The Increasing Accumulation of Pb Content in Marine Waters

Dongfang Yang¹, ², *, Dong Lin¹, Hong Zhu¹, Xianpeng Yuan¹, and Haixia Li¹

¹Accountancy School, Xijing University, Xi’an 710123, China;
²North China Sea Environmental Monitoring Center, SOA, Qingdao 266033, China;
*dfyang_dfyang@126.com

Abstract: Based on the investigation data of waters in Jiaozhou Bay in May, August and October, 1992, Pb content and horizontal distribution at surface waters in Jiaozhou Bay were studied in this paper. The results showed that the range of Pb content in Jiaozhou Bay was 3.87-37.90 μg/L corresponding to Class II, III and IV in accordance with Sea Water Quality Standard. It illustrated that in terms of Pb content in May, August and October, the entire waters in Jiaozhou Bay experienced low, medium and high pollution. The Pb content in Jiaozhou Bay was transported in four ways - ships and wharf, overland runoff, rivers and open ocean current, which was 16.34 μg/L, 14.85 μg/L, 13.25-37.90 μg/L and 13.25-37.53 μg/L respectively, shown in model diagrams. The transfer process of Pb content from the sources to the destinations was depicted in this paper to prove that Pb content causes pollution to the environment and ecology during temporal and spatial transfer.

1. Introduction
Heavy metal Pb is widely used in industry and agriculture. The continuous emission of Pb content to land, ocean and atmosphere brings about the pollution to global environment and ecology [1-6]. Hence, it is significant to analyze the pollution, pollution source and transfer process of Pb content in near ocean waters in a quantitative way [1-6]. According to the investigation data of 1992, horizontal distribution and source of the Pb content in Jiaozhou Bay were analyzed(Figure 1), and the water quality, source, source amount, transfer path and transfer process of Pb content in Jiaozhou Bay were studied, providing scientific reference for research on the source, pollution and transfer process of Pb in Jiaozhou Bay.
2. Investigated Waters, Materials and Methodology

2.1. The Natural Environment of Jiaozhou Bay.
Located in the southern Shandong Peninsula, at 120°04′-120°23′E and 35°58′-36°18′N, Jiaozhou Bay is a typical semi-closed bay bounded by Tuan Island and Xuejia Island and connected with the Yellow Sea, with an area of about 446 km² and an average water depth of about 7m. There are more than a dozen rivers running into the sea in Jiaozhou Bay, including Da gu River, Yanghe River, Haibo River, Licun River and Loushan River in Qingdao City. They are all seasonal rivers, which means they have obvious seasonal changes in terms of hydrological characteristics [7-8].

2.2. Materials and Methodology.
The investigation data of Pb content in Jiaozhou Bay in May, August and October, 1992 was provided by Beihai Monitoring Center, State Oceanic Administration. Samples of water were obtained from 13 sites in Jiaozhou Bay: 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 2104, 2105 and 2106 (Figure 1) in May, August and October, 1992, respectively. Besides, the samples were taken according to the depth of water (from surface and bottom layers when >10m, and surface layer when <10m) for investigation. What’s more, the research was done according to Specifications on Ocean Monitoring (1991) [9].

3. Results

3.1 Pb Content.
The Pb content in Class I, II, III and IV Sea Water Quality Standard was 1.00 μg/L, 5.00 μg/L, 10.00 μg/L and 50.00 μg/L, respectively. And in May, August and October, the range of Pb content in Jiaozhou Bay was 3.87-37.90 μg/L, so it was in Class II, III and IV.

In May, the range of Pb content in Jiaozhou Bay was 5.54-37.90 μg/L (Table 1). The first highest value of 37.90 μg/L occurred in the estuary nearshore waters of Licun River at site 58. Thus, Pb content was high in site 56, 57, 58, 2105 and 2104, the estuary nearshore waters of Licun River and northeastern bay, with a range of 12.84-37.90 μg/L, which was in Class IV. The second highest value range of 18.50-20.79 μg/L occurred in bay mouth at site 52 and 53, which matched the standard of Class IV. And the third highest value range of 14.50-16.34 μg/L appeared in the estuary nearshore waters of Haibo River at site 59 and 61, which agreed with the standard of Class IV. In addition, the lowest value range, 5.54-7.37 μg/L, was in eastern, central and southeastern bay at site 60, 55 and 2106, which exceeded the standard of Class II but corresponded to that of Class III. In a word, Pb content in May was relatively high in the entire Jiaozhou Bay and was in Class II, III and IV Sea Water Quality Standard.

In August, the Pb content range in Jiaozhou Bay was 5.53-37.53 μg/L (Table 1). The first highest value of 37.53 μg/L emerged in bay mouth at site 52, which agreed with the standard of Class IV. The highest value range of 11.30-27.44 μg/L existed in nearshore waters surrounding the bay at site 54, 55, 56, 57, 58, 59, 60, 61, 2104, 2105 and 2106, which matched the standard of Class IV. The lowest value range was 5.53 μg/L in central bay at site 55, which exceeded the standard of Class II but tallied with that of Class III. In short, in August, Pb content was high, matching Class III and IV.

In October, the range of Pb content in the bay was 3.87-14.85 μg/L (Table 1). The first highest value range of 14.79-14.85 μg/L was in northwestern and northern bay at site 56 and 57, which matched the standard of Class IV. The second highest value range of 13.25 μg/L appeared in bay mouth at site 52, which agreed with the standard of Class IV. The third highest value range of 13.25 μg/L existed in the estuary nearshore waters of Licun River at site 58, corresponding to the standard of Class IV. The lowest value range was 3.87-9.80 μg/L in eastern bay at site 54, 60, 61, 2106, 2105, and 2104, which tallied the standard of Class II and III. In brief, Pb content in October was relatively low in the entire Jiaozhou Bay with a range, which agreed with Class II, III and IV.

Hence, in May, August and October, the variation range of Pb content in Jiaozhou Bay was 3.87-37.90 μg/L, tallying with the water quality of Class II, III and IV. And it indicated that in May,
August and October, the entire Jiaozhou Bay waters experienced low, medium and high pollution of Pb (Table 1).

| Pb content in sea water/μg·L⁻¹ | May     | August | October |
|-------------------------------|---------|--------|---------|
| Sea Water Quality Standard    | Class III and IV | Class III and IV | Class II, III and IV |

Figure 2 Pb content distribution at the surface in Jiaozhou Bay in May(μg/L)

3.2 The Horizontal Distribution at Surface Layer.
In May, the highest value of 37.90 μg/L emerged in estuary nearshore waters of Licun River at site 58, forming a high content range with the estuary nearshore waters of Licun River as the center as well as a series of semicircles at different gradients. Pb content decreased progressively from 37.90 μg/L at center to 18.27 μg/L at northeastern bay, 13.72 μg/L at northern bay and 7.37 μg/L at central bay (Figure 2). The highest value of 16.34 μg/L was in eastern nearshore waters at site 61, which formed a high content range with eastern nearshore waters as the center and a series of semicircles at different gradients. And Pb content decreased continuously from 16.34 μg/L at center to 14.50 μg/L at estuary nearshore waters of Haibo River and 7.37 μg/L at central bay (Figure 2). In bay mouth at site 52, the highest value was 20.79 μg/L, forming a high content range with bay mouth as the center in addition to a series of semicircles at different gradients. Pb content decreased steadily from 20.79 μg/L at center to 14.50 μg/L at northwestern inside bay mouth and 5.54 μg/L at northeastern inside bay mouth (Figure 2).

In August, the highest value of 37.53 μg/L existed in bay mouth at site 52, forming a high content range with the bay mouth as the center in addition to a series of semicircles at different gradients. Pb content decreased continuously from 37.53 μg/L at center to 6.98 μg/L at northwestern inside bay mouth and 11.30 μg/L at northeastern inside bay mouth (Figure 3). The value of 25.45 μg/L was in estuary nearshore waters of Haibo River at site 59, forming a high content range with estuary waters as the center and a series of semicircles at different gradients. Pb content decreased steadily from 25.45 μg/L at center to 13.91 μg/L at southwestern estuary and 20.61 μg/L at northeastern estuary (Figure 3). In estuary nearshore waters of Licun River at site 58, the value was 26.21 μg/L, which formed a high content range with estuary waters as the center, beside a series of semicircles at different gradients. In estuary nearshore waters of Loushan River at site 2104, the value was 26.92 μg/L, forming a high content range with estuary waters as the center, apart from a series of semicircles at different gradients. In estuary nearshore waters of Dagu River at site 56, the value was 26.81 μg/L, which formed a high
content range with estuary waters as the center and a series of semicircles at different gradients.

In October, the value range of 14.79-14.85 μg/L appeared in northwestern and northern bay at site 56 and 57, forming a high content range with northwestern and northern bay as the center as well as a series of semicircles at different gradients (Figure 4). In bay mouth at site 52, the highest value 13.25 μg/L, formed a high content range with bay mouth as the center besides a series of semicircles at different gradients. Pb content decreased progressively from 13.25 μg/L at center to 9.47 μg/L at northwestern inside bay mouth and 9.67 μg/L at northeastern inside bay mouth (Figure 4). Further, in estuary nearshore waters of Licun River at site 58, the value was 13.25 μg/L, forming a high content range with estuary waters as the center apart from a series of semicircles at different gradients (Figure 4).

4. Discussion

4.1 The Water Quality.
In May, August and October, the range of Pb content in Jiaozhou Bay was 3.87-37.90 μg/L, which was in Class II, III and IV, proving that in May, August and October, the entire Jiaozhou Bay waters experienced low, medium and high pollution of Pb.
In May, the range of Pb content in Jiaozhou Bay was 5.54-37.90 μg/L, indicating that there existed serious and medium pollution in waters of Jiaozhou Bay. In estuary nearshore waters of Licun River and northeastern bay, the range of Pb content was 12.84-37.90 μg/L, showing that the water quality reached the standard of Class IV, which means waters were severely polluted. Similarly, the range 18.50-20.79 μg/L and 14.50-16.34 μg/L in bay mouth and estuary nearshore waters of Haibo River respectively showed the severe pollution. In eastern, central and southeastern bay, the range of Pb content was relatively low 5.54-7.37 μg/L, which shows that the water quality reached the standard of Class III. In other words, there was medium pollution.

In August, the range of Pb content was as high as 5.53-37.53 μg/L corresponding to standards of Class III and IV, indicating that Jiaozhou Bay waters were polluted in medium and severe way. The Pb content 37.53μg/L at bay mouth and 11.30-27.44μg/L at nearshore waters surrounding the bay match the standard of Class IV, which means waters are severely affected by pollution. In central bay, the Pb content was relatively low 5.53 μg/L, showing that the water quality reached the standard of Class III; that is to say, there was medium pollution.

In October, the range of Pb content was as low as 3.87-14.85 μg/L, which agreed with standards of Class II, III and IV, showing that there was low, medium and severe pollution in waters of Jiaozhou Bay. The range 14.79-14.85 μg/L and 13.25 μg/L respectively in northwestern and northern bay, and bay mouth and estuary nearshore waters of Licun River proved that the water quality reached the standard of Class IV, which means waters had severe pollution. In eastern and northeastern bay, the Pb content was 3.87-4.21 μg/L, indicating that the water quality matched the standard of Class II. In other words, there was low pollution. And in other waters farther from high-value and low-value waters, such as southwestern bay, the range of Pb content was 6.41-9.47 μg/L, indicating that the water quality corresponded to the standard of Class III. Waters were affected by medium pollution.

4.2 Sources.
In May, the high-content area was formed in estuary nearshore waters of Licun River with the Pb content of 37.90 μg/L, showing that the pollution source was Licun River. Further, the high-content area in eastern nearshore waters with the content of 16.34 μg/L proved that the source was ships and wharf. Besides the high-content area existing in bay mouth with the content of 20.79 μg/L indicated that the pollution was from open ocean current.

In August, the high-content area appearing in bay mouth with the high content of 37.53 μg/L showed that the source was open ocean current.

In October, the high-content area was formed in northwestern bay with the Pb content of 14.79 μg/L, indicating that the pollution source was Dagu River. In addition, the high-content area in northern bay with the content of 14.85 μg/L showed that the pollution was from overland runoff. Furthermore, the high-content area formed in bay mouth with the content of 13.25 μg/L proved that the source was open ocean current. What’s more, the high-content area existing in estuary nearshore waters of Licun River with the content of 13.25 μg/L indicated that the pollution came from Licun River.

In conclusion, there were four sources of Pb content in Jiaozhou Bay - ships and wharf, overland runoff, rivers and open ocean current, which were 16.34 μg/L, 14.85 μg/L, 13.25-37.90 μg/L and 13.25-37.53 μg/L respectively. The transportation in these four ways exceeded the standard of Class III, but matched that of Class IV - severe pollution (Table 2).

| Sources                  | Ships and wharf | Overland runoff | Rivers     | Open ocean current |
|--------------------------|-----------------|-----------------|------------|--------------------|
| Pb content/μg·L⁻¹        | 16.34           | 14.85           | 13.25-37.90| 13.25-37.53        |

4.3 Transportation Paths of Pb Content.
The main sources of Pb content in Jiaozhou Bay were ships and wharf, overland runoff, rivers and
open ocean current. In these four ways, Pb content was transported to the land, open ocean and waters in Jiaozhou Bay by human activities. Firstly, Pb content was emitted to the ocean via the transportation of ships and wharf, which was 16.34 μg/L. Secondly, Pb content was sent out to land via the transportation of rainwater and overland runoff, which was 14.85 μg/L. Thirdly, Pb content was discharged to land and ocean via the transportation of rivers on land, which was 13.25-37.90 μg/L. Fourthly, Pb content was emitted to land and transported to waters via open ocean current, which was 13.25-37.53 μg/L. The four paths for transportation of Pb content to ocean waters in Jiaozhou Bay are displayed (Figure 5).

![Figure 5 The transport paths of Pb contents into ocean](image)

The relatively low Pb content of 14.85 μg/L transported to ocean via overland runoff showed little Pb content emission to land. Besides, the relatively high Pb content of 16.34 μg/L moved to ocean via ships and wharf proved higher Pb content emission to ocean with the increasing ships. In addition, the high Pb content of 13.25-37.90 μg/L transported to ocean via rivers indicated the high Pb content accumulating by rivers on land. Further, the high Pb content of 13.25-37.53 μg/L transported to ocean via open ocean current showed that the Pb content was transported continuously via ships and wharf, overland runoff and rivers from the land to ocean, causing serious pollution to ocean.

4.4 The Sources and Destinations of Pb Content.
The great use of products containing Pb caused many emissions to the atmosphere, land and ocean. The Pb content in the atmosphere was sedimented to land and ocean then transported to ocean waters. In addition, in ocean waters, Pb content was transported from high-content area to low-content area. In Jiaozhou Bay, the sources of Pb content mainly included ships and wharf, overland runoff, rivers and open ocean current, displaying four different transfer paths of Pb content.

Based on the above transfer paths of Pb content, the transfer process was put forward in this paper. Firstly, Pb was emitted into the atmosphere then sedimented to land and ocean. Secondly, Pb content was moved to the ocean via ships and wharf. Thirdly, Pb content was transported to the ocean via overland runoff. Fourthly, Pb content was transported to the ocean via rivers. Lastly, in ocean waters, Pb content was transported from high-content area to low-content area. Therefore, the Pb content in ocean waters includes the Pb content stored in ocean waters and sedimented on the sea floor. Overall, the transfer process of Pb content was presented (Figure 6).
5. Conclusion
In May, August and October, the range of Pb content in Jiaozhou Bay was 3.87-37.90 μg/L, which corresponded to the water quality of Class II, III and IV. It indicated that in May, August and October, the whole Jiaozhou Bay waters experienced low, medium and high pollution of Pb.

In May, the range of Pb content was 5.54-37.90 μg/L, indicating that there existed medium and severe pollution in waters of Jiaozhou Bay. In estuary nearshore waters of Licun River and Haibo River, northeastern bay and bay mouth, the range of Pb content showed serious pollution. While in eastern, central and southeastern bay, the range of Pb content proved medium pollution to waters.

In August, the range of Pb content was as high as 5.53-37.53 μg/L, indicating that there was medium and severe pollution in waters of Jiaozhou Bay. The Pb content at bay mouth and nearshore waters surrounding the bay caused serious pollution to waters. And in central bay, the Pb content showed medium pollution to waters.

In October, the range of Pb content was as low as 3.87-14.85 μg/L, indicating that there existed low, medium and serious pollution in waters of Jiaozhou Bay. The range in northwestern and northern bay, and bay mouth and estuary nearshore waters of Licun River proved that waters were severely polluted. In eastern and northeastern bay, the Pb content caused low pollution to water. Besides, in other waters, such as southwestern bay, the range of Pb content showed that waters were affected by medium pollution.

There were four sources of Pb content in Jiaozhou Bay - ships and wharf, overland runoff, rivers and open ocean current, which caused severe pollution.

From land, ocean to waters in Jiaozhou Bay, the transfer of Pb content displayed four different paths. Firstly, Pb content was discharged to the ocean via ships and wharf transportation. Secondly, Pb content was emitted to land via the transportation of rainwater and overland runoff. Thirdly, Pb content was emitted to the ocean via river transport. Fourthly, Pb content was transported from high-content waters to low-content waters. The four paths were shown in the model diagram.

The transfer process of Pb content was put forward in this paper. Firstly, Pb was emitted into the atmosphere, then sedimented to land and ocean. Secondly, Pb content was transported to the ocean via ships and wharf. Thirdly, Pb content was transported to the ocean via overland runoff. Fourthly, Pb content was transported to the ocean via rivers. Lastly, in ocean waters, Pb content was transported from high-content area to low-content area. Thus, Pb content caused pollution to the environment and
ecology during the temporal and spatial transfer.

Acknowledgements
This research was sponsored by Doctoral Degree Construction Library of Guizhou Nationalities University and Research Projects of Guizhou Nationalities University ([2014]02), Research Projects of Guizhou Province Ministry of Education (KY [2014] 266), Research Projects of Guizhou Province Ministry of Science and Technology (LH [2014] 7376).

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