Diuron concentrations along shorelines of Ishigaki and Iriomote islands, Japan

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Abstract　Diuron (DCMU; 3-(3,4-dichlorophenyl)-1,1-dimethylurea) concentrations were analyzed at 24 sites along shorelines of Ishigaki and Iriomote Islands in September 2019. The diuron concentrations ranged from ＜0.6 to 32 ng l^{-1}. Slightly high concentrations of diuron as 32 and 19 ng l^{-1} were observed at a fishing port in Iriomote and a mooring point for boats in Ishigaki, respectively, implying contamination likely from antifouling paints of boats. A slightly high concentration (14 ng l^{-1}) of diuron was also found in the estuary of Arakawa River in Ishigaki Island, which implies land sources. In Iriomote Island, diuron concentrations were low (≤1 ng l^{-1}) at all sites except for the port site. These results indicate generally low levels (below toxic levels for organisms) of diuron contamination at least at the timing of the present study.

Keywords　Herbicide, Antifouling paints, Booster biocides, Yaeyama

Introduction

　Diuron (DCMU; 3-(3,4-dichlorophenyl)-1,1-dimethylurea) is widely used as a herbicide in farming and booster biocide of antifouling paint for boats. Diuron inhibits photosystem II of plants (Allen et al. 1983; Pfiste and Schreiber 1984), and also shows toxicity to a wide range of organisms (Nebeker and Schuytema 1998; Haynes et al. 2000; Jones 2005; Negri et al. 2005; Magnusson et al. 2008; Gallucci et al. 2015) and endocrine disruption in fish (Pereira et al. 2015). There has been already evidence showing disturbances to natural ecosystems caused by diuron pollution (Jones et al. 2003; Bengtson Nash et al. 2005; Duke et al. 2005; McMahon et al. 2005; Yamamuro 2012). Along with the development of analytical techniques to detect low concentrations of diuron in seawater after the 2000s (Martínez et al. 2000; Lamoree et al. 2002; Gatidou et al. 2005; Saleh et al. 2014), marine pollution by diuron has been reported

throughout the world (McMahon et al. 2005; Ali et al. 2014; Batista-Andrade et al. 2016; Lam et al. 2017) including Japan (Okamura et al. 2003; Balakrishnan et al. 2012; Sheikh et al. 2012; Yamamuro 2012; Kaonga et al. 2015).

　In Japan, Okinawa prefecture most abundantly discharged diuron among all prefectures during 2001−2018, estimated as 13.8 ± 4.3 ton $year^{-1}$ (PRTR 2021). Yaeyama Islands is in Okinawa prefecture, and consists of two major islands (Ishigaki and Iriomote islands) and multiple small islands, and its diverse biome in coral reefs, seagrass meadows and mangrove forests are conserved as the Iriomote-Ishigaki National Park. For conservation of these ecosystems, assessment of environmental disturbance factors is important. Previously, distribution of diuron concentrations was reported in the Todoroki River estuary in Ishigaki Island (Sheikh et al. 2012). However, there have been no reports about the broad distribution of

diuron covering the whole Ishigaki and Iriomote islands. In this paper, we present diuron concentrations along shorelines of Ishigaki and Iriomote islands.

Materials and methods

Sampling was conducted from 13th to 14th, and on 29th September 2019 in Ishigaki and Iriomote islands, respectively. On and before the sampling days, there was light rainfall, as 0–8 mm day^{-1} from 10th to 14th at Ishigaki and 0–31.5 mm day^{-1} from 25th to 29th September at Iriomote (https://www.data.jma.go.jp/obd/stats/etrn/). Seawater samples were collected from quays in fishing ports at Sts. 2, 16, and 24, while at other stations we accessed the water's edge by walking on intertidal sand flats or beaches. The water depths at the sampling locations were ~20–60 cm. Glass bottles were directly put into the water to collect seawater, then capped with PTFE sealing for determinations of diuron. Salinity was measured using an AAQ-RINKO (AAQ-175, JFE-Advantec Co. Ltd.). The samples were cooled on ice and transported to the laboratory of Yaeyama Field Station (Japan Fisheries Research and Education Agency, FRA), into which a surrogate standard (deuterium diuron at 10 μg l^{-1}) was added. Then, the samples were sent by refrigerated transport to the laboratory of Hatsukaichi Field Station (FRA) for analysis. Analysis of diuron concentrations in the environmental water samples was performed according to the method of Harino et al. (2005) with modification for using a tandem mass spectrometry. The seawater samples were filtered using glassfiber filters (GF/C, Whatman, diameter: 45 mm, pore size: 1.2 μm) to remove particles. Then, diuron in the filtrate of 580–590 ml volume was concentrated using columns (Oasis HLB Plus Short Cartridge, 225 mg, Waters), followed by elution using 10 ml methanol and evaporated to a final volume of 1 ml. After addition of an internal standard (atrazine $^{13}C_3$ at 10 μg l^{-1}), the concentrations were analyzed by liquid chromatography (LC) (LC-30AD Nexera X2 system, Shimadzu Corp.). Separation was carried out on an Inertsil ODS-4 column (2.1 mm i.d. × 150 mm, 5 μm, GL Science Inc.). The composition of the mobile phase was a gradient from 5 mmol l^{-1} ammonium acetate solution (solution A) to 5 mmol l^{-1} ammonium acetate in methanol (solution B) (50％ solution B linear to 95％ solution B for 10 min and held for 5

min) with flow rate of 0.2 ml min^{-1}. The injection volume was 10 μl. Electrospray mass spectrometry (MS) analysis was carried out (LCMS-8030; Shimadzu Corp.). The analytes were ionized by electrospray ionization in the positive-ion mode. LC-MS/MS was performed in the multiple reaction-monitoring mode. We monitored the ion of m/z 233.05 as the precursor ion and the ion of m/z 72.00 as the product ion. The recovery rate in seawater analysis of diuron were determined as follows; seawater for the recovery test was spiked with a specified amount of the diuron (1 ng l^{-1}) and pretreated as for the seawater analysis using 500 ml sample. The recovery test was performed six times, and the standard deviation of the diuron concentration (SD: 0.06 ng l^{-1}), coefficient of variation (CV: 4.5％) and average recovery rate (123％) were determined. Using this value of standard deviation, the method detection limit (MDL) and the method quantification limit (MQL) were calculated as SD×t-value (degree of freedom: n－1, p: 0.05) × 2 and SD×10, respectively, which were 0.2 and 0.6 ng l^{-1}, respectively. Recovery of the surrogate standard was 88％–118％ in the diuron analysis.

Results and discussion

Salinity was 24.5–32.9 (Fig. 1), indicating influence of freshwater inflows at all sampling sites, such as from small streams, rivers, or groundwater. Diuron concentrations were above MQL (＞0.6 ng l^{-1}) at 11 of 24 sites (Fig. 1), which ranged from 1 to 32 ng l^{-1}. Because toxic levels of diuron are ＞100 ng l^{-1} for most organisms (Devilla et al. 2005; Negri et al. 2005; DeLorenzo and Fulton 2012), diuron concentrations in this study were more than three times lower than the toxic levels.

The highest concentration was 32 ng l^{-1} at Shirahama fishing port (St. 16), followed by 19 ng l^{-1} at Fumida in Nagura Bay (St. 8) and 14 ng l^{-1} at the mouth of the Arakawa River (St. 10). There were fishing boats and moored diving boats at St. 16 and St. 8, respectively, so that these high concentrations were probably affected by contamination from the boats. Contamination of diuron from antifouling paints of boats has been often reported elsewhere (Okamura et al. 2003; Kaonga et al. 2015), and our results also indicate that these sources were one of important sources of diuron in this area.
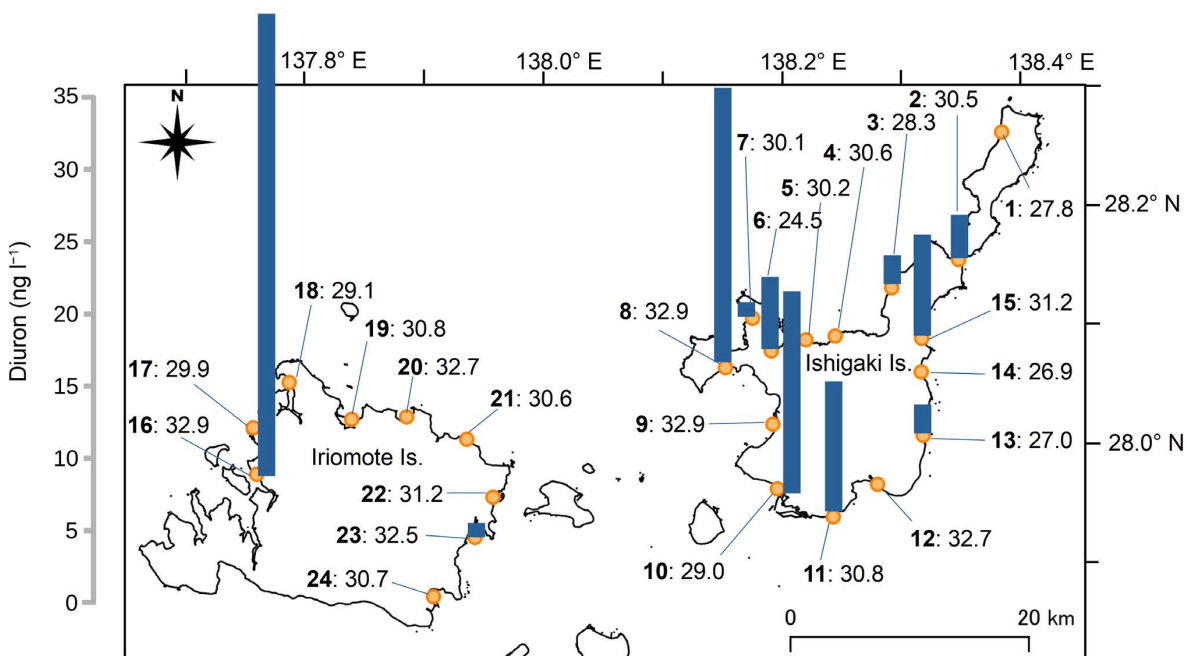
Fig. 1 Concentrations of diuron (bars) at each sampling site (points). Points without bars indicate that the concentration was below the method quantification limit (<0.6 ng l^{-1}). Salinity is shown after station numbers.

Most of the sites in Iriomote Island except St. 16 contained low levels of diuron (≤ 1 ng l^{-1}). This may have reflected the low levels of human activity in Iriomote Island. While, slightly higher concentrations were observed in Ishigaki Island, mainly in the southern city areas (14 and 9 ng l^{-1} at St. 10 and 11, respectively) in addition to St. 8. Particularly, St. 10 is located at the Arakawa River mouth and implies the origin from the herbicide use on land.

These results suggest that diuron contamination along shorelines of Ishigaki and Iriomote islands were generally at low levels and were comparable to those reported previously in Shiraho (close to St. 13 in this study), Ishigaki Island (Sheikh et al. 2012). The concentration of diuron was lower than the reported ecotoxicity threshold values (0.08−1.2 μg l^{-1}, Warne et al. 2018). However, diuron concentrations in coastal waters can show large temporal rises (Sheikh et al. 2012), particularly after heavy rainfall, which could bring land-derived diuron (e.g., herbicides used in sugarcane fields) to the sea (Camenzuli et al. 2012; Ali et al. 2014). Because our survey was only one-time under relatively limited rainfall and did not evaluate these temporal variations, potential pollution from land mass under heavy rains or throughout seasons should be further investigated in the future. From our results, ports and river estuaries were implied as relatively susceptible to diuron contamination and important sites for monitoring in this region. In addition, it is also important to evaluate potential risks of contamination by other herbicides (e.g., metribuzin) and pesticides (e.g., fipronil) which are used in the agriculture in this area.

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Compliance

There were no special matters to be declared about compliance.

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