

FRESHWATER DISCHARGE INTO THE EAST FRISIAN WADDEN SEA: GEOCHEMISTRY OF HUMIC MATTER-RICH WATERS

S. Kölsch, S. Gebhardt, F. Terjung, G. Liebezeit,
R. Reuter, J. Rullkötter & H.-J. Brumsack

Introduction

In the NW German Wadden Sea a high variability of many physical (e. g., salinity, temperature) and chemical parameters (e. g., DOM, Mn, Fe) of the water column can be observed on tidal as well as seasonal time scales. To understand these dynamics it is of vital importance to know the sources for dissolved and particulate major and trace elements, nutrients and dissolved organic matter (DOM) of the Wadden Sea water column.

The backbarrier tidal flats have three main water sources: (i) the North Sea, (ii) pore water draining off the tidal flats during ebb tide, (iii) freshwater discharge from small coastal tributaries. The freshwater is low in salinity, but specifically enriched in some trace metals. Furthermore, it represents an important source for terrestrial dissolved organic matter (DOM). DOM is a ubiquitous component of natural surface waters. Organic substances are transported from land to coastal marine environments *via* river discharge and contribute significantly to the carbon pool of coastal waters. Moreover, DOM in natural waters is of environmental importance for processes such as dissolution and mobilisation of xenobiotics and heavy metals.

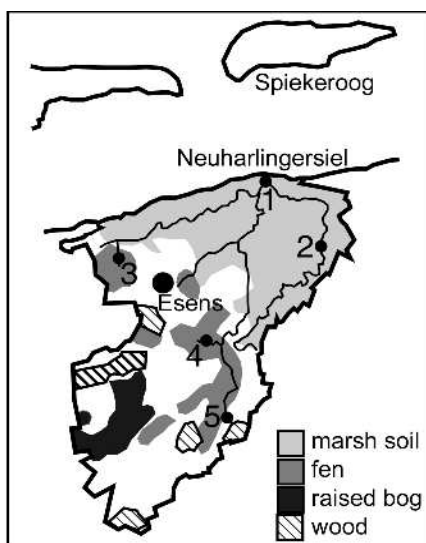


Fig. 1. Soil map of catchment area and selected sampling locations.

Freshwater discharge volumes can be estimated either from the opening times of the flood gates or indirectly from salinity changes in the backbarrier area of Spiekeroog Island. By our investigations we want to elucidate whether the freshwater input has a significant influence on the geochemistry of the Wadden Sea water column. The aim of our project is to quantify the terrestrial input of major and trace elements, nutrients and dissolved organic matter (DOM) *via* the freshwater contribution.

Geographical setting

The only significant direct freshwater input into the Spiekeroog backbarrier area originates from the automated flood

gates of Neuharlingersiel. The catchment area of the freshwater environment is about 125 km². Rainfall in the region is 827 mm/a according to the long-term average of 1961-1990 taken at the city of Aurich.

The catchment area rises to less than 5 m, in large parts less than 2 m above sea level. It consists of fens, areas of sandy marsh soils close to the coast and a few patches of forest. Most open areas are used as farmland, mainly for dairy cattle. Fig. 1 shows a soil map of the catchment area with the main water courses and 5 of the 10 sampling locations.

Material and methods

For inorganic geochemical investigations water samples were taken monthly at 10 locations in the catchment area and in shorter intervals at Neuharlingersiel. Filtration of samples was performed for analysis of particulate major and trace elements (0.4 µm GF Filters, HNO₃/HF/HClO₄ acid digestions, ICP-OES and ICP-MS), DOC (0.7 µm GF filters, multi N/C 3000, Analytic Jena), particulate carbon (0.7 µm GF filters, Ströhlein coulomat) dissolved trace metals (0.45 µm SFCA syringe filters, ICP-OES, ICP-MS) and yellow substance fluorescence (GF 50 filters, Shimadzu RF 1501, 308 nm excitation). After correction of the fluorescence spectra for the wavelength-dependent sensitivity of the instrument, readings were taken at 420 and 450 nm. These data were normalized to the total intensity of the water Raman scattering band, thus yielding fluorescence data with intensities denoted as Raman units (DERMANN *et al.*, 1994). Conductivity and pH were measured on unfiltered samples.

Inorganic nutrients were determined according to GRASSHOFF *et al.* (1998) on filtered samples (Whatman GF/C).

For organic geochemical investigations water samples were filtered at 0.45 µm (tangential flow filtration). The high-molecular-weight material of the DOM was isolated by column chromatography with XAD-8 resin. The XAD technique provides humic acids (HA), fulvic acids (FA) and hydrophobic neutrals (HoN).

The isolated humic material samples were characterised by pyrolysis in both absence and presence of TMAH (tetramethylammonium hydroxide). Samples were pyrolysed (Curie point, 590°C) for 10 s. Gas chromatography was done with temperature programming from 40°C to 280°C at 4°C/min.

Mass spectral analyses were carried out on an Agilent MSD 5973N using EI ionisation (70 eV) and a mass range of 50-650 u. Identification of the products was based on the NIST spectral library and mass spectral interpretation.

Inorganic geochemical properties of the water samples

As the chemical composition of water depends on the source, the chosen sampling sites cover all soil types. Table 1 shows average values for several parameters for five representative sampling sites.

The samples from the different sites show high variations in salinity, pH, DOC, POC, SPM and dissolved and particulate Mn and Fe. Locations on the marsh soils near to the coast are influenced by sea spray and saline groundwater (Altharlingersiel). These samples show pH values between 7 and 8, medium DOC contents (ca. 1.3 mmol/l) and increased salinities (average 0.8-0.9, individual Neuharlingersiel samples up to 1.7). Fe is removed from solution with increasing salinity and is enriched on particles. In the fen areas the water is slightly acidic (pH 6-7). At one location (Stuhlleide) the DOC content is rather high, at a different location (Kortenhörn) the DOC content is surprisingly low. At

Location	Neuharlingersiel (1)	Altharlingersiel (2)	Kortenhörn (3)	Stuhlleide (4)	Jackstede (5)
	sea water infl.	sal. ground water infl.	fen	fen	forest
SPM (mg/l)	48.2 (30.6)	67.5 (28.1)	13.2 (6.8)	21.2 (6.8)	18.5 (21.1)
pH	7.8 (0.5)	7.7 (0.3)	6.2 (0.2)	6.8 (0.2)	5.4 (0.4)
Sal (psu)	0.9 (0.38)	0.82 (0.26)	0.19 (0.04)	0.17 (0.03)	0.1 (0.02)
DOC (mmol/l)	1.24 (0.20)	1.27 (0.21)	0.62 (0.40)	1.56 (0.50)	3.88 (0.65)
C part. (%)	10.3 (3.8)	6.7 (2.4)	19.6 (2.0)	18.5 (1.9)	23.5 (7.9)
Fediss. (µmol/l)	12.5 (7.1)	2.4 (3.0)	42.4 (23.0)	45.5 (19.1)	35 (15.9)
Mndiss. (µmol/l)	3.92 (1.60)	5.73 (2.16)	3.22 (0.44)	3.25 (0.82)	2.45 (0.61)
Fe ₂ O ₃ part. (%)	10.2 (2.6)	9.2 (0.8)	31.5 (8.3)	21.0 (3.6)	5.8 (1.6)
Mnpart. (ppm)	1984 (1725)	1054 (496)	165 (82)	1279 (1664)	230 (95)
Fepart. (µmol/l)	61.3 (78.0)	77.4 (22.9)	52.2 (18.0)	55.7 (26.2)	13.5 (21.3)
Mnpart. (µmol/l)	1.02 (0.95)	1.29 (0.85)	0.04 (0.03)	0.49 (0.94)	0.07 (0.10)

Table 1. Average values (Mar 02–Mar 03, particulate Mn and Fe locations 2–5 Mar 02–Aug 02) of several parameters for five representative sampling sites. Standard deviations are given in parentheses to show the variability.

both locations the dissolved and particulate Fe content is very high.

The acidic water in a fen area removes Fe from the soil. The humic substances in the water can complexate and stabilise the Fe and other trace metals in solution. The water from one sampling location at a small ditch running from a forest exhibits the highest DOC content (3-6 mmol/l), the lowest pH (4.5-6) and a very high amount of particulate carbon. The dissolved Fe at this location is almost as high as in the fen area, but the particles contain considerably less Fe.

2002 a distinct pore water input would be needed to explain the Mn concentrations observed in the Wadden Sea.

Inorganic nutrients

The inorganic nutrients reactive phosphate, dissolved inorganic nitrogen (sum of nitrite, nitrate and ammonia) and silicate show high winter and low summer values in the course of the year 2002 (Fig. 3). Lowest nutrient concentrations were measured at Kortenhörn and Jackstede whereas Altharlingersiel, especially for phosphate, generally showed the highest concentrations.

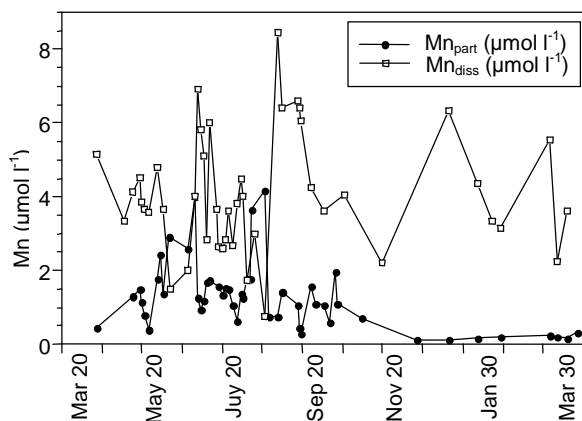


Fig. 2. Seasonal variation of particulate and dissolved manganese at Neuharlingersiel.

The catchment water merges downstream the Neuharlingersieltief, where it is accumulating until being discharged into the harbour and the Wadden Sea. The water at this sampling location (Neuharlingersiel) represents a mixed sample of the whole catchment area with a certain sea water influence especially close to the flood gates. In general the Neuharlingersiel samples show a similar signature compared to those from Altharlingersiel. The dissolved Mn in Neuharlingersiel is highly variable and shows no seasonality. A slight but not very significant correlation of dissolved Mn with salinity can be observed (R=0.61). Unlike dissolved Mn the particulate Mn shows seasonal variation. In summer particles are enriched in Mn, with a high variability. In winter the particulate Mn load is on a constantly lower level (Fig. 2). This is presumably caused by the lower activity of Mn-oxidising microorganisms in winter.

A simple balance calculation was made based on the salinity variations in the Wadden Sea to assess the importance of freshwater as a source for Mn in the Spiekerroog backbarrier area (DELLWIG *et al.*, this volume). This calculation shows that in situations like February 2002 the freshwater contribution would be sufficient, but in August

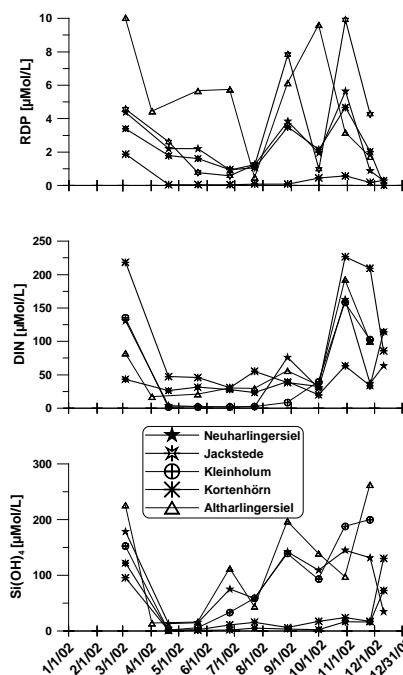


Fig. 3. Seasonal variation of inorganic nutrients at five sampling stations in the drainage area of the Neuharlingersiel deep (RDP – reactive dissolved phosphate, DIN – dissolved inorganic nitrogen).

Although the data suggest a largely biological control of nutrient contents additional processes appear to also exert an influence as can be seen in the variability in reactive phosphate in autumn and early winter and the increase in silicate concentrations already in summer at three stations.

Fluorescence of DOM

Approximately 70% of the dissolved organic matter in water consists of humic substances. When excited in the ultraviolet,

it emits a spectrally broad fluorescence band with a maximum at 420 to 450 nm, depending on the composition and origin of the material. The fluorescence spectra of humic substances represent the summation of signals from many different fluorescent molecules. Only a few aliphatic and alicyclic molecules exhibit fluorescence in the UV and visible region. Among the structural characteristics that give rise to fluorescence are those containing conjugated double bonds or aromatic rings. However, fluorescence spectroscopy cannot be used for the direct determination of functionality in humic substances.

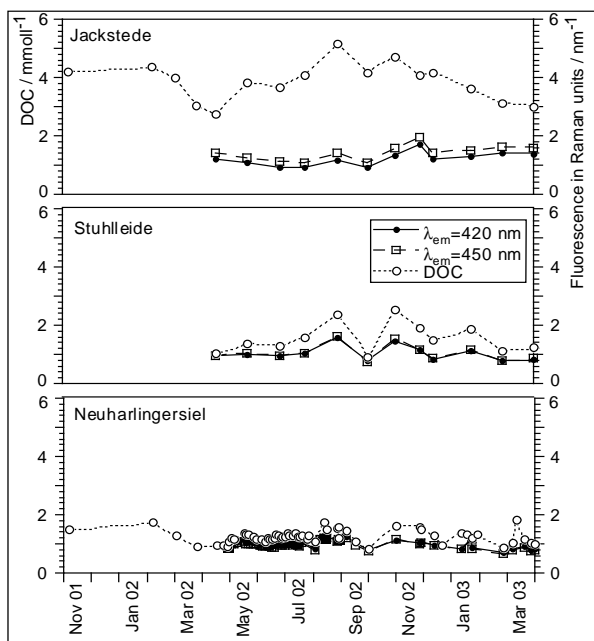


Fig. 4. Seasonal variation of DOC and fluorescence in samples from Neuharlingersiel (sea water infl.), Stuhlleide (fen) and Jackstede (forest).

The measurements of dissolved organic carbon (DOC) reveal a seasonal variation of these compounds in samples from different locations. Minima can be observed in spring and less distinctly in autumn. Fig. 4 shows a comparison of DOC and fluorescence.

Fluorescence emission spectra with 308 nm excitation are characterised by an emission maximum in the 420-450 nm region. Spectra taken from Stuhlleide (fen) samples show an emission maximum at 420 nm, and they correlate well with DOC ($R=0.93$). At Neuharlingersiel (sea water influenced) there is still a correlation of DOC and fluorescence, the emission is again at a maximum at 420 nm, but the correlation coefficient is much lower ($R=0.74$). The Jackstede (forest) samples, however, show an emission maximum shifted towards higher wavelengths ($\lambda=450$ nm). Moreover, there is no noticeable correlation between DOC and fluorescence. The ratio of DOC to fluorescence is much higher at Jackstede (approx. 2.8) than at Neuharlingersiel (approx. 1.2) and Stuhlleide (approx. 1.5), which shows that the fluorophores in the DOC pool of Jackstede have not only a different origin but also less intense fluorescence properties. The shift of the emission maximum indicates a change of the fluorophore composition. This is supposed to be due to the different structures of woodland- and marshland-derived yellow substance and needs to be further investigated.

Organic geochemical properties of the water samples

DOM in rivers exhibits a wide compositional diversity reflecting different organic matter sources related to the

bioproduction in the drainage area, seasonal variations and anthropogenic influence. The major part of DOM in natural waters consists of humic matter which is formed during degradation of plant- and animal-derived organic matter as a result of various abiotic and microbial transformation processes. As a consequence, humic matter has a complex polymer-like structure.

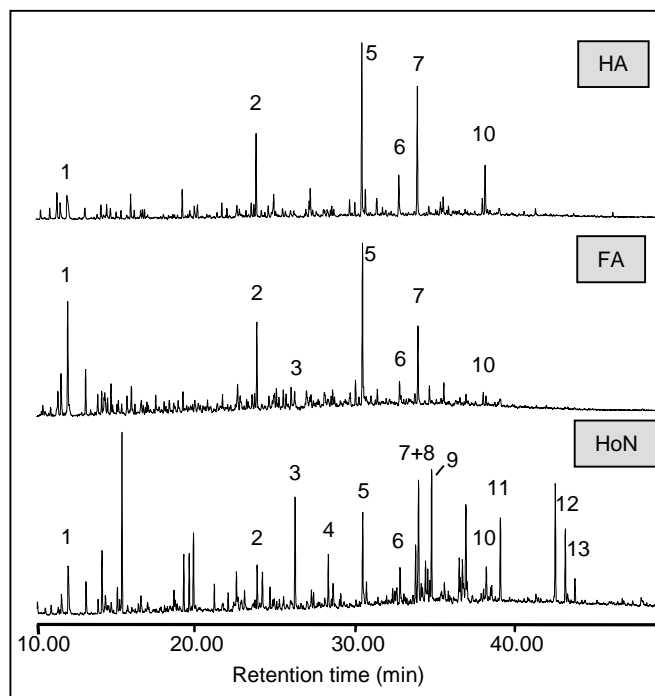


Fig. 5. TIC chromatograms of humic acids (HA), fulvic acids (FA) and hydrophobic neutrals (HoN) after pyrolysis at 590°C (with TMAH) (numbers: see Table 1).

To investigate this complex macromolecular matter in more detail, a pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) method was developed. It provides detailed structural information, but also has limitations in analysing polar functional groups. A poor chromatographic behaviour of the polar degradation products and secondary thermal reactions, like decarboxylation, lead to loss of essential information on the original macromolecule. The principle aim of pyrolysis in combination with TMAH treatment (tetramethylammonium hydroxide) is to avoid thermal decarboxylation and to improve chromatographic separation by converting carboxylic and phenolic hydroxyl groups into their methyl derivatives (CHALLINOR, 2001). Pyrolysis is now available as a method which allows application on a routine basis. The data given below outline the potential of this analytical tool in future investigations.

Conventional pyrolysis shows a large number of different compounds. The identified compounds of isolated fractions have different abundances and cover a wide variety of chemical structures which are mainly substituted aromatics such as benzenes, phenols and furans. The sum of these three product groups represents about 80% of all identified compounds.

Pyrolysis with TMAH results in a wide variety of methyl ethers of phenols and methyl esters of benzene-carboxylic acids. Fig. 5 shows the comparison between humic acids, fulvic acids and hydrophobic neutrals. Among the main aromatic products are methyl derivatives of different phenols, alkylphenols and phenolic acids, whereas aliphatic products are dominated by monocarboxylic (mainly C_{12} , C_{14} , C_{16} and C_{18}) and dicarboxylic acids (mainly C_4 - C_5), which indicate the

importance of ester linkages between the different structural subunits of aquatic humic matter. Cyclic compounds and nitrogen-containing products are also present.

(A)	HA	FA	HoN
Aliphatics	6.2	23.8	48.8
Lignin derived	68.5	44.5	14.7
Other aromatics	12.7	17.9	17.4

(B)	
1	Butanedioic acid, dimethyl ester
2	4-Methoxybenzoic acid methyl ester
3	1,2-Benzenedicarboxylic acid, dimethyl ester
4	Dodecanoic acid, methyl ester
5	3,4-Dimethoxybenzoic acid methyl ester
6	2-Propenoic acid, 3-(4-methoxyphenyl)-, methyl ester
7	3,4,5-Trimethoxybenzoic acid, methyl ester
8	Tetradecanoic acid, methyl ester
9	Tetradecanoic acid, 2-methyl-, methyl ester
10	Propenoic acid, 3-(3,4-dimethoxyphenyl), methyl ester
11	Hexadecanoic acid, methyl ester
12	Octadecenoic acid, methyl ester
13	Octadecanoic acid, methyl ester

Table 2. (A) Relative proportions (%) of the main degradation products of humic acids, fulvic acids and hydrophobic neutrals. (B) Some of the most abundant pyrolysis compounds (see Fig. 5).

Comparison of the relative abundances of the main product groups (Table 2) was made based on peak heights in the total ion current (TIC) chromatograms. The humic and fulvic acid fractions appear to consist of structurally similar organic matter dominated by lignin-derived compounds.

In both fractions the methyl esters of p-hydroxybenzoic acid (peak 2), vanillic acid (pPeak 5) and syringic acid (peak 7) are the degradation products with the highest abundance. The high number of methyl ethers of phenols indicates the significant contribution of lignin. The humic acid fraction shows the highest proportion of monomeric lignin-derived degradation products, whereas the aliphatic compounds are most abundant in the hydrophobic neutrals fraction.

Conclusions

To understand the tidal and seasonal dynamics of the Wadden Sea, coastal freshwater contributions were analysed in order to quantify the terrestrial input of major and trace elements, nutrients and dissolved organic matter (DOM) via the Neuharlingersiel flood gate.

The samples from different sites show high variations in salinity, pH, DOC, POC, SPM and dissolved and particulate Mn and Fe content, depending on the soil type. The dissolved Mn at Neuharlingersiel is highly variable and shows no seasonality. The particulate Mn shows seasonal variations with minima during winter presumably caused by the lower activity of Mn-oxidising microorganisms in the cold season.

DOC shows seasonal variations with minima in spring and autumn. In most samples it correlates with fluorescence, but with different DOC/fluorescence ratios. This is an indicator for the variable composition of DOM.

DOM shows a broad spectrum of different compounds. There are three main degradation product groups obtained by pyrolysis with TMAH, aliphatics, lignin-derived and other aromatics. The highest proportion of lignin-derived aromatics was found in the humic acid fraction., whereas the hydrophobic neutrals fraction shows the highest abundance of aliphatic compounds.

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¹S. Kölsch, ¹S. Gebhardt, ²F. Terjung, ³G. Liebezeit, ²R. Reuter, ¹J. Rullkötter, & ¹H.-J. Brumsack, ¹Institute of Chemistry and Biology of the Marine Environment (ICBM), Carl von Ossietzky University of Oldenburg, P.O. Box 2503, D-26111 Oldenburg, Germany; ²Marine Physics Group, Institute of Physics, Carl von Ossietzky University of Oldenburg, Carl-von-Ossietzky-Straße 9-11, D-26129 Oldenburg, Germany; ³Senckenberg TERRAMARE, Schleusenstrasse 1, D-26382 Wilhelmshaven; e-mail: s.koelsch@icbm.de.