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Long-Term (1996–2006) Variation of Nitrogen and Phosphorus and Their Spatial Distributions in Tianjin Coastal Seawater

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Abstract The spatio-temporal varying characteristics of dissolved inorganic nitrogen, reactive phosphate (RP), chemical oxygen demand (COD), and dissolving oxygen (DO) in Tianjin coastal seawater were investigated based on observation from May 1996 to October 2006. The concentrations of dissolved inorganic nitrogen (DIN), RP and COD ascended gradually and their varying ranges were 0.103–2.432, 0.009–0.12, and 0.8–2.9 mg L^{-1}, respectively. While DO in seawater decreased from 8.9 to 6.1 mg L^{-1} gradually. Those indicated that human-induced eutrophication occurred and the seawater quality deteriorated. The spatial distributions of DIN, RP and COD were largely uniform, where isopleths generally descended from estuarine zones and bays to the central areas and from northern area to southern area, indicating that continental input is the dominant source of those pollutants. Especially, peak zones of those pollutants usually appeared near estuaries, Tianjin harbors, and dumping site of dredged sediment, which indicates that the urban and industrial sewage, shipping waste, dredged soil were the main sources for those contaminants in seawater.

Keywords Inorganic nitrogen · Reactive phosphate · Tianjin · Long-term variation

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Tianjin city is located at the northern China and the west of the Bohai Bay. It is the third largest industrial and commercial city in China. The urban sewage and industrial wastewater of Tianjin were drained into the Bohai Sea by Haihe River, Yongding River, Duliujian River and so on. Tianjin is a famous littoral city with the greatest harbor in China. Tianjin coastal sea has an area of 3,000 km^2 and a coastline of 153 km.

During the recent two decades, with rapid economic development, the seashore area of Tianjin has achieved much more than before in port construction, chemical industry, shipbuilding industry and coastal aquaculture. Meanwhile, the coastal eco-environment is seriously contaminated by the anthropogenic activities and the seawater quality deteriorated gradually.

In recent years, many studies have been carried out on the pollution status of Chinese coastal sea, including Jiaozhou Bay, Shenzhen Bay, South China Sea (Fu et al. 2007; Chen and Jiao 2007; Chen et al. 2006). Those studies mainly focused on heavy metals, PAHs, PCBs, surfactant and various pollutants in marine sediment. The studies on the seawater pollution of Bohai Bay (the coastal sea of Tianjin) were less than those of other marine areas in China. Wang and Wang (2007) had found that the concentrations of Pb, Hg, Cu and As in the seawater of Bohai Bay were significantly higher than those in other marine areas of the Bohai sea due to larger anthropogenic input. According to China ocean environmental quality bulletin (http://www.soa.gov.cn), the environmental quality of Tianjin coastal sea deteriorated at a rapid pace during the last decade and the inorganic nitrogen, and reactive phosphate were considered as the dominant pollutants, which will lead to seawater eutrophication and high frequent occurrence of algal blooms in seawater. The eutrophication problem is one of the most serious environmental issues in sea aquatic ecosystem and in long term this will profoundly influence the marine ecosystem structure (Lancelot et al. 1987). Since the algal blooms occurred in Taihu Lake and Caohu Lake in China, the eutrophication problem of inland lakes has attracted many researchers' interest (Yang et al. 2007; Wang et al. 2007). However, to our knowledge, there is rare study investigating the eutrophication problem of China coastal seawater though eutrophication is the principal factor influencing the seawater quality in China (http://www.soa.gov.cn).

The present paper is filling this gap and giving detailed information on the long-term variation and spatial distribution of nutrient elements including inorganic nitrogen and reactive phosphorus in the area of Tianjin coastal sea. Twenty-one sites (located from 117°37′ E to 118°00′ E, from 38°36′ N to 39°11′ N) located throughout the Tianjin coastal sea were selected as the sampling sites (Fig. 1). To investigate the influence of the inflowing rivers, dredged soil, and harbors on the distribution of inorganic nitrogen and reactive phosphates in Tianjin coastal sea, five sites near the estuarine zone of five rivers (sites of 2,7,12, 13 and 17), one site near dredged soil (site 18), two sites near Tianjin Harbor (sites of 6 and 8) were selected as the sampling sites, respectively. To evaluate seasonal variation of seawater quality, seawater samples were collected in three periods of one year, i.e., spring (May), summer (August) and autumn (October).

Materials and Methods

The seawater sampling procedure was based on the Standard Method of GB3097-1997. One liter of surface water was collected in glass bottles. All samples were transported to the laboratory, where water samples were filtered immediately with 0.45 μm (effective pore size) filters. Filtered water samples were extracted and analyzed within 3 days. The filters were stored at −20°C refrigerator.

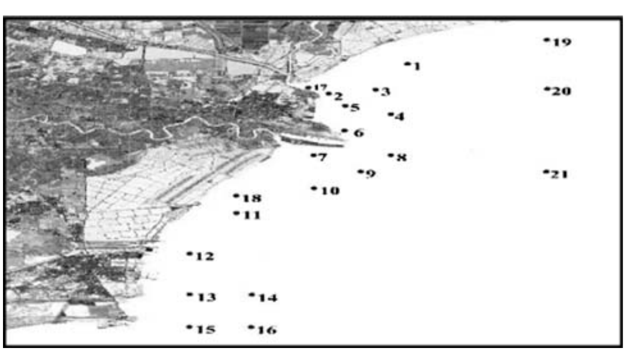


Fig. 1 Twenty-one sampling sites distributing throughout the Tianjin coastal sea

The parameters of water quality, including ammonium nitrogen (NH_4-N), nitrate nitrogen (NO_3-N), nitrite nitrogen (NO_2-N), reactive phosphates (RP), dissolved oxygen (DO), and chemical oxygen demand (COD), were measured in this study. Inorganic nutrients were determined directly after sampling, following classical spectrophotometric methods, i.e., Strickland and Parsons (1972) for NO_3-N, Grasshoff et al. (1983) for PO_4 and Koreleff (1969) for NH_4-N. The detection limits of NH_4-N, NO_3-N, NO_2-N and RP were 0.004, 0.007, 0.003 and 0.002 mg L^{-1}, respectively, in this study. And the analysis methods of COD and DO in seawaters were strongly based on the National Standard methods of GB17378.4-1998. Sea water's COD was measured by alkalic potassium permanganate and DO was measured by ometric method.

Results and Discussion

The spatio-temporal varying characteristics of inorganic nitrate (NO_2^-, NO_3^-, and NH_4^+), reactive phosphate, COD and DO were shown and elucidated in this section. The results of those parameters shown in long-term variations were the average values of all data obtained at twenty-one sites in every year. The result of each site in spatial distribution of every year was the average value of the data in three sampling periods.

As shown in Fig. 2, the nitrate nitrogen (NO_3-N) was the dominant component of inorganic nitrogen, followed by ammonium nitrogen (NH_4-N) and nitrite nitrogen (NO_2-N) in Tianjin coastal sea. The concentrations of NO_3-N, NH_4-N and NO_2-N in seawater were the minimum in 1996 with concentrations of 65.2 ± 32.7, 59.6 ± 43.8, and 17 ± 15.5 μg L^{-1}, respectively. As time goes on, concentrations of NO_3-N, NH_4-N and NO_2-N increased gradually and reached their maximum of 394 ± 291 302 ± 249 and

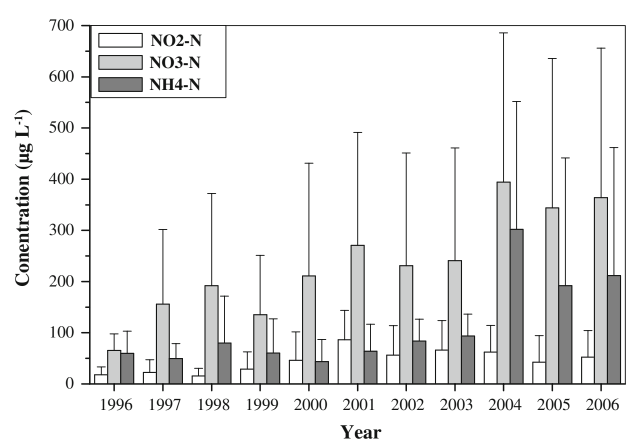


Fig. 2 Temporal variations of NO_2^-, NO_3^- and NH_4^+ from the year of 1996 to 2006 in Tianjin coastal sea

86 ± 57 μg L^{-1}, at the years of 2001, 2004 and 2004, respectively, which were almost six-times higher than their minimum levels. After the year of 2004, the concentrations of NO_3-N, NH_4-N and NO_2-N remained at the stable level in the following year. In Fig. 3, an annual ascending tendency was found in the concentration of inorganic nitrogen with its minimum (143 ± 68 μg L^{-1}) at 1996 and its maximum (699 ± 410 μg L^{-1}) at 2004. After 2004, the concentration of DIN showed an annual decreasing tendency, which might attribute to the increasing of treatment capacity of urban sewage in Tianjin.

The spatial distribution of inorganic nitrogen in Tianjin coastal Sea in 1996, 2000 and 2005 was shown in Fig. 4. In the year of 1996, the concentration of inorganic nitrogen was high (with average concentration of 200 μg L^{-1}) in the north of Tianjin costal sea including the sampling sites (1, 2, 4, 5, and 17) near the estuary of Haihe River and its adjacent area and low (with average concentration of 50 μg L^{-1}) in the southern oceanic area such as the sampling sites (7, 8, 9, 13, 16, 21) at offshore sea. From the year of 1996 to 2005, the difference of DIN concentrations between the northern area and southern area faded away gradually. In the year of 2005, the DIN concentration at the 11 sampling sites (account for 54%) was higher than 500 μg L^{-1}, which was slightly inferior to the grade-four sea water quality standard of China. Moreover, the sea water near the estuaries of Yongding River (sites of 2 and 17), Haihe River (sites of 6 and 7) and Duliujian River (site 12) with DIN concentrations above 800 μg L^{-1}, which indicated the discharge from those rivers was the dominant source of DIN in seawater and the significant increase of DIN input from rivers inflow in the year of 2005.

As shown in Fig. 3, the concentration of RP increased from its minimum (15.8 μg L^{-1}) at the year of 1996 to its maximum (32.9 μg L^{-1}) at the year of 2004, which indicates that the water quality of Tianjin coastal sea was deteriorated gradually and cannot reach to the grade-two sea water quality standard of China after the year of 2004 (as shown in Table 1). The horizontal distribution of RP indicated that in the year of 1996 RP concentration was higher in the northern area of Tianjin coastal sea compared with those in the southern area and showed its peak concentration near the Northern coastal sea, which was contaminated by industrial sewage from the Hangu city. In the year of 2001, the spatial distribution of RP was similar with that in 1996 but the peak zone appeared in the site 2 near the estuarine zone of Yongding River other than the site 1 near Hangu coastal sea. Moreover, two peak zones including site 1 and site 2 appeared in the spatial distribution of 2005 with the maximum concentrations of 85 μg L^{-1} and 71 μg L^{-1}, respectively. It should be noted that the RP concentrations in the inshore sea were

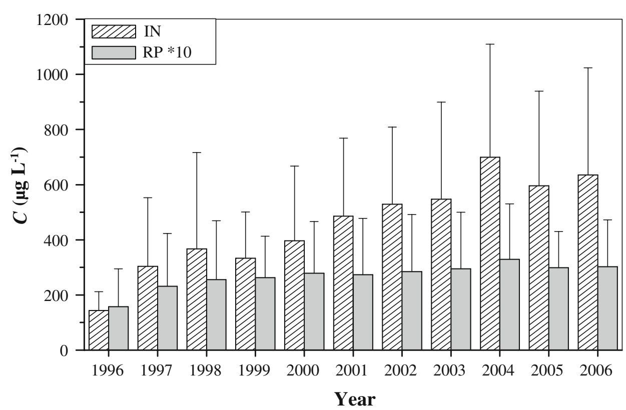
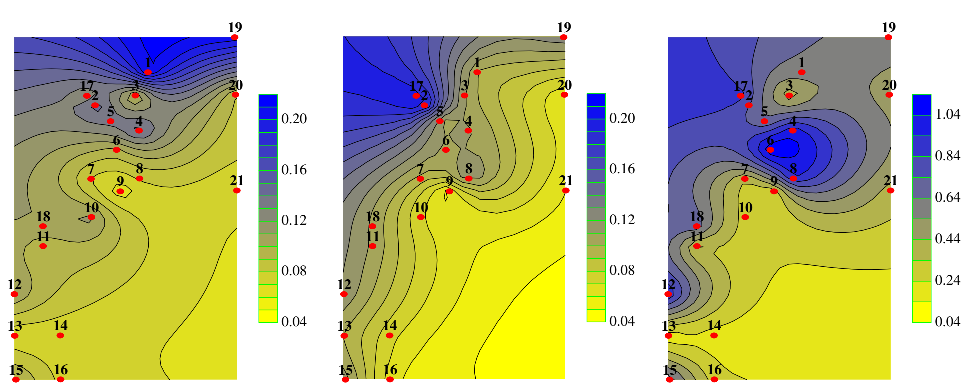


Fig. 3 Temporal variations of inorganic nitrogen (DIN) and reactive phosphate (RP) from the year of 1996 to 2006 in Tianjin coastal sea. The value of RP in plot was the ten-time of actual value

Table 1 Sea water quality standard of China for inorganic nitrogen and reactive phosphate

Sea-water quality standard	Grade-one	Grade-two	Grade-three	Grade-four
Inorganic nitrogen (μg L^{-1})	≤200	≤300	≤400	≤500
Reactive phosphate (μg L^{-1})	≤15	≤30	≤30	≤45
COD (mg L^{-1})	≤2	≤3	≤4	≤5
DO (mg L^{-1})	>6	>5	>4	>3

Fig. 4 Spatial distribution of concentration of inorganic nitrogen in Tianjin coastal sea in 1996, 2000 and 2005, respectively. (isopleths are mg L^{-1})



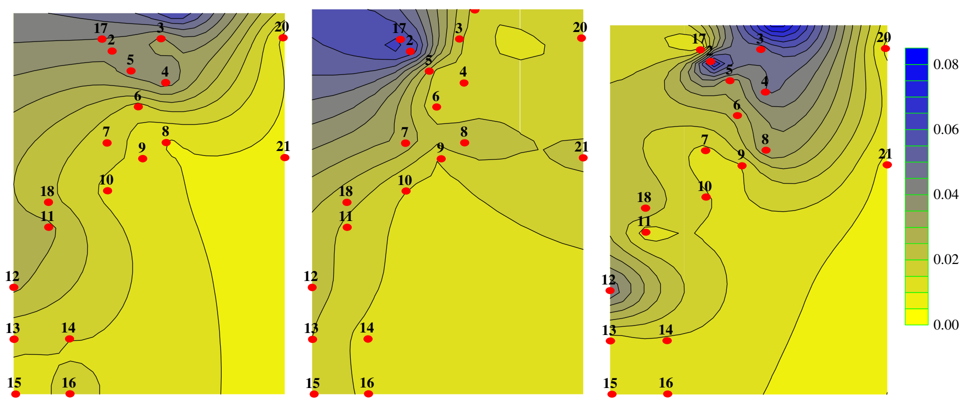


Fig. 5 Spatial distribution of concentration of reactive phosphate in Tianjin coastal sea in 1996, 2001 and 2005, respectively. (isopleths are mg L^{-1})

considerably higher than those of offshore sea in the 3 years, as shown in Fig. 5.

As shown in Fig. 6, the COD in Tianjin coastal sea increased from 1.26 mg L^{-1} in 1996 to 1.67 mg L^{-1} in 2006 and the DO decreased from 8.68 mg L^{-1} in 1996 to 7.28 mg L^{-1} in 2006. The varying tendencies of COD and DO indicated that the water quality of Tianjin coastal sea was deteriorating gradually, which is consistent with the conclusion from the tendency of DIN and RP. However, in terms of COD and DO, the seawater quality was superior to the Grade-one sea water quality standard of China, which implied the pollution from COD and DO in Tianjin seawater was minor compared with those from DIN and RP. The spatial distribution of COD (Fig. 7) in the year of 1996 indicated that the COD was higher in the sea near Tianjin harbor (site 6 and 8 with concentration of 1.5 mg L^{-1}) and marine aquaculture (site18 with concentration of 1.4 mg L^{-1}). In the year of 2001, the COD concentration in the estuarine zone of Yongding River (site 2 and 17 with concentration of 2.4 mg L^{-1}) was significantly higher than those of other area in Tianjin coastal area and also higher than those in 1996. In the year of 2005, the COD in almost all sampling sites were elevated compared with those same sites in 1996 and 2001, especially, the sites near Tianjin harbor and the estuarine zone of Yongding River with peak concentrations of 3.5 and 3.2 mg L^{-1}.

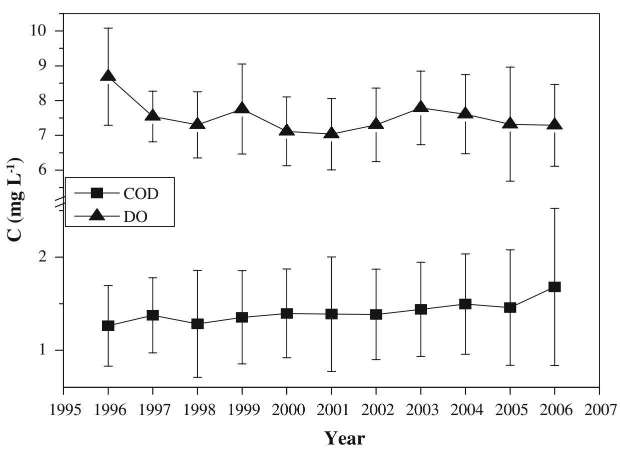


Fig. 6 Temporal variations of COD and DO from the year of 1996 to 2006 in Tianjin coastal sea

The temporal variations of DIN, RP, and COD in Tianjin coastal sea were almost similar with each other and all showed an ascending tendency while DO concentration decreased with the time. Those temporal variations indicated that the seawater was severely contaminated and the seawater quality was gradually deteriorated especially by the nutrient compositions (DIN and RP). Continental input and river inflow was considered as the dominant sources for DIN and RP. The annual average import of DIN, RP,

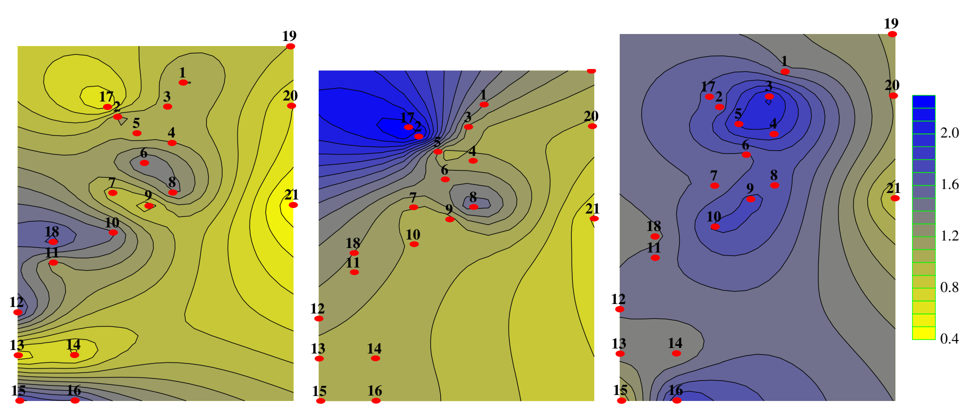


Fig. 7 Spatial distribution of concentration of COD in Tianjin coastal sea in 1996, 2001 and 2005, respectively. (isopleths are mg L^{-1})

and COD from sewage along the Tianjin coastal Sea was about 10,597 t, 684 t, and 443751t, respectively, in 2004 (SOA, 2004). In addition, industrial wastewater, shipping wastewater, discharge form dredged sediment, wastewater from marine aquaculture and so on were the important sources of the seawater pollutants.

As mentioned above in this section, in terms of DIN and RP, the water quality of Tianjin coastal sea was inferior to the Grade-three and even Grade-four Sea water quality standard of China while in terms of COD and DO the water quality was just inferior to the Grade-one in 2006. This phenomenon confirmed that the DIN and RP were the dominant pollutants in Tianjin coastal sea as the SOA conclusion.

As shown in Figs. 4 and 5, the spatial distributions of DIN and RP were extremely similar in the same year, which indicated DIN and RP had the common sources. It was reported that anthropogenic nitrogen in rivers mainly originates from the leaching of fertilized agricultural soils, from domestic wastewater discharge, and from atmospheric deposition while phosphorus is mainly linked to domestic wastewater (Brion et al. 2004). The similar distributing patterns of DIN and RP indicated that domestic wastewater was the common source for DIN and RP. In the years of 1996, the peak levels of DIN and RP appeared near estuarine zone of Yongding River, which indicated the rivers in flow was responsible for the high levels of DIN and RP. Yongding River is the drainage river of urban wastewater from Beijing city and Tanggu city. The spatial distribution of DIN and RP of 2001 was similar with that of 1996 but the peak concentrations were higher than those of 1996. Up to 2005, the distributing patterns of DIN and RP were quite different with those of 2001 and 1996. Peak zones appeared not only near estuarine zone of Yongding River but also near Tianjin harbor, estuarine zone of Haihe River and Duliujian River, Tanggu industrial district and the dumping site of dredged soil (site 18). In the spatial distribution of DIN and RP, isopleths largely descended from the inshore sea to the offshore, indicating continental inputs significantly elevates the levels of DIN and RP. Moreover, in the spatial distribution of 2005, some offshore sea (site 19) also with high DIN concentration indicated the continent input was not the only influence on pollutant levels. Wang and Wang (2007) reported that the dynamics of sea water masses or the biochemical processes can also influence the distributing pattern of oceanic pollutants.

The ascending tendency of average COD value in Tianjin coastal sea with the time indicated that the concentration of organic material in sea water was elevated gradually. The spatial distribution of COD in 1996 show high COD levels near Tianjin Harbor (sites 6 and 8) and the marine aquaculture (such as sites of 10 and 18), where many organic material was discharged. In the year of 1996, the estuarine zones were not the area with peak COD level while in 2001 the estuarine zones of Yongding River were the area with high COD level (near 2.20 mg L^{-1}). The spatial distribution of COD in 2006 was quite different with those of 1996 and 2001. COD level of most coastal sea (16 sites) was higher than 1.70 mg L^{-1} in 2005 but there were only 2 sites in 1996 and 2001. As shown in Fig. 7, the peak COD level appeared in the estuarine zones, which indicated the input from river drainage was the dominant source for COD in those years. DO in sea water has a negative correlation with COD. So the varying patterns of isopleths in DO spatial distribution were contrary to those of COD (Fig. 8).

From the long-term observation of Tianjin coastal seawater, it can be concluded that the seawater quality was deteriorated gradually. Inorganic nitrogen and reactive phosphate were considered as the dominant pollutants which had negative influence on seawater quality. In terms of DIN and RP, the seawater quality of Tianjin coastal sea were inferior to the Grade-four and Grade-two sea water quality standard of China, respectively, in most area of Tianjin coastal seawater in 2006. The spatial distributions of DIN, RP and COD were largely uniform, where isopleths generally descended from northern area to southern area and from estuarine zones and bays to the central areas. Conversely, for dissolved oxygen relatively high concentration was appeared in offshore areas but inshore area.

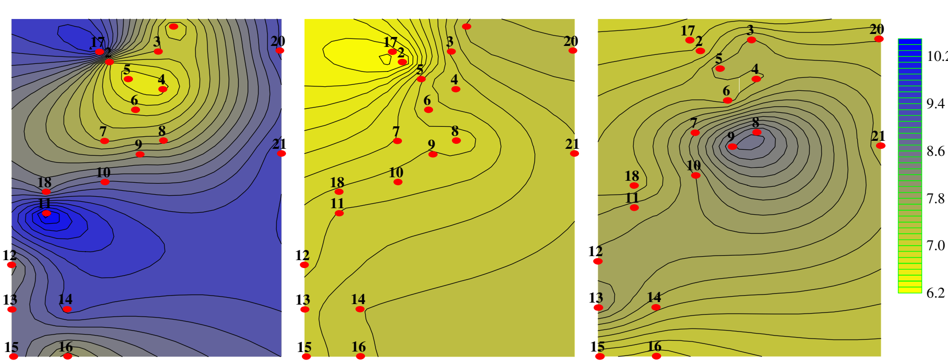


Fig. 8 Spatial distribution of concentration of DO in Tianjin coastal sea in 1996, 2001 and 2005, respectively. (isopleths are mg L^{-1})

Those varying pattern indicated the continent input from human activities was the dominant source to those pollutants. In addition, the discharge form the dredged soil was an important source.

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