), Harimanada (St-10: 34 40N, 134 45E, St-11: 34 35N, 134 40E, St-12: 34 31N, 134 36E), and Osaka bay (St-13: 34 39N, 135 20E, St-14: 34 35N, 135 14E, St-15: 34 29N, 135 09E, St-16: 34 25N,

Table 1. Descriptions of major rivers flow into the Seto Inland Sea

| River name | Name of Coastal sea where river flow in | River length (km) | Catchment area (km ²) | Prefectures in catchment area | Population in catchment area | Water flow (m ³ /s) |
|-----------------|---|-------------------|-----------------------------------|---------------------------------------|------------------------------|--------------------------------|
| Kurose River | Akinada | 51 | 239 | Hiroshima | 300,000 | 3.17 |
| Ashida River | Fukuyama | 111 | 2,670 | Hiroshima, Okayama | 273,000 | 61.8 |
| Takahashi River | Bingonada | 86 | 860 | Okayama, Hiroshima | 269,000 | 12.7 |
| Kako River | Harimanada | 96 | 1,730 | Hyogo | 820,000 | 45.9 |
| Yodo River | Osaka Bay | 75 | 8,240 | Kyoto, Osaka, Shiga, Mie, Nara, Hyogo | 11,650,000 | 268 |

135 04E). In 2009 samples were taken from the same areas but excluding Akinada. In St-9A the marine samples were collected in 2008 only while in 2009 the samples were collected in St-9. These sampling stations were chosen in the place where a short distance from major river estuaries. Table 1 provides general descriptions regarding major rivers that drain into the five coastal sea areas in the Seto Inland Sea. Descriptions on the Kurose river were provided by Hiroshima Prefecture office (2002) and descriptions of other rivers such as the Ashida, Takahashi, Kako and Yodo rivers were from the Ministry of Land, Infrastructure and Transport, Japan (2005). The Yodo river, which serve as a drainage route for the living and economical activities of 11 million people in the Kyoto, Osaka and Hyogo district of Japan, is the largest river in the Seto Inland Sea. Harbor water samples were collected at the quays of the Hiroshima Port, Kure Port, Onomichi Port and Kobe Port in the October 2009.

Sample preparation

Surface seawater (0–2 m) was collected using Niskin samplers by a Rosset system attached with CTD sensors (Sea Bird, SBE-9 plus) and successively filtered through a glass fiber filter paper (GC-50, Advantec). Harbor water samples were collected by hand using brown glass bottles that were rinsed with surface water prior to sampling.

Target compounds were extracted from the samples using an automated solid phase extraction (SPE) apparatus (Model: S.P.C.CONT, Waters Corporation) according to the method of Itagaki *et al.*, (2000), with some modification. The cartridges (Sep-Pak C-18, Waters Corporation) were pre-conditioned with 5 ml dichloromethane, 5 ml methanol and 10 ml Milli-Q water prior to use. One liter sample was passed through the cartridge column at a flow-rate of 10 ml/min. The cartridges were then washed with 10 ml Milli-Q water and the target compounds were eluted into a test tube with 5 ml of dichloromethane. The solvent was evaporated under a stream of nitrogen gas until almost complete dry, followed by re-dissolved in 1 ml acetone. Next, the acetone solvent was evaporated to 100 μ l, after which the solution was diluted to 2 ml with 1:1 methanol and Milli-Q water.

Sediments were collected with a Smith-Macintire type

sampler and stored at 4°C in the dark until analysis. Approximately 10 g of wet sediment samples were leached by shaking with 25 ml acetonitrile for 30 min, after which the samples were centrifuged for 10 min at 2000 rpm. The supernatant was extracted and concentrated to 5 ml using a rotary evaporator at 40°C. Next, the samples were cleaned using solid phase extraction and eluted with 5 ml of dichloromethane. Finally, the purified samples were concentrated to about 200 μ l under a gentle stream of nitrogen gas and re-dissolved in 2 ml 1:1 methanol and Milli-Q water.

Plankton samples were collected at each station by vertically towing of 100 μ m mesh size plankton net (Rigoshia & C. Ltd., Saitama, Japan). Samples were passed through glass fiber filter (GC-50, Advantec), after which the filter paper was cut into small pieces that were subsequently sonicated in 30 ml of methanol for 10 min. Next, the solvent was eluted into separatory funnel, after which 5% NaCl (300 ml) and 75 ml of dichloromethane were added to the mixture. The dichloromethane was then separated from the mixture and evaporated under a stream of nitrogen until almost completely dry, after which the residue was re-dissolved in 1 ml acetone. Finally, the acetone solvent was evaporated to 100 μ l, after which it was diluted to 2 ml with 1:1 methanol and Milli-Q water.

Moisture content of sediment and plankton was estimated by weight losses within overnight drying at 110°C in oven. Analyte recoveries were estimated by analyzing seawater and sediment samples fortified with standard solutions of Diuron and Irgarol compounds. When 1 μ g/L of each pesticides was added to 1000 ml of seawater ($n = 3$), the recovery rate was determined to be $88 \pm 10\%$ for Diuron and $87 \pm 12\%$ for Irgarol. When 500 μ g of each pesticides was added to 10 g of sediments ($n = 3$), the recovery rates for Diuron and Irgarol were 92 ± 7.5 and $90 \pm 10\%$, respectively. The recovery rate for plankton was not measured, because of low sample volume.

Analytical method

The prepared samples were analyzed by an HPLC system equipped with a pump (LC-10Ai, Shimadzu), a sample injector (Rheodyne Model 9725) with sample loop size 50 μ l and an UV-Vis detector (SPD-10A, Shimadzu). The oven temperature was 40°C (CTO-10A Shimadzu)

Table 2. Concentration of Diuron and Irgarol in sea waters, sediments and planktons in Seto Inland Sea, Japan

| St. No. | 2008 | | | 2009 | | | | | |
|---------|----------------------------------|------------------------------------|------------------------------------|----------------------------------|------------------------------------|------------------------------------|----------------------------------|------------------------------------|------------------------------------|
| | Diuron concentration | | | Diuron concentration | | | Irgarol concentration | | |
| | Sea water ($\mu\text{g/L}$) | Sediment ($\mu\text{g/g dw}$) | Plankton ($\mu\text{g/g dw}$) | Sea water ($\mu\text{g/L}$) | Sediment ($\mu\text{g/g dw}$) | Plankton ($\mu\text{g/g dw}$) | Sea water ($\mu\text{g/L}$) | Sediment ($\mu\text{g/g dw}$) | Plankton ($\mu\text{g/g dw}$) |
| St-1 | 0.049 | 0.080 | 0.256 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| St-2 | 0.044 | 0.015 | 0.180 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| St-3 | 0.038 | 0.010 | 0.082 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| St-4 | 0.038 | 0.061 | 0.191 | 0.059 | 0.090 | 0.452 | 0.059 | 0.068 | 0.201 |
| St-5 | 0.034 | 0.020 | 0.122 | 0.044 | 0.040 | 0.241 | 0.044 | 0.035 | 0.112 |
| St-6 | 0.014 | 0.012 | 0.076 | 0.018 | 0.020 | 0.090 | 0.018 | 0.016 | 0.030 |
| St-7 | 0.032 | 0.026 | 0.160 | 0.034 | 0.075 | 0.150 | 0.031 | 0.063 | 0.060 |
| St-8 | 0.011 | 0.061 | 0.090 | 0.027 | 0.050 | 0.112 | 0.023 | 0.031 | 0.060 |
| St-9 | n.d. | n.d. | n.d. | 0.023 | 0.020 | 0.080 | 0.011 | 0.011 | 0.020 |
| St-9A | 0.012 | 0.020 | 0.150 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| St-10 | 0.034 | 0.030 | 0.452 | 0.043 | 0.030 | 0.455 | 0.036 | 0.037 | 0.301 |
| St-11 | 0.013 | 0.010 | 0.211 | 0.032 | 0.010 | 0.203 | 0.022 | 0.020 | 0.151 |
| St-12 | 0.011 | 0.010 | 0.075 | 0.016 | 0.010 | 0.075 | 0.015 | 0.020 | 0.122 |
| St-13 | 0.062 | 0.084 | 0.454 | 0.061 | 0.080 | 0.453 | 0.055 | 0.063 | 0.361 |
| St-14 | 0.045 | 0.040 | 0.356 | 0.052 | 0.045 | 0.345 | 0.041 | 0.024 | 0.152 |
| St-15 | 0.031 | 0.028 | 0.293 | 0.041 | 0.025 | 0.283 | 0.032 | 0.020 | 0.095 |
| St-16 | 0.024 | 0.015 | 0.241 | 0.032 | 0.020 | 0.251 | 0.021 | 0.015 | 0.080 |

n.d.: no data.

and the system had a Supelcosil LC-18, 250 mm \times 4.6 mm ID column (Supelco, particle size 5 μm). A guard column (Supelcosil LC-18, 5 μm , 20 mm \times 4.0 mm ID) was fitted before the analytical column. A mixture of acetonitrile and Milli-Q water (60:40) was used as the mobile phase with isocratic elution. The flow rate of eluent was maintained at 1 ml/min and the UV detector wavelength for Diuron and Irgarol was 254 nm and 223 nm, respectively. The retention time of Diuron and Irgarol in the HPLC analysis was 5.1 min and 9.7 min respectively. The detection limit of Diuron was 0.002 $\mu\text{g/L}$, 0.00015 $\mu\text{g/g dw}$ and 0.0003 $\mu\text{g/g dw}$ in seawater, sediment and plankton samples, respectively while for Irgarol was 0.001 $\mu\text{g/L}$, 0.000176 $\mu\text{g/g dw}$ and 0.0003 $\mu\text{g/g dw}$ in these marine samples. The reproducibility analysis of this study for Diuron was $\pm 3.6\%$ and Irgarol was $\pm 3.8\%$ at each 1 $\mu\text{g/L}$ of pesticides.

RESULTS AND DISCUSSION

Concentration in seawaters

The concentrations in seawater, sediment and plankton samples are presented in Table 2. The Diuron concentrations in surface water in October 2008 ranged from 0.011 to 0.062 $\mu\text{g/L}$ (average 0.031 $\mu\text{g/L}$). In October 2009, ranged from 0.016 to 0.061 $\mu\text{g/L}$ (average 0.037 $\mu\text{g/L}$), while those of Irgarol ranged from 0.011 to 0.055 $\mu\text{g/L}$ (average 0.031 $\mu\text{g/L}$). The highest concentrations of Diuron and Irgarol were found at St-13 in the Osaka bay, which is the nearest sampling site from the Yodo river.

Direct contamination of the bay also likely occurred from the shipyard by compounds due to ship painting and normal leaching from areas near the estuary. The next highest concentrations were observed in samples in the regions of Fukuyama (St-4 in 2009), Akinada (St-1 in 2008) and Harimanada (St-10 in 2008 and 2009), which were characterized by consistently high levels of Diuron and Irgarol. In all the coastal sea areas studied, concentrations of Diuron and Irgarol were high at the sampling points near river mouth.

Concentration in sediments

Diuron and Irgarol were detected in all of the collected sediments (Table 2). The highest concentrations were measured in samples taken from the enclosed river mouths of Osaka Bay (0.084 $\mu\text{g/g dw}$ of Diuron (St-13) in 2008) and in Fukuyama (0.090 $\mu\text{g/g dw}$ of Diuron and 0.068 $\mu\text{g/g dw}$ of Irgarol (St-4) in 2009). Diuron was detected in the range of 0.1–13 and 0.1–1.42 $\mu\text{g/g dw}$ in sediment from the European estuaries and its offshore sites, respectively (Comber *et al.*, 2002). In addition, Harino *et al.* (2005) reported that the Diuron concentration in sediment from the coastal area of Osaka Bay ranged from <0.00064 –1.35 $\mu\text{g/g dw}$. Many studies have reported the presence of Irgarol in sediment. For example, Albanis *et al.* (2002) reported a maximum Irgarol concentration of 0.233 $\mu\text{g/g}$ of sediment from a Greek bay. In addition, Thomas *et al.* (2000) reported Irgarol in samples collected from offshore British sites at levels of 0.001–0.04 $\mu\text{g/g}$. Voulvoulis *et al.* (2000) reported Irgarol levels of 3.1–

Table 3. Consumption of Diuron in different utilization at Chugoku and Kinki districts of Japan, year 2007 and 2008

| Prefecture /Years | Rice field | | Orchards | | Vegetables | | Golf ground | | Forest | | Residential areas | | Others | | Total | |
|-------------------|------------|------|----------|------|------------|------|-------------|------|--------|------|-------------------|-------|--------|-------|-------|------|
| | 2007 | 2008 | 2007 | 2008 | 2007 | 2008 | 2007 | 2008 | 2007 | 2008 | 2007 | 2008 | 2007 | 2008 | 2007 | 2008 |
| Osaka | 75 | 15 | 150 | 39 | 70 | 3.2 | — | — | — | — | 1400 | 11000 | 7900 | 11295 | 9357 | |
| Hyogo | — | — | — | — | 90 | — | — | — | — | — | 250 | 1900 | 1800 | 1990 | 2050 | |
| Okayama | — | — | 130 | 150 | 40 | 51 | — | — | — | — | 63 | 2100 | 190 | 2270 | 454 | |
| Hiroshima | — | — | 980 | 590 | 62 | 32 | — | — | — | — | 750 | 5800 | 6100 | 6842 | 7472 | |

Unit: kg/year.

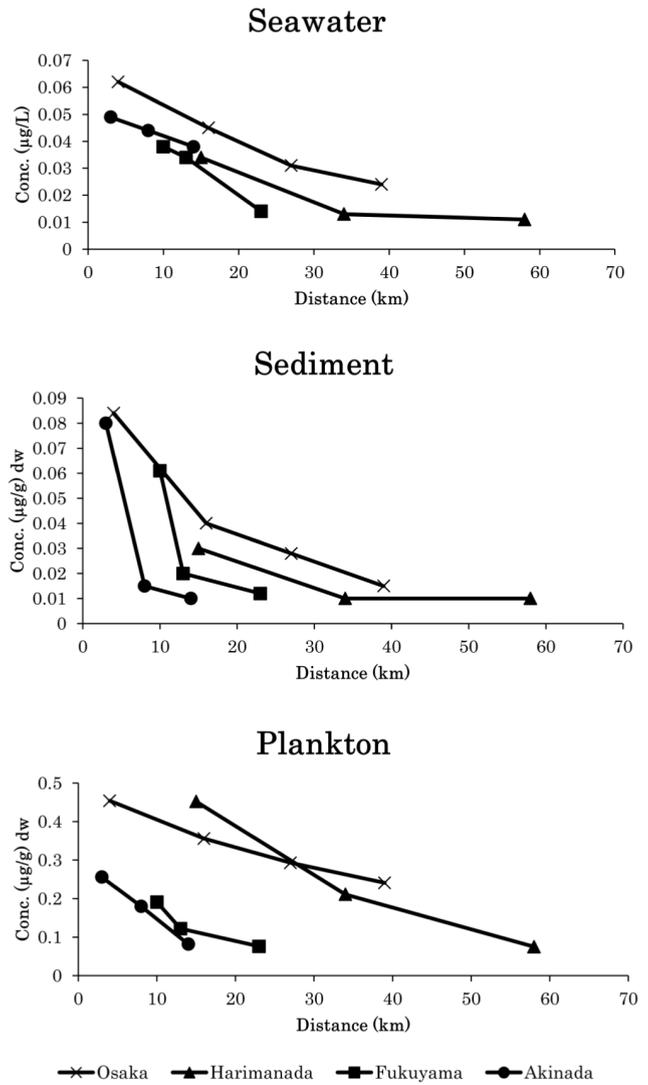


Fig. 2. Change in Diuron concentrations with distance from the river mouth at all stations during October 2008.

222, 3.1–14 and 2–220 µg/g in the River Blackwater, the North Sea and the Baltic Sea respectively. The concentration of Diuron and Irgarol observed in the present study are within the range of values previously reported for sediments.

Concentration in planktons

The concentration of Diuron in plankton was higher than Irgarol concentration in all stations except St-12. The Diuron concentration in plankton in 2008 and 2009 were ranged from 0.075 to 0.455 µg/g dw and in 2009, Irgarol concentration in plankton ranged from 0.020 to 0.361 µg/g dw (Table 2). The highest concentrations of Diuron were 0.452 and 0.454 µg/g dw of the samples obtained from both Harimanada and Osaka bay in 2008 respectively. The

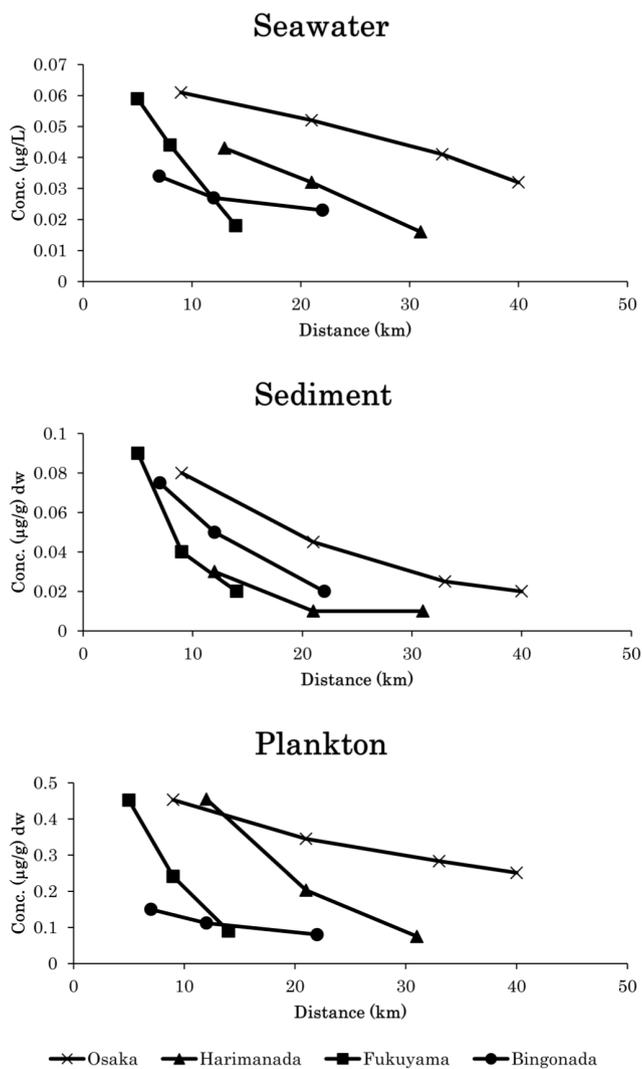


Fig. 3. Change in Diuron concentrations with distance from the river mouth at all stations during October 2009.

same concentrations of Diuron were also observed in samples obtained from Fukuyama, Harimanada and Osaka bay in 2009. The highest Irgarol concentrations of $0.361 \mu\text{g/g dw}$ were observed in samples obtained from Osaka bay in 2009. It was suspected that the usages of pesticides in the Osaka bay area are quite higher than the other coastal areas in Seto Inland Sea. Harino *et al.* (1999) reported a maximum organotin concentration of $2.39 \mu\text{g/g dw}$ in plankton from Port of Osaka and this is the only data, which is available for plankton samples in the Seto Inland Sea. This information implies that various antifouling pesticides occur in the Osaka bay area with moderately high concentrations.

Sources of Diuron and Irgarol in the Seto Inland Sea

The usages of Diuron in different prefectures that are

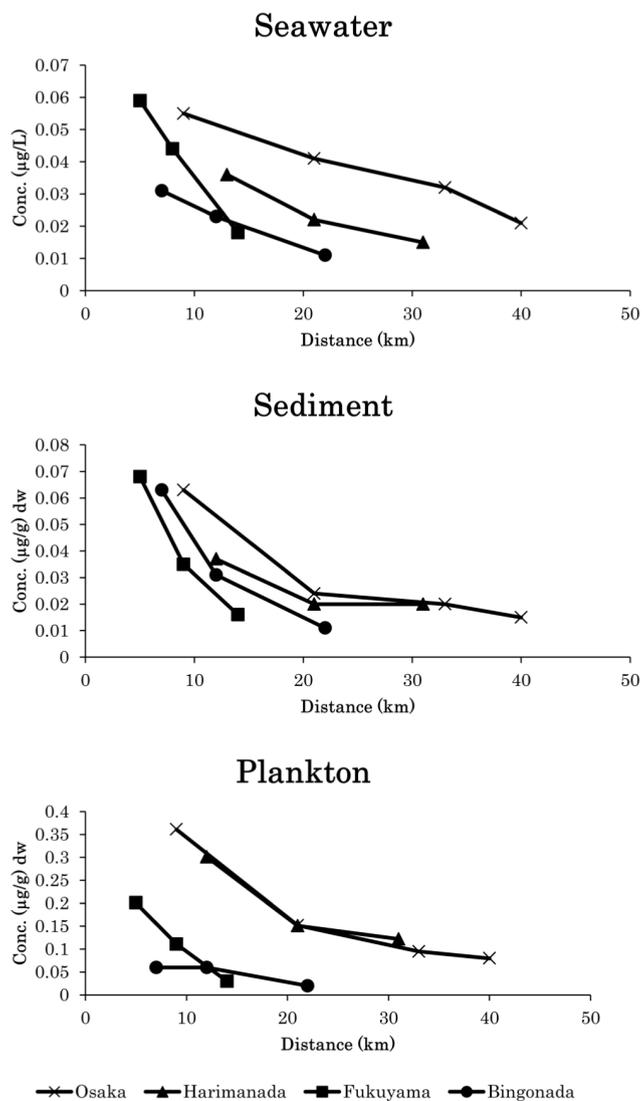


Fig. 4. Change in Irgarol concentrations with distance from the river mouth at all stations during October 2009.

facing to the Seto Inland Sea are reported in Table 3 (Organization for Research and Communication on Environmental Risk of Chemicals, Japan, 2007, 2008). Diuron was consumed by various agricultural and residential activities, and other activities such as weed control in and nearby roads and railways. Total consumption amounts of Diuron in 2007 and 2008 were 11295 and 9357, 1990 and 2050, 2270 and 454, and 6482 and 7472 kg/year for Osaka, Hyogo, Okayama and Hiroshima prefectures, respectively. Because of the essential role which pesticides now have in modern farming and the intensity of agriculture, a very large proportion of this land receives Diuron varying from several applications each year. The comparative different usage of Diuron will lead to riverine discharge into the respective estuaries.

Table 4. Diuron and Irgarol concentration in harbor and marina waters

| Sample | Diuron ($\mu\text{g/L}$) | Irgarol ($\mu\text{g/L}$) | Classification | Reference |
|----------------|-------------------------------|--------------------------------|----------------|------------------------------|
| Kure Port | 1.78 | 0.74 | Harbor | This study |
| Hiroshima Port | 1.70 | 1.05 | Harbor | This study |
| Onomichi Port | 2.12 | 0.14 | Harbor | This study |
| Kobe Port | 2.03 | 1.85 | Harbor | This study |
| Osaka Coast | 0.65 | 0.53 | Harbor | Harino (2004) |
| Wakayama Coast | 2.05 | 0.13 | Marina | Okamura <i>et al.</i> (2003) |
| Mie Coast | 3.05 | 0.078 | Harbor | Okamura <i>et al.</i> (2003) |
| U.K. Coast | 1.25 | 0.28 | Marina | Thomas <i>et al.</i> (2000) |

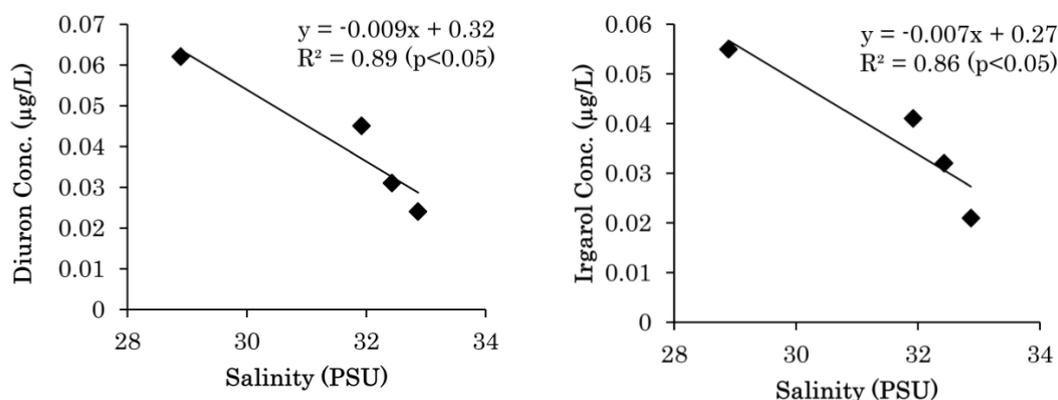


Fig. 5. Correlation between the concentrations of Diuron and Irgarol with salinity of Osaka Bay in 2009.

The distance pathway of Diuron and Irgarol concentration in the sea waters, sediments and planktons varied widely between each sampling station as shown in Figs. 2, 3 and 4. The results for all stations appeared to indicate a steady decrease in concentrations between river mouths to offshore areas. The Osaka bay area showed the highest Diuron concentration, which could be attributed to the input from the Yodo River. Irgarol can be sourced from anti-fouling paints on boats and ships.

The utilization of Diuron on land and its accumulation in the marine environment through the regular discharge from rivers are considerable to occur. Okamura *et al.* (2003) discussed that there is a possibility that some freshwaters collected from marinas might have received agricultural drainage containing Diuron. Hu *et al.* (1999) demonstrated that both the raw and treated water from Niigata public waterworks treatment plant contained Diuron at concentration levels of 0.02–0.25 $\mu\text{g/L}$. It seems that the origin of Diuron detected at the treatment plant is not ascribed to antifouling use. In Germany, more than 80% of the total herbicide load in the effluent from an urban wastewater treatment plant consisted of Diuron, which was mainly used in urban weed control (Nitschke and Schussler, 1998). Diuron has been reported in fresh-

water environments at relatively high concentrations as follows: 42 $\mu\text{g/L}$ in lagoon water, Italy (Gennaro *et al.*, 1995), 20.7 $\mu\text{g/L}$ in filed runoff, 18.2 $\mu\text{g/L}$ in stream water, and 10.9 $\mu\text{g/L}$ in USA groundwater (Field *et al.*, 1997).

In this study we identified the consumption of amount of Diuron on the land in the four prefectures, which are facing to the Seto Inland Sea, are significant (Table 3). Sakugawa *et al.* (2010) reported that concentration of Diuron in the river waters of Hiroshima prefecture was 0.35–3.6 $\mu\text{g/L}$ (average 0.69 $\mu\text{g/L}$) and the half-life of Diuron was 9–38 days when natural sunlight (October–December 2006) was irradiated to the water samples. While its half-life time by biodegradation was 602–814 days. They concluded that a significant portion of Diuron discharged into river water is transported into the Seto Inland Sea, without any or little degradation. Therefore Diuron derived from the use on land by various human activities could significantly contaminate the Seto Inland Sea.

Irgarol contamination from the Mediterranean Sea has recently been reported at concentration levels of 0.01–1.7 $\mu\text{g/L}$ in the marinas and ports and 0.0015–0.017 $\mu\text{g/L}$ in open coastal areas (Readman *et al.*, 1993; Tolosa *et al.*, 1996). In the coast of Sweden and U.K., Irgarol was also

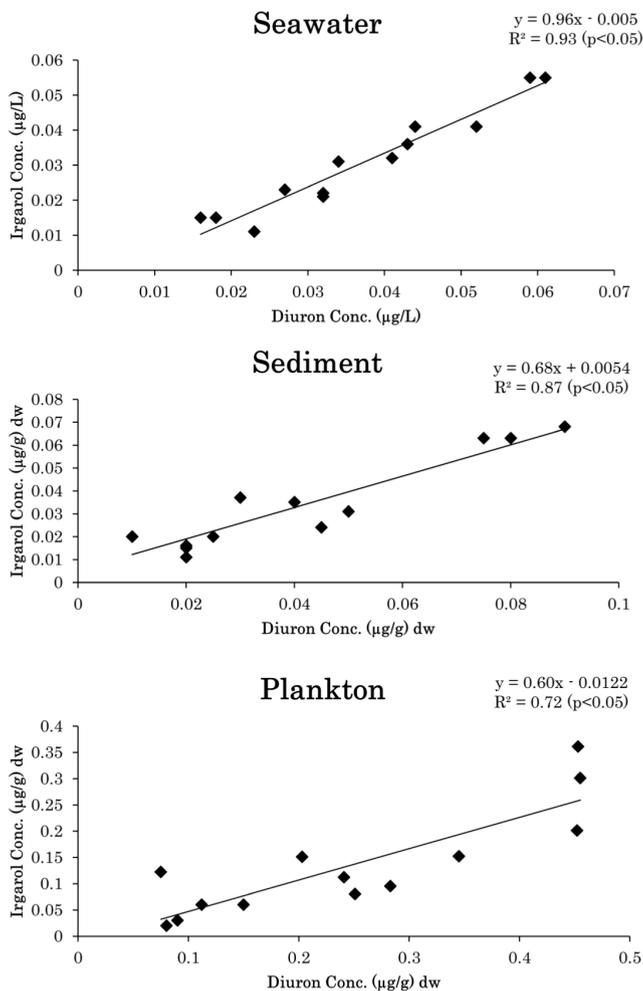


Fig. 6. Correlation between the concentrations of Diuron and Irgarol in 2009.

found in the marina waters (0.016~0.682 $\mu\text{g/L}$) and in the coastal waters (0.002~0.011 $\mu\text{g/L}$) (Gough *et al.*, 1994; Dahl and Blanck, 1996; Zhou *et al.*, 1996). Contamination by Irgarol of the European freshwater environment was noted at levels of 0.001~0.145 $\mu\text{g/L}$ (Toth *et al.*, 1996). Therefore, Irgarol at current levels in the Seto Inland Sea is comparable to those in other countries. It is likely that Irgarol would largely come from utilizations as antifouling paints for boats and ships (Okamura *et al.*, 2003).

To identify the sources of Diuron and Irgarol, seawater samples were collected from the port of Kure, Hiroshima, Onomichi and Kobe in the October 2009 (Table 4). The concentration ranges of Diuron and Irgarol measured were 1.70~2.12 and 0.14~1.85 $\mu\text{g/L}$, respectively. Our analytical values of these pesticides are similar to those determined by previous investigators (Table 4). Much higher concentrations of these pesticides in the port seawaters

than offshore seawaters (Table 2) indicate that some portion of Diuron and Irgarol in the sea may come from the port area by the use of antifouling paints. The relationship between pesticides with salinity was investigated. The good correlations were observed between Diuron ($R^2 = 0.89$) and Irgarol ($R^2 = 0.86$) with salinity (Fig. 5). This also shows the coasts of Seto Inland Sea are sources of these pesticides occurring in seawaters, sediments and planktons.

Correlations were examined between Diuron and Irgarol concentrations using the data points from this study. Linear relationships between two pesticides were appeared in seawaters, sediments and planktons (Fig. 6). Moreover, the concentration ratios between these two pesticides were almost same among seawater, sediment and planktons (0.60~0.96). These results suggest that the dynamics of the two pesticides in coastal sea areas may be quite similar. The octanol-water partition coefficients (Pow) is used to estimate hydrophobic or hydrophilic nature of organic compounds and also used for an indicative of bioaccumulation in the water environment. The logarithm of Pow of Diuron and Irgarol were almost same, 2.9 and 2.8 respectively (Harino, 2004). Therefore it can at least say that similar chemical properties of these two pesticides may result in similar distribution patterns in the Seto Inland Sea. The coastal area of Japan receives agricultural runoff, wastewater and local industries runoff, as well as runoff from urban domestic usage. Only a few quantitative data on commercial ship-bottom paints used in the Seto Inland Sea are currently available in the open literature. Further studies are required to clarify the sources of Diuron and Irgarol in the coastal area of Japan.

CONCLUSIONS

Diuron and Irgarol were detected in environmental samples collected from the Seto Inland Sea in Japan. During October 2008 and 2009, the average concentrations of Diuron and Irgarol were 0.034 $\mu\text{g/L}$ and 0.031 $\mu\text{g/L}$ in the seawater, 0.036 $\mu\text{g/g dw}$ and 0.033 $\mu\text{g/g dw}$ in the sediment, 0.228 $\mu\text{g/g dw}$ and 0.134 $\mu\text{g/g dw}$ in the planktons, respectively. In addition, the Diuron and Irgarol concentrations were highest near the vicinity of estuary and harbor in all the coastal sea areas. The sources of these pesticides were likely agricultural, urban runoff and antifouling paints. Since, a fraction would be transported offshore and eventually into the open ocean. Although our results are preliminary, they represent an important first approximation of the extent of offshore transport of pesticides in the Seto Inland Sea. Generating more refined estimations would require sampling several times during the year to account more accurately for temporal variations.

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