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研究ノート

Comparative Study of Chemical Oxygen Demand and Total Organic Carbon in Omura Bay

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大村湾海水における過マンガン酸カリウム消費量と全有機炭素の比較検討

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要 旨

化学的酸素要求量（COD）と全有機炭素量（TOC）を測定することにより、大村湾における有機汚濁レベルを評価した。本研究では、2008年５月から2010年５月にかけ、水深別（０、２、６、10m）に５地点（湾口部、湾央部、湾奥部３地点）より採水し、両者を測定した。その結果、COD は 0.68～3.94 mg/L（平均 1.95mg/L）、TOC は 0.811～2.170mg/L（平均 1.345mg/L）となり、COD では試料の約半数が環境基準の 2 mg/L 以上を示したのに対し、TOC ではほぼ全試料で 2 mg/L 以下となり、COD と比べて低値を示した。両者とも表層で高く、深度とともに低い傾向を示した。Pearson の積率相関分析を行った結果、両者の間には正の相関がみられた（相関係数：0.604）。また、海水交換が十分でないと示唆される湾奥部ほど、両者の相関性が高くなる傾向がみられた。以上の結果より、閉鎖性海域ほど両者の相関性が高く、TOC の測定は水質汚濁を把握するには有効であることが示唆された。

キーワード

化学的酸素要求量、全有機炭素、相関、大村湾

Summary

The organic pollutant levels in Omura Bay were evaluated by measuring chemical oxygen demand (COD) and total organic carbon (TOC). We investigated these factors in Omura Bay from May 2008 to May 2010, in order to clarify the relationship between them. Samples were collected from four depths (0, 2, 6, and 10 m) at five sites. The COD values ranged from 0.68 to 3.94 mg/L with a mean value of 1.95 mg/L, while the TOC values ranged from 0.811 to 2.170 mg/L with a mean value of 1.345 mg/L. Although half of the samples showed high COD values (>2.0 mg/L), most of the samples showed low TOC values (<2.0 mg/L). The samples from the upper layer showed higher COD and TOC values than the samples from the middle or bottom layers. A significant positive correlation between the COD and TOC values was obtained (0.604); furthermore, a strong correlation between these parameters was observed for the samples obtained from the inner bay. These results suggest that measuring TOC may be useful for estimating the degree of pollution in enclosed coastal sea areas.

Key words

chemical oxygen demand, total organic carbon, correlation, Omura Bay

Introduction

Many types of chemicals released from domestic and industrial waste ultimately accumulate in the sea; thus, determining the concentration of organic pollutants in seawater is important. In Japan, pollution levels are evaluated in seawater by measuring the hydrogen ion exponent (pH) and the levels of dissolved oxygen (DO), chemical oxygen demand (COD), total coliform, and n-hexane extracts. The COD has been used as a typical water-quality indicator for organic pollution, and the environmental quality standard for seawater was determined to be a COD level <2.0 mg/L. In 2008, only 76.4% of seawater samples met this environmental standard; this result was much poorer than that for rivers (92.3%).[1] The result of samples obtained from enclosed water areas, such as lakes, inner bays and inland seas, was particularly low.

As illustrated in Figure 1, Omura Bay is a mostly enclosed inner bay that is connected to the Sasebo Bay by the Hario narrows and the Haiki narrows. COD measurements in Omura Bay have been higher than the environmental water quality standard (2.0 mg/L) since 1976, although the COD values of the rivers that flow into Omura Bay have not increased. This data suggest that refractory organic chemicals may have accumulated in Omura Bay.

Although the COD is one of the most important parameters for assessing industrial and environmental waste water, the use of this parameter has some limitations, such as the fact that the decomposition ratio differs widely depending on organic compounds[2] and the fact that COD measurements can be somewhat inaccurate even if performed by the same person. If the oxidation conditions of the COD method using potassium permanganate are too acidic (COD_{Mn}), then a large amount of chloride ions are likely to interfere with the COD measurements ;[3-4] therefore, a large amount of silver nitrate must be used to pretreat the seawater in order to prevent such interference. In the case of alkaline conditions (COD_{OH}), chloride ions do not interfere with the COD measurements.[4] In Japan, the organic pollutant levels in seawater is evaluated by measuring COD using potassium permanganate, whereas it is evaluated by measuring COD using potassium dichromate (COD_{Cr}) in the United States and the European Union ; consequently, COD values measured in Japan are difficult to compare directly with those measured in the United States and the European Union. Moreover, the toxic waste containing $KMnO_4$ or $K_2Cr_2O_7$ that is used in the process of the measuring COD must be subsequently disposed. Considering these limitations, an index of organic pollutants other than COD measurements is needed.

The water quality standards for tap water were revised in 2003 and the total organic carbon (TOC) value was adopted as a new standard replacing $KMnO_4$ consumption, which had been used to evaluate organic pollution for about 100 years. TOC refers to the amount of carbon bound in an organic compound. With this method, operator variability among measurements can be reduced using an automatic TOC analyzer. Previously, TOC was measured by subtracting the inorganic carbon (IC) content from the total carbon (TC) content ; thus, the TOC of seawater was difficult to measure because of the high IC content. However, the nonpurgeable organic carbon (NPOC) method can measure TOC directly by acidifying samples to below pH3.0 and then purging the sample with CO_2-free air. Although the automated TOC method is useful for measuring organic pollutants in seawater, little is known about the relationship between COD and TOC values of seawater.[5] Therefore in this study, we focused on clarifying the relationship between COD and TOC in Omura Bay.

Experimental Method

Samples As shown in Figure 1, five different sampling sites were designated in Omura Bay, and samples were collected from the upper (0-m), middle (2-m and 6-m), and lower (10-m deep) layers. The samples were collected in May, September, and November of 2008, February, May, August and November of 2009, and February of 2010. Samples were stored at 4℃ until the analysis.

Chemicals Potassium hydrogen phthalate, which was used as the standard for TOC measurement, was purchased from nacalai tesque (Kyoto, Japan). Other chemicals were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). All chemicals were prepared with special grade reagents.

COD and TOC Measurements The organic pollutant level based on the COD was measured by potassium permanganate method at 100℃ according to the COD_{OH} method.[4] TOC was measured using the NPOC method with a TOC analyzer (TOC–V_{CSN} ; Shimadzu Corp., Kyoto, Japan). A Pearson product-moment correlation coefficient was used to determine the relationship between the COD and TOC. A p-value of less than 0.05 was considered to indicate statistical significance.

Results and Discussion

The COD and TOC data of the seawater samples collected from Omura Bay are listed in Table 1.

The COD values ranged from 0.68 to 3.94

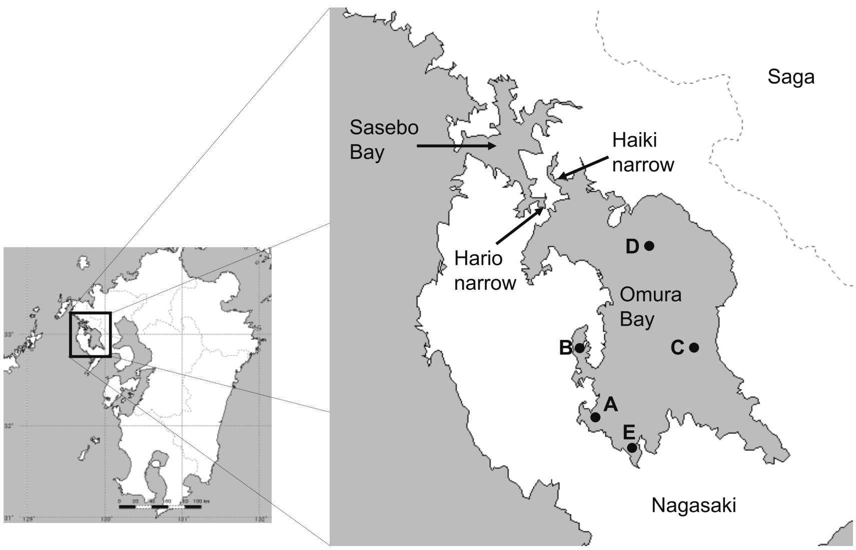


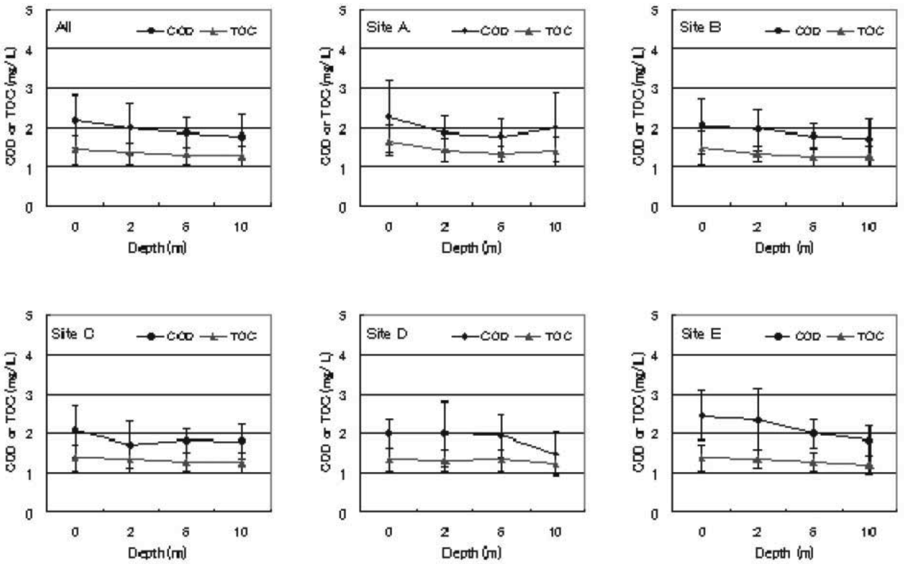
Fig. 1. Geographic locations of the sampling sites in Omura Bay

mg/L with a mean value of 1.95 mg/L, while the TOC values ranged from 0.811 to 2.170 mg/L with a mean value of 1.345 mg/L. The average COD values were higher than the TOC values for each site and depth tested, and the average ratio of COD/TOC ranged from 1.27 to 1.66 with a mean value of 1.45. Examples of the depth patterns of the average COD and TOC values are presented in Figure 2.

The COD and TOC values were higher in the upper layer than in the middle or bottom layer, and the distribution of the TOC values was similar to that for the COD values at each site. As shown in Figure 3, a significant positive correlation between the COD

Table 1. COD and TOC values in seawater samples from Omura Bay

Sampling Location	COD (mg/L)			TOC (mg/L)			Ratio of COD/TOC
	min	max	average	min	max	average	
All	0.68	3.94	1.95	0.811	2.170	1.345	1.45
Site A	0.80	3.94	1.98	1.033	2.143	1.460	1.36
Site B	0.76	3.26	1.86	0.909	2.170	1.328	1.40
Site C	0.92	3.10	1.85	0.847	1.912	1.438	1.29
Site D	0.68	3.84	1.81	0.811	1.723	1.433	1.27
Site E	1.12	3.48	2.17	0.865	1.803	1.306	1.66
0 m	0.80	3.94	2.18	0.880	2.170	1.453	1.50
2 m	0.92	3.84	1.99	0.811	2.062	1.358	1.47
6 m	1.16	3.06	1.87	0.823	1.618	1.298	1.44
10 m	0.68	3.94	1.77	0.865	2.143	1.270	1.39



The error bars show the standard deviation of the samples measured at each location and depth.

Fig. 2. Depth variations in COD and TOC values at different locations in Omura Bay

and TOC values was obtained with a coefficient of 0.604.

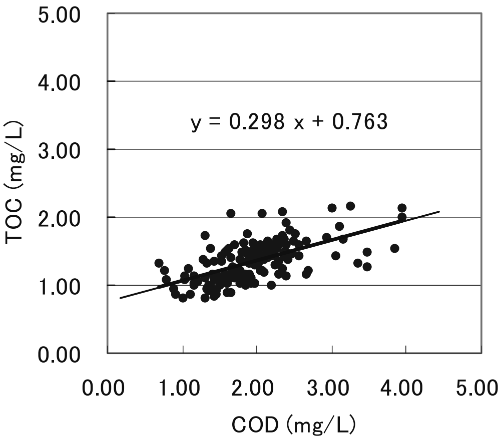


Fig. 3. Relationship between COD and TOC values in seawater samples from Omura Bay (n=156)

The results of correlation analyses comparing the COD and TOC values are summarized in Table 2.

Notable differences in the correlation coefficients (from 0.438 to 0.801) were obtained at the various sites, especially in the inner bay (site A). And a low correlation was obtained at site D ($p<0.05$), which is in the middle of Omura Bay. A previous study reported that the presence of a higher correlation between the COD and TOC in a lake than in a river was due to the fact that the water in the lake was stagnant, whereas the water in the river flowed.[6] Because the tidal range in Omura Bay is relatively small,[7] the inner bay sites at A, B, C and E do not exchange as much seawater as at site D. These results suggest that measuring TOC may be useful for estimating the degree of pollution in enclosed coastal sea areas.

Although the COD and TOC have been used as indices of organic pollutants, the COD measurements represent all chemicals in the water that can be oxidized, whereas the TOC represents the amount of organic carbon. Moreover, the decomposition ratio determined using the COD method varies greatly, depending on the organic compounds,[2] whereas that of the TOC is no problem because of high temperature combustion, indicating that it does not depend on the decomposition rate of the pollutants. The TOC indicates the total organic carbon in water, but organic compounds may also

Table 2. Correlation between COD and TOC and statistically significant regressions in Omura Bay

Sampling Location	Number	Regression line	Correlation coefficient (95% Confidence Limits)	Significant difference
All	156	y=0.298x+0.763	0.604 (0.493～0.695)	p<0.0001****
Site A	32	y=0.385x+0.696	0.801 (0.627～0.899)	p<0.0001****
Site B	32	y=0.294x+0.784	0.512 (0.199～0.731)	p=0.0027**
Site C	28	y=0.424x+0.533	0.741 (0.509～0.873)	p<0.0001****
Site D	32	y=0.195x+0.936	0.438 (0.106～0.638)	p=0.0121*
Site E	32	y=0.262x+0.739	0.604 (0.323～0.787)	p=0.0003***
0 m	39	y=0.363x+0.662	0.664 (0.441～0.810)	p<0.0001****
2 m	39	y=0.212x+0.937	0.512 (0.234～0.713)	p=0.0009***
6 m	39	y=0.274x+0.785	0.487 (0.202～0.696)	p=0.0017**
10 m	39	y=0.241x+0.874	0.588 (0.335～0.762)	p<0.0001****

*$p<0.05$, **$p<0.01$, ***$p<0.001$, ****$p<0.0001$

contain nitrogen or phosphorus. Therefore, the TOC method cannot measure the oxygen consumption by all organic compounds. In this study, half of the samples showed a high COD values (>2.0 mg/L), but most of the samples showed low TOC values (<2.0 mg/L). So it was suggested that the water pollution with organic compounds in Omura Bay is little, and be assumed that reducing material was existed in Omura Bay.

Because COD methods are officially used to monitor pollutant levels in seawater, a simple switch to TOC methods would be difficult and might cause confusion. Nonetheless, if a correlation can be obtained, it may be possible to estimate the COD from the TOC, so continuous analysis is needed in order to clarify the relationship between them. Our next concern is the relationship between COD and TOC in various seawaters. The present results should be useful in confirming the relationship between COD and TOC.

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