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CENTER FOR PHYSICAL SCIENCES AND TECHNOLOGY
INSTITUTE OF PHYSICS

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**STUDY OF AEROSOL PARTICLE ORIGIN AND DISPERSION BY ISOTOPE
RATIO MASS SPECTROMETRY**

Summary of doctoral dissertation
Physical sciences, physics (02P)

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VILNIAUS UNIVERSITETAS

FIZINIŲ IR TECHNOLOGIJOS MOKSLŲ CENTRO
FIZIKOS INSTITUTAS

Andrius Garbaras

**ATMOSFEROS AEROZOLIO DALELIŲ KILMĖS IR SKLAIDOS TYRIMAS
STABILŲ IZOTOPŲ MASIŲ SPEKTROMETRIJOS METODU**

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Introduction

Topicality of the problem

The development of industry, transport, agriculture and power engineering inevitably create problems related to the impact of generated waste on the environment as well as other undesirable processes. The atmosphere is the main component of the Earth's climate system because changes occurring due to the human economic activity result in serious environmental impacts in all components of the ecosystem as well as the Earth's climate self-regulation system is disturbed. The most objective parameter characterizing the Earth's climate equilibrium state is the dynamics of the average Earth's temperature variation. The present scientific research has shown that due to the active human economic activity the Earth's temperature over the twentieth century increased by 0.76 °C [1] and it this value is highest during the recent millennium. It has been shown that the essential changes of the climate are caused by the greenhouse effect, and phenomena of the Earth's thermal balance change are determined by atmospheric aerosol particles. The impact of these processes is substantially opposite, i.e. the greenhouse effect increases the average temperature of the Earth, while aerosols reduce it. Aerosol particles reflect the solar radiation, change conditions of water droplet formation in clouds and the precipitation regime. Thus, the Earth's albedo level is changed. These phenomena determine the reliability of the climate change forecasts, therefore, the research on the atmosphere aerosol becomes increasingly relevant, while the necessity and perspective of new scientific knowledge about natural and anthropogenic aerosols, are determined by the demand for more precise characterization of the atmospheric aerosol particle formation and processes determining their growth up to the sizes having impact on the light absorption and dispersion processes, thus changing the Earth's radiation balance and significantly influencing the cloud formation dynamics through water vapor condensation nuclei.

Despite intensive scientific research over the recent decade, fundamental mechanisms and physical and chemical phenomena determining the aerosol particle formation from gaseous phase and the origin of organic matter in these particles are not completely clear up to now. The interest in atmospheric aerosols, containing carbon, is

increasing. Therefore, it is very relevant to experimentally confirm the statements that aerosol properties and behavior in the processes occurring in the atmosphere are determined by organic compounds formed during biomass and fossil fuel burning or natural compounds formed in forests, on the sea surface, etc. Black carbon which is present in aerosol particles, due to its high surface sorption ability and optical properties is important to atmospheric processes, e.g. cooling, cloud formation.

New methodological investigations and development of the experimental aerosol research equipment also become relevant. Significant results are obtained by methods of aerosol particle spectroscopy, optical investigation methods, chemical methods, powerful computer engineering resources, models and programs for forecasting the air mass transport and processing of experimental results are applied. Application of mass spectroscopy methods and the experimental equipment in atmospheric aerosol particle research should be mentioned separately. The aerosol mass spectroscopy method provides unique possibility of measuring the composition of organic matter in the aerosol particle spectrum region of our interest. The isotope ratio mass spectroscopy method allows using carbon, nitrogen, oxygen, and hydrogen stable isotope ratios as markers in solving problems of the atmosphere aerosol particle dynamics and balance. The latter method is selected as the main one in pursuing objectives and tasks set up in this work.

Objective and tasks of the work

The objective of this work was to investigate the origin, sources and formation of organic compounds and black carbon in atmospheric aerosol particles and to develop new research methods.

To attain this objective the following tasks have been formulated:

- Development of the identification method for the aerosol origin and source by investigating the carbon isotope mass ratios.
- Illustration of possibilities of the carbon isotope ratio method by identifying the aerosol particle origin during the air mass long-range transport at the Preila Environmental pollution research station.
- Investigation of variation of the black carbon amount in aerosol particles in the diesel engine exhaust depending on the engine working parameters and fuel composition.
- Investigation of the carbon isotope ratio variation in natural aerosol depending on the aerosol particle size distribution.
- Determination of the partial contribution of natural and anthropogenic particles in aerosol by investigation of stable carbon and radiocarbon isotope ratio changes during continental and marine air mass transport.

Novelty of the work

For the first time the partial contribution of natural marine origin and anthropogenic aerosol particles during marine and continental air mass transport by measuring $\delta^{13}\text{C}$ variation with the isotope ratio mass spectrometer and radiocarbon (^{14}C) concentrations with the accelerator mass spectrometer in atmospheric aerosol particle samples has been determined.

By employing a multi-stage impactor and a stable isotope mass spectrometer, for the first time the influence of natural aerosol particle sources has been evaluated for aerosol particles of different size.

By investigating the isotope ratio changes in black carbon emitted by the transport

(powered by diesel fuel), the influence of biodiesel fuel supplements on the black carbon concentration in exhaust has been evaluated for the first time.

Author's contribution

Methodology of the isotope ratio measurement has been mastered, samples necessary for measurements were collected, the equipment for the size-segregated aerosol particle sampling was prepared, the primary sample treatment was performed and samples were measured. Moreover, the values of the carbon isotope ratios in samples were measured. Primary versions of scientific papers were prepared taking active participation in interpreting investigation results and drawing conclusions.

Approbation of the work

The research results obtained during Ph.D. studies were reported in 5 scientific publications and presented at 10 conferences.

Author's publications related to the thesis:

1. D. Ceburnis, A. Garbaras, S. Szidat, M. Rinaldi, S. Fahrni, N. Perron, L. Wacker, S. Leinert, V. Remeikis, M. C. Facchini, A. S. H. Prevot, S. G. Jennings, and C. D. O'Dowd, Quantification of the carbonaceous matter origin in submicron marine aerosol particles by dual carbon isotope analysis, *Atmospheric Chemistry and Physics Discussion*, Vol. 11, pp. 2749-2772 (2011);
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3. A. Garbaras, J. Andriejauskiene, R. Bariseviciute, and V. Remeikis, Tracing of atmospheric aerosol sources using stable carbon isotopes, *Lithuanian Journal of Physics*, Vol. 48, No. 3, pp. 259-264 (2008).
4. A. Garbaras, I. Rimšelytė, K. Kvietkus, and V. Remeikis, $\delta^{13}\text{C}$ values in size-

segregated atmospheric carbonaceous aerosols at a rural site in Lithuania, Lithuanian Journal of Physics, Vol. 49, No. 2, pp. 229-236 (2009).

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Author's publications methodologically related to the thesis:

1. V. Remeikis, A. Plukis, R. Plukienė, A. Garbaras, R. Barisevičiūtė, A. Gudelis, R. Gvozdaitė, G. Duškesas, L. Juodis, Method based on isotope ratio mass spectrometry for evaluation of carbon activation in the reactor graphite, Nuclear engineering and design, Vol. 241, No. 10, pp. 2697-2703 (2010);
2. G. Trakimas, T. D. Jardine, R. Barisevičiūtė, A. Garbaras, R. Skipitytė, V. Remeikis, Ontogenetic dietary shifts in European common frog (*Rana temporaria*) revealed by stable isotopes, Hydrobiologia (accepted).

Presentations at conferences:

1. A. Garbaras, R. Bariseviciute, J. Matijosius, S. Pukalskas, T. Sneideris, V. Remeikis, Biofuel combustion product inventory by stable isotope ratio mass spectrometry, International Aerosol Conference 2010, Helsinki, Finland, Abstract P2M22.
2. D. Ceburnis, A. Garbaras, S. Szidat, S. Fahrni, N. Perron, L. Wacker, M. Rinaldi, A. Prevot, L. Stephan, G. Jennings, V. Remeikis, C. Facchini, C. O'Dowd, Unambiguous origin of aerosol organic matter by 13C and 14C analysis, International Aerosol Conference 2010, Helsinki, Finland, 8E5.
3. D. Ceburnis, A. Garbaras, S. Szidat, A.S.H. Prevot, C. Facchini, C.D. O'Dowd, North Atlantic marine boundary layer organic aerosol: sources and fluxes, Halifax, July 2010.
4. A. Garbaras, V. Remeikis, I. Garbarienė, K. Kvietkus, and D. Čeburnis, Total carbon isotopic values at background and urban sites in Lithuania during summer 2008, European Geosciences Union General Assembly 2010, Vienna, Austria.
5. A. Garbaras, R. Barisevičiūtė, T. Šneideris, V. Remeikis, Stable carbon isotope ratio measurements in aerosol particles, generated from various internal combustion

- engines, 7th international conference of young scientists on energy issues, 2010, Kaunas, Lithuania.
6. D. Ceburnis, C. D. O'Dowd, A. Garbaras, V. Remeikis, M. Rinaldi, S. Szidat, S. Fahmi, A.S.H. Prevot, N. Perron, L. Wacker and S. Leinert, Proof of biogenic origin of marine aerosol by ^{13}C and ^{14}C analysis, 19th Annual VM Goldsmith Conference, 2009, Davos, Switzerland, *Geochimica et cosmochimica acta*, Vol. 73 (13), pp. A201-A201 (2009).
 7. A. Garbaras, I. Rimselyte, K. Kvietkus, A. Plukis, and V. Remeikis, Bulk carbon isotopic ratio of size-resolved aerosol at background and urban sites in Lithuania, European Geosciences Union General Assembly 2009, Vienna, Austria.
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 9. A. Garbaras, R. Barisevičiūtė, A. Plukis, V. Remeikis, GC-IMRS use in pollution sources, 2007, 37-th Lithuanian National Physics conference.
 10. A. Garbaras, A. Milukaitė, A. Plukis, I. Rimšelytė, R. Barisevičiūtė, V. Remeikis, PAH $^{13}\text{C}/^{12}\text{C}$ ratios in aerosols, 2007, 37-th Lithuanian National Physics conference.

The content of the dissertation

The dissertation consists of 90 pages and comprises an introduction, three chapters with 31 figures and 12 tables, conclusions and a list of 93 quoted references.

Statements to be defended

1. The carbon isotope ratio in anthropogenic origin aerosol particles corresponds to the isotope ratio of burnt fuel (biomass and fossil fuel), and this parameter well represents the source of atmospheric aerosol particles.
2. Vegetative organic carbon is prevailing in the aerosol particles, smaller than 1 μm . In the aerosol particles larger than 1 μm a carbonate component is observed. In aerosol particles of all sizes, the carbon isotope ratio of the vegetative organic origin component does not change.
3. Ethanol as a supplement of diesel fuel does not change the amount of the elemental carbon in vehicle exhaust.
4. The aerosol particles in the marine air mass are about 80 % of marine biogenic and 20 % of fossil fuel origin. The aerosol particles in the continental air mass are about 30 % of marine, 40 % of fossil fuel and 30 % of continental non-fossil fuel origin.

Review

In **chapter one** a short review of the carbon cycle, stable carbon isotope abundance in nature, and their reactivity and fractionation mechanisms is presented. A short historical review of the isotopic ratio measurement equipment is given. Aerosol particle formation and growth mechanisms are described. Investigations of organic and elemental carbon in size segregated aerosol particles and their origin are presented extensively. The origin of these compounds is natural or anthropogenic, while elemental carbon is formed during burning. This type of carbon can be formed during burning of fossil fuel or biomass, but the knowledge about partial contribution of carbon chemical forms in aerosol particles of different size is scarce.

Experimental

In **chapter two** methods of the carbon isotope ratio measurements in the aerosol particles from the environment or exhaust are presented. Experiments were carried out at two background stations in Lithuania (Preila and Rūgšteliškis) and in Ireland (Mace Head). Samples of anthropogenic aerosol particles were collected in ordinary cars and using the experimental set-up – the engine with the control system *KI-5543*. Aerosol particles were collected on filters or by MOUDI (Micro-Orifice Uniform Deposition Impactor). Measurements of aerosol particle organic fraction were performed with *Aerodyne Research* aerosol mass spectrometer. Carbon isotope ratio measurements in size-segregated aerosol particles were performed using an elemental analyzer (*Flash EA 1112*) connected with an isotope ratio mass spectrometer *ThermoFinnigan Delta Plus Advantage*.

Investigation of carbon isotopic ratio variation in the atmospheric aerosol particles by the mass spectrometry method

In **chapter three** experiments, research findings related to the carbonaceous aerosol particle origin, their formation in different environments, discussions and physical interpretation are presented. Methodology, potential and limits of application for the atmospheric aerosol particle origin identification are justified and illustrated experimentally.

In **subchapter 3.1** the variation of carbon isotope ratio values in total and PM_{2.5} aerosol particles at the Preila Environmental pollution research station is provided. Location and time of aerosol particle sampling are indicated in the first paragraph of this subchapter. It is shown that during this period, air mass transport from the west dominated at the Preila site, though some air masses were transported from the northern or southern directions. The air mass transport to the Preila station from the eastern or southeastern directions was not observed. Bearing in mind that collected samples were of the coarse aerosol fraction with the lifetime of the order of one day, from backward air mass trajectory analysis it is evident that during this sampling period most of the sampled aerosols were transported with marine air masses from the Baltic Sea. For this air mass transport scenario carbon isotopic ratio values $\delta^{13}\text{C}$ were from $-24.7 \pm 0.3 \text{ ‰}$ to $-26.4 \pm 0.2 \text{ ‰}$. From the experimental data (*Figure 1*) it follows that the average $\delta^{13}\text{C}$ value is $-25.5 \pm 0.7 \text{ ‰}$ for the total aerosol mass. Because the total aerosol mass is mostly influenced by the mass of largest particles, it is evident that this $\delta^{13}\text{C}$ value characterizes aerosol particles from local areas. This value indicates that the aerosol formation is affected by the marine and other natural precursors, for which the isotopic ratio value is common in this region, i.e. with relatively clean atmospheric marine air and background environment.

During the second sampling period aerosol particles with an aerodynamic diameter less than $2.5 \mu\text{m}$ were collected. During this period air masses were transported from the eastern (Ukraine and Byelorussia), northwestern (Scandinavia and Baltic Sea) directions and local spread over Lithuania, Latvia, Poland and Kaliningrad (Russia)

territories. For this period the air masses backward trajectories for 72 hours were analyzed. $\delta^{13}\text{C}$ values of aerosol particles collected on filters at the Preila Environmental pollution research station were measured and ranged from $-24.0 \pm 0.1 \text{ ‰}$ to $-30.9 \pm 0.2 \text{ ‰}$. Variation of $\delta^{13}\text{C}$ values was related to air mass transport scenarios. Examples of air mass backward trajectories and $\delta^{13}\text{C}$ values of aerosol particles are shown in Figure 2. The measured $\delta^{13}\text{C}$ values can be separated into three groups which can be related to the backward air masses trajectories. Considering that the $\delta^{13}\text{C}$ average value of aerosol from the local region was $-25.5 \pm 0.7 \text{ ‰}$ (Fig. 1), it is evident that the middle data group consists of a mix of aerosol particles from the marine environment and anthropogenic pollution sources.

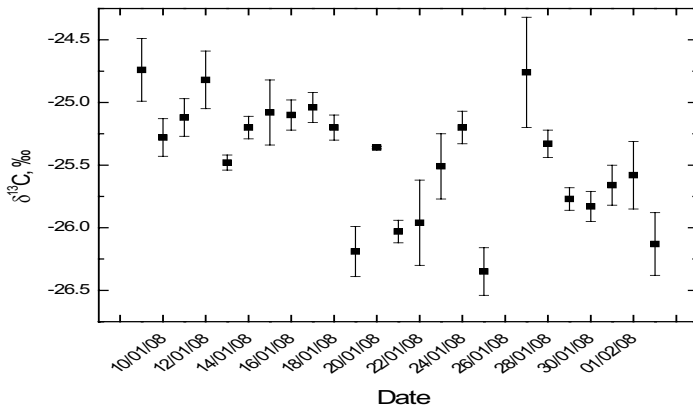


Figure 1. $\delta^{13}\text{C}$ of bulk aerosols at the Preila background station during 9 January to 2 February, 2008.

The upper data group indicates aerosol particles mostly of the marine origin with $\delta^{13}\text{C}$ values ranging from $24.0 \pm 0.1 \text{ ‰}$ to $-25.4 \pm 0.3 \text{ ‰}$. The bottom data group (eastern air mass transport events) clearly indicates anthropogenic pollution sources. During the experiment the most negative $\delta^{13}\text{C}$ values were observed when air mass transport was only from the continent. Such $\delta^{13}\text{C}$ values and continental transport show that transported aerosol particles were formed during burning. It is stated that sources of these particles were from burning of oil products or biomass, the carbon isotopic ratio of which is about -30 ‰ . Taking into consideration measured $\delta^{13}\text{C}$ values and air mass trajectories it is concluded that $\delta^{13}\text{C}$ values of aerosol particles depend on the air mass

transport direction and atmospheric processes occurring during transport. Experimental data very closely coincide with the carbonaceous aerosol concentration variation earlier measured at the Preila site [2]. The highest concentrations of carbonaceous aerosol were observed in the continental air masses, and the lowest ones in the marine air masses. It confirms that transported aerosol particles consist partly of the fossil fuel combustion products, $\delta^{13}\text{C}$ values of which are lower than -30 ‰.

In **subchapter 3.2** results of experimental investigation dedicated to the size segregated aerosol particles formation at the background site, where the main aerosol particle source is natural environment, are presented. Variation of elemental and organic carbon concentrations in atmospheric aerosol particles of 0.056-18 μm size and its relation with carbon isotopic ratios were experimentally observed by analyzing data of samples collected at the Rūgšteliškis Integrated monitoring station. For measurements of total and elemental carbon isotopic ratios aerosol particles were collected with the MOUDI impactor.

Variation of carbon fractions (OC, EC) in different size atmospheric aerosol particles is described. It is shown that the ultrafine particle size range (stage 11, $D_p = 0.056 - 0.1 \mu\text{m}$) made up < 5%. The accumulation mode particles (stages 10 – 6, $D_p = 0.1 - 1.8 \mu\text{m}$) including particles directly emitted and/or grown by coagulation and condensation processes amounted to about 70%, and the coarse size range (stages 5 – 1, $D_p = 1.8 - 18 \mu\text{m}$) including contributions of soil erosion, resuspension and abrasion processes – to about 30% of the mean TC concentration (Figure 3). Concentrations of organics were in the range of 1–25.4 $\mu\text{g m}^{-3}$, with an average of 5.6 $\mu\text{g m}^{-3}$ and a standard deviation of 3.7 $\mu\text{g m}^{-3}$. The changes in concentration of organic matter may be explained by the influence of long-range transport of aerosol particles. Figure 4 shows that the highest concentrations of organic aerosol particles were measured during 13-14 July when the air masses were coming mainly from Southern Europe.

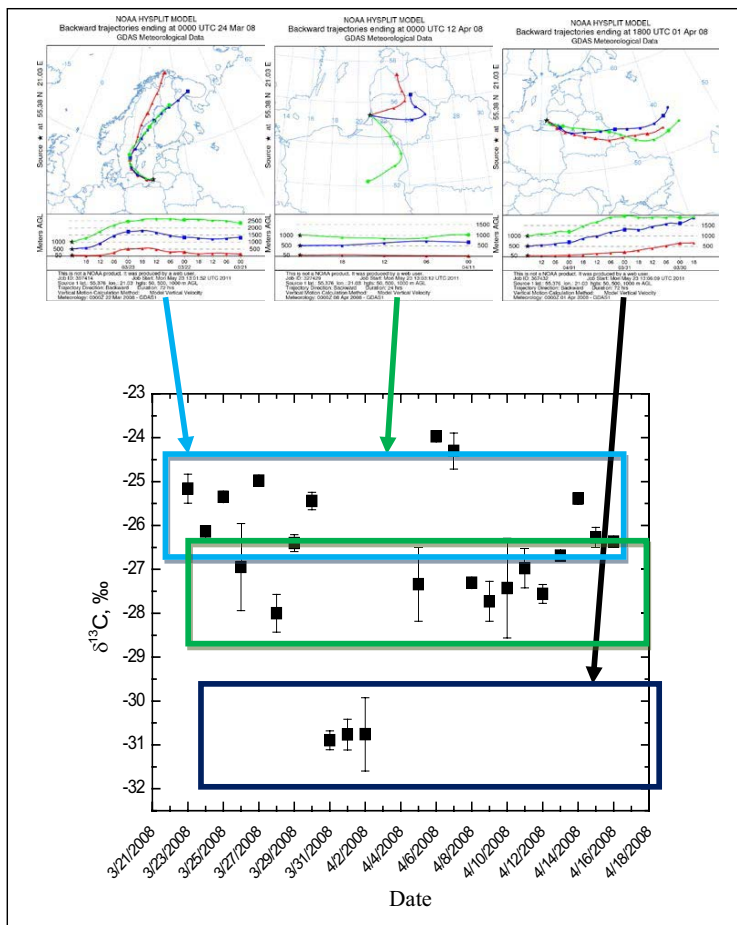


Figure 2. $\delta^{13}C$ values in PM_{2.5} aerosol particles, collected at Preila from 23/03/2008 to 16/04/2008. Backward air mass trajectories are presented above.

Those concentrations were noticeably higher than concentrations registered when air masses passed over Western Europe (19–20 July). The concentration considerably decreased (22 July) when air masses were coming from the North Atlantic, passing over the Baltic Sea. Generally, data revealed large variations in concentrations of organic species ranging within an order of magnitude depending on the air mass origin and history.

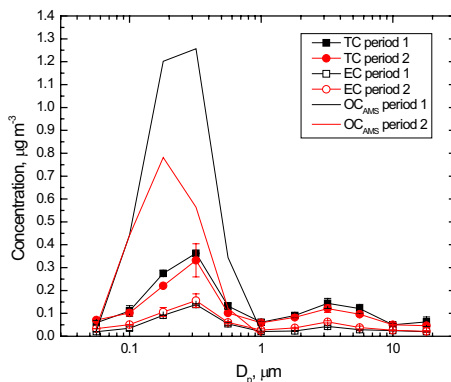


Figure 3. TC and EC mass concentrations in different size aerosol particles.

The derived mass spectra in comparatively clean air mass having passed over the North Atlantic and the Baltic Sea and in polluted air mass having arrived from Southern Europe differ mainly in relative intensity rather than in the presence or absence of specific peaks. The largest contributions to the spectrum came from mass fragments characteristic of oxidized organic compounds such as m/z 44 coupled with m/z 18, signatures of di- and polycarboxylic acid, in addition to mass fragments 43 and 55 which are associated with other types of oxidized organic compounds including aldehydes and ketones. During the period when air mass came from Southern Europe and has passed over polluted urban areas the relative abundance of peaks m/z 43 was larger than in the mass spectrum from the Northern Atlantic air mass. This mass spectrum has a significant intensity peak m/z 29 attributed to the saturated alkanes. It is shown that these peaks indicate that rural oxidation products might be mixed together with oxidized urban aerosol.

Levoglucosan ($m/z=60$) is a good indicator of biomass burning [3]. Absence of levoglucosan in the mass spectrum indicated that in the submicron range the main source of aerosol particles was not biomass burning.

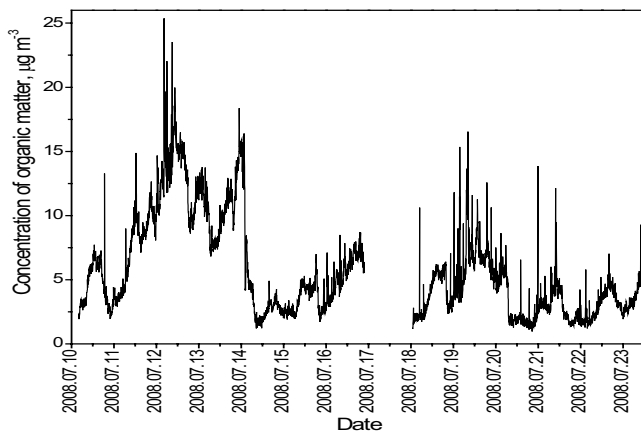


Figure 4. Concentrations of organic matter in aerosol particles at Rūgšteliškis IMS during 10-24 July 2008.

Measurements have shown that using Q-AMS and MOUDI OC ($OC=TC-EC$) values differ from 2 to 9 times. Cabada et al. [4] showed that more than 50% of the organic matter (OM) can be lost from the MOUDI aluminum foils during the summertime. OM losses during the summer are mainly due to volatilization of material due to higher ambient temperatures and higher concentrations of secondary organic species. For the determination of the OC/EC ratio we used OC concentrations registered by Q-AMS, and those of EC collected by MOUDI and later measured by EA-IRMS. The size distribution measured with the Q-AMS and MOUDI has been recalculated to the geometric mean diameter.

The OC/EC values are found to be with a maximum of 13.1 on stage 9 ($D_p = 0.18 - 0.32 \mu\text{m}$) in the accumulation mode during period 1. OC/EC ratios of > 10 in the accumulation particle mode are typical of background sites [5]. However, on stage 6 ($D_p = 1 - 1.8 \mu\text{m}$) the OC/EC ratio of 1.2 was observed (Table 1). This low value can be caused by soot emissions of domestic fires and aged traffic emissions transported over longer distances. OC and EC concentrations in aerosol particles of the accumulation mode are shown in Figure 3. Fresh traffic emissions from the near surroundings could not be detected as an important source as can be seen in the relatively low EC fraction of the particle mass on impactor stages 10 and 11. Measurements at sites being strongly dominated by traffic resulted in an OC/EC ratio of nearly 0.3 [6].

Table 1. TC, EC and OC_(AMS)/EC in the aerosol particles at the Rūgšteliškis site.

Stage No.	D, μm	Period 1 (10 – 18 July 2008)			Period 2 (10 – 18 July 2008)		
		TC, μg m ⁻³	EC, μg m ⁻³	OC _(AMS) /EC	TC, μg m ⁻³	EC, μg m ⁻³	OC _{AMS} /EC
1	18	0.06	0.02		0.05	0.02	
2	10	0.05	0.02		0.05	0.03	
3	5.6	0.12	0.03		0.10	0.04	
4	3.2	0.14	0.04		0.12	0.06	
5	1.8	0.09	0.02		0.08	0.04	
6	1	0.06	0.02	1.1	0.06	0.03	0.1
7	0.56	0.13	0.05	6.3	0.10	0.06	2.0
8	0.32	0.36	0.14	9.1	0.33	0.16	3.6
9	0.18	0.27	0.09	13.1	0.22	0.11	7.4
10	0.1	0.11	0.03	12.7	0.10	0.05	8.7
11	0.056	0.06	0.02	1.3	0.07	0.03	1.3

In the ultrafine particle size mode OC/EC ratios were about 1.3. This value shows that combustion processes significantly contribute to this size mode.

In the second part of **subchapter 3.2** values of stable carbon in size segregated aerosol particles are presented. The averaged $\delta^{13}\text{C}$ value at the Rūgšteliškis rural site was -27 ‰ with clear transit from the accumulation to coarse mode. The $\delta^{13}\text{C}$ value of about -26.5 ‰ for summer samples was reported in Zurich [7].

Measurement data show bimodal distribution of TC and EC in both investigation periods. In the accumulation mode, $\delta^{13}\text{C}$ values ranged from -22.9 to -26.3 ‰ (average value -24.7 ± 1 ‰) for EC and from -26.7 to -30.4 ‰ for TC. Comparable carbon isotopic ratios on all stages in the accumulation mode show that aerosol particles in this mode had the same source. The OC isotopic ratio was derived from TC, EC isotopic ratios (Figure 5). OC $\delta^{13}\text{C}$ value of -31.1 ± 1.4 ‰ is typical of dominant local plants (coniferous wood). From presence of oxidized organics matter in AMS spectra it is not possible to state that the biogenic or anthropogenic source is dominant. By combining AMS and isotopic ratio data it is evident that in the accumulation mode aerosol particle precursors had biogenic origin.

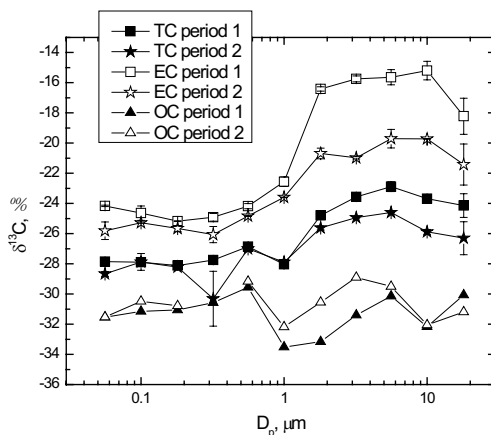


Figure 5. $\delta^{13}\text{C}$ variation in aerosol particles collected with MOUDI. Dashed line represents estimated OC isotopic ratios.

TC $\delta^{13}\text{C}$ values ranged from -22.8 to -26.3 ‰ and those of EC from -15.2 to -21.4 ‰ of aerosol particles in the coarse mode. Such positive carbon isotopic values indicate that in coarse mode TC consists of mixture of EC, OC and unknown third constituent. Naturally, materials with higher $\delta^{13}\text{C}$ values are carbonates, which could be transferred with dust from surrounding areas at the Rūgšteliškis site due to elevated air temperatures with no precipitation, and they probably determined such positive $\delta^{13}\text{C}$ values in coarse mode aerosols.

In **subchapter 3.3** the influence of traffic related anthropogenic emissions on the net balance of the atmospheric aerosol particles is considered. Using $\delta^{13}\text{C}$ values as a tracer in the whole atmospheric aerosol particle mass, particles with the carbon isotopic ratio typical of autotransport emissions (exhaust) were studied. Investigations of relevant to traffic pollution, i.e. the influence of vehicle motor working characteristics and fuel composition on the aerosol particle formation and transformation in the environment, were carried out.

During the experiment, changes in the carbon isotopic ratio in the fuel and its combustion products (aerosol particles and CO_2 gas) were measured. The vehicle models selected for investigation of the relation between vehicle emitted aerosol particles, CO_2 and used fuel are described in *Table 2*.

Table 2. Characteristics of the vehicles.

Type of fuel	Vehicle model	Year of production	Working volume, l	Cleaning system
Diesel	Hyundai H1	2000	2.5	EGR
Diesel	Volkswagen Transporter	2000	1.9	Catalyzer
Diesel	Mercedes-Benz C250	1996	2.5	
Diesel	Volkswagen Golf	1985	1.6	
Gasoline	Honda Civic	2000	1.6	TW
Gasoline	Volvo V70	1994	2	
Gasoline	Fiat Temptra	1994	1.8	
E85	Toyota Corolla	1995	1.3	Catalyzer
Gasoline/LPG	Toyota Corolla	1995	1.3	Catalyzer
Gasoline/LPG	Volkswagen Golf	1993	1.8	

EGR: exhaust gas recirculation system.

TW: three-way functional catalytic converter.

LPG: liquefied petroleum gas.

The investigations of combustion products of the diesel engine using ethanol-diesel blend with various engine working parameters are presented. The engine control system *KH-5543* with the 4-cylinder diesel engine which are located in the Vilnius Gediminas Technical University, Faculty of Transport Engineering Department of automobile transport were used (see experimental set-up in Figure 6 and diesel engine specifications in Table 3).

Isotopic analysis of the diesel fuel in Lithuania and neighboring countries (Byelorussia, Ukraine, Czech Republic) shows that the carbon isotopic composition of this fuel is similar (see *Table 4*). It is stated that crude oil for diesel production is of Russian origin. In general, the isotopic composition of fuel in the Baltic countries and Eastern Europe differs from that in Western Europe (*Table 4*).

Table 3. Diesel engine specifications.

Type	In-line 4-cylinder
Working volume V_h , cm ³	1896
Compression ratio	19.5
Maximum power P_e , kW	66 (at 4000 rev/min)
Maximum torque M_s , Nm	180 (2000...2500 rev/min)
Idling torque, Nm	780...860

These differences clearly show that fuel in Eastern and Western Europe is of different origin. The carbon isotope fractionation between fuel and emitted aerosol

particles or CO_2 in exhaust is denoted as $\Delta^{13}\text{C}_{(\text{aerosol} - \text{fuel})}$ and $\Delta^{13}\text{C}_{(\text{CO}_2 - \text{fuel})}$, respectively. It is determined that aerosol particles, produced in the internal combustion engine, were enriched with ^{13}C compared with the used fuel. For diesel fuel this enrichment was $\Delta^{13}\text{C}_{(\text{aerosol} - \text{fuel})} = 2.1 - 2.9 \text{ ‰}$.

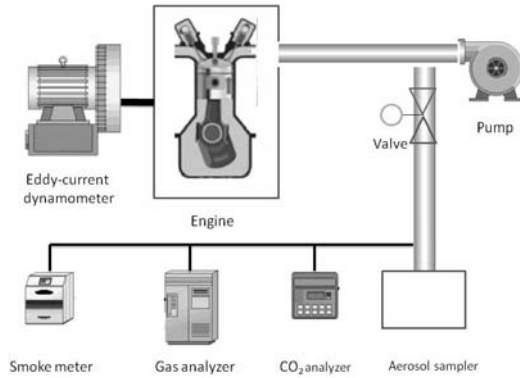


Figure 6. Schematic diagram of the experimental set-up.

It shows that fractionation between diesel fuel and aerosol particles does not depend on the engine type, but rather on the engine state (older cars fractionated to a lesser extent). For the gasoline cars fractionation was more prominent and the most important factor which defined the extent of fractionation was presence of a catalytic converter. For gasoline cars $\Delta^{13}\text{C}_{(\text{aerosol} - \text{fuel})}$ was determined to be 2.25 ‰ without a catalytic converter and 6.4 ‰ with a catalytic converter. A catalytic converter besides converting CO to CO₂ oxidizes unburned hydrocarbons. During oxidation due to the weak bond strength between $^{12}\text{C}-^{12}\text{C}$ compared to $^{13}\text{C}-^{12}\text{C}$ it is easier to form $^{12}\text{CO}_2$ than $^{13}\text{CO}_2$. The rest particles become enriched with ^{13}C . Larger fractionation between fuel and aerosol particles indicates the burning quality of the engine and efficiency of cleaning exhaust system. Fuel type E85 (85 % of ethanol and 15% of gasoline) is not common in Lithuania. Using this fuel aerosol particles undergo a smaller isotopic fractionation compared to the gasoline despite the fact that a catalytic converter was present in the car.

Table 4. $\delta^{13}\text{C}$ of diesel and gasoline.

Sample location and measurement year	Measured $\delta^{13}\text{C}$, ‰
<i>Diesel</i>	
Basel, Switzerland, 7% bio, 2009	-26.93±0.08
Ferney-Voltaire, France, 2009	-25.8±0.3
Battenheim Total Excell, France, 2009	-27.2±0.2
Moilbron, Germany, 7% bio, 2009	-27±0.30
Kiev, Ukraine, 2008	-31.1±0.4
Praha, Czech Republic, 2009	-31.1±0.1
Lithuania, diesel for farmers, 2009	-31.56±0.08
China, 2009	-27.17±0.04
Lithuania, 2010	-31.55±0.14
Byelorussia, 2010	-30.90±0.03
Lithuania, 2009	-31.4±0.5
Lithuania, 2007	-30.5±1.10
Lithuania, 2009	-31.1±0.4
Paris, France [8]	-27.9±0.5
<i>Gasoline</i>	
<i>Lithuania, E85, 2010</i>	-28.6±0.7
Lithuania, 2010	-30.1±0.3
Japan, 2010	-26.6±0.10

Further the investigation of partitioning between fuel and exhaust CO_2 is presented. The results have shown that exhaust CO_2 gas, produced during combustion of fuel, is depleted in ^{13}C , compared to the fuel used. $\delta^{13}\text{C}_{\text{CO}_2}$ ranged from -30.9 ‰ (gasoline and E85) to -32.9 ‰ (diesel car). $\Delta^{13}\text{C}_{(\text{CO}_2 - \text{fuel})}$ had random distribution for different fuels and varied from -0.7 ‰ to -2.3 ‰. The fractionation extent for CO_2 was similar for diesel and gasoline but differed as much as twice for E85 fuel. Diagram, representing partitioning between fuels, aerosol particles and exhaust CO_2 , is presented in Figure 7.

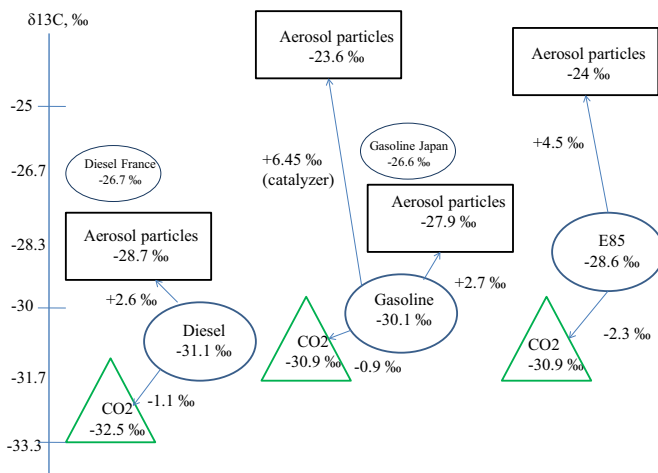


Figure 7. Stable carbon isotopic fractionation between fuel, aerosol particles and CO₂ gas in the internal combustion engines.

In the next paragraph of **subchapter 3.3**, the influence of ethanol on aerosol particle formation processes in the exhaust gas during combustion of diesel and ethanol mixture is investigated. For the investigation of combustion products, diesel and diesel fuel with ethanol were used, and their carbon isotopic ratios are described in Table 5.

Three types of fuel were used during the experiment: diesel and diesel mixed with 10 % and 40 % of ethanol (by mass). Two values of the load (49 Nm and 98 Nm) and the engine revolutions per minute (RPM) (1820 rev/min and 2010 rev/min) were used. Fractionation between the diesel fuel and emitted aerosol particles was 1.6 ‰ (1820 rev/min) and 2.1 ‰ (2020 rev/min) when the load was 49Nm, and 2.9 ‰ (1820 rev/min) and 3.2 ‰ (2020 rev/min) when the load was 98 Nm. Larger fractionation between the diesel fuel and emitted aerosol particles shows that combustion is more efficient at the higher engine load and RPM.

Table 5. $\delta^{13}\text{C}$ of diesel fuel and amount of ethanol used in the experiment.

Fuel	$\delta^{13}\text{C}$, ‰
Diesel	-30.65 ± 0.05
90 % of diesel and of 10 % ethanol	-30.3 ± 0.5
60 % of diesel and of 40 % ethanol	-29.1 ± 0.5
Ethanol	-25.2 ± 0.9

It is shown that diesel and diesel with 10% of ethanol have similar $\delta^{13}\text{C}$ values. But in exhaust particles the carbon isotopic ratio varies depending not only on the engine working conditions but on the fuel composition as well. The isotopic ratio difference between aerosol particles and diesel with 10% of ethanol was 2.7 ‰ (1820 rev/min) and 3.2 ‰ (2020 rev/min) at 49 Nm load and it was of smaller magnitude at 98 Nm load.

In **subchapter 3.4** a potential in organic matter apportionment between three principal sources: marine, terrestrial (non-fossil) and fossil fuel due to unique isotopic signatures is demonstrated. It is known that biogenic carbon is important during cloud formation processes and has direct link with the plankton, cloud formation and climate change. Clear marine environment can be affected by the anthropogenic pollution due to long-range transport from the continent. In subchapter investigation of submicron marine aerosol origin by the marker method is presented. Stable carbon and radiocarbon isotopic ratios and concentrations are used for the identification of the aerosol particles and the air mass origin.

Submicron ($D_p < 1.5 \mu\text{m}$) marine aerosol samples were collected over the NE Atlantic at *Mace Head* from January to November 2006 and on the *RV Celtic Explorer* during June–July 2006.

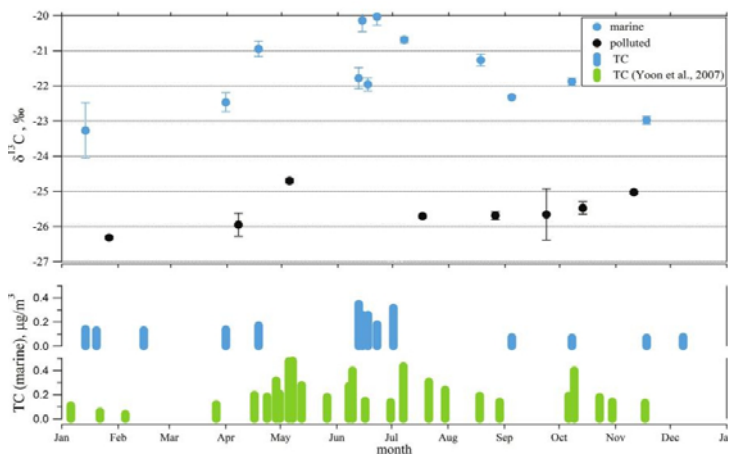


Figure 8. Seasonal pattern of $\delta^{13}\text{C}$ in clean marine and polluted samples during 2006 at Mace Head (top panel). The clean marine total carbon concentration (TC) for the 2006 data (middle panel) and for 2002–2005 are also shown [9] (bottom panel).

The samples were treated for carbon isotope analysis to quantify the biogenic marine carbon (i.e. carbon derived from marine plants), continental non-fossil fuel carbon (i.e. carbon derived from terrestrial plant emissions and/or biomass burning emissions), and fossil fuel carbon emissions. The carbon isotopic composition of the carbonaceous aerosol is assumed to be practically stable during transport from source-to-receptor sites, even if they undergo chemical transformations. Isotopic fractionation has, indeed, been demonstrated [10] which would compromise the above assumption, however, the suggested effect would mainly manifest itself via secondary aerosol formation due to preferential condensation of compounds depleted in heavy isotope. Most of the studies, however, conducted to elucidate marine organic aerosol origin [11,12] pointed to the dominant primary source of marine organic aerosol which should not be affected by isotopic fractionation and, therefore, isotopic fractionation is probably of limited importance to the source attribution.

The source quantification was performed using isotope mixing equations applied to both $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ isotope ratios as follows:

$$\delta^{13}\text{TC} = \delta^{13}\text{TC}_{\text{marine}} \times k_1 + \delta^{13}\text{TC}_{\text{cont}} \times k_2 + \delta^{13}\text{TC}_{\text{fossil}} \times (1 - k_1 - k_2) \quad (3)$$

$$\Delta^{14}\text{TC} = \Delta^{14}\text{TC}_{\text{marine}} \times k_1 + \Delta^{14}\text{TC}_{\text{cont}} \times k_2 + \Delta^{14}\text{TC}_{\text{fossil}} \times (1 - k_1 - k_2) \quad (4)$$

where k_1, k_2, k_3 are contributions of marine, continental and fossil fuel sources.

For marine, continental and fossil sources, the respective $\delta^{13}\text{C}$ ratios were -20‰, -26‰, -29‰, and 50‰, 100‰, -1000‰ for $\Delta^{14}\text{C}$ ratios.

The results of the ^{13}C isotope analysis are shown in Fig. 8. The clean marine aerosol samples revealed distinctly different $\delta^{13}\text{C}$ isotopic ratios when compared to polluted samples. Marine $\delta^{13}\text{C}$ values were in the range of -20‰ to -23.3‰, with least negative values occurring during summer months (periods of high biological activity) while polluted sample values exhibited more-negative values over a much smaller range of -24.7‰ to -26.3‰ with little seasonality seen. The less-negative values of $\delta^{13}\text{C}$, corresponding to the enrichment in ^{13}C , occur during the period of peak organic aerosol enrichment associated with peak biological activity. This enrichment results from carbon isotopic fractionation occurring during photosynthetic carbon assimilation whereby marine plants get enriched in ^{13}C relative to terrestrial plants due to limited supply of inorganic carbon in water during peak biological activity. The isotopic shift in $\delta^{13}\text{C}$ to less-negative values during summer results from plankton accelerated carbon fixation

during bloom conditions. This interpretation is supported by the corresponding $\delta^{13}\text{C}$ ratios of particulate organic carbon (-26.5 to -20.2‰) [13].

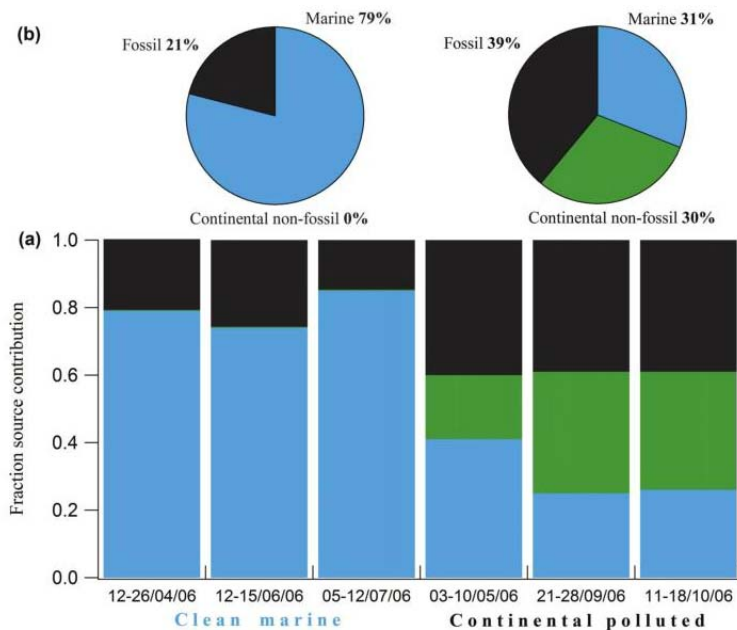


Figure 9. (a) Source contribution to organic matter in marine and polluted air samples in terms of fossil fuel carbon (black), non-fossil fuel continental carbon (dark green), and marine biogenic carbon (blue) sources; (b) same as (a) except average source values over all samples for marine and continental air masses.

In clean marine air, larger negative values during winter are most likely due to higher availability of inorganic carbon when biological activity and water temperature are lowest. Similarly, the more-negative values during summer observed in samples during a significant storm on board *RV Celtic Explorer* most likely resulted from mixing of organic material from greater depths where the competition for inorganic carbon is lower.

Distribution of $\delta^{13}\text{C}$ values suggested a lower estimate of marine sector $\delta^{13}\text{C}$ value which should be at least -20‰ or less negative to accommodate any contribution of terrestrial sources. Without $\Delta^{14}\text{C}$ it is impossible to separate the contribution of fossil

fuel sources and then continental non-fossil sources. In a similar way it is not possible to separate the marine sources using $\Delta^{14}\text{C}$ data alone. Combining both isotopes allows a separation of all three sources in a tightly constrained manner. Using Eqs. (3) and (4) and a subset of six samples where both isotope ratios were measured, the contribution of three principal sources was estimated and presented in Figure 9a. For three of the marine samples, between 74% and 85% of the total carbon was of marine origin, the remainder being fossil fuel carbon with no continental (non-fossil carbon) component evident. This marine contribution even makes up 76–87% considering only the OC fraction. On average, as shown in Figure 9b, carbon in marine samples comprised 80% of marine biogenic carbon and 20% of fossil fuel carbon while in non-marine air masses, carbon is attributed to 40% of fossil fuel, 30% of continental (non-fossil carbon) and 30% of marine biogenic carbon.

Conclusions

1. The carbon isotope ratio in anthropogenic origin aerosol particles corresponds to the isotope ratio of burnt fuel (biomass and fossil fuel), and this parameter is suitable for identification of the aerosol particle source. In the aerosol particles from the environment in the size range up to 1 μm , vegetative organic carbon is prevailing. The largest organic and elemental carbon ratio value (OA/EA=13.1) was observed in the accumulation mode, in the particle size interval from 0.18 μm to 0.32 μm . Such value is typical of background localities. $\delta^{13}\text{C}$ values of elemental carbon in the accumulation mode varied from -22,9 ‰ to -26,3 ‰, while organic carbon $\delta^{13}\text{C}$ values were about -28 ‰. From the carbon isotope ratio values it has been determined that the elemental carbon precursors in aerosol particles were from burning products, while the source of organic carbon was volatile organic compounds from vegetation.
2. In the aerosol particles larger than 1 μm the carbonate component is observed. In the range of all sizes the carbon isotope ratio of vegetative organic origin component does not change. By combining aerosol mass and isotope ratio mass spectrometry methods it has been determined that in aerosol particles of the accumulation mode (in the size interval from 0.056 to 1 μm) from 80 % to 90 % of carbon is of organic (vegetative) origin.
3. The measured $\delta^{13}\text{C}$ values in diesel fuel and diesel fuel with 10 % and 40 % of ethanol varied from -29 ‰ to -30,7 ‰. It has been determined that the isotope fractionation between fuel and aerosol particles was 1.3 ‰ and did not depend on the engine load and revolutions per minute, when diesel fuel with 40 % of ethanol was used. Such fractionation factor between this type of fuel and aerosol particles indicates that ethanol did not participate in the aerosol particle formation.
4. The method of identifying the aerosol particles from marine, biomass and continental fossil fuel burning products has been developed and experimentally realized. It has been shown that in clean air over the North Eastern Atlantic Ocean the marine biogenic submicron carbonaceous particle source dominates (80 %). In continental air masses on average there are 30 % of marine aerosol particles, 40 % from fossil fuel and 30 % from biomass burning aerosol particles.

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Santrauka

Žemės atmosfera yra svarbiausia klimato sferos dalis ir jautriausias antropogeninei taršai aplinkos sandas. Atmosferoje vykstantys procesai pakeičia ekosistemose per šimtmečius nusistovėjusius procesus – stebime įvairias globalinės klimato kaitos sukeltas pasekmes.

Mokslinė šio darbo idėja nukreipta į įvairiapusį atmosferos aerolio dalelių savybių ir prigimties tyrimą bei tyrimo metodų plėtrą, pasiremiant naujausiomis aplinkotyros mokslo žiniomis, akcentuojant pastarojo dešimtmečio masių spektrometrijos pasiekimus. Šio darbo tikslas yra organinių medžiagų ir juodosios anglies atmosferos aerolio dalelėse kilmės, aerolio sudėties ir formavimosi tyrimai bei naujų tyrimo metodų plėtra. Darbe eksperimentiškai įrodyta, kad anglies izotopų santykis antropogeninės kilmės aerolio dalelėse atitinka deginamo kuro izotopų santykį ir šis parametras tinka, identifikuojant aerolio dalelių šaltinį. Šis izotopų santykis, kaip metodinė priemonė, buvo panaudotas tiriant įvairios prigimties aerolio sudėtį, savybes ir kilmę. Tiriant aerolio daleles tolimojoje oro pernašoje stebėjome elementinės anglies $\delta^{13}\text{C}$ verčių kaitą akumuliacinėje modoje nuo $-22,9\%$ iki $-26,3\%$, organinės anglies $\delta^{13}\text{C} = -28\%$. Iš $\delta^{13}\text{C}$ verčių nustatyta, jog elementinės anglies pirmtakai aerolio dalelėse buvo degimo produktai, organinės anglies šaltinis – lakūs organiniai junginiai iš augalų. Vietinės kilmės dalelių, didesnių už $1\ \mu\text{m}$, stebėta karbonatinė komponentė. Apjungus masių ir izotopų santykių masių spektrometrijos metodus įvertinta, kad akumuliacinėje modoje aerolio dalelėse iki 90% anglies yra organinės (augalinės) kilmės.

Parodyta, kad švariame ore virš Šiaurės Rytų Atlanto vandenyno dominuoja (80%) jūrinis biogeninis submikroninis anglių dalelių šaltinis. Kontinentinėse oro masėse yra vidutiniškai 30% jūrinės kilmės, 40% iš iškastinio kuro ir 30% iš biomasės susidariusių aerolio dalelių.

Tiriant transporto indėlių į antropogeninio aerolio balansą aplinkoje, įvertinta kuro sudėties ir variklio darbo režimo įtaka aerolio formavimosi procesams. Išmatuotos $\delta^{13}\text{C}$ vertės dyzeline ir dyzeline su 10% ir 40% etanolio kito intervale nuo -29% iki $-30,7\%$. Nustatyta, kad izotopų persiskirstymas tarp kuro ir aerolio dalelių buvo $1,3\%$ ir nepriklausė nuo variklio apkrovos ar sūkių, naudojant dyzeliną su 40% etanolio. Tai reiškia, kad esant tokiai izotopų persiskirstymo vertei etanolis nedalyvavo aerolio dalelių susiformavime.

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