# Communications

Preliminary results of dissolved organic carbon concentration measurements in the Vistula river mouth using high-temperature catalytic oxidation\*

OCEANOLOGIA, No. 38 (3) pp. 395–403, 1996. PL ISSN 0078–3234

Salinity Dissolved organic carbon High-temperature catalytic oxidation Gulf of Gdańsk

WALDEMAR GRZYBOWSKI Institute of Oceanography, Gdańsk University, Gdynia

### Abstract

Some 100 measurements of dissolved organic carbon (DOC) concentrations were made in the water in the Vistula river mouth area using high-temperature catalytic oxidation. The results ranged from 4.8 to 22.4 mg dm<sup>-3</sup>. No relationship was detected between DOC and salinity within the 0.9–7.6 PSU salinity range.

### 1. Introduction

The attention which is at present being given to the dissolved organic carbon (DOC) in sea water derives from the still-growing evidence of its effects on chemical and biological processes in the sea and from the increased interest being shown in the oceanic carbon cycle. A crucial condition for successful research into these issues is the accurate measurement of the carbon concentration.

The introduction of high-temperature catalytic oxidation (HTCO) to DOC determination in seawater and the report on the elevated DOC concentrations in the northern Pacific obtained by means of this technique

 $<sup>^{*}</sup>$  This research was supported by Gdańsk University internal grant No. BW/1380–5–0014–5.

(Sugimura and Suzuki, 1988) have evoked considerable interest and debate on the reliability of data obtained using other techniques. As a result, several reports on the wet chemical oxidation method (WCO) (Menzel and Vaccaro, 1964) have been published (Gershey *et al.*, 1979; Ogawa and Ogura, 1992; Ridal and Moore, 1993; Sharp *et al.*, 1993) which cast some doubt on its ability to completely oxidise seawater organics. Even though Sugimura and Suzuki's results have been questioned (mainly because instrument blanks were underestimated (Benner and Strom, 1993; Suzuki, 1993; Cauwet, 1994)), the HTCO technique is currently regarded as reliable and remains a very common means of DOC determination in seawater.

The present paper reports the first data on DOC concentrations in the Gulf of Gdańsk obtained with HTCO. The research was focused on the area in the close vicinity of the Vistula river mouth, permitting samples over a broad salinity range to be analysed. With the exception of the results from two sampling points (Pęcherzewski and Ławacz, 1976) no data on DOC concentrations in this area have been published so far.

The objective was to estimate the vertical distribution and range of DOC concentrations, as well as to establish whether the DOC concentrations demonstrate any correlation with the salinity in the part of the Gulf of Gdańsk influenced by Vistula river water.

### 2. Experimental

The water samples were collected on board the r/v 'Oceanograf II' of Gdańsk University, during three cruises in April, May and November 1995. The locations of the sampling points are given in Tab. 1.

Seawater was collected in 10 l Niskin bottles. The DOC subsamples were immediately filtered through precombusted (450°C, 12 h) and preweighed Whatman GF/F glass fibre filters. The filtered water was poured into precombusted, 50 ml glass bottles, sterilised with 0.05 ml saturated HgCl<sub>2</sub> solution and closed with ground glass stoppers. All bottles were rinsed with the relevant sample water before being filled. The samples were stored in a refrigerator (4°C) and analysed within two weeks of collection.

The inorganic carbon was removed from the samples, prior to HTCO analysis, by acidification to pH = 2.5-3.0 (HCl, Merck, Suprapure) and purging with high-purity nitrogen for 5 min.

The instrument used in this study was the commercially available Shimadzu Total Organic Carbon Analyser (model 5000). The analytical procedure given in the instrument manual was followed. The quartz furnace

Table 1. Dissolved carbon concentrations, salinity, sampling depths, dates and coordinates . of the

	14			7.5 <b>4.8</b>				30					7.5	5.5
	12							16			7.4	6.8		
	10		7.5 <b>16.0</b>					14			7.4	5.8	7.3	5.5
	×		7.4 <b>15.1</b>					13			7.4	7.6		
	7	7.1 <b>5.8</b>			7.0 <b>7.3</b>			12			7.4	8.6		
	9					7.0 <b>5.3</b>		10		7.3 8.9	7.3	10.5		
	5	7.0 <b>13.5</b>	7.3 <b>22.2</b>					$\infty$	7.4 <b>6.5</b>	7.2 6.3	7.1	6.1	7.0	9.2
	4			6.6 7.0				7					7.0	8.8
	3	6.8 <b>21.5</b>			6.7 8.4		6.9 <b>8.0</b>	9	7.0 <b>10.9</b>	7.1	7.1	5.9		
	2	4.5 <b>17.2</b>	6.6 <b>6.6</b>	$\begin{array}{c} 6.0 \\ \textbf{12.8} \end{array}$	6.6 <b>14.7</b>	6.4 <b>21.6</b>		4	$\begin{array}{c} 6.2 \\ 14.5 \end{array}$	7.0 6.8	6.9	5.9	7.0	6.5
		4.4 <b>9.8</b>		5.7 8.6	4.5 <b>5.1</b>	1.9 <b>10.5</b>	3.0 10.2	2	2.8 10.1	5.9 7 2	6.2	13.4	7.0	6.0
	0	4.0 <b>10.5</b>	2.6 <b>10.2</b>	5.8 8.1	2.7 <b>11.7</b>	1.5 $12.5$	2.5 7.4	0	2.5 <b>16.8</b>	5.8 7 0	6.3	14.3	7.0	12.6
	[m]	[PSU] [PPM]	[PSU] [PPM]	[PSU] [PPM]	[PSU] [PPM]	[PSU] [PPM]	[PSU] [PPM]	[m]	[PSU] [PPM]	[PSU]	[PSU]	[PPM]	[PSU]	[PPM]
	depth	salinity DOC	salinity DOC	salinity DOC	salinity DOC	salinity DOC	salinity DOC	depth	salinity DOC	salinity DOC	salinity	DOC	$\operatorname{salinity}$	DOC
Location		$54^{\circ}22.0$ $18^{\circ}54.3$	$54^{\circ}22.8$ $18^{\circ}55.3$	$54^{\circ}21.5$ $18^{\circ}55.7$	$54^{\circ}21.8$ $18^{\circ}55.9$	$54^{\circ}22.4$ $18^{\circ}56.2$	$54^{\circ}22.0$ $18^{\circ}56.3$		$54^{\circ}22.9$ $18^{\circ}56.4$	$54^{\circ}23.1$ $18^{\circ}56.6$	$54^{\circ}23.6$	$18^{\circ}56.6$	$54^{\circ}27.9$	$18^{\circ}50\ 2$
$\operatorname{Date}$		18.05.1995							16.11.1995					

(continued)	
1.	
Table	

tube was filled with the highly sensitive version of the platinum catalyst constituting an exchangeable, standard part of the instrument. The carrier gas was high-purity oxygen flowing through the combustion tube at a rate of 150 ml min<sup>-1</sup>. Sample transfer was effected using the motorised syringe of the autoinjector. The injected volume was 0.100-0.250 ml, 4 injections being done for each sample.

The standards used in the measurements were prepared in Milli-Q water (Millipore Milli-Q unit) using reagent grade potassium hydrogen phthalate. The DOC concentration detected in freshly prepared Milli-Q water did not exceed 0.10  $\pm$  0.02 mg dm<sup>-3</sup>. The calibration curve was determined before each series of measurements from the set of four standards. The results were calculated from the peak areas. Expressed as a coefficient of variance, the calibration curve precision was below 3%. The blank of the procedure determined by DOC concentration analysis in filtered, sterilised, acidified and nitrogen-purged Milli-Q water was  $0.20 \pm 0.05 \text{ mg dm}^{-3}$ . No difference in DOC concentration was detected in Milli-Q water with or without a double volume addition of HCl and HgCl<sub>2</sub>. The intra-sample precision expressed as a relative standard deviation  $(RSD_{n-1})$  of the results from 4 injections of water from one bottle did not exceed 2%. In order to assess the sampling repeatability (the inter-sample precision), extra replications were taken from selected points during the cruises. The standard deviation (n = 4 to 5) determined for the several water samples collected from the same depth ranged from 0.2 to 0.6 mg dm<sup>-3</sup>. SD values were independent of DOC concentrations, although the lowest repeatability was recorded in the sets of 0 m depth samples.

## 3. Results and discussion

Tab. 1 shows the dissolved organic carbon concentration data obtained during three cruises in 1995.

The sampling points were concentrated in the area of the Vistula river mouth, which was probably the reason for the very high scatter of the results: these ranged from 4.8 to 22.4 C mg dm<sup>-3</sup>. The extreme DOC values (above 20 mg dm<sup>-3</sup>) presented in Tab. 1 were detected at three adjacent points at similar depths during the same cruise. Therefore, the possibility of accidental sample contamination seems very small.

The majority of the results significantly exceed the DOC concentrations reported from the Gulf of Gdańsk proper (*i.e.* not directly affected by the river Vistula). Pempkowiak *et al.* (1984) report values within the 4.8–7.1 range (4 samples, salinity 7.4–7.8 PSU), and Pęcherzewski and Lawacz's (1976) results (no salinity data) ranged from 6.5 to 12.6 mg dm<sup>-3</sup>. In the present study the carbon content in the samples least affected by river water (the bottom layer of the highest salinity) was as low as  $4.8 \text{ C} \text{ mg dm}^{-3}$ .

The Pęcherzewski and Ławacz (1976) paper also contains DOC concentration data determined at two points in the vicinity of the Vistula mouth. Their results lay in the 9 to 11 mg dm<sup>-3</sup> range and were supplemented by Vistula water DOC concentrations within the 6.0–6.5 mg dm<sup>-3</sup> range.

The very high DOC concentrations presented in this paper cannot be explained by the influence of the Vistula river water with its high-organic load. The extensive study by Pempkowiak and Kupryszewski (1980) contains data from year-long measurements: the highest DOC concentration measured in Vistula river water was 13.3 mg dm<sup>-3</sup>, and the average monthly value did not exceed 10 mg dm<sup>-3</sup>. There is little probability that earlier results were underestimated due to the lower efficacy of the technique applied (WCO). That problem was encountered mainly in low-organic ocean water of high salinity and was partly explained by the limited oxidation capability of persulphate radicals in the presence of  $Cl^{-1}$  ions (Peyton, 1993). Wet chemical oxidation applied in the analysis of freshwaters yielded results comparable with HTCO (Ogawa and Ogura, 1992; Benner and Hedges, 1993).

The possible reason for the very high DOC concentrations observed could be the existence of a permanent halocline. The evolving density barrier retards the migration of colloidal DOC. The occurrence of the halocline, however, is the only constant factor; the depth and horizontal range are subject to rapid and irregular changes caused by wind and river run-off. Therefore, DOC can accumulate only when this barrier is temporarily stable. The accumulation of organic-rich particles at the halocline (Cauwet, 1991; Sempere and Cauwet, 1995) supports the bacteriological activity, which is the local source of DOC. It is worth noting that the highest DOC values given in Tab. 1 were detected at depths which can be approximately ascribed to the halocline.

Some of the high DOC values were detected in the surface samples, a fact which can explained by the sampling procedure: the use of the typical sampling bottles, which are immersed open, may result in contamination of the samples with the organic-rich surface film (Zsolnay, 1978; Wangersky, 1993). The surface microlayer (literally the '0 m depth' sample) inevitably coats the inner walls of the sampling bottle, thus increasing the DOC content of the surface water samples in a haphazard fashion.

Fig. 1 illustrates the relationship between DOC and salinity in the water samples collected during three cruises in the Vistula river mouth area.



Fig. 1. DOC – salinity correlation for the Vistula river mouth area during the 'Oceanograf II' cruises in 1995 (n – number of samples, r – correlation coefficient)

The values of the correlation coefficients suggest that there is no relationship between salinity and DOC in the vicinity of the Vistula mouth. There are several reports on non-conservative DOC distribution in estuaries (Aminot *et al.*, 1990; Cauwet, 1991; Miller *et al.*, 1993; Sempere and Cauwet, 1995). Pempkowiak *et al.* (1984) found no correlation between DOC and salinity in southern Baltic and Gulf of Gdańsk water either. On the other hand, gradual DOC dilution with increasing salinity has been observed (Mantoura and Woodward, 1983; Whitehouse *et al.*, 1989).

While analysing the DOC – salinity relationships, one has to be conscious of the fact that DOC measurements are burdened with an inconsistency in the definition: 'dissolved' commonly means passing through the 0.7  $\mu$ m pore size of the Whatman GF/F glass fibre filter. Besides the truly dissolved phase, the 'solute' may contain colloids (Ogura, 1977), small particles and bacteria (Taguchi and Laws, 1988; Koike *et al.*, 1990; Williams *et al.*, 1993). In this case, the analysed DOC simultaneously undergoes dilution, flocculation, particulate adsorption and precipitation upon contact with water of a higher salinity (Sholkovitz, 1976; Whitehouse *et al.*, 1989). The filtration method used does not differentiate between the products of these processes, so the influence of salinity cannot be fully assessed.

There are other possible reasons for this apparently non-conservative behaviour of DOC. One of them could be the biological processes affecting readily biodegradable, land-derived organic carbon. These processes are influenced more by nutrient concentration than by salinity. Another explanation might be wind-derived mixing in shallow water disturbing the halocline, thus causing the 'patchiness' in the DOC distribution.

#### References

- Aminot A., El-Sayed M. A., Kerouel R., 1990, Fate of natural and anthropogenic dissolved organic carbon in the macrotidal Elorn Estuary (France), Mar. Chem., 29, 255–277.
- Benner R., Hedges J. I., 1993, A test of the accuracy of freshwater DOC measurements by high-temperature catalytic oxidation and UV-promoted persulfate oxidation, Mar. Chem., 41, 161–165.
- Benner R., Strom M., 1993, A critical evaluation of the analytical blank associated with DOC measurements by high-temperature catalytic oxidation, Mar. Chem., 41, 153–160.
- Cauwet G., 1991, Carbon inputs and biogeochemical processes at the halocline in a stratified estuary: Krka River, Yugoslavia, Mar. Chem., 32, 269–283.
- Cauwet G., 1994, HTCO method for dissolved organic carbon analysis in seawater: influence of catalyst on blank estimation, Mar. Chem., 47, 55–64.
- Gershey R. M., Mackinnon M. D., Williams P. J. le B., Moore R. M., 1979, Comparison of three oxidation methods used for the analysis of the dissolved organic carbon in seawater, Mar. Chem., 7, 289–306.
- Koike I., Hara S., Terauchi K., Kogure K., 1990, Role of sub-micrometre particles in the ocean, Nature, 345, 242–244.
- Mantoura R. F. C., Woodward E. M. S., 1983, Conservative behaviour of riverine dissolved organic carbon in the Severn Estuary: chemical and geochemical implications, Geochim. Cosmochim. Acta, 47, 1293–1309.
- Menzel D. W., Vaccaro R. F., 1964, The measurement of dissolved organic and particulate carbon in sea water, Limnol. Oceanogr., 9, 138–142.
- Miller A. E. J., Mantoura R. F. C., Suzuki Y., Preston M. R., 1993, Preliminary study on DOC in the Tamar Estuary, UK, using UV-persulphate and HTCO techniques, Mar. Chem., 41, 223–228.
- Ogawa H., Ogura N., 1992, Comparison of two methods for measuring dissolved organic carbon in sea water, Nature, 356, 696–698.
- Ogura N., 1977, High molecular weight organic matter in seawater, Mar. Chem., 5, 535–549.
- Pempkowiak J., Kupryszewski G., 1980, *The input of organic matter to the Baltic from the Vistula River*, Oceanologia, 12, 79–98.
- Pempkowiak J., Widrowski H., Kuliński W., 1984, Dissolved organic carbon and particulate carbon in the Southern Baltic in September 1983, Proc. 14th Conf. Baltic Oceanogr., Polish SCOR Comm., Gdynia, 699–713.
- Peyton G. R., 1993, The free-radical chemistry of persulfate-based total organic carbon analysers, Mar. Chem., 41, 91–103.

- Pęcherzewski K., Lawacz W., 1976, Preliminary results of investigations on the quantity of dissolved and particulate organic carbon in the waters of the southern Baltic, Zesz. Nauk. UG, Oceanografia, 4, 25–44, (in Polish).
- Ridal J. J., Moore R. M., 1993, Resistance to UV and persulphate oxidation of dissolved organic carbon produced by selected marine phytoplankton, Mar. Chem., 42, 167–188.
- Sempere R., Cauwet G., 1995, Occurrence of organic colloids in the stratified estuary of the Krka river (Croatia), Est. Coast. a. Shelf Sci., 40 (1), 105–114.
- Sharp J. H., Suzuki Y., Munday W. L., 1993, A comparison of dissolved organic carbon in North Atlantic Ocean nearshore waters by high temperature combustion and wet chemical oxidation, Mar. Chem., 41, 253–259.
- Sholkovitz E., 1976, Flocculation of dissolved organic and inorganic matter during the mixing of river water and sea water, Geochim. Cosmochim. Acta, 36, 834–845.
- Sugimura Y., Suzuki Y., 1988, A high-temperature catalytic oxidation method for the determination of non-volatile dissolved organic carbon in seawater by direct injection of a liquid sample, Mar. Chem., 24, 105–131.
- Suzuki Y., 1993, On the measurement of DOC and DON in seawater, Mar. Chem., 41, 287–288.
- Taguchi S., Laws E. A., 1988, On the microparticles which pass through glass fiber filter type GF/F in coastal and open waters, J. Plankton Res., 10, 999–1008.
- Wangersky P. J., 1993, Dissolved organic carbon methods: a critical review, Mar. Chem., 41, 61–74.
- Williams P. M., Bauer J. E., Robertson K. J., Wolgast D. M., 1993, Data report on DOC and DON measurements made at SIO, 1988–1991, Mar. Chem., 41, 271–281.
- Whitehouse B. G., Macdonald R. W., Iseki K., Yunker M. B., McLaughlin F. A., 1989, Organic carbon and colloids in the Mackenzie River and Beaufort Sea, Mar. Chem., 26, 371–378.
- Zsolnay A., 1978, Caution in the use of Niskin bottles for hydrocarbon samples, Mar. Pollut. Bull., 9, 23–24.