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Insoluble Particles in the Snowpack of the Ob River Basin (Western Siberia) a 2800 km Submeridional Profile

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Abstract: Snowpack exhibits properties that make it a unique natural archive of airborne pollution. The data on insoluble particles in the Ob River catchment (Western Siberia) snowpack are limited. Insoluble particles in the snowpack of Western Siberia were studied at 36 sites on a 2800 km submeridional profile from the city of Barnaul to Salekhard in February 2020. Snow samples were collected over the full depth of the snow core, from the surface of the snow cover to the boundary with soil, except for the lower 1–2 cm. After the filtration of melted snow through a 0.45-µm membrane, the particle composition was studied using a scanning electron microscope with an energy microprobe. In the background areas, the concentration of insoluble particles in the snow was below 2 mg/L. Significantly higher particle concentrations were encountered near cities and hydrocarbon production areas. Particulate matter in snow mainly consists of biogenic and lithogenic particles mixed with anthropogenic particles (ash and black carbon aggregates). The proportion of anthropogenic particles increases near cities and areas of active hydrocarbon production.

Keywords: insoluble particles; snowpack; West Siberia; scanning microscopy; lithogenic particles; biogenic particles; anthropogenic particles; long-range transport; pollution; gas flaring

1. Introduction

Atmospheric transport of suspended particles is a quick route to the release of many substances (including pollutants) into the environment [1–5]. Snowpack is a unique natural archive of particles deposited from the atmosphere [6–15]. The snow washes out insoluble aerosol particles (lithogenic, biogenic, and anthropogenic) from the atmosphere as well as soluble compounds, including various pollutants [16–30].

The snow remains at the soil surface and thus records all atmospheric input during the glacial period of the year. In boreal and subarctic regions, both dissolved and particulate fractions of snow water reflect the chemistry of the winter atmosphere, when the land is covered by snow and the water surfaces are covered by ice. During winter, the input of mineral compounds from adjacent regions is minimal, and the main factor controlling the chemical composition of snow is long-range, atmospheric transfer and transportation of anthropogenic particles over hundreds and thousands of kilometers from regional towns [19,21–35].

In the large and geographically homogeneous territories of Western Siberia, which present relatively similar levels of snow deposition during the winter seasons (i.e., from 100 mm of water in the south to 140–150 mm of water in the north), particulate matter has been actively studied in industrially developed areas (for example, in Novosibirsk, Tomsk, Kemerovo, and Nizhnevartovsk) [23,36–43]. Several studies on insoluble particles in the snowpack of relatively background areas of Western Siberia have been also conducted [16,44–49]. However, until now, large meridional or latitudinal transects of snow particulate composition have been rather limited (e.g., [46,47]). The latter studies demonstrated a systematic variation in the snow particle concentration and chemical composition across a sizable N–S transect and allowed the influence of aerosol generation from provinces to be traced and the local signals of anthropogenic pollution to be deciphered. These studies, however, were limited to the upper 0–5 cm snow layer, so they cannot be used for global mass balance calculations of dust transport and deposition in Siberia during the winter. To fill this gap, here, we collected the snow over the full depth of the snowpack, from the surface to the upper 1–2 cm above the ground. The aim of the work was to determine the concentrations of insoluble particles in the snow cover of the Ob catchment basin on the submeridional profile from the south of Western Siberia to the Ob mouth and to estimate the ratio of lithogenic, biogenic, and anthropogenic particles.

2. Materials and Methods

Insoluble particles in the snowpack of Western Siberia were studied at 36 sites on a 2800 km submeridional profile from the city of Barnaul to the city of Salekhard from 8 to 19 February 2020 (Table S1, Figure 1).

When interpreting the data obtained, we took into account the locations of associated gas flares, whose density is quite high in the region. The locations of the flares were determined from satellite data using the NASA Fire Information for Resource Management System [50]. This system provides information on high-temperature points, which are determined using radiometers (Visible Infrared Imaging Radiometer Suit (VIIRS)) installed on satellites. Access to the archive of coordinates of high-temperature points was obtained through [51] for specific boundaries of the region (52–70° N and 60–95° E) and the period of the year (February 2020). The positions of gas flares on the studied transect are also marked in Figure 1.

Due to the large latitudinal extent of the study area, the establishment of permanent snow cover was different among regions. According to the National Centers for Environmental Information of USA [52], in the south of the study area the snow cover was established on 27 October 2019. As we moved northward in the area of sampling sites 6–15, the formation of snow cover occurred on October 18–19. In the sampling area of the northernmost sites, namely 16–32, the snow cover was established in the period from October 16 to 17, 2019. Therefore, the period of accumulation of aerosol particles from the moment of snow cover formation to the moment of sampling is at least 3 months for the entire study area. Since we sampled the snow over full depth of the column, we collected all snow accumulated from the beginning till the data of sampling, i.e., over approximately 4 months. It is also worth noting that melting of the snow cover did not occur during the cold period, even in the south of the territory.

Sampling sites were situated at a distance of more than 500 m from the roads and more than 20 m from the nearest trees. For example, the selected location at point 31 is shown in Figure 2. The majority of roads are so-called winter roads (‘zimnik’), which are only used for several months per year and exhibit quite a low traffic density. Snow samples were taken from snow pits made by a pre-cleaned plastic shovel from the surface of the snow cover to the boundary with soil, except for the lower 1–2 cm (Figure 3), in double Milli-Q water pre-clean polyethylene bags, and they were transported in the frozen state to a laboratory in Tomsk. During sampling, a careful procedure was followed to avoid contamination from surrounding equipment and operators. Single-use vinyl gloves and clean laboratory overcoats were used during sampling and handling. The sampling was always performed by two people: one operating the shovel and loading the snowpack into plastic bags and the other holding the bags and immediately closing them with double plastic clamps. The density of snow was measured via sampling by standard 10 cm diameter plastic tube over the full depth of the snow core.

In the laboratory, the snow was melted at room temperature and immediately filtered through pre-weighed lavsan nuclear filters with a diameter of 47 mm and a pore diameter of 0.45 µm using pre-cleaned Nalgene 250 mL filter units and a manual PVC-made vacuum pump. The filter membranes were immediately frozen and freeze-dried prior to analysis.

The particle composition was studied using a VEGA 3 SEM scanning electron microscope (Tescan, Brno, Czech Republic); the elemental composition of the particles was determined using an EDX X-Max energy-dispersive X-ray microanalyzer (Oxford Instruments, Great Britain). The SEM-EDS spectra were recorded at an accelerating voltage of 20 kV. The spectrum accumulation time for the element maps was 480 s. Calibration and quantitative optimization of the X-ray spectra were performed using the Si Ka line at 1.73982 kV.

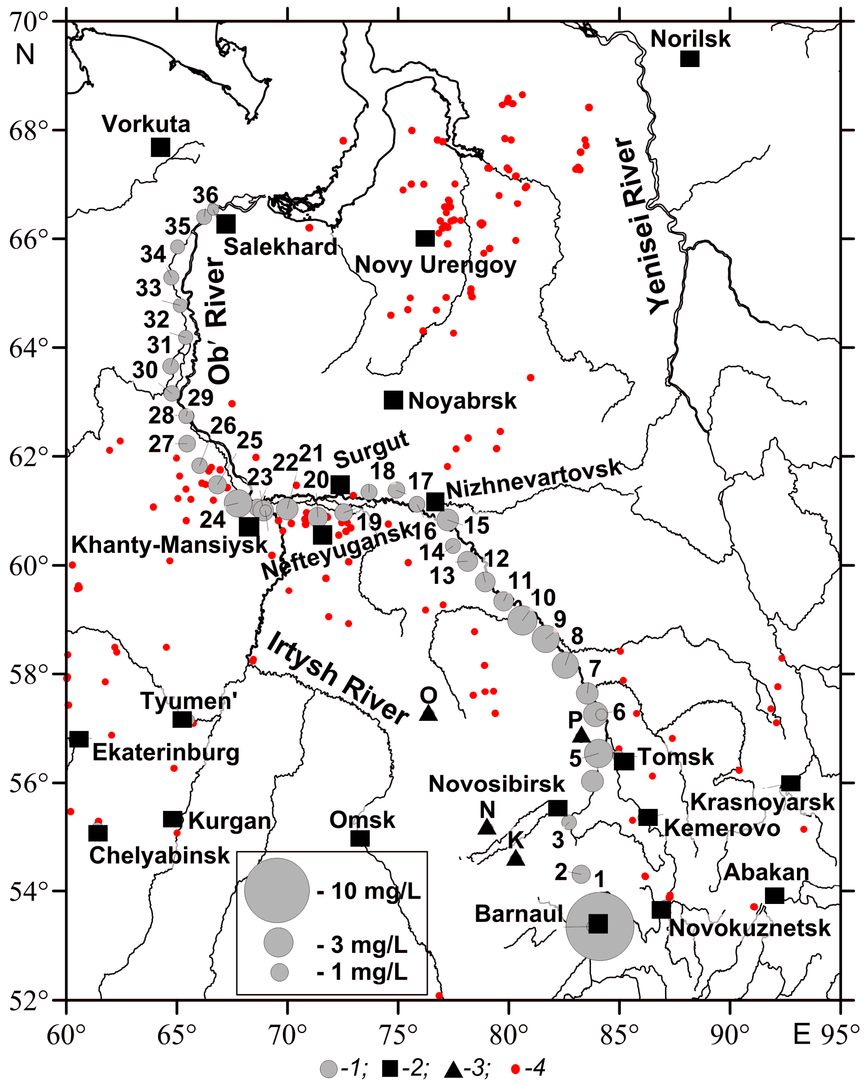

Figure 1. Studied area: 1—positions of the sampling sites (sizes of circles reflect the concentrations of particulate matter); 2—large cities; 3—sites of snowpack studies in [49]; 4—the positions of gas flaring taken from [51].

Figure 2. Sampling site 31 on a high floodplain on the left bank of the Ob river. Photo was taken by O.S. Pokrovsky.

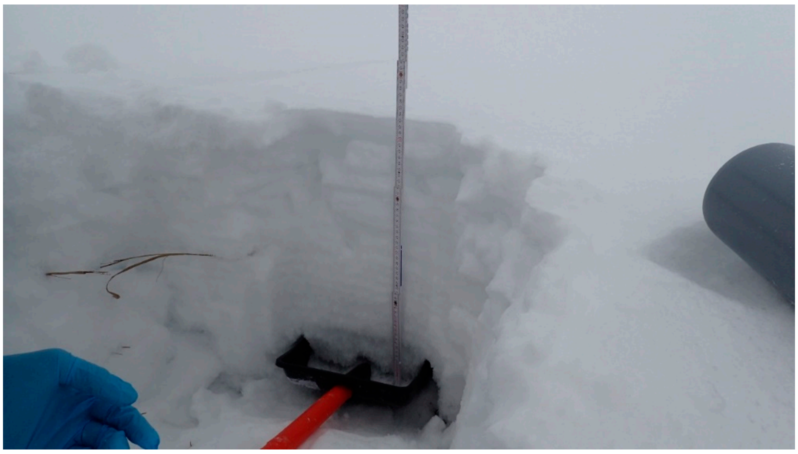

Figure 3. Sampling in snow pit at site 23. Photo was taken by O.S. Pokrovsky.

3. Results

The highest concentration of insoluble particles in snow water was encountered at site 1, near the city of Barnaul. This site is situated on a cultivated agricultural field (cropland), part of which was not covered with snow. Therefore, a local transfer of microparticles blown out of the soil by the wind was probable. At the remaining 35 sites, the concentration of insoluble particles varied from 0.48 to 3.42 mg/L (Table S1), with an average of 1.47 mg/L and a standard deviation of 0.86 mg/L. At site 2, on the cultivated agricultural field, the concentration of suspended matter was 1.32 mg/L, and at point 3, in the floodplain of the small river Chaus, it was 0.66 mg/L. At sites 4–10, located in relatively populated areas, the concentration of insoluble particles ranged from 2 to 3.42 mg/L. Further along the route, with the exception of site 24, the concentration of particles was less than 2 mg/L, and from site 28 to site 36, it was even less than 1 mg/L. Site 24 was located in the taiga near the city of Khanty-Mansiysk.

Particulate matter in snow mainly consists of biogenic (mostly plant fibers) and lithogenic (mostly clay minerals, feldspars, and quartz) particles mixed with anthropogenic particles (ash and black carbon aggregates). Clay minerals are mainly represented by montmorillonite, chlorite, and illite; feldspars are mainly represented by plagioclase and orthoclase. The proportion of anthropogenic particles rises near cities and areas of active hydrocarbon production. The most typical types of insoluble particles are shown in Figure 4. Additionally, SEM images and energy-dispersive spectra of selected particles are presented in Figure S1.

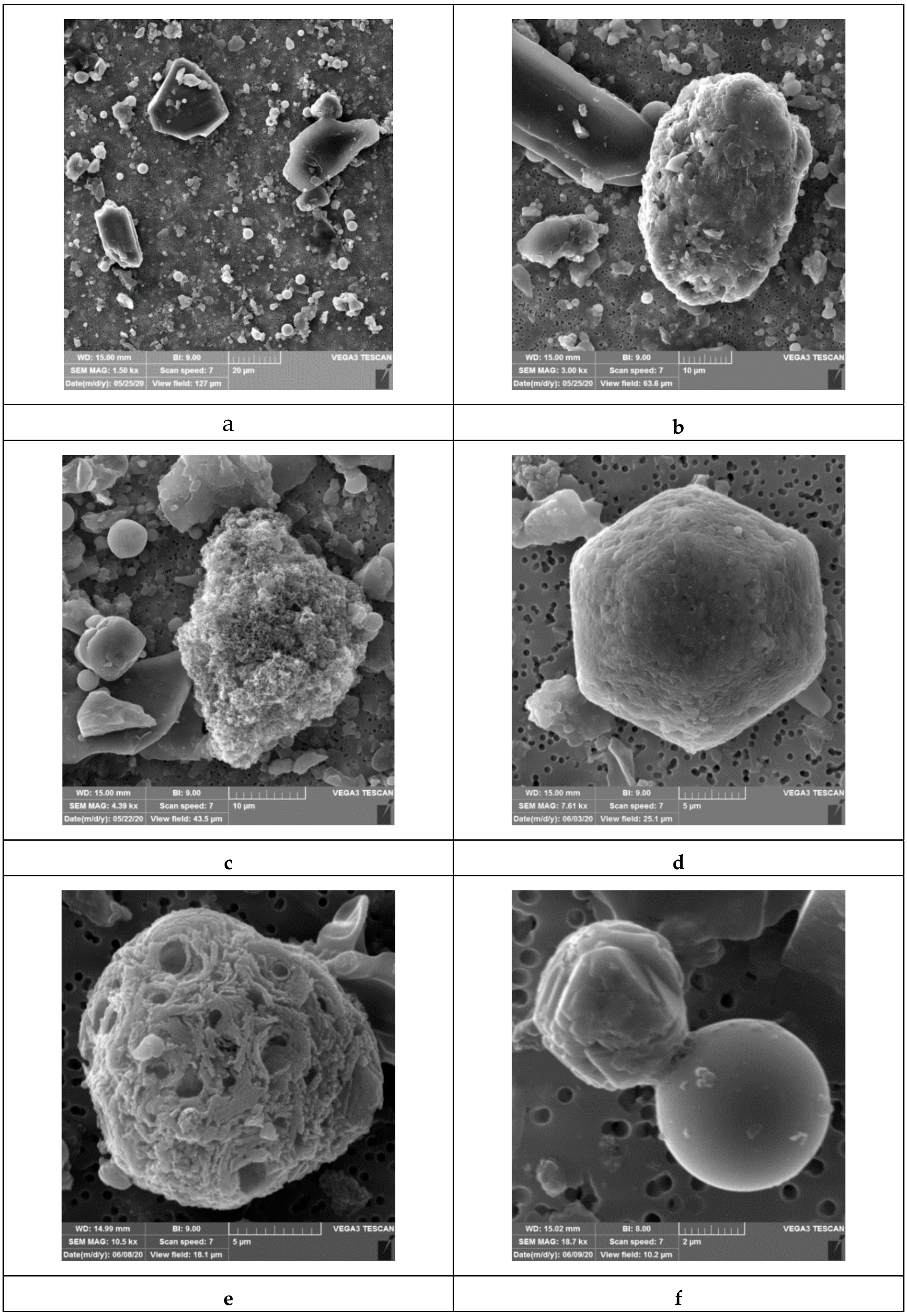

Figure 4. Typical insoluble particles in the Western Siberia snowpack: **a**—relatively large grains of plagioclase and smaller particles of clay minerals and ash; **b**—plagioclase particle with signs of intensive secondary replacement; **c**—black carbon particle aggregate; **d**—corundum microcrystal; **e**—porous carbonaceous ash particle; **f**—splice of metal slag (top) and aluminosilicate fly ash.

Samples of insoluble particles at sites 1–5 are saturated with mineral particles up to 30–50 μm in size, among which feldspars and clay particles of 4–6 μm prevail. The proportion of quartz particles in this interval is insignificant. The samples contain a significant amount of ash and a small amount of biogenic material. In the interval of the route from site 6 to site 15, the samples contain a large number of biogenic particles (mostly plants fibers larger than 20 μm), some ash and smaller proportion of mineral particles. Among mineral fraction, clay particles up to 10 μm in size prevail over feldspars. In the interval of sites 14–18, a synchronous increase in the amount of black carbon aggregates and ash is noted. From site 16 to site 27, the proportion of biogenic particles in the samples decreases, while the proportion of mineral matter remains almost constant. Clay particles up to 5 μm in size make up the bulk of the mineral matter in the samples. In this interval, the proportion of quartz particles increases; well-formed corundum crystals appear in many samples. Besides, all samples from this route interval exhibit a variety of anthropogenic particles. Northward of site 28, the number of biogenic particles in the samples continues to decrease, but it increases at the two end points of the transect. The total amount of all particles in the samples also decreases towards the extreme north, but the ratio of mineral and biogenic particles changes insignificantly. Among the mineral particles in samples from sites 28–36, there is a high proportion of quartz and clay particles about 10 μm in size. The amount of ash particles in this part of the transect continues to decrease in comparison with more southern regions.

4. Discussion

The concentration of insoluble particles in the snow cover of the Ob River basin in February 2020 was relatively low at most sites (from 0.48 to 3.42 mg/L), which corresponds to the level of many background regions of the Arctic and Subarctic [17,26,44]. At only one site (No. 1, near the city of Barnaul), the concentration achieved a level of 10.8 mg/L, which was presumably linked to local-range wind transport of dust from the agriculture field (cropland) that was not covered by snow and taiga. It is also possible that insoluble particles were delivered to this site by long-range atmospheric transport from the snow-free semi-desert and desert regions of Central Asia [53,54].

In the winter of 2005–2008, the concentration of insoluble particles in the snow cover of the Khanty-Mansiysk region varied from 0.2 to 397 mg/L; for 340 samples, the average value was 11.7 mg/L and the median value was 4 mg/L [44]. According to these authors, the highest concentration of particles in the snow cover occurred near the cities of Nizhnevartovsk and Surgut. Outside the cities, the concentration of insoluble particles ranged from 2 to 16 mg/L, increasing near to the associated gas flares and roads. At the four background points (Figure 1) in the southeast of Western Siberia (each at a distance of more than 100 km from major cities) at the end of winter in 2012–2018, the concentration of insoluble particles varied from 2.1 to 5.8 mg/L (on average, 4.1 mg/L with a standard deviation of 0.3 mg/L, 12 samples) [49]. In February 2014, the insoluble particles were studied in the upper 5 cm of snow cover in the Western Siberian Lowland across a 1700 km latitudinal gradient [46,47]. The concentration of particles in snow water ranged from 0.4 to 67 mg/L. The highest values were encountered in the vicinity of Tomsk, Surgut, and Noyabrsk; the lowest ones were located at 65° N.

The comparatively low concentrations of insoluble particles at the studied sites in the snowpack of the Ob River basin in February 2020 are apparently related to the fact that, in this expedition, the sampling sites were farther from roads and settlements than in the 2014 expedition [46]. Furthermore, the depth-integrated concentration of particles assessed in the present study may be lower than the upper 0–5 cm used in previous work [46]. Short-term deposition events linked to long-range transport of dust aerosols at the end of winter 2014 were probably not pronounced over the winter 2020.

The composition of the insoluble particles strongly depends on the processes of short- and long-range aeolian transport of the mineral grains. Differences in the mineralogical and granulometric composition of soils and parent rocks in the southern and northern parts of the study area may be linked to variable enrichment of atmospheric aerosols by mineral particles from different lithological provinces. Parent rocks in the southern part of the transect are mainly represented by loams [55,56]. In this area, the soils have a high content of feldspars (25–48%); whereas the content of quartz is slightly lower (19–47%) [57]. Soils in the north of the investigated transect are represented by sands and sandy loams [58–60]. Quartz is the predominant component of the mineralogical composition of soils in the north of Western Siberia (80–98%). The content of feldspars and plagioclases in the soils of this territory reaches no more than 18% [58].

In the taiga and tundra zones of western Siberia, podzols are widely distributed. They are characterized by the accumulation of weather-resistant minerals in the upper eluvial part of the profile [58]. One of these minerals is corundum, which is often found in samples located north of site 16. With the activation of deflation processes, the upper soil horizons are destroyed and the atmospheric suspension is enriched with erosion products. When certain areas are not covered with snow in winter, dust blown out of the soil can get into the nearby snow cover.

The main sources of ash particles and black carbon are gas flares, motor vehicles, and heating systems [44]. The content of black carbon and spherical ash particles (combustion spheres) increases in the regions of sites 14–18, where many gas flares are located (Figure 1). Chemical pollution of the atmosphere from the flaring of associated petroleum gas causes a well-known negative environmental impact from the oil production complex in Western Siberia and a number of other regions [61,62]. This negative impact is especially pronounced in the arctic and subarctic regions with their vulnerable ecosystems, where climatic changes occur most quickly [61,63–65].

At the end of the winter season in 2014–2016, studies of black (elemental) carbon (EC) in the snow cover of the Arctic territories of Russia (using the White Sea and Western Siberia watershed as an example) were carried out [66]. In February–March 2014, in Western Siberia, the highest concentrations of EC were observed near the large industrial center of Tomsk and in areas of active gas flaring in the Yamalo-Nenets Autonomous District. Overall, high values of anthropogenic black carbon emissions into the atmosphere are characteristic of the sparsely populated areas of the Tomsk Region and Yamalo-Nenets and Khanty-Mansi Autonomous Districts, whose industry is based on oil and gas production and where gas flaring is widely developed [67–70].

5. Conclusions

The concentration of insoluble particles in the snowpack of the Ob River basin in February 2020 was found to be at a relatively low level at most sites investigated (from 0.48 to 3.42 mg/L). This level corresponds to the background values in many regions of the Arctic and Subarctic. The comparatively low concentrations of insoluble particles at the studied sites in the snowpack of the Ob River basin in February 2020 are apparently related to the fact that, in this expedition, the sampling sites were farther from roads and settlements than in the 2014 expedition [46,47], and in 2020, there was no long-range aeolian transport of dust from areas open due to snow.

Particulate matter in snow consists mainly of biogenic (mostly fragments of plants) and lithogenic particles mixed with anthropogenic particles (ash and black carbon aggregates). Differences in the mineralogical and granulometric compositions of soils and parent rocks in the southern and northern parts of the study area contribute to the enrichment of atmospheric suspension with mineral suspension with sharp differences in the mineralogical composition. Feldspars and quartz dominate in the southern part and northern part of the transect, respectively. The content of plant debris was not found to vary significantly over the studied transect. The proportion of anthropogenic particles was found to rise near cities and areas of active hydrocarbon production and gas flaring without any clear latitudinal pattern.

In general, there was no strong pollution of the snowpack along the 2800 km submeridional profile in the Ob River basin in February 2020.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4433/11/11/1184/s1. Table S1. Positions of Snow Sampling Sites, Snow Depth, and Concentration of Insoluble Particles in the SnowPack (C, mg/L) in February 2020; Figure S1. Scanning electron microscope photography (SEM images) of selected insoluble particles and their energy-dispersive X-ray spectra (the probe zone is shown by a white rectangle: a,b—fragments of plants; c–f—ash; g–m—minerals (g—silica; h—quartz; I—biotite; j—saponite; k—augite; l, m—corundum); n—ash.

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