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Bioassay-directed identification of toxicants in sediments of Liaohe River, northeast China☆

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A B S T R A C T

Contaminants accumulated in sediments may directly harm benthic organisms, however, the specific contaminants responsible for adverse effects have been poorly described. In this study, a bioassay-directed analysis combined with toxicity tests and chemistry analysis was conducted to determine the compounds eliciting the greatest toxicological effect in the sediments in Liaohe River, northeast China. A total of 24 sediment samples were examined to determine their acute toxicity to midge *Chironomus tentans* (*C. tentans*). Of these samples, 15 exhibited significant toxicity, with a mortality of 23%–93% ($p < 0.05$). Numerous contaminants, including 16 polycyclic aromatic hydrocarbons, 32 polychlorinated biphenyls, 20 organochlorine pesticides, 6 organophosphate pesticides, 8 pyrethroids, and 5 heavy metals were analyzed. On the basis of toxic unit (TU) analysis results, pyrethroids may contribute to the toxicity of 9 of the 15 toxic samples with concentrations of >1 TU. The significant correlation between the TUs of pyrethroids and the mortality of *C. tentans* ($r^2 = 0.74$, $p < 0.01$) confirmed the major role of pyrethroids in toxicity. The selected sediment samples responding to piperonyl butoxide and low temperature with the increased toxicity exhibited the characteristics of pyrethroids. The bioassay-based screening framework provided strong evidence that pyrethroids were the primary cause of sediment toxicity in Liaohe River. Further studies should therefore be conducted to regulate this important class of pollutants.

1. Introduction

Over the past several decades, rapid economic growth and urbanization have resulted in the deterioration of water quality in aquatic ecosystems in China. As such, the central and local governments of China have focused on water quality improvements; however, authorities have placed minor considerations on aquatic sediments in terms of practical water quality management. Sediments are important components of aquatic ecosystems providing habitat and feeding and spawning areas for aquatic organisms; sediments are also major repositories of chemical pollutants. High contaminant concentrations that accumulated in sediments are harmful to benthic organisms. Moreover, contaminated sediments adversely affect aquatic resources by causing ecological and economic damages, such as habitat degradation and costly remediation and disposal actions (Ho and Burgess, 2013). Therefore, sediment contamination should be characterized to promote sediment assessment and management during decision making.

Liaohe River is a heavily polluted river in northeast China. It consists of four big rivers, namely, Liao River, Taizi River, Hun River, and Daliao River. The middle- and down-stream of Liaohe River are the largest industrial bases of metallurgy, machinery, petrochemical, and building materials in northeast China. The pollution status of contaminants, including polycyclic aromatic hydrocarbons (Guo et al., 2007), organochlorine pesticides (Wang et al., 2007), polychlorinated biphenyls, polybrominated diphenyl ethers, polychlorinated dibenzo-*p*-dioxins (Lv et al., 2015; Zhang et al., 2010), short-chain chlorinated paraffins (Gao et al., 2012), and metals (He et al., 2015), in the sediments of Liaohe River have been extensively investigated. These studies have offered a good understanding of the occurrence and distribution of contaminants in this area but have provided limited information on their potential hazards to aquatic organisms. Hence, sediment-contact tests, which involve the exposure of benthic organisms to bulk sediments, are performed to assess the integrated effects of sediment-bound

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contaminants (Chapman and Anderson, 2005). When a positive toxic result is observed in a sediment, the sources of toxicity should be identified to determine the specific contaminants that need immediate attention and thus protect aquatic organisms and ecosystems (Anderson et al., 2010; Donnachie et al., 2014). Ke et al. (2015) examined sediments from Liao River to evaluate acute toxicity in midge larvae (*Chironomus riparius*) and found that As and Cd are probably associated with sediment toxicity. However, the identified toxicants have not been effectively confirmed, and the link between contaminant exposures and sediment toxicity remains unclear. To the best of our knowledge, limited data are available regarding the identification of active toxicants and establishment of cause-effect relationship. Specifically acting toxicants are difficult to identify because of the complexity of sediment matrix. Limited time and resources have also prompted researchers to devote appropriate mitigation efforts on highly toxic chemicals.

The primary objective of this study was to examine the spatial distribution and magnitude of sediment toxicity to midge *C. tentans* in Liaohe River. The specific contaminants responsible for the toxicity were further explored. Additionally, the relationship between contamination levels and toxic effects was discussed by integrating bioassays with chemical analysis. This study provided comprehensive insights into ecological hazards posed by sediments in Liaohe River, and helped screen the priority pollutants in this area. This bioassay-based screening framework is of ecological and economic importance to assist reliable mitigation and management measures.

2. Materials and methods

2.1. Sample collection

Twenty-four sediment samples (0–10 cm) were collected from Liaohe River with a Van Veen grab sampler in June 2014. Among these samples, nine (L1-L9) were from Liao River, five (H1–H5) from Hun River, six (T1–T6) from Taizi River, and four (D1-D4) from Daliao River (Fig. 1). At each sampling site, three replicate samples were collected, passed through a 2 mm mesh sieve, and then homogenized. Collected sediments were placed into sealed polyethylene bags, and transported on ice to the laboratory where they were stored at 4 °C for toxicity testing and at −20 °C for chemical analysis, respectively.

2.2. Chemical analysis

The pollutants including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), organophosphate pesticides (OPs), pyrethroids and inorganic heavy metals were selected as representatives of hazardous pollutants, due to their widespread distribution in sediment and potential toxicity to aquatic biota. The target compounds are shown in Table S1 in the supplementary materials. In addition, concentrations of acid-volatile sulfide (AVS) and simultaneously extracted metals (SEMs), total organic carbon (TOC) contents and sediment grain size (Table S2) were also analyzed. The details of chemicals and reagents, chemical analysis procedure and quality assurance and control are described in the supplementary materials.

2.3. Bulk sediment toxicity test

C. tentans (Diptera: Chironomidae), a native species in Liaohe River, was used as the test organism. The midges obtained from Ecotoxicology Laboratory of Nankai University were laboratory-cultured in accordance with standard protocols (USEPA, 2000). Sediment samples were screened for toxicity by using 10-day survival tests for *C. tentans*. In brief, 50 g of sediments was placed in three replicate beakers, and each beaker was filled with 200 mL of reconstituted water prepared by adding salts to Milli-Q purified water (USEPA, 2007). After sediments were settled overnight, 10 s- or third-instar larvae were randomly introduced to each beaker and fed with 6 mg of finely ground Tetrafin Goldfish Flakes per day. Tests were performed at 23 °C with a 16L: 8D photoperiod, and the overlying water was renewed twice daily. Temperature and dissolved oxygen were monitored on a daily basis; conductivity, pH, and ammonia were measured at the beginning and the end of the test. The samples containing dissolved oxygen with amounts decreased to 2.5 mg/L were gently aerated. Each test batch was accompanied by control sediments obtained from a drinking water reservoir. After 10 days, surviving larvae were sieved and counted; their ash-free dry mass (AFDM) was determined following the standard methods (USEPA, 2000).

2.4. Estimation of toxicity

The contribution of each contaminant to sediment toxicity was evaluated using a toxicity unit approach. The concentrations of contaminants in sediments were converted to TUs by dividing the 10-day sediment median lethal concentration (LC_{50}) for midges on an organic carbon-normalized basis [Eq. (1)]. Conservative sediment benchmarks were used for metals, PAHs, and PCBs because of a lack of sediment toxicity data.

$$TU = \frac{\text{Contaminant concentration in sediment/TOC}}{LC_{50}\ \text{or sediment benchmark/TOC}} \quad (1)$$

The TUs of metals were calculated on the basis of consensus-based probable effect concentrations (PECs). AVS-SEM models were also used to evaluate the toxicity contributed by metals (Table S3). The TUs of PAHs were estimated in terms of equilibrium-partitioning sediment benchmarks (ΣESBTUs; Table S4). For PCBs, the PEC of total PCBs was considered (Table S5). The sediment LC_{50} of pesticides was obtained from previous studies and listed in Tables S6–S8. For the TUs of hexachlorocyclohexane (HCH), the concentration of gamma isomer was used because other isomers exhibit lower aquatic toxicity (Eaton and Klaassen, 2001). LC_{50} of allethrin was unavailable; as such, a screening-level toxicity value was computed by using an equilibrium partitioning approach based on a water-column 24 h LC_{50} value (ECOTOX database) (Moran et al., 2011). The TUs of heavy metals were expressed as the average of five metals. For each class of organics, the TUs of individual contaminant were added to assess mixture toxicity. Moreover, the combined toxicity of pesticides was estimated based on concentration addition (Belden et al., 2007). The approximation of concentration was 0.5 TU when mortality likely occurred; this value was also considered a threshold, that is, at >0.5 TU, a contaminant was assumed potentially responsible for mortality (Weston et al., 2004).

2.5. Confirmation

Several lines of evidence were utilized to confirm possible toxicants. One approach was statistical correlation; in this approach, the estimated TUs of contaminants were plotted against the observed mortality. TU evaluation and statistical analysis suggested that pyrethroids may be the primary cause of toxicity; therefore, a focused toxicity identification evaluation (TIE), including piperonyl butoxide (PBO) addition and temperature manipulation, was applied to confirm their toxicity. PBO enhances

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