The influence of agriculture on the chemical composition of aeInstitute of Oceanography, University of Gdansk, Division

Martyna Malinowska [1]*, Anita U. Lewandowska [1], Michalina Bielawska[1]

[1] Institute of Oceanography, University of Gdansk, Division of Marine Chemistry and Environmental Protection, Av. M. Piłsudskiego 46, 81-378 Gdynia, Poland

* martynakali@gmail.com,

University of Gdańsk

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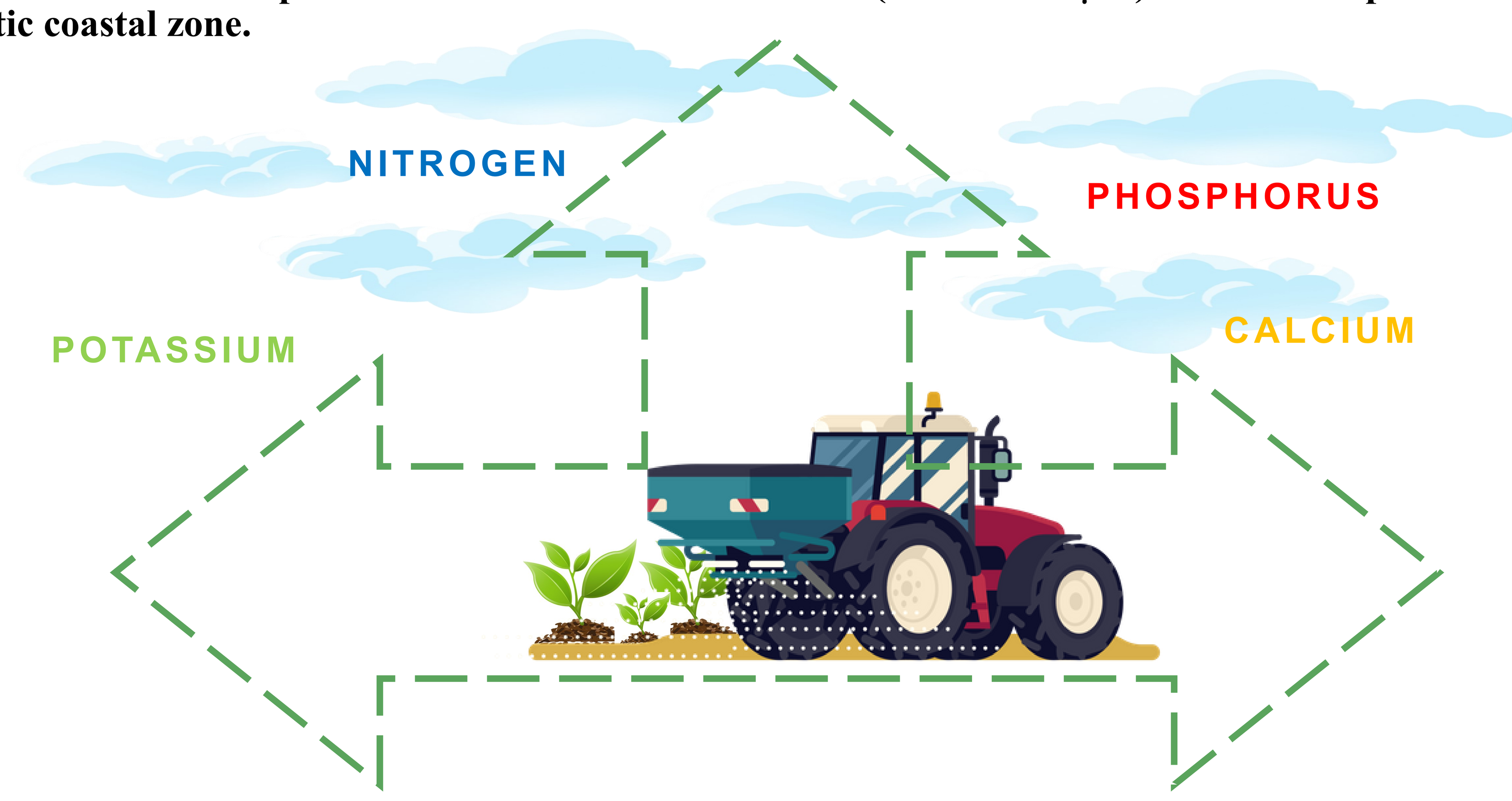
Introduction

In order to improve the quality of the soil, the size and appearance of plants, various types of fertilizers are used in Poland, which are rich in nitrogen, phosphorus, calcium and potassium. In the case of granular fertilizers, the release of their components into the atmosphere is associated with wind discharge and re-emission from the surface of the fields. In turn, compounds contained in liquid fertilizers can be directly adsorbed on atmospheric aerosols during their spraying in the atmosphere. Atmospheric pollution with compounds emitted in agricultural areas occurs not only during field fertilization. It also takes place after each disturbance of the soil structure, e.g. when plowing the soil, when solid layers of sediment are pulled up, which are then transferred to the atmosphere. Such agricultural activity may have a negative impact on the chemical composition of atmospheric aerosols, which can be transported by air masses away from the regions of agricultural sources. **This study investigated the effect of agriculture on the chemical composition of aerosols of various sizes (<0.45 to 10 µm) in the atmosphere of the Baltic coastal zone.**

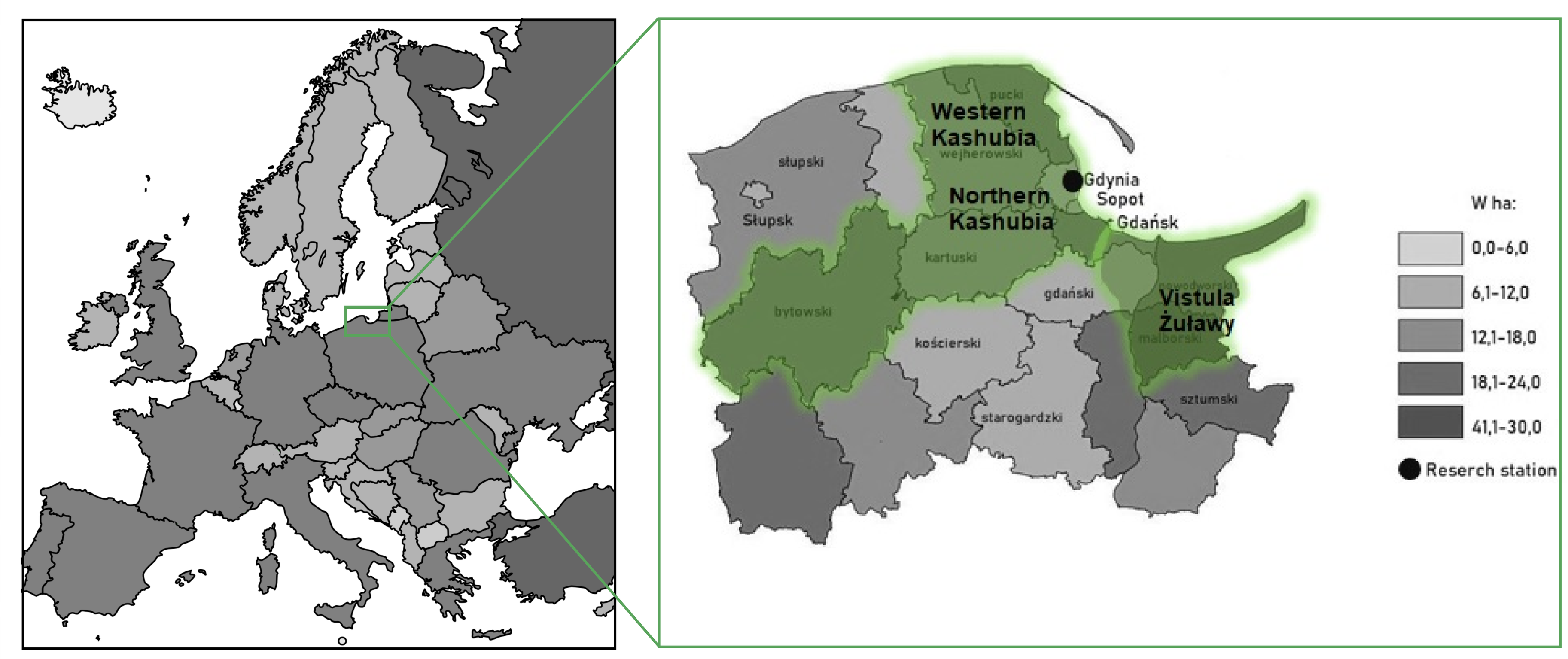


Materials and methods

Sampling location. Aerosol samples were collected in Gdynia, on the territory of the Faculty of Oceanography and Geography of the University of Gdańsk (54°30'N, 18°32'E). The building is located in the urbanized part of the city, 560 m from the shoreline of the Baltic Sea (Gdańsk Bay).

Sample collection. Aerosol samples were collected in the period from 19/04/2016 to 17/08/2016 (vegetative period). Samples were carried out in a five-hour cycle, outside the rush hours (10:00 am.-3:00 pm.). It was aimed at eliminating the source related to the transport as much as possible.

Identification Aerosols were collected using a Tisch Environmental, Inc. high-flow impactor (model: TE-235). It operates at a nominal flow of 1.132 $m^3 \cdot min^{-1}$ (40 scfm; 68 $m^3 \cdot h^{-1}$), at a pressure of 760 mm Hg and a temperature of 25°C. Aerosols were collected on TE-QMA Micro Quartz filters, 14.3cm x 13.7cm in size (aerosols from 0.49 µm to 10 µm). The smallest particles, below 0.49 µm were collected on a Whatman 41 filter, which had a size of 20.3cm x 25.4cm. Before use, all filters were preheated (580°C, 6h) and then conditioned in a desiccator for 24 hours (Rh: 45% ± 5%; 20°C ± 5°C).



Results and discussion

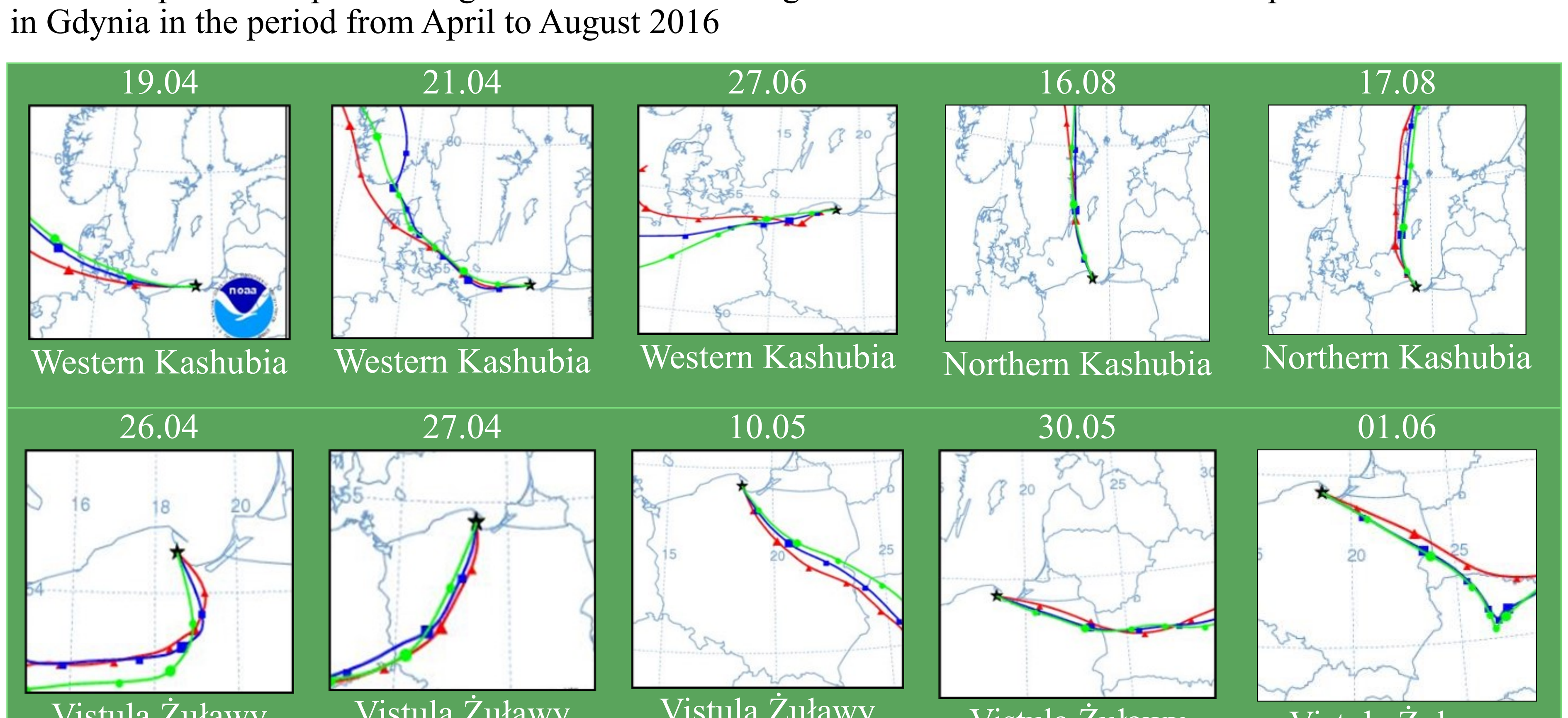
During the entire measurement period, the average PM10 concentration in the five-hour measurement cycle was 47.27 $\mu g \cdot m^{-3}$. The lowest mean value of PM10 concentration (4.10 $\mu g \cdot m^{-3}$) was obtained in the range of aerosol sizes from 1.5 to 3.0 µm in diameter. The maximum mean concentration of PM10 was 18.63 $\mu g \cdot m^{-3}$ and it was obtained in the range of aerosols with the largest diameter (7.2-10 µm) (Tab.1). The minimum concentration of PM10 was 26.00 $\mu g \cdot m^{-3}$ and it was recorded on May 12.05.2016 while the maximum concentration was 65.89 $\mu g \cdot m^{-3}$ and it was obtained on April 19.04 (Tab.2).

In the five-hour cycle of mesaurements carried out in Gdynia in the period from 19/04/2016 to 17/08/2016, calcium ions dominated among the analyzed PM10 ionic components (91.2%). The median Ca^{2+} concentration was also the highest and amounted to 2.81 $\mu g \cdot m^{-3}$. The remaining ions constituted on average: NO_3^-- 3,5%, PO_4^{3-}- 4,8%, a K^+- 0,5% of the PM10 mass. During the research period, the median NO_3^- concentration was 0.06 $\mu g \cdot m^{-3}$. The extreme values of the concentration of these ions in PM10 have been recorded: 1.10 $\mu g \cdot m^{-3}$ (10.05), 1.09 $\mu g \cdot m^{-3}$ (27.04), 1.06 $\mu g \cdot m^{-3}$ (26.04), 1.03 $\mu g \cdot m^{-3}$ (12.05) and 0.89 $\mu g \cdot m^{-3}$ (19.04). The median concentration of 0.17 was $\mu g \cdot m^{-3}$. There were no extreme values for phosphate ions. The median concentration of potassium ions (K^+) was 0.1 $\mu g \cdot m^{-3}$. The extreme values for K^+ reached 0.18 $\mu g \cdot m^{-3}$ (19.04), 0.16 $\mu g \cdot m^{-3}$ (26.04 and 17.08).

Table 1. Average values and concentration range (min-max) of PMx and selected ionic components depending on the size of aerosols collected in Gdynia in the period from April to August 2016

Parameter [$\mu g \cdot m^{-3}$]	Aerosol size [µm]					
	<0.49	0.49-0.95	0.95-1.5	1.5-3.0	3.0-7.2	7.2-10
PMx	9.83 (5.95-13.16)	4.14 (0.42-6.93)	4.19 (1.44-7.77)	4.10 (1.79-6.52)	4.95 (2.61-7.53)	18.63 (6.18-39.07)
NO_3^-	0.25 (0.02-0.87)	0.05 (0.01-0.10)	0.06 (0.01-0.17)	0.04 (LoQ-0.11)	0.08 (0.01-0.30)	0.19 (0.02-0.68)
PO_4^{3-}	0.08 (0.02-0.19)	0.13 (0.02-0.22)	0.19 (0.14-0.28)	0.19 (0.07-0.33)	0.17 (0.04-0.31)	0.17 (0.05-0.30)
K^+	0.04 (0.01-0.09)	0.01 (LoQ-0.03)	0.01 (LoQ-0.05)	0.02 (LoQ-0.05)	0.01 (LoQ-0.03)	0.01 (LoQ-0.03)
Ca^{2+}	5.64 (2.17-8.21)	2.23 (0.36-5.46)	2.32 (0.12-5.66)	2.08 (0.12-3.93)	2.89 (0.37-5.26)	2.44 (0.19-5.25)

Table 2. Episodes of potential agriculture source of origin of PM10 and its chemical components measured in Gdynia in the period from April to August 2016



The percentages of NO_3^-, K^+, Ca^{2+}, as well as their min concentrations, were the highest in aerosols with a diameter below 0.49 µm (Tab. 1). Nitrate ions accounted for 37.3%, potassium ions 40.0%, and calcium ions 32.6% by weight of the aerosols in this particle size range. The highest percentage of PO_4^{3-} was recorded in aerosols with a diameter ranging from 0.95 to 1.5 µm (20.4%) and from 1.5 to 3.0 µm (20.5%). However, the mean concentration of phosphate ions was very similar for particles larger than 0.95 µm and ranged from 0.17 to 0.19 $\mu g \cdot m^{-3}$. Particles smaller than 0.95 µm were characterized by twice lower mean concentration values, ranging from 0.08 $\mu g \cdot m^{-3}$ (<0.49 µm in diameter) to 0.013 $\mu g \cdot m^{-3}$ (0.49-0.95 µm).

During the entire research period, episodes of high concentrations of the analyzed ionic PM10 components were selected, which could be related to agricultural activity in the neighboring areas. The air masses from over the Western Kashubia applied pollutants on April 19 and 21, June 27, and August 16 and 17, 2016. At that time, wind velocities ranged from 1.1 to 3.3 $m \cdot s^{-1}$ what is characteristic for local to the regional origin of air pollution (Lewandowska et. al., 2013). In turn, the air masses from the Żuławy Wiślane region, which could transport pollutants of agricultural origin, occurred on April 26 and 27, May 30 and 30, and June 1, 2016. In this case, winds with a force indicating the transfer of pollutants on a regional scale (from 2.5 to 4.2 $m \cdot s^{-1}$) prevailed.

Conclusions

1. The highest mean concentrations of NO_3^-, K^+ and Ca^{2+} occurred in aerosols below 0.49 µm in diameter (0.26 $\mu g \cdot m^{-3}$, 0.04 $\mu g \cdot m^{-3}$ and 5.85 $\mu g \cdot m^{-3}$, respectively). Phosphates showed a high average concentration (0.19 $\mu g \cdot m^{-3}$) in aerosols with a diameter from 1.5 to 3.0 µm.
2. The highest concentrations of nitrate ions in aerosols over Gdynia occurred both during advection from the Western Kashubia and Vistula Żuławy in early spring, before sowing when the plants begin to grow long, which requires nitrogen fertilization.
3. The concentration of phosphates in aerosols over Gdynia increased slightly from spring to summer 2016, also in situations when air masses were flowing from the West Kashubia and Vistula Żuławy regions. This could be a consequence of introducing these ions into the soil with fertilizers in order to increase the resistance of plants to pathogens.
4. Advection from the area of Vistula Żuławy, where sea-origin sludge rich not only in salt but also in calcium compounds, played a key role in shaping high concentrations of calcium ions in aerosols over Gdynia in the discussed research period.
5. Potassium ion concentrations were the lowest among all the analyzed compounds in aerosols collected from April to August 2016 in the atmosphere over Gdynia. It could have been a consequence of the effective uptake of these compounds by plants from the soil.