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Highlighted Article

The bioconcentration factor of perfluorooctane sulfonate is significantly larger than that of perfluorooctanoate in wild turtles (*Trachemys scripta elegans* and *Chinemys reevesii*): An Ai river ecological study in Japan

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Abstract

Turtles rank high in the river food chain, and are suitable for predicting the bioconcentrations of chemicals through the food chain. *Trachemys scripta elegans* ($N = 46$) and *Chinemys reevesii* ($N = 51$) were captured in a river in Japan, from September to October 2003 and April to June 2004. Surface water samples were collected simultaneously from the same sites at which the turtles were caught. Serum perfluorooctane sulfonate (PFOS) ranged from 2.4 to 486 μg/L, while water PFOS levels ranged from 2.9 to 37 ng/L. The geometric mean (GM) (geometric standard deviation, GSD) of the bioconcentration factor (BCF) of PFOS was 10,964 (2.5). In contrast, the perfluorooctanoate (PFOA) level in water ranged from 16.7–87,100 ng/L, and serum PFOA ranged from <0.2 to 870 μg/L. The GM (GSD) of the BCF of PFOA was 3.2 (7.9). Furthermore, the BCF of PFOA decreased as the PFOA level in the surface water increased. PFOS could be preferentially bioconcentrated in biota, and PFOA, slightly bioconcentrated.

Keywords: Perfluorooctane sulfonate; Perfluorooctanoate; *Trachemys scripta elegans*; *Chinemys reevesii*; Bioconcentration factor; River; Serum

1. Introduction

Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) are ubiquitous environmental contaminants found in water, air borne dust, wildlife, and humans (Hansen et al., 2002; Saito et al., 2004; So et al., 2004; Sasaki et al., 2003; Martin et al., 2002, 2004; Giesy and Kannan, 2001; Olsen et al., 2003, 2004; Harada et al., 2004, 2005). They are synthetic surfactants used in a variety of industrial applications (Kissa, 2001), and are also formed through the degradation or metabolism of certain other synthetic perfluorochemical products (Dinglasan et al., 2004; Ellis et al., 2004). PFOA and PFOS seem to be terminal products because they are reported to be resistant to photolysis and biodegradation by activated sludge (Organisation for Economic Cooperation and Development (OECD), 2002; USEPA, 2003). PFOA has been reported to cause diverse toxic effects in zooplankton and laboratory animals, including primates (Butenhoff et al., 2002; Kudo and Kawashima, 2003; Sanderson et al., 2003, 2004; Lau et al., 2004).

Recent environmental surveys have shown that PFOA is rarely found in wildlife, whereas PFOS is ubiquitously present (Kannan et al., 2002; Martin et al., 2004). One possible reason for such a discrepancy is that PFOA has a lower bioconcentration factor (BCF) than PFOS.

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A large difference in the BCFs of these two compounds has been reported in laboratory fishes. A laboratory assessment reported that the BCF of PFOA was 27 ± 9.7 in the blood of rainbow trout, while that of PFOS was 4300 ± 570 (Martin et al., 2003a). Boulanger et al. estimated that the field-based BCF of PFOA was 150–2300 using concentration data from Etobicoke Creek fish liver samples and water from the Great Lakes, which have limitations due to geographical discordance and an accidental aqueous film forming a foam spill in Etobicoke Creek (Boulanger et al., 2004; Moody et al., 2002). It remains unknown whether these differences in the BCFs in limited species are applicable to other species and can explain the rare occurrence of PFOA compared with PFOS in wild animals.

We recently reported that surface waters in the Kinki District of Japan are more contaminated with PFOA than those in other districts (Saito et al., 2004). In particular, the Ai River (located in Settsu city, Kinki District) was found to be the most heavily PFOA-contaminated river in the world, by comparison with other values reported to date (Boulanger et al., 2004). In the Ai River, there is an upstream-to-downstream gradient of PFOA concentrations along the river, and we can therefore assess the BCFs at various concentrations of PFOA.

In this study, we investigated the BCFs of PFOS and PFOA in turtles in the Ai River system. Turtles are located in the highest rank of the food chain in the river ecological system and have small territories. Thus, the BCFs of the turtles covered a wide range of PFOA concentrations. The present study provides insight into the bioconcentration of PFOA in comparison with that of PFOS.

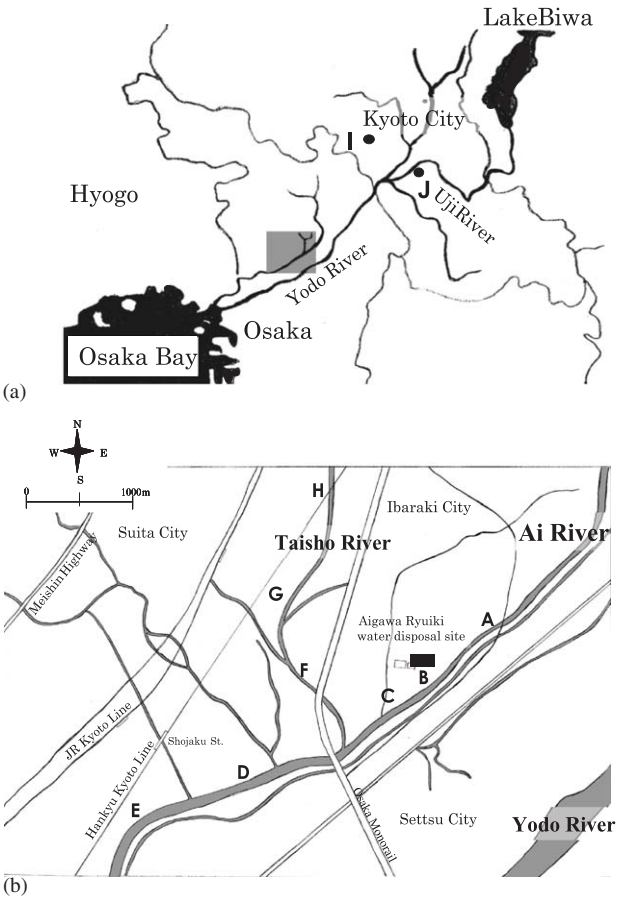

Fig. 1. Study area and sampling sites. The individual letters indicate the sampling sites, and correspond to those in Tables 1 and 2: (a) Broad illustration of the study area in the Kinki district in Japan. The area in the gray square is magnified in (b). (b) Magnified illustration of the Ai River system. The black square indicates the Aigawa Ryuiki water disposal site.

2. Materials and methods

2.1. Reagents

Heptadecafluorooctane sulfonic acid potassium salt (FW.538.22), used as a standard for PFOS, and pentadecafluorooctanoic acid ammonium salt (FW.431.10), used as a standard for PFOA, were purchased from Fluka (Milwaukee, WI, USA). The purities of these standards were greater than 98%. We did not correct the reported concentrations according to the purity. 1H,1H,2H,2H-Tetrahydroperfluorooctane sulfonate was synthesized as an internal standard (Wako Pure Chemicals, Osaka Japan), and its purity was greater than 99%. Rat sera were purchased for matrix blanks (Sigma Aldrich Japan).

2.2. Turtle capture and blood sampling

Trachemys scripta elegans ($N = 46$) and *Chinemys reevesii* ($N = 51$) were captured with baited traps in the Ai River (located in Settsu city, Japan, Fig. 1), one of its branches, and other uncontaminated sites from September to October 2003 and April to June 2004. After capture, we recorded the body weight, sex, age, and carapace length of each turtle. Their ages were determined using the rings (annuli) on their scales based on the assumption that only one ring or annulus is formed annually (Germano and Bury, 1998). Blood samples were collected by heart puncture through the plastron (Stephens and Creekmore, 1983). Serum was separated from the red blood cells and other cellular components by centrifugation at 3000 rpm for 5 min. All serum samples were stored at $-20\,^{\circ}C$ until use.

2.3. Water sampling

Water samples were collected simultaneously from each location when turtles were captured. At each site, two 2-L samples were collected in disposable polyethylene terephthalate containers with a narrow-mouth bottle top and a screw cap as previously reported