Table 1. Brief characteristics of instruments in aerosol complex.

Instruments	Main characteristics	
	RV "Akademik Fedorov"	RV "Professor Khljustin"
SPM sun photometers	AOD and water vapor content of the atmosphere with uncertainties of 0.01-0.02 and 0.1 g/cm^2, respectively. Field of view angle is 1.5-2.5°. Passband maxima of filters are at:	
	381, 373, 405, 500, 550, 673, 775, 870, 933, 1045, 1249, 2132 nm	341, 367, 439, 501, 547, 676, 777, 871, 938, 1044, 1553, 2136 nm
Particle counters	GRIMM 1.108.	AZ-10.
	Particle number and mass concentrations in 15 size ranges from 0.3 to 20 μm: 0.3-0.4; 0.4-0.5; 0.5-0.65; 0.65-0.8; 0.8-1.0; 1.0-1.6; 1.6-2.0; 2.0-3.0; 3.0-4.0; 4.0-5.0; 5.0-7.5; 7.5-10; 10-15; 15-20 μm. Tolerance Ranges: count correlation at 1 μm ± 5%; relative mass deviation ± 5% to reference unit.	Particle number and mass concentrations in 6 diameter ranges from 0.3 to 10 μm: 0.3-0.4; 0.4-0.5; 0.5-1.0; 1.0-2.0; 2.0-5.0; 5.0-10 μm. Tolerance Ranges: ± 30%.
Aethalometers (Kozlov et al., 2008)	Mass concentration of Black Carbon in particles of submicron range. Sensitivity is 10 $ng \cdot m^{-3}$.	
The vacuum diaphragm pump HBM 1.2	Bleeding the air at a speed of 0.02 $m^3 \cdot min^{-1}$	
One frequency polarization lidar (Bukin et al., 2007; Shmirko et al., 2010)		S- and p- polarization of backscattered signal was recorded with spatial resolution of 1.5 m along laser beam. Maximal height of sounding was about 4000 m daytime and about 5000 nighttime. Temporal resolution of recorded profiles was approximately 7 seconds.
Automated meteorological complex AMK-03 (http://meteosap. ru)		Meteorological parameters: air temperature (T); relative humidity of air (RH); atmospheric pressure (P); horizontal wind speed (WS) and wind direction; vertical wind speed (w).

Table 2. Geographic positions of regions and periods of sun photometer measurements.

Area no.	Geographic characteristic	Latitude	Longitude	Time
1	Coastal station *Barentsburg* (Spitsbergen archipelago)	78°N	14°E	Aug. 21-Sep. 7
2	Northeastern margin of Kara Sea	82°N	98°E	Sep. 14
3	Coastal station *Polyarka* (Tiksi) – coast of Laptev Sea	72°N	129°E	Aug. 26-Sep. 21
4	Northeastern margin of Laptev Sea	80°N	150°E	Sep. 2
5	De Long Strait – Chukchi Sea	69°N	179°W	Aug. 13
6	Bering Sea (along coasts of Russia)	60°N	170°E	Sep. 4, Sep. 26-28
7	Near Pacific coast of Kamchatka	52°N	159°E	Jul. 31, Sep. 1-3
8	Coastal station *Vladivostok* – coast of Japan Sea	43°N	132°E	Jul. 27-Sep. 6

5 Chemical composition of the atmosphere on the route of RV *Akademik Fedorov* and *Professor Khljustin*

In addition to the measurements of the optical and microphysical characteristics of aerosol, on the route of two expeditions (Fig. 1) we collected air samples for a subsequent analysis of ion and elemental composition of aerosol, as well as the content of gaseous impurities. In the preliminary analysis of the chemical composition of samples on the route of RV *Akademik Fedorov*, we considered data for the water basin of the Barents Sea (region *B*), as well as three sub-regions in high-latitude part of the route (within the region *A*): 1) area northward of Severnaya Zemlya and Franz Josef Land archipelagos (81-84°N, 68-111°E); 2) the northwestern part of the Laptev Sea (77-80°N, 107-126°E); 3) the northeastern margins of the Laptev Sea (78-81°N, 127-155°E). In analysis below, the average characteristics of chemical composition of aerosol will be considered for the region *A* as a whole.

The chemical composition of aerosol in cruise of RV *Professor Khljustin* was determined according to samples, collected on the filters PTFE for five Far East seas: the Japan, Okhotsk, Bering, Chukchi, and East Siberian Seas. The last two seas, though adjoining the Far East of Russia, refer to Arctic seas. We will use this name in the given paper just for brevity of the general name. Taking into account the difference in meteorological conditions over Far East seas, the average characteristics of the chemical composition of aerosol were estimated separately for the forward and backward routes of the vessel and for each region as a whole.

5.1 Ion composition of aerosol

Preliminary analysis of aerosol samples, collected in high-latitude part of the route of RV *Akademik Fedorov* (region *A*) showed that most ions had higher concentrations in northwestern part of the Laptev Sea (the mean concentrations $\Sigma_{ions} = 1.71$ µg·m^{-3}). However, the existing differences in concentrations are not large and much smaller than the standard deviations. Therefore, the average characteristics of the chemical composition of aerosol were calculated for the region *A* as a whole (Table 6.).

Much larger difference in ion composition is observed for two samples, collected in water basin of the Barents Sea (region *B*): both summed content (the average $\Sigma_{ions} = 0.61$ µg·m^{-3}), and concentrations of individual ions (except K$^+$) are about two times smaller than the average concentrations over the Arctic Ocean. The data in the region *B* had insufficiently representative statistics and, as such, were excluded from further analysis.

From comparison with our previous data in other Arctic regions we can draw the following conclusions. The averaged summed ion content in the region *A* well agrees with data obtained in July-August 2011 in Barentsburg (Spitsbergen Archipelago, ~78°N) (Golobokova et al., 2013): the average $\Sigma_{ions} = 1.41$ µg·m^{-3}. In more southern seas, adjoining continent, the ion content is much larger (Polkin et al., 2011a): by about an order of magnitude (17.1 µg·m^{-3}) over the subarctic White Sea, and by almost a factor of 6 (8.9 µg·m^{-3}) over the Kara Sea. Clearly, the atmosphere of these seas is under a stronger influence of continental aerosol sources, contributing about 38% in the White Sea, 30% in central regions of the Kara Sea, and 60-80% in coastal water basins of the Kara Sea (Polkin et al., 2011a).

The average ion concentrations in aerosol composition over Far East seas vary in quite a wide range (see Table 6.). The average ion concentrations differ not only among separate seas, but also in the same regions on the forward and backward routes of RV *Professor Khljustin*. The ions Na$^+$, Mg^{2+}, K$^+$, Cl$^-$ and SO$_4^{2-}$ exhibit the strongest variations. For the first half of the cruise, the total sum of ions and contents of individual ions distinctly show a tendency of their latitudinal distribution (Fig. 12). As the ship moved from low to high latitudes, the total concentration of ions in the near-water aerosol decreased by approximately 30%. A little weaker gradient (a decrease by 13%) was observed during transit from the Okhotsk to Bering Sea.

Data, collected on backward route of the vessel, exhibited stronger spatiotemporal variations in ion content, and the regularity of their latitudinal growth was not distinctly manifested. This was primarily because, on backward route, in the aerosol composition there was a much (a factor of 2–9) larger contribution from sea-derived ions, i.e., Na$^+$, Mg^{2+} and Cl$^-$, the generation of which was caused by stronger sea surface roughness, rather than by the geographic position of the region.

Despite the strong variations and difference in the data between the forward and backward routes of

RV *Professor Khljustin*, the average (over regions) ion concentrations nonetheless exhibit a tendency of their northward decrease.

We also note that the average ion concentrations in Far East sector of the Russian Arctic (Chukchi and East Siberian Seas) are close in value to the average data in the central part (region *A*). That is, the variations and differences in ion composition over Arctic seas were mainly caused not by spatial inhomogeneities, but, rather, by weather features in the periods of measurements.

The maritime component of sodium and chloride ions predominated in aerosol composition on the route of both expeditions (*Akademik Fedorov* and *Professor Khljustin*). Their maximal percentages of the total sum of ions were 70.8% over the Arctic Ocean and 57.9% over Far East seas. This agrees with data from Chinese National Arctic Research Expedition (FCNARE, 1999 и 2003) (Sun, 2002; Xu et al., 2005), performed along the route close to that of RV *Professor Khljustin*. Percentage of sea-derived ions was 60.2% in FCNARE expeditions.

For other ions (except for Na^+ and Cl^-) the concentrations can be lined up as follows (in order of decreasing): $NH_4^+ > K^+$, $Mg^{2+} > Ca^{2+}$ in high-latitude regions of Arctic; $K^+ > Mg^{2+} > Ca^{2+} > NH_4^+$ in the Bering, Chukchi, and East Siberian Seas; and $K^+ > Ca^{2+} > Mg^{2+} > NH_4^+$ in the Japan and Okhotsk Seas. The SO_4^{2-} concentrations are larger than NO_3^- concentrations in all regions of the Northern Sea Route.

A characteristic feature of ion composition of aerosol over the Japan and Okhotsk Seas is very high concentrations of K^+, exceeding those over Arctic seas by about an order of magnitude. Possibly, this is due to the effect of active volcanoes of the Kamchatka Peninsula and Kuril Islands, which predominately release magmas of moderate-potassium type (Ponomareva et al., 2012). In contrast to our data, no elevated percentage of K^+ was observed in FCNARE expedition (Sun, 2002; Xu et al., 2005): with respect to average percentage composition, NH_4^+ and SO_4^{2-} ions (summing to 27%) were ranked next behind Na^+ and Cl^- in this case.

Still another salient feature is higher NO_3^- concentrations obtained in FCNARE: 0.94 $\mu g \ m^{-3}$ for the Japan Sea, and 0.11 $\mu g \ m^{-3}$ for the Okhotsk and Bering Seas. Sun (2002) and Xu (2005) suggest that the NO_3^- ions are indicators of anthropogenic impact, and their elevated content over the Japan Sea was also reported elsewhere (see, e.g., Sasakawa et al., 2005). The NO_3^- concentrations over the Japan Sea, measured in our expedition, were much lower than in FCNARE data, but they were also higher than over other seas. Presumably, our measurements were performed only in the northern part of the Japan Sea, less subject to anthropogenic outflows, explaining smaller NO_3^- concentrations. It should be also be remembered that, given limited number of samples collected in separate regions, chemical analysis results may substantially differ among diverse expeditions, reflecting not the specific character of the region, but rather specific features of meteorological conditions (and, primarily, air transports) in particular periods of measurements.

We used the well-known formulas to calculate the percentages of sea-salt (ss-) and non-sea-salt (nss-) sulphates (EMEP, 1996):

$$[nss\text{-}SO_4^{2-}] = [SO_4^{2-}] - 0.06028 \ [Na^+]$$
$$[ss\text{-}SO_4^{2-}] = [SO_4^{2-}] - [nss\text{-}SO_4^{2-}] \quad (6)$$

where $[SO_4^{2-}]$ is the sulphate concentration, $[Na^+]$ is the sodium concentration in aerosol; 0.06028 is the relationship of concentrations SO_4^{2-}/Na^+ for ions of seawater; the initial content of components is represented in molar concentration ($mol \cdot L^{-1}$).

The calculations showed that seawater was the main source of sulphates on the routes of two expeditions. Among the high-latitude regions, the high percentage (up to 100%) of ss-SO_4^{2-} was observed mainly over the Laptev Sea, where air came from the central part of the Arctic Ocean. The minimal percentage of ss-SO_4^{2-} in aerosol was recorded on September 13-17, 2013 northward of Severnaya Zemlya Archipelago. The percentage of non-sea-salt sulphates (nss-SO_4^{2-}) reached 74% in this region.

On the route of RV *Professor Khljustin*, the maximal percentage (100%) of ss-SO_4^{2-} in aerosol was observed over the East Siberian, Bering, and Japan Seas on backward route of vessel under the conditions of growing wind speed (15-20 m/s) and sea roughness (Beaufort numbers of 3-4). The large percentage (up to 88.7%) of non-sea-salt sulphates was recorded over the Japan Sea during an extended vessel drift in the region of Sakhalin Island.

It is well known that series of concentrations of elements in seawater and maritime aerosol coincide. According to the Dittmar law, the quantitative relationships between principal components of the main salt composition are always constant in seawater samples. We quantitatively estimated the differences in relationships of the Ca^{2+}, K^+, Mg^{2+}, Cl^-, SO_4^{2-} concentrations with respect to sodium ion in aerosol (aer) and seawater (sw):

$$K_i = [(C_i / Na^+)_{aer}] / [(C_i / Na^+)_{sw}], \tag{7}$$

where (C_i / Na^+) is the concentration of the i th element with respect to Na^+, and K is the enrichment coefficient (Tsunogai et al., 1972).

The ratios $(K^+/Na^+)_{aer}$ and $(Ca^{2+}/Na^+)_{aer}$ larger than in seawater were recorded on the route of RV *Akademik Fedorov*. Maximal enrichment of aerosol, especially by potassium (by up to a factor of 18), was observed on August 23-24, 2013 at northern margins of the Kara Sea (in the region of Severnaya Zemlya islands). Analysis of 10-day trajectories of motion of air masses showed that, in this period, they formed and came (at 3-km level) to the region of measurements from the following directions: from Western Europe across Kola Peninsula on August 23; and over water basin of the Arctic ocean along the trajectory of Svalbard – Franz Josef – New Siberian Islands – Taimyr on August 24. At lower heights, the air masses moved within the Arctic Ocean. Thus, using these data, it is difficult to identify the sources or causes for such potassium-rich substances.

The literature, available to us, provides no unambiguous data on the sources of K- and Ca-enriched substances in this region of the Arctic Ocean, located hundreds to thousands of kilometers away from continent. Fractionation of sea salts from snow and ice is known to be one of mechanisms by which aerosol particles are enriched, especially by sulphates and sodium (Domine et al., 2004; Hara et al., 2012). Ship emissions usually influence the arrival of pollutants to the Arctic atmosphere (Zhan et al., 2014); however, ships usually cruise southward of the regions considered here. Far-range transports of pollutants from northern margins of continent may also have effect. For instance, observations at coastal station Kevo, Northern Finland (from 1964 to 1978) revealed, together with nonferrous metals in mosses (indicators of atmospheric air pollution), also tenfold increase in potassium, which is the main marker of biomass burning. In addition, Na, K, and Ca arrive at this region from different Kola industrial areas (Yli-Tuomi et al., 2003). Enrichment of sphagnum mosses by components of aerotechnogenic pollution is observed in polar regions of Russia (Shevchenko et al., 2006). Supply of pollutants to the central regions of Arctic together with air masses from Northern Europe and industrial centers of Russia was repeatedly indicated in (Vinogradova et al., 2007; Vinogradova, 2014).

On the route of RV *Professor Khljustin*, maximal enrichment ($K = 13$-34) was revealed, as expected, for K^+ ions over water basins of the Japan and Okhotsk Seas. The enrichment coefficient was also high for calcium: the ratio $(Ca^{2+}/Na^+)_{aer}$ exceeded $(Ca^{2+}/Na^+)_{sw}$ by a factor of 2-15. Maximal enrichment of sulphates in aerosol was observed over the Bering Sea on August 28: $(SO_4^{2-}/Na^+)_{aer}$ exceeded $(SO_4^{2-}/Na^+)_{sw}$ by as much as the factor of 67. On that day, air masses passed across Kamchatka Peninsula before reaching the sampling point. Maximal enrichment of aerosol by sulphates is observed occasionally in the Bering Sea and, as such, is atypical for this region.

The excess of $(SO_4^{2-}/Na^+)_{aer}$ was, on the average, a factor of 5 over the Japan Sea and a factor of 2-3 over other seas. Emissions of sulfur-containing gases from magmas are one of the sources of sulphates in the region of active volcanoes (Ponomareva et al., 2012). Moreover, as compared to northern seas, the atmosphere of the Japan and Okhotsk Seas experiences stronger anthropogenic impact not only due to regional sources, but also as a consequence of trans-boundary transport of pollutants from China, Korea, and Japan (Luangjame, 2013; Toyama et al., 2013). Our studies of aerosol component, performed in the Japan and Okhotsk Seas in 2009 and 2010 (Polkin et al., 2011c), showed that dust, anthropogenic, and smoke outflows from Asian continent were responsible for up to a factor of 136 enrichment of aerosol particles in the Japan Sea by sulphates and for up to the factors of 60 and 81 enrichment by potassium and calcium.

Because of the considerable dependence of aerosol characteristics on hydrometeorological conditions, given the limited time and the number of samples taken, we could not determine the average chemical composition, characteristic for separate seas. Therefore, we will conclude this section by presenting ion concentrations averaged over three larger sea water basins, where no less than ten aerosol samples were

collected:

1) remote regions of Arctic (region A, n=14), which are less subject to the effect of continental aerosol outflows, while their own sources are weak;

2) polar and subpolar seas (the Chukchi and Bering Seas, n=15), which, although located near Asian coasts, are nonetheless characterized by low-intensity aerosol sources;

3) Far East seas at midlatitudes (the Japan and Okhotsk Seas, n=10), most subject to the effect of continental aerosol outflows.

From these results (see Fig. 12) it follows that the average concentrations of most ions and their sum increase in the above-mentioned sequence of three regions. For instance, the summed concentration of ions, as compared to the Arctic Ocean, increases by 73% over the Bering and Chukchi Seas, and by a factor of 2.5 over the Japan and Okhotsk Seas. Exceptions are the ions NH_4^+ and NO_3^-, the average concentration of which is most low over the Bering and Chukchi Seas (smaller than in remote regions of the Arctic Ocean). Another salient feature is characteristic for ions SO_4^{2-}, the concentration of which is nearly the same in southern and northern Far East seas.

5.2. Elemental composition of aerosol

First measurements of elemental composition in solid-phase aerosol, performed in 1985-1988 on the Wrangel and Severnaya Zemlya islands, made it possible to obtain information on aerosol composition and sources in the Russian sector of Arctic. Subsequent studies determined: the mineral and chemical composition of solid-phase aerosol, the aerosol particle size distribution, the transport pathways of eolian material, and the degree of pollution of the Arctic atmosphere by anthropogenic pollutants; also, these data were used to identify the groups of elements associated with terrigenous (Fe, Al, Mn), marine (Na, Cl), and anthropogenic (Co, Sb, Zn, Pb) sources (Shevchenko, 2006; Vinogradova and Ponomareva, 2007).

In oceanic waters, practically all elements are in dissolved form and play an important role in formation of the chemical composition of maritime aerosol. Analysis of elemental composition of water-soluble aerosol fraction (see Table 7 and Fig. 13) demonstrated the variety and wide (reaching 4-5 orders of magnitude) variability range of absolute concentrations of elements. The highest concentrations of most elements were characteristic for aerosol over the Sea of Japan, and the lowest concentrations for aerosol over the East Siberian Sea. The concentrations of Fe, Cd, Sb, Ti, and Mo over the Arctic Ocean (region *A*) are equal to or higher than those over Far East seas. The situation was opposite for Cu, Al, V, Ni, Pb, and Li, the concentrations of which were smaller in the region *A*.

For the average summed content of elements, a common tendency is northward decrease: Σ_{TE} ranges from 54 to 60 ng·m^{-3} over midlatitude seas and from 17 to 32 ng·m^{-3} over polar and sub-polar Far East seas, and Σ_{TE} is about 19 ng·m^{-3} in the high-latitude area of the Arctic Ocean.

With respect to content of water-soluble elements in the aerosol composition, we can single out three groups: 1) with concentrations from several tens to several tenths of ng·m^{-3}, 2) from several tenths to several hundredths of ng·m^{-3}, and 3) from several thousandths to analytical zero. Metals of predominately terrigenous origin, i.e., Fe, Zn, Al, Ba, as well as Cu and Sr, refer to the first group. The elements in the first group totaled 93.4 % of all analyzed microelements. The second group included Ni, Cd, Cr, Se, Pb, V, Mo (5.6% of the total composition), which are mostly the markers of anthropogenic pollution. The third group consists of Ti, Co, Sb, Li, As (0.6% of the total composition). Elements in this group originate from both natural and anthropogenic sources.

For insoluble fraction of Arctic aerosols, Shevchenko (2006) showed that the content of most terrigenous chemical elements (Na, Al, K, Ca, Fe, Co, and Ba) in aerosol composition is lower than the average values, characteristic for Earth's crust; while the content of such elements as Cr, Cu, Zn, As, Se, Br, Ag, Sb, Ni, and Pb is much higher, suggesting their predominately anthropogenic origins. Moreover, it is indicated that some elements with high concentrations (Zn, Se, and Fe) may be both anthropogenic and coming from natural sources.

The data obtained were used to estimate the relative content of soluble elements in the total sum of ions (Table 6) and elements (Table 7) of water-soluble aerosol fraction. The calculations showed that the average content of elements decreases in the northern direction (except in the Bering Sea): 1.9% in the

Japan Sea, 1.5% in the Okhotsk Sea, 0.8% in the Bering Sea, 1.7% in the Chukchi Sea, 1.6% in the East Siberian Sea, and 1.4% in the region A. In the Far East sector, the maximal percentage of soluble elements was recorded on July 30 over the Okhotsk Sea (up to 13.8%) and on August 14 over the Chukchi Sea (up to 8.6%). In the region A (RV *Akademik Fedorov*) the percentage of soluble elements was maximal at the northeastern margins of the Laptev Sea.

Deficient information on measurements of elemental composition of water-soluble aerosol fraction in these regions (and especially over the Arctic Ocean) complicates the data comparison. Therefore, the composition of water-soluble aerosol fraction in the region A was compared with that of solid aerosol suspensions (soluble and insoluble particles) in the western part of the Russian Arctic during summer-fall period of 2006 (Goryunova and Shevchenko, 2008). The comparison showed that the Na, Ca, Co, Ni, Se, As, Sr, Sb, and Ba concentrations in water-soluble fraction (our data) are smaller than in solid-phase aerosol suspension. The soluble percentage was, on the average, 11.4-19.2% for sodium, 7.9-18.8% for calcium, and about 4% for barium. The soluble percentages for other elements vary in wider ranges. The maximal percentages were found to be 39.7-60% for selenium, 0.5-30% for nickel, and about 5% (4.8-6.2) for antimony. Other percentages had been 0.1-4.2% for cobalt, 1.0-1.6 for arsenic, and 0.1-4.3% for strontium. Despite their low concentrations, these elements play very important role in wildlife. When entering the environment, the elements penetrate trophic chains, accumulate in plant and animal organisms, become involved in metabolic cycles, and cause diverse physiological distortions.

In analogy to the main ions in aerosol, we also calculated the enrichment coefficients of concentrations of elements with respect to sodium ($K = (C_i/Na)_{aer}/(C_i/Na)_{sw}$. On the whole, on both routes, the enrichment of particles for most chemical elements in soluble aerosol fraction was lower than the average values, characteristic for seawater. High enrichment is revealed for seven elements, namely, Zn, Cu, Al, Fe, Mn, Cr, and Cd. With respect to intensity of pollution of aerosol by these elements, the study regions can be lined up as follows: Okhotsk Sea, Arctic Ocean, Chukchi Sea, Japan Sea, Bering Sea, and East Siberian Sea.

Aerosol component with enriched elements was recorded on entire route of RV *Akademik Fedorov*. The enrichment coefficients for the elements varied in the following ranges: $K = 8.8$-794 for Cd, $K = 1.2$-264 for Cr, $K = 4.8$-72.8 for Zn, $K = 2.0$-34.4 for Cu, $K = 1.1$-1.6 for Ni, $K = 0.1$-45.3 for Al, and $K = 2.7$-88.8 for Fe. The maximal enrichment of particles was observed northward of the Severnaya Zemlya Archipelago from September 11 to 18. According to works (Yli-Tuomi et al., 2003; Shevchenko, 2006; Vinogradova and Ponomareva, 2007; Vinogradova, 2014), the main suppliers of heavy metals to the central Arctic are Murmansk region (Ni, Cu, Cd), Arkhangelsk region (Zn, Cr), Nenets Autonomous Okrug (Zn, Pb, Cr, Cu), Sverdlovsk region (Cd, As, Zn, Cr), Norilsk industrial region (Ni, Pb), and Kola Peninsula (Zn, Sb, As, In).

We note that high enrichment of aerosol particles by elements may be also observed in regions farther removed from anthropogenic sources. For instance, enrichment by Al, Fe, Mn, Ni, Cd, and Se was revealed in the Eastern sector of the coastal part of Antarctica between China's Zhongshan Station and Australia's Casey Station (Xu et al., 2014). The coefficients of enrichment by Al, Fe, and Ni near the stations ($K < 10$) turned out to be comparable to or lower than data, which we obtained in the Arctic region A ($K = 1$-100). High enrichments by Cd in the southern and northern polar regions are in the same range of values ($100 < K < 1000$). The two high-latitude regions showed considerable difference in the coefficients of enrichment by Se: the average $K = 1.3$ in the region A, and K is greater than 10^4 in the region of Antarctic stations.

On the route of RV *Professor Khljustin*, high enrichment coefficients, reaching 3-4 orders of magnitude, were recorded for Zn and Cr. For zinc, the largest enrichment coefficients were observed over water basins of the Okhotsk ($K = 36$-1204) and Chukchi Seas ($K = 17$-352). Over other Far East seas, the enrichment coefficients for Zn varied in the range of two orders of magnitude ($K = 10$-97). The maximal pollution by chromium compounds was recorded in the atmosphere of the Bering Sea ($K = 10$-1143). Over other seas, the enrichment coefficients for Cr had the following values: $K = 73$-181 for the Japan Sea, $K = 90$-224 for the Okhotsk Sea, $K = 23$-412 for the Chukchi Sea, and $K = 77$ for the East Siberian Sea. High enrichment for Cu (by 2-3 orders of magnitude) was revealed over water basins of all Far East seas ($K = 13$-351), for Cd over the Okhotsk ($K = 15$-305) and Chukchi Seas ($K = 10$-171), and

for Al over the Okhotsk Sea ($K = 42\text{-}328$). We note that Cu and Cd mainly represent markers of anthropogenic emission; while Al is more indicative of terrigenous particle supply to the atmosphere. Maximal enrichment of aerosol by manganese was detected over the Okhotsk ($K = 194\text{-}217$) and Chukchi ($K = 20\text{-}198$) Seas. An elevated intensity of aerosol enrichment by iron was observed over the Japan ($K = 13\text{-}34$), Okhotsk ($K = 9\text{-}40$), and Chukchi ($K = 1\text{-}80$) Seas.

An important role in determining the pollution level of atmospheric air is played by processes of trans-boundary transport of suspended particles and pollutants from adjoining territories. Far East seas are on the pathway of pollutant transport both from Eurasia and North America (see, e.g., Hov et al., 2007; Rudis, 2010; Vinogradova, 2014). In the contemporary period, pollutant outflows from China exert ever growing effect (Streets et al., 2000; Ohara et al., 2007). However, in this work we did not pursue the trajectory analysis of motion of air masses and the quantitative estimation of the effect some or other pollution sources have on samples collected in separate seas.

5.3 Small gaseous impurities

Small gaseous impurities and, especially, acid-forming gases, strongly influence the Earth's radiation budget, oxidizing or self-cleaning capacity of the atmosphere, aerosol formation, growth, and properties, and air quality. The average concentrations of gaseous impurities (HCl, HNO_3, SO_2, NH_3) in the study regions are presented in Table 8.

In the atmosphere of Far East seas, on the average, the concentrations of acid-forming gases HCl, SO_2, and HNO_3 decreased when going from warm (Okhotsk and Japan Seas) to Arctic seas (East Siberian and Chukchi Seas). Concentrations of HCl had decreased by approximately a factor of 4, SO_2 concentrations by a factor of 11, and HNO_3 concentrations from 0.45 $\mu g \cdot m^{-3}$ to analytical zero, consistent with works (Sun, 2002; Xu et al., 2005). The regularity of northward decrease in concentration largely showed up owing to data acquired on forward route. This was also favored by meteorological conditions over the Chukchi Sea on August 12-20 (see Fig. 9 d, e): high relative humidity, wind decline into a perfect calm, washing-out effect of precipitation, etc. On the backward route, the HCl, SO_2, and HNO_3 concentrations varied with latitude in different ways, with a lower level of mean concentrations being observed in midlatitude seas. Seemingly, this divergence was due to different weather conditions and air mass types, as well as to smaller number of samples collected on backward route (e.g., only one sample was taken in the Japan Sea).

The NH_3 concentrations were characterized by relatively low and nearly the same level, less than 0.1 $\mu g \cdot m^{-3}$, on the average, on the most part of the route of RV *Professor Khljustin*. The NH_3 concentrations were higher only at polar latitudes on backward route, up to 0.21 $\mu g \cdot m^{-3}$ over the Chukchi Sea.

Comparison with content of gaseous impurities, obtained during preceding expeditions (Polkin et al., 2011c) in the Japan Sea during spring 2009 and in the Okhotsk Sea during August 2010 allowed us to make the following conclusions. The average HNO_3 concentrations are in best agreement with new data: they were 0.6 $\mu g \cdot m^{-3}$ in 2009 and 0.66 $\mu g \cdot m^{-3}$ in 2010. Average HCl concentrations, obtained earlier (1.7 and 4.3 $\mu g \cdot m^{-3}$), are close to average data for backward route of RV *Professor Khljustin*. Much larger SO_2 and NH_3 concentrations were observed in 2009 and 2010 expeditions. For instance, the average SO_2 concentrations were 39.7 and 10.8 $\mu g \cdot m^{-3}$ over the Japan and Okhotsk Seas respectively. The fact that the average concentrations of gaseous impurities strongly differ between forward and backward routes (see discussion above) and among diverse expeditions indicates that these abundances vary in wide range and depend strongly on direction of air transport. Despite their averaging over individual seas, the obtained compositions of the samples more reflect the specific features of a particular period of measurements rather than peculiarities of the region of measurements.

With respect to content of gaseous impurities, the atmosphere of high-latitude region *A* (RV *Akademik Fedorov*) is somewhat different from Far East seas. The HCl concentrations in high-latitude region are much lower and in a good correspondence to latitudinal decrease of this impurity over Far East seas. The average HNO_3 content turned out to be about the same as that over the Japan and Okhotsk Seas. The SO_2 and NH_3 concentrations had been surprisingly high in remote region of the Arctic Ocean, though several-fold smaller than over the Japan and Okhotsk Seas during 2009/2010 expeditions (Polkin

et al., 2011c). It is especially difficult to explain so strong difference in impurity content between region *A* and the East Siberian and Chukchi Seas, which are close both in latitude and in climatic conditions.

In the absence of other data for Arctic region *A*, we performed comparison with (a) measurements of gaseous impurities in Ny-Ålesund at Svalbard during spring 2003 (Ianniello et al., 2007); (b) results of monitoring in midlatitude background region of the Lake Baikal (Golobokova et al., 2011). The impurity concentrations in the region *A* turned out to be larger even than maximal values in Ny-Ålesund: by a factor of 1.6 for HNO_3 and by more than a factor of 6 for HCl and SO_2. However, this comparison is not quite correct because of the difference in sampling techniques. It is more unambiguous to perform comparison with data for the Lake Baikal, where the same methods and instruments were used for measurements. The average concentrations in the Lake Baikal during different periods of time vary from 0.6 to 4.8 $\mu g \cdot m^{-3}$ for SO_2, from 0 to 0.07 $\mu g \cdot m^{-3}$ for HNO_3, and are about 0.8 $\mu g \cdot m^{-3}$ for NH_3. That is, the average SO_2, HNO_3, and NH_3 concentrations in the region *A* are comparable with data in background continental region.

This, of course, leaves the question as to why gaseous impurities in region *A* have elevated content and needs a confirmation (which is also true for other characteristics). We hope that measurements in new Arctic expedition NABOS-2015 (August-September 2015) along an analogous route will help to clarify the question.

In addition to individual analysis of content of gaseous impurities, we also considered their joint variations with concentration of sum of ions. Interrelation between summed concentrations of gaseous impurities and ions (with correlation coefficient of 0.68) manifested on the route of RV *Akademik Fedorov*. Over Far East seas (RV *Professor Khljustin*), the SO_2 concentrations well correlate with the concentrations of methanesulfonic acid (correlation coefficient of 0.77), probably because dimethyl sulfide oxidizes to form SO_2. Moreover, there was a weak negative correlation between concentrations of NH_3 and sum of gases HCl, SO_2, and HNO_3. These interrelations may indicate that chemical processes flow between these components. However, the available information is still insufficient to make firm conclusions.

5.4 Fluxes of chemical substances to sea surface

The obtained results (see Table 6-8) were used to estimate the vertical fluxes of water-soluble substances to the sea surface. In the flux calculations in Arctic zone (region *A*, East Siberian, Chukchi, Bering Seas), we used the values, known from literature data: dry deposition velocity geometric mean, equaling $1.9 \cdot 10^{-3}$ $m \cdot s^{-1}$ for the open sea (Nilsson and Rannik, 2001); and deposition velocity of particles, equaling $2 \cdot 10^{-2}$ $m \cdot s^{-1}$ for coastal regions (Duce et al., 1991; Shevchenko, 2006). Table 9 presents flux calculations for two groups of marine water basins: Arctic Seas and Far East seas at temperate latitudes.

The fluxes of substances, coming from the atmosphere together with different ions (under heading Ions in Table 9), were determined for the sum of Na, K, Mg, Ca, Cl, N, and S. Nitrogen was recalculated in the sum of nitrates and ammonium ions, and sulfur was recalculated from sulphates. Fluxes of trace elements (TE) were calculated for the sum of Al, Ti, V, Cr, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Pb, Ba, Be, B, Li, Mn, and Sr concentrations. In the calculation of substances, supplied together with gaseous impurities (GI), we took the sum of the Cl, N, and S concentrations, calculated from gaseous species HCl, HNO_3, NH_3, and SO_2 respectively. In the calculations, we used the maximal deposition velocities of gases over water surface for each of the gaseous impurities: $2.6 \cdot 10^{-2}$ $m \cdot s^{-1}$ for HNO_3, $2.2 \cdot 10^{-2}$ $m \cdot s^{-1}$ for NH_3, $2.1 \cdot 10^{-2}$ $m \cdot s^{-1}$ for SO_2 (Zhang et al., 2003), and $1.3 \cdot 10^{-2}$ $m \cdot s^{-1}$ for HCl (Clark et al., 1984).

Use in the calculations of particle deposition velocities, differing by an order of magnitude ($1.9 \cdot 10^{-3}$ and $2 \cdot 10^{-2}$ $m \cdot s^{-1}$), naturally translates to an order of magnitude difference in fluxes. In this regard, when comparing the vertical fluxes of substances, supplied together with aerosol substance and gaseous impurities, we will use, as was conventional in a number of works (Duce et al., 1991; Shevchenko, 2006), the aerosol particle deposition velocity of $2 \cdot 10^{-2}$ $m \cdot s^{-1}$. From these data it follows that, both in Arctic and Far East seas, maximal amount of substance is supplied to the surface together with gaseous impurities. On the average, deposited ions accounted for about 24.7%, trace elements accounted for 0.4%, and small gaseous impurities accounted for 74.9% of the total amount of substances (Ions+TE+GI), coming from the atmosphere. The maximal fluxes of substances together with ions were

observed in the water basin of the Chukchi and Bering Seas (28 and 30%), and minimal fluxes were observed over the Japan Sea (16%). Among the ions, maximal contribution (66-83%) to substance fluxes comes from maritime component, i.e., Na and Cl. Fluxes of substances, supplied together with ions to the surface of the Arctic seas, are quite close to analogous data from the monitoring station Primorskaya (2.11 mg·m^{-2} day^{-1}) (EANET, 2011).

A different relationship is observed in the distribution of fluxes of gaseous impurities in these regions. Over the Arctic ocean (region A), HCl accounts for about 16%, the sum (NH_3+HNO_3) accounts for about 22%, and SO_2 accounts for 62%. Over Far East seas, the main contribution (up to 97%) to the substance fluxes is due to Cl.

In the total sum (Ions+TE+GI), the average substance fluxes over the Japan and Okhotsk Seas are three times larger than over Arctic seas. As was already noted in sections 5.1-5.3, these regions experience strong effect of continental sources of aerosol and gases. The substance fluxes over the Bering Sea occupy an intermediate position between Arctic seas and more southern seas.

For comparison purposes, we present estimates (Shevchenko, 2006), according to which the average vertical aerosol flux in Arctic is about 600 mg·m^{-2}·year^{-1} (or 1.64 mg·m^{-2}·day^{-1}) and incorporates salt, terrigenous, and organic parts. The elemental composition of insoluble fraction is reported by the author to be, on the average, 0.39 mg·m^{-2}·day^{-1}, i.e., ¼ part. Hence, the remaining part (1.25 mg·m^{-2} day^{-1}) is accounted for by salt and organic parts of aerosol. According to our estimates (see Table 9), soluble-part fluxes alone (Ions + TE) are 2.2 mg·m^{-2} day^{-1}, almost a factor of two larger. The discrepancy seems to be because the method for flux estimation (Shevchenko, 2006) used a number of model assumptions. Our calculations are based on real measurements, but they characterize just a separate period and region of measurements; therefore, they may differ from average fluxes for entire Arctic.

We considered separately the vertical fluxes of sulfur and nitrogen, deposited together with aerosol substance (S_{aer}, N_{aer}) and gaseous impurities (S_{gas}, N_{gas}) (see Table 10). A tendency for flux intensity to decrease from south to north is apparent in delivery of sulfur together with aerosol substance (S_{aer}). Other components of sulfur and nitrogen fluxes (N_{aer}, S_{gas}, N_{gas}) keep latitudinal decrease in north direction only as far as East Siberian Sea, and over Arctic ocean (A) they sharply increase (by more than an order of magnitude). This jump is a consequence of anomalously high NH_4^+, SO_2, and NH_3 concentrations (see 5.1 and 5.3) in high-latitude region A, which are not explained yet.

Using available literature data, we performed a comparison with vertical sulfur and nitrogen fluxes in the northeastern part of the Atlantic Ocean near Bermuda (Sievering et al., 1989) and with data from continental region, i.e., from Primorskaya monitoring station (EANET, 2011). The comparison showed that the deposition of the summed sulfur ($S_{aer}+S_{gas}$) in the area of Bermuda (0.43-0.52 mg·m^{-2} day^{-1}) satisfactorily agrees with our data for Bering and Okhotsk Seas. The average intensities of fluxes of sulfur (0.68 mg·m^{-2} day^{-1}) and nitrogen (0.37 mg·m^{-2} day^{-1}) at Primorskaya station are close to our data for Far East seas at midlatitudes.

The intensity of nitrogen fluxes in soluble aerosol fraction (N_{aer}) was compared with data, obtained by Jung et al. (2013) in the subarctic western North Pacific Ocean (0.25 mg·m^{-2} day^{-1}). This value is comparable with N_{aer} fluxes in the high-latitude Arctic (region A), but is several-fold larger than over Far East seas.

We conclude by noting once again that these results rely on a small number of samples collected for separate regions, and reflect the chemical composition of the aerosol atmosphere in specific periods of measurements. Therefore, these characteristics are estimative in character and need a confirmation and further interpretation.

Table 6. Average characteristics of ion composition of atmospheric aerosol on the route of RV *Akademik Fedorov* and *Professor Khljustin* (numerator indicates the average ion content in µg·m^{-3} and standard deviations; denominator indicates the average values on the forward and backward routes, n is the number of samples; and $\sum_{ions}$ is the summed ion content).

Ions	Area					
	Region *A*, (n = 14)	East Siberian Sea, (n =1/1)	Chukchi Sea, (n =6/2)	Bering sea, (n =3/4)	Okhotsk Sea, (n = 3/2)	Japan Sea, (n = 4/1)
Na$^+$	0.34±0.24	0.27±0.13 / 0.18/0.38	0.62±0.98 / 0.29/1.58	0.62±0.62 / 0.38/0.80	1.00±1.66 / 0.34/1.99	0.65±0.40 / 0.49/1.30
NH$_4^+$	0.13±0.07	0.00	0.00	0.02±0.02 / 0.01/0.02	0.01±0.02 / 0.02/0.00	0.05±0.01 / 0.05/0.04
K$^+$	0.04±0.06	0.18±0.11 / 0.10/0.26	0.08±0.11 / 0.04/0.19	0.26±0.41 / 0.06/0.41	0.28±0.43 / 0.39/0.11	0.48±0.20 / 0.45/0.61
Mg^{2+}	0.03±0.02	0.02±0.01 / 0.02/0.03	0.07±0.11 / 0.03/0.18	0.06±0.05 / 0.04/0.08	0.13±0.24 / 0.03/0.28	0.05±0.02 / 0.05/0.07
Ca^{2+}	0.04±0.02	0.04±0.01 / 0.03/0.053	0.05±0.06 / 0.03/0.10	0.07±0.06 / 0.03/0.10	0.10±0.10 / 0.10/0.11	0.12±0.05 / 0.13/0.10
Cl$^-$	0.66±0.36	0.48±0.25 / 0.31/0.66	0.80±0.91 / 0.53/1.60	1.09±1.14 / 0.66/1.41	1.63±2.57 / 0.58/3.21	1.10±0.67 / 0.82/2.23
Br$^-$	0.01±0.01	0.001±0.0 / 0.001/0.009	0.002±0.004 / 0.001/0.006	0.002±0.002 / 0.001/0.003	0.005±0.010 / 0.001/0.011	0.004±0.004 / 0.004/0.003
NO$_3^-$	0.03±0.04	0.001 / 0.001/0.0	0.005±0.010 / 0.007/0.0	0.011±0.020 / 0.0/0.019	0.005±0.011 / 0.0/0.013	0.110±0.085 / 0.103/0.140
SO$_4^{2-}$	0.11±0.07	0.069±0.003 / 0.068/0.071	0.25±0.35 / 0.13/0.60	0.84±0.89 / 0.34/1.22	0.42±0.47 / 0.29/0.61	0.58±0.21 / 0.66/0.28
Σ_{ions}	1.39±0.75	1.06±0.52 / 0.72/1.45	1.88±2.50 / 1.06/4.26	2.97±1.96 / 1.52/4.06	3.58±5.07 / 1.75/6.33	3.14±1.09 / 2.75/4.67

Table 7. Average values (± SD) of concentrations [ng·m^{-3}] of water-soluble elements in aerosol along the route of RV *Akademik Fedorov* and *Professor Khlyustin* (July-September, 2013).

Element	Area					
	Arctic ocean (*A*)	East Siberian Sea	Chukchi Sea	Bering Sea	Okhotsk Sea	Japan Sea
Fe	6.06±4.22	0.55±0.061	2.1±1.5	2.0±1.0	2.6±3.1	6.1±5.0
Zn	8.71±4.81	10.3±5.8	20.3±13.7	11.0±2.1	35.5±31.4	36.1±11.6
Al	0.70±1.33	0.29±0.032	1.6±2.3	5.1±7.2	5.6±6.7	2.2±0.8
Cu	1.08±0.72	3.0±1.6	2.9±1.1	3.9±2.1	5.2±5.2	8.1±3.1
Sr	0.65±0.38	1.06±0.72	0.61±0.74	0.64±0.54	1.10±1.29	1.03±0.31
Mn	-	0.20±0.18	1.19±1.04	0.11±0.16	1.40±1.99	1.51±1.71
Ba	0.99±0.44	1.05±0.076	1.0±0.4	1.0±0.3	0.97±0.50	2.1±0.3
Ni	0.27±0.25	0.21±0.08	0.62±1.13	0.32±0.35	0.41±0.51	0.98±0.46
Cd	0.36±0.19	0.050±0.030	0.074±0.029	0.14±0.21	0.09±0.05	0.11±0.06
Cr	0.100±0.074	0.031±0.031	0.078±0.076	0.37±0.41	0.14±0.13	0.24±0.06
Se	0.141±0.068	0.23±0.07	0.10±0.13	0.050±0.078	0.06±0.08	0.22±0.14
Pb	0.086±0.038	0.16±0.03	0.22±0.06	0.25±0.16	0.28±0.23	0.41±0.12
V	0.024±0.010	0.15±0.03	1.22±2.84	0.093±0.069	0.16±0.17	0.74±0.67
Mo	0.047±0.019	0.024±0.010	0.023±0.014	0.016±0.016	0.023±0.024	0.039±0.025
Ti	0.064±0.189	0.00	0.009±0.023	0.003±0.007	0.00	0.026±0.036

Co	0.003±0.013	0.007±0.010	0.005±0.010	0.002±0.006	0.007±0.010	0.015±0.011
Sb	0.126±0.438	0.014±0.001	0.023±0.016	0.013±0.004	0.046±0.048	0.065±0.049
Li	0.0049±0.0079	0.044±0.041	0.049±0.053	0.023±0.022	0.040±0.040	0.077±0.037
As	0.0057±0.0042	0.014±0.013	0.012±0.017	0.005±0.012	0.023±0.042	0.034±0.035
Be	0.00	0.0012±0.0021	0.0002±0.0005	0.0001±0.0002	0.0002±0.0004	0.0002±0.0003
Σ_{TE}	19.42	17.39	32.13	25.04	53.65	60.10

Table 8. The average concentrations of small gaseous impurities in the atmosphere [$\mu g \cdot m^{-3}$] on the route of RV *Akademik Fedorov* and *Professor Khljustin* (numerator indicates the total average in the region and standard deviations; denominator indicates the average in the forward and backward directions).

Area	HCl	HNO_3	SO_2	NH_3
Arctic ocean *(A)*	0.91±0.46	0.46±0.16	4.31±2.55	0.73±0.28
East Siberian Sea	4.8±2.9 / 2,7/6,8	0,00	0.06±0.00 / 0,06/0,06	0.07±0.08 / 0,01/0,13
Chukchi Sea	5.8±3.5 / 6,3/4,6	0,00	0.13±0.14 / 0,11/0,20	0.12±0.09 / 0,09/0,21
Bering Sea	9.5±6.5 / 15,7/4,8	0.11±0.19 / 0,26/0,00	0.15±0.15 / 0,26/0,07	0.04±0.02 / 0,03/0,04
Okhotsk Sea	16.3±11.7 / 24,7/3,6	0.40±0.36 / 0,66/0,00	0.45±039 / 0,70/0,09	0.04±0.02 / 0,05/0,04
Japan Sea	20.9±12.4 / 24,5/6,4	0.45±0.44 / 0,56/0,01	0.66±037 / 0,81/0,05	0.05±0.03 / 0,05/0,03

Table 9. Diurnally average vertical fluxes of water-soluble substances together with aerosol and gaseous impurities [$mg \cdot m^{-2} day^{-1}$] according to data of measurements in Arctic and Far East seas (RV *Akademik Fedorov* and RV *Professor Khljustin*).

Area	Deposition velocity				
	$1.9 \cdot 10^{-3}$ m s^{-1}		$2.0 \cdot 10^{-2}$ m s^{-1}		
	Ions	TE	Ions	TE	GI
Arctic seas					
Arctic ocean (region *A*)	0,21	0,003	2,17	0,034	6,28
East Siberian Sea	0,17	0,003	1,75	0,030	5,41
Chukchi Sea	0,28	0,005	2,94	0,056	6,64
Far East seas (moderate latitude)					
Bering Sea	-	-	4,14	0,043	10,64
Okhotsk Sea	-	-	5,68	0,093	18,48
Japan Sea	-	-	4,59	0,104	23,74

Table 10. Diurnally average vertical fluxes of sulfur and nitrogen together with aerosol and gaseous impurities [$mg \cdot m^{-2} \cdot day^{-1}$] according to data of measurements in Arctic and Far East seas (RV *Akademik Fedorov* and *Professor Khljustin*).

Area	S_{aer} (SO_4^{2-})	N_{aer} ($NH_4^+ + NO_3^-$)	S_{gas} (SO_2)	N_{gas} ($NH_3 + HNO_3$)	$S_{aer} + S_{gas}$	$N_{aer} + N_{gas}$
Arctic seas						
Arctic ocean (region *A*)	0.06	0.19	3.91	1.37	3.97	1.56
East Siberian Sea	0.04	0.00	0.05	0.11	0.09	0.11
Chukchi Sea	0.14	0.002	0.12	0.19	0.26	0.192
Far East seas (moderate latitude)						
Bering Sea	0.48	0.03	0.14	0.12	0.62	0.15
Okhotsk Sea	0.24	0.02	0.41	0.26	0.65	0.28

| Japan Sea | 0.33 | 0.11 | 0.60 | 0.30 | 0.99 | 0.41 |