Atmosphere Aerosol, Phytoplankton and its Influence on Climate Forming in the Pacific Ocean

Atmosphere Aerosol, Phytoplankton and its Influence on Climate Forming in the Pacific Ocean: Measurement New Methods

Edited by

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EDITOR'S NOTE

Dear colleagues!

We are glad to present you with **Atmosphere Aerosol, Phytoplankton and Its influence on climate forming in the Pacific Ocean: New Measurement Methods**. It is a collection of new articles by young academics, students and PhD students, who participated in the First International Sailing University Conference on Climate Forcing, held on the board of the sailing training ship Nadezhda in the Sea of Japan and the Sea of Okhotsk at the end of summer 2010.

This collection was written by young researchers with encouragement and great support from their scientific advisors, and it presents a vivid overview of current problems in the research fields of atmosphere aerosol, phytoplankton communities, volcano activities and hydroacoustics, moreover it examines the influence of climate changes on phytoplankton communities.

This research work and the entire expedition would not have taken place without support from the Ministry of Education and Science of the Russian Federation and its contributions and grants to the young academics and scientific groups (State contracts: P163, 02.740.11.0439, 14.740.11.0139).

The idea and the entire concept of the Sailing University in the Far East of Russia as a unique combination of exciting on-board investigations and creative educational processes belongs to Dr. Oleg Bukin, Vice-Rector for Research of the Maritime State University. The results of his great contribution to the development of scientific programmes for young academics are present here.

Victoriya Yurchik
Director of the Department of Scientific and Educational Projects,
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PREFACE

This volume contains all papers presented on the board of the sailing ship Nadezhda by PhD students and researchers who participated in the annual scientific expedition of the International Sailing University 2010, organized by the Maritime State University named after Admiral G.I. Nevelskoy.

The Sailing University of the Maritime State University is intended to combine scientific experimental research methods with education processes, and to provide an international forum for young researchers and academic advisors.

Preliminary results were obtained in the Sea of Japan, the Sea of Okhotsk and in the Pacific Ocean within the period from August 3 till September 3, 2010. This collection presents a comprehensive coverage of the critical issues related to global climate changes, which were very noticeable in the seawater of the North-Eastern outlying areas of the Pacific Ocean during our latest expedition, where the Sailing University traditionally carries out its research activities.

This collection aims to elaborate on the research methods and on hardware used and tested throughout the expedition. Climate forcing and its influence on formation of phytoplankton communities was part of the expedition carried out in the Sea of Japan and the Sea of Okhotsk.

Dust storms in the continental areas of China and Mongolia, volcanic eruptions, and anthropogenic impact are of considerable influence on the ocean and atmosphere systems; while continental and volcano aerosol makes an impact on mineral nutrients for phytoplankton communities in seawater. The phytoplankton communities of the Sea of Okhotsk, where one of the largest bio recourses is concentrated, participate in the formation of atmospheric radioactive components, as this can be well observed in the area of Kashevarov Bank and Krusenstern Bank. Our scientific research aims to investigate the dynamics of the phytoplankton communities' behaviour under the impact of the climate forcing components typical of this region, i.e. tropic cyclones, dust storms, volcano aerosol emissions, and ozone layer changes.

On the other hand, the research intends to inspect how phytoplankton communities influence radioactive components in the near-water layer of the atmosphere (aerosol, carbon dioxide, methane) in order to determine

the potential of this influence on photosynthetic activity of the phytoplankton cells, which in turn could possibly affect climate changes.

Students, young researchers and PhD students have prepared all the articles presented here, in cooperation with their academic advisors who also participated in the expedition and research activities. This way of training young researchers appears to be extremely effective, as all natural experiments are jointly carried out, and all lectures are devoted to the matter being under scientific investigation.

Dr. Oleg Bukin,
Vice-rector for Research, Professor
Maritime State University named after Admiral G. I. Nevelskoy;
Director of the International Sailing University

INTRODUCTION

OLEG A. BUKIN

Research results edited and collected in this book were obtained during the 10th scientific expedition of the International Sailing University on the board of the sailing ship Nadezhda in September 2010.

Since 1997, Maritime State University (Vladivostok, Russia) has been organizing scientific expeditions of the Sailing University. Mostly, research programs are focused on critical issues concerning the atmosphere and upper ocean layer monitoring, as well as the current state of phytoplankton communities. The Sailing University's goal is to research the main processes of the atmosphere and ocean that make contribution to the North-Eastern part of the Pacific Ocean climate formation; to determine how marine ecosystems react to those still ongoing climate changes; as well as to identify the role of phytoplankton communities in climate formation in the abovementioned area. Our key interests include potential use of phytoplankton communities for stabilization of sharp climate changes and investigation into their influence on the ocean carbon cycle. It is impossible to solve this problem without development of the new physical methods for atmosphere and ocean monitoring, therefore young researchers together with their academic advisors were assemble new equipment in order to apply new research methods, which are being tested in each scientific expedition. Consequently, the results of our former scientific expeditions as well as the Nadezhda's circum navigation (2003–2004) have become part of the Sailing University scientific programme. Articles written by Ekaterina Sokolova et al. and Maxim Shinkarenko present new equipment development in order to investigate the ocean upper

layer. The former work presents the development of Laser Induced Breakdown Spectroscopy (LIBS), which was implemented to investigate the elemental composition of seawater and phyto-plankton cells. The above-mentioned method has been being developed for a long period of time, but in this case nanosecond pulse duration lasers were used in order to find out the quantity of the smallest element concentrations (10^{-3} g/l) in seawater and phytoplankton cells. Authors illustrate that LIBS lasers with femtosecond pulse duration usage increase test-sensitivity by two degrees, i.e. this method is extremely effective for investigation of the photosynthetic apparatus of phytoplankton cells, especially when the influence of various elements on the development rate of the phytoplankton communities is taken into account. Maxim Shinkarenko’s work presents new equipment development in order to research phytoplankton concentration fields in the upper ocean layer: presented are testing results of the new pumpable two-frequency laser fluorimeter, which provides measurements of the seawater (phytoplankton included) fluorescence spectrums on the running vessel by excitation of two length waves of the laser radiation. This research made possible to elaborate on methodology in order to separate dissolved organic matter reproduced by fresh phytoplankton cells (young dissolved organic matter). Such methodology was created in order to appraise the effectiveness of the phytoplankton cells’ photosynthetic apparatus during the production of organic matter. Konstantin Kluger’s article presents processing methodology of the sea water fluorescence three-dimensional spectrum. The work of the PhD student Ivan Doroshenkov presents preliminary results of the fluorescence spectrums recorded throughout this expedition, aiming at studying dynamics of the research processes of degradation for the dissolved organic matter in seawater, as well as at defining the phytoplankton role in the reproduction processes of dissolved organic matter, and its significance in the carbonic cycle in the ocean.

The works of PhD students Igor Stepochkin, Vasily Kachur, and Victoriya Saklakova present the development of measurement algorithms for sea colour data. They also intend to develop methods for comparison

of satellite data and onboard measurements, and present the development results for semianalitic, empiric algorithms, and the other ones based on comparison of laser and solar induced fluorescence. The abovementioned works refer to the research of the effectiveness of satellite definition for the dissolved organic matter by the phytoplankton community. Presented is a detailed description of the data base, which collects important information and makes possible to process data on-line. Preliminary analysis of the atmosphere monitoring (satellite data, on-board photometric measurement and lidar) is presented in the article by the senior researcher Konstantin Shmirko. This analysis had been carried out within a period before Peak Sarychev eruption on the Kurile Islands, and after it (the eruption took place in June 2009, and was the biggest on the Kurile Islands for the last 300 years). The abovementioned research seeks to investigate how the volcanic eruption influenced the condition of phytoplankton communities in the Sea of Okhotsk. Another aspect of the interaction of phytoplankton communities with the atmosphere processes is presented in article by the student Alexey Bobrikov, who attempts to find out the experimental connection between atmosphere aerosol and phytoplankton concentrations in the lower underlayer of the atmosphere above the ocean. This work presents the results of the preliminary analysis, received during this expedition to the Kashevarov Bank area (the Sea of Okhotsk) and the Krusenstern Bank (the Pacific Ocean).

Andrey Storozhenko, a PhD student, describes the methods of acoustic measurements aimed at investigating the dynamics of the sonic scattering layer in the photic layer of the ocean, in order to observe and analyse the phytoplankton communities' dynamics and their reaction to various processes. The work by the PhD student Ilya Bukin, and the senior researcher Dmitry Lyakhov, analyses possible ways of using a remotely operating vehicle, equipped with the laser fluorimeter, in order to register seawater areas with high methane concentrations. Such works are to create a complex apparatus for research of the gas hydrates deposits and investigation of carbonic cycles in the ocean.

Quantitative Elemental Determination in Water by Femtosecond Laser-Induced Breakdown Spectroscopy

Sergey Golik, Alexey Ilyin
and Ekaterina Sokolova

Examination of the phytoplankton cell photosynthesis system condition and monitoring of concentration of sea water elements that limit phytoplankton cell development require an operative measurement method for determination of chemical elements concentration at the microgram-per-liter level. For this purpose, in our research we suggested and developed the method of nanosecond laser spectroscopy, that allowed for measurements of chemical elements in the liquid and phytoplankton cells at the 10^{-3} – 10^{-4} g/l level, which ensures its usability for real-time sea water and phytoplankton communities monitoring [1,2]. However, this method did not allow for the measurements of biogenous elements that limit phytoplankton cell development, and this prompted us to carry out a series of experiments aimed at determination of element concentration at the level of 10^{-6} g/l.

Research of elemental composition requires preliminary identification of spectral and molecular lines of plasma induced on the surface of sea water and distilled water. This research was carried out with an apparatus described in work [3].

Spectra of optical breakdown on the surface of water samples under normal atmospheric conditions were obtained for pulse duration – the *super-short* one, less than 50 fs, and the *subpicosecond* one of approximately 650 fs. Figure 1 shows the optical breakdown spectrum on the water surface induced with a laser pulse of 50 fs and registered without ICCD gating. This case reveals an intensive continuous spectrum resulting from a super-continuum generation, as well as Bremsstrahlung and recombination radiation. Figure 2 shows an averaging of 20 measurements of optical breakdown spectrum on the sea water surface induced with a laser pulse of 50 fs, registered with a time delay of 20 ns after laser pulse action. Laser pulsing was 10 Hz, exposure time of ICCD camera was 1 μs.

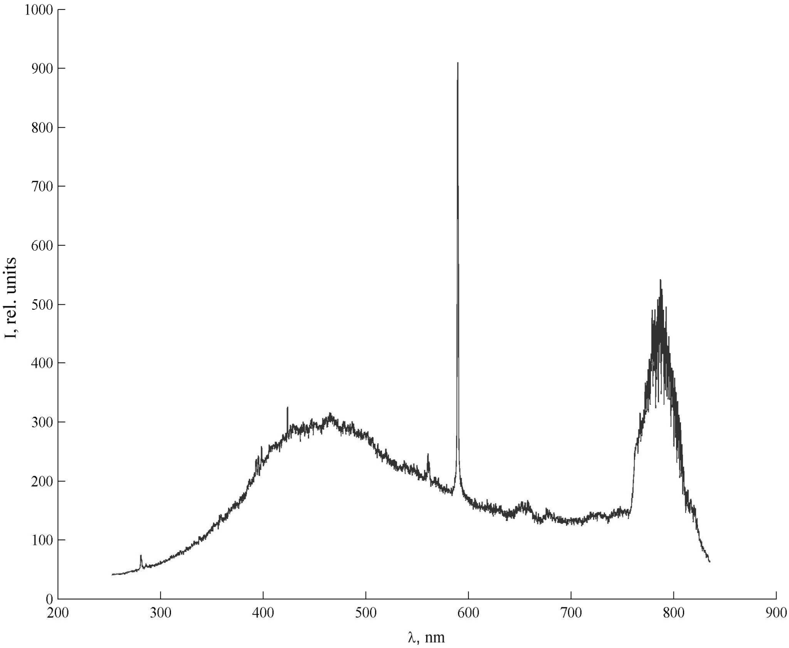

Fig. 1 – Spectrum of optical breakdowns on sea water surface with laser pulse duration of 50 fs, registered without gating.

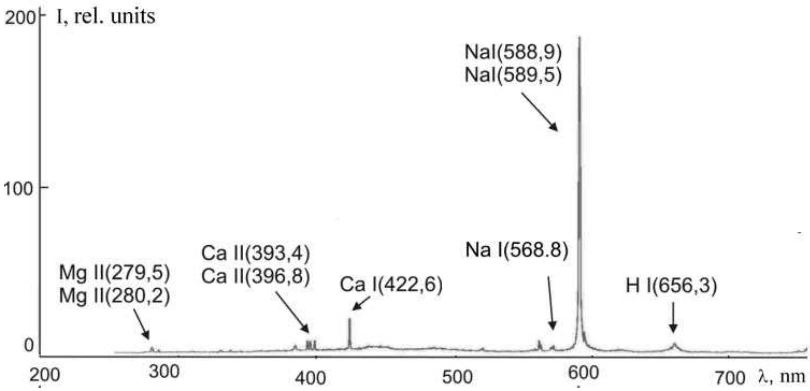

Fig. 2 – Spectrum of optical breakdown on sea water surface with laser pulse duration of 50 fs, time delay is 20 ns.

This case shows the absence of an intensive continuum. Emission lines of sea water macro-composition are registered. Let us note that all spectrums shown in this paper are not calibrated to the spectral sensitivity of recording equipment.

Optical breakdown spectra induced by pulses of 650 fs on the surface of sea and distilled water samples under normal atmospheric conditions, being an averaging of 20 laser pulses, are shown on figures 3 and 4 respectively. Within the given spectra were identified emission lines of sea water macro-composition (Ca, Mg, Na, K, H) as well as O and N lines. Figure 4 shows the distilled water spectrum induced by laser pulses of 650 fs under normal atmospheric conditions. H, N, and O lines were singled out in the distilled water spectrum. Displayed spectrums do not show lines of other elements in sea water, as their registration requires either special signal accumulation, or higher spectral resolution [3].

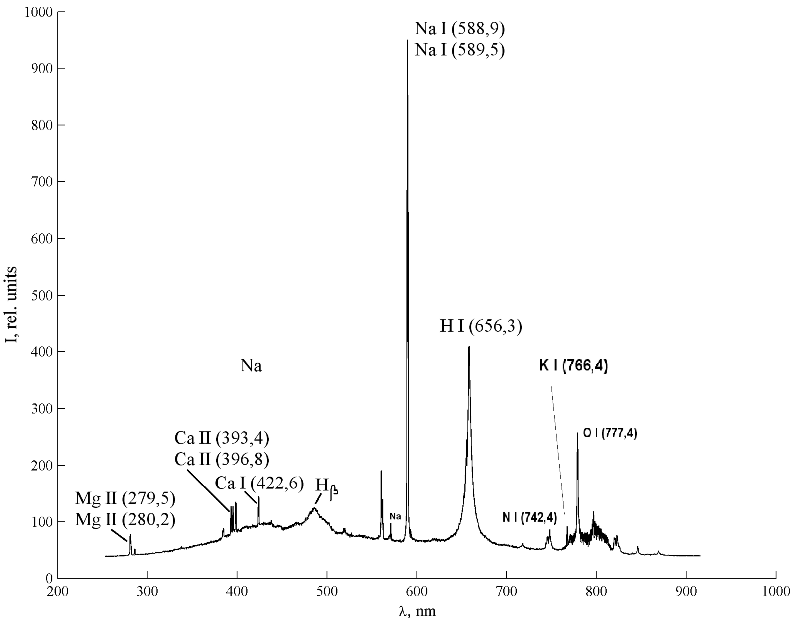

Fig. 3 – Optical breakdown spectrum on sea water surface, laser pulse duration is 650 fs, time delay is 40 ns.

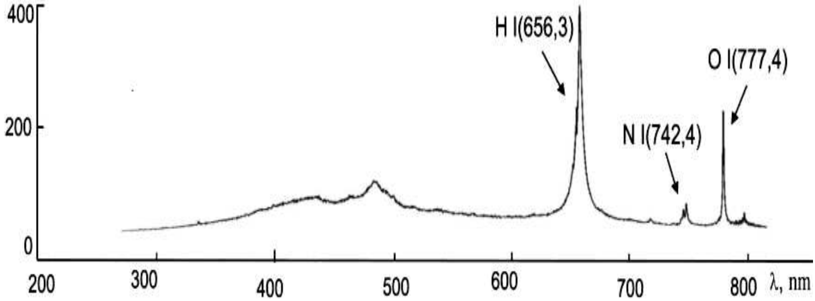

Fig. 4 – Optical breakdown spectrum on distilled water surface, laser pulse duration is 650 fs, time delay is 40 ns.

The experimental complex presented in work [3] was used for identification of spectral lines of phytoplankton cells in the femtosecond optical breakdown. Phytoplankton samples settled down on ash-free filters, so-called “white ribbon”, with an average pore size and high filtration speed. The volume of filtered sea water was 1 litre for each sample. Figure 5 shows laser plasma spectrums generated on the surfaces of studied filters with biological objects. For comparison, this paper shows research results of the two filtered sea water samples, one of them being one year old.

The spectrum was recorded with a time delay of 45±2,5 ns in relation to laser pulse, each 100 laser pulses being accumulated. At registration of the plasma spectrum within the wavelength from 560 to 600 nm and 740-780 nm, a neutral filter with 2.0 OD (Newport) was installed in front of the spectrograph slit; a neutral filter with 1.0 OD (Newport) was used for the rest of the range.

On the basis of spectral line table, data emission lines of the following elements were identified: K, Mg, Na, Ca, Cl, Fe, C_2, CH, O, H, N. Spectrums obtained showed relation of signal intensity (emission line intensity) to continuum intensity (SBR) on the scale not less than 10:1, also due to low intensity of the continuum, unlike that of the traditional nanosecond laser-induced breakdown spectroscopy. It is necessary to note that FeI emission lines under these conditions of excitation were not registered in sample #1 settled on the filter, which is presumably due to the decomposition of phytoplankton cells in sea water and with their passing through 10-micron filter pores. Sample #2, taken directly before its examination shows a high number of lines in the line spectrum of plasma, their intensity being higher than in sample #1 and in sea water.

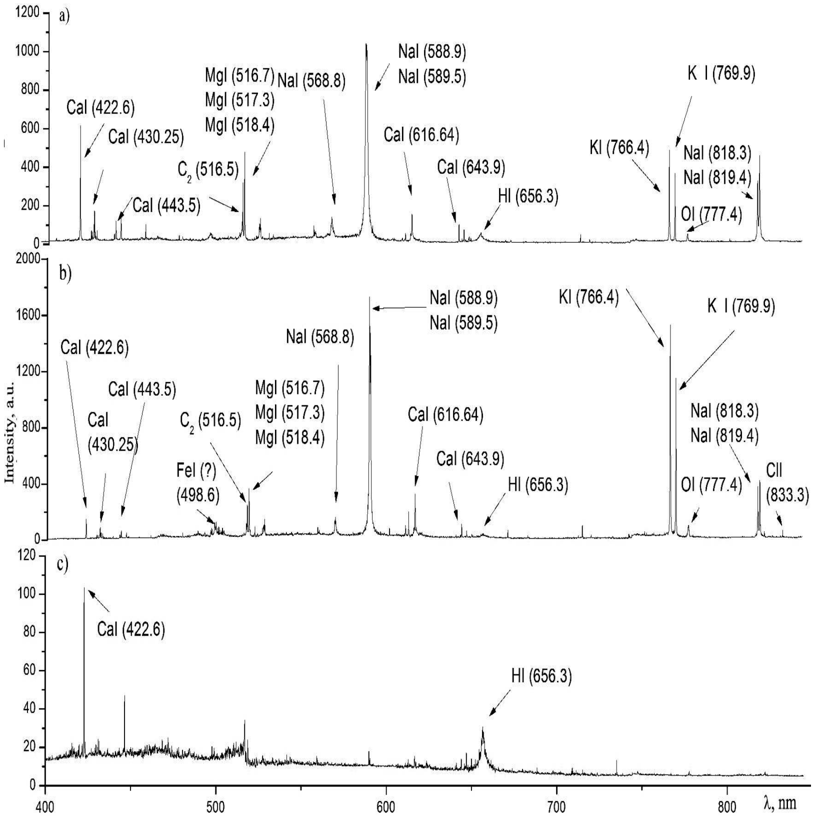

Fig. 5 - LIBS of filter samples: a) filter with sea water sample #1, b) filter with sea water sample #2, c) clean filter.

To analyze and assess minimally detectable concentrations of chemical elements in aqueous medium were used the State standard reference samples (SSRS) of water solutions of natrium ion water solutions (SSRS 7474-98) with the concentration of 0,95-1,05mg/cm^3 and calcium ion solutions (SSRS 7682-99). These elements were selected due to their high concentration in sea water and presence on LIBS spectrum of atomic and ion lines, which are clearly registered in cases of nano and femtosecond breakdown.

Dependence of Na I line intensity (588,9 nm) on concentration in the SSRS water solution helped research the limit of signal detection for Na.

Figure 6 shows averaging of 7 LIBS measurements of the SSRS Na spectrum. The spectrum was obtained with laser pulse of 100 Hz, and laser pulse duration of 650 fs. Energy pulse was 1.1 mJ, pulse duration was grope time delay of 75 ns, exposure time was 500 ns. The signal was accumulated on 800 laser pulses. Na emission line intensity on the wavelength of 588.9 nm was 40±8,5 relative units, the relative measurement error being 21% for this concentration. Thus, in defining the minimally detected concentration as a value of 3σ background signal, we obtained the Na atom detection limit: ~ 10^{-6} g/l [3].

Similarly, dependence line intensity of calcium II (393,4 nm) on concentration in the SSRS water solution helped research the limit of signal detection for calcium. The spectrum was obtained with laser pulsing of 1 kHz, pulse duration of 50 fs, energy per pulse of 1 mJ, and pulses time delay of 75 ns. Exposure time was 500 ns for each laser impulse, the signal was being accumulated during 4 seconds, and as a result 4000 laser pulses were summarized. Ca emission line intensity on the wavelength of 393,4 nm constituted (144±16) relative units, the relative measurement error for this calcium concentration in water being 11,1%. Thus, in defining the minimally detected concentration as a value of 3σ background signal, we obtain the Ca atom detection limit: ~ $2\cdot10^{-5}$ g/l.

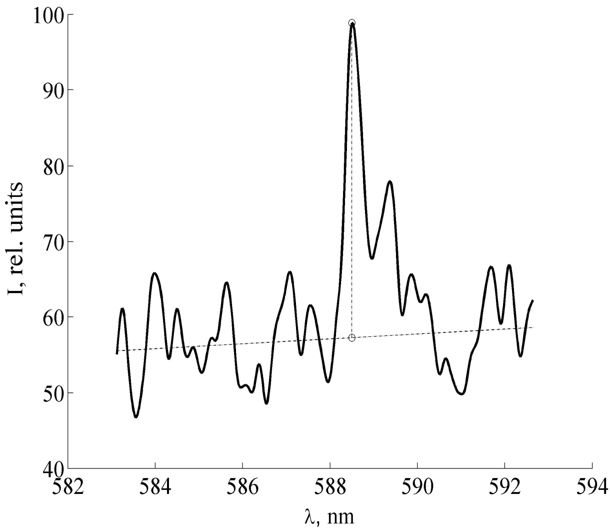

Fig. 6 - LIBS of NaCl water solution with Na concentration of $4\cdot10^{-6}$ g/l

Conducted experiments revealed that unlike in the case of nanosecond excitation, the detection limit for Ca and Na atoms with one-pulse femtosecond breakdown with the same analytical wavelength is two order magnitude weaker (see table 1). Further, the femtosecond breakdown increased sensitivity of spectrum definitions during analysis of vital biogenous elements, ferrum, for instance, the minimally detected concentration of which is far less reliable when nanosecond excitation is used.

Table 1. Comparison of minimally detected concentrations.

Element	Wave length, mn	Concentration, g/l (from work[4])	This work, g/l
Na I	588,9	$5\cdot10^{-4}$	10^{-6}
Ca II	393,4	$3\cdot10^{-4}$	$2\cdot10^{-5}$

Thus, firstly, the method of femtosecond laser-induced breakdown spectroscopy with signal time gating allows for registration of elemental composition of phytoplankton cells. Secondly, registration of microelements in samples deposited on filters is made possible. And, thirdly, this method confirms the necessity of carrying out the sea water and phytoplankton cell analysis directly after sampling.

The typical fluorescence time of femtosecond emission lines breakdown is considerably shorter compared with the nanosecond one. However, due to generation of stable femtosecond laser plasma on the surface of studied samples and the high ratio of line intensity to the continuum, the femtosecond LIBS showed high reliability and result reproducibility for concentration measurements of chemical elements in liquid.

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Observation Results of Aerosol Dynamics in Atmosphere of Sea of Japan and Sea of Okhotsk

Konstantin Shmirko

Recent times have seen close attention paid to studies of processes linked with climate changes. On a first-priority basis, this is relevant to dynamics of radioactively active atmosphere components, which include trace gases (ozone, CO_2, methane, water vapor, etc.), and atmospheric dust/volcanic/anthropogenic aerosol. An increasing number of volcanic eruptions and their increasing capacity during maximum value periods of volcanic activity cycles are thought to be the main cause of global temperature changes. This results in higher emissions of greenhouse gases and volcanogenic aerosols into atmosphere, which in turn brings about radiation balance changes.

Within a period from 2007 till present, the IACP FEB RAS lidar station has been monitoring volcanic aerosol distribution, caused by Okmok, Kasatochi and Sarychev Peak volcanoes. In all these cases, at the atmospheric tropopause level and lower, aerosol layers capable of changing the relation between flux difference of incoming and outgoing radiation at the tropopause level were observed, which results in troposphere temperature condition change. This influence directly depends on vertical distribution of scattering layers. The objective of this article is to highlight in what atmospheric changes the eruption of Sarychev Peak volcano on Matua Island resulted. We used data from shipborne lidar measurements together with spaceborne ones. In the latter case we used data from Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observation (CALIPSO) satellite provided by NASA: http://www-calipso.larc.nasa.gov/

Two scientific research expeditions were carried out in 2009 and 2010. The first voyage aboard the Senite towards the volcano took place two weeks after its eruption in July 2009. The second voyage took place a year after the first expedition, within a period from August 3 to September 2, 2010, aboard the training tall ship Nadehzda. The following atmosphere parameter measurements were continuously carried out aboard the ship throughout its entire route: aerosol optical depth, vertical distribution of backscattering and extinction coefficients, particle size distribution function as well as samplings for chemical testing.

A shopborne mobile lidar was used to obtain vertical profiles of the backscattering signal (Fig.1a). The receiving system diameter was 150 mm. Backward scattering signal registration was carried out with a 14-bit 10mhz AD converter. The transmission unit was based on the Nd:YAG Brilliant-Ultra laser (by Quantel) with pulse energy being equal to ~45 mJ. Laser impulse frequency was 15 Hz. Backscattering signal measurements were effectuated in clusters of 1000 impulses (in cases of altitudinal sounding), and of 100 impulses, when dynamics of light-scattering layers were being taken into account. The background signal measurements were taken for their further subtraction before each set of measurements.

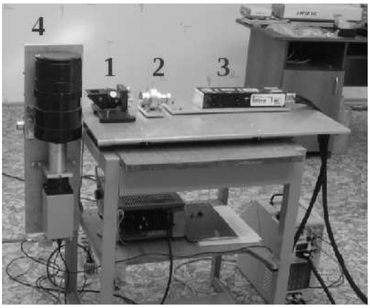


Fig.1a Shipborne mobile lidar:
1 sine V-block; 2 collimator; 3 laser head;
4 receiver.

Fig.1b Sun photometer with sun tracking system.

Passive atmosphere sounding was carried out with a portable direct sun photometer (made in Tomsk) (Fig.1b), synchronously with lidar sounding, when possible. Measurements were taken hourly when the weather was clear (the lidar profile does not support nebulosity).

Apart from optical remote sounding, we carried out contact measurements of parameters of the atmospheric surface layer, which included measurements of particle size distribution function, atmospheric aerosols and black carbon concentration. Such measurements were carried automatically on an hourly basis.

Figure 2 shows expedition routes. On the map, green dots indicate lidar measurements, while yellow circles show spectrophotometric measurements.

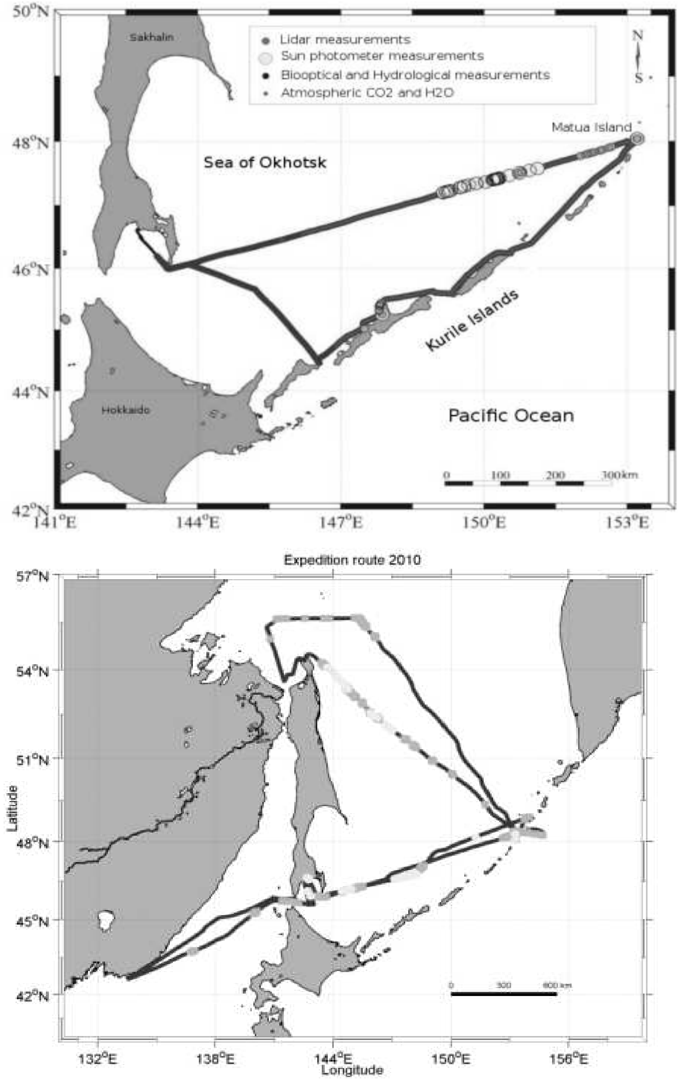


Fig.2 Routes a) 2009, b) 2010

Spatial resolution of satellite lidar data was 300 meters between profiles. However, their accumulation was necessary to obtain a high-quality signal of backward scattering. Being interested in the atmosphere condition in the vicinity of Matua Island, we were obtaining the lidar signal composite profile via averaging profiles within a circle of a 200 km radius.

Data obtained during expeditions can be conventionally divided into two types, belonging to either “pure” or “agitated” atmosphere. We define the “pure” atmosphere as a case when lidar profiles do not show strongly marked nebulosity, their integral coefficient of backward scattering being equal to, or less than 0.01 sr^{-1} m^{-1} Analogously, “agitated” atmosphere implies such situations when lidar profiles do not show strongly marked nebulosity, while its integral coefficient of backward scattering is bigger than 0.01 sr^{-1} m^{-1}. Values of backward scattering integral coefficient, which is used as a classification criterion, were obtained via statistic processing of lidar data of previous expeditions (2004, 2006, 2008).

Main (background) lidar profiles reflect the conditions typical of the Sea of Okhotsk and the Sea of Japan atmosphere:

- planetary boundary layer (PBL) lies within the range from 340m to 1000m (stable boundary layer lies within range from 170m to 340m);
- atmospheric aerosol is majorly concentrated in lower PBL levels;
- rather stable aerosol stratification is observed, its change being caused by meteorological processes.

After the eruption of Sarychev Peak volcano, a large amount of pyroclastics was emitted into the atmosphere. It reached the tropopause heights and formed a permanent aerosol layer there (Fig. 4a). Apart from considerable height from 8 to 12 km and high values of backscattering coefficient along the entire aerosol layer depth, the depolarization factor value equaled 0.2, which corresponds to non-spherical particles of dry origin (the volcanic one, in this case). This atmospheric condition was being observed throughout June-July 2009.

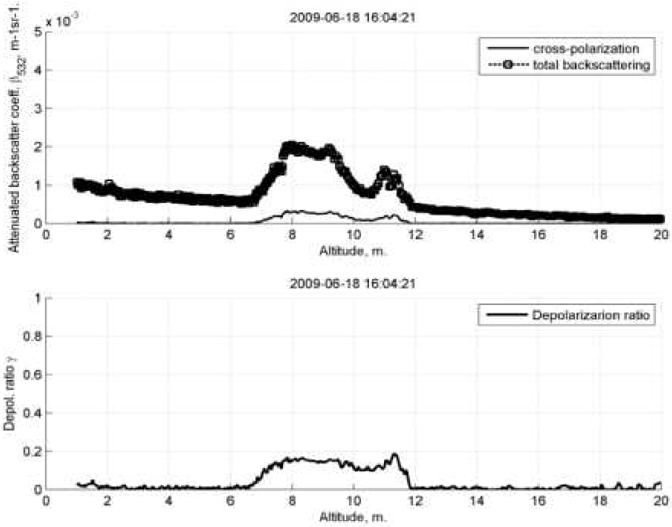


Fig.4a First successful shot produced by CALIPSO after volcanic eruption

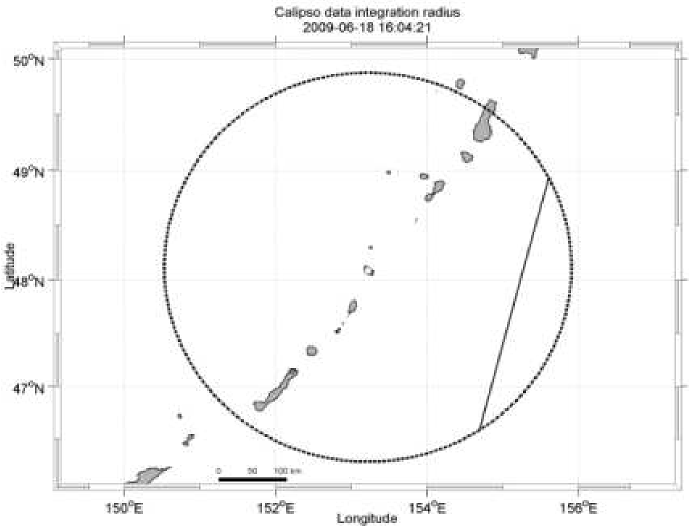


Fig. 4b Averaging area

Figure 5 shows lidar measurements taken during the expedition to the volcano in June 2009. The closer to the volcano, the more apparent the aerosol layer became at the height of 8-9.5 km, revealing the tendency of going even lower. Near the volcano itself, obtention of high-quality vertical profiles was not possible because of considerable ash emissions. A large amount of aerosol emitted into the atmosphere resulted in its stratification, and the planetary boundary level expanded its boundaries as aerosol was inflowing.

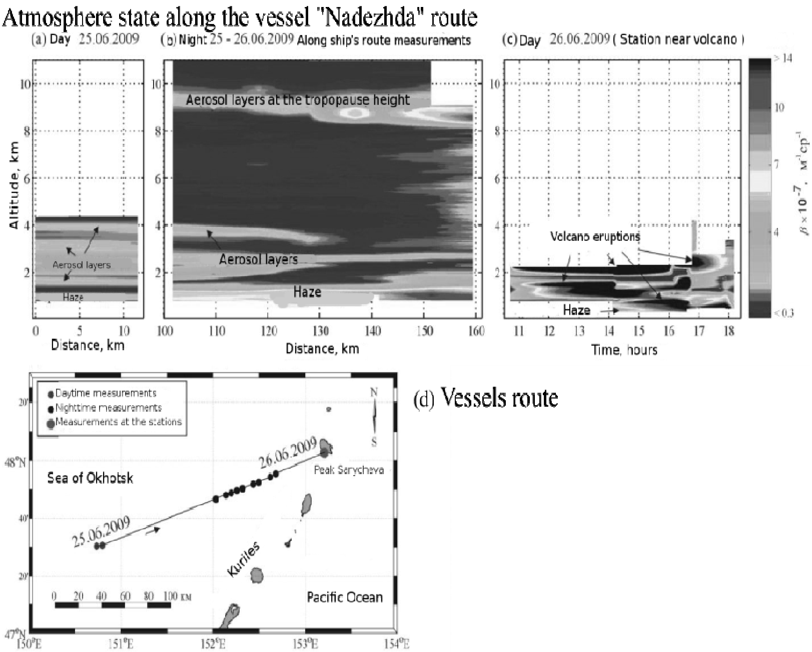
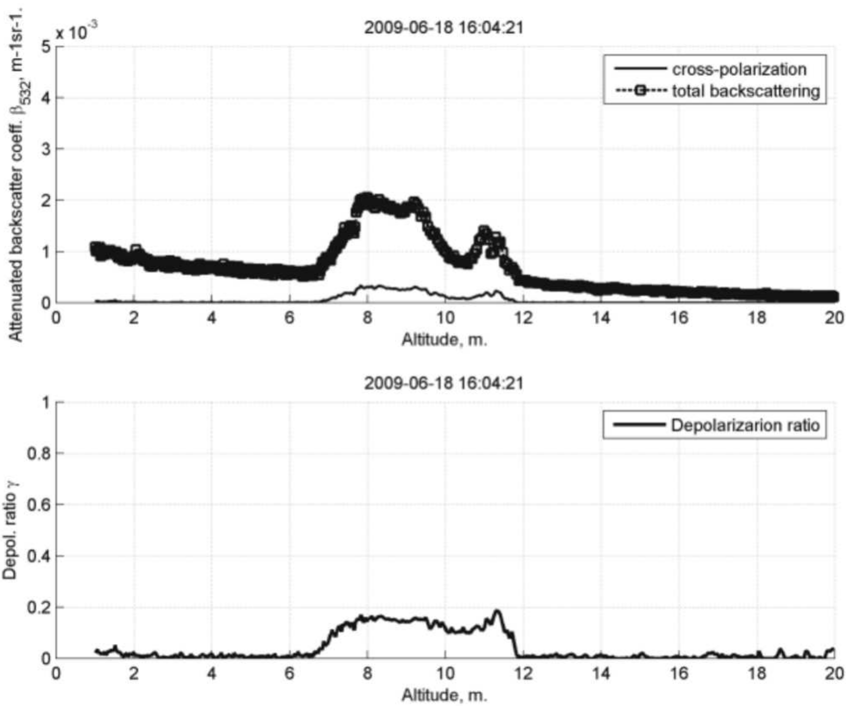


Fig. 5 Lidar experiment near Sarychev Peak volcano

The planetary boundary layer had a complex multi-layered structure. At that time we registered at least three sub-layers inside PBL of same origin – from ash and water vapor emissions. The first layer was located at 300 meters above the sealevel, the second and third had altitudes of 1500 and 2000 meters. The first 2 km were completely attenuated by atmosphere constituents, and we were unable to retrieve data from above 2 km. The planetary boundary layer at that time was located at the 2 km height. It should be noted that the marine boundary layer is located at the altitude less than 700-1100 m.

Due to the high values of aerosol concentration and optical thickness in the planetary boundary layer, there are possibilities in intensive gas exchange between atmosphere and the sea upper-top layer, as well as volcanic aerosol disposition onto the water surface.

Figure 6 shows CALIPSO satellite data we analyzed to explore the atmosphere structure at the higher altitudes.



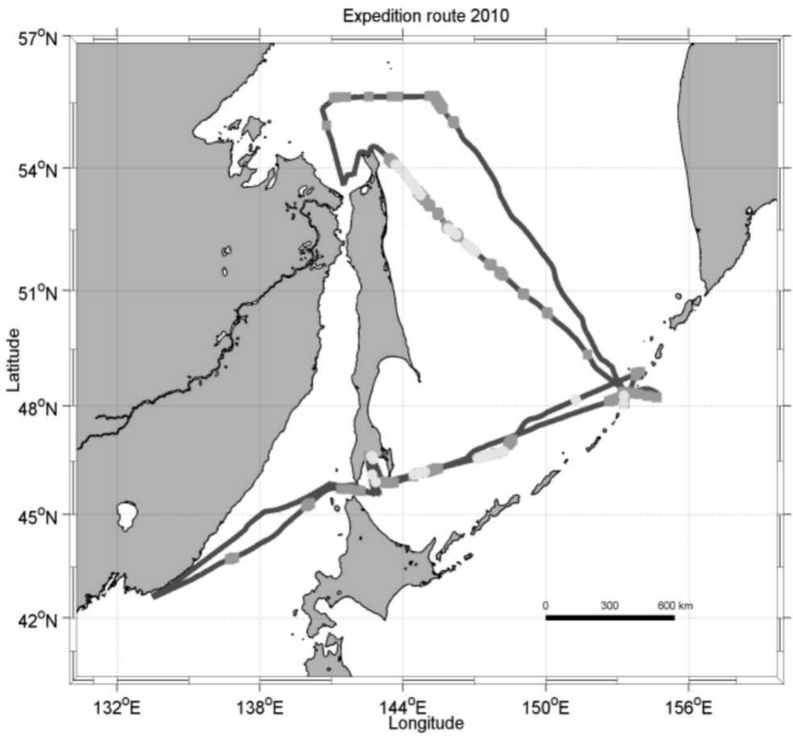


Fig.6 Vertical profile of backscattering signal (June 25, 2009) and integration range

That day CALIPSO satellite data clearly showed the aerosol layer position at the height of 8.5 km. Moreover, it was clear that the atmospheric bottom layer had been filled with aerosol up to the height of 2 km.

Expedition carried out in 2010 showed that the atmosphere in the vicinity of Matua Island had restored its intermediate qualities. Apart from the boundary layer and tropopause, aerosol traces were not present anymore. Residual aerosol could account for the layer at the tropopause height. At that time, the planetary boundary layer had no sub-layers and its altitude was 700 m.