Water Research 113 (2017) 22–31

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Influence of blooms of phytoplankton on concentrations of hydrophobic organic chemicals in sediments and snails in a hyper-eutrophic, freshwater lake

Wei Shi [a], Nanyang Yu [a], Xia Jiang [b], Zhihua Han [a, c], Shuhang Wang [b], Xiaowei Zhang [a, *], Si Wei [a], John P. Giesy [a, d, e, f, g], Hongxia Yu [a, **]

[a] State Key Laboratory of Pollution Control and Resource Reuse, School of Environment, Nanjing University, Nanjing, People's Republic of China
[b] Key Laboratory of Environmental Protection of Lake Pollution Control, Chinese Research Academy of Environmental Science, Beijing, People's Republic of China
[c] Ministry Environment Protection China, Nanjing Institute Environment Science, Nanjing, People's Republic of China
[d] Department of Veterinary Biomedical Sciences, Toxicology Centre, University of Saskatchewan, Saskatoon, Saskatchewan, Canada
[e] Department of Zoology, Center for Integrative Toxicology, Michigan State University, East Lansing, MI, USA
[f] School of Biological Sciences, University of Hong Kong, Hong Kong Special Administrative Region
[g] Department of Biology and Chemistry, State Key Laboratory in Marine Pollution, City University of Hong Kong, Hong Kong Special Administrative Region

ARTICLE INFO

Article history:
Received 19 September 2016
Received in revised form
24 January 2017
Accepted 29 January 2017
Available online 31 January 2017

Keywords:
Eutrophication
Chemodynamics
Sedimentation
Polycyclic aromatic hydrocarbons
Pesticides
Biodegradable contaminants

ABSTRACT

Blooms of phytoplankton, which are common in freshwater ecosystems, might not only affect quality of water but also influence biogeochemical processing of pollutants. Based on three years of field observations in sediments of Tai Lake, China, concentrations of organochlorine (OC) pesticides and polycyclic aromatic hydrocarbons (PAHs) in areas where blooms occurred were 2.4 and 3.4 times greater than concentrations in areas without blooms. Concentrations of octylphenol (OP), nonylphenol (NP) and bisphenol A (BPA) in areas where blooms did not occur were 3.8, 4.4 and 2.6 times greater than concentrations in areas where blooms did occur. To explain the differences, simultaneous, seasonally determinations of the water-sediment-phytoplankton-snails disequilibria were determined empirically. Greater sinking and lesser diffusion were shown to be probable drivers of the burial of δ-HCH, 4-ring and 5-ring PAHs in surface sediments of areas in which blooms occurred, being as much as 0.58, 38 and 45 g month^{-1}. Large biodegradation and low burial was shown to be the probable reason of the inverse proportion of NP, OP and BPA in both water and sediment to biomass which might be due to the enhanced metabolic capacity of bacterial community associated with algae blooms. These phenomena further influence the persistent hydrophobic organic chemicals in the snail species (*Bellamya quadrata*) being greater in winter but lesser in summer, which is probably due to the positive relationship with the concentrations in sediment when snails were dormant and with the concentrations in water after dormancy. Thus, in Tai Lake, the fate and distribution of persistent and biodegradable contaminants in sediments and snails is influenced by blooms of phytoplankton, which should be included in models of environmental fates of contaminants.

1. Introduction

Sources and fates of hydrophobic organic chemicals (HOCs), especially more persistent organic pollutants (POPs) in the environment is deserving increasing attention. Efforts to control sources of predominant organic pollutants and eliminate emissions have been implemented in many countries, including China (Breivik et al., 2004). Due to the reduced production and use of polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT), hexachlorocyclohexane (HCH) and other organochlorine chemicals that has historically been issues, concentrations of these POPs have been decreasing in air, water and biota (Tieyu et al.,

* Corresponding author. School of the Environment, Nanjing University, Nanjing, 210023, People's Republic of China.
** Corresponding author. School of the Environment, Nanjing University, Nanjing, 210023, People's Republic of China.
E-mail addresses: zhangxw@nju.edu.cn (X. Zhang), yuhx@nju.edu.cn (H. Yu).

http://dx.doi.org/10.1016/j.watres.2017.01.059
0043-1354/

2005; Carlson et al., 2010). However, sediments can serve as secondary sources of POPs and are important in the environmental fates of chemicals.

To predict their environmental fate, models of HOCs should include their mobilization to and from sediments (Streets et al., 2006). Understanding of biogeochemical processes is indispensable for migration of HOCs to sediments of aquatic environments. Aquatic macro-organisms such as salmon, and seabirds have been demonstrated to transfer contaminants to sediments and some recent work has highlighted the role of phytoplankton (Krmmel et al., 2003; Blais et al., 2005; Everaert et al., 2015). A theoretical assessment to understand influences of plankton on transformation of organic contaminants, especially POPs, from air to water and sediments has been developed (Dachs et al., 1999). A series of studies, based on concentrations from simultaneously collected environmental compartments, have suggested that uptake of POPs by marine phytoplankton with subsequent transfer of bound POPs to sediment promotes fluxes of POPs from sediment-to-water, water-to-biota and air-to-water (Meijer et al., 2006; Galbn-Malagn et al., 2012; Berrojalbiz et al., 2011a). For example, results of a recent study demonstrated that, in the North Sea, biomass of phytoplankton are positively correlated with the annual maxima of PCB concentrations in sediments and are negatively correlated with concentrations of PCB in blue mussels (*Mytilus edulis*) (Everaert et al., 2015).

In freshwater ecosystems, blooms of phytoplankton, which was characterized by increased biomass of phytoplankton in water, can influence sedimentation of organic pollutants (Krmmel et al., 2003; Carstensen et al., 2007; Janetski et al., 2012). Organic contaminants in bottom sediments can be buried by accumulating sediment, or recycled to the water column, or re-distributed to depositional zones under influence of blooms of phytoplankton (Fernandez et al., 1999). These contaminants sediments are believed to influence contaminants in benthonic organisms (Hughes et al., 1999). Although well-described in theory and a field evidence has also shown the effects of biomass on distributions of PCBs in zooplankton and fish, but influences of increased biomass on accumulation of organic contaminants by freshwater benthonic organisms was still less well understood (Meijer et al., 2006).

Some blooms of phytoplankton in freshwater system are primarily formed by cyanobacteria, which might cause not only sedimentation but also dilution and degradation of organic contaminants (Paerl et al., 2011; Subashchandrabose et al., 2013). Due to dilution as the same mass of pollutants are partitioned into a larger mass of phytoplankton if mass of POPs in the system remaining constant, concentrations of some POPs in phytoplankton were inversely proportional to biomass of phytoplankton due to dilution as the same mass of pollutants are partitioned into a larger mass of phytoplankton if mass of POPs in the system remains constant (Larsson et al., 1990). Although this phenomenon has been well-characterized for POPs such as PCBs and organochlorine (OC) pesticides, field evidence for effects of dynamics of phytoplankton on more degradable compounds was lacking. Previous studies have indicated that bacteria-phytoplankton dynamics in lakes might result in biodegradation of organic contaminants (Stets and Cotner, 2008; Sundh, 1992). However, the empirical evidence of the effectiveness of biological process on biodegradable organic pollutants and their occurrence in sediments are limited.

Tai Lake (Ch: *Taihu*), the third largest freshwater lake in China, is a wide, shallow, hyper-eutrophic lake, that has been affected by expansion of economies, industrialization and urbanization (Paerl et al., 2011; James et al., 2009), and is thus influenced by both eutrophication and organic pollution. Concentrations of POPs have been observed to be greater in sediments of more eutrophic areas in the northern part of the lake (Wang et al., 2003). While inputs from rivers is still the primary source of contaminants, relative proportions of contaminants in sediments and benthic organisms associated with greater biomass of phytoplankton during blooms were lacking.

The objectives of the study, results of which are presented here, were to: 1) examine spatial occurrences and sources of organic residues of varying persistence in sediments of Tai Lake, China. 2) determine temporal and inter-annual variability in distribution, fate and disequilibria of persistent and degradable contaminants in sediment and biota as functions of coupling with primary producer biomass dynamics.

2. Materials and methods

2.1. Chemicals

Eight OC pesticides, sixteen polycyclic aromatic hydrocarbons (PAHs), bisphenol A (BPA), nonylphenol (NP) and octylphenol (OP) were purchased from Sigma Chemical (Co., St. Louis, MO, USA). Internal standards including ^{13}C-PCB 141, acenaphthene-d10, pyrene-d10, bisphenol A-d14 and dibenzo (a,h)anthracene-d14 were purchased from AccuStandard (New Haven, CT, USA). Information of these chemicals is provided in Table S1 in supporting information (SI).

2.2. Study area

The study was conducted in Tai Lake, China (Fig. 1). Locations 1 and 2 were located in the eastern part of the lake where fewer cyanobacteria occur. Locations 4, 5 and 9 were in the vicinity of outlets from northern areas of Tai Lake, which is characterized by accumulation of cyanobacteria. There are few incidental sources of pollution in the northern portion of Tai Lake. Riverine inputs were one of the primary sources of pollution at Locations 6, 7 and 8 (Yang and Liu, 2010). Locations 3, 10 and 11were in the central open water area of Tai Lake, which is remote from sources of pollution and thus the least contaminated part of Tai Lake.

2.3. Sampling and preparation

To describe spatial variations of organic contaminants, surface sediments (0–2 cm, 2000 g wet mass (wm)) were collected in Nov. 2009, 2010 and 2011 at the above mentioned 11 locations. The season during which blooms developed was from April to late October, with greater biomass occurring from early May to late October. To further confirm driving factors and temporal variety of distributions of organic contaminants, surface sediment and water were collected simultaneously from locations 3, 4, 5, 9, 10 and 11, in April, July and October of 2013. Samples of phytoplankton were also collected from areas in which blooms of phytoplankton were occurring, including locations 4, 5 and 9. Snails (*Bellamya quadrata*), one of the most common benthonic organisms in Tai Lake, were collect at the beginning and end of blooms (during April and October, 2013) to describe variability of organic contaminants in benthonic organisms related to blooms. Water, sediments, phytoplankton and *B. quadrata* were given codes that consisted of a letter followed by locations and time (see Supporting Information (SI) Methods for details).

Samples of sediments were collected by use of a gravity corer. Phytoplankton which consisted primarily of cyanobacteria was collected by use of a plankton net (mesh size, 10 μm; diameter of net opening, 20 cm). Five samples were collected from each area and composited into a single sample. Five liters of water, 2000 g (wm) of surface sediment, 2000 g of phytoplankton and 1000 g of *B. quadrata* (wm) were collected at each location and transported

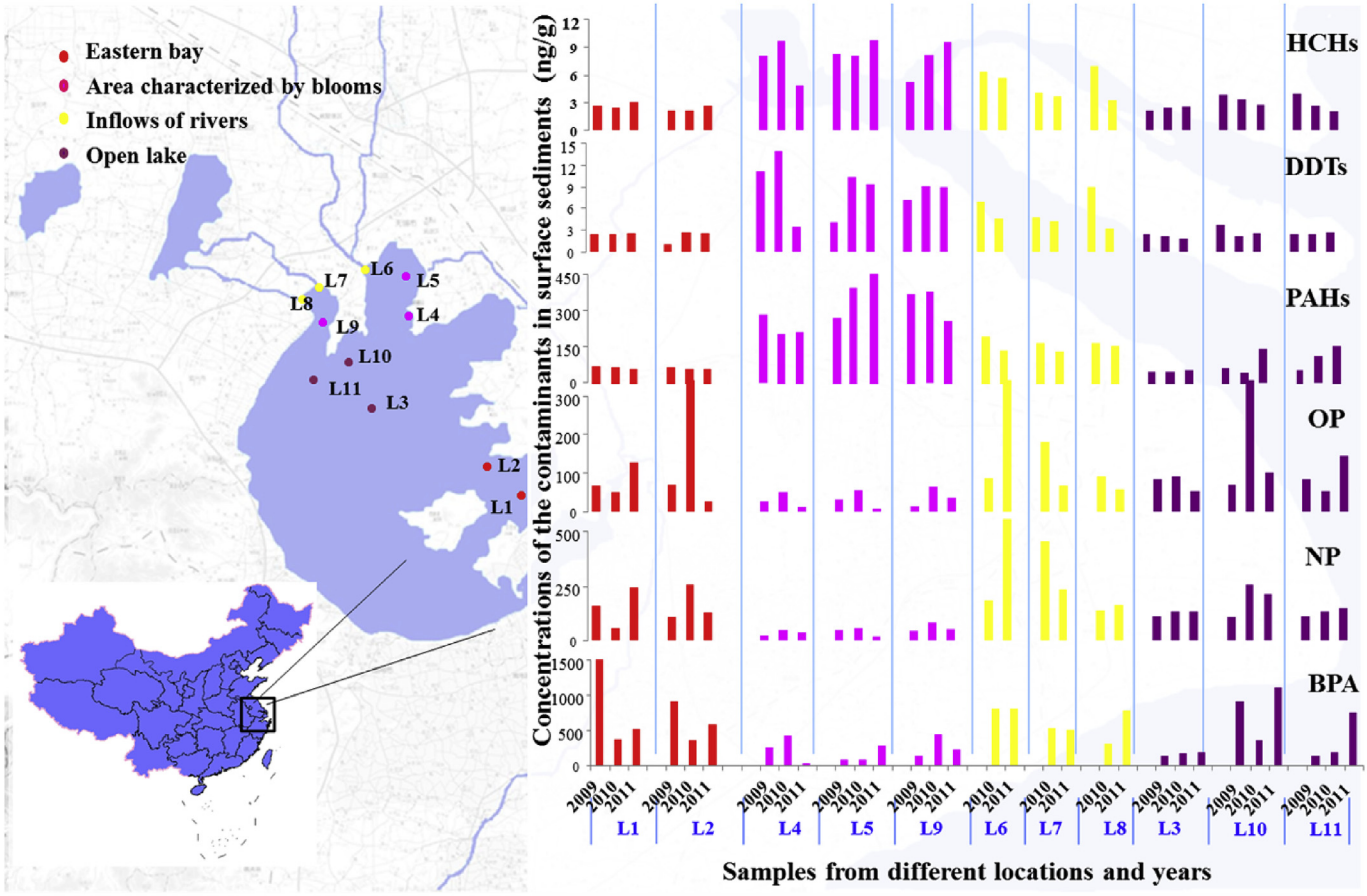


Fig. 1. Distribution of Organochlorine (OCs) pesticides, polycyclic aromatic hydrocarbons (PAHs), nonylphenol (NP), octylphenol (OP) and bisphenol A (BPA) in surface sediments of Tai Lake, China in spatial variations examination. Concentrations were measured during the late cyanophyceae bloom season of 2009, 2010 and 2011. Samples from east bay, area characterized by blooms, inflows of rivers, open lake were colored by red, fuchsia, yellow and purple, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

immediately to the laboratory. Transparency and depth of water were obtained *in situ*. Water temperature, pH, dissolved oxygen (DO), concentrations of chlorophyll *a* (Chla) and transparency were measured *in situ* by use of an YSI Environmental Monitoring System 6600 (YSI Incorporated, Yellow Springs, OH, USA). Concentrations of Chla were used as a proxy for phytoplankton biomass (Everaert et al., 2015).

Sediments, phytoplankton, *B. quadrata* and water were extracted and fractionated by use of previously described methods (Khim et al., 1999; Snyder et al., 1999; Shi et al., 2012). Briefly, 15-g aliquots of sediment, phytoplankton and *B. quadrata* were extracted by use of Accelerated Solvent Extraction (Dionex® ASE 300, Dionex, Idstein, Germany) after frozen dried and extracts were purified with a gel permeation chromatography column (GPC; Bio-Beads® S-X3, J2 Scientific, AccuPrep® MPS, 20 cm length and 3 cm i.d). Solid phase extraction (SPE) was performed for 5 L water samples using 500 mg Oasis HLB cartridges (Waters, USA) after filtration to extract the dissolved organic contaminants. GPC and SPE fractions were concentrated and passed through 10 g of activated Florisil (60–100 mesh size; Sigma Chemical Co., St. Louis, MO, USA) packed in a glass column (10 mm i.d.) for clean-up and fractionation. Detailed information about sampling and preparation of sample is shown in SI.

2.4. Instrumental analyses

Organochlorine pesticides and PAHs were quantified by use of a Thermo series II gas chromatograph equipped with a triple quadrupole mass spectrometer (San Jose, CA, USA) operating in multiple-reaction monitoring (MRM) mode. NP, OP and BPA were quantified using a reverse-phase high-performance liquid chromatography with tandem mass spectrometric (Thermo Electron Corporation, San Jose, CA, USA). Concentrations of all residues are reported on a dry mass basis. More detailed information for instrumental analysis, procedural blank and QA/QC is listed in Table S2.

2.5. Calculation of sinking, diffusion and burial

Vertical settling of HOCs from the water column depletes the photic zone of dissolved concentrations, through flux of HOCs to the surface sediments (Jurado and Dachs, 2008). Vertical flux of HOCs out of the water column (F_{Sink} [mg m^{-2} d^{-1}]) (Bauerfeind et al., 2009; Dachs et al., 2000) was calculated (Equation (1)).

$$F_{sink} = F_{OM} \times C_P \quad (1)$$

Where, C_p is the concentration in phytoplankton [mg kg^{-1}]). F_{OM} is sinking flux of biogenic material [mg m^{-2} d^{-1}]. By assuming that F_{OM} is equal to vertical flux of organic carbon (F_{OC}), F_{OC} [mg m^{-2} d^{-1}]) can be calculated (Equation (2)).

$$\log(F_{OC}) = 1.82 + 0.62\log(Chla) \quad (2)$$

Where, Chla is the concentration of Chla [mg m^{-3}]. It was then possible to estimate rates of removal of HOCs removed by sinking from concentrations of Chla in area where blooms of phytoplankton was occurring from May to October, and the average concentrations of residues measured in plankton. Rates of diffusion and burial were calculated based on the previous study (Meijer et al., 2006; See equations S1 to S3 in SI).

2.6. Estimation of biodegradation

Probabilities of rapid aerobic biodegradation of organic compounds in the presence of mixed populations of microorganisms were estimated by use of the *Estimation Program Interface* (EPI) Suite from US Environmental Protection Agency. Six types of relationships were used, including: Linear, Non-Linear, Ultimate Biodegradation Timeframe, Primary Biodegradation Timeframe, MITI Linear and MITI Non-Linear.

2.7. Data analyses

To detect relative similarities of profiles of pollutants and specific properties in sediments, principal component analysis (PCA) was performed using Simca-P 11.5 software (Umetrics, Sweden). All concentrations of classes of organic contaminants including OC pesticides, 2-, 3-, 4-, 5-, and 6-ring PAHs, NP, OP and BPA were included in the analysis. To give all variables the same importance variables were "auto scaled". This was done by subtracting the mean from each variable then each variable was divided by its standard deviation. Numbers of significant components were given by the eigenvalue limit of 2. The relevant loadings describe how the original variables contribute to each principal component. Correlations of contaminants and Chla were analyzed by use of Origin 8.5 (Origin software Inc., San Clemente, CA, USA). Homogeneity of variances and normality of data were tested by use of Levene's Test and Shapiro-Wilks normality test, respectively. When necessary, data were log-transformed to obtain homogeneity of variances and normality. When these assumptions were met, significant differences between different groups of samples were analyzed by one-way analysis of variance (ANOVA), followed by Duncan's multiple comparisons test (SPSS 11).

3. Results and discussion

3.1. Spatial variations of organic contaminants from whole lake

For samples collected from the three years' field investigation, concentrations of OC pesticides, PAHs, NP, OP and BPA were detectable in surface sediments (Fig. 1). Total concentrations of DDTs and HCHs ranged from 2.0 to 9.7 ng/g, dry mass and 1.0–14 ng/g dry mass (Table S3), which are comparable with results of other studies (Peng et al., 2005). Total concentrations of PAHs were less than 450 ng/g dry mass (Table S4). Mean concentrations of HCHs, DDTs and PAHs in surface sediments from areas where blooms were occurring, including locations 4, 5 and 9, were 2.4-, 2.5- and 3.4-fold greater than concentrations in sediments from areas where blooms were not occurring, including locations 1, 2, 3, 10 and 11. These concentrations were also greater than concentrations in sediments from riverine inputs near locations 6, 7 and 8. Among the chemicals studied, 5-ring PAHs in sediments from areas where blooms were occurring exhibited the greatest differences, which were 7.4 times greater than those from the area where blooms were not occurring. These results are consistent with those of previous studies which indicated that areas where blooms were occurring, in the norther portion of Tai Lake, were more polluted (Wang et al., 2003). Measurable concentrations of NP, OP and BPA were observed in all sediments, with concentrations ranging from 4.8 to 34, 16 to 5.6 $\times$ 10^2 and 29 to 1.5 $\times$ 10^3 ng/g dry mass, respectively (Table S4). Greatest concentrations were found in sediments near riverine inputs. Mean concentrations of BPA were greater than those from sediments of Xiamen Bay and the Pearl River Delta in southeastern China. This is due to production of BPA from dozens of chemical plants in the vicinity of Tai Lake. Mean concentrations of OP, NP and BPA from areas where there were no blooms of phytoplankton were 3.8-, 4.4- and 2.6-fold greater than concentrations in areas where blooms occurred. There is little historical data regarding NP, OP and BPA in surface sediments of freshwater lakes in China, thus the data presented here establish a baseline for future monitoring and management of these compounds in this area (Liu et al., 2011).

Principal component analysis (PCA) used for concentrations of residues in sediments classified three principle groups (Fig. 2). Sediments from areas in which blooms occurred at Locations 4, 5 and 9, were classified as a distinct region. Loadings were primarily contributed by γ-HCH, δ-HCH, *p, p'*-DDE, *o, p'*-DDT, 4- and 5-ring PAHs and other persistent chemicals (class 1) (Fig. 2A). Areas near where rivers enter the lake, at locations 6, 7, and 8, were classified and characterized by greater concentrations of 2- and 3-ring PAHs (class 2). Other areas were characterized by greater concentrations of NP, OP and BPA (class 3). Regions where rivers enter the lake were characterized by a different profile of contaminants than the area where blooms of phytoplankton occurred, which indicated additional contribution for contaminants in those areas where blooms occurred. PCA loadings separated persistent HOCs including HCHs, DDTs and 4-, 5- and 6-ring PAHs (Fig. 2B). NP, OP, and BPA being more degradable were also separated (Chang et al., 2004; Ying and Kookana, 2003; Heitkamp and Cerniglia, 1989).

3.2. Temporal changes in concentrations of persistent contaminants

Disequilibria of concentrations of residues in water-sediment-phytoplankton, studied by use of simultaneous samplings, at locations 3, 4, 5, 9, 10 and 11 in April, July and October of 2013, were used to determine sources of contaminants in sediments (Fig. 3, Table S5). For locations 4, 5 and 9, where blooms occurred, concentrations of γ-HCH, δ-HCH, p, p'-DDE, 4- and 5-ring PAHs in sediments significantly increased during the season in which blooms occurred. Concentrations of Chla in water were correlated with concentrations of δ-HCH ($r^2 = 0.58$, $p < 0.05$), p, p'-DDE ($r^2 = 0.35$, $p < 0.05$), 4-PAHs ($r^2 = 0.44$, $p < 0.05$) and 5-ring PAHs ($r^2 = 0.31$, $p < 0.05$) in surface sediments (Fig. 4). These results are consistent with persistent chemicals at these locations being classified as class 1 locations by the PCA. This result indicated that increased biomass in areas where blooms occurred contributed to greater concentrations of persistent contaminants in surface sediments. This observation is consistent with results of previous studies, which indicated that phytoplankton can influence the mobilization and fate of organic contaminants in aquatic environments (Galbn-Malagn et al., 2012).

Concentrations of HCHs and PAHs were observed in water during simultaneous sampling, ranged from 2.3 to 13 and 0.39–6.0 ng/L, respectively. Concentrations of DDTs were less than the DL (Table S6). Correlations of concentrations of HCHs and PAHs in the water with biomass were not statistically significant, and

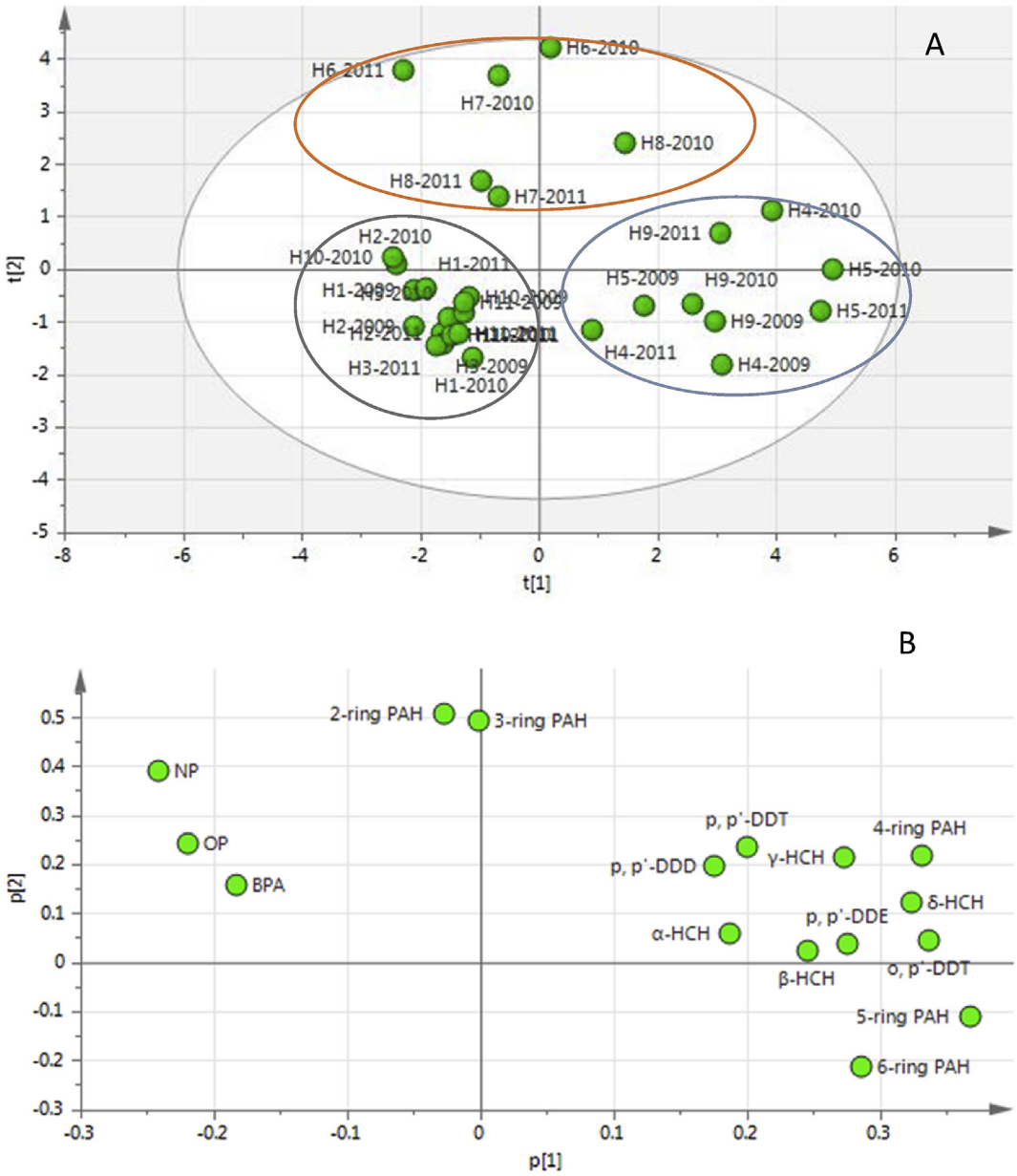


Fig. 2. Principal component analysis for sediment samples detected during the later stages of cyanophyceae bloom season from 2009, 2010 and 2011. (A) The detected organic chemicals contributing to sample clusters (class 1 is blue, class 2 is red, class 3 is green). Samples are named as "H, Number1-Number2" (letter representing type of matrix, while the first number represents the location where the sample was taken and the second number represents the date of collection). (B) Loading plot of the detected organic chemicals contributing to sample clusters. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

exhibited spatial and temporal variability in dissolved concentrations, which indicated the combined result of both flux from air to water and water to sediment. This is consistent with results for HCHs in sea water in the North Atlantic where blooms occurred (Zhang et al., 2012).

Concentrations of DDTs, PAHs and some HCHs in phytoplankton (Table S7) in the area where blooms occurred, at locations 4, 5 and 9, were inversely proportional to concentrations of Chla (SI Figure S1), which is consistent with the "biomass dilution" hypothesis. Associations for δ-HCH, 5- and 6-ring PAHs were stronger ($r^2 = 0.36$, $p < 0.05$), while other chemicals exhibited weaker relationships. Generally, the more hydrophobic the congener, the stronger the decrease of concentrations in phytoplankton. The slope "m" depends on physical-chemical properties of compounds. This is reflected in the different values of m fitted for δ-HCH, 4-ring, 5-ring and 6-ring PAHs, which has the same trend with the octanol water partition coefficient (Kow) of different compounds (Figure S1). Larger values for m suggest greater control of these hydroponic compounds by plankton biomass. Lesser concentrations of persistent organic pollutants (POPs) have also been reported in phytoplankton when biomass in oceans and lakes was greater (Galbn-Malagn et al., 2012; Berrojalbiz et al., 2011b). This result is consistent with the results of the present study.

3.3. Drivers of persistent chemicals in sediments

The surface layer of sediment can receive inputs from sinking particles, by diffusion from the water column and removal processes include resuspension, diffusion to the water column and burial to deeper (more permanent) sediment (Fig. 5). Among these

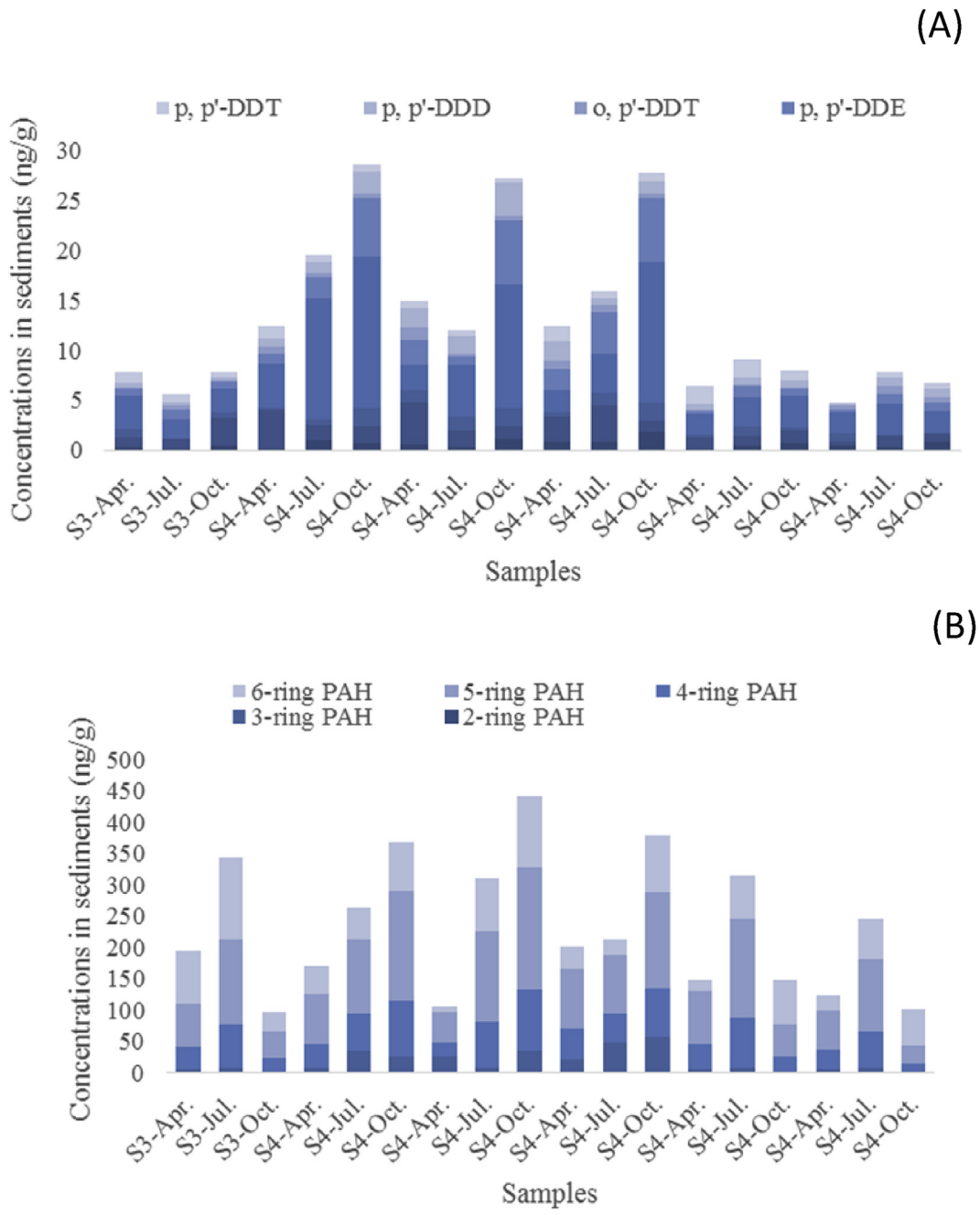


Fig. 3. Temporal variations of organic contaminants from location 3, 4, 5, 9, 10 and 11, collected during April, July and October in 2013. (A) Concentrations of HCHs and DDTs in surface sediments. (B) Concentrations of PAHs in surface sediments.

process sinking and diffusion from sediment to water were considered to be dominant processes. Results of previous studies have indicated that sinking contributes 93–98% of water to sediment flux and diffusion contributes 68–100% for sediment to water flux for PCBs (Meijer et al., 2009). To determine which factors were driving scavenging and sedimentation of organic pollutants, vertical sinking flux and diffusion of HCHs, DDTs and PAHs were calculated. Sinking flux ranged from 3.0 to 8.0 ng m^{-2} d^{-1}, 1.3 to 3.7 ng m^{-2} d^{-1} and 42 to 91 ng m^{-2} d^{-1} for HCHs, DDTs and PAHs, respectively, in the region of maximum blooms of phytoplankton (SI Table S8). These fluxes are similar to those previously determined by use of a sediment trap to measure fluxes of Hexachlorocyclohexane in Tai Lake (Chi et al., 2008). Sediment to water diffusion fluxes ranged from 5.1 to 12 ng m^{-2} d^{-1} and 6.6 to 45 ng m^{-2} d^{-1} for HCHs and PAHs (not available for DDTs because of the undetectable concentrations) (SI Table S9). Generally, diffusion flux for lighter compounds were greater than those for heavier compounds. Integrated fluxes indicated that, for δ-HCH, 3- ring, 4-ring and 5-ring PAHs, the overall sinking was greater than the overall sediment to water diffusion transfer (Fig. 5). Predicted sediment burial indicated the same trend (SI Table S10). Total approximations of burial including sinking and diffusion were as much as 0.58, 38 and 45 g $month^{-1}$ for δ-HCH, 4-ring and 5-ring PAHs for Meiliang Bay, which was the most eutrophic region with an area of 129.3 km^2. Larger sinking and lesser diffusion is the probable driver of accumulation of these HOCs in sediments.

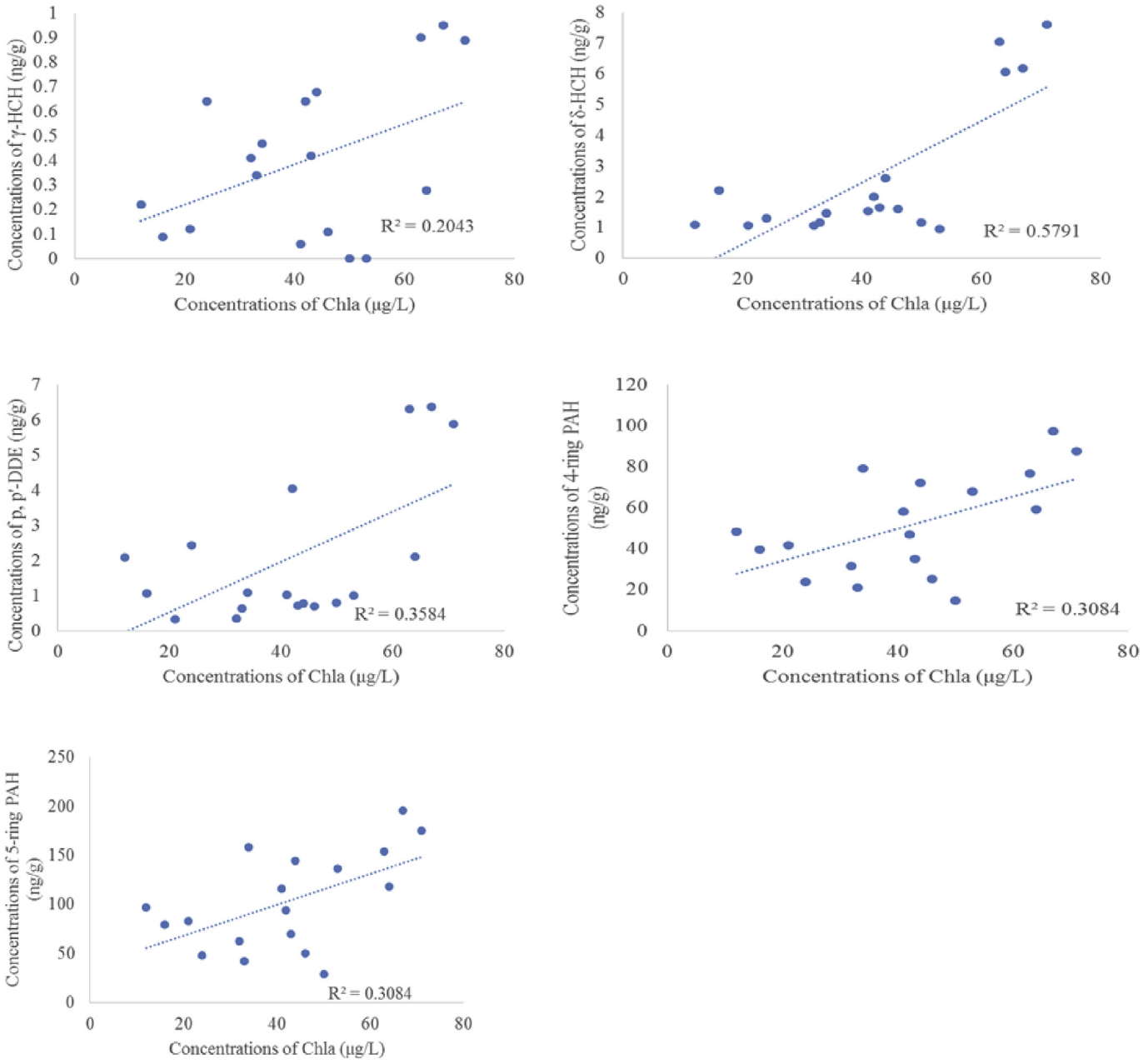


Fig. 4. Correlation of persistent contaminants in surface sediments and Chla in the water column for correlation coefficients at location 3, 4, 5, 9, 10 and 11, collected during April, July and October in 2013.

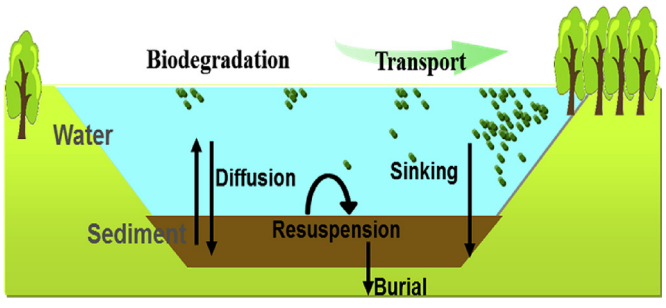


Fig. 5. Migration and transformation of organic pollutants in a eutrophic, freshwater lake mediated by phytoplankton migrations.

Results of previous studies have suggested that persistent HOCs associate mainly with organic particles in the water and the greater rate of sedimentation caused by phytoplankton would result in contaminants being moved to sediments where they could be buried and that eutrophication would enhance this flux of material from the water column (Berglund et al., 2001; Gunnarsson et al., 2000). Moreover, results of a recent study suggest that alterations in communities of fishes, caused by eutrophication, could directly affect aquatic communities and aquatic ecosystem function but might also indirectly affect migration and transformation of contaminants by altering aquatic biomass (Jones et al., 2013). Thus, blooms of phytoplankton and related biomass might be one of the reasons for the greater amounts of persistent HOCs observed in sediments in blooming area, especially during the period of biomass climax.

3.4. Influence of blooms on concentrations of biodegradable contaminants

Lesser concentrations of degradable compounds including NP, OP and BPA, observed during simultaneous samplings, were in sediments from areas where blooms were occurring and concentrations of contaminants were inversely proportional to concentrations of Chla in the water column (Fig. 6). Concentrations of NP, OP and BPA were less than the detection limit (DL) in all samples of phytoplankton. This indicated a weak accumulation in phytoplankton and the related weak sedimentation. Results of previous studies have indicated that these contaminants degraded relatively rapidly in sediment and water, and are more rapidly degraded by microbes at higher temperatures (Tanghe et al., 1998; Ying et al., 2003). Concentrations of these degradable chemicals including NP, OP and BPA in the water of more eutrophic areas were inversely proportional to the mass of phytoplankton ($r^2 > 0.47$, $p < 0.05$) (SI Figure S2). This is in accordance with the distribution of degradable chemicals in sediments, which is similar to that observed previously for lesser molecular weight PAHs in sea water (Berrojalbiz et al., 2011b).

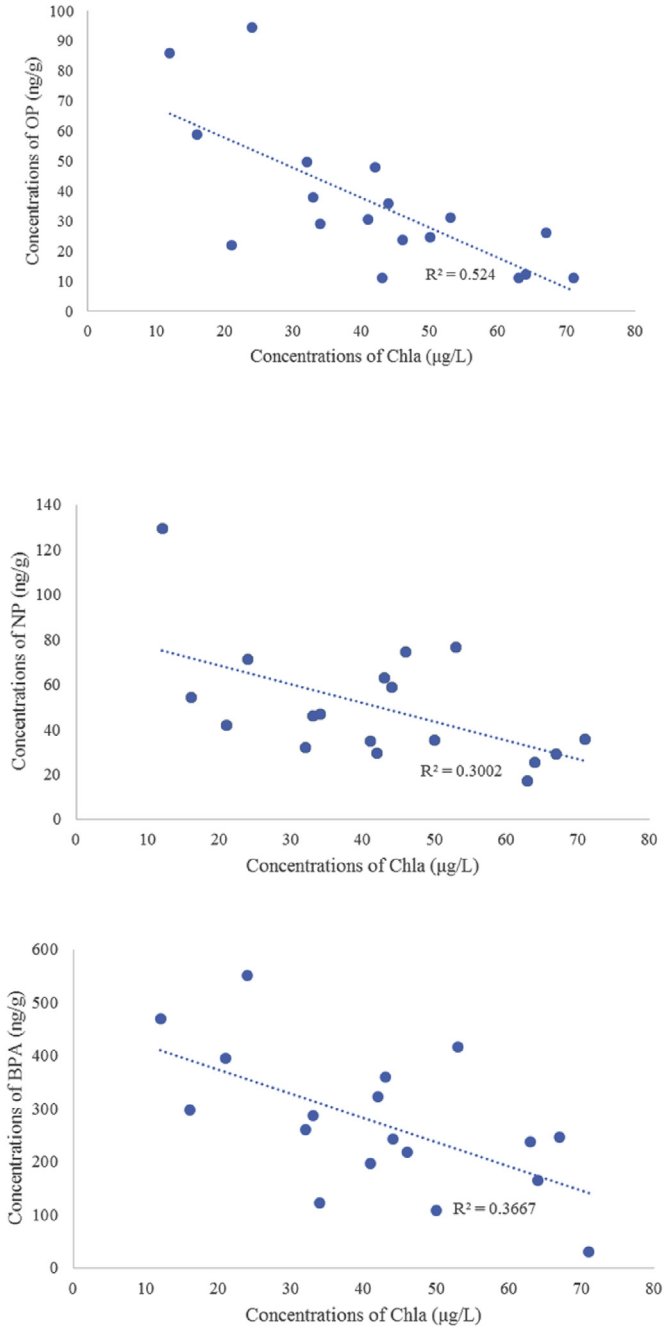


Fig. 6. Correlation of biodegradable contaminants in surface sediments and Chla in the water column for correlation coefficients at location 3, 4, 5, 9, 10 and 11, collected during April, July and October in 2013.

Effective degradation during periods of greater biomass of phytoplankton and associated bacteria which is greater during greater blooms of phytoplankton and higher temperature, may be the reason for the results of NP, OP and BPA in freshwater (Gasol and Del Giorgio, 2000; Kirchman et al., 1991). Results of previous field studies have shown that greater supplies of N and P during the season when blooms occur can also enhance biodegradation of chemicals (Graham et al., 2000). Values of k_{ow} were similar among the chemicals studied. However, NP, OP and BPA were more degraded than other more persistent chemicals (SI Table S11). Results of studies in marine systems also indicated biodegradation of some contaminants by phytoplankton or bacteria (Becquevort and Smith Jr, 2001). The proportion of bacteria were considered as the most important cause (Van Wambeke et al., 2002; Lancelot et al., 2000). Weak sedimentation and increased degradation can probably induce the observed phenomenon for NP, OP and BPA.

3.5. Influence of blooms of phytoplankton on contaminants in *B. quadrata*

Concentrations of HCHs, DDTs and PAHs in *B. quadrata* collected in April from areas in which blooms occurred (locations 4, 5 and 9), were 1.6-, 4.7- and 1.8-fold greater than those from areas in which blooms did not occur (locations 3, 10 and 11), respectively. This result is consistent with greater concentrations of contaminants observed in sediments at these locations (SI Table S7). Concentrations of HOCs in areas where blooms occurred decreased significantly after the season during which blooms occurred (SI Figure S3). This result is different from the greater concentrations of contaminants in sediments caused by greater biomass during blooms. A recent study has demonstrated a similar negative correlation between concentrations of PCBs in sediments and in blue mussels at large spatiotemporal scales in the North Sea. This was likely reason to be related to the cleansing phenomenon during blooms and filtering of water by blue mussels from the overlying water, which is independent of sediment concentrations (Jiao et al., 2013). The lesser concentrations observed during the present study might also due to the filter feeding of *B. quadrata*. *B. quadrata* had a dormant phase in the sediments before April every year, during which they filter relatively polluted pore water resulting in greater concentrations of contaminants in tissues. Also, shortages of food and a faster metabolism of accumulated fatty tissues in winter might also contribute. This dormant phase in sediments might cause greater concentrations of contaminants in benthonic organisms in more polluted areas in which blooms occurred. After dormancy, *B. quadrata* came out of sediments, and filtered cleaner water because of the increased biomass and sedimentation, resulting in decreased concentrations in tissues. The trend observed is a combination of the living habits of biota and blooming-driven equilibrium partitioning between the water, sediment, and biota. Important to note is that April is the most popular season to eat *B. quadrata* and other snails because they are fleshy and tender at that time. To reduce ingestion of contaminants by humans, it is suggested that *B. quadrata* should be collected in April from areas where blooms do not occur and in October from areas in which blooms do occur.

4. Conclusions

Spatio-temporal coupling between the seasonal dynamics of blooms of phytoplankton and organic contaminants in sediments and a mollusk were determined for a eutrophic, freshwater lake. Spatial differences in concentrations of HOCs between areas in which blooms occur and those they do not occur have been theoretically described. Here, we provide the field verification to demonstrate that biomass from blooms of phytoplankton contributes to increasing concentrations of persistent HOCs in sediments or enhancing decreasing of degradable contaminants by either subjecting HOCs to greater sinking and lesser diffusion or by subjecting them to trophic transfer in a shallow, eutrophic, freshwater lake. A positive correlation between persistent HOCs in *B. quadrata* and sediments were found in April, which is probably related to the dormant under surface of sediment. Furthermore, a negative correlation with concentrations in sediments and a positive correlation with concentrations in water was found in October, which might be due to the filter-feeding behavior after dormant, being staying on the surface of sediments. This is the first evidence to confirm that the influence of biomass on the disruption of organic contaminants in sediments and benthic snails is essential for the areas in which blooms occurred in Tai Lake.

Acknowledgment

This work was supported by Natural Science Foundation of China (21577058 & 21307054), Nonprofit industry research subject (201409040), Natural Science Foundation of Jiangsu Province (BK20130551 and BK20130100), Major Science and Technology Program for Water Pollution Control and Treatment (2012ZX07101-003), and the Collaborative Innovation Center for Regional Environmental Quality. Prof. Giesy was supported by the program of 2012 “High Level Foreign Experts” (#GDW20123200120) funded by the State Administration of Foreign Experts Affairs, the P.R. China to Nanjing University and the Einstein Professor Program of the Chinese Academy of Sciences. He was also supported by the Canada Research Chair program, a Visiting Distinguished Professorship in the Department of Biology and Chemistry and State Key Laboratory in Marine Pollution, City University of Hong Kong.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.biomaterials.2017.01.045.

References

Bauerfeind, E., Nthig, E.M., Beszczynska, A., Fahl, K., Kaleschke, L., Kreker, K., Klages, M., Soltwedel, T., Lorenzen, C., Wegner, J., 2009. Particle sedimentation patterns in the eastern Fram Strait during 2000-2005: results from the Arctic long-term observatory HAUSGARTEN. Deep Sea Res. 56 (9), 1471–1487.

Becquevort, S., Smith Jr., W., 2001. Aggregation, sedimentation and biodegradability of phytoplankton-derived material during spring in the Ross Sea, Antarctica. Deep Sea Res. 48 (19), 4155–4178.

Berglund, O., Larsson, P., Ewald, G., Okla, L., 2001. Influence of trophic status on PCB distribution in lake sediments and biota. Environ. Pollut. 113 (2), 199–210.

Berrojalbiz, N., Dachs, J., Del Vento, S., Ojeda, M.J., Valle, M.C., Castro-Jimenez, J., Mariani, G., Wollgast, J., Hanke, G., 2011b. Persistent organic pollutants in Mediterranean seawater and processes affecting their accumulation in plankton. Environ. Sci. Technol. 45 (10), 4315–4322.

Berrojalbiz, N., Dachs, J., Ojeda, M.J., Valle, M.C., Castro-Jiménez, J., Wollgast, J., Ghiani, M., Hanke, G., Zaldivar, J.M., 2011a. Biogeochemical and physical controls on concentrations of polycyclic aromatic hydrocarbons in water and plankton of the Mediterranean and Black Seas. Glob. Biogeochem. Cycles 25 (4).

Blais, J.M., Kimpe, L.E., McMahon, D., Keatley, B.E., Mallory, M.L., Douglas, M.S., Smol, J.P., 2005. Arctic seabirds transport marine-derived contaminants. Science 309 (5733), 445-445.

Breivik, K., Alcock, R., Li, Y.-F., Bailey, R.E., Fiedler, H., Pacyna, J.M., 2004. Primary sources of selected POPs: regional and global scale emission inventories. Environ. Pollut. 128 (1), 3–16.

Carlson, D.L., De Vault, D.S., Swackhamer, D.L., 2010. On the rate of decline of persistent organic contaminants in lake trout (Salvelinus namaycush) from the great lakes, 1970-2003. Environ. Sci. Technol. 44 (6), 2004–2010.

Carstensen, J., Henriksen, P., Heiskanen, A.S., 2007. Summer algal blooms in shallow estuaries: definition, mechanisms, and link to eutrophication. Limnol. Oceanogr. 52 (1), 370–384.

Chang, B., Yu, C., Yuan, S., 2004. Degradation of nonylphenol by anaerobic microorganisms from river sediment. Chemosphere 55 (4), 493–500.

Chi, J., Wang, Q.Y., Huang, J.J., Huang, G.L., 2008. Sedimentation and seasonal variation of hexachlorocyclohexanes in sediments in a eutrophic lake, China. J. Environ. Sci. Heal. B 43 (7), 611–616.

Dachs, J., Eisenreich, S.J., Hoff, R.M., 2000. Influence of eutrophication on air-water exchange, vertical fluxes, and phytoplankton concentrations of persistent organic pollutants. Environ. Sci. Technol. 34 (6), 1095–1102.

Dachs, J., Eisenreich, S.J., Baker, J.E., Ko, F.C., Jeremiason, J.D., 1999. Coupling of phytoplankton uptake and air-water exchange of persistent organic pollutants. Environ. Sci. Technol. 33 (20), 3653–3660.

Everaert, G., De Laender, F., Goethals, P.L., Janssen, C.R., 2015. Multidecadal field data support intimate links between phytoplankton dynamics and PCB concentrations in marine sediments and biota. Environ. Sci. Technol. 49 (14), 8704–8711.

Fernandez, P., Vilanova, R.M., Grimalt, J.O., 1999. Sediment fluxes of polycyclic aromatic hydrocarbons in European high altitude mountain lakes. Environ. Sci. Technol. 33 (21), 3716–3722.

Galbn-Malagn, C., Berrojalbiz, N., Ojeda, M.-J., Dachs, J., 2012. The oceanic biological pump modulates the atmospheric transport of persistent organic pollutants to the Arctic. Nat. Commun. 3, 862.

Gasol, J.M., Del Giorgio, P.A., 2000. Using flow cytometry for counting natural planktonic bacteria and understanding the structure of planktonic bacterial communities. Sci. Mar. 64 (2), 197–224.

Graham, D., Miley, M.K., Denoyelles, F., Smith, V.H., Thurman, E.M., Carter, R., 2000. Alachlor transformation patterns in aquatic field mesocosms under variable oxygen and nutrient conditions. Water Res. 34 (16), 4054–4062.

Gunnarsson, J., Bjrk, M., Gilek, M., Granberg, M., Rosenberg, R., 2000. Effects of eutrophication on contaminant cycling in marine benthic systems. Ambio 29 (4), 252–259.

Heitkamp, M.A., Cerniglia, C.E., 1989. Polycyclic aromatic hydrocarbon degradation by a Mycobacterium sp. in microcosms containing sediment and water from a pristine ecosystem. Appl. Environ. Microbiol. 55 (8), 1968–1973.

Hughes, T., Szmant, A.M., Steneck, R., Carpenter, R., Miller, S., 1999. Algal blooms on coral reefs: what are the causes? Limnol. Oceanogr. 44 (6), 1583–1586.

James, R.T., Havens, K., Zhu, G., Qin, B., 2009. Comparative analysis of nutrients, chlorophyll and transparency in two large shallow lakes (Lake Taihu, PR China and Lake Okeechobee, USA). Hydrobiologia 627 (1), 211–231.

Janetski, D.J., Chaloner, D.T., Moerke, A.H., Rediske, R.R., Okeefe, J.P., Lamberti, G.A., 2012. Resident fishes display elevated organic pollutants in salmon spawning streams of the Great Lakes. Environ. Sci. Technol. 46 (15), 8035–8043.

Jiao, D., Xie, C., Lv, Y., Zhang, N., Zhao, F., Li, R., 2013. Feeding habits of Bellamya purificata and its function in water purification system of ecological ditch. Yu Ye Xian Dai Hua 40 (2), 17–21 (in Chinese).

Jones, T.A., Chumchal, M.M., Drenner, R.W., Timmins, G.N., Nowlin, W.H., 2013. Bottom-up nutrient and top-down fish impacts on insect-mediated mercury flux from aquatic ecosystems. Environ. Toxicol. Chem. 32 (3), 612–618.

Jurado, E., Dachs, J., 2008. Seasonality in the "grasshopping" and atmospheric residence times of persistent organic pollutants over the oceans. Geophys. Res. Lett. 35 (17), 1–5.

Khim, J.S., Kannan, K., Villeneuve, D.L., Koh, C.H., Giesy, J.P., 1999. Characterization and distribution of trace organic contaminants in sediment from Masan Bay, Korea. 1. Instrumental analysis. Environ. Sci. Technol. 33 (23), 4199–4205.

Kirchman, D.L., Suzuki, Y., Garside, C., Ducklow, H.W., 1991. High turnover rates of dissolved organic carbon during a spring phytoplankton bloom. Nature 352 (6336), 612–614.

Krmmel, E., Macdonald, R., Kimpe, L., Gregory-Eaves, I., Demers, M., Smol, J., Finney, B., Blais, J., 2003. Aquatic ecology: delivery of pollutants by spawning salmon. Nature 425 (6955), 255–256.

Lancelot, C., Hannon, E., Becquevort, S., Veth, C., De Baar, H., 2000. Modeling phytoplankton blooms and carbon export production in the Southern Ocean: dominant controls by light and iron in the Atlantic sector in Austral spring 1992. Deep-Sea Res. 47 (9), 1621–1662.

Larsson, P., Okla, L., Woin, P., 1990. Atmospheric transport of persistent pollutants governs uptake by holarctic terrestrial biota. Environ. Sci. Technol. 24 (10), 1599–1601.

Liu, J., Wang, R., Huang, B., Lin, C., Wang, Y., Pan, X., 2011. Distribution and bioaccumulation of steroidal and phenolic endocrine disrupting chemicals in wild fish species from Dianchi Lake, China. Environ. Pollut. 159 (10), 2815–2822.

Meijer, S.N., Dachs, J., Fernandez, P., Camarero, L., Catalan, J., Del Vento, S., Van Drooge, B., Jurado, E., Grimalt, J.O., 2006. Modelling the dynamic air-water-sediment coupled fluxes and occurrence of polychlorinated biphenyls in a high altitude lake. Environ. Pollut. 140 (3), 546–560.

Meijer, S.N., Grimalt, J.O., Fernandez, P., Dachs, J., 2009. Seasonal fluxes and temperature-dependent accumulation of persistent organic pollutants in lakes: the role of internal biogeochemical cycling. Environ. Pollut. 157 (6), 1815–1822.

Paerl, H.W., Xu, H., McCarthy, M.J., Zhu, G., Qin, B., Li, Y., Gardner, W.S., 2011. Controlling harmful cyanobacterial blooms in a hyper-eutrophic lake (Lake Taihu, China): the need for a dual nutrient (N & P) management strategy. Water Res.

45 (5), 1973–1983.
Peng, X., Zhang, G., Zheng, L., Mai, B., Zeng, S., 2005. The vertical variations of hydrocarbon pollutants and organochlorine pesticide residues in a sediment core in Lake Taihu, East China. Geochem-Explor. Env. A 5 (1), 99–104.
Shi, W., Hu, X., Zhang, F., Hu, G., Hao, Y., Zhang, X., Liu, H., Wei, S., Wang, X., Giesy, J.P., 2012. Occurrence of thyroid hormone activities in drinking water from eastern China: contributions of phthalate esters. Environ. Sci. Technol. 46 (3), 1811–1818.
Snyder, S.A., Keith, T.L., Verbrugge, D.A., Snyder, E.M., Gross, T.S., Kannan, K., Giesy, J.P., 1999. Analytical methods for detection of selected estrogenic compounds in aqueous mixtures. Environ. Sci. Technol. 33 (16), 2814–2820.
Stets, E.G., Cotner, J.B., 2008. The influence of dissolved organic carbon on bacterial phosphorus uptake and bacteria-phytoplankton dynamics in two Minnesota lakes. Limnol. Oceanogr. 53 (1), 137–147.
Streets, S.S., Henderson, S.A., Stoner, A.D., Carlson, D.L., Simcik, M.F., Swackhamer, D.L., 2006. Partitioning and bioaccumulation of PBDEs and PCBs in lake Michigan. Environ. Sci. Technol. 40 (23), 7263–7269.
Subashchandrabose, S.R., Ramakrishnan, B., Megharaj, M., Venkateswarlu, K., Naidu, R., 2013. Mixotrophic cyanobacteria and microalgae as distinctive biological agents for organic pollutant degradation. Environ. Int. 51, 59–72.
Sundh, I., 1992. Biochemical composition of dissolved organic carbon derived from phytoplankton and used by heterotrophic bacteria. Appl. Environ. Microbiol. 58 (9), 2938–2947.
Tanghe, T., Devriese, G., Verstraete, W., 1998. Nonylphenol degradation in lab scale activated sludge units is temperature dependent. Water Res. 32 (10), 2889–2896.
Tieyu, W., Yonglong, L., Hong, Z., Yajuan, S., 2005. Contamination of persistent organic pollutants (POPs) and relevant management in China. Environ. Int. 31 (6), 813–821.
Van Wambeke, F., Heussner, S., Diaz, F., Raimbault, P., Conan, P., 2002. Small-scale variability in the coupling/uncoupling of bacteria, phytoplankton and organic carbon fluxes along the continental margin of the Gulf of Lions, Northwestern Mediterranean Sea. J. Mar. Syst. 33, 411–429.
Wang, H., Wang, C., Wu, W., Mo, Z., Wang, Z., 2003. Persistent organic pollutants in water and surface sediments of Taihu Lake, China and risk assessment. Chemosphere 50 (4), 557–562.
Yang, S.-Q., Liu, P.-W., 2010. Strategy of water pollution prevention in Taihu Lake and its effects analysis. J. Gt. Lakes. Res. 36 (1), 150–158.
Ying, G.-G., Kookana, R.S., 2003. Degradation of five selected endocrine-disrupting chemicals in seawater and marine sediment. Environ. Sci. Technol. 37 (7), 1256–1260.
Ying, G.-G., Kookana, R.S., Dillon, P., 2003. Sorption and degradation of selected five endocrine disrupting chemicals in aquifer material. Water Res. 37 (15), 3785–3791.
Zhang, L., Bidleman, T., Perry, M.J., Lohmann, R., 2012. Fate of chiral and achiral organochlorine pesticides in the North Atlantic bloom experiment. Environ. Sci. Technol. 46 (15), 8106–8114.

Supporting Information:

Influence of blooms of phytoplankton on concentrations of hydrophobic organic chemicals in sediments and snails in a hyper-eutrophic, freshwater lake

Wei Shi,[a] Nanyang Yu,[a] Xia Jiang,[b] Zhihua Han,[a,c] Shuhang Wang,[b] Xiaowei Zhang,[a, *] Si Wei,[a] John P. Giesy, [a,d,e,f,g] and Hongxia Yu[a, *]

[a] State Key Laboratory of Pollution Control and Resource Reuse, School of Environment, Nanjing University, Nanjing, People's Republic of China.

[b] Key Laboratory of Environmental Protection of Lake Pollution Control, Chinese Research Academy of Environmental Science, Beijing, People's Republic of China.

[c] Ministry Environment Protection China, Nanjing Institute Environment Science, Nanjing, People's Republic of China.

[d] Department of Veterinary Biomedical Sciences and Toxicology Centre, University of Saskatchewan, Saskatoon, Saskatchewan, Canada.

[e] Department of Zoology, and Center for Integrative Toxicology, Michigan State University, East Lansing, MI, USA.

[f] School of Biological Sciences, University of Hong Kong, Hong Kong, SAR, People's Republic of China.

[g] Department of Biology and Chemistry and State Key Laboratory in Marine Pollution, City University of Hong Kong, Hong Kong, SAR, People's Republic of China.

AUTHOR INFORMATION

Corresponding Author

Prof. Xiaowei Zhang, PhD: School of the Environment, Nanjing University, Nanjing, 210023, China. E-mail: zhangxw@nju.edu.cn

Prof. Hongxia Yu, PhD: School of the Environment, Nanjing University, Nanjing, 210023, China. E-mail: yuhx@nju.edu.cn

ACKNOWLEDGMENT

This work was supported by Natural Science Foundation of China (21577058 & 21307054), Nonprofit industry research subject (201409040), Natural Science Foundation of Jiangsu Province (BK20130551), Major Science and Technology Program for Water Pollution Control and Treatment (2012ZX07101-003), Specialized

Research Fund for the Doctoral Program of Higher Education(20130091120013), and the Collaborative Innovation Center for Regional Environmental Quality. Prof. Giesy was supported by the program of 2012 "High Level Foreign Experts" (#GDW20123200120) funded by the State Administration of Foreign Experts Affairs, the P.R. China to Nanjing University and the Einstein Professor Program of the Chinese Academy of Sciences. He was also supported by the Canada Research Chair program, a Visiting Distinguished Professorship in the Department of Biology and Chemistry and State Key Laboratory in Marine Pollution, City University of Hong Kong.

Table S1 Name, CAS no. and purity of tested chemicals.

Chemicals	Abbreviation	CAS no.	Log Kow	Purity (%)
α-HCH		319-84-6	3.72	99.5%
β-HCH		319-85-7	3.72	99.5%
γ-HCH		58-89-9	3.72	99.5%
δ-HCH		319-86-8	3.72	99.5%
p,p'-DDT		50-29-3	6.91	99.5%
o,p'-DDT		789-02-6	6.91	99.5%
p,p'-DDD		72-54-8	6.91	99.5%
p,p'-DDE		72-55-9	6.91	99.5%
Naphthalene	Nap	91-20-3	3.30	99%
Acenaphthylene	Acy	208-96-8	3.94	99%
Acenaphthene	Ace	83-32-9	3.92	99%
Fluorene	Flu	86-73-7	4.18	99%
Phenanthrene	Phe	85-01-8	4.46	99%
Anthracene	Ant	120-12-7	4.45	99%
Fluoranthene	Flt	206-44-0	5.16	99%
Pyrene	Pyr	129-00-0	4.88	99%
Benz[a]anthracene	B[a]A	56-55-3	5.76	99%
Chrysene	Chr	218-01-9	5.81	99%
Benzo[b]fluoranthene	B[b]F	50-32-8	6.13	99%
Benzo[k]fluoranthene	B[k]F	207-08-9	6.11	99%
Benzo[a]pyrene	B[a]P	50-32-8	6.13	99%
Dibenz[a,h]anthracene	DBA	53-70-3	6.75	99%
Indeno[1,2,3-c,d]pyrene	Ind	193-39-5	6.75	99%
Benzo[g,h,i]perylene	B[ghi]P	191-24-2	6.63	99%
Nonylphenol	NP	25154-52-3	4.5	99.5%
Octylphenol	OP	27193-28-8	5.5(calculated)	99.5%
Bisphenol A	BPA	80-05-7	3.32	99.5%

Table S2. Recoveries and limit of quantification (LOQ) for chemicals.

Chemicals	Water (n=3)			Sediment (n=3)			Biota (n=3)		
	LOQ (ng/L)	Procedural recovery Recovery±RSD (%)	Matrix spike recovery Recovery±RSD (%)	LOQ (ng/g)	Procedural recovery Recovery±RSD (%)	Matrix spike recovery Recovery±RSD (%)	LOQ (ng/g)	Procedural recovery Recovery±RSD (%)	Matrix spike recovery Recovery±RSD (%)
α-HCH	0.35	90±5%	93±7%	0.01	92±2%	94±5%	0.06	95±2%	102±9%
β-HCH	0.31	91±4%	96±8%	0.01	98±3%	99±6%	0.05	99±4%	102±6%
γ-HCH	0.29	86±6%	91±9%	0.03	93±7%	97±5%	0.07	92±5%	98±8%
δ-HCH	0.27	89±5%	94±3%	0.09	96±8%	99±7%	0.06	94±2%	98±11%
p,p'-DDT	0.14	86±3%	89±7%	0.06	101±8%	101±12%	0.05	93±6%	99±9%
o,p'-DDT	0.18	98±3%	102±7%	0.01	95±2%	99±7%	0.08	96±4%	100±10%
p,p'-DDD	0.33	91±9%	98±13%	0.03	102±2%	102±7%	0.04	87±7%	94±8%
p,p'-DDE	0.52	88±6%	97±12%	0.02	96±5%	100±8%	0.07	92±2%	94±6%
Nap	0.97	63±9%	64±11%	0.63	68±4%	77±11%	0.77	71±9%	74±9%
Acy	0.28	81±4%	84±8%	0.13	104±6%	102±9%	0.19	98±7%	99±6%
Ace	0.24	93±5%	95±4%	0.22	105±4%	104±8%	0.28	102±3%	99±9%
Flu	0.38	113±14%	114±4%	0.17	82±7%	89±9%	0.37	83±5%	92±10%
Phe	0.19	80±7%	84±8%	0.13	93±5%	96±5%	0.25	88±6%	94±7%
Ant	0.22	86±5%	96±13%	0.15	81±8%	86±6%	0.44	82±9%	94±13%
Flt	0.06	96±18%	99±8%	0.17	84±3%	90±8%	0.45	84±7%	95±12%
Pyr	0.08	91±11%	97±8%	0.28	89±4%	95±11%	0.58	87±3%	94±8%
B[a]A	0.11	94±2%	99±7%	0.44	90±8%	95±8%	0.59	96±4%	99±7%
Chr	0.12	83±9%	93±12%	0.72	86±9%	93±11%	0.76	86±8%	93±11%
B[b]F	0.09	89±3%	96±13%	0.15	98±3%	101±9%	0.11	93±2%	98±8%
B[k]F	0.06	87±7%	94±13%	0.13	96±4%	100±7%	0.14	99±6%	102±7%
B[a]P	0.07	87±5%	94±9%	0.17	92±6%	98±8%	0.29	91±4%	104±13%
Ind	0.06	83±5%	89±9%	0.13	98±8%	102±9%	0.17	97±8%	100±8%
DBA	0.05	89±9%	95±9%	0.17	92±3%	97±10%	0.47	92±9%	98±9%
B[ghi]P	0.05	82±5%	91±10%	0.15	99±5%	105±8%	0.21	93±4%	101±9%
NP	2.87	83±2%	93±10%	4.14	92±5%	98±7%	6.28	87±2%	94±9%
OP	2.38	84±6%	89±7%	6.83	99±2%	102±8%	10.05	89±5%	96±8%
BPA	4.93	91±2%	96±8%	8.19	98±4%	104±9%	10.56	93±4%	96±6%

Table S3. Distribution of organochlorine (OC) pesticides in surface sediments and phytoplankton (ng/g, dm). Concentrations were measured during the late bloom season of 2009, 2010 and 2011. Samples are named as Letter, Number1-Number2 (letter representing type of matrix, while the first number represents the location where the sample was taken and the second number represents the date of collection).

	α-HCH	β-HCH	γ-HCH	δ-HCH	p, p'-DDE	o, p'-DDT	p, p'-DDD	p, p'-DDT
H1-2009	0.03	1.12	0.03	1.46	0.85	0.01	0.59	0.95
H1-2010	0.47	1.11	0.04	0.79	1.75	0.70	0.03	0.03
H1-2011	0.12	0.63	0.33	1.90	0.91	0.67	0.51	0.48
H2-2009	0.07	0.45	0.28	1.34	0.39	0.31	0.07	0.26
H2-2010	0.16	0.44	0.28	1.21	0.23	1.49	0.84	0.17
H2-2011	0.07	0.63	0.10	1.85	1.59	0.38	0.22	0.42
H3-2009	0.40	0.43	0.14	1.21	0.81	1.42	0.07	0.09
H3-2010	0.27	0.41	0.61	1.07	0.46	0.88	0.56	0.25
H3-2011	0.10	0.84	0.03	1.49	1.11	0.11	0.07	0.52
H4-2009	0.14	0.48	0.34	6.95	4.04	5.73	0.36	0.92
H4-2010	0.51	1.93	1.31	5.87	6.84	2.14	0.26	4.76
H4-2011	0.38	1.46	0.20	2.69	1.44	1.34	0.26	0.49
H5-2009	0.01	1.20	0.54	6.41	0.67	0.98	1.65	0.87
H52010	1.25	2.42	1.44	2.83	5.71	3.20	0.11	1.32
H5-2011	0.39	0.82	0.89	7.61	0.35	4.39	2.81	1.71
H6-2010	0.01	0.43	0.66	5.21	1.02	3.29	0.90	1.54
H6-2011	0.08	0.16	0.04	5.31	0.33	0.77	1.03	2.42
H7-2010	0.80	0.96	0.83	1.46	1.46	0.61	2.07	0.52
H7-2011	0.30	0.96	0.44	1.86	0.40	0.69	0.90	2.21
H8-2010	0.33	0.71	1.49	4.30	3.55	4.66	0.54	0.24
H8-2011	0.21	0.92	0.36	1.71	0.54	0.97	0.55	1.05
H9-2009	0.39	0.73	0.67	3.39	1.50	3.18	1.21	1.28
H9-2010	0.03	0.62	0.16	7.30	2.43	4.76	0.88	1.09
H9-2011	0.42	2.19	0.40	6.44	0.52	5.32	2.25	0.85
H10-2009	0.04	1.53	0.36	1.85	0.74	1.91	0.50	0.46
H10-2010	0.35	0.59	0.32	2.11	0.44	0.98	0.18	0.46
H10-2011	0.36	0.36	0.41	1.60	0.18	0.70	0.70	0.93
H11-2009	0.20	0.44	0.60	2.62	0.58	1.18	0.23	0.51
H11-2010	0.14	0.53	0.26	1.68	0.79	1.21	0.22	0.26
H11-2011	0.46	0.01	0.36	1.15	0.24	1.19	0.74	0.63

Table S4. Distribution of polycyclic aromatic hydrocarbons (PAHs), nonylphenol (NP), octylphenol (OP) and bisphenol A (BPA) in surface sediments and phytoplankton (ng/g, dm). Concentrations were measured during the late bloom season of 2009, 2010 and 2011 (letter representing type of matrix, while the first number represents the location where the sample was taken and the second number represents the date of collection).

	2-ring PAH	3-ring PAH	4-ring PAH	5-ring PAH	6-ring PAH	OP	NP	BPA
H1-2009	N.D.	17.36	32.73	14.20	4.80	65.75	155.96	1500.00
H1-2010	N.D.	15.25	28.02	14.20	9.00	47.85	56.71	379.58
H1-2011	N.D.	19.57	16.49	19.58	4.48	126.05	244.78	516.84
H2-2009	N.D.	17.80	29.14	10.68	10.40	69.94	107.57	903.47
H2-2010	N.D.	14.49	28.94	14.44	1.12	340.20	252.67	352.97
H2-2011	N.D.	16.80	26.70	13.20	2.60	26.25	126.36	570.41
H3-2009	N.D.	21.35	7.63	8.68	8.20	82.62	113.26	142.72
H3-2010	N.D.	20.90	7.20	16.60	2.60	92.34	129.96	167.24
H3-2011	N.D.	19.60	10.20	18.60	7.20	52.00	133.42	188.13
H4-2009	N.D.	5.79	61.53	130.04	82.08	24.78	22.28	244.78
H4-2010	N.D.	26.33	72.78	86.20	13.60	47.85	47.85	429.05
H4-2011	N.D.	26.67	87.76	78.96	17.96	11.13	35.50	29.43
H5-2009	N.D.	13.88	88.87	147.56	18.06	31.20	43.50	76.80
H5-2010	N.D.	25.90	104.86	225.02	37.32	54.78	57.87	72.13
H5-2011	N.D.	11.93	74.56	259.04	99.10	4.78	15.70	281.69
H6-2010	2.42	67.70	101.92	16.96	0.50	85.33	183.58	811.81
H6-2011	1.33	38.47	60.03	34.60	0.42	339.23	557.30	813.40
H7-2010	1.17	68.56	61.62	31.12	1.34	181.21	452.19	536.95
H7-2011	N.D.	60.07	61.35	9.58	0.24	66.69	230.38	503.24
H8-2010	1.17	68.56	61.62	31.12	1.34	90.57	137.58	320.15
H8-2011	1.15	58.75	70.27	19.80	3.20	56.12	163.36	786.81
H9-2009	N.D.	11.69	116.47	171.20	64.32	14.78	39.55	143.80
H9-2010	N.D.	6.76	108.19	248.98	11.50	63.26	82.62	442.72
H9-2011	N.D.	57.32	76.84	91.04	31.26	33.56	49.65	240.44
H10-2009	N.D.	27.11	16.04	16.80	2.30	69.94	107.57	903.47
H10-2010	N.D.	26.61	5.68	7.38	1.62	340.20	252.67	352.97
H10-2011	N.D.	1.64	25.19	71.18	40.22	98.84	214.64	1102.17
H11-2009	N.D.	33.13	8.38	9.50	1.32	82.62	113.26	142.72
H11-2010	N.D.	25.00	7.20	21.80	10.60	52.00	133.42	188.13
H11-2011	N.D.	0.84	14.65	56.30	37.06	143.98	144.83	742.34

Table S5. Temporal variations of organochlorine (OC) pesticides, polycyclic aromatic hydrocarbons (PAHs), nonylphenol (NP), octylphenol (OP) and bisphenol A (BPA) in surface sediments (ng/g, dm) from April to October in 2013.

Location	Time	α-HCH	β-HCH	γ-HCH	δ-HCH	p, p'-DDE	o, p'-DDT	p, p'-DDD	p, p'-DDT	2-ring PAH	3-ring PAH	4-ring PAH	5-ring PAH	6-ring PAH	OP	NP	BPA
3	Apr.	0.26	1.06	0.84	3.32	0.72	0.15	0.42	1.10	N.D.	5.69	34.95	69.90	84.84	118.13	160.96	1291.75
3	Jul.	0.22	0.9	N.D.	1.92	1.00	0.40	0.36	0.74	N.D.	9.03	68.09	136.18	131.68	134.21	143.41	652.85
3	Oct.	0.4	2.78	0.68	2.34	0.64	0.18	0.30	0.50	N.D.	1.97	21.08	42.16	32.36	83.79	113.69	779.33
4	Apr.	0.16	3.9	0.18	4.40	1.06	0.66	0.85	1.30	N.D.	7.55	39.60	79.20	44.00	121.00	109.85	1166.60
4	Jul.	1.01	1.48	0.56	12.14	2.11	0.46	1.10	0.69	N.D.	34.93	59.13	118.26	51.54	19.81	23.18	163.46
4	Oct.	0.78	1.64	1.78	15.22	5.89	0.35	2.31	0.71	N.D.	26.67	87.76	175.52	78.96	11.00	14.59	78.32
5	Apr.	0.54	4.18	1.28	2.58	2.44	1.31	1.99	0.65	N.D.	25.15	23.92	47.84	8.90	129.36	154.39	747.49
5	Jul.	0.34	1.62	1.36	5.22	0.78	0.35	1.85	0.50	N.D.	8.62	72.28	144.56	84.88	60.11	36.13	232.16
5	Oct.	1.20	1.18	1.90	12.38	6.39	0.37	3.39	0.49	N.D.	34.92	97.65	195.30	113.82	10.82	13.56	139.03
9	Apr.	0.82	2.54	0.44	2.18	2.08	0.85	2.07	1.42	N.D.	21.55	48.39	96.78	35.58	181.55	230.53	960.03
9	Jul.	0.88	3.58	1.28	3.98	4.06	0.78	0.65	0.73	N.D.	46.84	47.14	94.28	23.08	21.91	25.42	285.87
9	Oct.	1.84	1.18	1.80	14.08	6.32	0.52	1.25	0.85	N.D.	57.32	76.84	153.68	91.04	33.56	49.65	240.44
10	Apr.	0.18	1.14	0.24	2.12	0.32	0.04	0.54	1.82	N.D.	5.58	41.62	83.24	17.18	109.18	165.37	931.43
10	Jul.	0.44	1.02	0.94	2.94	1.09	0.22	0.69	1.69	N.D.	9.00	79.1	158.2	69.18	150.6	164.9	493.02

												3	6		3	2	
10	Oct.	0.72	1.32	0.22	3.20	0.70	0.18	0.70	0.93	N.D.	1.64	25.19	50.38	71.18	98.84	214.64	1102.17
11	Apr.	0.38	0.46	0.82	2.12	0.34	0.32	0.20	0.16	N.D.	6.02	31.44	62.88	24.32	111.70	123.07	885.17
11	Jul.	0.32	1.12	0.12	3.08	1.02	0.75	0.89	0.52	N.D.	7.90	58.15	116.30	63.62	62.48	56.74	506.81
11	Oct.	0.92	0.72	N.D.	2.30	0.79	0.64	0.74	0.63	N.D.	0.84	14.65	29.30	56.30	143.98	144.83	742.34

Table S6. Temporal variations of organochlorine (OC) pesticides, polycyclic aromatic hydrocarbons (PAHs), nonylphenol (NP), octylphenol (OP) and bisphenol A (BPA) in the water (ng/L) from April to October in 2013.

Location	Time	α-HCH	β-HCH	γ-HCH	δ-HCH	c, p'-DDE	o, p'-DDT	p, p'-DDD	p, p'-DDT	2-ring PAH	3-ring PAH	4-ring PAH	5-ring PAH	6-ring PAH	OP	NP	BPA
3	Apr.	0.60	3.30	N.D.	3.97	N.D.	N.D.	N.D.	N.D.	N.D.	1.10	0.10	0.02	0.01	11.11	62.75	358.92
3	Jul.	1.37	3.69	N.D.	5.96	N.D.	N.D.	N.D.	N.D.	N.D.	1.19	0.17	0.08	0.02	31.13	76.31	415.98
3	Oct.	1.05	3.51	0.62	7.93	N.D.	N.D.	N.D.	N.D.	N.D.	1.68	0.65	0.05	0.03	37.74	45.76	286.36
4	Apr.	0.05	1.52	0.06	1.70	N.D.	N.D.	N.D.	N.D.	N.D.	0.60	0.57	0.06	0.00	58.95	54.23	298.20
4	Jul.	0.38	0.56	0.21	4.77	N.D.	N.D.	N.D.	N.D.	N.D.	4.01	0.84	0.08	0.00	12.15	25.21	164.44
4	Oct.	0.30	0.62	0.70	5.96	N.D.	N.D.	N.D.	N.D.	N.D.	2.67	0.62	0.12	0.01	11.13	35.50	29.43
5	Apr.	0.20	1.64	0.49	0.99	N.D.	N.D.	N.D.	N.D.	N.D.	2.45	0.25	0.00	0.00	94.39	70.99	550.87
5	Jul.	0.13	0.62	0.53	2.00	N.D.	N.D.	N.D.	N.D.	N.D.	0.69	1.10	0.12	0.00	35.84	58.90	242.04
5	Oct.	0.46	0.43	0.72	4.86	N.D.	N.D.	N.D.	N.D.	N.D.	2.94	0.87	0.16	0.02	26.18	29.20	245.78
9	Apr.	0.32	0.99	0.16	0.83	N.D.	N.D.	N.D.	N.D.	N.D.	1.94	0.75	0.04	0.00	85.95	129.39	469.78
9	Jul.	0.33	1.38	0.50	1.53	N.D.	N.D.	N.D.	N.D.	N.D.	4.48	0.47	0.03	0.00	47.85	29.50	322.24
9	Oct.	0.70	0.42	0.68	5.52	N.D.	N.D.	N.D.	N.D.	N.D.	5.21	0.69	0.12	0.01	11.07	16.94	237.27
10	Apr.	N.D.	0.35	0.82	4.41	N.D.	N.D.	N.D.	N.D.	N.D.	0.25	0.02	0.06	0.06	22.01	41.61	394.15
10	Jul.	1.65	4.56	N.D.	3.68	N.D.	N.D.	N.D.	N.D.	N.D.	0.86	0.03	0.01	0.00	28.90	46.60	122.97
10	Oct.	0.77	1.30	0.83	1.67	N.D.	N.D.	N.D.	N.D.	N.D.	0.71	0.23	0.08	0.03	23.81	74.61	218.49

11	Apr.	1.02	2.37	1.25	7.43	N.D.	N.D.	N.D.	N.D.	N.D.	0.81	0.12	0.03	0.01	49.70	31.87	260.96
11	Jul.	0.47	1.80	N.D.	5.32	N.D.	N.D.	N.D.	N.D.	N.D.	0.91	0.06	0.04	0.01	30.48	34.94	197.20
11	Oct.	0.67	1.40	0.63	3.25	N.D.	N.D.	N.D.	N.D.	N.D.	1.26	0.09	0.07	0.02	24.48	35.30	108.25

Table S7. Temporal variations of organochlorine (OC) pesticides, polycyclic aromatic hydrocarbons (PAHs), nonylphenol (NP), octylphenol (OP) and bisphenol A (BPA) in phytoplankton and *Bellamya quadrata* (ng/g, dm) from April to October in 2013.

Location	Time	α-HCH	β-HCH	γ-HCH	δ-HCH	p, p'-DDE	o, p'-DDT	p, p'-DDD	p, p'-DDT	2-ring PAH	3-ring PAH	4-ring PAH	5-ring PAH	6-ring PAH	OP	NP	BPA
phytoplankton																	
4	Apr.	0.11	2.16	0.21	8.27	3.21	1.13	0.11	N.D.	N.D.	6.02	6.25	6.88	2.17	N.D.	N.D.	N.D.
4	Jul.	0.08	1.10	0.15	6.83	3.15	1.06	0.11	N.D.	N.D.	2.85	3.61	2.75	1.23	N.D.	N.D.	N.D.
4	Oct.	N.D.	1.12	0.08	7.37	1.15	0.47	N.D.	N.D.	N.D.	1.75	3.14	2.17	0.88	N.D.	N.D.	N.D.
5	Apr.	0.27	1.21	0.15	8.21	2.15	1.02	N.D.	N.D.	N.D.	2.98	4.51	2.83	1.10	N.D.	N.D.	N.D.
5	Jul.	0.11	2.04	0.26	8.08	2.28	1.17	0.20	N.D.	N.D.	5.08	5.78	1.96	0.54	N.D.	N.D.	N.D.
5	Oct.	N.D.	0.46	0.24	7.07	2.27	1.20	0.24	N.D.	N.D.	1.51	1.37	1.93	0.70	N.D.	N.D.	N.D.
9	Apr.	0.18	1.10	0.39	8.06	2.37	1.48	0.34	N.D.	N.D.	3.60	4.15	3.72	2.58	N.D.	N.D.	N.D.
9	Jul.	0.14	1.07	0.29	7.05	1.30	0.89	0.27	N.D.	N.D.	1.91	1.31	2.34	0.77	N.D.	N.D.	N.D.
9	Oct.	N.D.	0.28	0.24	7.34	1.31	0.71	0.21	N.D.	N.D.	1.91	1.97	1.39	0.47	N.D.	N.D.	N.D.
Bellamya quadrata																	
3	Apr.	1.05	1.43	1.11	50.07	1.25	0.82	N.D.	N.D.	N.D.	5.64	25.89	24.69	17.63	N.D.	N.D.	N.D.
3	Oct.	0.71	0.87	0.56	48.22	0.83	0.43	N.D.	N.D.	N.D.	5.12	15.46	20.13	10.41	N.D.	N.D.	N.D.
4	Apr.	0.61	6.38	0.33	80.15	2.14	3.27	0.12	N.D.	N.D.	7.11	40.03	52.31	12.91	N.D.	N.D.	17.90
4	Oct.	0.35	3.18	0.16	50.12	1.34	0.46	N.D.	N.D.	N.D.	3.61	18.77	24.69	5.42	N.D.	N.D.	N.D.
5	Apr.	1.77	5.62	1.69	51.34	4.23	4.51	0.12	N.D.	N.D.	16.09	24.31	30.17	12.64	N.D.	N.D.	11.47
5	Oct.	0.89	3.11	0.76	25.64	3.37	2.17	0.11	N.D.	N.D.	8.54	13.72	16.98	5.42	N.D.	N.D.	N.D.
9	Apr.	3.12	4.32	0.88	52.39	4.12	3.64	0.31	N.D.	N.D.	27.91	43.22	48.16	19.23	N.D.	N.D.	15.19
9	Oct.	1.89	3.21	0.42	20.12	1.98	2.07	0.25	N.D.	N.D.	6.98	23.14	19.67	4.65	N.D.	N.D.	N.D.
10	Apr.	0.60	0.78	0.43	40.68	0.85	0.74	N.D.	N.D.	N.D.	3.26	19.14	19.49	13.40	N.D.	N.D.	N.D.
10	Oct.	0.53	0.96	0.66	23.71	0.32	0.21	N.D.	N.D.	N.D.	1.22	7.98	11.36	2.80	N.D.	N.D.	N.D.
11	Apr.	0.98	0.56	1.01	31.76	0.46	0.67	N.D.	N.D.	N.D.	4.17	20.91	25.95	6.10	N.D.	N.D.	N.D.
11	Oct.	0.78	0.86	1.33	30.57	0.34	0.51	N.D.	N.D.	N.D.	3.71	23.87	18.96	5.44	N.D.	N.D.	N.D.

Supporting Information, Table S8 Vertical sinking flux of organochlorine (OC) pesticides and polycyclic aromatic hydrocarbons (PAHs) out of the water column (ng m^{-2} d^{-1})

Vertical flux	Location 9-2013			Location 4-2013			Location 5-2013		
	April	July	Oct	April	July	Oct	April	July	Oct
α-HCH	0.06	0.09	-	0.04	0.07	-	0.05	0.19	-
β- HCH	0.34	0.72	0.24	0.80	0.96	1.04	0.97	0.84	0.41
γ- HCH	0.12	0.19	0.21	0.08	0.13	0.07	0.12	0.10	0.21
δ- HCH	2.49	4.73	6.33	3.05	5.95	6.84	3.83	5.67	6.33
p, p'-DDE	0.73	0.87	1.13	1.18	2.74	1.07	1.08	1.48	2.03
o, p'-DDT	0.46	0.60	0.61	0.42	0.92	0.44	0.55	0.70	1.07
p, p'-DDD	0.10	0.18	0.18	0.04	-	-	0.09	-	0.21
p, p'-DDT	-	-	-	-	-	-	-	-	-
2-ring PAH	0.60	-	-	-	-	-	-	-	-
3-ring PAH	11.09	12.79	16.44	22.17	24.84	16.26	24.06	20.58	13.53
4-ring PAH	12.79	8.81	16.94	23.02	31.42	29.14	27.41	31.14	12.24
5-ring PAH	11.47	15.67	11.95	25.36	23.97	20.15	9.29	19.50	17.27
6-ring PAH	7.95	5.18	4.05	8.00	10.72	8.20	2.55	7.61	6.31

-: not available (because the concentrations were lower than the LOQ).

Supporting Information, Table S9 Sediment-to-water diffusion of organochlorine (OC) pesticides and polycyclic aromatic hydrocarbons (PAHs) out of the sediment (ng m^{-2} d^{-1})

Vertical flux	Location 9-2013			Location 4-2013			Location 5-2013		
	April	July	Oct	April	July	Oct	April	July	Oct
α-HCH	0.40	1.13	1.74	1.01	1.12	0.70	1.07	0.40	0.91
β- HCH	0.81	2.70	3.58	2.07	1.63	2.21	1.15	1.90	2.99
γ- HCH	1.04	0.52	3.03	0.96	0.63	0.79	1.30	0.85	2.60
δ- HCH	2.89	3.81	3.78	3.09	2.24	4.61	2.29	4.77	3.15
p, p'-DDE	-	-	-	-	-	-	-	-	-
o, p'-DDT	-	-	-	-	-	-	-	-	-
p, p'-DDD	-	-	-	-	-	-	-	-	-
p, p'-DDT	-	-	-	-	-	-	-	-	-
2-ring PAH	11.42	3.04	3.10	6.30	1.66	0.75	4.72	4.36	0.95
3-ring PAH	8.14	8.05	6.22	11.84	9.70	2.57	16.77	17.57	5.59
4-ring PAH	3.59	3.45	3.09	4.94	3.68	1.88	16.56	9.26	6.47
5-ring PAH	10.68	3.27	2.52	7.87	2.58	1.12	7.42	4.58	1.52
6-ring PAH	-	-	0.50	-	-	0.28	-	-	0.29

-: not available (because the concentrations were lower than the LOQ).

Supporting Information, Table S10 Estimated sediment burial of organochlorine (OC) pesticides and polycyclic aromatic hydrocarbons (PAHs) (ng m^{-2} d^{-1})

Vertical flux	Location 9-2013			Location 4-2013			Location 5-2013		
	April	July	Oct	April	July	Oct	April	July	Oct
α-HCH	0.01	0.01	0.02	0.00	0.01	0.01	0.01	0.00	0.01
β- HCH	0.03	0.04	0.01	0.04	0.01	0.02	0.04	0.02	0.01
γ- HCH	0.00	0.01	0.02	0.00	0.01	0.02	0.01	0.01	0.02
δ- HCH	0.02	0.04	0.14	0.04	0.12	0.15	0.03	0.05	0.12
p, p'-DDE	0.00	0.04	0.06	0.01	0.02	0.06	0.02	0.01	0.06
o, p'-DDT	0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.00	0.00
p, p'-DDD	0.02	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.03
p, p'-DDT	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00
2-ring PAH	0.01	0.04	0.02	0.00	0.04	0.03	0.00	0.00	0.02
3-ring PAH	2.16	4.68	5.73	0.76	3.49	2.67	2.51	0.86	3.49
4-ring PAH	4.84	4.71	7.68	3.96	5.91	8.78	2.39	7.23	9.76
5-ring PAH	3.56	2.31	9.10	4.40	5.15	7.90	0.89	8.49	11.38
6-ring PAH	0.39	0.74	3.13	0.48	0.17	1.80	0.54	0.84	4.81

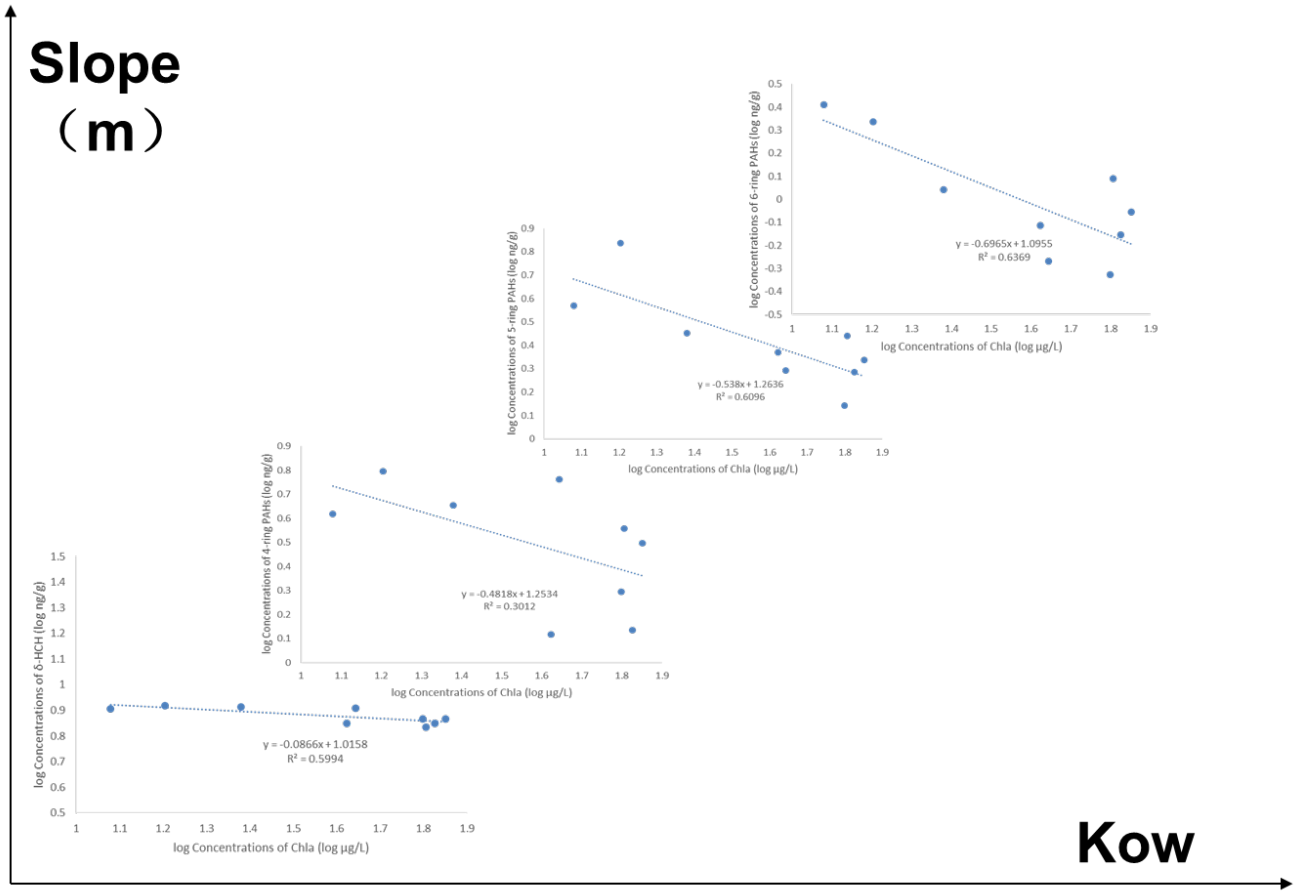
Supporting Information, Table S11 Biodegradability of the detected biodegradable contaminants.

Name	Biodegradability				Classification	
	Linear	Non-Linear	MITI Linear	MITI Non-Linear	Ultimate Biodegradation	Primary Biodegradation
α-HCH	-0.059	0.000	-0.0712	0.000	1.517	2.825
β-HCH	-0.059	0.000	-0.072	0.000	1.517	2.825
γ-HCH	-0.059	0.000	-0.072	0.000	1.517	2.825
δ-HCH	-0.059	0.000	-0.072	0.000	1.517	2.825
p, p'-DDE	0.009	0.000	-0.154	0.001	1.737	2.857
o, p'-DDT	-0.250	0.000	-0.203	0.000	1.196	2.482
p, p'-DDD	0.062	0.000	-0.220	0.001	1.658	2.786
p, p'-DDT	-0.250	0.000	-0.203	0.000	1.196	2.482
Nap	1.006	0.999	0.397	0.447	2.330	3.320
Acy	0.675	0.700	0.321	0.252	2.863	3.628
Ace	0.784	0.878	0.191	0.190	2.709	3.488
Flu	0.784	0.878	0.191	0.190	2.709	3.488
Phe	0.982	0.999	0.264	0.195	2.219	3.248
Ant	0.982	0.999	0.264	0.195	2.219	3.248
Flt	-0.006	0.000	0.197	0.108	1.953	2.854
Pyr	-0.006	0.000	0.197	0.108	1.953	2.854
B[a]A	-0.018	0.000	0.132	0.068	1.895	2.816
Chr	-0.018	0.000	0.132	0.068	1.895	2.816
B[b]F	-0.030	0.000	0.060	0.035	1.842	2.782
B[k]F	-0.030	0.000	0.060	0.035	1.842	2.782
B[a]P	-0.030	0.000	0.0601	0.035	1.842	2.782
Ind	-0.041	0.000	-0.0114	0.018	1.789	2.747
DBA	-0.042	0.000	-0.0009	0.021	1.785	2.744
B[ghi]P	-0.042	0.000	-0.0009	0.021	1.785	2.744
OP	0.813	0.797	0.1431	0.1339	2.6937	3.501
NP	-0.398	0.000	0.5812	0.3499	2.5161	3.580
BPA	0.687	0.465	0.2956	0.1559	2.5953	3.444

For Linear Model, Non-Linear Model, MITI Linear Model and MITI Non-Linear Model, the value represents biodegradability. A probability greater than or equal to 0.5 indicates --> biodegrades fast. A probability less than 0.5 indicates --> Does not biodegrade fast. For Ultimate Biodegradation Timeframe and Primary Biodegradation Timeframe models, result represents classifications of rates: 5.00 -> hours, 4.00 -> days, 3.00 -> weeks, 2.00 -> months, 1.00 -> longer.

Table S12 Physical parameters in Tai Lake, China, in 2013

Sampling time	Locations	Temperature (℃)	pH	Dissolved oxygen（mg/L)	Turbidity（NTU）	Total depth (m)	Concentrations of Chla (μg/L)
April 2013	Location 3	14.4	7.73	6.75	31.8	2.5	43
	Location 4	19.3	7.81	7.23	27.7	2.2	16
	Location 5	18.2	7.4	6.8	22.8	1.8	24
	Location 9	15.7	7.54	5.99	24.5	1.9	12
	Location 10	17.1	8.1	6.9	24.5	2.9	21
	Location 11	19.7	7.84	8.56	22.8	3	32
Jul. 2013	Location 3	27.44	7.75	7.05	23.1	3	53
	Location 4	30.9	8.04	9.27	21.1	2.1	64
	Location 5	27.8	8.3	7.3	24.7	2.3	44
	Location 9	28.8	7.98	7.31	23.7	1.8	42
	Location 10	30.2	8.2	8.71	23.5	2.7	34
	Location 11	29.6	8.69	10.02	21.1	3.1	41
Oct. 2013	Location 3	28.3	7.6	8.3	24.5	3.2	33
	Location 4	24.8	8.39	7.54	21.5	1.7	71
	Location 5	28.9	8.77	8.67	37.5	1.6	67
	Location 9	24.3	8.71	8.08	22.1	1.55	63
	Location 10	23.7	8.16	6.48	18.8	2.08	46
	Location 11	22.7	8.7	7.24	19.2	2.65	50



Supporting Information, Figure S1. Correlation between δ-HCH, 4-, 5- and 6-ring PAHs in phytoplankton and Chla in the water column in blooming areas including location 4, 5 and 9 collected during April, July and October in 2013.

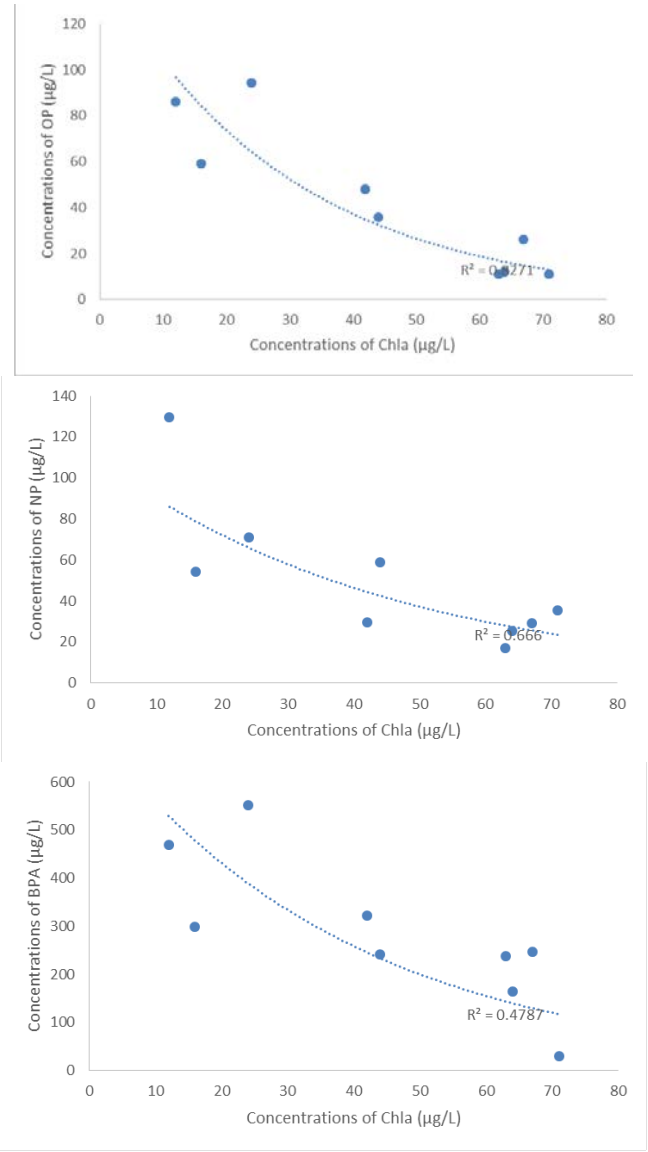
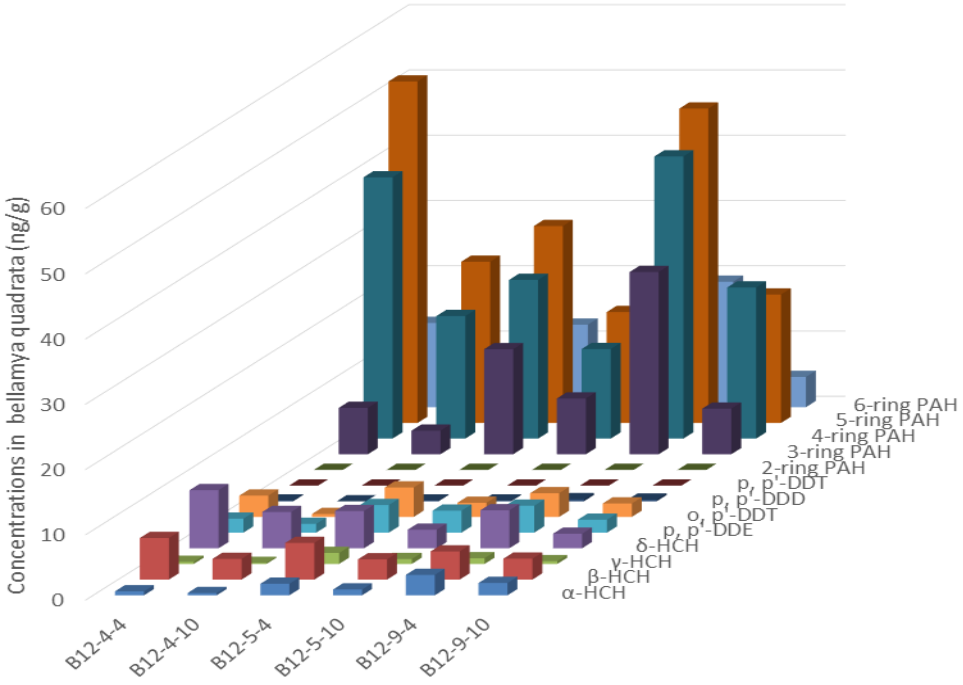


Figure S2 Correlation of biodegradable contaminants in the water and Chla in the water column for correlation coefficients at location 4, 5 and 9 collected during April, July and October in 2013.



Supporting Information, Figure S3. Concentrations of organic chemicals in *Bellamya quadratas* (ng/g) at blooming areas in April and October.

EXPERIMENTAL SECTION

Sampling. Phytoplankton nets were pre-cleaned with Milli-Q water and placed into a zip-sealed bag until opening on board for sampling. Nets were also washed with on site water samples for 3 times before sample collection. Sampling depth was from below the maximum of chlorophyll a (Chla) density depth to the surface. Unfiltered samples of phytoplankton in blooms were placed in brown glass bottles. Concentrations of Chla in water were measured *in situ* once two hours every day. The concentrations were averaged for each month.

Surface sediments (0-2 cm) were collected by use of a sediment gravity corer. Three cores were collected at each location at the same time, and about 2,000 g (wet mass) were composited from the surficial 2 cm. Any pebbles and twigs were removed before mixed thoroughly. Samples of sediment and phytoplankton were sent to the laboratory on ice and then freeze-dried within 24 h to minimize alteration of sample constituents and avoid the need to preserve or stabilize samples. Ground samples were stored at -20°C until extraction. Water (5 L) was collected at each location and placed into brown glass bottles. Samples were transported and stored at 4 °C and extracted within 24 h. The associated bottles were combusted at 450 °C for 4 h, then pre-cleaned with high-purity n-hexane (Merck Darmstadt, Germany), dichloromethane (Tedia Co. Ltd, Fairfield, OH, USA), acetone (Tedia Co. Ltd, Fairfield, OH, USA), methanol (Tedia Co. Ltd, Fairfield, OH, USA) and Milli-Q water. Bottles were also washed with water samples for 3 times before sample collection.

Sample preparation. For sediment and phytoplankton samples, 15 g of sediment or biota samples were extracted with Accelerated Solvent Extraction (Dionex ASE 300, Dionex, Idstein, Germany) with three extraction cycles of hexane/dichloromethane/acetone (4:4:1) at 100 °C and 103.4 bar with 10 min static time. Extracts were concentrated to 2 mL by rotary evaporation in a thermostatic bath and treated with activated copper granules to remove sulfur from the raw extracts (REs). Extracts were then added to a gel permeation chromatography column (GPC; Bio-Beads S-X3, J2 Scientific, AccuPrep MPS, 20 cm length and 3 cm i.d). For lipid and chlorophyll removal, the extracts were eluted with cyclohexane/ethyl acetate (1:1 v/v) and the elution from 2.7 to 25 min was collected. Sediment sample and phytoplankton sample pre-extracted with hexane, dichloromethane, acetone and methanol by ASE for 6 times were used as procedure blank for sediment and phytoplankton respectively. The blank samples were also extracted according to the procedure above-mentioned.

Water sample was not filtered. Solid phase extraction (SPE) was performed for each water sample (5L) using two tandem Oasis HLB cartridges (500 mg/ 6mL, Waters, USA). Cartridges were activated and conditioned with 10 ml of high-purity hexane, dichloromethane, acetone, methanol and Mili-Q water sequentially. Water was extracted under vacuum at a flow rate of 5-8 mL/min. Approximately 1 L of sample was passed through two tandem cartridges to avoid over filtration, and ten cartridges were used for the water samples from one site ((5L/1L)×2 cartridges=10 cartridges). Then the column was dried completely under a gentle stream of

nitrogen gas (99.999% pure). Chemicals were eluted with 10 mL hexane, 10 mL hexane: dichloromethane (1:1), followed by 10 mL acetone: methanol (1:1). The SPE extracts were combined into a composite sample and concentrated by rotary evaporation (type TVE-1000, EYELA, Tokyo, Japan) in a thermostatic bath. The milli-Q water used as procedure blanks was also extracted according to the procedure above-mentioned.

The GPC fractions and SPE extracts were concentrated and passed through 10 g of activated Florisil (60–100 mesh size; Sigma Chemical Co., St. Louis, MO, USA) packed in a glass column (10mm i.d.) for further clean-up and fractionation. The first fraction (F1) was eluted with 100 mL of high-purity hexane. The second fraction (F2) was eluted with 100 mL hexane/dichloromethane (4:1). The third fraction (F3) was eluted with 100 mL dichloromethane/methanol (1:1).

Instrumental Analysis. Organochlorine pesticides and sixteen priority PAHs were analyzed using a Thermo series II GC equipped with a triple quadrupole mass spectrometer operating in multiple- reaction monitoring (MRM) mode. Helium was used as carrier gas and flow rate was set at 1.0 mL/min. A pulsed splitless injector was used for injecting 1.5 μL of extract for analyzing phthalate esters. An Rtx-5MS column (30 m × 0.25 mm, film thickness 0.25 μm) was used for chemical separation for the target chemicals. Temperature of the inlet was set as 250 ℃. For PAHs, The initial oven temperature was set as 80 ℃, held at 80 ℃ for 2 min, heated to 180 ℃ at 15 ℃/min, held at 180 ℃ for 15 min, then heated to 300 ℃ at 15 ℃/min, and held at 300 ℃ for 5 min. For OCs, the oven temperature was set at 150 ℃, heated to 290 ℃ at 4 ℃/min, then heated to 310 ℃ at 15 ℃/min, and held at 310 ℃ for 5 min.

NP, OP and BPA were quantified using a reverse-phase high-performance liquid chromatography with tandem mass spectrometric (Thermo Electron Corporation, San Jose, CA, USA). The methanol and water (1:4, v/v) was used as the mobile phase from 0 min to 5 min, and methanol was used as the mobile phase from 5 min to 11 min. The flow rate was set as 200 μL/min. The temperature of column was set at 30 ℃.

QA/QC. During the process of instrumental analysis, internal standards including ^{13}C-PCB 141, acenaphthene-d10, pyrene-d10, bisphenol A-d14 and dibenzo(a,h)anthracene-d14 were added to the tested extracts before instrumental analysis for quality control of OC pesticides, PAHs and phenols. The regression coefficients (r^2) of calibration curves for all target chemicals were greater than 0.99.

Blank runs of the chromatograph and direct injections of dichloromethane or methanol were made to check the presence of target compounds in the chromatographic system. None of the target compounds was present in the chromatograms. In the present study, procedural blank analyses were initially carried out with Milli-Q water, pre-extracted sediment and phytoplankton for water, sediment and phytoplankton samples respectively. A procedural blank was performed for each batch of samples to check lab contamination. The limit of quantification (LOQ) was set at the laboratory LOQ which was ten times of S/N. All the contaminants in the procedural blanks were lower than the LOQ.

When sampling in each site, Milli-Q water, pre-extracted sediment and phytoplankton operated as the procedure of the sampling of water samples were used as the field blanks. Firstly, these field blanks were treated using the same methods with samples. Then they were detected by instrumental analysis. All target analytes in field blank were below their corresponding LOQs.

The procedural recovery and matrix spike recovery tests were conducted by spiking each target compounds into procedure blank samples and on field samples. The spiked levels for sediments and phytoplankton were 1, 5 and 20 ng/g, dm for OCs, PAHs and phenols. The spiked levels for water were 1, 5 and 20 ng/L for OCs, PAHs and phenols, respectively. Three replicates were conducted for QA/QC. The LOQs, procedural recoveries and matrix spike recoveries are shown in Table S2.

During sample analysis, quality control samples were consisted of duplicate samples, calibration check standards and solvent blanks. Duplicate samples were used to assure the precision and accuracy of each batch of samples, and the deviations of duplicate samples were less than 20%. Calibration check standards were run after every ten sample to check the instrument. If the calibration check standards were out of ± 20% of its theoretical value based on the calibration curve, a new calibration curve was prepared. Solvent blanks were run prior to every ten sample to check the instrumental background.

Diffusion and burial. The flux of dissolved compounds due to diffusion between sediment and water ($F_{seddiff}$ [ng m^{-2} d^{-1}]) is caculated as follows (Equation S1).

$$F_{seddiff} = -k_{seddiff}(C_w - \frac{Cs}{K_{sed}}) \quad \text{(S1)}$$

where C_S is the concentration in sediment [ng kg^{-1}], K_{sed} is the sediment water partition coefficient [m^3 kg^{-1}] calculated based on the study of (Meijer et al. 2006) using f_{oc}=0.041. C_s/K_{sed} was taken as the dissolved concentration in the pore water of the sediment [ngm^{-3}]. $k_{seddiff}$ is the sediment water diffusion coefficient [m d^{-1}], which was estimated from previous detection in Tai Lake as 0.08 (Zhu et al., 2007; Qiao et al. 2008; Fan et al., 2001)

The flux of compound from the surface sediment layer to the permanent sediment layer estimated (Equations S2 and S3).

$$F_{burial} = F_{settling}C_s \quad \text{(S2)}$$

$$F_{settling} = F_{OM} \times 2 \text{ kg } m^{-2} d^{-1} \quad \text{(S3)}$$

By assuming that F_{OM} is equal to vertical flux of organic carbon (F_{OC})

Bioconcentration of contaminants by phytoplankton. Knowledge of bioconcentration of organic contaminants by phytoplankton is essential to understanding factors that control bioaccumulation and biomagnification in the food web of the lake (Kelly et al., 2007). Lower levels of the trophic web could induce longer persistence and magnification potential for the organic contaminants, which could also lead to biomagnification and greater concentrations and potential risks to health of predators (Berrojalbiz et al., 2011). The bioconcentration factor (BCF)

value for lipophilic chemicals decreased slightly at the same location with time, which showed greater variability for different chemicals and such that it is difficult to understand the transfer trends in water and phytoplankton. This is consistent with the results of a study in Lake Maggiore in Italy (Nizzetto et al., 2012). Variations in BCF during blooms of cyanophyceae are due, in part, to changes in overall abundance of phytoplankton as well as the species present in the assemblage (Stange et al., 1994). Initially blooms consisted primarily of *Microcystis*, which was then followed by *Chlamydomonas spp.* in Tai Lake. Thus, greater variability in concentrations measured in the water column would be introduced, which is consistent with what is observed. As a result, BCFs were less useful for evaluation of transfers of lipophilic chemicals from water to phytoplankton.

Transfer trends in water and phytoplankton. The water-phytoplankton flux is useful to give estimates of contaminants those derived from the decrease of water column concentrations. When $F_{P\text{-}W}$ was calculated for lipophilic chemicals, $F_{P\text{-}W}$ was negative during the season when blooms of algae occurred and the net flux was from water to phytoplankton. Therefore, the water-to-phytoplankton system was presumably in disequilibrium during blooms. This trend became especially strong during the period of maximum biomass. Lipophilic chemicals with larger $\log K_{ow}$ values exhibit stronger associations with the BCF for phytoplankton (BCF_M, $m^3\ kg^{-1}$, see SI Methods for details). During the period of maximum biomass, the flux into phytoplankton of γ-HCH, *p, p'*-DDE and 5-ring PAH was greater. Greater fluxes of biogenic matter during the summer deplete concentrations in the water column, which results in a greater decrease in concentrations of lipophilic chemicals during periods of algae blooms. Results of previous studies have indicated that, annual blooms of phytoplankton could sink to the sediment as they die. It is suspected that, during the life cycle of cyanophyceae lipophilic chemicals are accumulated, and when algae die and settle to the bottom, organic chemicals were withdrawn from the water column and increased the concentrations in surface sediments in more eutrophic portions of lakes.

References

Berrojalbiz, N.; Dachs, J.; Del Vento, S.; Ojeda, M. J.; Valle, M. C.; Castro-Jimenez, J.; Mariani, G.; Wollgast, J.; Hanke, G., Persistent organic pollutants in Mediterranean seawater and processes affecting their accumulation in plankton. *Environ. Sci. Technol.* 2011, *45*, (10), 4315-4322.

Fan C.; Zhang L.; Qu W., Lake sediment resuspension and caused phosphate release-a simulation study. *J. Environ. Sci.* 2001, 13(4):406-410

Kelly, B. C.; Ikonomou, M. G.; Blair, J. D.; Morin, A. E.; Gobas, F. A., Food web-specific biomagnification of persistent organic pollutants. *Science* 2007, *317*, (5835), 236-239.

Nizzetto, L.; Gioia, R.; Li, J.; Borga, K.; Pomati, F.; Bettinetti, R.; Dachs, J.; Jones, K. C., Biological pump control of the fate and distribution of lipophilic organic pollutants in water and plankton. *Environ. Sci. Technol.* 2012, *46*, (6), 3204-3211.

Qiao M.; Huang S.; Wang Z., Partitioning Characteristics of PAHs Between Sediment and Water in a Shallow Lake. J Soils Sediments. 2008, 8(2): 69 – 73

157 Stange, K.; Swackhamer, D. L., Factors affecting phytoplankton species-specific differences in
158 accumulation of 40 polychlorinated biphenyls (PCBs). *Environ. Toxicol. Chem.* 1994, *13,* (11),
159 1849-1860.
160 This information is available free of charge via the Internet at http://pubs.acs.org/
161 Zhu, G.; Qin B.; Gao G.; Zhang L.; Luo L.; Zhang Y.;,Effects of hydrodynamics on phosphorus
162 concentrations in water of Lake Taihu, a large, shallow, eutrophic lake of China. *Hydrobiologia.*
163 2007, 581:53–61