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Original Research

Iron Wet Deposition in the Coastal Zone of the Gulf of Gdańsk (Poland)

D. Dunajska*, L. Falkowska, P. Siudek, G. Sikorowicz, A. Lewandowska, D. Pryputniewicz, R. Magulski, M. Kowacz

Department of Marine Chemistry and Environmental Protection, Institute of Oceanography, University of Gdańsk, al. Marsz. J. Piłsudskiego 46, 81-378 Gdynia, Poland

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Abstract

The concentrations of total iron were determined in the 30 rainwater samples collected at Gdynia station, located in the coastal zone of Gulf of Gdansk. The samples were assembled from December 2002 to November 2003. Total iron concentrations were measured using a colorimetric method with bathophenanthroline. The concentrations of major rain components (Na^+, NO_3^-, Cl^-, SO_4^{2-}) were also determined. Concentrations of Fe_{tot} ranged from 0.26 $\mu g \cdot dm^{-3}$ to $0.51 \cdot 10^{-3}$ $\mu g \cdot dm^{-3}$. The total annual flux of Fe_{tot} was 11.22 $mg \cdot m^{-2} yr^{-1}$, which suggests that wet deposition can be one iron source for phytoplankton in the Southern Baltic. Iron in rain came from both terrestrial areas and seawater. Particularly at E&SE winds the swash zone saturated with marigenic aerosols was a significant source of iron. In these causes an anthropogenic influence on rain acidification was found to be minimal.

Keywords: iron, wet deposition, acid rain, coastal zone of Southern Baltic

Introduction

Iron is an element essential for the biochemical and physiological activity of marine phytoplankton due to its role in many metabolic processes, i.e. photosynthesis, nitrate reduction, nitrogen assimilation, N_2 fixation and oxidation reactions [1-3]. Iron presents often at low ambient concentrations in seawater (0.05–2 nM), therefore it can limit primary production and regulate ecosystem structure in large areas of the ocean [1, 2]. The atmosphere is a source of particulate and dissolved iron for HNLC regions (High Nutrients, Low Chlorophyll) and coastal surface seawaters [1, 4]. Iron removed from the atmosphere by wet or dry deposition stimulates growth of phytoplankton and increases a flux of organic matter from the euphotic layer to the deep ocean [1, 2, 4]. The washed-out aerosols are considered to be the major iron source in oceans and apparently account for ~80% or more of the total atmospheric deposition [4, 7]. Photochemical processes and the contact of iron with acidic aerosols during material transport in the atmosphere can transform mineral iron into dissolved Fe(III) and Fe(II) [7]. Therefore, most often rain consists of dissolved iron, inorganic and organic forms, and additionally of colloidal and particulate iron [7]. Only Fe(II) species play an important role in phytoplankton growth. Due to the rapid changes of pH, ionic strength and solubility of aerosols occurred in the atmosphere-seawater boundary layer the dissolved Fe(II) undergoes again transformation into colloidal and particulate Fe(III). If atmospheric iron deposited to iron-limited surface seawaters became bioavailable, then rain could stimulate the growth of phytoplankton [1, 2, 3].

Until 1900 the Baltic Sea was considered to be a mesotrophic reservoir. At present the Baltic is an eutrophic sea because of a four-fold increase in N input and an eight-fold increase in P input from outside sources. It is possible that eutrophication to some extent depends on iron input. The assessments show that an annual input by

*Corresponding author; e-mail: dede@sat.ocean.univ.gda.pl

geological processes and river outflows were 25,000 $t \cdot yr^{-1}$ in the beginning of the 1990s, whereas anthropogenic outflows, mines and industries introduced 319,000 $t \cdot yr^{-1}$ into the Baltic [8]. Until now determinations of iron concentrations are limited to Baltic sediments and seawater [9, 10]. Papers about atmospheric deposition have not been found. The main aim of this work was to recognize preliminary total iron concentrations in rain and to estimate the iron flux from the atmosphere.

Materials and Methods

Sampling

The 30 rain samples were collected at a routine measurement station located at a land-based station in Gdynia (φ= 54°31'N, λ= 18°48.86'E, Fig. 1). The station was situated at the edge of the roof of the Institute of Oceanography of Gdansk University, above the tree crowns at a height of c. 20 m a.s.l.. The building is about 1 km away from the coastal line of the Gulf of Gdańsk. Gdynia, with a population of 250,000 citizens, is located close to agricultural and industrial centers (shipyards, port facilities, food-processing and chemical plants). Near Gdynia are two other sizeable cities - Gdańsk and Sopot. Together with Gdynia, they make up the so-called 'Tri-city' area.

The collections of samples were carried out during December 2002 - November 2003. Usually the intervals between rainfall events varied from 4 days to 2 weeks. Meteorological parameters, such as the type of wet deposition, rainfall amount, wind direction, wind speed, relative air humidity and air temperature were measured.

Procedures

The rain sample collector consisted of a 1 dm^3 polyethylene bottle with small vent and teflon funnel of precipitation area equal to 31.4 cm^2. The bottle was tightly joined with the funnel and sealed by a teflon-ring. Before sampling each bottle was treated by 1.0 M hydrochloric acid during 24 hours, then rinsed 3 times with distillated and de-ionized water and dried at 80ºC. Both rain pH and conductivity were measured directly after sample collection. The pH measurement was conducted by a glass electrode and two standard solutions of pH 4.0 and 7.0. The conductivity of rain samples was measured using an InoLab Cond Level 1 conductmeter at 20ºC. In the case of snow or sleet depositions, the samples were melted in a tightly closed bottle at room temperature. All samples were kept in the dark in polyethylene bottles at 4° C until analyzed but not longer than two weeks.

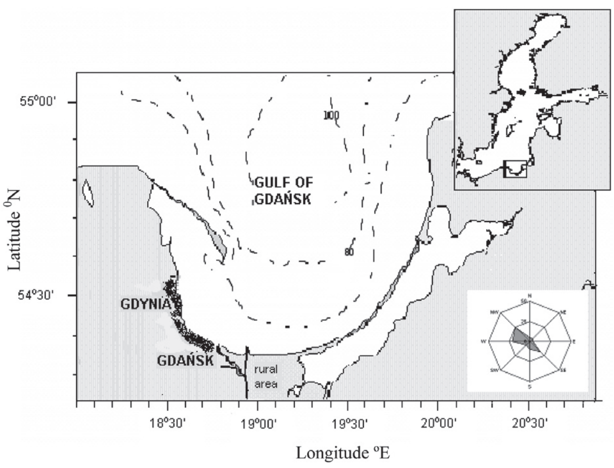

Fig. 1. The geographical location of the Gdynia sampling station and the wind rose (2002-03).

Analytical Methods

Total iron concentrations were determined spectrophotometrically using bathophenanthroline (4,7-Diphenyl-1,10-phenanthroline) in acetone solution [11-13], 10% hydroxylamine hydrochloride solution and acetate buffer solution. Before analysis acetate buffer and hydroxylamine hydrochloride solution were extracted by shaking vigorously with adequate chemicals [13]. Polyethylene vials were treated by 4.0 M hydrochloric acid to prevent the adhering of iron to bottle wall. The measurement of Fe(III) relied on its reduction to Fe(II) by a hydroxylamine hydrochloride solution. The absorbance of bright red complex Fe(II) with bathophenanthroline was measured on Cadas Spectrophotometer using a 50-mm cell at 533 nm. According to Falkowska et al. [13] water samples cannot be preserved by their acidification, therefore the iron concentrations were determined in un-acidified and unfiltered rain samples. The pH of sample during reaction should be mildly acidic. The limit of detection using this method was 0.11 µg Fe dm^{-3}, estimated as three times the standard deviation of repeated measurements on samples. Major components of atmospheric deposition such as sodium, nitrate, chloride and sulphate ions were also determined in rain samples. The measurement of sodium ion concentrations was performed by Atomic Absorption Spectrophotometry (ASA) using an Analyst 300 (Perkin Elmer spectrophotometer). The limit of detection was 3.0 $\mu g \cdot dm^{-3}$. Standard deviations (SD) for the lowest and highest sodium concentrations were 61.0 $\mu g \cdot dm^{-3}$ and 0.69 $mg \cdot dm^{-3}$, respectively. All other ion concentrations were measured by a colorimetric method using a spectrophotometer. The determination of chlorides consisted of the formation of color $Fe[CSN]_3$ complex in perchloric acid presence [14]. The limit of detection for chloride determination was 0.13 $mg \cdot dm^{-3}$. The SD values for lowest and highest concentrations were 44.0 $\mu g \cdot dm^{-3}$ and 0.18 $mg \cdot dm^{-3}$, respectively. Nitrate analyses were performed by reduction in the presence of hydrazine and reaction of the reduced compound with sulfanilic acid and N-(-1-Naphthyl)-ethylenediamine dihydrochloride [15]. The detection limit for this method was 51.0 $nmol \cdot dm^{-3}$, and the SD for lowest concentrations was 56.0 $\mu g \cdot dm^{-3}$, 0.32

mg·dm^{-3} for highest concentrations. Sulphates were precipitated by a barium perchloride solution in the presence of ethanol, then complexed with an excess of barium ions and thorin [16]. The limit of detection for sulphates using this method was 0.86 mg·dm^{-3}. All methods used in this study are applied in the Baltic monitoring and recommended by HELCOM[1].

Results and Discussion

Ion Concentrations in Rain

Among 30 collected samples, three of them consisted of sleet; one occurred in winter, and two samples in early spring. The amount of precipitation varied from 0.3 mm to 33.8 mm per sampling period. The lowest wet deposition occurred in February and confirmed the long-term weather trend for the Gdynia area [17]. Relatively short intervals of droughts going on 4-14 days were also observed in March, April, May and August 2003. The pH of rain samples varied between 4.5-6.6. Average wind speed varied from 1.2 up to 10.7 m·s^{-1}. Relative air humidity averaged about 75%. The greatest average temperature was 18.8^{o}C in summer and 6.8^{o}C in autumn. In winter average air temperature did not fall below -4^{o}C.

The concentrations of total iron varied from 0.26 µg·dm^{-3} to 0.51 mg·dm^{-3} annually, but such extreme values appeared only once in winter. Minimum iron concentration was observed in summer. The median total iron concentration was 19.40 µg·dm^{-3}. The low and high quintiles of iron distribution were 5.25 µg·dm^{-3} and 36.88 µg·dm^{-3}, respectively (Fig. 2). Concentrations of major ions were generally 4 orders of magnitude higher than concentrations of iron and changed within a wide range during the year. The median concentration of sulphates was 7.31 mg·dm^{-3}, and lower median concentration had nitrates (4.85 mg·dm^{-3}). Among major rain components the concentration of chloride and sodium ions characterized the lowest variability of statistical parameters. The median concentrations of these ions were 5.82 mg·dm^{-3} and 1.80 mg·dm^{-3}, respectively (Fig. 2).

Total iron concentrations varied from 17.70 µg·dm^{-3} to 0.51 mg·dm^{-3} in winter. The greatest concentration, 0.51 mg·dm^{-3}, was determined for a sample containing sleet. This sample occurred only once in that season and was collected after the 9th day of a drought. Such great iron concentration resulted from short shower rain events, where the sum of precipitation amount in all was 1.14 mm during 25 days of February. In winter it was noticed that after long and intensive rainfall the next sample had very low iron concentrations despite large volume of collected rain. This indicates that previous rainfalls were more effective with the washout of aerosols from the atmosphere. The same phenomena were also marked in the other seasons.

The ion concentrations measured in the coastal station of the Gulf of Gdańsk are presented in Table 1. The greatest seasonal weighted average concentrations of total iron were detected in winter 2002 (107.13 µg·dm^{-3}) and spring 2003 (32.97 µg·dm^{-3}) (Table 1). The major components of wet deposition were nitrates and sulphates, but their greatest concentrations were in winter.

Statistical Analyses

The factor analyses were carried out in order to better characterize our variables. For annual data, the first factor

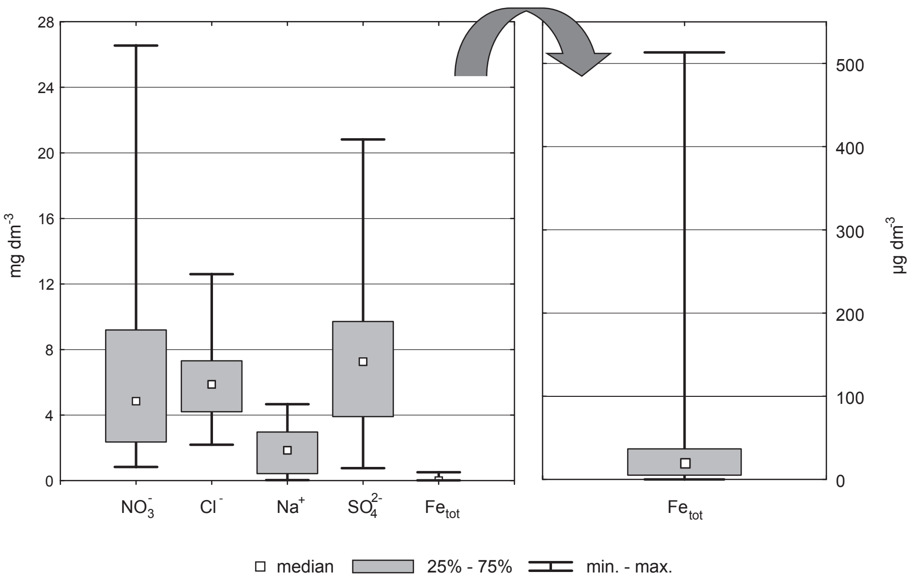

Fig. 2. Statistical characteristic of ion concentrations in rain from Gdynia coastal station (2002-2003).

[1]Helsinki Commission, Baltic Marine Environment Protection Commission.

Table 1. Seasonal characteristic of ion concentrations in rain samples.

Season	Date start	Date stop	Sample amount	Σ H [mm]	Mean pH	Fe_{tot} [μg·dm^{-3}]	SD[a] [μg·dm^{-3}]	NO_3^-	Cl^-	Na^+	SO_4^{2-}
								[mg·dm^{-3}]			
Winter	17.12.02	14.03.03	5	38.7	5.4	107.10[b]	215.31	9.65	3.01	2.14	9.54
Spring	24.03.	23.06.	10	101.4	5.5	32.97	30.82	3.21	5.98	1.47	4.14
Summer	23.06.	24.09.	10	121.5	4.9	19.46	19.71	3.08	5.63	1.01	6.44
Autumn	01.10.	27.10.	5	52.6	5.1	10.74	10.58	5.98	6.94	2.23	5.30

[a] SD=92.08 μg·dm^{-3} for annual data, but without the sample with greatest iron concentration in winter SD= 22.75 μg·dm^{-3}.
[b] Calculating the seasonal weighted average concentration of Fe_{tot} the sample containing sleet was neglected. At the time an weighted average of Fe_{tot} concentration was 25.18 μg dm^{-3} at SD=13.85 μg dm^{-3}.

Table 2. Loadings of the normalized Varimax rotation of chemical components and physical air parameters.

Parameters	Annual				Cold season			Warm season		
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3
Pressure [hPa]	0.293	**0.687**	0.408	0.015	**0.872**	-0.068	-0.387	**0.762**	-0.415	0.156
Wind speed [m s^{-1}]	0.288	0.250	**0.775**	0.003	**0.987**	-0.010	-0.094	0.225	0.269	**-0.749**
Temperature [°C]	**-0.902**	0.120	-0.113	-0.041	-0.446	0.093	**0.855**	0.209	-0.405	-0.544
Relative humidity [%]	0.102	**-0.798**	0.025	0.158	-0.060	**0.945**	0.202	**-0.914**	-0.244	0.088
Conductivity [μS cm^{-1}]	0.564	0.159	0.100	**-0.728**	0.100	0.144	**-0.962**	0.451	**0.851**	0.156
pH	-0.224	**0.808**	-0.141	0.095	-0.134	**-0.911**	0.284	**0.757**	-0.167	-0.014
H [mm]	-0.318	**-0.760**	-0.241	0.030	**-0.787**	0.098	0.170	**-0.877**	0.029	-0.075
Fe_{tot} [mg dm^{-3}]	0.094	-0.053	-0.105	**-0.681**	0.245	0.477	**-0.784**	0.029	**0.825**	0.185
NO_3^- [mg dm^{-3}]	**0.707**	-0.095	0.447	-0.409	0.361	0.212	**-0.896**	-0.269	**0.787**	-0.192
Cl^- [mg dm^{-3}]	0.239	0.055	**-0.898**	0.015	-0.545	0.224	**0.762**	0.165	0.208	**0.811**
Na^+ [mg dm^{-3}]	**0.845**	0.191	-0.261	0.041	**0.750**	0.291	-0.244	0.242	-0.042	**0.910**
SO_4^{2-} [mg dm^{-3}]	0.200	0.083	-0.107	0.578	0.111	**-0.770**	0.303	-0.425	0.369	0.487
Eigenvector	3.726	2.391	1.724	1.659	6.754	3.097	1.578	3.994	3.089	2.367
% total Variance	28.67	18.39	13.26	12.77	51.96	23.82	12.14	30.72	23.76	18.21

was attributed to chemical composition of wet deposition created by anthropogenic (nitrates) and marigenic sources (sodium ions) (Table 2). The second was ascribed to the dynamics of atmospheric processes, and the third presented at the influence of the Gulf of Gdansk on chemical compositions of rain. High loadings of concentration of chlorides (-0.898) and wind speed (0.775) pointed at marine source of aerosols. In cold and warm seasons there occurred the same relationships. In cold season the natural source of marine salts and its role in rain neutralization were more important than in the other season, where the marine source was also, but the anthropogenic and terrigenic sources had greater importance in the formation of chemical compositions of rain.

Coefficients of statistical linear correlation for these same seasons confirmed relationships showed by the factor analysis. In cold season the significant statistical linear correlations between iron concentration and both wind direction (r=0.97[2]), and nitrate concentrations (r=0.85) were noticed. On the one hand these relationships unambiguously indicated the role of closely situated marine source, and on the other hand showed the terrestrial source. In the second season Fe_{tot} concentration correlated only with conductivity (r=0.74), which in connection with pH and amount of rain suggested high efficiency of the iron washout.

The marine source of iron ions was occurred in both seasons. This fact was confirmed by the coexistence of

[2]For all presented in this paper statistical linear coefficients the significance (p) level was below 0.05.

Table 3. Loadings of the normalized Varimax rotation of rain components and physical air parameters for different ranges of pH.

Parameters	pH							
	4.6-5.1[a]			5.1-5.6[b]			5.6-6.1	
	Factor 1	*Factor 2*	*Factor 3*	*Factor 1*	*Factor 2*	*Factor 3*	*Factor 1*	*Factor 2*
Pressure [hpa]	*0.507*	**-0.710**	*0.343*	**0.817**	*0.344*	*0.071*	*-0.606*	*-0.579*
Wind speed [m s^{-1}]	*0.125*	**-0.961**	*0.259*	**0.978**	*-0.045*	*0.077*	*0.131*	**0.991**
Temperature [°C]	**-0.930**	*-0.020*	*0.223*	**-0.672**	*0.303*	**0.658**	**-0.926**	*-0.376*
Relative humidity [%]	*0.289*	*0.345*	**-0.897**	*0.001*	*0.427*	**0.707**	*0.072*	**-0.997**
Conductivity [µS cm^{-1}]	**0.889**	*0.005*	*0.140*	*-0.005*	*0.211*	**-0.967**	*0.052*	**0.843**
H [mm]	**-0.719**	**0.876**	*-0.084*	**-0.739**	*-0.055*	*0.188*	**0.640**	*0.295*
Fe_{tot} [mg dm^{-3}]	**0.644**	**0.609**	**0.657**	*0.304*	**0.877**	*0.372*	**-0.968**	*0.220*
NO_3^- [mg dm^{-3}]	**0.840**	*-0.425*	*-0.146*	*0.587*	*0.075*	**-0.694**	*0.511*	*0.462*
Cl^- [mg dm^{-3}]	*-0.075*	*-0.150*	*-0.489*	**-0.631**	*0.526*	*0.112*	*-0.307*	**0.653**
Na^+ [mg dm^{-3}]	**0.905**	**0.842**	*-0.223*	*0.215*	**0.866**	*-0.236*	**0.637**	*0.027*
SO_4^{2-} [mg dm^{-3}]	*0.005*	*0.148*	*0.331*	*0.201*	**-0.790**	*0.293*	**0.695**	*-0.279*
Eigenvector	*5.705*	*3.276*	*1.906*	*4.853*	*3.759*	*2.278*	*5.481*	*4.349*
% total Variance	*43.88*	*25.20*	*14.66*	*37.91*	*28.91*	*17.52*	*42.16*	*33.45*

[a]The Jansen classification (1988), [b]The modification of the Jansen classification; the upper value of pH is 5.6 and means the carbonate balance $HCO_3^{2-} \rightarrow CO_3^{2-}$ in water, when CO_{2atm} is 350 ppm.

sodium and chloride ions (Table 2) and significant statistical correlation between them (r=0.78). The molar ratio of Cl:Na in rain samples from cold season was similar to that in the Baltic seawater of 1.18.

After splitting the annual data set into the pH-dependent subgroups, factor analysis showed strong correlation between iron concentration and such parameters as precipitation amount, air temperature, nitrate and sodium concentrations (Table 3). The ranges of pH were established by classification of Jansen [18], who divided precipitation into classes of acidity. We separated additionally two ranges of pH from 5.1 to 5.6 and from 5.6 to 6.1. The pH value of 5.6 characterizes the carbonate balance ($HCO_3^{2-} \rightarrow CO_3^{2-}$) in water, when CO_{2atm} is 350 ppm. Thus pH=5.6 was threshold value pointing out the natural rain acidification.

In range of low pH (4.6-5.1) acid rainfalls were a result of anthropogenic and marigenic ion occurrence. The second factor for this pH range reflected the iron marine source. The third was attributed to an effective washout of iron compounds from the atmosphere. According to Millero et al. [19] mineral iron undergoes the process of transformation into ionic form at low pH.

In pH range of 5.1-5.6 the first factor showed important role of air circulation, and the second indicated the common origin of iron and sodium, different than sulphates origin. The role of neutralization by marine salts pointed out the third subgroup of pH. Factor 1 and 2 let us see terrigenic and anthropogenic sources of rain compounds remote off the Gulf of Gdańsk.

Origin of Iron Aerosols

Southeastern winds predominate over the Gdynia area in winter and spring. This direction provided a higher concentration of ions in rain presumably from the Gulf of Gdańsk and the 'Tri-city' area compared to the northwestern winds. This fact was confirmed by the factor analysis (Table 2). Correlations between Fe_{tot} concentration and wind speed were found in pH-dependence subgroups (Table 3). Because the rain from cold season was collected at E&SE winds and had higher pH than these from the W&NW, it can be concluded that seawater was the important source of sea salt (NaCl) and iron. Especially significant were the swash zone where aerosols are generated. This zone of the Gulf of Gdansk is under strong influence of the Vistula River, providing water abundant with iron [20]. Terrigenic sources supporting iron from remote areas were also important, but less effective than local ones. Terrigenic and anthropogenic aerosols were brought by westerly winds from land, which prevailed in summer and autumn (Table 1).

It is worth stressing that pH of rainwater at wind from the Gulf of Gdańsk was not as acidic as at winds from the land in summer. This fact was verified by the factor analysis for two sectors of wind directions (Table 4). The first factor for E&SE winds suggested the concern of anthropogenic and terrigenic aerosols washed-out by rain. Although anthropogenic nitrates were responsible for rain acidification, marine salts

Table 4. Loadings of the normalized Varimax rotation of chemical rain components and physical air parameters for eastern and western winds.

Parameters	**E & SE** *Mean Vw=1.98 m·s⁻¹* *H=13.7 mm* *[Fe]=3.58-97.6 µg·dm⁻³*		**W & NW** Mean Vw=2.37 m·s⁻¹ H=11.0 mm [Fe]= 0.26 - 97.7 µg dm⁻³			
	pH = 5.1-5.6		**pH = 5.1-5.6**		**pH = 4.6-5.1**	
	Factor 1	*Factor 2*	*Factor 1*	*Factor 2*	*Factor 1*	*Factor 2*
Pressure [hPa]	-0.614	0.053	**0.995**	0.104	**0.754**	0.016
Wind speed [m s^{-1}]	0.365	**-0.899**	**0.988**	0.153	0.522	-0.139
Temperature [°C]	**0.772**	0.523	-0.577	**0.817**	**-0.903**	0.144
Relative humidity [%]	-0.472	-0.065	-0.209	**0.978**	0.210	-0.394
Conductivity [µS cm^{-1}]	-0.037	0.224	-0.120	**-0.993**	**0.710**	0.156
H [mm]	0.308	0.237	**-0.645**	0.191	**-0.753**	0.180
Fe_{tot} [mg dm^{-3}]	**0.734**	-0.296	0.501	**0.865**	0.589	-0.093
NO_3^- [mg dm^{-3}]	**0.801**	-0.313	0.494	**-0.869**	**0.814**	0.114
Cl^- [mg dm^{-3}]	0.057	**0.908**	**-0.870**	0.494	-0.349	**-0.655**
Na^+ [mg dm^{-3}]	0.156	**0.919**	**0.998**	-0.062	**0.798**	-0.516
SO_4^{2-} [mg dm^{-3}]	-0.370	-0.543	**0.986**	-0.169	-0.022	**-0.713**
Eigenvector	4.717	3.300	8.253	4.746	5.355	2.364
% total Variance	36.28	25.38	63.48	36.51	41.19	18.18

were strong parameter neutralizing wet deposition and they stopped decreasing of pH to too low values. At winds from this sector pH in rain samples did not have less than 5.1. Probably marine salts raised pH to 5.6, i.e. the value revealed the carbonate balance especially in winter and spring seasons. East winds were characterized by lower speed (average V_w=1.98 m·s^{-1}), an average rainfall amount of 13.7 mm, and iron concentrations varied from 3.58 to 9.76 µg·dm^{-3}.

In the sector of W&NW winds the factors indicated on anthropogenic and terrigenic origin of ions washed-out by rain, while the dynamics of the atmosphere highlighted itself strongly when pH was above 5.1 than below this value (Table 4). Therefore, local anthropogenic source will generate the strongest acidificator of rain (chloride, sulphate and nitrate aerosols). More effective washout of terrigenic iron appeared during short rainfall of small volume when air temperature and relative air humidity were high. An average west wind speed was 2.37 m·s^{-1}, average rainfall amount was 11.0 mm and iron concentrations varied from 0.26 µg·dm^{-3} to 97.7 µg·dm^{-3}.

Atmospheric Iron Fluxes – Influence on Phytoplankton Growth

Iron limits primary production in the Baltic during the vegetation season. As Sunda and Huntsman [21] have pointed out, oceanic diatoms were able to grow at Fe concentration of 168 pg dm^{-3} while the coastal *Thalassiosira psuedonana* and *T. weissflogii* needed Fe concentrations of 2.24 and 6.72 ng dm^{-3}, respectively, to achieve the same iron-limited growth rate. A second acceleration in iron uptake rates of *T. pseudonana* was at total iron concentrations above 56 µg·dm^{-3} and no other species showed any acceleration of iron uptake [21]. The concentration of bioavailable iron in the Baltic of >20 µg·dm^{-3} [22] was high enough to allow species such a *Nodularia spumigena* and other diazotrophic cyanobacteria like *Aphanizomenon* sp. to bloom, in spite of their high iron demands. The experiments carried out in the coastal zone of the Southern Baltic demonstrated that during the vegetation season the deficiencies of phosphorus, nitrogen and iron compounds were observed [10, 23, 24]. In spring Sikorowicz et al. [10] detected 24-h cyclic decreases in iron concentrations below 5.60 µg·dm^{-3} in open water of the Basin of Gdańsk. According to Pohl et al. [25] Fe(III) concentrations in the surface seawater of the Gulf of Gdańsk varied from below the limit of detection to 35.11 µg·dm^{-3}. In this region the average iron concentration estimated by Pempkowiak et al. [9] was 0.10 µg·dm^{-3}. It is likely that iron limits the growth of primary producers, particularly in open seawaters of the Basin of Gdańsk. In situations where river waters supplied large loadings of iron to the coastal zone, the atmosphere could enrich terrestrial input and simultaneously sustain the primary production in marine

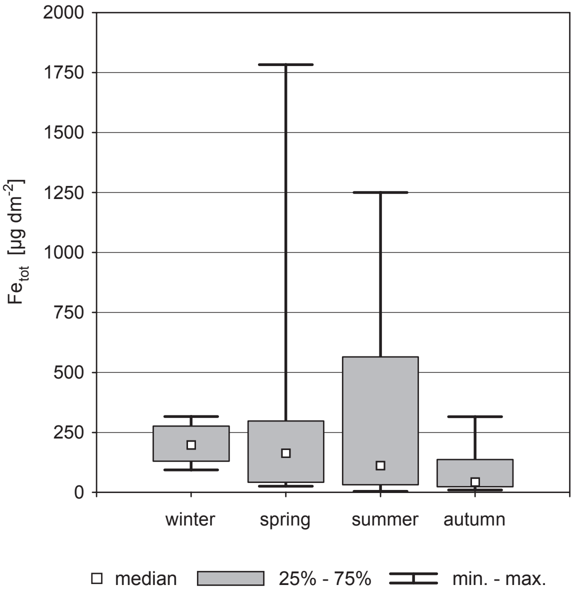

Fig. 3. Statistical characteristic of total iron flux in wet deposition in the coastal zone of the Gulf of Gdańsk (single and maximum value of Fe flux in winter was excluded).

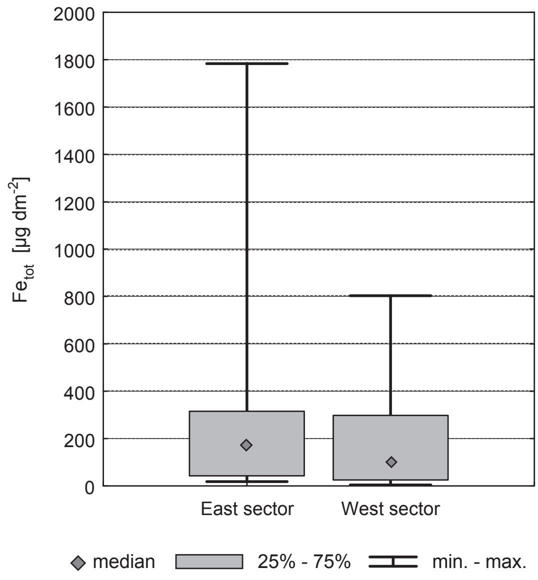

Fig. 4. The mean iron fluxes from East and West wind sectors (the sample of the greatest iron flux occurred only once in the sampling period was excluded from data set).

areas remote from the coastal zone. The latest bibliography [1-7] indicates the atmosphere as the most important source of iron in open seawaters.

The total annual flux of Fe$_{tot}$ was 11.22 mg·m^{-2} yr^{-1}, but wet deposition supplied the most sulphates (2.11 g·m^{-2}yr^{-1}) and chlorides (1.95 g·m^{-2}yr^{-1}) in the coastal zone of the Gulf of Gdańsk. The total annual flux of nitrates was 1.62 g·m^{-2}yr^{-1} and sodium 510.06 mg·m^{-2}yr^{-1}. Seasonally the median values of Fe$_{tot}$ fluxes were relatively greater in winter (0.23 mg·m^{-2}yr^{-1}) and spring (0.16 mg·m^{-2}yr^{-1}) compared to fluxes in summer (0.11 mg·m^{-2}yr^{-1}), and autumn (47.0 µg·m^{-2}yr^{-1}) (Fig. 3).

In spring and summer seasons of the iron requirement the atmosphere can sustain primary production and ipso facto contribution to the intensification of eutrophication. Frequently rainfall, characterizing itself by high flux of iron, occurred in spring and summer.

For local eastern circulation the atmosphere supplied the median iron flux of 207.17 µg·m^{-2} in rain, whereas at W&NW wind direction iron flux was 93.87 µg Fe m^{-2} (Fig. 4). The sample of the greatest iron flux occurred only once in the sampling period and was excluded from data. Then iron flux at east wind direction was 168.73 µg m^{-2}.

We collected 314.17 mm of rainfall amount and estimated the total flux of iron on 11.22 mg·m^{-2} yr^{-1} in the coastal zone of the Gulf of Gdańsk. In hydrological year 2002/03 the amount of rain was 600 mm, which means 52.4% of rainfall amount was collected. Because iron ions play an important role in the limiting of primary production [1-3, 6, 21, 22], authors willing to estimate more precisely an magnitude of the atmospheric input of that element, the correction of value of wet deposition was made. After correction an annual iron flux in rainfall was 21.43 mg·m^{-2} yr^{-1}. The same order of magnitude of iron flux was estimated in Wilmington station in USA (25.2 mg·m^{-2} yr^{-1}) [26] and in the Inter-tropical Convergence Zone (ITCZ) (76.3 mg·m^{-2} yr^{-1}) [27]. In central Barents region Chekushin and coworkers [28] estimated annual iron flux from 8.13 mg·m^{-2}yr^{-1} to 3.52 g·m^{-2}yr^{-1}.

Conclusions

The coastal zone of the Gulf of Gdańsk was characterized by low total iron concentrations in wet deposition (0.26 µg·dm^{-3} – 0.51 mg·dm^{-3}). It decided about relatively small flux of iron from the atmosphere in comparison to the others regions. A wide range changeability of Fe$_{tot}$ concentrations in rain over the Gulf of Gdańsk indicated the complicated physical processes determining the wash-out of aerosols by rain. The effectiveness of iron wash-out from the atmosphere increased with decreasing pH and amount of precipitation. The total annual iron flux was 11.22 mg·m^{-2}yr^{-1} at 314.17 mm of rainfall amount. Iron level in rain was not significant in the coastal zone, but wet deposition could be an important source of iron in open part of the Gulf of Gdańsk, where riverine waters did not reach. Therefore, iron deposited during rainout events had a significant impact on primary production in remote areas of the Gulf of Gdańsk.

Iron aerosols were terrigenic and anthropogenic in origin, but in many cases the swash zone saturated by marigenic aerosols may have a great meaning as a source of this metal in air over the coastal zone.

References

1. MARTIN J.H., FITZWATER S.E. Iron deficiency limits phytoplankton growth in the North-east Pacific subarctic. Nature **321,** 341, **1988**.
2. LINDLEY S.T., BARBER R.T. Phytoplankton response to natural and experimental iron addition. Deep-Sea Res. II **45**, 1135, **1998**.
3. COALE K.H., JOHNSON K.S., FITZWATER S.E., BLAIN S.P.G., STANTON T.P., COLEY T.L. IronEx-I, an in situ iron-enrichment experiment: Experimental design, implementation and results. Deep-Sea Res. II **45**, 919, **1998**.
4. TINDALE N.W., PEASE P.P. Aerosols over the Arabian Sea: Atmospheric transport pathways and concentration of dust and sea salt. Deep-Sea Res. II **46,** 1577, **1999**.
5. MARING H.B. AND DUCE R.A. The impact of atmospheric aerosols on trace metal chemistry in open ocean surface seawater. I. Aluminium. Earth & Plan. Sci. Let. **84,** 381, **1987**.
6. COALE K.H., FITZWATER S.E., GORDON S.E., TANNER S., CHAVEZ S., FERIOLI F.P., SAKAMOTO C., ROGERS P., MILLERO F., STEINBERG P., NIGHTINGALE P., COOPER D., COCHLAN W.P., LANDRY M.R., CONSTANTINOU J., ROLLWAGEN G., TRASVINA A., KUDELA R. A massive phytoplankton bloom induced by an ecosystem-scale iron fertilization experiment in the equatorial Pacific Ocean. Nature **383,** 495, **1996**.
7. HANSON A.K., TINDALE N.W., ADEL-MOATI M.A.R. An Equatorial Pacific rain event: influence on the distribution of iron and hydrogen peroxide in surface waters. Mar. Chem. **75,** 69, **2001**.
8. GLASBY G.P., SZEFER P. Marine pollution in Gdansk Bay, Puck Bay and the Vistula Lagoon, Poland. Sci. Tot. Env. **212(1)**, 49, **1998**.
9. PEMPKOWIAK J., CHIFFOLEAU J-F., STANISZEWSKI A. The Vertical and Horizontal Distribution of Selected Trace Metals in the Baltic Sea off Poland. Est. Coast. & Shelf Sci. **51,** 115, **2000**.
10. SIKOROWICZ G., FALKOWSKA L., BURSKA D., DUNAJSKA D., PRYPUTNIEWICZ D., MAGULSKI R. Dial changes of nitrogen, phosphorus and iron compounds in Southern Baltic Sea (June 2001). Oceanology, in press, **2005**.
11. CLARK L.J. Iron(II) determination in the presence of iron(III) using 4,7-diphenyl-1,10-phenanthroline. Anal. Chem. **34 (3)**, 348, **1962**.
12. Analytical Methods Committee. General method for the determination of iron with 4,7-Diphenyl-1,10-phenanthroline (Bathophenanthroline), Analyst **103**, 521, **1978**.
13. FALKOWSKA L., BOLALEK J., LYSIAK-PASTUSZAK E.. Chemical analyses of seawater 2. The University of Gdansk Publishing, pp.78-80, **1999**. (In Polish)
14. EMEP. Co-Operative Programme For Monitoring And Evaluation of the Long Range Transmission of Air Pollutants in Europe, Manual for Sampling and Chemical Analysis, Chem. 3, **1977**.
15. PN (Polish Norm). Water and wastes. Determination of pollutants in atmospheric precipitation. Analysis of nitrates ions by colorimetric method. Normalizing Publishing Alfa, PN-91/C – 04642/05, **1992** (in Polish).
16. Alfa. Water and wastes. Determination of pollutants in atmospheric precipitation. Analysis of sulphate ions by colorimetric method. Normalizing Publishing, PN-91/C – 04642/03, pp. 1-4, **1992** (in Polish).
17. OWCZAREK M. Characteristic of climate parameters of Gdynia during 1951-1997. IMGW Publishing: Warsaw, Wiadomości Instytutu Meteorologii i Gospodarki Wodnej XXIII(1), **2000**. (in Polish).
18. JANSEN W., BROCK A.A., KNACK J. Acidic rain – origin, consequence. Aura **4,** 18, **1988**. (in Polish)
19. MILLERO F.J., YAO W., AICHER J. The speciation of Fe(II) and Fe(III) in natural waters. Mar. Chem. **50,** 21, **1995**.
20. Environmental conditions in the Polish zone of the Southern Baltic Sea during 2000. Institute of Meteorology and Water Management Publishing, pp. 175-190, **2001**. (in Polish)
21. SUNDA W.G., HUNTSMAN S.A. Iron uptake and growth limitation in oceanic and coastal phytoplankton. Mar. Chem **50**, 189, **1995.**
22. RYDIN E., HYENSTRAND P., GUNNERHED M., BLOMQVIST P. Nutrient limitation of cyanobacterial blooms: an enclosure experiment from the coastal zone of the northwest Baltic proper, Mar. Ecol. Prog. Ser. **239**, 31, **2002**.
23. FALKOWSKA L., BOLAŁEK J., NOWACKI J. Nutrients and oxygen in the Gulf of Gdańsk. Stud. Ocean. Mat. KBM PAN **64,** 131, **1993**.
24. FALKOWSKA L., BURSKA D., BOLAŁEK J., ROGUSZCZAK D. Short-term changes in nutrient and oxygen concentration in the water column of the Gdańsk Deep (Baltic Sea) in spring. Part 1. Nutrient and oxygen concentrations in relation to the density stratification. Oceanology **40(2),** 83, **1998**.
25. POHL C., HENNINGS U., PETERSOHN J., SIEGEL H. Trace metal budget, transport, modification and sink in the transition area between the Order and Peene Rivers and the Southern Pomeranian Bight. Mar. Poll. Bull. **36(8),** 598, **1998**.
26. KIEBER R.J., WILLIAMS K., WILLEY J.D., SKRABAL S., AVERY JR. G.B. Iron speciation in coastal rainwater: concentration and deposition to seawater. Mar. Chem. **73,** 83, **2001**.
27. HELMERS E. AND SCHREMS O. Wet deposition of metals to the tropical North and the South Atlantic Ocean. Atm. Env. **29(18),** 2475, **1995**.
28. CHEKUSHIN V.A., BOATYREV I.V., DE CARITAT P., NSKAVAARA H., REIMANN C. Annual atmospheric deposition of 16 elements in eight catchments of the central Barents region. Sci. Tot. Env. **220,** 95, **1998.**