Conference paper

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Elemental composition of dust aerosols near cement plants based on the study of samples of the solid phase of the snow cover

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Abstract: This study is focused on the quantification of dust load on snow cover and chemical elements content in the solid phase of snow cover in the impacted areas of cement plants (the south of Western Siberia). Applying the instrumental neutron activation analysis, we identified chemical composition in the samples of the solid phase of snow cover. The results demonstrated that the dust load corresponded to the permissible pollution levels in the living zones. Dust pollution level varied from moderately hazardous to highly hazardous in the north-western impacted zone of the cement plants and raw material open pits. It was found that the predominant chemical element is Ca, as well as a group of rare-earth (Yb, Tb, Sm, La, Ce, etc.) elements in the solid phase of snow cover from the impacted zone of the cement plants.

Keywords: Aerosols; atmospheric precipitation; chemistry and climate; cement plant; dust load; elemental composition; particulate matter; snow cover.

Introduction

At present, air pollution is an urgent problem. One of the sources of air pollution is the cement industry, due to the high emissions of fine dust that can be transported over long distances by wind flows. Many researchers have shown the relevance of studying the influence of the cement industry on the environment. Brazilian scientists have identified the effect of cement dust on flowering plants (*Cedrela fissilis*) and found that when deposited and accumulated, cement dust reduces the amount of chlorophyll in plants and causes aging and premature fall of leaves. The impact of cement dust caused a change in the mineral composition of the leaves: there was an increase in the contents of Ca, Mg and Mn, a decrease in the levels of B, Cu and Fe [1]. Scientists from Nigeria studied 2.5 and 10 μm particulate matter measured with the AEROCET 531S instrument and calculated an air quality index. They found that kilns and chimneys of cement mills were the main sources of air emissions from cement plant production processes. Air quality near the plant boundaries was rated as good for $PM_{2.5}$, PM_{10} and CO, while for SO_2 it was rated as moderate in 71 % of points and good in only 29 % of points. For NO_2, about 64 % of the sampling sites have good air quality. In living zones (7 % of sampling sites), air quality was assessed as "unhealthy for vulnerable groups" (people with asthma or other respiratory diseases,

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the elderly and children are the most at risk groups) [2]. In the Polish city of Kielce, located in the area of three cement plants and limestone quarries, studies were carried out to analyze the physical and chemical properties and chemical composition of the snow cover. When measuring the concentrations of PM_{10} particles, it was found that during 19 days of the experiment, an excess of the permissible concentration level was observed and the highest concentrations exceeded the maximum daily concentration by more than three times. Analysis of the pH values of snowmelt water samples showed that they were in the range from 6.55 to 9.23, which indicates a significant contribution of the cement industry and mining industries [3]. Scientists from Novosibirsk conducted research on snow cover in the area of influence of the cement plant in Iskitim for several years (2012, 2013, 2014, 2017) and determined the contents of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, NO_3^{-}, SO_4^{2-}, inorganic dust in samples [4, 5].

Snow cover is used by many researchers to assess the technogenic impact on the environment due to its long-term occurrence and the ability to accumulate and retain pollutants [6–8].

The aim of this work is to carry out a comparative analysis of the elemental composition of samples of the solid phase of snow cover in the impacted zones of cement plants located in the south of Western Siberia.

Methods and materials

Sampling of snow cover

The objects of study were cement plants located in the south of Western Siberia – in the Kemerovo region (Topki town) with an annual cement production of 3.7 million tons (cement plant 1) and in the Novosibirsk region (Isktim town) with an annual production capacity of 2.1 million tons of cement (cement plant 2) (Fig. 1). The studied plants use wet production technology.

In February 2016, snow samples were taken in the vicinity of cement plant 1 and the living zone of cement plant 1. Snow cover sampling sires were located according to the vector system, taking into account the

Fig. 1: Location of the studied cement plants in Western Siberia (Topki – cement plant 1, Iskitim – cement plant 2; Russia; source: maps open source, modified).

prevailing wind direction (southwest). In total, 15 samples of snow cover were taken. At the beginning of March 2019, snow samples were collected in the vicinity of cement plant 2 in accordance with the prevailing wind direction (southwest). In total, 16 samples were taken in the study area. Snow cover samples were taken in zones of influence of cement plants 1 and 2, open pits for the extraction of raw materials, as well as in living zones of the study areas. The background area is considered with the area of Sredny Vasyugan, which has the status of a West Siberian background territory [9].

Preparation of snow cover samples

Snow cover samples were collected by the pit method for the entire thickness of the snow cover, excluding 5 cm above the soil to avoid contact with the ground. The weight of each sample averaged 18 kg. The work on the selection and preparation of snow samples was carried out in accordance with the some works [9–13]. The melting of the snow cover samples took place at room temperature in plastic basins; as a result of the melting, the resulting snow melt water was filtered through paper filters of the "blue ribbon" type. The solid phase of snow cover obtained after filtration was dried together with the filter and sieved through a sieve with a mesh size of at least 1 mm. After sample preparation, the solid phase of snow cover was weighed.

Analysis of snow solid phase samples and data processing

The elemental composition of samples was identified by the method of instrumental neutron activation analysis (INAA), which makes it possible to determine 28 chemical elements. A total of 29 samples were studied with INAA.

To assess the state of the environment, ecological and geochemical indicators were calculated in accordance with published works [12–15]. The calculation of the dust load Pn, (mg/(m^2 day)) was made according to the formula:

$$P_n = P_0/(Sxt)\,, \tag{1}$$

where, P_n is dust load; P_0 is the mass of the solid phase of snow cover (mg); S is the area of the pit (m^2); t is the time representing the stable snow cover formation duration up to sampling day (*d*). According to the accepted dust load gradation [10, 11] the degree of pollution and the level of environmental hazard of the territory were determined.

The concentration coefficient (K_c) of a chemical element shows the degree of its concentration in the solid phase of snow relative to the background content and is calculated by the formula [11]:

$$\kappa_c = C/C_b\,, \tag{2}$$

where, K_c is the concentration coefficient; C is the element content in the solid phase of snow (mg kg^{-1}); C_b is the background element content in the solid phase of snow (mg kg^{-1}) [11]. Based on the obtained values of the concentration coefficients, geochemical series of associations of chemical elements are constructed, which are a set of chemical elements, ordered as the values of the concentration coefficients decrease. Geochemical associations of chemical elements can characterize a possible source of environmental pollution.

Based on the obtained values of the concentration coefficient, the total pollution factor is calculated by the formula [10, 11]:

$$Z_c = \sum\kappa_c - (n-1)\,, \tag{3}$$

where K_c is the concentration coefficient; n is the number of elements taken in the calculation at $K_c \geq 1.5$. The values of the total indicator of pollution are compared with the gradation according to the level of pollution (Table 1).

Table 1: Gradation by dust load and total pollution factor [10, 11].

P_n, mg/(m^2·day.)	Z_c	Pollution level
Less than 250	Less than 64	Permissible
251–450	64–128	Moderately hazardous
451–850	128–256	Hazardous
More than 851	More than 256	Highly hazardous

Results

Dust load

We revealed permissible, moderately hazardous, hazardous and highly hazardous levels of pollution of the snow cover in accordance to the dust load calculations. The background dust load for the West Siberian region (Sredny Vasyugan village) is 7 mg/(m^2 day) [9].

In the living zones of the study areas, where cement plants 1 and 2 are located, the values of dust load correspond to a low degree of pollution and exceed the background values by 3.9 and 10.4 times, respectively (Table 2).

In the impacted zones cement plants 1 and 2, moderately hazardous and highly hazardous pollution levels are formed. These values are probably related to the annual production capacity of the plants under consideration. The greatest distribution of dust load in the impacted zone of cement plant 2 occurs in the northwest direction, which is possibly related to the peculiarities of the relief of this territory – the cement plant is located on the river bank [4, 5].

In the area of the open pit for the extraction of limestone and clay, the values of the dust load are different: in the area of the cement plant 1 corresponds to an moderately hazardous pollution level, otherwise, we observed the highly hazardous pollution level in the area of the cement plant 2. As the distance from cement plants 1 and 2 in the north direction, there is a tendency for a decrease in dust load (Table 2). The contribution to the dust load is made by the extraction of raw materials by the open method, as well as the transportation of the extracted raw materials by large-sized equipment.

Elemental composition

We identified a group of chemical elements which exceeded the background values in the impacted zone of cement plants. The group of these chemical elements includes Ca, Yb, Tb, Zn, Sm, La. As a result of calculating the concentration coefficients, we made the geochemical series of associations of chemical elements (Table 3).

In the impacted zones of the studied cement plants and residential areas, we found the highest concentration coefficient for calcium. Ca content is exceeded background values in 28 times in the impacted zone of

Table 2: Average values of dust load on snow cover in the impacted zone of cement plants.

Zone	P_n, mg/(m^2·day.)	Pollution level [10, 11]	P_n, mg/(m^2·day.)	Pollution level [10, 11]
	Cement plant 1		Cement plant 2	
Northwest zone of influence of the cement plant	1322	Highly hazardous	413	Moderately hazardous
Open pit	274	Moderately hazardous	932	Highly hazardous
Living zone	28	Permissible	73	Permissible

Table 3: Average geochemical rows of chemical elements associations in the solid phase of snow cover from the impacted zone of cement plants.

	Geochemical row in accordance with the concentration coefficients	
Zone	**Cement plant 1**	**Cement plant 2**
Northwest impacted zone of the cement plant	$Ca_{28,3} - U_{6,6} - Yb_{4,9} - La_{3,2} - Sr_{3,1} - Tb_{2,9} - Sm_{2,9} - Ce_{1,9}$	$Ca_{22,9} - Yb_{5,2} - Tb_{4,7} - Zn_{4,3} - Sb_{3,9} - La_{3,1} - Sm_{2,7} - U_{2,3} - Ce_{2,0}$
Open pit	$Ca_{31,3} - Sr_{3,6} - U_{3,5} - Yb_{3,1} - Tb_{2,2} - La_{1,8} - Sm_{1,8}$	$Ca_{23,2} - Tb_{4,0} - Yb_{3,6} - Zn_{3,3} - Sb_{2,3} - Sm_{2,2} - La_{2,1} - Ce_{1,7}$
Living zone	$U_{17,6} - La_{12,1} - Yb_{10,9} - Tb_{9,3} - Ca_{9,0} - Sm_{7,5} - Ba_{7,0} - Ce_{6,1} - Sr_{5,0} - Na_{4,3} - Ta_{3,2} - Zn_{2,6} - Th_{2,5} - Hf_{1,9} - Lu_{1,9} - Co_{1,7} - Sb_{1,6} - Cs_{1,6}$	$Ca_{14,6} - Zn_{4,6} - Tb_{4,0} - Yb_{3,8} - Sm_{3,5} - La_{3,1} - Sb_{2,8} - Sr_{2,1} - Ce_{1,9} - Cr_{1,7}$

Note: values of concentration coefficient ≥1.5.

cement plant 1, whereas Ca contents were about 23 times higher than the background value in the samples from the impacted zone of cement plant 2. These the highest contents might be associated with the production capacities of the studied plants. In the samples from living zones located near cement plant 1, the values of Ca content is higher the in the samples collected in the living zones near cement plant 2. This difference might be explained by the territorial location of the plants in urban areas. The cement plant 2 is located directly in the city, otherwise, the cement plant 1 is located far from residential areas.

The predominance of calcium in most areas is associated with the use of the main raw material for the production of cement as limestone ($CaCO_3$). Earlier we found that the mineral composition of the studied is characterized by calcite (from 70 to 95 %), as well as quartz (from 4 to 6 %) and cement clinker minerals as brownmillerite (from 4.5 to 15 %) and hathrurite (about 29 %) [16].

Kokovkin V.V. and Raputa V.F. [4] showed that the composition of the dust of a reinforced concrete plant includes such chemical elements as U, Yb, Ba, Ca, Hf, Sr, Tb, La, Ta, Sm, Ce, Th, Na. A large proportion of rare-earth elements (La, Ce, Eu and Yb) are concentrated in the non-magnetic fraction of cement dust [9]. Sources of rare-earth and radioactive elements can be emissions of the coal-fired boiler houses and residential heating in a living zone, because these element was found in coal [17].

In addition, clay, which is also used as raw materials in the cement plants, can be a possible source of rare earth-elements in the studied samples [18]. In addition, the found chemical elements can incorporate into the snow cover as a result of the use of various raw materials, such as granular slag, iron-containing additives, clays and limestone.

The Z_c values showed the permissible pollution level (Table 4). We identified the moderately hazardous pollution level in the living zones located near the cement plant 1. It could be connected with the presence of additional sources of chemical elements input, such as coal combustion on the local boiler houses. The largest contribution to the total pollution factor is made by Ca due to high values of K_c. Concentration coefficients of Yb, Tb, U, Zn and other elements were also contribute in pollution level. The highest values of the Z_c were recorded at a distance of 3.8 km from the cement plant 1 and 0.4 km from cement plant 2. The minimum values of the total pollution factor are formed in the samples collected in the distances from 1 to 4.7 km from the cement plant 1 and 1.7 km from the cement plant 2.

Table 4: Average values of total pollution factor in the impacted zone of cement plants.

Zone	Z_c	
	Cement plant 1	**Cement plant 2**
Northwest impacted zone of the cement plant	47	43
Open pit	41	36
Living zone	90	33,1
Average	59	37

Conclusion

Thus, we found that the values of dust load do not differ significantly in the impacted areas of the cement plants and vary from permissible to highly hazardous pollution levels. Hazardous and highly hazardous pollution levels are typical for the impacted zone of cement plants, as well as for open pit of the raw materials. Permissible pollution levels are observed mainly in the residential parts of the studied areas.

We found that Ca has predominant values relative to background concentrations in the solid phase of snow cover. This is probably due to the use of the main raw material component as limestone, which contains calcium. In addition, a group of rare-earth elements was identified as marker elements. The source of these chemical elements may be clay, which is also used in the process of cement production. Moreover, a possible source of rare-earth and radioactive chemical elements can be emissions of the coal-fired boiler houses and domestic heating.

The values of the total pollution factor in the studied zones vary from 33 to 90, which corresponds to permissible and moderately hazardous pollution level, correspondently. The maximum values of the total pollution factor are determined in the samples collected in 3.8 km from the boundaries of cement plant 1 and 0.4 km from the boundaries of cement plant 2. Ca makes the largest contribution to the values of the total pollution factor, as the main chemical element in raw material used.

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