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ORGANIC AND ELEMENTAL CARBON IN COASTAL AEROSOL OF THE BALTIC SEA

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Investigation of organic (OC) and elemental (EC) carbon in atmospheric aerosol was performed at the Preila Environmental pollution research background station on 19–28 June 2006. In parallel, the measurement of black carbon by the reflectometric method was carried out. The sources of carbonaceous compounds were detected by using air mass backward trajectories. The highest concentrations of OC and EC were transported with air masses of the southwestern direction, from the "black triangle" (bordering areas of Czech Republic, Germany, and Poland), and the lowest concentrations of carbonaceous compounds were associated with air masses from the Atlantic Ocean. The input of westerly air mass exceeded 50% of total pollution, which is in agreement with earlier determined peculiarities of background pollution formation in the Baltic region.

Keywords: organic carbon, elemental carbon, black carbon, coastal aerosol, air mass backwards trajectories

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1. Introduction

Chemical structure of aerosol is important not only due to its impact on humans and environment but also due to its contribution to the earth climate. The main components of aerosol influencing the climate can be soot (elemental carbon or black carbon (BC) depending on the method of measurement), organic carbon, and sulphates [1]. It is known that the total aerosol mass in the city atmosphere exceeds aerosol mass of a rural site by 33–40% due to organic and black carbon components in aerosol [2]. Investigations during the last decades have indicated that the amount of organic carbon may comprise up to 40–60% of urban aerosol [3] and up to 6–16% of that at the coastal site of the Baltic Sea [4]. The concentration of black carbon at the Ireland coastal station Mace Head was relatively low, but varied in a wide range: from 0.05 to 2.5 μg·m^{-3}. Separate episodes of high black carbon concentration were observed with air masses from the western part of Europe, where emission of black carbon was evaluated to be $(482\pm140)\cdot10^3$ tons per year [5]. It was suggested that about half of black carbon emission is associated with fossil fuel burning [6]. High amount of water insoluble substances were observed in aerosol particles of high dispersity (Aitken's and accumulation modes) during the periods of high biological activity – "blooming" of phytoplankton. It allowed the authors to suggest that aerosol at the coastal Atlantic Ocean station contains a large amount of organic compounds of biological origin (lipids, proteins, and others) [7]. Data on total carbonaceous compounds (TC), organic carbon, and elemental carbon concentrations in aerosol are scarce. They are mostly obtained at urban sites, though global aerosol effects can be cleared up by investigating the background sites.

The aim of this study is to determine concentrations of organic and elemental carbon in coastal aerosol and to evaluate the origin of these carbonaceous compounds by investigation of certain synoptic episodes at the Preila background station.

2. Experimental

Sampling site. The investigation of carbonaceous compounds was performed at the Preila Environmental pollution research background station located on the Curonian Spit, on the coast of the Baltic Sea in the period of 19–28 June, 2006. *Analysis*. Thermal-optical analytical technique was used for determination of organic and elemental carbon [8]. Because of the high temperature during the analysis, PALLFLEX 2500At-UP quartz-fibre filters were used for aerosol sample collection. To remove possible carbon con-

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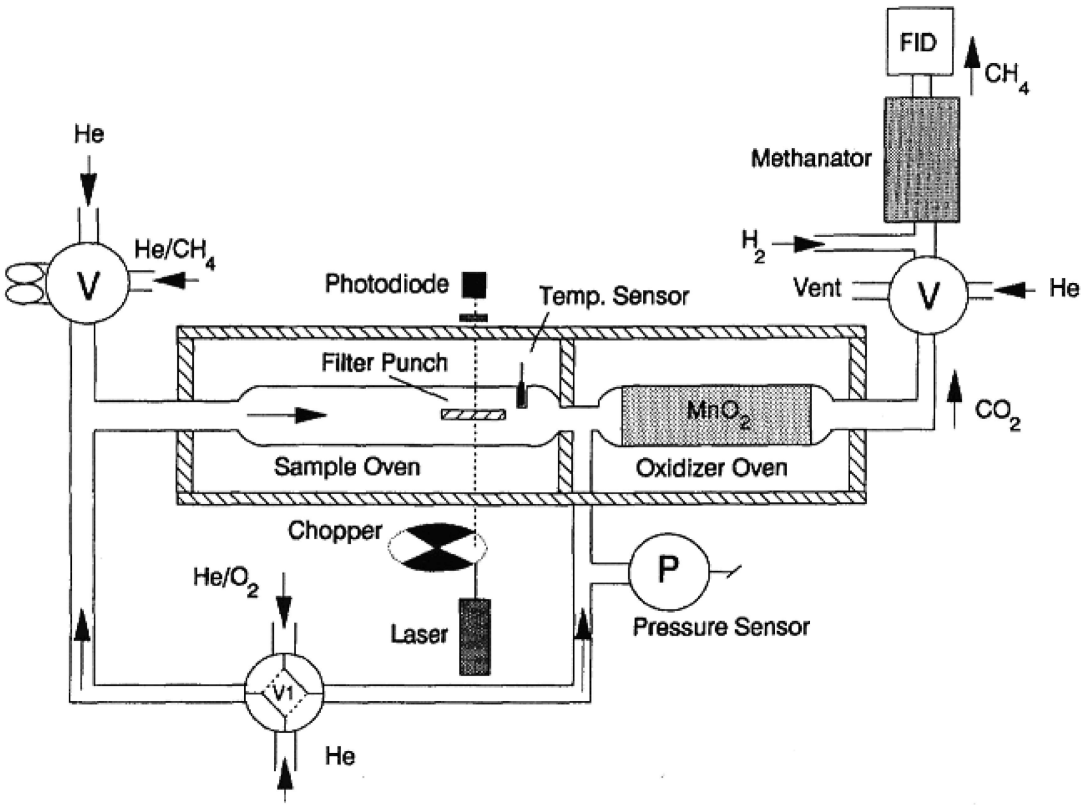

Fig. 1. Scheme of thermal-optical instrumentation [8].

tamination, quartz-fibre filters were precleaned in a furnace at the temperature of 600 °C. Atmospheric aerosols were sampled daily with the low-speed aspiration equipment at the rate of 2–3 m^3h^{-1}. After sampling the quartz-fibre filters were folded twice, placed into an aluminium envelope and placed for storage in a cooler until analysis.

The thermal-optical analysis is based on oxidation of organic and elemental carbon to CO_2 and further reduction to methane (CH_4), which is determined with the flame-ionization detector (FID). The scheme of thermal-optical analysis is presented in Fig. 1. Due to characteristics of the thermal-optical method, the separation of organic, carbonate carbon (CC), and elemental carbon is performed by temperature and space control. The analysis proceeds in two steps. In the first step, the 1.5 cm^2 rectangular portion of the quartz-fibre filter is placed in a porcelain bed and at a fixed rate is passed to the sample oven, where temperature is increased to about 820 °C in the pure helium atmosphere. Then organic and carbonate carbon is volatilized and oxidized catalytically in a bed of MnO_2 to CO_2 at 900 °C, and later CO_2 is reduced to CH_4 in a methanator with Ni at 450 °C. The flame ionization detector was used for carbon determination which was quantified as methane. Calibration of FID was achieved through injection of known volume of methane into the sample oven. During the second step of the analysis, the EC measurement is performed. The oven temperature is reduced, oxygen and helium mix (10:90) is introduced, and pyrolytic carbon (PC) is removed. Then the oven temperature is raised to 860 °C for EC oxidation to CO_2, which further is reduced to CH_4. Concentrations of organic and elemental carbon are determined as $\mu g\,C/cm^2$ of aerosol deposit area on the filter. The detection limit of this method was 0.02 $\mu g{\cdot}m^{-3}$. Repeatability of the method was $\pm 7\%$. The He–Ne laser allows continuous monitoring of filter transmittance observation during thermal-optical analysis defining the split line between OC and EC in thermogram (Fig. 2).

The optical measurement of elemental carbon was also performed by the refractometric method with the spectrometer "Specol ZV" equipped with its supplement R 45/0. The application of the refractometric method for elemental carbon (black carbon) measurement provides higher values of concentration compared with elemental carbon values obtained by the thermal-optical method due to chemical compounds in aerosol influencing the optical reflectance. Some researchers suggest introducing an error of 20% [9] or a coefficient, which might be constant for certain location or for some particular air mass [10].

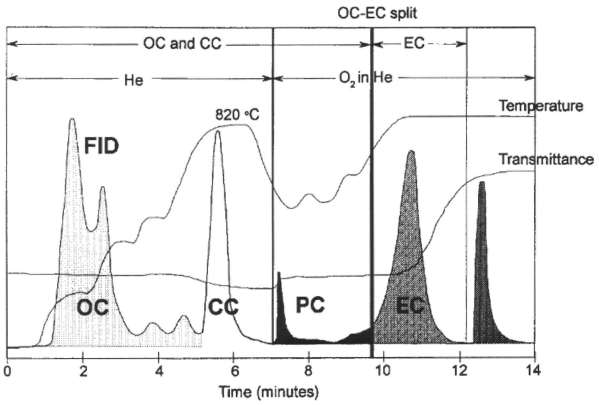

Fig. 2. Thermogram of thermal-optical analysis [8].

Meteorological data. Wind direction and 72-hour or 96-hour air mass backward trajectories at the height of 20, 500, and 1000 m above ground level for each day were constructed by the atmospheric model HYSPLIT and the archive of the meteorological database NOAA (National Oceanic and Atmospheric Administration), which are accessible on the Internet [11].

3. Results and discussion

The results of carbonaceous compound investigation are presented in Table 1. The concentrations of organic carbon and elemental carbon differed even 10 times at the same place, but concentrations of separate carbonaceous compounds determined during the period of investigation corresponded to the level of concentrations observed at other background sites [12, 13]. The average concentration of OC and EC is in the interval of concentrations observed earlier at the Preila background station in 1985–1994 but they are lower compared to the data of earlier investigations [14, 15]. It may be a result of the total decrease in emissions and concentrations of different pollutants during the last decade in atmospheric air in Europe. Reliable correlation ($r_{\rm cor} = 0.73$, $p < 0.1$) between organic and elemental carbon can be observed. It allows us to suggest that aerosol hydrocarbons and soot reach the Preila background station usually from the same sources of pollution. The EC/TC ratio was used as an indicator of anthropogenic sources at the investigation site, because elemental carbon is primary and chemically stable pollutant from fuel burning sources. This ratio is usually lower at the background sites and higher at the urban sites [12, 16]. In our case of investigation the EC/TC ratio varied between 0.04 and 0.43. This ratio shall be further considered in detail by investigating the pollutant transport to the Preila background station.

In parallel, exposed filters were analysed by the refractometric method for determination of black carbon as well. The average concentration of BC was determined by this method to be about 36% higher compared with the EC average concentration determined by the thermal-optical method. The largest difference (38.5–66.7%) between EC and BC concentrations was observed in samples No. 2, 3, and 4 (Table 1). These samples were associated with high concentration of organic compounds suppressing reflection of light.

Transport of both carbonaceous compounds to the investigation site was considered in relation to the certain air mass backward trajectories and wind directions. The highest concentrations of carbonaceous pollutants were determined on 20, 21, and 22 of June, when southwestern air masses from the "black triangle", which includes some part of the Czech Republic, Germany, and Poland or industrial region of Silesia,

Table 1. Concentrations of carbonaceous compounds (μg·m^{-3}), air mass backward trajectories, and wind directions.

Sample	Date	Pollutants				Ratio	Direction	
	2006.06	TC	OC	EC	BC	EC/TC	Air mass trajectory	Wind
1	19	0.80	0.75	0.05	0.06	0.06	SE	W, SW
2	20	3.20	3.06	0.14	0.29	0.04	SW	S
3	21	2.82	2.66	0.16	0.26	0.06	SW	S
4	22	2.14	2.05	0.09	0.27	0.04	SW	S
5	23	0.16	0.09	0.07	0.04	0.43	N	W
6	24	0.65	0.56	0.09	0.09	0.14	NW	W, NW
7	25	1.32	1.22	0.10	0.13	0.08	NW, W	W
8	26	1.92	1.85	0.07	0.09	0.04	NW, W	W, SE
9	27	0.75	0.64	0.11	0.17	0.15	NW, W	N
10	28	0.10	0.06	0.04	0.04	0.40	N	N
	Mean	1.39	1.29	0.09	0.14	0.14		
	Std. dev.	1.09	1.06	0.04	0.10	0.15		

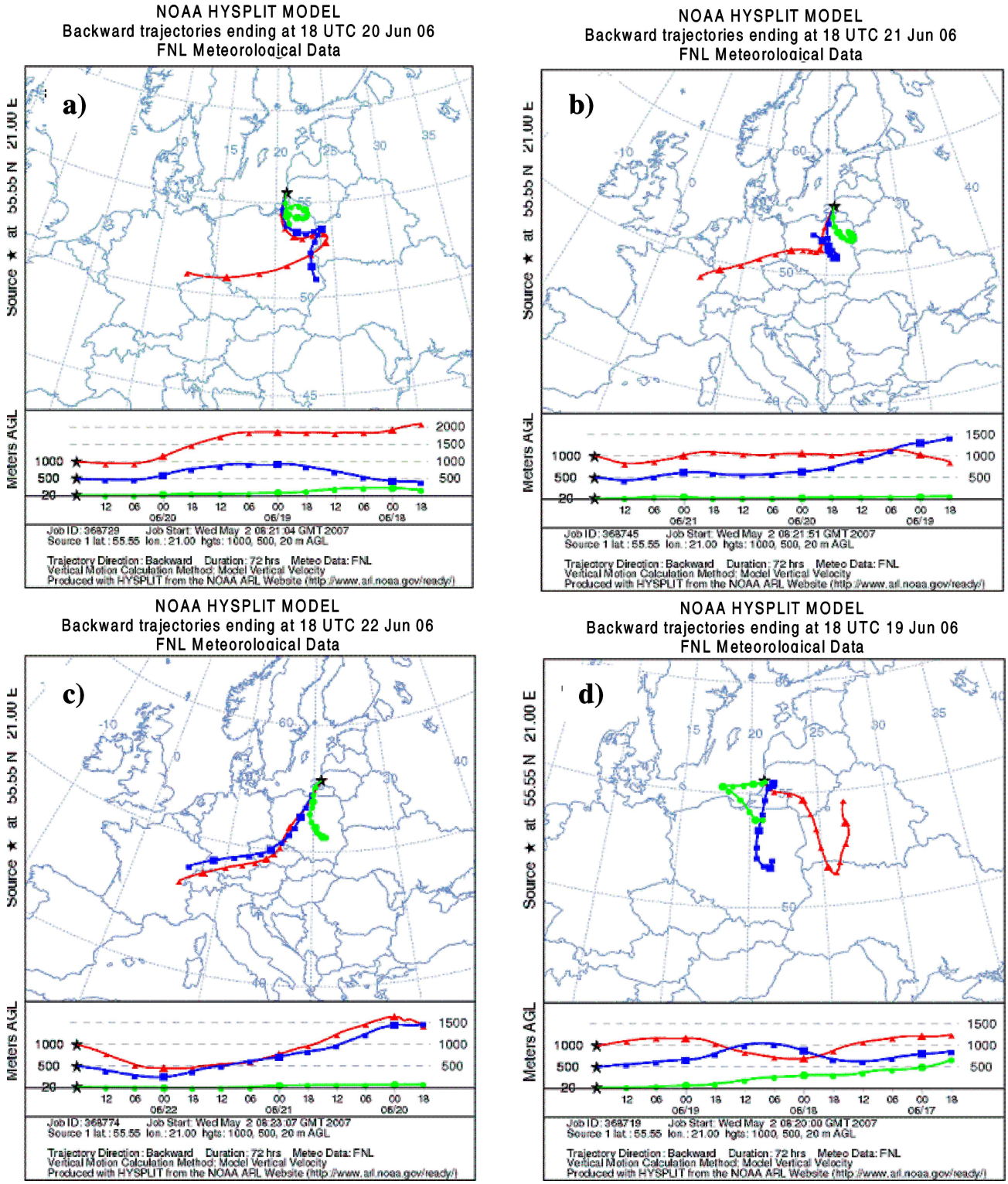

Fig. 3. Backward trajectories of air masses associated with highest concentrations of OC and EC at the Preila background station on (a–c) 20–22 June 2006 and (d) a characteristic episode of southeastern direction air mass transport on 19 June 2006.

Table 2. Average concentrations of carbonaceous compounds ($\mu g \cdot m^{-3}$) transported by different air masses and separate input of each air mass direction to the air pollution of the Preila background station during the investigation period.

	Average concentrations				Ratios of concentrations			Inputs of carbonaceous compounds by different air masses, %			
Pollutant	N	SE	NW	SW	C_{SW}/C_N	C_{NW}/C_N	C_{SE}/C_N	N	SE	NW	SW
TC	0.13	0.80	1.62	2.72	20.9	12.5	6.2	2.5	15.2	30.7	51.6
OC	0.08	0.75	1.4	2.59	32.4	17.5	9.4	1.6	15.1	31.1	52.3
EC	0.06	0.05	0.08	0.13	2.2	1.3	0.8	18.8	15.6	25.0	40.6
BC	0.04	0.06	0.11	0.27	6.8	2.8	1.5	8.3	12.5	22.9	56.3

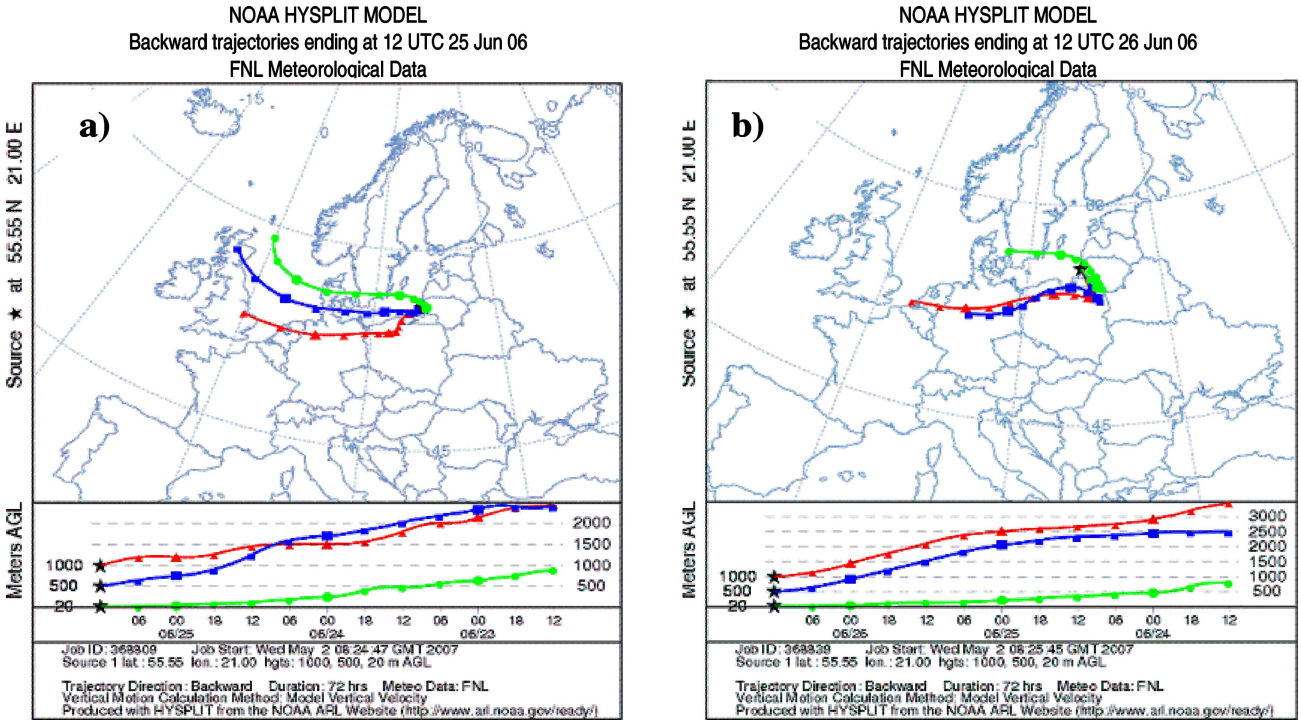

Fig. 4. Air mass backward trajectories at the Preila background station on (a) 25 and (b) 26 of June 2006.

and southern winds from Nida and Kaliningrad region were prevailing (Fig. 3(a–c)). This combination of air masses and ground boundary level winds transported the most polluted air to the Preila background station [15, 17]. Furthermore, it can be seen that air masses of the 500 and 1000 m height (indicating long-range transport of pollutants) mainly coincide, while air masses of the 20 m height (indicating local ground boundary wind) are usually of the other direction. This fact needs a separate analysis of air masses and winds in each investigation episode.

On 19 June air mass of 1000 m height was coming from northwestern part of Ukraine via Belarus and was passing the Preila background station when western wind was prevailing. It was a characteristic and rare episode of pollution associated with southeastern air masses (Fig. 3(d)). Relatively low concentration of carbonaceous compounds has been observed during this period, though these air masses are of continental origin. Similar concentrations were observed on 25 and 26 June with air masses transported from the northern part of West Europe with minor influence of southern mining regions (Fig. 4(a, b)). During these analysed periods, the EC/TC ratio was low and varied between 0.04 and 0.06 because of comparatively high concentration of organic carbon in air masses from industrial regions. We suggest that during the air mass transport over the continent, organic carbon fraction is relatively stable and its high amount might be observed in an aged atmospheric air mass sample.

Lowest concentrations of EC and OC were determined at the background station on 23 and 28 of June, when air masses from the Atlantic Ocean via England, the North Sea, and the Baltic Sea were pass-

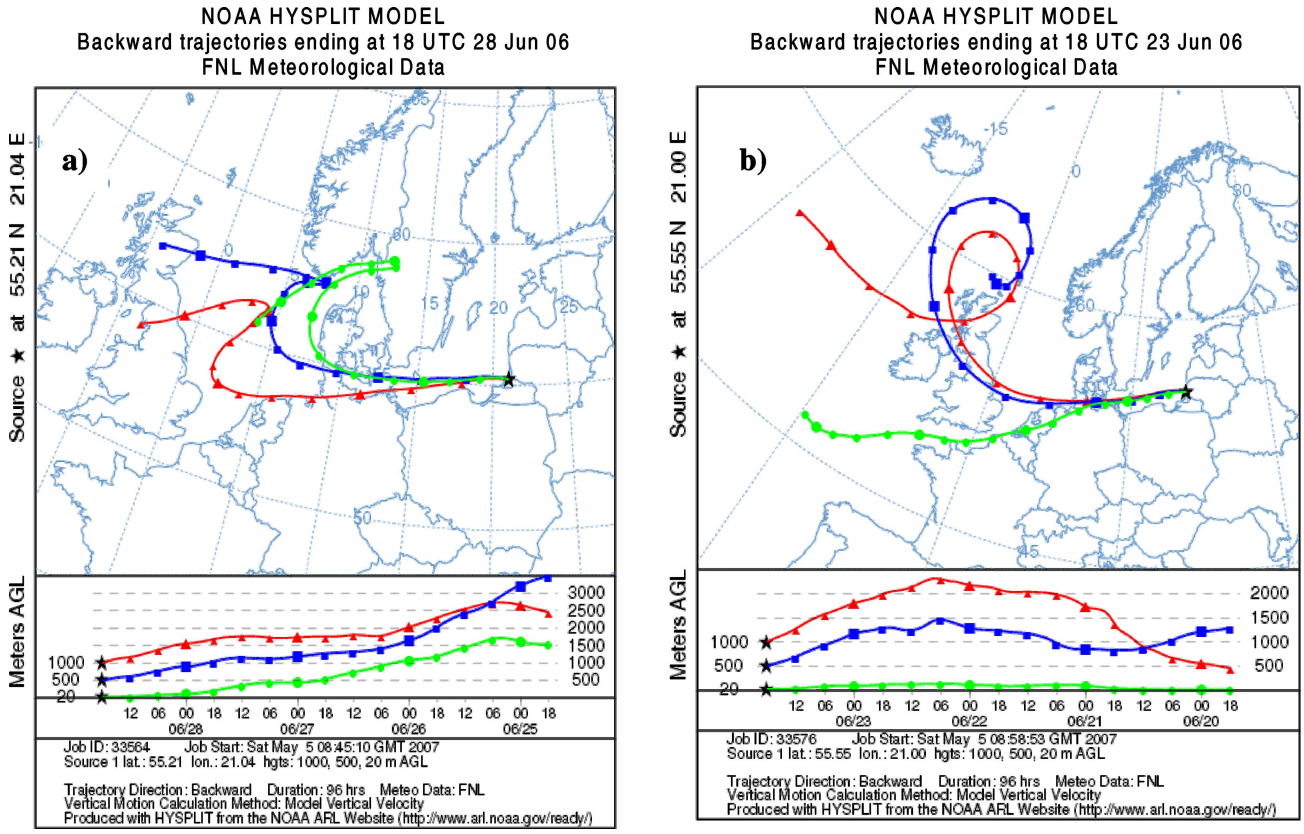

Fig. 5. Backward trajectories of air masses associated with the lowest concentrations of carbonaceous pollutants at the Preila background station on (a) 28 June and (b) 23 June 2006.

ing the investigation site during the periods of marine western winds (Fig. 5(a, b)). Exclusively high EC/TC ratio observed during this period indicated the anthropogenic origin of carbonaceous pollutants. This can be explained by 96-hour air mass backward trajectories which show that air masses have been enriched with elemental carbon passing over industrial regions of England and have been important for the formation of high pollution episodes in Lithuania [18]. The low concentration of OC in these air masses can indicate a very effective washout process of hydrocarbons and long lifetime of EC in the marine atmosphere.

The relative load of carbonaceous compounds transported by different air masses is presented in Table 2. Data of investigation indicate that the main part of organic and elemental carbon is transported to Preila with southwestern and western air masses. These air masses are comparatively frequent in the Baltic region and the contribution of carbonaceous compounds within those air masses is 40–56%. This fact confirms peculiarities of transport of other pollutants to this background site [15]. Western air masses originating from the northern part of West Europe have transported from 22.9 to 31% of carbonaceous substances. Eastern air masses are rare in the Baltic region and their input comprises only 12–15% of carbonaceous pollutant amount. Northern air masses coming from the Atlantic Ocean via England have carried insignificant amount of pollutants. Furthermore, we can note that the EC/TC ratio in northern air mass is high enough to assume that these carbonaceous compounds are more of anthropogenic than of biological origin. These investigations were performed in warm season. In wintertime an increase in carbonaceous substances, particularly of elemental carbon, may be evident.

4. Conclusions

The reliable correlation between organic and elemental carbon indicates that both carbonaceous substances reach the Preila background station mostly from the same sources of pollution. The main part of carbonaceous compounds are carried to the Preila background station by air masses from the southwestern part of Europe. Carbonaceous compounds in south-western air mass may comprise more than 50% of total carbonaceous compounds reaching the background station by air masses from different directions. The low amount

of organic carbon carried to the recipient site with the northern air masses from the Atlantic Ocean via northern part of UK indicated an intensive washout process of hydrocarbons over the marine atmosphere. Furthermore, the relatively high EC/TC ratio in aerosol, associated with northern air masses, suggests more anthropogenic than biogenic origin of aerosol at the Preila background station.

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ORGANINĖ IR ELEMENTINĖ ANGLIS BALTIJOS JŪROS PAKRANTĖS AEROZOLYJE

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Santrauka

Organinė ir elementinė anglis atmosferos aerozolyje buvo tirta 2006 m. birželio 18–28 dienomis Preilos Aplinkos užterštumo tyrimų stotyje. Organinės ir elementinės anglies koncentracijos buvo įvertintos termooptiniu metodu. Lygiagrečiai reflektometriniu metodu buvo atlikti juodosios anglies matavimai. Turinčių anglies junginius aerozolio dalelių, įvertinant jų šaltinius, pernaša analizuota naudojant atgalines oro masių pernašos trajektorijas 1000, 500 ir 20 m virš žemės paviršiaus. Trajektorijos skaičiuotos NOAA (*National Oceanic and Atmospheric Administration*, JAV) HYSPLIT modelio metodika [11]. Rasta, kad didžiausios organinės ir elementinės anglies koncentracijos aerozoliuose buvo susijusios su pietvakarinėmis oro masėmis, praslinkusiomis virš „juodojo trikampio" (Lenkijos, Čekijos, Vokietijos pasienio teritorija), o žemiausios – su oro masėmis nuo Atlanto vandenyno. Organinė ir elementinė anglis, nešama vakarinių oro masių, Preilos foninėje stotyje sudarė daugiau nei 50% visos anglį turinčių medžiagų taršos. Gauti rezultatai atitinka Pabaltijo atmosferos užterštumo fono formavimosi dėsningumus, nustatytus anksčiau kitiems teršalams.