

# Monosaccharides in the water of the Gulf of Gdańsk

OCEANOLOGIA, 43 (2), 2001.  
pp. 247–256.

© 2001, by Institute of  
Oceanology PAS.

## KEYWORDS

Monosaccharides  
Baltic Sea  
Seawater

WALDEMAR GRZYBOWSKI  
AGNIESZKA MAKSYMIOUK  
Institute of Oceanography,  
University of Gdańsk,  
al. Marszałka Piłsudskiego 46, PL-81-378, Gdynia, Poland;  
e-mail: grzyb@panda.bg.univ.gda.pl

Manuscript received 20 February 2001, reviewed 23 April 2001, accepted 9 May 2001.

## Abstract

The concentration of monosaccharides in samples collected in the Gulf of Gdańsk area was determined in water filtered through  $\sim 0.8 \mu\text{m}$  pore size filters. Seawater concentrations ranged from about 0.2 to 1.1 mg C dm<sup>-3</sup>, the highest values being detected at the mouth of the river Vistula. Seasonality was detectable in the data distribution; the majority of autumn values lay within the 0.2–0.4 range while concentrations in the spring samples were higher and the values more widely scattered. Measurements of monosaccharide concentrations at selected points during the whole observation period showed that values increased from spring to autumn as much as 5-fold. Concomitant analyses in Vistula river water yielded concentrations from 0.4 to 1.2 mg C dm<sup>-3</sup>. These latter values were all higher than those recorded in seawater in the corresponding months.

## 1. Introduction

Saccharides comprise the largest class of chemically identified constituents of dissolved organic matter (DOM) in seawater (Williams 1975). Their estimated proportion in the dissolved organic carbon (DOC) pool ranges from  $\sim 15\%$  (Heinrichs & Williams 1985, Senior & Chevolet 1989) to  $\sim 35\%$  (Burney et al. 1982). Even at low concentrations they provide

an important food source for heterotrophic bacteria, participate in several metabolic functions, and are dominant structural constituents of planktonic organisms. Dissolved total saccharides consist of combined saccharides (i.e. oligo- and polysaccharides) and free monosaccharides. This last fraction, along with dissolved free amino acids, is the most bio-reactive component of marine DOM.

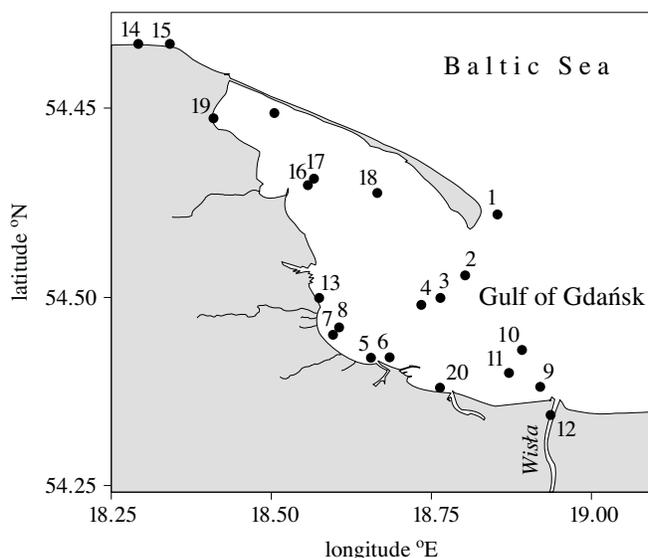
Despite the importance of monosaccharides to the bio-mediated organic carbon turnover, relatively little is known about their abundance in the marine environment, mainly because of analytical difficulties. The commonly used MTBH method (Johnson & Sieburth 1977) and its modifications (Pakulski & Benner 1992) involves a large number of procedural steps, which renders it tiresome in routine use. The method used in the present paper was introduced and successfully applied to seawater samples by Myklestad et al. (1997). Its advantage over the MTBH lies in the fact that no pre-concentration or desalting is necessary, and measurements are not affected by salinity. The method, however, cannot be applied to waters with a high  $\text{Fe}^{2+}$  content (i.e. anoxic pore waters) and does not yield the molar composition of monosaccharides.

The very limited information on sugars in the Baltic Sea available so far (Kerstan 1994) does not include any data concerning the Gulf of Gdańsk. The aim of the present study was to survey the range of dissolved monosaccharide concentrations in this area. Additionally, an attempt was made to discern the role of biological processes by analysing samples collected in periods of different biological activity.

## 2. Experimental

The location of the sampling sites is shown in Fig. 1.

Samples of water from the river Vistula were collected in midstream from the ferry at Świbno, approximately 3 km from the river mouth (point 12). Some of the samples were collected from the beach or from piers with a polyethylene pail (points 13–15 and 19–20). The ‘open water’ samples were collected from the r/v ‘Oceanograf’ with a 5 dm<sup>3</sup> Niskin bottle; samples were taken about 1 m below the water surface and 1–2 m above the bottom. Prior to sampling the bottle was flushed with seawater. The samples were passed through Whatman GF/F glass fibre filters ( $\sim 0.8 \mu\text{m}$  pore size) within 4 hours of sampling and stored in glass bottles in a refrigerator until analysis (no longer than 8 hours). The filters, the bottles and the all-glass filtration set were previously rinsed with distilled water and sterilised by combusting at 450°C overnight.



**Fig. 1.** Location of sampling sites in the Gulf of Gdańsk

The analytical procedure and reagent compositions are given in Myklestad (1997). In general, the method is based on the reduction of ferricyanide by sugars;  $\text{Fe}^{2+}$  is then determined colorimetrically after reaction with 2,4,6-tripirydydyl-s-triazine (TPTZ) (Avigad 1968). The reagents and standard solutions were made up in re-distilled water. The ferric chloride solution was prepared directly before analysis. All samples were analysed in triplicate at the least. Analyses of one set of samples included blanks and at least one standard solution. Colorimetric measurements were carried out in 10 mm cuvettes with re-distilled water as a blank sample. The monosaccharide concentrations obtained from the glucose calibration curves were converted to organic carbon concentrations: (1 mg of glucose = 0.4 mg C).

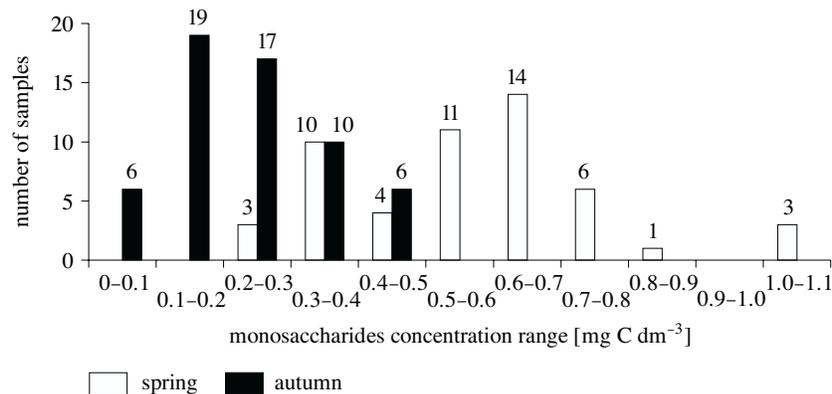
### 3. Results

The field measurements were preceded by methodological investigations designed to estimate the precision obtainable. An important finding was the high blank value detected in Milli-Q water produced in the set supplied with distilled water but not with the UV oxidation module. The blank values were up to 5-fold higher than those measured in freshly prepared re-distilled water. That problem was reported by Borch & Kirchman (1997), who suggested irradiating Milli-Q water containing added  $\text{H}_2\text{O}_2$  with sunlight.

The detection limit defined as the triple standard deviation of the blank measured in re-distilled water was  $0.03 \text{ mg C dm}^{-3}$ . The calibration

curves were obtained from standard solutions of glucose with  $0.5 \text{ mg dm}^{-3}$  intervals. The linearity of the curves expressed as  $r^2$  ranged from 0.971 to 0.999 up to  $2 \text{ mg dm}^{-3}$  of glucose. The coefficient of variation measured for quadruple sub-samples of a single seawater sample did not exceed 3%; this value increased up to 15% when separate samples of the same water masses were collected.

Fig. 2 shows the distribution of monosaccharide concentrations in the whole data set (excluding the river water samples) split into groups of samples collected in autumn and spring.

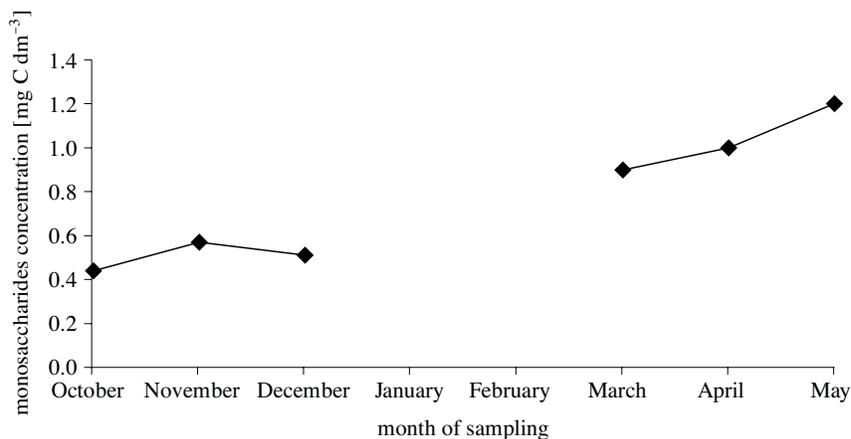


**Fig. 2.** Distribution of monosaccharide concentrations measured in seawater samples collected in the Gulf of Gdańsk area

The variability of the data was high, and differences between the lowest and highest concentrations approached one order of magnitude. Comparison of surface and bottom samples showed that, in general, concentrations were higher in the former. Nevertheless, the differences were very small ( $0.08 \text{ mg C dm}^{-3}$ ) and did not depend on the depth of the sampling point.

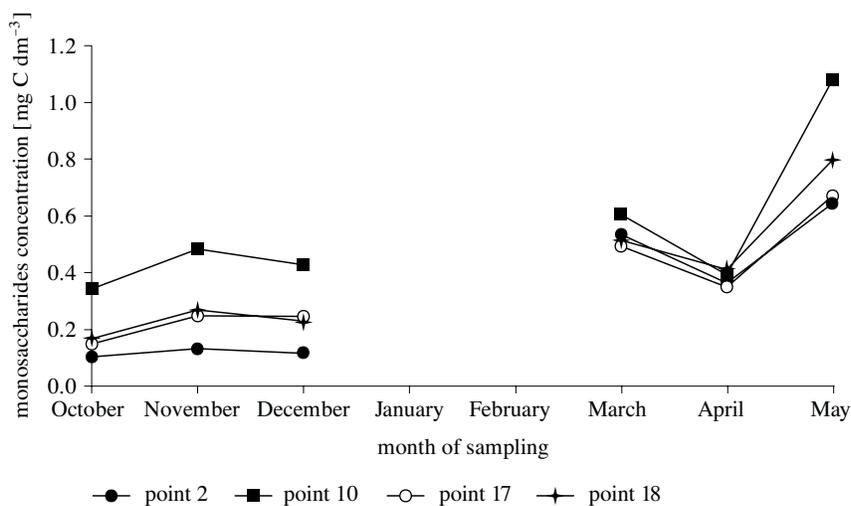
As can be seen in Fig. 2, the values were distributed bi-modally. The concentrations of all the autumn samples were  $< 0.5 \text{ mg C dm}^{-3}$ , while those of all the spring samples were  $> 0.2 \text{ mg C dm}^{-3}$ . The lowest concentrations were detected in samples collected beyond the Gulf of Gdańsk proper, i.e. surface water at Cape Rozewie (points 14 and 15).

The highest values were measured in water collected at points 9, 10 and 11, which were located near the Vistula mouth. The samples were affected by river water (salinity  $< 7 \text{ PSU}$  and a significantly higher absorbance). Fig. 3 illustrates the monosaccharide concentrations in Vistula river water during the study period (owing to technical problems no samples were taken in January and February).



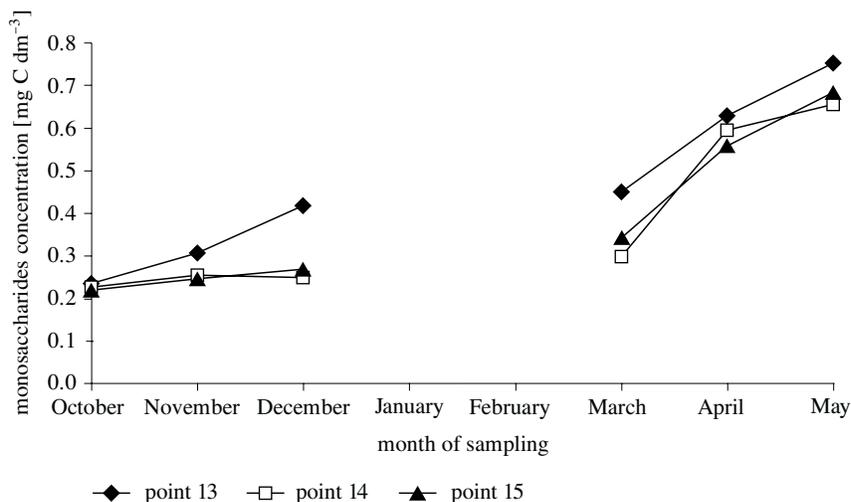
**Fig. 3.** Concentration of monosaccharides in Vistula river water

The values obtained were higher than those recorded in seawater in the corresponding sampling periods. The variability of the data was also significantly lower. In this case too, the spring concentrations were higher. In order to gain a more detailed insight into the temporal variations, the measurements of monosaccharide concentrations were repeated at selected sampling points. Fig. 4 shows the changes in the surface water at the ‘open water’ sampling points.



**Fig. 4.** Monosaccharide concentrations in surface water at sampling points 2, 10, 17, 18 in the Gulf of Gdańsk (see Fig. 1)

The features common to this pattern were the relatively constant concentrations during the autumn followed by higher values in spring. During this period the temporary decrease in monosaccharide concentration in April was followed by a significant increase in May. Such a pattern, however, was not recorded in the beach samples (Fig. 5)



**Fig. 5.** Monosaccharide concentrations in water at sampling points 13, 14, 15 in the Gulf of Gdańsk (see Fig. 1)

In this group of samples, monosaccharide concentrations increased monotonically, as was the case in riverine water (see Fig. 3). The relative increase at all sampling points did not exceed 500% and was higher than that in river water.

#### 4. Discussion

The seawater monosaccharide concentrations (in mg C dm<sup>-3</sup>) reported in the literature vary over a wide range of concentrations, from 0.001–0.025 (Sakugava & Handa 1985) and 0.003–0.03 (Rich et al. 1996), through 0.01–0.09 (Pakulski & Benner 1994), to 0.05–0.18 (Bhosle et al. 1998). It should be stressed, however, that direct comparison of published absolute values may not always be possible owing to the diversity of analytical methods (Borch & Kirchman 1997) and the different operational definitions of dissolved matter (filtration through 0.2  $\mu\text{m}$  pore size membrane filters *versus*  $\sim 0.8 \mu\text{m}$  pore size glass-fibre filters).

Besides being about one order of magnitude higher than these literature values, the data given in the present paper are also elevated as compared with those measured in some coastal areas: values ranged from 0.06–0.6 in

Trondheimsfjord water (Borsheim et al. 1999) to 0.04–0.12 in San Francisco Bay (Murrell & Hollibaugh 2000).

Monosaccharide concentrations in Gulf of Gdańsk water are on average twice as high as those reported by Kerstan (1994) for open Baltic Sea samples, where the highest values did not exceed  $0.3 \text{ mg C dm}^{-3}$  (analysis done by the MTBH method). It should be noted, however, that concentrations within this range were recorded in samples collected beyond the Gulf of Gdańsk (points 14 and 15). This concentration range is close to that found in a comparable environment, that is to say, estuarine waters strongly affected by riverine water with a high organic content: Senior & Chevelot (1989) report monosaccharide concentrations up to  $0.45 \text{ mg C dm}^{-3}$  in samples whose DOM content is slightly lower than that in Gulf of Gdańsk water.

The high values given here are due to the higher organic matter content in the samples analysed. While the DOC concentrations reported for Gulf of Gdańsk water exceed  $10 \text{ mg dm}^{-3}$  (Pęcherzewski & Ławacz 1976, Grzybowski 1996), the highest values in the open Baltic water range from  $7 \text{ mg dm}^{-3}$  (Pempkowiak et al. (1984) to  $4 \text{ mg dm}^{-3}$  (Ferrari et al. 1996) (the latter data were obtained in samples filtered through a  $0.2 \mu\text{m}$  pore size filter) and in ocean water are about  $1 \text{ mg dm}^{-3}$  (Pakulski & Benner 1994). The influence of organic matter on monosaccharide content is further confirmed by the fact that their highest concentrations were found in Vistula river water, where the DOC content may be as high as  $20 \text{ mg dm}^{-3}$  (Grzybowski 1996).

Assuming the highest DOC values to be  $10 \text{ mg dm}^{-3}$ , the proportion of monosaccharides in the organic pool of Gulf of Gdańsk water may vary from 1 to 10%. Percentages within that range were recorded both in oceanic (Pakulski & Benner 1994) and coastal waters (Senior & Chevelot 1989, Borsheim et al. 1999, Murrell & Hollibaugh 2000).

As in the case of organic matter, the monosaccharide content depends on the biological processes occurring in the marine environment. The data presented here show an increase from autumn to spring values. Obviously, the observed 4- to 5-fold increase cannot be attributed to the respective change in DOC concentrations. One of the probable reasons could be the extracellular release of carbohydrates from phytoplankton. Such an effect has been recorded during field observations of the phytoplankton bloom (Ittekkott et al. 1981) and in laboratory experiments (Biersmith & Benner 1998). In the present study, primary production was not assessed concomitantly with the monosaccharide analysis. However, records of maximum chlorophyll concentrations in May are available for the study area (Latała 1996, Niemczyk 1999).

For technical reasons, samples for investigating temporal variation were taken at only a few points, so the data illustrating month-to-month changes are too sparse to formulate sound conclusions. The recorded sequence of monosaccharide concentrations may be due to factors other than biological ones (e.g. mixing of water masses). However, it is noteworthy that a pattern resembling that in Fig. 4 (a spring decrease in concentration followed by an increase) has been observed by Borsheim et al. (1999) in surface water in the inner part of the Trondheimsfjord. This may have occurred as a result of an intensive bacterial uptake triggered by a temperature rise in April. A further increase in concentration may have been due to senescent algal blooms (Ittekkott et al. 1981) when the supply of monosaccharides from cell lysis exceeded bacterial demand. The lack of such a pattern in river water and in the beach samples (Figs. 3 and 5) suggests that primary production plays a minor role in those environments, and that terrestrial sources of monosaccharides are dominant.

To summarise, the monosaccharide concentrations in water from the Gulf of Gdańsk exceed those recorded in water from the Baltic Proper. The highest values were detected in Vistula river water and in areas adjacent to the river outlet. The seasonality in the data distribution suggests that they may be affected by biological processes. However, this conclusion should be regarded as circumstantial because the biological characteristics of the water masses analysed are unavailable.

## References

- Avigad G., 1968, *A modified procedure for the colorimetric ultramicro determination of reducing sugars with the alkaline ferricyanide reagent*, Carbohydr. Res., 7, 94–97.
- Bhosle N.B., Bhaskar P.V., Ramachandran S., 1998, *Abundance of dissolved polysaccharides in the oxygen minimum layer of the Northern Indian Ocean*, Mar. Chem., 63, 171–182.
- Biersmith A., Benner R., 1998, *Carbohydrates in phytoplankton and freshly produced dissolved organic matter*, Mar. Chem., 63, 131–144.
- Borch N.H., Kirchman D.L., 1997, *Concentration and composition of dissolved combined neutral sugars (polysaccharides) in seawater determined by HPLC–PAD*, Mar. Chem., 57, 85–95.
- Borsheim K.Y., Myklestad S.M., Sneli J., 1999, *Monthly profiles of DOC, mono- and polysaccharides at two locations in the Trondheimsfjord (Norway) during two years*, Mar. Chem., 63, 255–272.
- Burney C.M., Davis P.G., Johnson K.M., Sieburth J.M., 1982, *Diel relationships of microbial trophic groups and in situ dissolved carbohydrate dynamics in the Caribbean Sea*, Mar. Biol., 67, 3111–322.

- Ferrari G. M., Dowell M. D., Grossi S., Targa C., 1996, *Relationship between optical properties of chromophoric dissolved organic matter and total concentration of dissolved organic carbon in the southern Baltic Sea region*, Mar. Chem., 55, 299–316.
- Grzybowski W., 1996, *Preliminary results of dissolved organic carbon concentration measurements in the Vistula river mouth using high-temperature catalytic oxidation technique*, Oceanologia, 38 (3), 395–403.
- Heinrichs S. M., Williams P. M., 1985, *Dissolved and particulate amino acids and carbohydrates in the sea surface microlayer*, Mar. Chem., 17, 141–163.
- Ittekott V., Brockman U., Michaelis W., Degenes E. T., 1981, *Dissolved free and combined carbohydrates during a phytoplankton bloom in the Northern North Sea*, Mar. Ecol. Progr. Ser., 4, 299–305.
- Johnson K. M., Sieburth J. M., 1977, *Dissolved carbohydrates in seawater. 1. A precise spectrophotometric method for monosaccharides*, Mar. Chem., 5, 1–13.
- Kerstan E., 1994, *Carbohydrates in the Baltic Sea*, Proc. 19th Conf. Baltic Oceanogr., Sopot, 604–619.
- Latała A., 1996, *Concentration and distribution of chlorophyll a in the Gdańsk Bay*, Proc. 13th Symp. Baltic Mar. Biologists, Gdynia, 42–52.
- Murrell M. C., Hollibaugh J. T., 2000, *Distribution and composition of dissolved and particulate organic carbon in Northern San Francisco Bay during low flow conditions*, Estuar. Coast. Shelf Sci., 51, 75–90.
- Myklestad S. M., Skanoy E., Hestmann S., 1997, *A sensitive and rapid method for analysis of dissolved mono- and polysaccharides in seawater*, Mar. Chem., 56, 279–286.
- Niemczyk E., 1999, *Chlorophyll a*, [in:] *Environmental conditions in the Polish zone of the Southern Baltic Sea during 1988*, Inst. Meteor. Water Managem., Gdynia, 199–202, (in Polish).
- Pakulski J. D., Benner R., 1992, *An improved method for the hydrolysis and MTBH analysis of dissolved and particulate carbohydrates in seawater*, Mar. Chem., 40, 143–150.
- Pakulski J. D., Benner R., 1994, *Abundance and distribution of carbohydrates in the ocean*, Limnol. Oceanogr., 39, 930–940.
- 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., Gdynia, 699–713.
- Pęcherzewski K., Ławacz W., 1976, *Preliminary results of investigations on the quantity of dissolved and particulate organic carbon in the waters of the southern Baltic*, Zesz. Nauk. Uniw. Gdańsk, Oceanografia, 4, 25–44, (in Polish).
- Rich J. H., Ducklow H. W., Kirchman D. L., 1996, *Concentrations and uptake of neutral monosaccharides along 140° W in the equatorial Pacific: contribution of glucose to heterotrophic activity and the DOM flux*, Limnol. Oceanogr., 41, 595–604.

- Sakugava H., Handa N., 1985, *Chemical studies on dissolved carbohydrates in the water samples collected from the North Pacific and Bering Sea*, *Oceanol. Acta*, 8, 185–196.
- Senior W., Chevolet L., 1989, *Studies of carbohydrates (or carbohydrate-like substances) in an estuarine environment*, *Mar. Chem.*, 32, 19–35.
- Williams P.J. le B., 1975, *Biological and chemical aspects of dissolved organic material in seawater*, [in:] *Chemical oceanography*, 2, J. P. Riley & G. Skirrow (eds.), Acad. Press, London, 301–363.