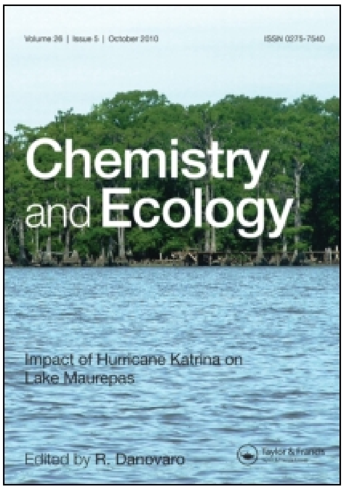

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Characterisation and classification of hoarfrost samples collected in Poland (2003-2005) by discriminant analysis

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Characterisation and classification of hoarfrost samples collected in Poland (2003–2005) by discriminant analysis

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A highly informative chemometrical method using linear discriminant analysis was employed in this paper for the characterisation and classification of hoarfrost samples collected in Poland. From the classification matrix, it was concluded that good discrimination (an overall 69% correct classification and 93% correct classification for the samples originated from Gdańsk) between hoarfrost samples of different origin could be achieved by using the ion concentrations retained in the model. Discriminant analysis was not only used for classifying the hoarfrost samples according to origin and location but also for detecting the most important variables that discriminate between the groups. It was found, according to different statistical parameters, that the highest contribution to the discriminatory power of the model was given by NO_3^- ($\lambda^* = 0814$; F $= 5.54$), PO_4^{3-}($\lambda^* = 0.888$; F $= 3.06$) and F^- ($\lambda^* = 0.892$; F $= 2.92$). The smallest contribution was observed for Mg^{2+} ($\lambda^* = 0.961$; F $= 0.98$). The results obtained in this study illustrate that discriminant analysis allows a rational classification and grouping of hoarfrost samples using chemical composition for their characterisation.

Keywords: hoarfrost; chemical composition; ionic balance; discriminant analysis

1. Introduction

The chemistry of solid phase atmospheric hydrometeors, which do not belong to a precipitation category, is a good index of local scale environmental pollution. This is particularly the case during the wintertime anticyclonic type of weather, when precipitation events of snow or rain tend to be weak or absent, while conditions for hoarfrost and rime formation are favourable. On such occasions hoarfrost is the major media for wet pollutant deposition. They are formed in two different ways: reversal of the sublimation process, and freezing of supercooled fog/cloud droplets on impact with any object met [1].

In the territory of Poland, hoarfrost is observed on less than 20 to more than 80 days per year [2] with minimum values in the northern (coastal) part and maximum in concave landforms of the

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southern and central regions, but on well exposed mountain summits it occurs on less than 10 days per year.

The primary goal of an environmental chemistry laboratory is to correctly perform analytical procedures that yield accurate and precise information to aid in correct and objective characterisation and diagnosis. In order to achieve reliable results, the environmental laboratory must include the ability to use basic supplies and equipment correctly, and an understanding of fundamental concepts is critical to any chemical test [2].

The volume of data generated by the environmental chemistry laboratory is enormous and must be summarised to be most useful to the analyst and decision makers. Consequently, the use of multivariate chemometrical methods is necessary as a way to handle the very large and complex data sets. Principal component analysis, cluster analysis, discriminant analysis and fuzzy clustering are the most applied multivariate methods for data processing and maximum information extraction [3–9].

Principal component analysis methods were applied, for example, to the classification of quality surface waters [10], estimation of interdependences among trace metals in cows' milk [11], and the distribution and mobility of metal in soils [12,13]. Relevant classifications of vegetable oils, tea samples and organic solvents were obtained by using discriminant analysis [14,15]. In the recent period, fuzzy clustering methods [16,17], including fuzzy principal component analysis [18–20], were successfully applied to the clustering of different environmental data.

The objective of this study was to attempt to classify hoarfrost samples by chemometric treatment of the data obtained from chemical compositions. In this order statistical correlation and discriminant analysis were applied to illustrate the correlation between variables (ions concentration) and to find out the (dis)similarities among samples at five different sites in Poland.

2. Experimental

Hoarfrost samples were collected from October 2003 to March 2005 at five different sites in Poland. Depending on the location of sample collection as well as background pollution emissions, the stations were divided as follows: rural inland (*Działdowo*, *Jeziory*), urban coastal (*Gdańsk*), and urban inland (*Grudziądz, Poznań*). Table 1 summarises the general characteristics of the sampling sites.

The hoarfrost samplers were made of polyethylene foil measuring 100 cm by 100 cm, spread on an insulation layer made of styrofoam and mounted in a wooden frame. To reduce the disturbing effect of ongoing dry deposition, the samplers were cleaned before exposure, rinsed with deionised water and wiped dry. Blank sample analyses revealed that the material of the collector surface did not have any measurable influence on the hoarfrost sample chemistry. Hoarfrost samples were collected in the morning after each deposition event. The samples were transferred to polypropylene containers (50 cm^3) using a polytetraflouroethylene (PTFE) scraper and then stored at low temperature without chemical preservatives because the analysis was performed immediately after the samples were delivered to the laboratory.

Selected anions (AS9-HC column, 2 × 250 mm; AutoSuppression® Recycle Mode ASRC®-ULTRA; conductivity detection; eluent 9.0 mM Na_2CO_3; flow rate 0.25 ml/min) and cations (CS12A column, 2 × 250 mm; AutoSuppression® Recycle Mode CSRS®-ULTRA; conductivity detection; eluent 20 mM methanesulfonic acid; flow rate 0.25 ml/min) were determined using ion suppressed chromatography (Dionex Corporation, USA) and quantified against synthetic rain standards: Reference Material No. 409 (BCR-409, Institute for Reference Materials and Measurements, Belgium) and Analytical Reference Material Rain-97 (National Water Research Institute, Environment Canada) [21]. The sample volume was too small to determine pH value.

Table 1. Detailed characteristics of the sampling sites.

Sampling site location	Geographic coordinates	Elevation [m a.s.l.]	Type of area	Site description	Pollution background
Działdowo	53° 14″ N 20° 10″ E	153	Rural	• Close to the road; • 2 km W of village; • 22, 000 citizens.	• Transportation routes; • Low emission from buildings burning of coal for household heating in the cold season; • Agriculture – region with the relative intensive NH_3 emission (poultry and cows).
Jeziory	52° 16″ N 16° 48″ E	82	Rural	• Urban agglomeration of Tricity; • Ecological Station Jeziory of the University of Poznań located within the Wielkopolski National Park; • 17 km SSW of a large urban agglomeration (Poznań); • Nearby leafy forest and Góreckie lake; • Uninhabited area.	• Low emission originating from two small villages adjacent to the Wielkopolski National Park: Stęszew 5 km WNW and Mosina 5 km SE and burning of coal for household heating in cold season; • Transportation routes around the WNP; • Potato processing plant and phosphorus fertiliser plant; • Region with relatively intensive NH_3 emission (pigs and cows); • Neighbourhood of Poznań agglomeration.
Gdańsk	54° 20″ N 18° 36″ E	71	Suburban	• Sampling site close to intersection of Armii Krajowej and łostowic streets; • Main road connecting Gdańsk centre with the Tricity ring road; • 5 km WSW of a Gdańsk city centre and 10 km NE of Gdańska Gulf; • 460,000 citizens.	• Urban agglomeration of Tricity; • Harbours, shipyards, Gdańsk refinery; • Low emission (close to the measure point) from buildings burning of coal for household heating in the cold season. • Transportation routes.
Grudziądz	53° 29″ 18° 46″ E	38	Urban	• Major intersection in the middle size city centre; • 99,000 citizens.	• Urban industrialised area; • Transportation routes; • Low emission (close to the measure point) from buildings burning of coal for household heating in the cold season; • Agriculture – region with relatively intensive NH_3 emission (due to intensive fertilisation).
Poznań	52° 24″ N 16° 55″ E	85	Urban	• Major intersection close to the city centre (Królowej Jadwigi and Świętego Marcina streets); • 800 m W of market square; • 574,000 citizens.	• Urban agglomeration; • Main transportation routes.

Data quality control was performed by evaluating the percentage difference of the ionic balance (PDI) and the sum of total inorganic ionic content (TIC). PDI was calculated as:

$$\mathrm{PDI} = \frac{Conc._{anions} - Conc._{cations}}{Conc._{anions} + Conc._{cations}} \times 100.$$

The acceptability criterion was set: PDI $\leq \pm 20\%$ [22,23]. TIC represents the sum of liquid phase concentration of SO_4^{2-}, NO_3^-, Cl^-, H^+, NH_4^+, Ca^{2+}, Mg^{2+}, Na^+ and K^+ [24]. The level of non-sea-salt sulfate ($nssSO_4^{2-}$) and non-sea-salt calcium ($nssCa^{2+}$) was estimated using the following equations: $nssSO_4^{2-} = SO_4^{2-} - (SO_4^{2-}/Na^+)_{seawater} \cdot Na^+$, and $nssCa^{2+} = Ca^{2+} - (Ca^{2+}/Na^+)_{seawater} \cdot Na^+$, where $(SO_4^{2-}/Na^+)_{seawater}$ and $(Ca^{2+}/Na^+)_{seawater}$ are the concentration ratio of SO_4^{2-} to Na^+ and that of Ca^{2+} to Na^+ in seawater, which are 0.12 and 0.044 (equivalent ratio), respectively [25].

3. Results and discussion

Discriminant analysis was applied as a method to hoarfrost samples for characterisation and identification using a data set consisting of 114 samples collected in Poland between 2003 and 2005. Information concerning chemical composition, select hydrochemical indices and the percentage contribution of select ions determined in hoarfrost samples are reported in Table 2.

The compounds determined and used to establish the similarities and differences between samples are presented in Table 3, together with their statistical characteristics. The values of statistical parameters in Table 3 illustrate a positive asymmetry and kurtosis (leptokurtic distribution) in all cases.

Also, in Table 4 it is easy to observe a strong correlation between some ion concentrations. After application of the standard discriminant analysis method to the data matrix, the variables presented in Table 4 were retained in the model. The statistics from this table illustrate the contribution to the discrimination of samples by the considered ion concentration according to different statistical parameters. High correlation between ions SO_4^{2-}, Na^+, Cl^-, Ca^{2+} indicates their similar sources of product of similar chemical reaction.

It is easy to observe that the greatest contribution is given by nitrate. The next highest are phosphate and fluoride. Hoarfrost samples collected from the terrain of the different stations were characterised by low NO_3^- ion quantities, which can be caused by the fact that hoarfrost is usually created during the night, when vehicular traffic is 2–3 times lower than during the day. The highest NO_3^- quantities were found to be in samples from agricultural terrain, which can be attributed to the use of nitrogen fertilisers in agriculture.

The smallest contribution (see Table 5) was obtained for Mg ($\lambda^* = 0.961$; $F = 0.981$). Also, a small contribution brings the PDI ($\lambda^* = 0.957$; $F = 1.09$).

A canonical correlation analysis has been done, which determined the successive functions and canonical roots. The maximum number of functions will be equal to the number of groups minus one, or the number of variables in the analysis, whichever is smaller. The eigenvalues (characteristic roots) and the corresponding standardised canonical discriminant function coefficients are shown in Table 6. The first function presented a relatively high eigenvalue (1.16). The eigenvalue drops to 0.919 for the second axis, and further, to 0.351, for the third axis.

The highest standardised discriminant coefficients correspond to SO_4^{2-}, nss SO_4^{2-}, Ca^{2+}, nss Ca^{2+} and S_C in root 1, and to Ca^{2+}, nss Ca^{2+}, SO_4^{2-}, $NH_4^+ + H^+$ and NH_4^+ in root 2. In root 3 the highest values are for Ca^{2+}, nss Ca^{2+}, SO_4^{2-} and $NH_4^+ + H^+$. In root 4, coefficients corresponding to Ca^{2+}, nss Ca^{2+}, SO_4^{2-}, nss SO_4^{2-}, $NH_4^+ + H^+$ and NH_4^+ are the highest. It can be observed that calcium and sulphate have a major contribution in all roots.

Table 2. Minimum, maximum and average analyte concentrations (meq/l) and selected hydrochemical indices in hoarfrost samples.

				Urban station		
		Rural inland		Urban inland		Urban coastal
Analyte		Działdowo	Jeziory	Grudziądz	Poznań	Gdańsk
N		18	19	24	10	43
Na^+	max	4.91	0.30	2.27	1.72	2.63
	mean	0.65	0.11	0.52	0.91	0.24
	min	0.024	0.017	0.047	0.37	0.039
	f (%)	100	100	75.0	100	100
NH_4^+	max	1.43	0.94	1.12	1.01	0.51
	mean	0.41	0.22	0.48	0.66	0.19
	min	0.038	0.016	0.26	0.31	0.0022
	f (%)	77.8	100	100	100	95.3
K^+	max	0.66	0.048	0.35	0.74	0.24
	mean	0.15	0.018	0.18	0.22	0.086
	min	0.0015	0.0018	0.074	0.053	0.0059
	f (%)	100	100	100	100	97.7
Mg^{2+}	max	1.39	0.067	1.20	0.53	0.092
	mean	0.47	0.030	0.29	0.22	0.057
	min	0.028	0.0058	0.083	0.062	0.028
	f (%)	100	100	79.2	100	37.2
Ca^{2+}	max	1.39	0.23	2.47	1.50	2.37
	mean	0.47	0.12	0.53	0.72	0.24
	min	0.028	0.050	0.042	0.077	0.040
	f (%)	100	100	100	100	72.1
F^-	max	0.27	0.012	0.14	0.050	0.68
	mean	0.083	0.0061	0.026	0.020	0.063
	min	0.0058	0.0011	0.0027	0.0063	0.026
	f (%)	83.3	57.9	91.7	90.0	90.7
Cl^-	max	3.77	0.68	2.94	2.20	2.24
	mean	0.59	0.17	0.74	1.13	0.33
	min	0.063	0.014	0.22	0.53	0.031
	f (%)	100	100	100	100	100
NO_2^-	max	<LOD	<LOD	0.015	<LOD	< LOD
	mean			0.0078		
	min			0.0030		
	f (%)			29.2		
NO_3^-	max	0.090	0.35	0.21	0.22	0.099
	mean	0.036	0.082	0.052	0.12	0.027
	min	0.0013	0.0060	0.012	0.045	0.0094
	f (%)	94.4	100	100	100	100
PO_4^{3-}	max	1.36	0.032	1.74	<LOD	0.49
	mean	0.36	0.016	0.39		0.14
	min	0.036	0.0062	0.0091		0.011
	f (%)	100	63.2	58.3		34.9
SO_4^{2-}	max	2.96	0.50	2.69	3.69	3.06
	mean	0.55	0.19	0.65	1.45	0.20
	min	0.058	0.075	0.27	0.34	0.0098
	f (%)	100	100	100	100	100
$SO_4^{2-} + NO_3^-$	MAX	3.00	0.73	2.91	3.73	3.16
	mean	0.59	0.27	0.70	1.57	0.23
	min	0.061	0.084	0.28	0.41	0.026

(*Continued*)

Table 2. Continued

				Urban station		
		Rural inland		Urban inland		Urban coastal
Analyte		Działdowo	Jeziory	Grudziądz	Poznań	Gdańsk
$NH_4^+ + H^+$	max	1.43	0.94	1.12	1.01	0.51
	mean	0.32	0.23	0.47	0.66	0.18
	min	4.37×10^{-5}	0.017	0.26	0.31	0.00032
S_C	max	8.75	1.57	6.06	4.95	5.69
	mean	1.67	0.50	1.78	2.73	0.69
	min	0.22	0.13	0.61	1.03	0.052
S_A	max	8.19	1.44	5.89	5.94	6.00
	mean	1.61	0.46	1.69	2.72	0.66
	min	0.21	0.10	0.58	0.95	0.058
TIC	max	16.9	3.01	11.9	10.9	11.7
	mean	3.28	0.96	3.47	5.45	1.36
	min	0.43	0.23	1.19	1.98	0.11
PDI(%)	max	9.33	13.9	7.35	9.11	8.57
	mean	4.44	5.19	4.00	4.70	4.48
	min	0.69	2.14	1.14	2.67	0.13
nss SO_4^{2-}	max	2.37	0.46	2.42	3.48	2.75
	mean	0.48	0.18	0.60	1.34	0.17
	min	0.049	0.070	0.22	0.29	0.0044
nss Ca^{2+}	max	1.21	0.22	2.37	1.46	2.25
	mean	0.44	0.11	0.51	0.68	0.23
	min	0.025	0.049	0.029	0.059	0.034

Notes: S_C - sum of cations.
S_A - sum of anions.
f - frequency of occurrence.

Table 3. Statistics of the measured variables.

	Mean	Median	SD	Skewness	Kurtosis
F^-	0.040	0.012	0.079	5.27	37.7
Cl^-	0.501	0.322	0.624	2.79	9.19
NO_3^-	0.051	0.028	0.060	2.53	6.92
PO_4^{3-}	0.125	0.007	0.271	3.46	14.6
SO_4^{2-}	0.459	0.227	0.664	2.88	8.77
Na^+	0.370	0.173	0.643	4.38	24.3
NH_4^+	0.310	0.262	0.281	1.29	1.92
K^+	0.114	0.083	0.120	2.58	9.40
Ca^{2+}	0.333	0.147	0.438	2.57	8.25
Mg^{2+}	0.093	0.047	0.156	4.01	22.7
S_C	1.22	0.835	1.38	2.68	9.18
S_A	1.18	0.766	1.36	2.67	8.57
S_A/S_C	0.960	0.922	0.091	1.42	1.29
TIC	2.40	1.62	2.74	2.66	8.80
PDI	4.51	4.60	2.12	0.979	2.94
nss SO_4^{2-}	0.415	0.209	0.604	2.88	9.00
nss Ca^{2+}	0.317	0.143	0.417	2.56	8.30
$SO_4^{2-} + NO_3^-$	0.510	0.275	0.688	2.73	7.86
$NH_4^+ + H^+$	0.312	0.262	0.280	1.30	1.95

Table 4. Table of correlation.

	F^-	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	S_A	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	S_C	S_A/S_C	TIC	PDI	nss SO_4^{2-}	nss Ca^{2+}	$SO_4^{2-} + NO_3^-$	$NH_4^+ + H^+$
F^-	1.00	0.13	−0.00	0.11	0.07	0.17	0.17	0.18	0.21	0.16	−0.04	0.18	0.05	0.18	−0.14	0.05	0.16	0.06	0.18
Cl^-		1.00	0.36	0.27	**0.82**	**0.94**	**0.89**	0.76	0.66	**0.81**	0.50	**0.94**	0.04	**0.94**	−0.09	0.79	0.79	**0.82**	0.76
NO_3^-			1.00	−0.08	0.37	0.37	0.25	0.55	0.11	0.38	0.23	0.38	−0.01	0.38	−0.05	0.38	0.38	0.44	0.56
PO_4^{3-}				1.00	0.24	0.44	0.45	0.31	0.41	0.36	0.34	0.46	0.01	0.45	−0.13	0.21	0.35	0.23	0.31
SO_4^{2-}					1.00	**0.93**	0.80	0.73	0.69	**0.84**	0.56	**0.91**	0.16	**0.92**	−0.05	1.00	**0.82**	1.00	0.73
S_A						1.00	**0.91**	**0.80**	0.74	**0.88**	0.58	**0.99**	0.10	1.00	−0.10	**0.91**	**0.86**	**0.93**	0.80
Na^+							1.00	0.64	0.60	0.73	0.38	**0.92**	0.01	0.92	−0.14	0.75	0.70	0.79	0.64
NH_4^+								1.00	0.61	0.65	0.48	0.81	−0.05	**0.81**	−0.06	0.72	0.63	0.75	1.00
K^+									1.00	0.50	0.60	0.72	0.15	0.73	0.04	0.68	0.48	0.67	0.61
Ca^{2+}										1.00	0.45	**0.88**	0.06	**0.88**	−0.16	**0.83**	1.00	**0.84**	0.64
Mg^{2+}											1.00	0.58	0.01	0.58	−0.07	0.57	0.44	0.56	0.47
S_C												1.00	0.03	1.00	−0.13	**0.88**	**0.86**	**0.91**	**0.81**
S_A/S_C													1.00	0.06	0.20	0.17	0.06	0.15	−0.05
TIC														1.00	−0.12	**0.90**	**0.86**	**0.92**	**0.81**
PDI															1.00	−0.03	−0.16	−0.05	−0.05
nss SO_4^{2-}																1.00	**0.82**	**0.99**	0.72
nss Ca^{2+}																	1.00	**0.83**	0.63
$SO_4^{2-} + NO_3^-$																		1.00	0.75
$NH_4^+ + H^+$																			1.00

Table 5. Variables in the model and the standardised canonical discriminant function coefficients.

Variables	Wilks	Partial λ^*	F-remove	p-level	Tolerance	1-Tolerance
nss SO_4^{2-}	0.155	0.930	1.82	0.131	0.00001	1.00
PO_4^{3-}	0.162	**0.888**	**3.06**	0.020	0.547	0.453
Mg^{2+}	0.149	0.961	0.981	0.422	0.142	0.858
NO_3^-	0.177	**0.814**	**5.54**	0.0005	0.494	0.506
nss Ca^{2+}	0.157	0.916	2.23	0.071	0.00001	1.00
NH_4^+	0.154	0.931	1.79	0.137	0.0007	0.999
S_A/S_C	0.158	0.911	2.36	0.058	0.705	0.295
F^-	0.161	**0.892**	**2.92**	0.025	0.772	0.228
SO_4^{2-}	0.155	0.931	1.81	0.134	0.00001	1.00
$NH_4^+ + H^+$	0.156	0.923	2.02	0.097	0.0007	0.999
Ca^{2+}	0.157	0.915	2.25	0.069	0.00001	1.00
S_C	0.156	0.921	2.07	0.090	0.0029	0.997
PDI	0.150	0.957	1.09	0.361	0.755	0.245

Table 6. Standardised coefficients for canonical variables.

	Root 1	Root 2	Root 3	Root 4
nss SO_4^{2-}	**−34.6**	16.7	46.1	**79.6**
PO_4^{3-}	0.227	−0.072	0.451	0.791
Mg^{2+}	−0.054	0.487	0.752	−0.239
NO_3^-	0.403	0.724	−0.187	0.391
nss Ca^{2+}	**27.7**	**−64.9**	**−117**	**−173**
NH_4^+	−2.60	**−6.05**	−16.2	**3.61**
S_A/S_C	−0.160	−0.454	−0.126	0.221
F^-	0.448	−0.189	−0.185	0.170
SO_4^{2-}	**38.9**	**−17.0**	**−51.9**	**−87.5**
$NH_4^+ + H^+$	2.56	**6.85**	**17.2**	**−3.82**
Ca^{2+}	**−28.4**	**68.7**	124	182
S_C	**−4.58**	−4.95	−3.93	−1.44
PDI	0.252	0.174	0.007	0.214
Eigenvalue	1.16	0.919	0.351	0.242
Cumulative proportion (%)	43.3	77.8	90.9	1.00

All hoarfrost sample collection sites were characterised by a rather large contribution of SO_4^{2-} ions. SO_4^{2-} ions are one of the most important indicators of pollution, since, similar to NO_3^- ions, they are responsible for the acidic properties of water created from hoarfrost. The contribution of NH_4^+ ions was the largest in samples collected in the agricultural area, which may be attributed to agricultural activities (ammonium fertilisers).

A rather high contribution of Ca^{2+} ions is connected to, among others, the general presence of this ion in dust, the exploitation of concrete roads and cement production. The percentage contribution of PO_4^{3-} ions in complete ion content was the highest in agricultural terrains, which, similar to NO_3^- and NH_4^+ ions, can be explained by the use of fertilisers in agricultural practice.

We can also visualise how the functions discriminate between groups by plotting the individual scores for the discriminant functions. This statement is well supported by the two-dimensional scatterplot using the discriminant scores of the samples along the different roots, as can be seen in Figure 1.

The classification result of this procedure is the classification matrix, which shows the number of samples that were correctly classified (on the diagonal of the matrix) and those that were

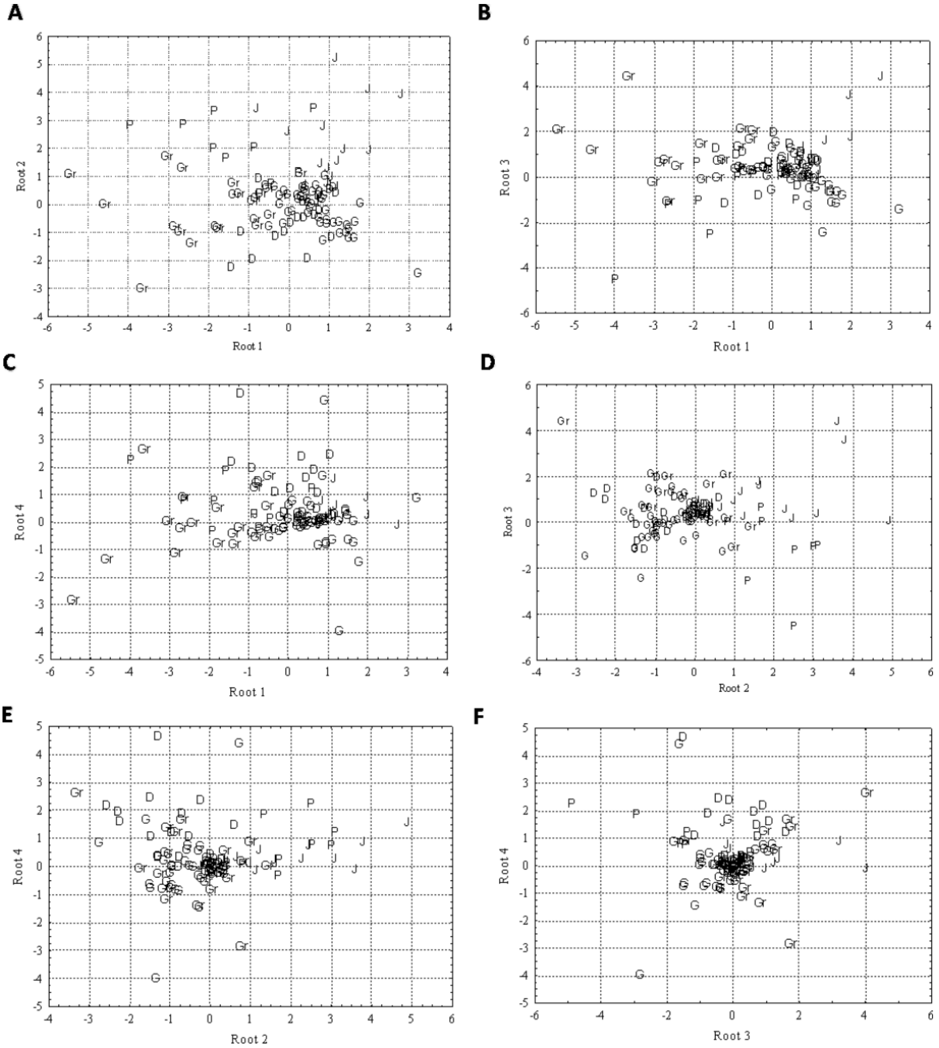

Figure 1. Scatterplot of canonical scores on the plan described by: A – root 1 and root 2, B – root 1 and root 3, C – root 1 and root 4, D – root 2 and root 3, E – root 2 and root 4, F – root 3 and root 4.

Table 7. Classification matrix.

	Percent	Działdowo	Gdańsk	Grudziądz	Jeziory	Poznań
Działdowo	50.0	**9**	9	0	0	0
Gdańsk	93.0	3	**40**	0	0	0
Grudziądz	58.3	3	5	**14**	0	2
Jeziory	52.6	0	8	0	**10**	1
Poznań	60.0	0	2	2	0	**6**
Total	69.3	15	64	16	10	9

misclassified. The classification matrix presented in Table 7 indicates a satisfactory separation of samples in a good agreement to their origin. The group which originated from Gdańsk, for example, showed that 93.0% of samples were well classified. All the other groups showed more or less a satisfactory separation ($>$50%).

4. Conclusions

Statistical correlation and discriminant analysis were applied to the study of hoarfrost samples collected in Poland from 2003–2005. The application of discriminant analysis allows the clarification of similarities among samples according to their origin and location. From the classification matrix, it was concluded that good discrimination (an overall 69% correct classification and 93% correct classification for the samples originated from Gdańsk) between hoarfrost samples from different sampling sites could be achieved by using the ion concentration retained in the model.

Looking at the data presented in part of the results, the appearance of the following relationships can be confirmed between analytes determined in hoarfrost samples collected from sites with different properties:

- Urban coastal areas: a group of strong correlations between sodium ions and chlorides, which is a natural consequence of the placement of these sites near the coast;
- Urban inland areas: correlations in one third of the cases, which can be caused by different agglomeration developments as well as their geographic placement;
- Rural inland areas: coefficient values larger than 0.75 for chosen ions or their sums, which can attest to the similarity of their sources of origin.

The obtained results give significant information of anionic and cationic sources in hoarfrost samples at urban, urban inland and rural sites, and confirm that environmental chemistry combined with the multidimensional interpretation of data gives an interesting and very useful way of sample correlations, interpretations, problem-solving and cost effectiveness.

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