Novorossiysk agglomeration landscapes and cement production: geochemical impact assessment

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Abstract. The article deals with assessing the environmental impact of marl mining and cement production in Novorossiysk city (Krasnodar krai, Russia). The existing methods of studying the environmental effects caused by the cement industry have been reviewed. Soil and aquatic vegetation sampling has been carried out and the gross concentration of metals in the samples has been defined. The research has been conducted in the certified and accredited laboratory using emission spectral analysis. The external control has been carried out via X-ray fluorescence analysis. Based on the collected data, main chemical pollutants in soil cover and water area near the cement plant have been identified. The contaminants released by urban enterprises and motor vehicle emissions, as well as fugitive dust from dumps and the cement factory, lead to multi-element lithogeochemical anomaly at geochemical barriers in soils. Accumulation of pollutants in soil depends on the type of land use and the area relief. The most contaminated aquatic landscapes have been identified in the inner bay. According to this information, the technical proposals can be prepared for environmental safety management in strongly polluted city areas, as well as for the reclamation design in the areas currently experiencing the negative impact of cement production.

1. Introduction

Novorossiysk city is located in the foothills of the North-West Caucasus on the Black Sea coast. The Novorossiysk industrial agglomeration consists of the city over 300,000 people, the eldest Russian cement factory "Novoroscement", the largest regional Novorossiysk seaport, as well as other enterprises and transport infrastructure objects. The cement factory was put into commission in 1882, and is currently producing 4 million tons per year. Open-pit mining of marl deposit in the agglomeration is a source of raw material for Portland cement manufacturing. According to the report "State and Protection of the Environment of the Russian Federation in 2011", the cement plant is recognized as a major air pollution source in the city.

The research is devoted to monitoring the environmental impact of cement factory, i.e. soil and water pollution. Dust emission is the key environmental pollution driver of a cement industry [2, 7, 17, 24, 25]. An impact of technogenic precipitations on geochemical landscapes is manifested in changing chemical element concentrations in soil [5, 11, 22], plant cover and agricultural lands [8, 13, 23], which can also affect human health in the course of environmental migration [20, 21]. Compared to those of other geochemical landscapes, urban soils experience the strongest technogenic load [1, 4, 6, 14–16]. In the studied landscapes, polluting element anomalies are formed and redistributed depending on the geomorphological conditions. The subsequent surface run-off leads to contamination of the water area [3, 9, 10, 19].

2. Materials and methods

The *transeluvial* (steep slopes), *transaccumulative* (low-angle gentle slopes), and *trans-superaquatic* (overwater slopes) geochemical landscapes are located in different geomorphological conditions in the Novorossiysk agglomeration (figure 1). These landscapes were ranged by the district building types: *single-storeyed*, *2–5 storeyed* and *5–10 storeyed*; the other studied areas were *industrial enterprise sites* (including cement factory, seaports, and railway station) and *wastelands*. As a result of intensive water contamination with toxic substances and increased turbidity, meso- and macro-benthos have almost completely disappeared from aquatic landscapes of Tsemes (Novorossiysk) bay. Landscapes with predominating brown algae *Cystoseira* are characterised by the greatest biomass. These landscapes are located along the both shores of the bay at the depth of 1.5–3.0 m.

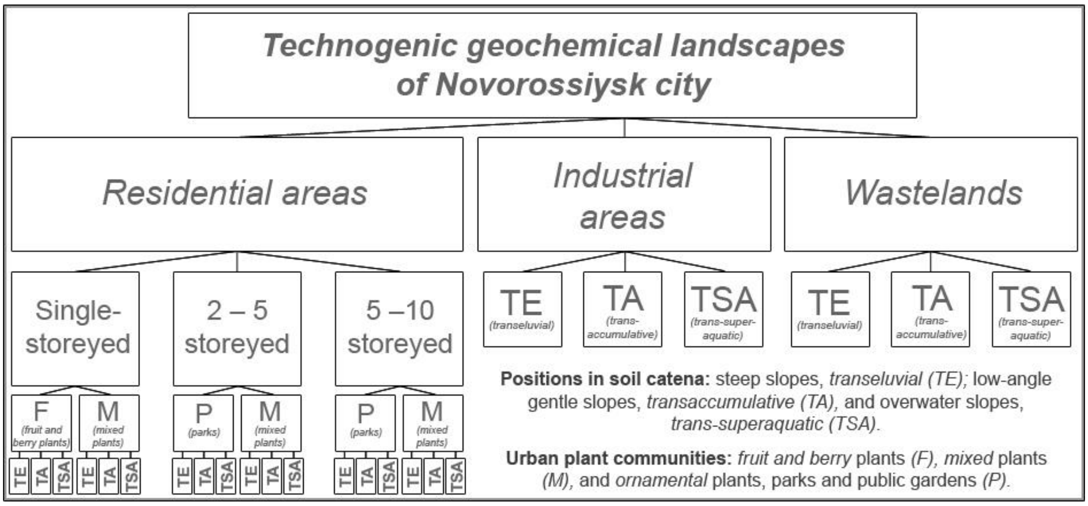

Figure 1. The division scheme of urban geochemical landscapes

Monitoring soil sampling (over 100 samples) was carried out twice, in 2014 and 2015. The samples were taken from the uppermost 10-cm soil horizons with a maximal intensity of geochemical processes in the landscape [12]. The brown algae used for aquatic landscape monitoring are the most sensitive to the changing environmental chemical content. The *Cystoseira barbata* algae used in the research are the most common in coastal aquatic landscapes coast of Novorossiysk. In 2009, 87 algae samples were collected in order to assess the current state of coastal landscapes of Tsemes bay, with the entire coastline being covered (figure 2). All spectral emission analyses of soil samples and seaweed ashes were carried out in the certified and accredited “Kavkazgeolsyomka” laboratory; and the external X-ray fluorescence control analysis was conducted in the Common Use Centre Laboratory of Mining University.

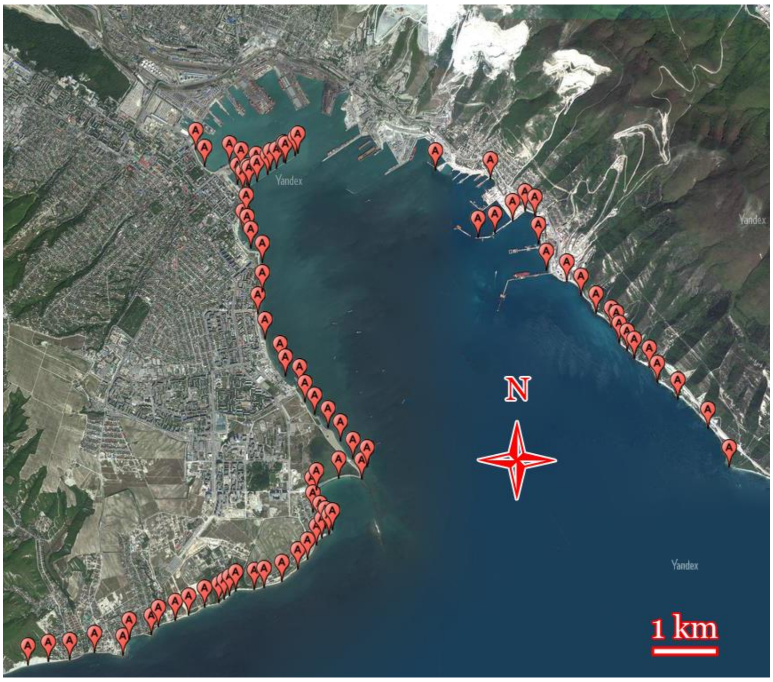

Figure 2. The schematic map of sampling points in Tsemes bay (based on the Yandex satellite image)

3. Results and discussion

Soil pollution was assessed separately in geochemical landscapes of residential areas, wastelands, and industrial sites. The joint effect of cement factory emissions, relief features and building height led to certain dispersion in elements' mean concentrations in soils of landscapes with various geomorphological conditions. The comparison between the *maximal* average concentrations and the *minimal* ones in the *residential area* shows that for 8 out of 22 studied elements the former is more than 1.5 times as much as the latter: *Pb* (4.5 times), *Sr* (1.7), *Ag* (2.2), *Cu* (1.7), *Zn* (2.5), *Ga* (1.5), *Sn* (1.6), and *Yb* (1.5). In soils of *wasteland* landscapes, under different morphological conditions, the excess of maximal average contents over minimal ones by more than 150 % was recorded for four elements only: *Zn* (1.7 times), *Pb*, *Co*, and *Ag* (1.6). We note that the maximal average contents of these elements in soils of *wastelands* are significantly lower than those in soils of *residential areas.* The distribution of the majority of chemical elements' average contents is more uniform in soils of *industrial areas*, including the main pollution source – the cement factory. The largest exceed of maximal average contents over minimal ones was recorded for two elements only: *Sn* (2.9 times) and *Pb* (1.7). The maximal average content of these elements in soils of *industrial areas* is higher than that in soils of *wastelands*, but lower than in *residential areas*.

Thus, *residential areas* mostly tend to be affected by the technogenic impact, resulting in the intensive soil pollution. The *maximal* for the entire city *average polluting element contents* were established in these areas. The greatest number of *unevenly distributed average element contents* was recorded in soils of *residential areas* under the influence of geomorphological and anthropogenic factors in combination. The concentrations of *Ag, Sn*, and *Mn* are maximal in soils of transeluvial landscapes in *residential areas* as compared with the whole considered area. At the same time, the minimal average contents in the uppermost parts of the slopes were defined for 10 elements: *Ag*, *Cu, Zn, Mo, Ti, Cr, Ga, Y, Yb,* and *Sc.* There has been a six-fold increase in the number of elements with the maximal mean contents, i. e. the number has changed for 18 *(Cu, Zn, Pb, Mo, Ba, Co, Ni, Ti, V, Cr, Ga, Li, Sr, Y, Yb, Sc, Zr,* and *Nb)* in soils of *transaccumulative* and *trans-superaquatic* landscapes of residential areas located below. This pollution is associated with relief characteristics [18]: the average contents in soils of upper slope parts were mainly due to the impact of pollutants precipitating after the sorption by cement industrial emissions.

The major part of defined element concentrations were lower in the ash of *Cystoseira* growing in the zones under the influence of biogenic terrestrial landscapes than in those influenced by technogenic landscapes. The highest average contents were noted at the observation points in the areas of urban wastewater treatment plant discharge (Aleksino settlement) and breakwater area, facing the greatest impact of precipitating cement plant emissions. The lowest contents of all the elements considered, except for *Mo*, are generally characteristic for *Cystoseira* of the western biogenic coast (table 1).

Table 1. The average element content in the ash of *Cystoseira barbata* in Novorossiysk bay, ppm

Part of Tsemes bay	Chemical element											
	Cu	**Zn**	**Pb**	**Co**	**Ni**	**V**	**Cr**	**Sn**	**Mo**	**Mn**	**Ti**	**Ba**
Western Biogenic	30.0	30.0	7.30	6.0	18.3	2.0	1.0	3.0	3.7	233	367	300
Myskhako	44.4	53.8	11.3	8.9	24.4	2.6	1.3	6.8	9.7	563	531	425
Aleksino	47.5	178	17.1	8.4	30.6	3.1	2.8	8.9	9.4	625	575	363
Central	51.8	57.3	13.8	8.2	22.7	2.6	1.2	6.0	6.2	464	636	455
Eastern Biogenic	41.7	48.3	10.3	6.5	22.5	3.0	1.0	7.0	5.3	583	617	467

The eastern biogenic coast is characterised by a slightly higher content of elements in comparison with the western one. The concentrations of five elements – *Cu* (41.7 ppm), *Zn* (48.3), *Pb* (10.3), *Co* (6.5), and *Cr* (1.0) are lower than those of *Cystoseira* sampled in the technogenic landscape influence zone. In this case, the concentrations of *Ni, V, Sn, Mo, Mn,* and *Ti* are close to the values typical for the coastal strip of Novorossiysk. Thus, the effect of pollutants precipitating from the air remains even on the coast with forest landscapes in the absence of direct technogenic impact. It should be noted that the cement plant is located on the eastern shore of the bay, and the increased metal content in algae may be related to the influence of atmospheric emissions.

Analysing the average element contents in *Cystoseira* ash samples of different years (table 2), we identified certain regularities of changes. The peaks of *Cu, Cr, Ni,* and *Mo* contents were observed in 2000 and 2009; *Mn, Ti,* and *Zn* – in 2009 only; *Pb* – in 2000 only. A slight increase in the average *V* content was noted in *Cystoseira* ash in 2004, and it remained at the same level in the samples of 2009. The increased content in the 2004 samples was also characteristic of *Sn*.

Table 2. The average Pb, Cr, Ni, and V content (with a 95% confidence level) in the ash of *Cystoseira barbata* in Novorossiysk bay, ppm

Year of sampling	Chemical element			
	Pb	**Cr**	**Ni**	**V**
1999	42.2±10.4	51.1±12.5	36.5±5.4	14.7±3.3
2000	46.1±13.0	58.5±7.6	45.9±5.7	11.5±1.1
2001	19.4±4.2	19.3±3.0	21.6±3.0	7.3±1.5
2002	12.0±2.0	13.5±3.0	19.1±2.0	6.3±1.1
2004	11.5±1.8	6.0±1.8	15.1±3.0	7.0±2.0
2009	10.2±3.0	7.5±2.4	22.8±6.0	7.0±3.0

Thus, based on the received data, it is possible to assume the persisting decrease tendency in the average contents of most studied elements in *Cystoseira* ash throughout 1999–2004, and elevated levels by 2009. Monitoring researches have shown that during the years 2001–2004 there were processes in the bay leading to a decrease of most investigated element contents in *Cystoseira* ash.

4. Conclusion

The urban soil pollution under the impact of mining and processing industry is determined by the local factors of chemical element migration and accumulation: geomorphological structures of urban area and types of land use. Monitoring researches in Novorossiysk city revealed that the change of these factors had caused a significant redistribution of chemical elements and their maximal accumulation in soils of residential areas. Pollutants are brought into the soil directly from the source of contamination, as well as due to the migration from landscapes located hypsometrically above.

The biogeochemical investigation allowed revealing the water areas of Tsemes bay that can be described as “relatively pure”– the western and eastern outer bay parts in the zones influenced by biogenic terrestrial landscapes. The inner bay part, experiencing the greatest impact of fugitive dust plant emissions, as well as the neighbouring Aleksino settlement, where urban wastewater treatment plants are located, may be recognised as the most polluted.

The pollutant migration factors should be accounted to determine the reasons for the landscapes to be particularly contaminated. The data obtained characterise the ecological and geochemical state of Novorossiysk urban environment, and allow developing the measures for improvement.

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