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Influence of salinity on COD measurements in coastal water management

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ABSTRACT

Chemical oxygen demand (COD) is an important parameter in water quality assessment. COD values by different determination methods were investigated in coastal rivers. The results show that there is no clear relationship between COD_{Cr} and COD_{Mn} in coastal areas. COD_{Cr} does not reflect the degree of pollution of coastal waters. As salinity increased, COD_{Cr} and acidic COD_{Mn} increased significantly, but there was little/no change observed for alkaline COD_{Mn}. Coastal zone water quality standards should be proposed to solve connection problems between marine quality standard and surface water quality standard.

Keywords: COD; Salinity; Coastal waters; Water quality standard

1. Introduction

Chemical oxygen demand (COD) is one of the most widely used parameters for water quality monitoring and assessment. It provides information about the readily oxidized fraction of the organic load or reduced compounds in waters, indicating the degree of water pollution [1]. COD therefore plays an important role in water pollution control and surface water management [2,3]. According to the species of oxidizing agents, COD can be divided into COD_{Cr} and COD_{Mn}, depending on whether potassium dichromate (K₂Cr₂O₇) or potassium permanganate (KMnO₄) is used as the oxidizing agent in the process of COD analysis [4]. K₂Cr₂O₇ has a stronger oxidation capability than KMnO₄, and is capable of completely

oxidizing most organic compounds in water. Generally, COD_{Cr} is applied in surface waters (e.g. lakes and rivers) and wastewater, and COD_{Mn} is applied in lightly polluted waters, e.g. reservoir, tap water, and seawater. For the determination of COD in coastal waters (river, estuary, and near shore bay), there is no commonly adopted method.

Rapid industrialization, urbanization, and population growth lead to pollution of rivers and estuaries and degradation of ecosystems; therefore, the water quality in the coastal zone is receiving more and more attention [5–7]. COD is the most commonly used indicator to evaluate water quality. However, because COD_{Cr} measurement is influenced by high concentrations of chloride or bromine ions [8,9], and COD_{Mn} does not reflect the actual degree of pollution, neither method is really applicable to brackish and saline waters. Previous studies on COD have mostly focused

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on how to improve the measurement accuracy e.g. [1–4,10], but relatively few have looked at how to select an appropriate method for a particular salinity [11–13]. In the coastal zone, estuaries vary from brackish to fully saline, and due to the high concentrations of chloride and bromine (which can be oxidized by $K_2Cr_2O_7$ under acid conditions), the COD_{Cr} values are elevated. Similarly, heavily polluted river water results in higher COD_{Mn} than actual values because of multiple dilutions before analysis. In this study, we applied a systematic testing of both COD methods in three rivers and a reservoir in Yantai (China) in order to determine if there is an optimum approach to measuring COD within the coastal zone, or whether all the existing methods are inappropriate.

2. Methods and materials

2.1. Samples collection and handling

Water samples were collected from a total of 20 sampling sites in Menlou Reservoir, Jiahe River, Guandonghe River, and Yuniaohe River in Yantai, China (Fig. 1). All sampling equipment and storage containers were cleaned with distilled water before use. Samples from ~20 cm below the water surface were taken using 500-mL polypropylene vials. Samples were collected without disturbing the sediment–water interface. The vials were fully filled with water, sealed with gas-tight screw-caps, and immediately kept in an adiabatic box with ice until further analysis. Before analysis, all samples were shaken in a sealed condition.

2.2. Measurements and methods

Reagents used were all of analytical grade or above, and deionized water (milli-Q) was used to

prepare reagent solutions. Concentrations of COD_{Cr} and COD_{Mn} were measured with the method specified in the standard methods for examination of water and wastewater [APHA, 1998] [14]. Dissolved oxygen (DO), pH, temperature (T), salinity, and oxidation reduction potential (ORP) were measured using a YSI Professional Plus Handheld DO and Temperature System purchased from TechTrend International Limited, USA. The relative standard deviation of the measurements was <8% based on triplicate water analyses.

2.3. Design of modeling test for influence of salinity on COD measurement

Based on salinity variations in coastal rivers, waters of different salinity were prepared with freshwater (sampled from upstream of the Yuniaohe River) and seawater (offshore area of the Yuniaohe River estuary). Three groups of experiments were set up to determine the different COD values (COD_{Cr} , acid COD_{Mn} , and alkaline COD_{Mn}): forty-five 500-ml beakers were divided into three groups of 15 beakers. For each group, different volume ratios of freshwater and seawater were added to these beakers to give a final salinity of 0.5 (100% freshwater), 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 18, 24, and 31 PSU (100% seawater), respectively. Then, the different COD were measured to investigate the influence of salinity.

3. Results and discussion

3.1. COD in different coastal rivers and their correlations

COD values (average of triplicate tests) for different sampling sites in the Guandonghe River and the Yuniaohe River are presented in Table 1. The concentrations of COD_{Cr} were 15–423 $mg\ L^{-1}$ in the Guandonghe River and 31–1,312 $mg\ L^{-1}$ in the Yuniaohe River. The concentrations of acidic COD_{Mn} and alkaline COD_{Mn} were 6–31 and 5–20 $mg\ L^{-1}$ in the Guandonghe River and 6–24 and 5–25 $mg\ L^{-1}$ in the Yuniaohe River. The highest values of COD_{Cr} were recorded in the estuarine sections of both rivers (sites P and T).

The standard electrode potential of Cl/Cl^- (1.36 V) and Br/Br^- (1.087 V) is much lower than the electrode potential of $Cr_2O_7^{2-}/Cr^{3+}$ (1.55 V), so Cl^- and Br^- in estuarine water can be oxidized by $K_2Cr_2O_7$ (Eqs. (1) and (2)) during the COD_{Cr} analysis process, resulting in elevated measurement values [8,15]. Furthermore, the organic matter in all water samples can be oxidized by acidic $K_2Cr_2O_7$ with the help of the silver sulfate catalytic effect (Eq. (3)). In this process, organic matter first oxidizes to organic

Fig. 1. Schematic graph showing sampling sites.

Fig. 2. Relationships among COD_{Cr}, acidic COD_{Mn}, and alkaline COD_{Mn} in the Jiahe River. (a), (c), and (e) were fitted by data excluding the highly saline point, and (b), (d), and (f) were fitted by the data of all sampling sites.

acid, then reacts with Ag⁺ to form organic acid salts, and then generates carbon dioxide and water. Finally, the organic carbon chains transfer to carbon dioxide and water. Therefore, without the presence of Ag⁺, organic matter can only be oxidized to organic acid. However, Cl⁻ and Br⁻ in brackish/saline water decrease silver availability by precipitation of solid AgCl and AgBr. This process restrains the reaction of organic acid into carbon dioxide and water because of Ag⁺ decrease, resulting in a lower COD_{Cr} value

lower than the actual value. But in comparison, the contribution of the former is larger than that of the latter, so the measurement value is higher than normal. Therefore, COD_{Cr} values are not suitable for coastal water quality assessment:

Fig. 3. Influence of salinity on different COD measurements.

Highest acidic COD_{Mn} was measured in the estuarine sites of the Guangdongge and Yuniaohe rivers. However, alkaline COD_{Mn} in these rivers was unstable, and the highest value was not in the estuarine site. This is primarily associated with the unique characteristics of water quality in estuaries and the oxidation strength of oxidants. Under the condition of acidic and alkaline solutions, the standard electrode potential of $\text{MnO}_4^-/\text{Mn}^{2+}$ is 1.49 and 0.588 V, respectively. So, Cl^- (Cl/Cl^- , 1.36 V) and Br^- (Br/Br^- , 1.087 V) in water samples could be oxidized by acidic KMnO_4 (Eqs. (4) and (5)) rather than alkaline $\text{K}_2\text{Cr}_2\text{O}_7$:

For each river, there was a big difference between different COD methods. For example, in the Guangdongge River, the concentrations of COD_{Cr} , acidic COD_{Mn} , and alkaline COD_{Mn} were ~ 430 , ~ 32 , and $\sim 20 \text{ mg L}^{-1}$, respectively. This may be related to the oxidation strength of oxidants and the degree of water pollution. $\text{K}_2\text{Cr}_2\text{O}_7$ used in the COD_{Cr} analysis is a strong oxidizing agent under acidic conditions (acidity is achieved by the addition of sulfuric acid). It can oxidize almost all organic matter, anions, and oxidizable inorganic materials in waters, including Cl^- , Br^- , and NO_2^- , resulting in high values in different COD analyses. However, alkaline KMnO_4 can merely oxidize some of the organic matter, NO_2^- and some reductive compounds [16]. Because Cl^- and Br^- can be oxidized by acidic $\text{K}_2\text{Cr}_2\text{O}_7$ and acidic KMnO_4 , the alkaline KMnO_4 method was applied in COD measurement in seawater or halogen containing wastewater [13].

Table 1

The COD values in the Guangdanghe and Yuniaohe rivers

	Sampling site	COD _{Cr} (mg L ⁻¹)	COD _{Mn} (mg L ⁻¹)	
			Acid method	Alkaline method
Guangdanghe river	M	15.11	5.96	5.02
	N	78.40	21.73	19.36
	O	122.30	25.65	20.24
	P	423.36	31.53	17.44
Yuniaohe river	Q	31.36	6.24	5.33
	R	86.24	23.84	24.56
	S	47.04	7.84	5.65
	T	1,312.42	23.05	4.86

In order to investigate the relationship between COD value and salinity, the analysis of waters in the whole watershed of the Jiahe River (from upstream, Menlou reservoir to estuary, Fig. 1) was conducted and the results are listed in Table 2. The concentrations of COD_{Cr}, acidic COD_{Mn}, and alkaline COD_{Mn} in the Jiahe River were 8–493, 3–18, and 3–11 mg L⁻¹, respectively, with the salinity variation of 0.3–14 PSU. In the estuary (site L), the concentrations of COD_{Cr} and acidic COD_{Mn} reached ~490 and ~18 mg L⁻¹, respectively, much higher than those in other sites. The value of salinity was ~14 PSU at the estuary, which was also much higher than that in other sites of the river. In contrast, COD_{Cr} and acid COD_{Mn} results were elevated at sites K and L (with high salinity), respectively. These phenomena confirmed the previous hypothesis that COD determination was greatly influenced by salinity except for alkaline COD_{Mn}.

Generally, COD_{Cr} is 2–7 times higher than COD_{Mn} in freshwater, so a rough COD_{Mn} value can be obtained through COD_{Cr} to assess water quality.

However, in this study, COD_{Cr} is orders of magnitude higher than COD_{Mn} in the sections with high salinity. Furthermore, there is no obvious correlation between COD_{Mn} and salinity in the river–estuary system. Therefore, it is not feasible to get a rough COD_{Mn} value from COD_{Cr}.

Empirically, many engineers use COD_{Cr} to estimate a COD_{Mn} value in engineering or fieldwork [17,18], but this estimation must rely on stable and simple water chemistry. In this study, the composition of river water was complex (river water plus discharges of wastewater plus tidal mixing with seawater at the seaward end), and there was no obvious positive correlation between COD_{Cr} with which to estimate COD_{Mn}. In order to observe the relationship between COD_{Cr}, acidic COD_{Mn}, and alkaline COD_{Mn} in the Jiahe River, linear fitting of different COD values at each sampling site (Fig. 1) is illustrated in Fig. 2. In this figure, (a), (c), and (e) were fitted by data excluding the highly saline point (sampling point L), and (b), (d), and (f) were fitted by the data of all sampling sites (point L involved).

Table 2

Parameters in different sampling sites of the Jiahe River valley

Site	DO (mg L ⁻¹)	Temp. (°C)	Cond. (ms cm ⁻¹)	Sal. (PSU)	pH	ORP (mV)	COD _{Cr} (mg L ⁻¹)	COD _{Mn} (mg L ⁻¹)	
								Acid	Alkaline
A	7.60	26.2	0.85	0.40	8.28	265.6	24.74	4.40	4.00
B	8.69	27.3	0.87	0.41	8.57	237.1	8.25	3.38	3.26
C	8.04	29.9	0.91	0.40	8.57	230.4	11.55	3.40	3.37
D	8.89	30.3	0.68	0.30	9.10	305.5	28.04	5.36	5.18
E	10.77	30.8	0.62	0.26	9.34	262.8	18.15	4.57	4.97
F	9.22	30.1	0.63	0.28	9.25	212.3	24.74	4.88	5.20
G	9.10	28.7	0.61	0.27	9.01	254.5	9.90	4.80	4.97
H	7.87	29.6	0.73	0.33	8.82	257.2	16.50	5.19	5.29
I	13.62	30.3	0.63	0.27	9.58	197.1	26.39	6.08	6.04
J	14.58	29.9	0.73	0.32	9.47	179.4	21.44	8.00	10.82
K	10.44	29.7	9.11	4.61	9.02	207.6	51.14	11.00	8.82
L	12.45	30.5	22.76	14.08	9.19	201.5	493.23	17.80	9.26

A detailed relationship among COD_{Cr} , acidic COD_{Mn} , and alkaline COD_{Mn} in the Jiahe River is illustrated in Fig. 2(a)–(f).

From Fig. 2(a), it can be seen that there was a linear correlation between COD_{Cr} and acidic COD_{Mn} ($R^2 \sim 0.7$), when excluding the highest salinity sample. Although there was a positive correlation between COD_{Cr} and acid COD_{Mn} in the Jiahe River, no obvious correlation was observed in the Guangdong River and the Yuniaohe River (figures not shown). Furthermore, in the Jiahe River, there was nearly no linear relationship (Fig. (c)), $R^2 \sim 0.3$ between COD_{Cr} and alkaline COD_{Mn} , even with the highest salinity point excluded. Therefore, it is not feasible to get the accurate alkaline COD_{Mn} value based on COD_{Cr} . From Fig. 2(e), the linear relationship (R^2) between acidic COD_{Mn} and alkaline COD_{Mn} was higher than that between COD_{Cr} and alkaline COD_{Mn} ($R^2 > 0.75$). This was mainly due to the effect of salinity on acidic COD_{Mn} being far less than that on COD_{Cr} (Fig. (c) and (d)), although the R^2 value was still decreased after the highly saline point was added (Fig. 2(f)). Overall, when the salinity increased, COD_{Cr} and acidic COD_{Mn} increased significantly while a little change was observed for alkaline COD_{Mn} . The coastal zone is a special geographical area, a transition zone from the ocean to the land, with two different unique attributes of sea and land [19]. So, it is unscientific to apply surface water quality standards or sea quality standards separately to assess the coastal water quality. In this study, in the estuaries of three rivers, high COD_{Cr} values were found to be mainly due to the high concentration of Cl^- , Br^- , and terrigenous contamination. Although the method of alkaline COD_{Mn} avoids the influence of tidal seawater, high analytical error occurs during the determination process because of multiple dilutions (heavily polluted water) and complex operation (water bath). Many efforts have been devoted to the development of the photoelectrochemical methods for the determination of COD [20,21]. Although these methods could avoid chloride interferences, and without any oxidizing agent addition, there is no unified evaluation criterion on COD in China. Therefore, it is necessary to find a unified method or standard to evaluate water quality in coastal zones.

3.2. Influence of salinity on COD measurement

In order to investigate the influence of salinity on COD measurement, the trend of different COD values obtained with salinity is plotted in Fig. 3. There is a linear increase in COD_{Cr} up to 5 PSU, but then an

exponential increase and more complex trend thereafter. Therefore, 5 PSU can be regarded as the threshold of salinity influence on COD_{Cr} measurement.

However, for acid COD_{Mn} measurement, there was a rapid linear increase with salinity up to 10 PSU, and then a leveling-off. This phenomenon can be explained because with the salinity increase, the Cl^- and Br^- in seawater can be oxidized by finite KMnO_4 . With the volume of seawater increase (along with salinity increase) in model water, finite KMnO_4 will be exhausted in the measurement process. So, when salinity exceeds 10 PSU, surplus Cl^- and Br^- are no longer oxidized and the acid COD_{Mn} gave similar values (Fig. 3). For alkaline COD_{Mn} , there is a linear trend here of a gradual decrease in the COD with increased salinity because the pollutants in freshwater were diluted by seawater in model water. Overall, the influence of salinity almost cannot be observed, it is mainly because of weak oxidation capability under alkaline conditions.

3.3. Application of COD in coastal water quality assessment and management

Currently, the selection of COD determination method is generally dependent on geographic position in the coastal zone. The $\text{K}_2\text{Cr}_2\text{O}_7$ and acid KMnO_4 methods are widely used in river water quality assessment and the alkaline KMnO_4 method is used for marine water quality assessment [22,23]. In the marine environment, reducible ions in seawater can be oxidized by $\text{K}_2\text{Cr}_2\text{O}_7$ and acid KMnO_4 leading to an inaccurate determination result. The content of reductive ions in surface water is generally low ($\text{Cl}^- < 500 \text{ mg L}^{-1}$), while in seawater it is up to $\sim 19,000 \text{ mg L}^{-1}$. Generally, according to the geographical position, intertidal zones in rivers and estuaries are always located inland, but the salinity in these sections may be similar to seawater. Therefore, the COD_{Cr} method is unsuitable for such surface water quality assessment. However, for environment management, these sections of the river system often fall under the jurisdiction of the local environmental protection agency, so the method of COD_{Cr} will often be blindly applied in water quality management.

In addition to the problem of managing the boundary between inland rivers and the sea itself, there is still no uniform evaluation criterion on COD in China. For example, the environmental quality standard for surface water is divided into five categories, while the marine water quality standard is divided into four grades (Table 3), and there are no similar criteria for COD [22,23]. Therefore, if COD was used to assess

Table 3

Comparison of COD in different water quality standards (unit: mg L⁻¹)

Level	Surface water		Marine water Alkaline COD _{Mn}
	COD _{Cr}	Acid COD _{Mn}	
I	≤15	≤2	≤2
II	≤15	≤4	≤3
III	≤20	≤6	≤4
IV	≤30	≤10	≤5
V	≤40	≤15	–

coastal water quality, it is difficult to judge the grade of water quality for coastal waters by this standard. For surface waters, the K₂Cr₂O₇ method and the acid KMnO₄ method are applied to determine the extent of water pollution, while the COD_{Mn} method is used on entering the estuary and off-shore area. Because there are no alkaline COD_{Mn} values in the rivers, it is difficult to identify the sources of COD and quantify its influence on coastal water quality.

4. Conclusions

COD_{Cr} is far higher than COD_{Mn} in waters with high salinity within the coastal zone. There is no obvious correlation between COD_{Mn} and salinity in the river–estuary–offshore system. It is not feasible to get a rough COD_{Mn} value from COD_{Cr} measurements, or at least this value does not reflect the real water conditions. The traditional use of geographical location as the dividing line for the method selection of COD measurement is not scientifically rigorous. Instead, a threshold of 5 PSU should be regarded as reference for COD measurement method selection. Although alkaline COD_{Mn} for coastal waters presents a steady linear relationship with salinity, it does not reflect real pollution degree because of its weak oxidation capability (most pollutants in surface water cannot be oxidized by KMnO₄ under alkaline conditions). Therefore, a special coastal water quality measurement standard should be developed to solve the linking problem of seawater quality standard and surface water quality standard, improving coastal water quality control and management.

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