CHEMICAL ENGINEERING TRANSACTIONS Volume 22, 2010
Editor Eliseo Ranzi

 ISBN 978-88-95608-13-6 ISSN 1974-9791
DOI: 10.3303/CET1022018

An Estimation of Sea Aerosol Part in Seashore Town Gelendzhik's Air in the 2009 Summer

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Keywords: Atmospheric pollution, Atmospheric aerosol, Chemical composition, Aerosol sources.

The evaluation and prediction of air quality in settlements requires our awareness of the main pollutant sources and their power changing with time (anthropogenic sources) or under the influence of environmental conditions (natural sources). In seaside cities, aerosol of sea origin is one of significant sources of air pollutants. Complex estimation of different atmospheric boundary layer pollutants in Gelendzhik was carried out in the first decade of July 2009. The conducted investigations showed that in the period of observations the portion of sea aerosol made up from 4 to 25% of the total aerosol. These data correlates well with similar data for the Mediterranean. It was found that pollutant concentrations in aerosol were considerably lower than the corresponding average daily maximum permissible concentrations values.

1. Introduction

The evaluation and prediction of air quality in settlements requires our awareness of the main pollutant sources and their power changing with time (anthropogenic sources) or under the influence of environmental conditions (natural sources). In seaside cities, aerosol of sea origin is one of significant sources of air pollutants (Almeida et al., 2005; Takahashi et al., 2008; Wu et al., 2003). Besides salts normally present in sea water, it can contain different dissolved chemical pollutants and microorganisms, which can get into the atmosphere as part of the sea spray aerosol. Therefore, first of all, it's necessary to determine the portion of particles of sea origin in the total aerosol. And, secondly, it's necessary to reveal what pollutants could be considered to originate from sea sources.
Complex estimation of different atmospheric boundary layer pollutants in Gelendzhik was carried out for fulfilling these tasks using three on-ground sampling sites, one on-board site in Gelendzhik bay, and aircraft based laboratory (Arshinov et al., 2009) at altitude 500 – 2200 m in the first decade of July 2009. Gelendzhik is situated on Russian Black Sea shore and have population about 100,000 and up to 2 millions guests

Please cite this article as: Safatov A.S., Arshinov M., Baklanov A.M., Buryak G.A., Generalov V.M., Kiselev S.A., Kozlov A.S., Malyshkin S.B., Olkin S.E., Reznikova I.K., Sergeev A.N., Belan B. and Simonenkov D., (2010), An estimation of sea aerosol part in seashore town gelendzhik's air in the 2009 summer, Chemical Engineering Transactions, 22, 113-118
DOI: 10.3303/CET1022018

during summertime. The town have no industry so main local aerosol sources are auto and sea transportations, cooking, soil, road dust, vegetation and sea water.

2. Materials And Methods

During the period of observation meteorological characteristics of atmosphere were recorded and concentrations of main gaseous atmospheric pollutants (O_3, CO, CO_2, SO_2 and NO_x) were measured using Vantage Pro2 Plus complex (Italy) and special gas analysers described in Sergeev et al., (2009).

Aerosol number and mass concentrations and size distribution in range 3 nm – 100 μm were determined using Diffusion Aerosol Spectrometer (DSA, Russia) and optical aerosol counter Grimm 1.109 (Germany). Atmospheric aerosol was sampled using fibrous AFA-HA-20 filters and 5-stages Anderson type impactor.

The concentrations of following pollutants in aerosol deposited onto fibrous filters were determined:

- elemental composition (*Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sr, Ti, Zn*) by atom absorption method C-115-M and Perkin Elmer 3110, USA;
- ions SO_4^{2-} - by ionic chromatography method using ionic chromatography device "Tsvet-3006", Russia;
- polycyclic aromatic hydrocarbons (PAH) – by high performance liquid chromatography method using Spectra-Physics SP8800-Spectra100, USA: naphthalene, acenaphtylene, fluorene, acenaphthene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, benzo(b)fluoranthene, pyrilene, benz(a)pyrene, 1,2,5,6-dibenzanthracene, benz(ghi)pyrilene;
- nonpolar hydrocarbons – by FT-IR spectroscopy method using Varian FTS 1000, USA;
- total protein – by fluorescent spectroscopy method with specific dye (You et al 1997) using spectroflourimeter Shimadzu RF-520.

Aerosol particles deposited in different impactor stages were investigated using SEM (LEO1430VP) with energy spectrometer "OXFORD" which allow to obtain information on particle elemental composition from back scattered electrons. This method allows us to detect only relatively large amounts of substance, and therefore, it cannot be used to study particles with a diameter of not less than approximately 100 nm, adsorption layers of organic and bioorganic compounds on the surface of larger particles. However, this method provides unique information on individual particles present in atmospheric aerosol.

Sea aerosol concentrations were estimated on the basis of *Na* and some other elements concentrations which exist in sea water (Bardouki et al., 2003; Koulouri et al., 2008). Biogenic aerosol concentrations were estimated on the basis of total protein concentrations (Safatov et al., 2006). Auto and sea transportations' discharges were estimated on the basis of PAH and some other elements concentrations (Smichowski et al., 2008). Aluminum and silicon oxides and some other "soil elements" are character for soil aerosols (Moreno et al., 2009).

3. Results And Discussion

The conducted investigations involved the estimation of daily average mass concentrations of aerosol in different fractions and the total aerosol mass in the near-ground atmospheric layer. Values of daily averaged PM_{10}, $PM_{2.5}$, and PM_1 were

calculated using data of particle counter Grimm 1.109 and particles density 2 g/cm^3 (particles density was estimated by comparison of particle counter and impactor data). As shown by Peters et al., (2006), the data obtained with this counter provide a good estimate of the mass particle size distribution at known density of particles.
Data on aerosol mass concentrations as well as total protein and sea aerosol concentrations are presented in the Table 1. It should be noted that the total mass of particles in that period practically coincided with PM_{10} value, the total PM values being not large.

Table 1 Data on daily averaged aerosol concentrations and concentrations of some aerosol components

Date of measurement	PM_{10}, μg/m^3	$PM_{2.5}$, μg/m^3	PM_1, μg/m^3	Sea aerosol, μg/m^3	Total protein, μg/m^3
02 July, 2009	25.82 ± 4.38	14.15 ± 2.31	5.16 ± 0.78	1.11 ± 0.44	0.64 ± 0.35
03 July, 2009	17.57 ± 3.93	9.12 ± 2.48	4.38 ± 1.19	1.72 ± 0.96	0.95 ± 0.32
04 July, 2009	16.57 ± 3.68	9.88 ± 1.35	5.53 ± 0.66	0.89 ± 0.84	0.94 ± 0.08
05 July, 2009	14.87 ± 3.09	9.47 ± 1.96	5.09 ± 1.31	4.04 ± 1.60	1.52 ± 0.40
06 July, 2009	16.37 ± 4.76	9.73 ± 2.19	5.32 ± 1.31	1.29 ± 0.49	1.44 ± 0.53

Data on atmospheric aerosol chemical composition and it mass concentrations show that atmospheric aerosol mass contained from 4 to 25% of sea aerosol and from 2.5 to 10% of biogenic aerosol during the period of observation (Table 1). Concentrations of different PAH, some chemical elements, and nonpolar hydrocarbons in aerosol samples did not exceed threshold values of its determination of the methods used (that's why these data were not included in Table 2). Consequently, the input of different transportation into aerosol pollution of the region is low during the period of observation. Pollutant concentrations in all near-ground aerosol samples did not reach 1% of the corresponding values of average daily maximum permissible concentrations (MPC). Increased *Ca*, *Ni* concentrations and one of *Na* were found in altitude samples collected as the airplane was flying along the coastal line at the altitudes of 1000 – 2000 m in the vicinities of the city of Gelendzhik on July 6. This could be accounted for by the discharge of cement works of the city of Novorossiysk, which, as follows from the examination of reverse paths of air masses motion, could reach the region under study in the period of carrying out aircraft probing of the atmosphere. The maximum total mass of aerosol particles determined as the total amount of controlled chemical elements and ions at that moment exceeded 37 μg/m^3 whereas in near-ground samples it always was less than 15 μg/m^3.
Photo 1 presents a typical photo of particles deposited in the impactor and the chemical composition of their regions. The analysis of particles found in different stages of the impactor demonstrated that the percentage of particles of sea origin, which simultaneously contain considerable amounts of *Na, Cl, Mn, Mg, S* and *O* (such as particle 1 in Photo 1), was only 3 – 10% among aerosols with particle size of > 0.1 μm. Particle 2 in this photo is most probably a bioaerosol particle as carbon and oxygen prevail in it, and particle 3 is of a soil origin as it simultaneously contains large amounts of *O, Si* and *Al* (we should also note a considerable amount of carbon present in this particle, which is probably due to soot making part of it or the adsorption layer of organic compounds on its surface). Microscopic examinations detected 60 – 80% of such particles. Particles with high *Pb* concentration could probably originate from different vehicles using lead-containing fuel and road dust.

Table 2 Average daily concentrations of chemical elements, SO_4^{2-} ion and total protein ($\mu g/m^3$) in surface samples of atmospheric air in the city of Gelendzhik in July 2009

Chemical Compounds	Sampling Date 02	03	04	05	06
Al	0.120	0.073	0.056	0.070	0.070
Ba	0.008	0.005	0.004	0.005	0.010
Ca	5.442	3.484	3.069	3.081	3.388
Co	0.003	0.003	0.012	0.012	0.013
Cu	0.114	0.057	0.026	0.101	0.151
Fe	0.124	0.008	0.069	0.025	0.008
K	0.235	0.152	0.167	0.201	0.182
Li	0.004	0.003	0.003	0.003	0.003
Mg	0.461	0.280	0.193	0.171	0.037
Mn	0.021	0.012	0.012	0.008	0.005
Mo	0.020	0.020	0.020	0.026	0.025
Na	0.435	0.677	0.353	1.360	0.599
P	0.137	0.040	0.076	0.057	0.053
Pb	0.045	0.144	0.079	0.073	0.118
SO_4^{2-}	3.775	4.000	3.127	3.981	2.777
Si	0.191	0.066	0.024	0.037	0.022
Sr	0.048	0.029	0.018	0.017	0.012
Ti	0.005	0.005	0.005	0.005	0.005
Zn	0.068	0.043	0.079	0.026	0.017
Total protein	0.64	0.95	0.94	1.52	1.44
Σ	11,894	10,049	8,332	9,257	7,495

Unfortunately, the accuracy of microscopic analysis is rather low because very great labor expenditures are required to obtain information on chemical composition of large amounts of individual particles. It is also difficult to determine the amount of particles of a complex shape as many particles have non-uniform chemical composition, etc. These are other reasons why it is extremely difficult to obtain similar information for different size fractions of particles.

Concentrations of the main gaseous atmospheric pollutants (O_3, CO, CO_2, SO_2 and NO_x) in that period proved to be considerably lower than the corresponding MPC values.

4. Conclusion

The conducted investigations showed that in the period of observations the portion of sea aerosol made up from 4 to 25% of the total aerosol, which correlates with similar data for the Mediterranean. It was found that pollutant concentrations in aerosol were considerably lower than the corresponding MPC values. As concentrations of the main gaseous atmospheric pollutants (O_3, CO, CO_2, SO_2 and NO_x) in that period were also considerably lower than the corresponding MPC values, it can be concluded that Gelendzhik was an ecologically clean city during the investigations.

5. Acknowledgments

This work was partially supported by Rosnauka (Contracts # 02.515.11.5087 and # 02.518.11.7153); Grant of Russian Academy of Sciences Presidium #16; Grant of

Russian Academy of Sciences, Department of Geosciences # 5; Grant of Rusian Foundation for Fundamental Researches # 08-05-92499.

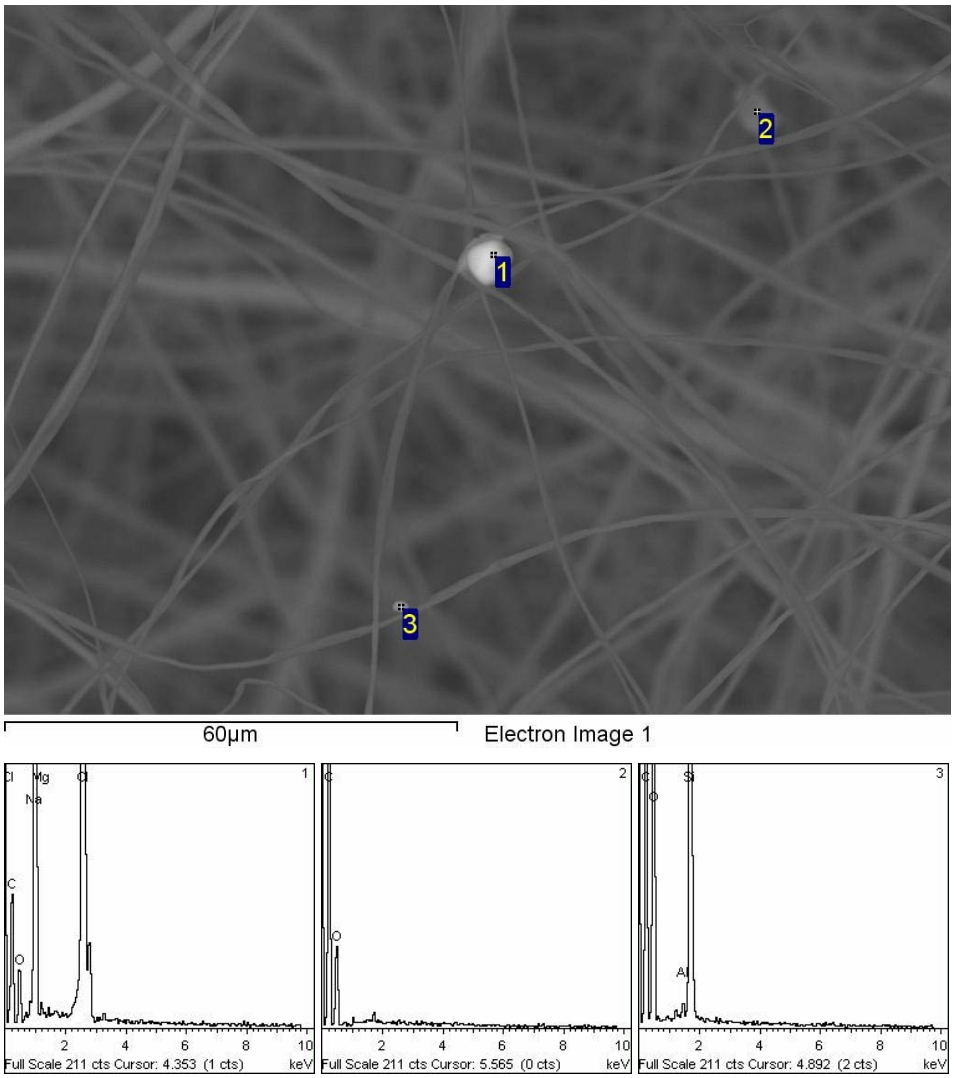

Photo 1. Aerosol particles deposited on one of the impactor stages and their chemical composition.

References

Almeida S.M., Pio C.A., Freitas M.C., Reis M.A. and Trancoso M.A., 2005, Source apportionment of fine coarse particulate matter in a sub-urban area at the Western European Coast. Atmos. Environ. 39, 3127.

Arshinov M.Yu., Belan B.D., Davydov D.K., Ivlev G.A., Kozlov V.S., Panchenko M.V., Penner I.E., Pestunov D.A., Safatov A.S., Simonenkov D.V., Tolmachev G.N., Fofonov A.V., Shamanaev V.S. and Shmargunov V.P., 2009, Aircraft

laboratory Antonov-30 “Optic-E”: 20-year investigations of the environment. Atmos. Ocean. Optics. 22, 950. (In Russian)

Bardouki H., Liakakoku H., Economou C., Sciare J., Smolik J., Ždimal V., Eleftherriadis K., Lazaridis M., Dye C. and Mihalopoulos N., 2003, Chemical composition of size-resolved atmospheric aerosols in the eastern Mediterranean during summer and winter. Atmos. Environ. 37, 195.

Koulouri E., Saarikoski S., Theodosi C., Markaki Z., Gerasopoulos E., Kouvarakis G., Makela T., Hillamo R. and Mihalopoulos N., 2008, Chemical composition and sources of fine and coarse aerosol particles in the Eastern Mediterranean. Atmos. Environ. 42, 6542.

Moreno T., Querol X., Alastuey A. and Gibbons, W. 2009, Identification of chemical tracers in the characterisation and source apportionment of inhalable inorganic airborne particles: an overview. Biomarkers. 14 (Suppl. 1), 17.

Peters T.M., Ott D. and O’Shaughnessy P.T., 2006, Comparaison of the Grimm 1.0108 and 1.0109 portable aerosol spectometer to the TSI 3321 aerodynamic particle sizer for dry particles. Ann Occup. Hyg. 50, 843.

Safatov A.S., Andreeva I.S., Buryak G.A., Marchenko V.V., Marchenko Yu.V., Olkin S.E., Reznikova I. K., Repin V.E., Sergeev A.N., Penenko V.V., Tsvetova E.A., Arshinov M.Yu., Belan B.D., Panchenko M.V., Tolmachev G.N., Baklanov A.M., Koutsenogii K.P., Makarov V.I. and Popova S.A., 2006, The results of 7-year monitoring of the biogenic components of atmospheric aerosol in Southwestern Siberia. Chem. Eng. Trans. 10, 401.

Sergeev A.N., Safatov A.S., Agafonov A.P., Andreeva I.S., Arshinov M.Yu., Belan B.D., Buryak G.A., Generalov V.M., Zakharova Yu.R., Lapteva N.A., Ol’kin S.E., Panchenko M.V., Parfenova V.V., Reznikova I.K., Simonenkov D.V., Teplyakova T.V. and Ternovoii V.A., 2009, Comparison of the presence of chemical and biomarkers in the surface microlayer in water areas of health resort zones of Lake Baikal and in atmospheric aerosol of this region. Atmos. Ocean. Opt. 22, 467.

Smichowski P., Gomez D., Frazzoli C. and Caroli S., 2008, Traffic-related elements in airborne particulate matter. Appl. Spectr. Rev. 43, 23.

Takahashi K., Minoura H. and Sakamoto K., 2008, Chemical composition of atmospheric aerosols in the general environment and around a trunk road in the Tokyo metropolitan area. Atmos. Environ. 42, 113.

Wu Y., Hao J., Fu L., Hu J., Wang Z. and Tang U., 2003, Chemical characteristics of airborne particulate matter near major roads and at background locations in Macao, China. Sci. Total. Environ. 317, 159.

You W.W., Haugland R.P., Ryan D.K. and Haugland R.P., 1997, 3-(4-Carboxybenzoyl)quinoline-2-carboxaldehyde, a reagent with broad dynamic range for the assay of proteins and lipoproteins in solution Annal. Biochem. 244, 277.