Influence of salinity on COD measurements in coastal water management

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Abstract: 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 the connection problems between the 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 parameter 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 ($K_2Cr_2O_7$) or potassium permanganate ($KMnO_4$) is used as the oxidizing agent in the process of COD analysis [4]. $K_2Cr_2O_7$ has a stronger oxidation capability than $KMnO_4$, and is able to completely oxidize 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 the 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 on how to improve the measurement accuracy and new measure method [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 will result in higher COD_{Mn} than actual values because of multiple dilutions before analysis. In this study we applied 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 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, Guangdanghe River and Yuniaohe River in Yantai, China (Fig. 1). All sampling equipments 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.

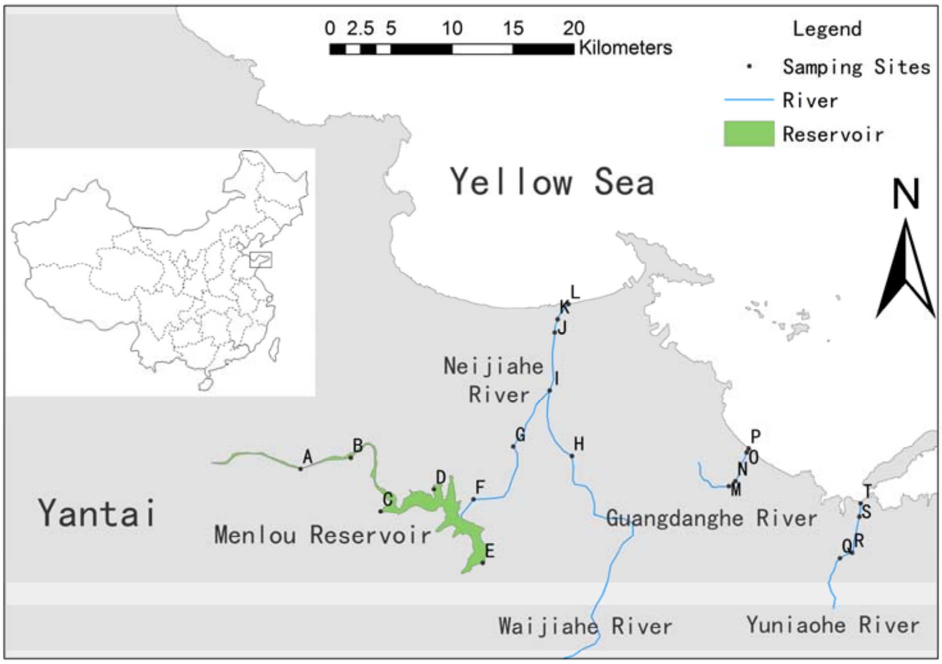


Fig. 1. Schematic graph showing the sampling sites

2.2 Measurements and methods

The reagents used were all 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 the 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 Dissolved Oxygen 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 Yuniaohe River) and seawater (offshore area of 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 fifteen beakers. For each group, different volume ratios of freshwater and seawater were added to these beakers to give 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 triplicates tests) for different sampling sites in Guangdanghe River and Yuniaohe River are presented in Table 1. The concentrations of COD_{Cr} were 15-423 mg L^{-1} in the Guangdanghe River and 31-1312 mg L^{-1} in the Yuniahohe River. The concentrations of acidic COD_{Mn} and alkaline COD_{Mn} were 6-31 mg L^{-1} and 5-20 mg L^{-1} in the Guangdanghe River and 6-24 mg L^{-1} 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).

Table 1 The COD values in the Guangdanghe and Yuniaohe Rivers

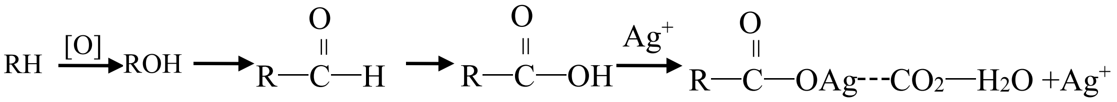
	sampling sites	COD_{Cr} (mg L^{-1})	COD_{Mn} (mg L^{-1})	
			Acid method	Alkaline method
Guangdanghe River	M	15.11	5.96	5.02
	N	78.40	21.73	19.36
	O	122.30	25.65	20.24
	P	423.36	31.53	17.44
Yuniaohe River	Q	31.36	6.24	5.33
	R	86.24	23.84	24.56
	S	47.04	7.84	5.65
	T	1312.42	23.05	4.86

The standard electrode potential of Cl/Cl^- (1.36 V) and Br/Br^- (1.087 V) are 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 the $K_2Cr_2O_7$ (Eq. 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 is first oxidized to organic 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, the Cl^- and Br^- in brackish/saline water decrease the silver availability by precipitation of solid AgCl and AgBr. This process restrain the reaction of organic acid into carbon dioxide and water because of

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

$$6Cl^- + Cr_2O_7^{2-} + 14H^+ \rightarrow 3Cl_2 + 2Cr^{3+} + 7H_2O \tag{1}$$

$$6Br^- + Cr_2O_7^{2-} + 14H^+ \rightarrow 3Br_2 + 2Cr^{3+} + 7H_2O \tag{2}$$



$$RH \xrightarrow{[O]} ROH \longrightarrow R\text{—}\overset{\overset{O}{\|}}{C}\text{—}H \longrightarrow R\text{—}\overset{\overset{O}{\|}}{C}\text{—}OH \xrightarrow{Ag^+} R\text{—}\overset{\overset{O}{\|}}{C}\text{—}OAg\text{---}CO_2\text{—}H_2O + Ag^+ \tag{3}$$

Highest acidic COD_{Mn} were measured in the estuarine sites of the Guangdanghe and Yuniaohe rivers. However, the alkaline COD_{Mn} in these rivers were 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 MnO_4^- / Mn^{2+} are 1.49 V and 0.588 V respectively. So Cl^- (Cl/Cl^-, 1.36 V), Br^- (Br/Br^-, 1.087 V) in water samples could be oxidized by acidic $KMnO_4$ (Eq. 4 and 5) rather than alkaline $K_2Cr_2O_7$.

$$10Cl^-+2MnO_4^-+16H^+\rightarrow 2Mn^{2+}+5Cl_2+8H_2O \tag{4}$$

$$10Br^-+2MnO_4^-+16H^+\rightarrow 2Mn^{2+}+5Br_2+8H_2O \tag{5}$$

For each river, there was a big difference between different COD methods. For example, in Guangdanghe River, the concentrations of COD_{Cr}, acidic COD_{Mn} and alkaline COD_{Mn} were ~430 mg

L^{-1}, ~32 mg L^{-1} and ~20 mg L^{-1}, respectively. This may be related to the oxidation strength of oxidants and the degree of water pollution. The $K_2Cr_2O_7$ used in 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 analysis. 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 $K_2Cr_2O_7$ and acidic $KMnO_4$, the alkaline $KMnO_4$ method was applied in COD measurement in seawater or halogen containing wastewater [13].

In order to investigate the relationship between COD value and salinity, analysis of waters in the whole watershed of the Jiahe River (from upstream, Menlou reservoir to estuary, Fig. 1) were conducted, and results are listed in Table 2. The concentrations of COD_{Cr}, acidic COD_{Mn} and alkaline COD_{Mn} in Jiahe River were 8-493 mg L^{-1}, 3-18 mg L^{-1} 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 mg L^{-1} and ~18 mg L^{-1} respectively, much higher than those in other sites. The value of salinity was ~14 PSU at estuary, 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). These phenomena confirmed the previous hypothesis that the 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}.

Table 2 Parameters in different sampling sites of Jiahe River valley

Sites	DO	Temp.	Cond.	Sal.	pH	ORP	COD_{Cr}	COD_{Mn} (mg L^{-1})	
	(mg L^{-1})	(□)	(ms cm^{-1})	(PSU)		(mV)	(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

Empirically, many engineers use COD_{Cr} to estimate a COD_{Mn} value in engineering or fieldwork [17,18], but this estimation must be 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 Jiahe River, linear fitting of different COD value at each sampling site (Fig. 1) was illustrated in Fig. 2. In this figure, (1), (3) and (5) were fitted by data excluding the highly saline point (sampling point L), (2), (4) and (6) were fitted by the data of all sampling sites (point L involved). Detailed relationship among the COD_{Cr}, acidic COD_{Mn} and alkaline COD_{Mn} in Jiahe River were illustrated in Fig. 2 (1) - (6).

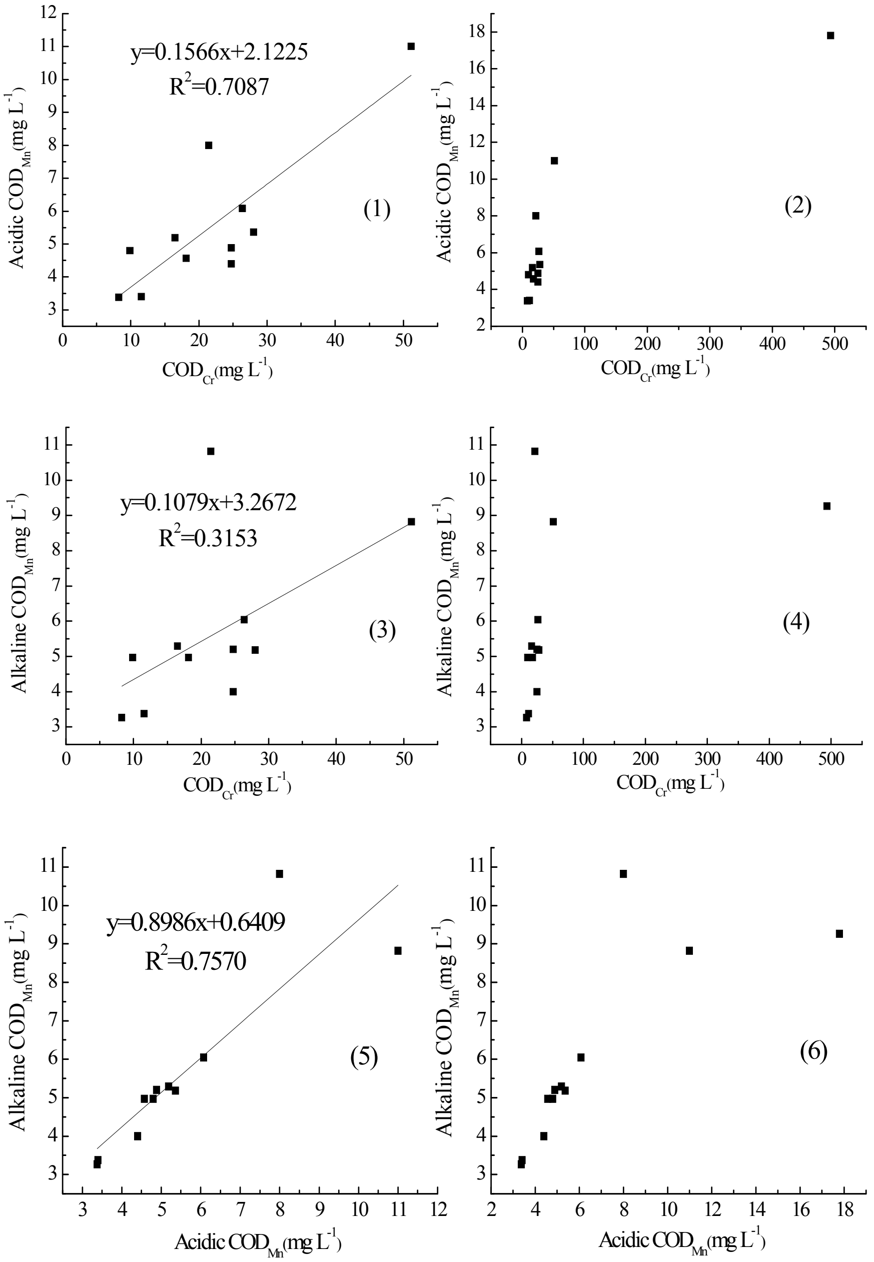


Fig. 2. The relationships among the COD_{Cr}, acidic COD_{Mn}, alkaline COD_{Mn} in Jiahe River

From Fig. 2 (1) , 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 Jiahe River, there was no obvious correlation was observed in Guangdanghe Rvier and Yuniaohe River (figures not shown). Furthermore, in Jiahe River, there was nearly no linear relationship (Fig. (3), R^2 ~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 the COD_{Cr}. From Fig. 2 (5), the linear relationship (R^2 between the 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. (3) and (4)), although the R^2 value was still decreased after the highly saline point was added (Fig. 2 (6)). Overall, with the salinity increases, COD_{Cr} and acidic COD_{Mn} increased significantly while 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 the 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 high concentration of Cl^-, Br^-, and terrigenous contamination. Although the method of alkaline COD_{Mn} avoids the influence of tidal seawater, high analytical error will occur during determination process because of multiple dilution (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 the water quality in coastal zone.

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 are plotted in Fig. 3. There is a linear increase in $\mathrm{COD}_{\mathrm{Cr}}$, up to 5 PSU, but then an exponential increase and more complex trend thereafter. Therefore, 5PSU can be regarded as the threshold of salinity influence on $\mathrm{COD}_{\mathrm{Cr}}$ measurement.

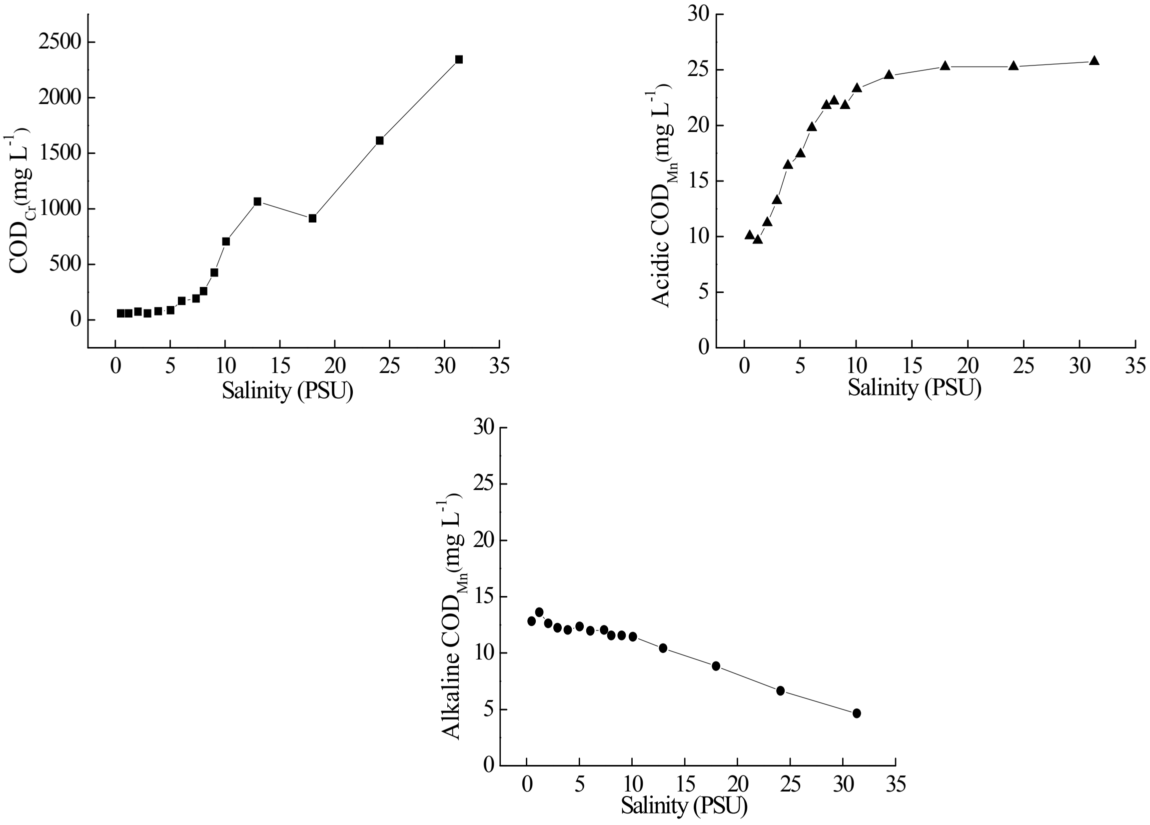


Fig. 3 The influence of salinity on different COD measurement

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 measurement process. So when the 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 gradual decreasing COD with increased salinity because pollutants in freshwater was diluted by seawater in model water. Overall, the influence of salinity is 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 $K_2Cr_2O_7$ 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 $K_2Cr_2O_7$ and acid $KMnO_4$, leading to an inaccurate determination result. The content of reductive ions in surface water is generally low ($Cl^- < 500$ mg L^{-1}), while in seawater it is up to ~19000 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 coastal water quality, it is difficult to judge the grade of water quality for coastal waters by this standard. For surface waters, $K_2Cr_2O_7$ method and acid $KMnO_4$ methods are applied to determine the extent of water pollution whilst 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.

Table 3 Comparison of COD in different water quality standards (unit: mg L^{-1})

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

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 $KMnO_4$ 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.

Acknowledgments

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