Bull Environ Contam Toxicol (2011) 87:307–311
DOI 10.1007/s00128-011-0335-7

Changes of Concentrations, Shipment Amounts and Ecological Risk of Pesticides in River Water Flowing into Lake Biwa

T. Tsuda · T. Igawa · K. Tanaka · D. Hirota

Received: 28 January 2011 / Accepted: 2 June 2011 / Published online: 15 June 2011

Abstract A survey of various pesticide contaminations was performed for water in Yanamune River flowing into Lake Biwa from 1988 to 2009. Ten pesticides (diazinon and fenitrothion as insecticides, iprobenfos and isoprothiolane as fungicides and chlornitrofen, thiobencarb, molinate, bromobutide, simetryne and pretilachlor as herbicides) were selected and concentration changes of the pesticides were evaluated based on their shipment amounts. Yearly maximum concentrations of eight of the pesticides in Yanamune River water were compared with their no observed effect concentration and their predicted no effect concentration values and initial ecological risk assessment was conducted for five pesticides (diazinon, fenitrothion, iprobenfos, isoprothiolane and thiobencarb) by their predicted no effect concentration values. All of the diazinon (0.01–0.28 μg/L) and fenitrothion (0.005–0.31 μg/L) concentrations from 1988 to 2007, the iprobenfos (2.7 and 2.4 μg/L) concentrations in 1988 and 1990 and the thiobencarb (0.24–2.7 μg/L) concentrations in 1988, 1992, 1993 and 1995 exceeded their predicted no effect concentration (PNEC) (0.00026, 0.00021, 1.0 and 0.17 μg/L) values.

Keywords Pesticide · River water · Concentration · Shipment amount · Ecological risk

We have already reported various pesticide contamination of water from seven rivers flowing into Lake Biwa (Tsuda et al. 1991, 1992, 1994, 1996, 1997, 1998; Takino et al. 1998). Recently, we again performed the same survey in water from Yanamune River once or twice from April to August in 2007 (Tsuda et al. 2009) and in water from 21 rivers around Lake Biwa from May to June in 2009. Many survey data of various pesticide contaminations could be collected in Yanamune River and 10 pesticides (diazinon and fenitrothion as insecticides, iprobenfos and isoprothiolane as fungicides and chlornitrofen (CNP), thiobencarb, molinate, bromobutide, simetryne and pretilachlor as herbicides) were detected at high frequency and concentrations. The 10 pesticides were selected and concentration changes of the pesticides were evaluated based on their shipment amounts (National Institute for Environmental Studies, Japan 2010). Further, yearly maximum concentrations of eight pesticides (diazinon, fenitrothion, iprobenfos, isoprothiolane, thiobencarb, molinate, simetryne and pretilachlor) in Yanamune River water were compared with their no observed effect concentration (NOEC) values in algae, water flea and fish (Ministry of the Environment, Japan 2010a; US Environmental Protection Agency 2010) as reference data for initial ecological risk assessment and the risk assessment (Ministry of the Environment, Japan 2010b) was conducted for five pesticides (diazinon, fenitrothion, probenfos, isoprothiolane and thiobencarb) using their predicted no effect concentration (PNEC) values (Ministry of the Environment, Japan 2010c).

Materials and Methods

Water samples were collected from Yanamune River flowing into Lake Biwa (Fig. 1) once or twice every month in 1988–1997 (Tsuda et al. 1991, 1992, 1994, 1996, 1997, 1998; Takino et al. 1998), once or twice from April to August in 2007 (Tsuda et al. 2009) and on May 29 in 2009.

T. Tsuda (✉) · T. Igawa · K. Tanaka · D. Hirota
Lake Biwa Environmental Research Institute,
5-34 Yanagasaki, Ohtsu, Shiga 520-0022, Japan
e-mail: tsuda-taizo@pref.shiga.lg.jp

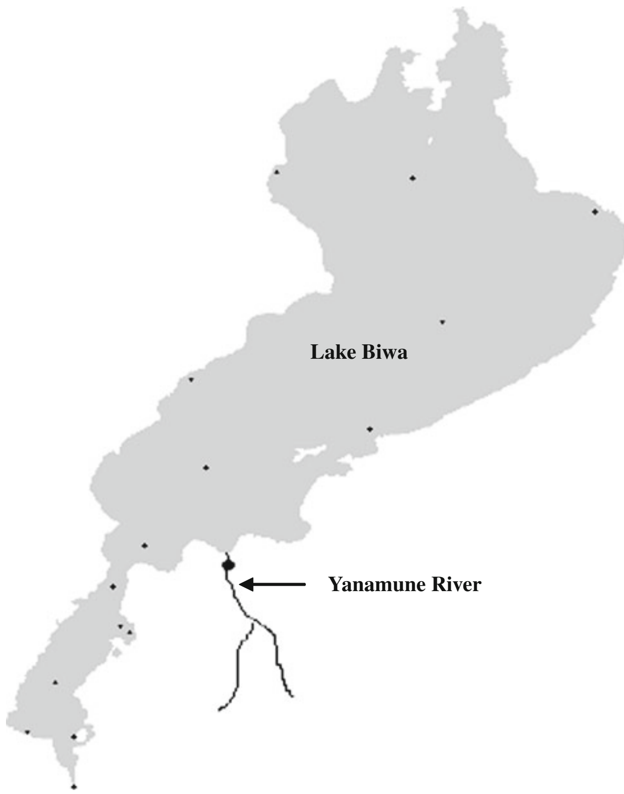

Fig. 1 Map of a sampling location

Water samples were analyzed immediately after sample collection.

In 1988–1997, analyses of the pesticides in the water samples were performed by the following procedure. A measured volume (1,000 mL) of the water was shaken with 100 mL of dichloromethane after addition of 50 g of NaCl. The organic layer was again shaken and filtered through anhydrous Na_2SO_4 and the aqueous layer was again shaken and filtered in the same manner. The combined filtrate was rotary-vacuum evaporated just to dryness at 40°C and the residue was dissolved in 1 mL of hexane. Detemination of the pesticides in the hexane solution was performed using selected ion monitoring (SIM) by gas chromatograpy-mass spectrometry (GC–MS). In 2007 and 2009, analyses were performed by the following procedure (Nakamura et al. 2008). A measured volume (500 mL) of water sample was passed through a Aqusis PLS-3 column and eluted with 4 mL of dichloromethane after drying with air stream at room temperature for 40 min. Detemination of the pesticides in the eluate was performed using SIM by GC/MS after evaporation to 0.5 mL. Average recoveries (n = 3) were 88%–108% for the 10 pesticides at a spiked level of 0.1 μg/L and quantification limits were 0.01 μg/L for all of the 10 pesticides.

Ecological risk assessment was conducted for yearly maximum concentrations of the five pesticides (diazinon,

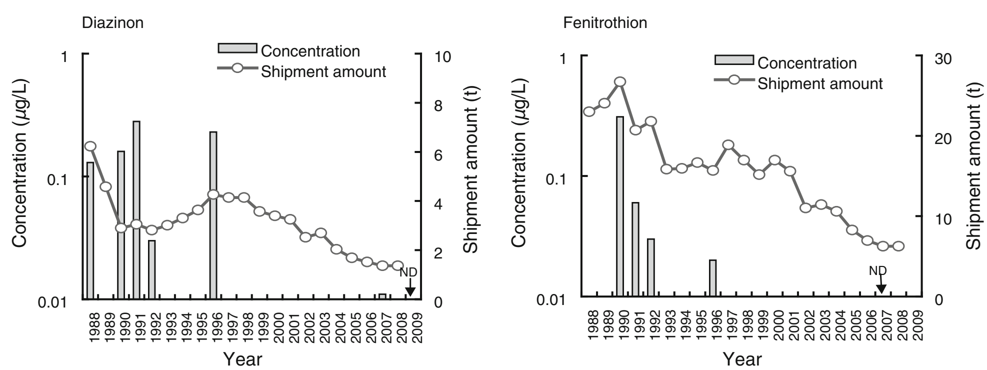

Fig. 2 Variations in shipment amounts of two insecticides in Shiga Prefecture and their yearly maximum concentrations in Yanamune River water

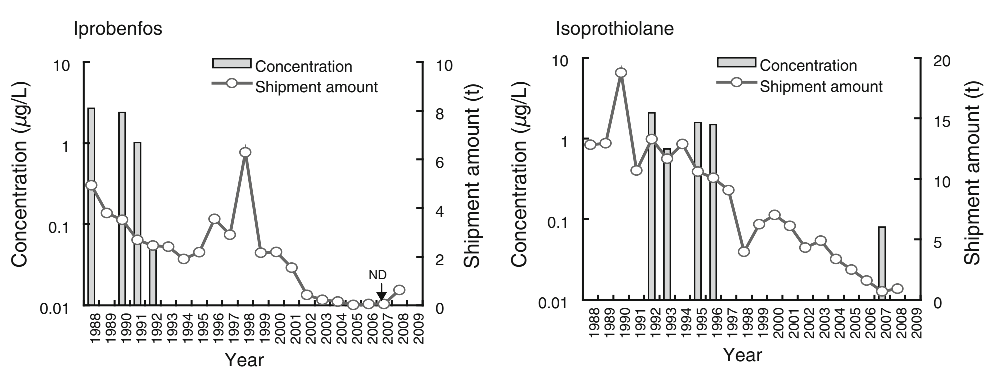

Fig. 3 Variations in shipment amounts of two fungicides in Shiga Prefecture and their yearly maximum concentrations in Yanamune River water

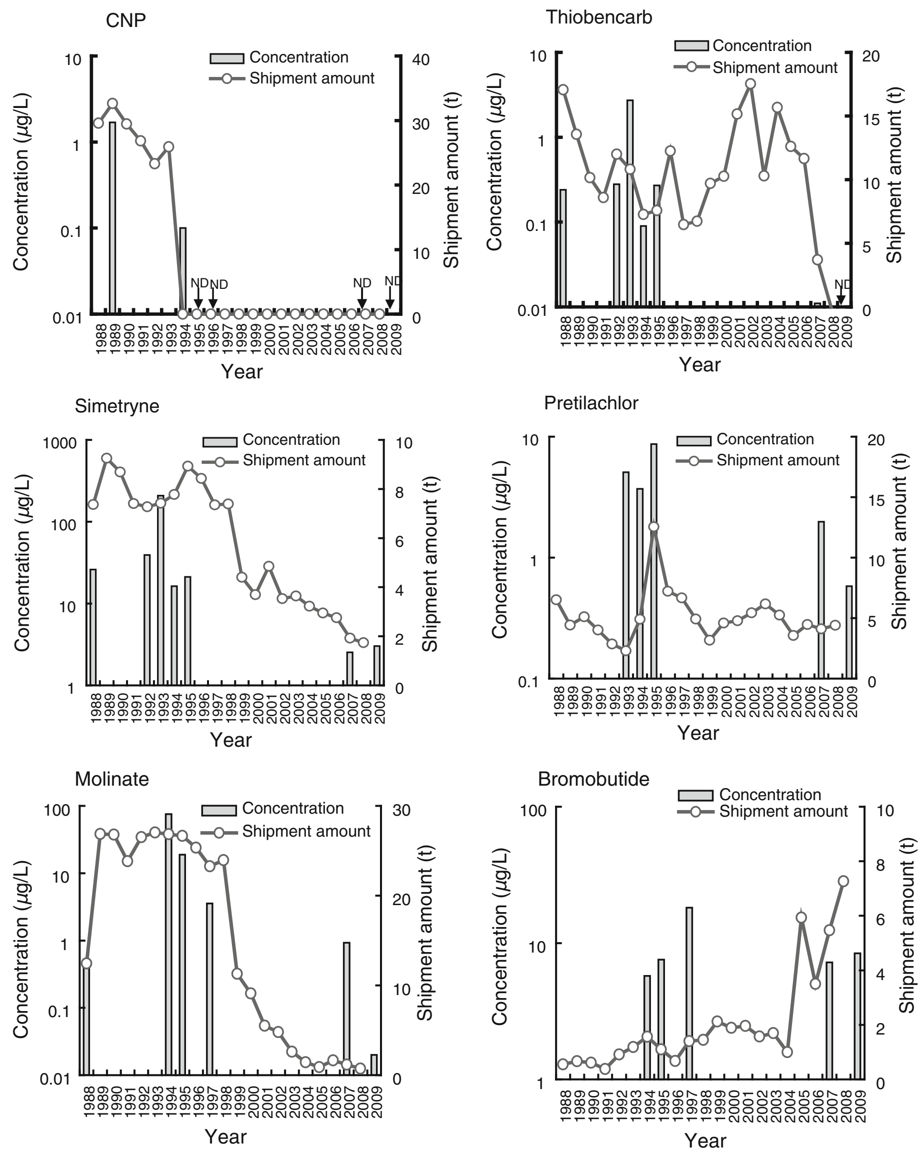

Fig. 4 Variations in shipment amounts of six herbicides in Shiga Prefecture and their yearly maximum concentrations in Yanamune River water

fenitrothion, iprobenfos, isoprothiolane and thiobencarb) detected in Yanamune River water by Guideline for Initial Environmental Risk Assessment of Chemicals (Ministry of the Environment, Japan 2010b). The pesticide concentrations in the river water were evaluated using their PNEC in this risk assessment method.

Results and Discussion

Variatons in yearly maximum concentrations of the two insecticides (diazinon and fenitrothion) in Yanamune River were compared with those in their shipment amounts (Fig. 2). Diazinon concentrations showed no tendency to increase or decrease from 1988 to 1996 but showed low values (0.01 μg/L and ND) in 2007 and 2009, respectively. The variations in shipment amounts of diazinon showed decreasing tendency after 1996 and this tendency was equal to those in the concentrations after 1996. On the other hand, fenitrothion showed decreasing tendency in both of the concentrations and the shipment amounts from 1990 to 2007.

Similarly, variations in the concentrations of the two fungicides (iprobenfos and isoprothiolane) in Yanamune River were compared with those in their shipment amounts (Fig. 3). Iprobenfos and isoprothiolane showed decreasing tendency in both of the concentrations and the shipment amounts from 1988 to 2007 for iprobenfos and from 1992 to 2007 for isoprothiolane, respectively.

Variations in shipment amounts of six herbicides in Shiga Prefecture and their yearly maximum concentrations in Yanamune River water are shown in Fig. 4. For CNP, the use in Japan was inhibited in 1994 and the shipment amount has been reported to be 0 t since 1994. The CNP

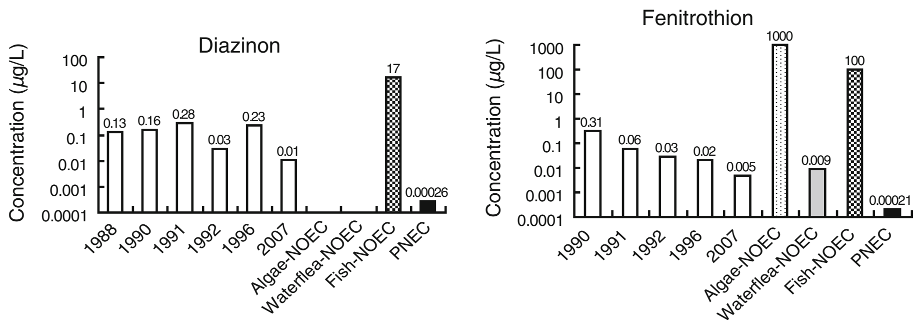

Fig. 5 Yearly maximum concentrations of two insecticides in Yanamune River water and their NOEC and PNEC values

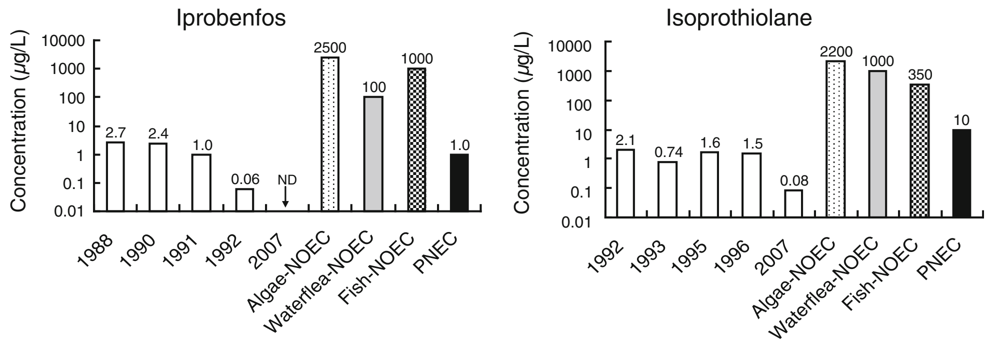

Fig. 6 Yearly maximum concentrations of two fungicides in Yanamune River water and their NOEC and PNEC values

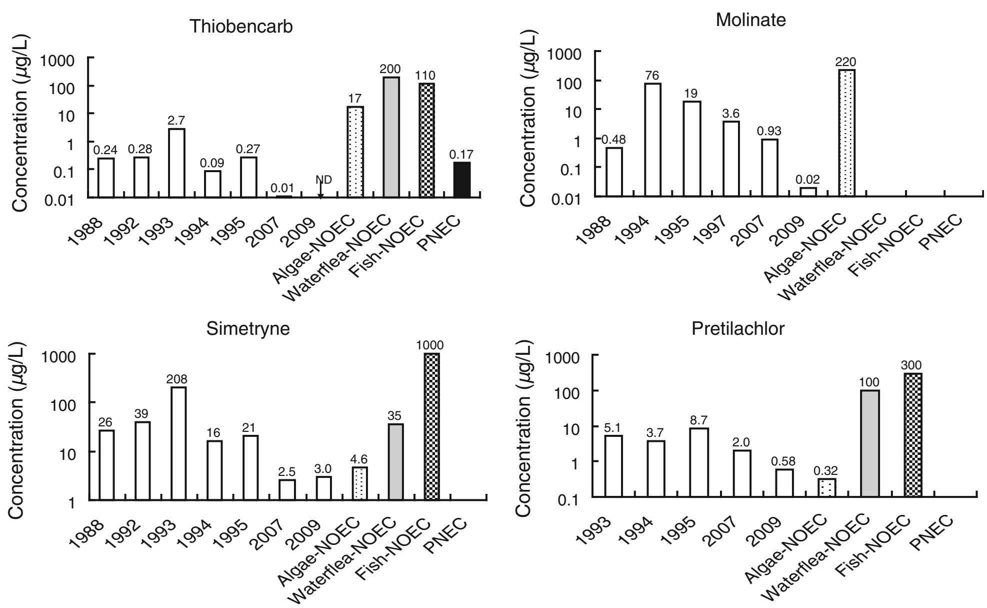

Fig. 7 Yearly maximum concentrations of four herbicides in Yanamune River water and their NOEC and PNEC values

concentrations were 1.7 μg/L in 1989, 0.1 μg/L in 1994, ND in 1995, 1996, 2007 and 2009. The decreasing tendency in the CNP concentrations was equal to that in the shipment amount. For thiobencarb, the shipment amount in Shiga Prefecture was 11.7 t in 2006 but decreased to 3.7 t in 2007 and 0 t in 2008 owing to self-control of the use in Shiga Prefecture. The thiobencarb concentrations were 0.09–2.7 μg/L from 1988 to 1995 and ND in 2009 in agreement with the shipment tendency. The shipment amounts of simetryne and molinate have been decreased since 1995 and the decreasing tendencies in their concentrations have been equal for simetryne but were considerably deviated in 2007 for molinate. The shipment amount of pretilachlor was nearly constant except in 1995 and the pretilachlor concentrations were almost constant. For bromobutide, the shipment amount has been increased since 2004 but the concentrations have been nearly constant.

Yearly maximum concentrations of eight pesticides (two insecticides, two fungicides and four herbicides) in Yanamune River from 1988 to 2009 were compared with their

NOEC and PNEC values in Figs. 5, 6, 7. All of the diazinon concentrations in the river water were less than the NOEC value of fish and all of the fenitrothion concentrations were less than the NOEC values of algae and fish. However, the fenitrothion concentrations from 1990 to 1996 exceeded the NOEC value of waterflea. For initial ecological risk assessment by PNEC, all of the diazinon and fenitrothion concentrations from 1988 to 2007 exceeded the PNEC values (0.00026 and 0.00021 μg/L). Many survey data of diazinon in river water have been reported in the world. For example, the diazinon concentrations were <0.005–0.51 μg/L in Selangor River, Malaysia (Leong et al. 2007), <0.002–0.01 μg/L in Po River, Italy (Agradi et al. 2000) and ND ~ 0.08 μg/L in Sacramento River, USA (Hall 2003). Many data of the diazinon concentrations exceeded the PNEC value (0.00026 μg/L) not only in Japan but also in the other countries.

All of the iprobenfos and isoprothiolane concentrations in the river water from 1988 to 2007 were less than the NOEC values of algae, waterflea and fish. For the initial risk assessment, all of the isoprothiolane concentrations were less than the PNEC value (10 μg/L). However, the iprobenfos concentrations in 1988 and 1990 exceeded the PNEC value (1 μg/L) and those in 1992 and 2007 were less than the PNEC value (1 μg/L).

All of the thiobencarb concentrations in the river water were less than the NOEC values of algae, waterflea and fish and all of the molinate concentrations were less than the NOEC values of algae. In the other countries, the molinate concentrations were <1–3.2 μg/L in Sacramento River, USA (Environmental Protection Agency 2002) and 0.004–0.36 μg/L in Po River, Italy (Agradi et al. 2000). Both of the data were similarly less than the NOEC values of algae. All of the simetryn concentrations were less than the NOEC value of fish. However, those from 1988 to 1995 exceeded the NOEC value of algae and those in 1992 and 1993 exceeded the NOEC value of the waterflea. All of the pretilachlor concentrations were less than the NOEC values of waterflea and fish but exceeded the NOEC value of algae. For the initial risk assessment, the thiobencarb concentrations in 1988, 1992, 1993 and 1995 exceeded the PNEC value (0.17 μg/L).

References

Agradi E, Baga R, Cillo F, Ceradini S, Heltai D (2000) Environmental contaminants and biochemical response in eel exposed to Po river water. Chemosphere 41:1555–1562

Environmental Protection Agency (2002) Rice pesticide use and surface water monitoring 2002. Environmental Hazards Assessment Program, EH02-09

Hall LW Jr (2003) Analysis of diazinon monitoring data from the Sacramento and Feather River watersheds: 1991–2001. Environ Monit Assess 86:233–253

Leong KH, Tan LLB, Mustafa AM (2007) Contamination levels of selected organochlorine and organophosphate pesticides in the Selangor River, Malaysia between 2002 and 2003. Chemosphere 66:1153–1159

Ministry of the Environment, Japan (2010a) Ecological interference examination of chemicals. http://www.env.go.jp/chemi/sesaku/01.html

Ministry of the Environment, Japan (2010b) Guideline for initial environmental risk assessment of chemicals. http://www.env.go.jp/chemi/risk/guideline_ia.pdf

Ministry of the Environment, Japan (2010c) Environmental risk assessment of chemicals Vol. 2. http://www.env.go.jp/chemi/report/h15-01/index.html

Nakamura T, Inoue A, Tanaka K, Tsuda T (2008) Results of pesticide surveys in water from Lake Biwa in 2006. Rep Lake Biwa Environ Res Inst 3:205–212 (in Japanese)

National Institute for Environmental Studies, Japan (2010) Web Kis-Plus Information on exposure to chemicals. http://db-out.nies.go.jp/kis-plus/index_1.php? Category d = 03000000&

Takino A, Tsuda T, Kojima M, Harada H, Nakajima A (1998) Survey on herbicides in water and fish from rivers in Shiga Prefecture. Rep Shiga Pref Inst Pub Health Environ Sci 33:96–98

Tsuda T, Aoki S, Kojima M, Harada H (1991) Pesticides in water and fish from rivers flowing into Lake Biwa. Toxicol Environ Chem 34:39–55

Tsuda T, Aoki S, Kojima M, Fujita T (1992) Pesticides in water and fish from rivers flowing into Lake Biwa (II). Chemosphere 24:1523–1531

Tsuda T, Aoki S, Kojima M, Fujita T (1994) Pesticides in water and fish from rivers flowing into Lake Biwa (III). Toxicol Environ Chem 41:85–90

Tsuda T, Inoue T, Kojima M, Aoki S (1996) Pesticides in water and fish from rivers flowing into Lake Biwa. Bull Environ Contam Toxicol 57:442–449

Tsuda T, Kojima M, Harada H, Nakajima A, Aoki S (1997) Herbicides in water and fish from rivers flowing into Lake Biwa. Toxicol Environ Chem 61:243–249

Tsuda T, Kojima M, Harada H, Nakajima A, Aoki S (1998) Pesticides and their oxidation products in water and fish from rivers flowing into Lake Biwa. Bull Environ Contam Toxicol 60:151–158

Tsuda T, Nakamura T, Inoue A, Tanaka K (2009) Pesticides in water, fish and shellfish from littoral area of Lake Biwa. Bull Environ Contam Toxicol 82:716–721

US Environmental Protection Agency (2010) ECOTOX Database. http://cfpub.epa.gov/ecotox/ecotox_home.cfm