Oceanologia (2015) 57, 168—176

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/oceano

ORIGINAL RESEARCH ARTICLE

DOC and POC in the southern Baltic Sea. Part II — Evaluation of factors affecting organic matter concentrations using multivariate statistical methods☆

Anna Maciejewska, Janusz Pempkowiak *

Marine Chemistry and Biochemistry Department, Institute of Oceanology, Polish Academy of Sciences, Sopot, Poland

Received 30 June 2014; accepted 17 November 2014
Available online 8 December 2014

KEYWORDS
Southern Baltic;
Organic carbon sources;
Quantitative contribution;
Biological activity;
Abiotic factors;
Cluster analysis (CA);
Principal component analysis (PCA);
Segment analysis

Summary This study is a continuation of the research on organic matter sources, distribution and dynamics in the southern Baltic Sea described in detail by Maciejewska and Pempkowiak (2014).

In this paper, cluster analysis, principal component analysis and segment analysis were used to assess relations among factors influencing organic matter concentration in the Baltic sea-water. The following sea-water properties, salinity (Sal), temperature (Temp), pH, concentrations of chlorophyll *a* (Chla) and phaeopigment *a* (Feo), were assessed, while dissolved (DOC) and particulate (POC) organic carbon were used as organic matter measures. Water samples were collected in the course of a three-year study (2009—2011) from the Gdańsk Deep, the Gotland Deep and the Bornholm Deep (Southern Baltic).

As a result, relations among both DOC and POC and the measured water properties were revealed. The cluster analysis leads to the discovery of the following structure of the analyzed water properties: DOC-pH, POC-Chla, without providing interpretation why the structure exists. Using the principal component analysis, factors influencing DOC and POC concentrations were classified as plankton activity and the inflows of saline and freshwater water masses as the study area. Segment regression analysis revealed that organic matter consists of labile and stable fractions and led to the quantification of relations between DOC and the measured sea-water properties. The following contributions to the DOC fluctuations were calculated: salinity — 11%,

☆ This study was supported by the Baltic-C a BONUS Plus EUFP6 Project, statutory activities of Institute of Oceanology PAN, Sopot, and the Polish Ministry of Science and Higher Education, Grant No. N N306 404338.

* Corresponding author at: Marine Chemistry and Biochemistry Department, Institute of Oceanology, Polish Academy of Sciences, ul. Powstańców Warszawy 55, 81-712 Sopot, Poland. Tel.: +48 58 5517281; fax: +48 58 3449669.

E-mail addresses: aninamac@iopan.gda.pl (A. Maciejewska), pempa@iopan.gda.pl (J. Pempkowiak).

Peer review under the responsibility of Institute of Oceanology of the Polish Academy of Sciences.

ELSEVIER Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.oceano.2014.11.003

chlorophyll *a* — 26%, phaeopigment *a* — 26%, POC — 38% in the growing season and 31%, 33%, 21% and 22% respectively in the non-growing season.

1. Introduction

Sea water comprises a variety of dissolved and particulate organic substances. Concentrations of organic substances depend on an equilibrium between their sources — biological activity and sinks — eg. respiration (Chen and Wagnersky, 1993; Chester, 2003; HELCOM, 2007; Hygum et al., 1997; Nagata, 2000; Otto and Balzer, 1998). Contrary to inorganic salts, the concentration of organic substances in sea-water is in the 1—15 mg/dm^3 range. Despite this, the number of individual, different, organic substances exceeds the number of inorganic ones (Hedges, 2002).

Even if most of the organic compounds present in sea-water are still unidentified, it is believed that organic substances play a key role in many natural processes in the marine environment including the vertical transport of biogenic elements and the accumulation of metals by biota. Moreover, organic matter can affect the chemical and physical properties of sea-water. For example organic matter makes water appear colored and/or cloudy, influences the speciation of chemical trace constituents and the alkalinity of sea-water (Almroth-Rosell et al., 2011; Dera, 1992; Emerson and Hedges, 2008; Hedges, 2002; Seager and Slabaugh, 2004; Segar, 2012). Organic matter plays a significant role in carbon cycling (Kuliński and Pempkowiak, 2012; Omstedt et al., 2014) in the Baltic.

The measure of organic matter in sea-water is organic carbon (OC). Organic carbon, for practical reasons, is divided into two fractions: particulate organic carbon (POC) and dissolved organic carbon (DOC). Both, POC and DOC, are mainly products of marine primary production, which is an important driver of the carbon cycle. POC and DOC concentrations in the Baltic Sea have been a subject of interest for many years (Burska et al., 2005; Dzierzbicka-Glowacka et al., 2010, 2011; Emelyanov, 1995; Ferrari et al., 1996; Grzybowski and Pempkowiak, 2003; Jurkovskis et al., 1976; Kuliński and Pempkowiak, 2008, 2011; Maciejewska and Pempkowiak, 2014; Pempkowiak, 1983; Pempkowiak et al., 1984, 2006). These reports indicate, in particular, the ranges of POC and DOC concentrations in the Baltic. In the Baltic Sea concentrations of organic compounds are 3—4 times higher than in the oceans. Moreover it has been established (Maciejewska and Pempkowiak, 2014) that POC and DOC fluctuate seasonally and change both vertically and in various regions of the sea. Recent studies (Kuliński and Pempkowiak, 2008; Maciejewska and Pempkowiak, 2014) show that several factors are related to organic carbon concentrations. These include salinity, sea-water temperature, pH, Chla, and pheo-*a*.

Results of studies on organic carbon concentrations in the Baltic sea indicate that organic substances occur in sea-water due to natural processes related to biota activities (excretion, respiration or decomposition) and transport (river runoff, water exchange with the North Sea). Moreover, Kuliński and Pempkowiak (2008) have already connected chlorophyll *a* and phaeopigment *a* concentrations with live phytoplankton biomass and phytoplankton mortality caused by zooplankton grazing, respectively. Furthermore they used salinity as a measure of riverine discharges and the North sea-water masses in the Baltic.

Recently a three-year study was performed to quantify organic carbon concentrations in Baltic sea-water, and to reveal factors influencing organic carbon concentrations. In a report by Maciejewska and Pempkowiak (2014), the methods of measurements, spatial and temporal OC variability, and factors related to concentrations of DOC and POC were described. It has been concluded that organic carbon concentration is, separately, related to water temperature, pH, and both chlorophyll *a* and pheopigment concentrations. However, factors affecting organic carbon within sea-water act simultaneously. Thus it is interesting to reveal a relative importance of the factors, as well as group the factors into clusters that affect organic carbon concentrations in a similar manner. A study on quantification of the relations between organic carbon concentrations and a battery of individual properties has been performed and the results are reported.

The aim of this paper is to investigate the complex relations between these individual factors and organic carbon concentrations. Data on temperature, DOC and POC, pH, Chla, pheo-*a*, and salinity concentrations are those already used by Maciejewska and Pempkowiak (2014). Multivariate statistical methods (cluster and factor analysis) and segment regression analyses were used to reveal the relations.

2. Material and methods

2.1. Study area

The Baltic Sea is one of the largest brackish seas in the world. It is located between 54°N 66°N parallel of latitude and 10°E 30°E meridian of longitude. The Gulf of Bothnia, Gulf of Finland, the Baltic Proper, and the Danish Straits are the major morphological parts of the sea. The salinity of the surface sea-water layer in the Baltic Proper is approx. 7.1 as a result of abundant precipitation, and the proximity of freshwater sources. Vertical sea-water density increases with depth and decreases in the north-east direction as a result of highly saline water mass inflows from the North Sea through the Danish straits (Voipio, 1981). Moreover, the Baltic Sea is one of the most productive ecosystems in the world due to the high riverine inflow of nutrients (HELCOM, 2007).

This study reports on the statistical analysis of DOC and POC concentration dynamics at three sites in the southern part of the Baltic Proper located in the Gdańsk Deep (54°50′N; 19°17′E), Gotland Deep (57°18′N; 19°53′E), and the Bornholm

Deep (55°10′N; 15°53′E). Vertically sea-water in the presented regions is stratified with stabile halocline, at the depth of 70 m, separating the upper well-oxygenated water layer from a sub-halocline, low oxygen or even anoxic, water layer.

2.2. Analytical methods

2.2.1. Sea-water sample collection and analysis

Sea-water samples were collected during cruises on r/v 'Oceania', r/v 'Alkor' and r/v 'Aranda' between March, 2009 and September, 2011. The following measurements were carried out: temperature and salinity of sea-water using a CTD Sea-Bird, 911-Plus; pH of sea-water using a WTW Multi 3400i pH meter. The samples were filtered through o.4 μm glass fiber filters. The concentrations of POC on the filters were measured using a CHN elemental analyzer Flash EA 1112 series coupled with an IRMS Delta V Advantage/Conflo IV mass spectrometer. Concentrations of DOC were measured in a HyPerTOC analyzer Thermo Electron Corp. Chlorophyll *a* and phaeopigment *a* measurements after acetone extraction and spectrophotometric detection were carried out in a Hitachi U-2800 spectrophotometer. Laboratory analyses of the sea-water samples are described in detail in Maciejewska and Pempkowiak (2014). The results obtained were characterized with respect to DOC and POC vertical and horizontal concentrations and relationships between DOC, POC and pH, temp, Chla, pheo, and salinity were used as proxies of processes influencing organic carbon (Maciejewska and Pempkowiak, 2014).

2.2.2. Statistical analysis

Cluster analysis is a tool that enables the sorting of objects in large data sets into groups and discover their structure without providing interpretation why the revealed groups exist (Bock, 1996). The aim of a cluster analysis is to find 'hidden' groups and present sets of objects within groups (clusters) with individuals that are similar to each other around one group. The use of cluster analysis enables the classification of related variables into one group. It is also possible to select groups that are different from each other (objects within one group are similar and are different from objects in other groups). The graphical result of this analysis is a hierarchical dendogram showing relationships between the analyzed variables. In this paper, cluster analysis was used to determine similarity between the following sea-water properties: salinity, temperature, pH, POC and DOC concentrations, chlorophyll *a* and phaeopigment *a* concentrations characterizing sea-water in the three regions in the southern Baltic Sea. This approach may reveal connections between the variables and classify the variables into the groups characterized by similar features (Bock, 1996; Norusis, 2012).

The cluster analysis was based on a data set comprising samples-objects from the Gdańsk Deep, the Gotland Deep and the Bornholm Deep. There are 167 water samples-objects, each characterized by 7 variables (1169 results). The cluster analysis based on the data set from the Gdańsk Deep included 76 objects, each characterized by 7 variables (523 results). Calculations were made using complete linkage and the Euclidean distance measured by means of the Statistica Data Analysis 6 software package.

2.2.3. Principal component analysis (PCA)

Principal component analysis is a statistical technique used to identify and describe relations between variables that characterize objects. This method enables the classification of variables in terms of a potentially lower number of unobserved variables called factors, without losing information. Thus PCA develops new virtual variables by reducing a number of actual variables and presents new variables-factors in a 2D relationship with covariance values. Similar to cluster analysis, in this study, PCA was used to analyze structure and classify the same sea-water properties: salinity, temperature, pH, POC and DOC concentrations, chlorophyll *a* and phaeopigment *a* concentrations. As a result a set of factors (principal components) will be found describing the analyzed data set features with reduced number of dimensions (Norusis, 2012). Every new component is characterized by covariance coefficients bringing information about the relationships between each of the factors and the input data set from the observation (Borgognone et al., 2001; Norusis, 2012). The PCA was carried out on the data set from the Gdańsk Deep, the Gotland Deep and the Bornholm Deep. There are 167 objects, each characterized by 7 variables (1169 results). The PCA based on the data set from the Gdańsk Deep included 76 objects, with each characterized by 7 variables (523 results). Calculations were made using the Statistica Data Analysis 6 software package.

2.2.4. Segment regression (breakpoint regression)

Segment regression is a method of regression analysis used to determine and quantify dependences between various independent variables and one dependent variable. In this method the data sets are divided into two groups (segments) separated by a 'breakpoint' — a threshold value. Each segment is described by different linear regression equations and indicates a different relationship between dependent and independent variables (Muggeo, 2003). In this study relationships between DOC as a dependent variable and salinity, chlorophyll *a*, phaeopigment *a*, and pH as independent variables were quantified according to Eqs. (1) and (2):

$$\mathrm{DOC_{M1}} = \alpha_1 \cdot S + \beta_1 \cdot C_{\mathrm{chla}} + \gamma_1 \cdot C_{\mathrm{feo}} + \delta_1 \cdot C_{\mathrm{POC}} + \varepsilon_1, \qquad (1)$$

$$\mathrm{DOC_{M2}} = \alpha_2 \cdot S + \beta_2 \cdot C_{\mathrm{chla}} + \gamma_2 \cdot C_{\mathrm{feo}} + \delta_2 \cdot C_{\mathrm{POC}} + \varepsilon_2, \qquad (2)$$

where $\mathrm{DOC_{M1}}$, $\mathrm{DOC_{M2}}$ [mg/dm^3] — computed DOC concentrations; S — salinity [psu]; C_{chla} [mg/m^3] — measured chlorophyll *a* concentrations; C_{feo} [mg/m^3] — measured phaeopigment *a* concentrations; pH — measured pH values; α_1, α_2, β_1, β_2, γ_1, γ_2, δ_1, δ_2 — regression coefficients; ε_1, ε_2 —regression constants.

As a result, the DOC concentrations' data set was separated into two sub-sets using a breakpoint concentration equal to 4.3 mg/dm^3. The breaking point divides samples into two groups: those collected in the vegetative period and those outside of the period (Kuliński and Pempkowiak, 2008; Maciejewska and Pempkowiak, 2014). To calculate the contributions of factors affecting DOC concentration changes the method used by Kuliński and Pempkowiak (2008) was used; first the range of DOC variability and the variability amplitudes for the investigated factors were identified. The results were multiplied by the adequate coefficients, and then divided by the result of DOC variability range, giving the percentage contributions of the individual factors to the DOC pool. Calculations were performed using the Statistica Data Analysis 6 software package.

Vegetative vs non-vegetative periods were discriminated according to the temperature and chlorophyll *a* concentrations as both these factors influence and result from phytoplankton activity, which in turn affect concentration of organic carbon. The 'break point' in the segment regression separates winter or stable organic carbon from organic carbon that comprises both labile and stable fractions.

3. Results

3.1. Cluster analysis results

3.1.1. Southern Baltic

The analyzed data set from the Gdańsk Deep, the Gotland Deep and the Bornholm Deep included 167 objects, each characterized by 7 variables (1169 results). The data from the cluster analysis are synthesized in a dendogram that illustrates the hierarchical structure of the set of variables and shows the similarity between them (Fig. 1). Two main groups of variables are obtained: the first containing mainly the "biotic" properties of sea-water (Feo, POC, Chla, DOC, pH-abiotic), these are closely related to phytoplankton activity (Maciejewska and Pempkowiak, 2014), and the second, which includes "abiotic properties" of sea-water {Sal, Temp}. Within the biotic cluster — smaller, "sub-clusters" — groups of properties {POC, Chla} and {DOC, pH} are clearly visible.

The composition of clusters shows the close relationship between POC and chlorophyll *a* concentrations. This can be readily accepted as the chlorophyll *a* concentration is an indicator of phytoplankton biomass in the water column (Kuliński and Pempkowiak, 2008; Wasmund and Uhlig, 2003) and phytoplankton biomass is the most important component of POC (Dzierzbicka-Glowacka et al., 2011). Thus phytoplankton biomass is a major factor influencing POC concentrations in the study area.

A strong relationship between DOC and pH was also established (Fig. 1). Sea-water pH depends on carbon dioxide partial pressure (Omstedt et al., 2014). CO_2 concentration decreases in the course of photosynthesis due to the absorption by phytoplankton and slow transfer of CO_2 from the atmosphere to sea-water. Thus the process of photosynthesis significantly modifies the pH of sea-water (Edman and Omstedt, 2013; Lampert and Sommer, 2001; Schneider et al., 2003). Intensive photosynthesis in sea-water leads not only to a decrease in CO_2 partial pressure resulting in increased pH (IPCC, 2007), but to a higher DOC concentration as well, due to the excretion of dissolved organic substances and cell lysis (Maciejewska and Pempkowiak, 2014). Data sets characterizing the Bornholm Deep and the Gotland deep comprise much less data. Moreover they lack a suitable coverage of seasons; below the halocline layer data are missing in the case of the Gotland Deep. Therefore just the Gdańsk Deep data were analyzed separately.

3.1.2. The Gdańsk Deep

A dendogram characterizing relations between properties in the "Gdańsk Deep data set" is presented in Fig. 2. Two main groups are distinguishable: {POC, Chla, DOC, pH} and {Sal, Feo, Temp}. The former comprises of two strongly related pairs: {POC, Chla} and {DOC, pH}, while the latter contains one such pair: {Feo, Temp}. The composition of the first cluster and connection between the first two pairs have already been explained (Section 3.1.1). Dzierzbicka-Glowacka et al. (2010) have indicated that zooplankton biomass increases in late summer and autumn, as a result of phytoplankton abundance. An increased concentration of zooplankton in the second half of a year was also reported in

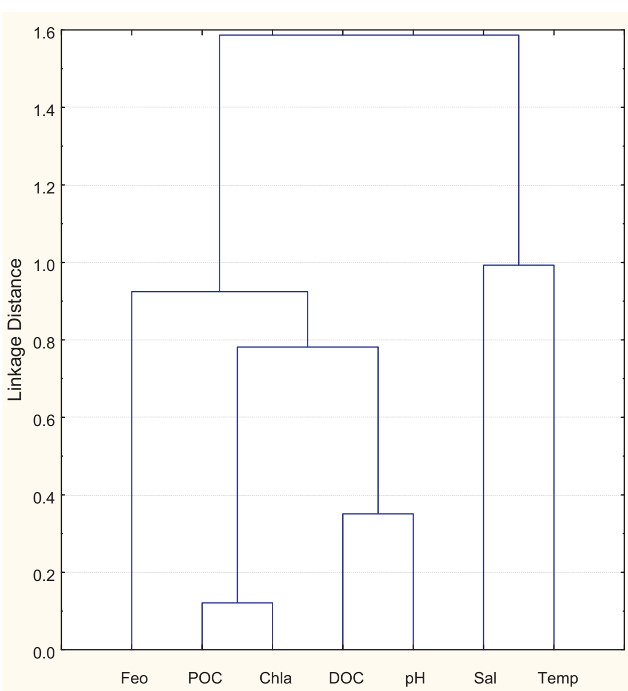

Figure 1 Dendogram illustrating the hierarchical structure of the variables resulting from the cluster analysis of the full data set.

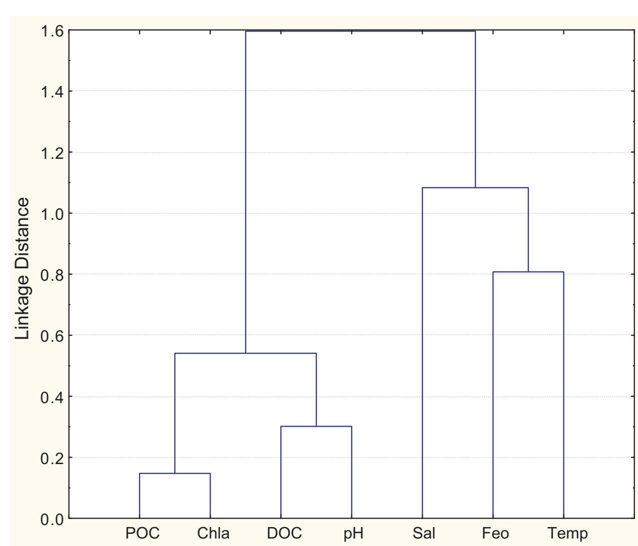

Figure 2 Dendogram illustrating the hierarchical structure of the set of variables resulting from the cluster analysis for the Gdańsk Deep data set.

numerous experimental studies (Brodeur and Ware, 1992; Steinberg et al., 2012).

It must be kept in mind that Chla is a measure of phytoplankton, while POC comprises phytoplankton and zooplankton and detritus as well. The two other components of POC act as a source of DOC. It would be much better to discriminate against phytoplankton in POC, however the uncertainty of calculations would increase substantially, and thus it was decided to use both Chla and POC in the segment analysis.

Sloppy feeding by zooplankton leads to phaeopigment *a* increase. Thus, the co-association of Feo and Temp, although not very strong, seems acceptable as the increase of sea-water temperature has a positive effect on the development of phytoplankton biomass (Maciejewska and Pempkowiak, 2014). The presence of phytoplankton in sea-water, in turn, has an impact on the zooplankton biomass development.

Thus the cluster analysis of "the Gdańsk Deep data set" led to the co-association of pheopigment (Feo) and temperature (Temp) in the "abiotic cluster". This indicates, as already mentioned above, the development of zooplankton activity in periods characterized by higher temperature (Maciejewska and Pempkowiak, 2014), confirming results of biogeochemical modeling (Dzierzbicka-Glowacka et al., 2011) and actual measurements. This is a significant change compared to the results of the "Southern Baltic data set", indicating a weaker relation between organic carbon and zooplankton biomass and activity.

3.2. Principal component analysis (PCA) results

3.2.1. Southern Baltic

Results of the PCA are presented on a two-dimensional graph with axis describing the first two factors (Fig. 3).

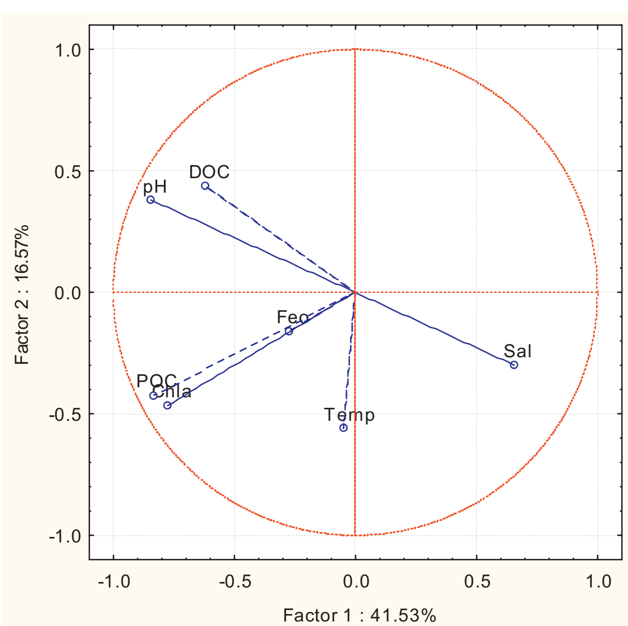

Figure 3 The two-dimensional graph in the space defined by factors F1 and F2 resulting from the PCA analyses of the southern Baltic data set.

Table 1 Factors loadings resulting from PCA analyses of the "Southern Baltic data set". Bold-statistically significant.

Variable	Factor loading		
	Factor 1	Factor 2	Factor 3
Temp	−0.05	**−0.56**	0.50
Sal	**0.65**	−0.30	0.12
pH	**−0.84**	0.38	0.11
Chla	**−0.78**	−0.46	−0.06
Feo	−0.28	−0.16	−0.32
DOC	**−0.62**	0.44	0.35
POC	**−0.84**	−0.42	−0.02

Factor 1 describes more than 41% of the data set variance, while Factor 2 — more than 16%. The correlation coefficients between individual variables and factors are presented in Table 1. Thus, PCA has revealed that DOC is closely related to pH while POC to Chla. Moreover, both pairs define Factor 1 as they are well correlated with each other. Factor 1 is negatively correlated to Sal (salinity). Negative dependence between salinity and organic carbon is easily understandable here, as increased salinity is caused by water of the North Sea low in organic carbon (Kuliński and Pempkowiak, 2008). Moreover, decreased salinity is due to the river run-off, rich with organic carbon (Kuliński and Pempkowiak, 2011). Factor 2 is associated with Temp and describes almost 17% of the variance. It might be interesting to point out that loadings of Chla (negative) and DOC (positive) are barely statistically significant. Feo has the smallest contribution to both factors and is associated with neither of the factors. Factor 3 was classified as insignificant.

Thus, the two factors, Factor 1 and Factor 2, are sufficient to explain almost 60% of the variance of the whole data set comprising seven sea-water properties.

3.2.2. The Gdańsk Deep

Fig. 4 shows results of PCA analyses of the "Gdańsk Deep data set". The first component (Factor 1) is responsible for about 45% of variance and is well correlated with the following sea-water properties: POC, Chla, DOC, pH, and Sal (same as in the PCA results of the "full" data set) (Fig. 3). The conclusion is supported by the role of Sal that defines Factor 1. This is easily understandable as the salinity of the water layer bellow the halocline is much larger than the salinity of the surface water layer where processes involved in production of both, DOC and POC, are the most intensive. On the other hand in zones affected by river run-off, rich with nutrients, salinity is lower, while primary production is higher. Thus lower salinity can be strongly associated with an abundance of dissolved and particularly organic carbon. Temp together with Feo is strongly correlated with Factor 2 describing more than 18% of variance. This feature is similar to the CA results and supports the conclusions drawn from the cluster analysis results. Factor 1 and Factor 2 explain almost 65% of the variance of the whole "Gdańsk Deep data set" coposed of seven sea-water properties.

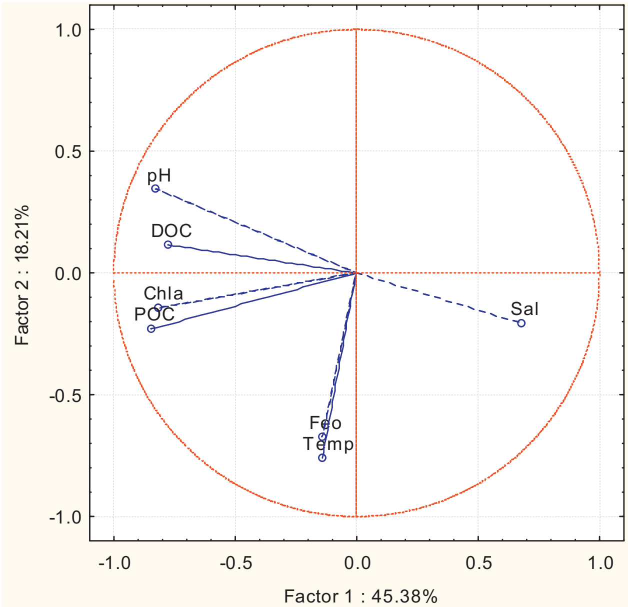

Figure 4 The two-dimensional graph in the space defined by factors F1 and F2 resulting from the PCA analyses of "Gdańsk Deep data set".

3.3. Segment regression

3.3.1. Southern Baltic

Segment analysis has been used to establish quantitative relations between the analyzed properties and DOC concentration in the sea-water. DOC concentration was set as a dependent variable while salinity (Sal), chlorophyll *a* concentration (Chla), phaeopigment *a* concentration (Feo) and POC concentration were used as independent variables (Kuliński and Pempkowiak, 2011; Nakano and Watanabe, 2005; Pempkowiak et al., 2006). These relations were established for two groups of the data, separated by a break point (DOC concentration) equal to 4.3 mg/dm^3. The first group compromises DOC concentrations <4.3 mg/dm^3 originating from the non-vegetative time period. The second set of data comprises concentrations of DOC, above the breaking point of 4.3 mg/dm^3, characterizing samples collected during the vegetative season. Two separate linear equations describing relationships of DOC concentrations and the independent variables were established:

$$DOC_{M1} = -0.122 \cdot Sal + 0.033 \cdot C_{Chla} + 0.106 \cdot C_{Feo} + 0.029 \cdot C_{POC} + 3.58, \quad (3)$$

$$DOC_{M2} = -0.045 \cdot Sal + 0.031 \cdot C_{Chla} + 0.206 \cdot C_{Feo} + 0.046 \cdot C_{POC} + 3.75. \quad (4)$$

Eq. (3) describes the dependence of DOC concentrations not exceeding 4.3 mg/dm^3 on the independent variables, while Eq. (4) defines the same dependence for DOC concentrations greater than 4.3 mg/dm^3. Coefficients calculated for DOC correlations with each particular environmental factor are shown in Table 2.

Calculated regression coefficients indicate an increase of DOC concentrations simultaneously with increasing concentrations of Chla, Feo, and POC. At the same time DOC concentrations decrease with increasing salinity. This, in general, supports qualitative conclusions based on the results of CA and PCA. However, the segment analysis defined quantitative dependences between the variables and the percentage contribution of each variable to DOC concentration changes. The concentration of chlorophyll *a*, in both linear regression equations, (3) and (4), is positively associated with DOC proving that phytoplankton biomass is a significant source of DOC. The larger the biomass of phytoplankton — the higher the concentration of chlorophyll *a* and DOC in the sea-water. Positive values of phaeopigment *a* and POC regression coefficients are in agreement with earlier considerations regarding DOC sources and sinks. A positive correlation between DOC and phaeopigment *a* can be observed and explained as Feo is a proxy of phytoplankton mortality caused by zooplankton (Collos et al., 2005a,b; Kuliński and Pempkowiak, 2008). Sloppy feeding is a direct source of DOC due to cells lysis. The correlation between DOC and POC results from the fact that POC is a measure of all particulate organic carbon species. A "degradation" of suspended organic matter by microorganisms is the likely mechanism that relates these two fractions. In Table 2 there are values not assigned to any particular variable. These are representative of the stable DOC persisting in sea-water throughout a year (Kuliński and Pempkowiak, 2008; Maciejewska and Pempkowiak, 2014).

Actual DOC concentrations and concentrations calculated, by means of the segment analysis, are well correlated with one another, with a correlation coefficient equal to 0.85.

4. Discussion

It is understandable that organic carbon concentrations in sea-water are influenced by several major, and even more minor, processes acting simultaneously. Some of them lead to increase of the concentrations, while others — to the

Table 2 Regression coefficients and calculated contribution of selected factors to the DOC pool.

Environmental factor	Regression coefficients	Value of regression coefficients		Contribution to DOC [%]	
		Non-growing season	Growing season	Non-growing season	Growing season
Salinity (S)	α	−0.122	−0.045	−31%	−11%
Chlorophyll *a* (C_{Chla})	β	0.033	0.031	32.7%	25.7%
Phaeopigment *a* (C_{Feo})	γ	0.106	0.206	21.5%	26.3%
POC (C_{POC})	δ	0.029	0.046	22.2%	37.8%
Concentration of stabile DOC	ε	3.58	3.75		

decrease. Relative importance of the factors has never been quantified. This study provides insight into relations among factors that simultaneously affect concentrations of both, DOC and POC in the Baltic sea-water. An effort to recognize the simultaneous influence of several factors, phytoplankton biomass, phytoplankton activity, zooplankton activity, water exchange with the North Sea and run-off, was undertaken. Despite decades of research the Baltic Sea it is not a sufficiently well-investigated area especially in regard to the distribution of organic carbon. The applied qualitative statistical techniques, cluster analyses and PCA, provided an answer to the question regarding relations among factors, that influence DOC and POC concentrations in the study area.

The cluster analysis established the same groups of variables associated with DOC and POC in the data set comprising results from three regions located in the southern Baltic Sea (the Gdańsk, Gotland and Bornholm Deep) and results from the "Gdańsk Deep": POC—Chla and DOC—pH (Table 3). The link between concentrations of POC and chlorophyll *a* is easily understandable as chlorophyll *a* is a measure of phytoplankton biomass in the marine environment, while phytoplankton biomass is the most important or the second-most important component of POC (Dzierzbicka-Glowacka et al., 2010). Similar conclusions were reached by Kuliński and Pempkowiak (2008) and Dzierzbicka-Glowacka et al. (2011) who analyzed the determinants of POC and DOC concentrations in the southern part of the Baltic Sea. Moreover there is a strong linear correlation between the two variables in the Baltic sea-water (Maciejewska and Pempkowiak, 2014).

The DOC—pH association indicates a close relationship between both variables. A decrease of CO_2 concentration significantly modifies the pH of sea-water (Edman and Omstedt, 2013; IPCC, 2007; Lampert and Sommer, 2001). Thus, pH is an indicator of phytoplankton activity that significantly influences DOC concentrations in the southern Baltic Sea (Kuliński and Pempkowiak, 2008).

PCA analysis "detected" relationships (described as a new factors) among several variables (POC, DOC, Chla, Feo, pH, Sal, and Temp). This statistical technique established multivariate relations between the listed variables and classified them to newly defined factors correlated with one or more primary variables (Table 2). The PCA also provided a semi-quantitative interpretation of the data set variance contributors.

Table 3 Groups of sea-water properties associated with DOC and POC as derived by the cluster analysis.

Organic carbon form	Cluster groups	
	Gdańsk, Gotland and Bornholm Deeps	Gdańsk Deep
DOC	DOC—pH	DOC—pH
POC	POC—Chla	POC—Chla

Similar to cluster analysis, the PCA pointed at close connections in pairs: DOC—pH and POC—Chla. Both pairs were correlated to Factor 1 that was classified as phytoplankton biomass and activity (Table 4). Salinity is negatively corelated with Factor 1 — the higher the salinity the lower pH, DOC, POC and Chla are observed. This is due to fresh, rich inorganic material and nutrients water discharges from rivers. This simultaneous reduction of salinity and increase of DOC occur in the upper sea-water layer. Moreover high seawater inflows from the North Sea, poor in organic compounds (Kuliński and Pempkowiak, 2008; Thomas et al., 2002) increase the salinity and decrease organic carbon concentrations. Factor 2 set by Temp (Southern Baltic) and by a pair Temp—Feo was classified as a zooplankton activity. Both factors explain almost 60% of the total variability in the original data (variance).

Segment analysis enabled a quantification of the relationships between the measured properties of sea-water. It was proven that DOC concentration is influenced by particular sea-water properties. Based on the segment regression equations, two data sets were selected: the first one characterized by concentrations of DOC ($<$4.3 mg/dm^3) observed in samples collected in the non-vegetative period, and the second one that comprised DOC concentrations characteristic of the vegetative season ($>$4.3 mg C/dm^3). The so-called "regression constant" amounted to some 3.65 mg C/dm^3 and was interpreted as the stabile fraction of DOC (Maciejewska and Pempkowiak, 2014). A high-positive correlation between DOC concentrations and the tested properties showed that DOC is strongly dependent on the activity of phytoplankton (Chla), zooplankton grazing (Feo) and POC (direct source of dissolved organic carbon). This supports conclusions drawn by Hoikkala et al. (2012). A negative

Table 4 Groups of variables characterized by statistically significant loadings with factors and percentage contribution to variance.

Factor	PCA results and interpretation					
	Southern Baltic			Gdańsk Deep		
	Variables	% of variance	Factor interpretation	Variables	% of variance	Factor interpretation
Factor 1	DOC—pH, POC—Chla, Sal	42%	Phytoplankton biomass and activity Vertical stratification	DOC—pH, POC—Chla, Sal	45%	Phytoplankton biomass and activity Vertical stratification
Factor 2	Temp	17%	Vertical stratification, seasonality	Temp—Feo	18%	Vertical stratification Zooplankton biomass

dependence between DOC and Sal in the two selected periods is due to the riverine run-off, rich in organic matter and nutrients and the highly saline, poor in organic matter, inflows of the North sea-water (Grzybowski, 2003; Kuliński and Pempkowiak, 2008; Pempkowiak and Kupryszewski, 1980). The most important source of DOC, in the vegetative season, was POC (38% contribution to the DOC increase) (Table 4). The lowest and inversely proportional effect on DOC was observed for Sal (11%). The high-negative contribution of Sal (31%) was associated with a DOC decrease in this period due to the combined effect of inflows from the North Sea and river run-off. Based on the high-correlation coefficient between the experimental and calculated concentrations of DOC (84%) it can be concluded that a simultaneous influence of several mechanisms influencing organic carbon has been quantified for the Southern Baltic. Obviously there are other factors that influence DOC in sea-water. These may include, but are not limited to dissolved organic substances, flocculation in the mixing zone of fresh and saline water (Grzybowski and Pempkowiak, 2003), variations of phytoplankton species characterized by DOC excretion rate, varying organic carbon — Chla ratios (Ston et al., 2002), the rate of labile organic matter mineralization, and climatic conditions: average temperature (Kuliński et al., 2011), cloudiness (Leipe et al., 2008; Meyer-Harms and von Bodungen, 1997), re-flux of organic matter from sediments (Kuliński and Pempkowiak, 2011; Winogradow and Pempkowiak, 2014), seeping groundwater (Szymczycha and Pempkowiak, 2014) and others. However these may be regarded as secondary factors, the primary being the activity of phytoplankton and zooplankton as well as river run-off and inflows of water from the North Sea.

References

Almroth-Rosell, E., Eilola, K., Hordoir, R., Meier, M.H.E., Hall, P.O.J., 2011. Transport of fresh and resuspended particulate organic material in the Baltic Sea — a model study. J. Mar. Syst. 87 (1), 1—12.

Bock, H.H., 1996. Probabilistic models in cluster analysis. Comput. Statist. Data Anal. 23, 5—28.

Borgognone, M.G., Bussi, J., Hough, G., 2001. Principal component analysis in sensory analysis: covariance or correlation matrix? Food Qual. Preference 12 (5—7), 323—326.

Brodeur, R.D., Ware, D.M., 1992. Long-term variability in zooplankton biomass in the subarctic Pacific Ocean. Fish. Oceanogr. 1 (1), 32—38.

Burska, D., Pryputniewicz, D., Falkowska, L., 2005. Stratification of particulate organic carbon and nitrogen in the Gdańsk Deep (southern Baltic Sea). Oceanologia 47, 201—217.

Chen, W., Wagnersky, P.J., 1993. High-temperature combustion analysis of dissolved organic carbon produced in phytoplankton cultures. Mar. Chem. 41 (1—3), 167—171.

Chester, R., 2003. Marine Geochemistry, 2nd ed. Blackwell Science, London, 506.

Collos, Y., Husseini-Ratrema, J., Bec, B., Vaquer, A., Hoai, T.L., Rougier, C., Pons, V., Souchu, P., 2005a. Phaeopigment dynamics, zooplankton grazing rates and the autumnal ammonium peak in a Mediterranean lagoon. Hydrobiologia 550, 83—93.

Collos, Y., Husseini-Ratrema, J., Bec, B., Vaquer, A., Hoai, T.L., Rougier, C., Pons, V., Souchu, P., 2005b. Pheopigment dynamics, zooplankton grazing rates and the autumnal ammonium peak in a Mediterranean lagoon. Hydrobiologia 550, 83—93.

Dera, J., 1992. Marine Physics. Elsevier, Amsterdam, 515.

Dzierzbicka-Glowacka, L., Kulinski, K., Maciejewska, A., Jakacki, J., Pempkowiak, J., 2011. Numerical modelling of POC dynamics in the southern Baltic under possible future conditions determined by nutrients, light and temperature. Oceanologia 53 (4), 971—992.

Dzierzbicka-Glowacka, L., Kuliński, K., Maciejewska, A., Pempkowiak, J., 2010. Particulate Organic Carbon in the southern Baltic Sea: numerical simulations and experimental data. Oceanologia 52 (4), 621—648.

Edman, M., Omstedt, A., 2013. Modeling the dissolved CO_2 system in the redox environment of the Baltic Sea. Limnol. Oceanogr. 58 (1), 74—92, http://dx.doi.org/10.4319/lo.2013.58.1.0074.

Emelyanov, E., 1995. Baltic Sea: Geology, Geochemistry, Paleoceanography, Pollution. P.P. Shishov Institute of Oceanology Russian Academy of Sciences, Kaliningrad, 119.

Emerson, S.R., Hedges, J.I., 2008. Chemical Oceanography and the Marine Carbon Cycle. Cambridge University Press, Cambridge, 453.

Ferrari, G.M., Dowell, M.D., Grossi, S., Targa, C., 1996. Relationship between the 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., 2003. Are data on light-induced ammonium release from dissolved organic matter consistent? Chemosphere 52, 933—936.

Grzybowski, W., Pempkowiak, J., 2003. Preliminary results on low molecular weight organic substances dissolved in the waters of the Gulf of Gdansk. Oceanologia 45 (4), 693—704.

Hedges, J.I., 2002. Why dissolved organic matter. In: Hansell, D.A., Carlson, C.A. (Eds.), Biogeochemistry of Marine Dissolved Organic Matter. Elsevier Science, San Diego, 1—33.

HELCOM, 2007. Climate change in the Baltic Sea Area. Baltic Sea Environ. Proc. 111, 54.

Hoikkala, L., Lahtinen, T., Perttila, M., Lignell, R., 2012. Seasonal dynamics of dissolved organic matter on a costal salinity gradient in the northern Baltic Sea. Cont. Shelf Res. 45, 1—45.

Hygum, B.H., Petersen, J.W., Søndergaard, M., 1997. Dissolved organic carbon released by zooplankton grazing activity — a high quality substrate pool for bacteria. J. Plankton Res. 19 (1), 97—111.

IPCC, 2007. Climate Change 2007. Synthesis Report. A Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel of Climate Change. Cambridge University Press, Cambridge, 73.

Jurkovskis, A.K., Formych, T.A., Grotanie, B.J., 1976. Cikl izmienienij fosfora, azota i organiczeski swiazannogo uglieroda w Ba1tijskom Morie. Okieanologia 16, 79—86.

Kuliński, K., Maciejewska, A., Dzierzbicka-Głowacka, L., Pempkowiak, J., 2011. Parameterisation of a zero-dimensional pelagic detritus model, Gdansk Deep, Baltic Sea. Rocznik Ochrony Środowiska 13, 187—206.

Kuliński, K., Pempkowiak, J., 2008. Dissolved organic carbon in the southern Baltic Sea: quantification of factors affecting its distribution. Estuarine. Coast. Shelf Sci. 78, 38—44.

Kuliński, K., Pempkowiak, J., 2011. The carbon budget of the Baltic Sea. Biogeosciences 8, 3219—3230, http://dx.doi.org/10.5194/bg-8-3219-2011.

Kuliński, K., Pempkowiak, J., 2012. Carbon Cycling in the Baltic Sea. Springer, Berlin, 132.

Lampert, W., Sommer, U., 2001. Ekologia wód śródlądowych. (Ecology in Freshwaters).Wydawnictwo Naukowe PWN, Warszawa, 415.

Leipe, T., Dippner, J.W., Hilles, S., Voss, M., Christiansen, C., Bartholdy, J., 2008. Environmental changes in the central Baltic Sea during the past 1000 years: inferences from sedimentary records, hydrography and climate. Oceanologia 50 (1), 23—41.

Maciejewska, A., Pempkowiak, J., 2014. DOC and POC in the Southern Baltic. Part I Evaluation of factors influencing sources distribution and dynamics of organic matter. Oceanologia 56 (3), 523—548.

Meyer-Harms, B., von Bodungen, B., 1997. Taxon-specific ingestion rates of natural phytoplankton by calanoid copepods in an estuarine environment (Pomeranian Bight, Baltic Sea) determined by cell counts and HPLC analyses of marker pigments. Mar. Ecol. Prog. Ser. 153, 181—190.

Muggeo, V.M., 2003. Estimating regression models with unknown break-points. Stat. Med. 22 (19), 3055—3071.

Nagata, T., 2000. Production mechanisms of dissolved organic matter. In: Kirchman, D.L. (Ed.), Microbial Ecology of the Oceans. Wiley-Liss, New York, 121—152.

Nakano, Y., Watanabe, Y.W., 2005. Reconstruction of pH in the surface sea-water over the North Pacific Basin for all seasons using temperature and chlorophyll-a. J. Oceanogr. 61, 673—680.

Norusis, M., 2012. IBM SPSS Statistics 19 Advanced Statistical Procedures Companion. Prentice Hall, Upper Saddle River, NJ, 464.

Omstedt, A., Humborg, Ch., Pempkowiak, J., Perttila, M., Rutgersson, A., Schneider, B., Smith, B., 2014. Biogeochemical control of the coupled CO_2—O_2 system of the Baltic Sea: a review of the results of Baltic-C. AMBIO 43, 49—59, http://dx.doi.org/10.1007/s13280-013-0485-4.

Otto, S., Balzer, W., 1998. Release of dissolved organic carbon (DOC) from sediments of the NW European Continental Margin (Goban Spur) and its significance for benthic carbon cycling. Prog. Oceanogr. 42, 127—144.

Pempkowiak, J., 1983. C_{18} reversed-phase trace enrichment of short- and long-chain (C_2—C_8—C_{20}) fatty acids from dilute aqueous solutions and sea water. J. Chromatogr. 258, 93—102.

Pempkowiak, J., Kupryszewski, G., 1980. The input of organic matter to the Baltic from the Vistula River. Oceano 12, 80—98.

Pempkowiak, J., Walkusz-Miotk, J., Be1dowski, J., Walkusz, W., 2006. Heavy metals in zooplankton from the Southern Baltic. Chemos 62, 1697—1708.

Pempkowiak, J., Widrowski, M., Kuliński, W., 1984. Dissolved organic carbon and particulate carbon in the Southern Baltic in September 1982. In: Proceedings XIV Conference of Baltic Oceanographers, IMGW, Gdynia, 699—713.

Schneider, B., Nausch, G., Nagel, K., Wasmund, N., 2003. The surface water CO_2 budget for the Baltic Proper: a new way to determine nitrogen fixation. J. Mar. Syst. 42 (1—2), 53—64.

Seager, S.L., Slabaugh, M.R., 2004. Chemistry for Today: General, Organic, and Biochemistry. Thomson Brooks/Cole, 342.

Segar, D.A., 2012. Introduction to Ocean Science, 3rd ed., First electronic edition, Version 3.0, 525.

Steinberg, D.K., Lomas, M.W., Cope, J.S., 2012. Long-term increase in mesozooplankton biomass in the Sargasso Sea: linkage to climate and implications for food web dynamics and biogeochemical cycling. Global Biogeochem. Cycles 26 (1), 1—16.

Ston, J., Kosakowska, A., Łotocka, M., Łysiak-Pastuszak, E., 2002. Pigment composition in relation to phytoplankton community structure and nutrient content in the Baltic Sea. Oceanologia 44 (4), 419—437.

Szymczycha, B., Pempkowiak, J., 2014. Could groundwater be a significant carbon source to the Baltic sea? Oceanologia 56 (2), 327—347.

Voipio, A., 1981. The Baltic Sea, vol. 30. Elsevier, Amsterdam, 148.

Wasmund, N., Uhlig, S., 2003. Phytoplankton trends in the Baltic Sea. J. Mar. Sci. 60, 177—186.

Winogradow, A., Pempkowiak, J., 2014. Organic carbon burial rates in the Baltic Sea sediments. Estuar. Coast. Shelf Sci. 138, 27—36.