Daria Grishina

MICROELEMENT COMPOSITION OF RAPAKIVI GRANITE AS AN OUTSIDE BUILDING MATERIAL AND THE EFFECT OF AIR POLLUTION ON COMPOSITION VARIATION

Case of Saint Petersburg

Bachelor's Thesis
Environmental Engineering

April 2014

MAMK
University of Applied Sciences

DESCRIPTION

Date of the bachelor's thesis
April 2014

Author(s)
Daria Grishina

Degree programme and option
Environmental Engineering

Name of the bachelor's thesis

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Abstract

This Bachelor thesis is commissioned by Geologian Tutkimuskeskus (GTK), Finland as a part of South-East Finland - Russia ENPI CBC Programme aiming to investigate efficient use of natural stone in the Leningrad region and South-East Finland. The chemical composition of granite, as a vastly used building material, falls inside the ENPI Programme interest providing the basis for creating an extensive database on chemical variations in granite composition which can be caused by different natural and human-induced factors.

Saint-Petersburg city center which is famous for its granite architectural ornamentation becomes the object of the thesis investigation, aiming to study the influence of major anthropogenic air pollution sources, defined through the literature review, on buildings and constructions found in the city center and made of rapakivi granite.

The results of chemical analysis of rapakivi granite samples obtained from 9 sampling points were further examined to determine macro and micro element composition variations in crust and fresh parts with their comparison to reference materials provided by previous research done within GTK projects.

The variations of macro elements composition show the natural processes of stone weathering at a low level (proved by a number of weathering indices); while the variations of micro elements present a certain accumulation of the following 14 elements in samples crust: Se, Bi, Cd, As, Pb, Ce, Zn, Cu, La, Ba, Sr, Mo, S, Sb.

The chemical elements found in excess amounts have an anthropogenic, mainly traffic-induced, origin. The general pathway of accumulation is through the deposition together with city dust. The contamination of urban air with heavy metals cause threat to human health increasing the risks of cancer cases, cardiovascular and respiratory diseases and built environment forming a dirty layer on building surfaces. As such, the problems of Saint-Petersburg air quality should attract more attention with aims of constant improvement in the future.

Subject headings, (keywords)
Urban air quality, particulate matter, traffic related air pollution, rapakivi granite, weathering indices

Pages	Language	URN
56 + 3 pages Appendix	English	

Remarks, notes on appendices

Tutor
Aila Puttonen

Employer of the bachelor's thesis
Geologian Tutkimuskeskus (GTK)

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1. INTRODUCTION

Saint-Petersburg is the largest center of economic, industrial, cultural and scientific life of Nova-Ladozhskii region. Besides, it is the fourth most populous city in Europe and the most northern of the largest cities in the world congregating all the challenges of urbanization activities. Thus, environmental problems of Saint Petersburg become essential for the city and for nearby territories which experience its tremendous anthropogenic influence.

Clear ambient air becomes one of the urgent issues of the highly populated megapolis. For a long time the situation with city air quality is stated to be poor being in the top list of the most polluted cities in Russia, according to ratings by RIA News (Obrazkova 2013). This observation bears a great significance from the ecological, political, cultural point of view. Definitely a high level of air pollution in Saint- Petersburg has a negative impact on local population health as the statistical observations report higher increase in cancer cases in the city than the average in the country in 2009 (Ecologicheskii sojuz 2009). Besides, due to meteorological movement of air masses, the pollutants may be transported for long distances affecting the amount of pollutants detected at European monitoring stations. Not surprisingly unprecedented load of air pollutants influences the cultural heritage preservation as it negatively affects natural stone buildings, iron constructions and historical monuments damaging materials by means of wet and dry deposition and facilitating natural weathering processes. As such the city demands development of stricter air quality standards intended for improvement and preventions of air pollution in the city and in Baltic Sea area as well.

The quality of air in city environment has attracted attention of environmentalists for a long time. The massive set of recent research proved the steady interconnections between the levels of air pollution and the illness and morbidity rates of the city residents together with the increased risks to cardiovascular and respiratory diseases. According to the World Health Organization, 40-50 % of human diseases are somehow connected with the change of the environment and, above all, with air pollution. (WHO 2005.)

A special attention in literature is drawn to particulate matter in the air as numerous publications are set describing the character of major urban airborne pollutants, their concentrations and identification of their primary sources together with their distribution. The reports are describing the air pollution behavior in the cities all around the globe. The article of Daniela Salvagio Manta et al., (2002) investigates the deposition processes of heavy metals in the city soil samples. Later the scientific observations of concentrations of heavy metals found in airborne dust were described by a German team (Zereini, Alt et al., 2005). The Swedish report pays attention to the major city airborne pollutants found in sediments (Jönsson 2011). The work of Spanish researchers describes the major fine and ultrafine particles which can be found in the ambient air of a city (Fernandez-Camacho, Rodrigues et al., 2012). Many detailed researches are done mainly concentrating on heavy metals depositing into soil and dust underlining their harmful effects on human health, and terrestrial and aquatic ecosystems.

Recently a new approach was suggested by an Italian group of researchers utilizing cement monuments as passive samples which are able to accumulate the deposits of air pollutants. Their investigation was based on two elements – platinum and rhodium - which are the main tracers of traffic-based air pollution. The analytical examinations proved that heavy traffic and modern catalytic converters have an adverse effect on monuments surfaces contaminating them with different pollutants which are depositing with particulate matter. Thus the authors are raising the questions of public health and cultural heritage preservation concerns. (Rampazzi, Giussani et al., 2010)

The studies of that kind give a background for further analyses of ecological state of a large city principally basing on the idea that building constructions are damaged by air pollution and might serve as indicators of this negative influence. So far, our report aims at investigating the chemical composition variations of rapakivi granite as a widely spread building material in Saint-Petersburg center defining the level of chemical weathering of natural stone as a reaction to chemical pollution in urban environment.

2 AIR QUALITY IN BIG CITIES

For the further analysis of the ecological state of Saint Petersburg on the basis of chemical weathering of rapakivi granite it is important to provide an insight into the major sources of urban air pollutants in Russian Federation determining the environmental situation of the city with a special attention to particulate matter as the key component facilitating the surface contamination.

2.1 The sources of urban pollution in Russia

The levels of air pollution of Russian cities are concluded to be very high with the 80% of emissions coming from anthropogenic activities (Bityukova, Kasimov 2012). It is determined by the processes of urbanization, which becomes a characteristic feature of developing countries and is naturally accompanied by rapid growth of urban population due to economic development of the country setting the priority to cities as economic, political, and cultural centers (Soubbotina 2004). As such, environmental problems of cities are connected with the concentration of large numbers of people, vehicles and industrial enterprises on a relatively small geographical area. Particularly in Russia the situation is worsening due to “combination of low efficiency and high power intensity, outdated industrial specialization and inherited transport networks” which are inefficient for ever-increasing traffic loads. (Bityukova, Kasimov 2012)

In Russia, the monitoring of air pollution levels in cities is regularly carried out by the State Service for Hydrometeorology and Environmental Monitoring since 1965. Nowadays 692 stationary monitoring points are organized in 252 cities of the country monitoring the concentrations of multiple air pollutants (Sverlova 2009; Ecologicheskii sojuz 2010). The State Manual for Air Quality Control (1991) prescribes the procedures for measuring of the following air pollutants: PM, CO, NO_2, SO_2, H_2F_2, Cl_2, HCl, P_2O_5, H_2S, CS_2, aerosols of H_2SO_4 and HPO_3, CH_2O, HCN, heavy metals (Fe, Cd, Cb, Ng, Mn, Ni, Cr, Zn, Pb, Te, Hg), inorganic compounds of As, nitrogen compounds, aromatic amines (РД 52.04.186-89). Each air monitoring station fulfills monitoring and measurement of a certain number of air pollutants (from 4 to 38) depending on the location and priorities.

According to the state air quality monitoring data of the Russian Federation the ambient air is evaluated by means of integrated index of air pollution which determines the impact of air pollution on population health. The index is calculated by State Hydrometeorology and Environmental Monitoring Agency as a sum of annual averaged impurities concentrations divided by the corresponding value of maximum permissible concentrations. This quantitative assessment of air pollution distinguishes the natural or baseline pollution and anthropogenic pollution as the index is expressed through the averaged impurities concentration, which varies in time in the atmosphere and depends on direct emissions from anthropogenic activities and natural emissions of pollutants. The impurities, measured in certain sampling points in a city during a day, a month or a year, undergo concentration analysis. The analysis allows separating substances which exceed the maximum permissible concentration (MPC) determining the severe air pollution making the results reliable for evaluation of chronic, long-lasting air pollution. (Sverlova 2009.)

In accordance to modern assessment methods the level of air pollution is considered to be low if the integrated index performs 0-4; the level of air pollution is increased if the index is 5-6; the level of air pollution is high if the index shows 7-13; and the level of air pollution is very high if the integrated index equals to or above 14 (Sverlova 2009).

In Overview of the environmental statement and pollution in the Russian Federation in 2012 it is stated that the levels of air pollution in cities remain high. In 138 cities (64 %) where the monitoring takes place the pollution levels were assessed as high and very high; merely 18 % of the cities showed low levels of pollutant concentrations. Only in 5 % of the cities the level of air pollution is low; and in 15 % of the cities natural pollution sources facilitate the impacts of man-induced influence worsening the air quality. Besides, in 214 cities (85 %), the average annual concentrations of at least one substance exceed MPC by one. (Roshydromet 2013; Makarova, Ionov et al., 2011.)

The State Agency regularly publishes a register with top-priority cities suffering the highest levels of air pollution. In 2012 the register included 28 cities with 19.1 mln people as the total number of inhabitants where the integrated index is equal or above 14. The main sources of air pollution in these cities are named to be oil-refinery industry, nonferrous-metal industry, chemical processing industry; additional contribution is done by coal-fired thermal stations and traffic. (Roshydromet 2013.)

TABLE 1: The main sources of anthropogenic air pollution and key pollutants (Segal 1987)

Air Pollution Source	**emitted aerosol**	**gaseous discharge**
Boilers and Industrial Furnaces	Ash, soot	NO_2, SO_2, CO, aldehyde, carboxylic acids, benzo(a)pyrene
Vehicle Engines	Ash	CO, NO_2, aldehydes, noncancerogenic hydrocarbons, benzo(a)pyrene
Oil-refining industry	Dust, ash	SO_2, H_2S,NH_3, NO_x, CO, hydrocarbons, mercaptans, acids, aldehydes, ketones, carcinogenic substances
Chemical process industry	Dust, ash	depending on the process (H_2S, CS_2, CO, NH_3, acids, organic substances, solvents, VOC, etc.)
Metallurgical engineering and chemical recovery carbonization	Dust, black iron oxide	SO_2, CO, NH_3, NO_x, fluoride compounds, nitriles, organic compounds, benzo(a)pyrene
Mining industry	Dust, ash	depending on the process (CO, fluoride compounds, organic substances)
Food-manufacturing industry	Dust	NH_3, H_2S (polyblend organic compounds)
Construction materials industry	Dust	CO, organic compounds

Anthropogenic pollution of urban air accounts for a greater variety of different sources emitting enormous amounts of various substances which cause the significant damage to the environment due to their saturation of the ability of the atmosphere to self-purificate. Nowadays thousands of anthropogenic origin pollutants can be traced in the atmospheric boundary layer. Due to continuing growth of industrial and agricultural development new toxic chemical compounds are releasing into the environment

(Maksakovskii 2008). The major sources of anthropogenic air pollution and the key pollutants are presented in Table 1.

Apart from the bulk amounts of respirable particulate matter and sulfur, nitrogen and carbon oxides, complex organic compounds, organochlorides, nitrogen compounds, technogenic radionuclides, viruses and microbes are among the main anthropogenic pollutants of urban air environment. Besides, the most dangerous dioxin, benzo(a)pyrene, phenols, formaldehyde, carbon disulfide are widespread in the air basin of Russia. Suspended solids are presented mainly by soot, calcite, quartz, hydrous micas, kaolinite, feldspar, sulfates and chlorides. There is a tendency of particulate matter found in the atmospheric ground layer of the European part of Russia to accumulate heavy metals including lead, tin, chromium, cobalt, nickel, strontium, phosphorus, scandium, calcium, beryllium, niobium, tungsten, molybdenum, lithium, beryllium, gallium, barium, zinc, manganese and copper. Some of them are potentially toxic for human health and ecosystems resistance. (WHO 2005; Roshydromet 2013.)

The data provided by the governmental agency demonstrate that the amounts of point-sources pollutants have a strong interconnection with the economic development of the country. As the industry remains a major factor that currently determines the ecological conditions of the cities in Russia, the amounts of pollutants vary steadily increasing and declining together with economic depressions in 1990 and 2008 and growths in 1999 - 2007 (Bityukova, Kasimov 2010). While the influence of nonpoint sources mainly coming from excess load of transport continues to be of great importance in the country as the volume of motor vehicle fleet has a firm incline to increase accounting for 233 passenger cars per 1000 inhabitants in 2009 according to UNECE Statistical Database (2009). The city environment witnesses the excessive private vehicle use as the amount of personal cars registered by State Automobile Inspectorate has increased by 6.4 % in 2012 by comparison with previous year (GIBDD 2012), and 51 % of the vehicles are older than 11 years (UNEP 2010) carrying on older combustion engines which make it difficult to meet the emission standard requirements. At the same time there is a gradual decrease in public transport use due to different reasons including undeveloped traffic routes, private ownership character of the service providers and lack of governmental subsidizing to the economic sector (Dimitrov 2004). In connection with this, traffic bears a great responsibility for almost all the air pollutants detected in some cities.

2.2 The level of air pollution in Saint-Petersburg

Nowadays high level of urban air pollution in Saint Petersburg has become one of the main consequences of negative anthropogenic impact on the environment. Generally the air quality is affected by industrial activities, transport and natural climatic conditions. (Anisimova 2008.)

From the point of view of weather conditions, Saint Petersburg has an adventurous location with comparison to other cities as it has marine climate with positive situation for emissions dispersion. For example, a steady decline in the concentration of impurities in the first half of the 90s is largely connected to the predominance of western quarter winds. Thus the meteorological factors are playing a certain role in air quality evaluation and modeling, though these conditions still have a negligible impact for the summarized ecological statement. (Anisimova 2008.)

Systematic monitoring of air quality in the city has been carried out by Hydrometeorology and Environmental Monitoring Agency at three stationary points since 1969. The four main impurities were monitored at that time including particulate matter, sulfur dioxide, nitrogen dioxide and carbon monoxide. With the time the amount of stationary monitoring points as well as the defined chemical compounds has increased in accordance to newer tasks and legislative standards applied for the process of organization and implementation of monitoring activities. By the end of the 1980s the measurement took place three times a day at 16 fixed monitoring stations registering 16 chemicals. Later, due to the lack of financing, this network was reduced to 7 stations measuring 9 pollutants, and in the end of the 1990s with the growth of environmental concerns monitoring activities were enlarged. (Ufimtseva, Terekhina 2005, 95-96.)

Nowadays, according to Report on Ecological Situation in Saint Petersburg (Golubeva, Sorokina 2013), there are 21 stationary monitoring points with automated systems of air quality control which satisfies the requirements set by Directive 2008/50/EU on ambient air quality and cleaner air for Europe. The monitoring points are located in different parts of the city evaluating the amounts of the city’s prioritized air pollutants, which are particulate matter, sulfur dioxide, carbon dioxide, phenols, formaldehyde, ammonia, benzo(a)pyrene, nitrogen dioxide, ozone, ethylbenzene, hydrogen chloride, benzene, hydrogen sulfide, xylene and some other components. Also the actual status of the urban airshed in Saint Petersburg is assessed as unsatisfactory in spite of numerous air protection programs implemented by the government. The reason for this is hidden not only in vast volumes of industrial emissions but also in rapidly increasing vehicle fleet in the city. It is recorded that in 2007 the maximum permissible concentrations for certain air pollutants exceeded the norm in 2-3 times. And in some areas of the city a tenfold excess was observed. (Anisimova 2008.)

It is stated that the total air emissions from stationary and nonpoint sources are characterized by the following data: in 2012 492,300 tons of air pollutants were emitted including particulate matter - 2,900 tons, SO_2 - 7,600 tons, CO - 358,000 tons, NO_x - 65,700 tons, CH_x - 10,600 tons, VOC -45,600 tons (Golubeva, Sorokina 2013).

Table 2 shows the air pollutants emissions data coming from stationary and nonpoint (vehicular and railroad traffic) in the city in 2012. The contribution of nonpoint pollution sources to the total emissions of air polluting substances comprises 89 %; among them particulate matter - 34 %, sulfur dioxide – 27 % , carbon dioxide – 95 %, nitrogen oxide (in terms of nitrogen dioxide) – 58 %, hydrocarbons without VOC (CH_x) – 17 %, and volatile organic compounds (VOCs) – 90 %. (Golubeva, Sorokina 2013, 5.)

TABLE 2: Air pollutants emissions from stationary and nonpoint sources in 2012, thousand tonnes (Golubeva, Sorokina 2013, 5)

	Total	**PM**	**SO_2**	**CO**	**NO_x**	**CH_x**	**VOC**
Stationary	68,9	1,9	5,6	19,1	27,7	8,8	4,7
Nonpoint	423,4	1,0	2,02	338,9	35,3	1,8	40,6
including: vehicular traffic	419,3	0,7	2,0	338,2	35,3	1,8	40,6
railroad traffic	4,1	0,3	0,02	0,7	2,7	0,01	0,3
Total	492,3	2,9	7,6	358	65,7	10,6	45,6
Emission per capita (kg/person)	98,5	0,6	1,5	71,6	13,1	2,1	9,1

The comparative data analysis of stationary air pollutants shows that the total amount of emissions has increased by 4 % (3,000 tonnes) in 2012 compared to the previous year. According to the Territorial Department of the Federal State Statistics for Saint Petersburg and Leningrad region the growth of emissions in 2012 compared to 2011 is determined by the growth of industrial production in Saint Petersburg. In 2012, the industrial production index in Saint Petersburg was estimated to be 104.3 % compared to year 2011. Index of mining activities was 107.3 %, processing industries - 104.7 %, the manufacture and distribution of electricity, gas and water - 100.5 % (Golubeva, Sorokina 2013, 6).

At the same time the total amount of emissions from nonpoint sources has increased by 10.4 % (44,500 tonnes) in 2012 by comparison with the previous year. The increase in air pollutants emissions from motor vehicles correlate strongly with the continuing growth of motor vehicle fleet. Table 3 shows the data of the number of vehicles registered in St. Petersburg in 2010, 2011 and 2012 collected by State Traffic Safety Inspectorate. Thus, the total number of vehicles in 2012, compared with 2011 has increased by 75,056 units (4.3 %), including cars - by 11,506 units, trucks - by 62,066 units, and buses - by 1,484 units. (Golubeva, Sorokina 2013, 7.)

TABLE 3: The number of vehicles according to State Traffic Safety Inspectorate (Golubeva, Sorokina 2013, 8)

Year	Passenger cars	Trucks	Buses	Total
2010	1,462,362	129,043	22,714	1,617,119
2011	1,525,967	138,967	20,965	1,685,899
2012	1,537,473	201,033	22,449	1,760,955
Increase (+) compared to 2011	+11,506	+62,066	+1,484	+75,056

As a result, motor vehicles and combustion processes become the major source of air pollution in Saint Petersburg. Unprecedented growth of passenger cars and trucks in recent years determines more than half of all harmful emissions entering the environment additionally giving rise for energy consumption concerns as well as for increased risks of road-related injuries and unsatisfactory public attitude due to high traffic density and constant traffic jams.

The contribution of air pollutants originated from traffic mainly depends on the type of gasoline used. As such, Table 4 presents the data of air pollution emissions in relation to engine type declared by the state agency (Golubeva, Sorokina 2013, 8).

TABLE 4: The contribution of traffic in relation to engine type to air emissions in Saint Petersburg, % (Golubeva, Sorokina 2013, 8)

Vehicle type	**Type of fuel**	
	Gasoline	**Diesel**
Passenger vehicles	50.4	0.2
Trucks	40.5	4.0
Buses	4.7	0.2

On average, with the estimated national fuel economy of 8.11 l / 100 km (UNEP 2010) and with average 15 thousand kilometers per year a gasoline car burns 1,5 tons of fuel and about 26 - 30 tons of air, including 4,5 tons of oxygen, which is 50 times more than a human needs. As a return a vehicle emits 700 kg/year of CO, 40 kg/year of nitrogen dioxide, 230 kg/year of unburned hydrocarbons, and 2-5 kg/year of solids (Kovalenko 2013).

A vehicle pollutes air not only with toxic components of exhaust gases and fuel vapors, but also with the products of tires wear and brake-shoe lining. The vapors from open fuel tanks are constantly ending up in the atmosphere which is the most obvious at the gas stations during summer periods. And the cars parked at the close proximity to the residential units cause the greatest hazard to public health. (Dimitrov 2004; Hjortenkrans, Bergbäck 2007.)

The numerous studies related to the topic proved that the volume of cancer cases is reported 3-4 times more often among the residents of the buildings located close to the roads carrying heavy traffic (up to 10 m) than among those who are living at a 50 m distance from the road (Kovalenko 2013). Besides, the long-term exposure to benzene and NO_2 (Raaschou-Nielsen, Hertel et al. 2001) and to CO, NO_x and $PM_{2,5}$ (Heck, Wu et al. 2013) is linked to the risks of lymphomas and leukemias in children.

Reasonably planned and circumspect organization of traffic flows in the city can significantly reduce air emissions from motor-vehicle transport. Small amount of underpasses and a large number of intersections, causing a backup of cars running at idle, lead to a sharp increase of air pollution. When a car is idling or warming up the engine, it becomes a source of increased air pollution due to instable work of the engine resulting in a larger proportion of incomplete combustion. Additionally, unreasonable speeding leads to over-enrichment of air-fuel mixture at acceleration mode that increases the emissions of unburned fuel and other products of incomplete combustion. Previously used city planning techniques especially obvious in historical parts of the city impede air circulation and contribute to the increased levels of pollution concentration in the streets. Therefore, the development of transport infrastructure in the city is one of the basic means to improve air quality. (Dimitrov 2004.)

2.3 Criteria air pollutants

There is a list of human health-based criteria air pollutants which was established by National Ambient Air Quality Standards and accepted worldwide. It enumerates five primary criteria pollutants - PM_{10}, CO, NO_2, SO_2, particulate lead and ground-level ozone. (Corbitt 1998; Cooper, Alley 2002.)

In December 2012, EPA issued a new document with a more precise differentiation of particular matter enlarging the list of criteria air pollutants by one. Since then, particulate pollution is grouped into two categories setting annual and 24-hour limits for PM_{10} and $PM_{2,5}$. (EPA 2012)

All the criteria air pollutants become commonly found in the polluted atmosphere as they are emitted in large quantities by industrial and transportation sources being mainly products of combustion of fossil fuels and industrial processes. These pollutants are blamed to cause smog, acid rains, health and the environment hazards together with materials damage. (Corbitt 1998; Cooper, Alley 2002.)

- Particulate matter. The effects of particulate matter are often evident as it can reduce visibility by the physical property to scatter light. Inhalation of particulate has adverse effects on human health increasing public mortality rate. Having natural and anthropogenic origin, solid and liquid particles form atmospheric aerosols which are composed of a variety of organic and inorganic elements. Only by EEA member countries, around 2,250 ktonnes of primary particulate matter were emitted in 2010 (EEA 2012). In a global scale the emission values are much larger attracting the attention for the further reduction. (Sb.)

- Carbon monoxide. A special place among gaseous impurities is taken by carbon dioxide the amount of which annually increases by 0.2 % .CO is emitted due to incomplete combustion of carbonaceous materials such as combustion of solid waste, exhaust gases and industrial emissions. Then it is oxidized to CO_2. Annually, around 1250 Mt of CO is released in the atmosphere where it reacts with other atmospheric components and contributes to the planet temperature rise and the greenhouse effect. (Sb.)

- Nitrogen compounds. Annually, around 20 Mt of nitrogen compounds are released in the atmosphere then undergoing chemical reactions. As such, when exposed to sunlight nitrogen monoxide is intensely oxidized by atmospheric reactions to nitrogen dioxide. In the atmosphere nitrogen oxide and nitrogen dioxide are in dynamic equilibrium transforming into each other as a result of photochemical reactions in which they act as catalysts. Their ratio in the air depends on the intensity of solar radiation, the concentration of oxidizing factors, and etc. (Sb.)

- Sulfur compounds. Sulfur dioxide (SO_2) is released into the atmosphere by industrial activities and with the exhaust gases of vehicles. In the atmosphere, it reacts with other compounds, in particular with hydrocarbons. The oxidation of sulfur dioxide to sulfur trioxide takes place in the atmosphere by catalytic and photochemical reactions. The end product is an aerosol or a solution of sulfuric acid in rainwater. In dry air oxidation of sulfur dioxide is extremely slow. In the presence of nitrogen oxides the oxidation rate of sulfur dioxide is increased regardless of humidity. (Sb.)

- Lead. It enters the atmosphere mainly in the form of lead halides and lead oxide (II) with the exhaust gases of vehicles causing a significant negative impact on subcellular, cellular and organ system levels. (Sb.)

- Ozone. Ground-level zone is very reactive due to its high oxidizing ability. In the urban air environment ozone appears as a secondary pollutant being a product of other pollutants reactions in presents of sunlight. (Sb.)

- Hydrocarbons. The group of hydrocarbons is not related to criteria air pollutants, though they attract special attention due to variety of chemical structures, abundance in the polluted air and the effects on ozone depletion. Depending on the volatility or vapour pressure the group is divided into volatile organic compounds and semi-volatile organic compounds. In this group methane takes a special position. Individual reactive hydrocarbons make a different contribution to ozone depletion. (Sb.)

3 PARTICULATE MATTER AND DUST IN AIR ENVIRONMENT

The surrounding ambient air always contains a certain amount of mechanically suspended dense particles, which form the airborne particulate matter. Some particles can be found even at high altitudes and at great distances from polluted areas in the atmosphere causing a significant impact on climate, visibility, ecosystems and building materials. The amount of particulate matter, its nature and degree of influence on the human health vary greatly and depend mainly on the location and source of particulate matter and on its composition. Recently, one of the major factors affecting the poor air quality in Saint Petersburg is related to the amount of particulate matter observed in the city’s atmosphere. (Kovalenko 2013.)

3.1 Overview of particulate matter

Generally, the term “particulate matter” refers to “a mixture of solid particles and liquid droplets found in the air” (EPA 2013). In other words particulate matter is a dispersed system with gaseous dispersion medium and solid disperse phase consisting of solid or liquid particles of different size in the air in suspension. It is originated from a vast variety of sources both natural and anthropogenic located in the vicinity of measurement area or separated by a certain distance and located in other countries.

According to William Hinds (1998) different terms are used for certain types of particles dispersed in a gas, depending on size, shape and behavioral characteristics - dust, soot, fumes, smoke, fog, haze, etc. For example, dust is a general term applied only to particulate matter which is divided into (a) sinking or settling mechanically disintegrated by crushing or grinding material where particles are exposed to gravitation forces as their size range from submicrometer to more than100 µm and (b)suspensions which are mechanically stable due to the particles size of 0.1-5 µm. Fumes contain both solid and liquid particles with size from 0.01 to 1 µm in diameter. They originate either from the substances volatilizing at high temperatures or from chemical reactions such as oxidation. The term smoke refers to a visible aerosol generated by incomplete combustion with liquid or solid particles usually less than 1 µm though tended to agglomeration. Mist and fog present a gaseous medium with liquid condensated or dispersed particles of 0.01-3 µm. (Hinds 1998.)

Particulate matter reaches the city environment due to the weathering of rocks, deflating of topsoil, forest fires, burning fuel from thermal power plants, ferrous and non-ferrous metallurgic industry, machine-building industry, building material enterprises, traffic. As a rule the concentration of particulate matter in cities or around industrial centers is much higher than in rural areas. (Hinds 1998.)

3.1.1 Chemical composition of particulate matter

The suspension of particulate matter are composed of different chemical compounds and elements including elemental and organic carbon, sulphate, nitrates, ammonium, sodium chloride, mineral dust, water. Trace components occurring in amounts less than 1 ng/m^3 are aluminum, calcium, carbon, iron, potassium, sodium, silicon. Often there are certain amounts of copper, zinc and titanium, and even lower content of antimony, beryllium, bismuth, chromium, cobalt, cesium, lithium, magnesium, nickel, rubidium, selenium, strontium, and vanadium. Besides, there is always organic material including bacteria and viruses. (Fernandez-Camacho, Rodrigues et al., 2012; Hinds 1998.)

Though chemical composition of particles depends on the source and the age (Puttonen 2011), most of the elements found in particulate matter are particularly hazardous for human health and the environment. Table 5 shows the classification of chemicals according to their harmful effects (Sverlova 2009).

TABLE 5: The classification of chemical elements according to their hazard category (Sverlova 2009)

Hazard category	The level of hazard	Chemical elements
I	extra hazardous substances	As, Cd, Hg, Pb, Zn, F, V
II	highly hazardous substances	B, Co, Ni, Li, Mo, Cu, As, Sb, Cr, Na, Se, Cl.
III	moderately hazardous substances	Ba, Fe, Mg, W, Sr, Ag
IV	low hazard substances	Al, Ti, Mn, S, Br.

Organic and inorganic pollutants can be emitted directly into the atmosphere due to combustion processes in thermal power plants, waste incineration facilities, household ovens, internal combustion engines, cement kilns, due to forest fires, or volcanic activities. Additionally, these chemicals can be released by evaporation from the open sources, or as a result of soil and dust resuspension. Literary they are called primary pollutants. Some of these chemicals undergo certain chemical reactions in the air with other pollutants due to photochemical processes generated by UV radiation and increase of the temperature. They form so-called secondary pollutants which might cause a more severe impact on the environment due to their toxicity and long retention time in the atmosphere. (Hinds 1998.)

Particles are usually composed of a mixture of chemical components both soluble and insoluble which are attached together due to absorption and adsorption processes. As such, respirable particles usually cause a multifunctional disorder to the organism’s tissues. Being washed down to the surface with water droplets it is accumulated in soils having a slow biodegradation potential. (Fernandez-Camacho, Rodrigues, etc. 2012.)

3.1.2 Mass concentration and particle size

The factors, which are commonly used to characterize total suspended particulates and which are significant for evaluating hazardous health impact, are the mass concentrations of particles with a diameter less than 10 µm (PM_{10}) and particles with a diameter less than 2.5 µm ($PM_{2.5}$). So that, PM_{10} presents a group of particles with the aerodynamic diameter < 10 µm; while $PM_{2.5}$ where the aerodynamic diameter is < 2.5 µm is often referred to a group of fine particles which also includes ultrafine particles with a diameter less than 1 µm. (Puttonen 2011; Hinds 1998.) The smaller the particle the more hazardous potential health impact it can expose due to inhalation and respiratory penetration ability and mediated toxicity.

The size and density of particulate matter determines its aerodynamic diameter which affects mainly its deposition rate: the larger the particulate matter aerodynamic diameter, the faster it settles resulting in a faster atmosphere self-cleaning. As such, particulate matter of a diameter of 0.1-1 µm may remain in the atmospheric air for many days or weeks and is respectively subjected to transportation over long distances with afterwards deposition to the Earth's surface. (Sverlova 2009; Puttonen 2011.)

The amount of particulate matter in the urban air environment varies with time and depends on meteorological parameters including weather condition, solar radiation, wind direction and speed and industrial activities (working days vs weekends and holidays) and road traffic intensity (morning-evening rush hours vs weekends and holidays) (Fernandez-Camacho, Rodrigues et al., 2012.)

The particulate matter is usually scavenging from the atmosphere by two processes of wet and dry precipitation. The decrease is observed under two conditions: (a) after rainfalls or after fog affection due to the processes of wet precipitation, and (b) with the increase in height due to gravitation forces. However, in the higher layers of the atmosphere the concentration of particles may increase due to outer space sources. (Puttonen 2011; Kovalenko 2013.)

The rain and snowfalls are an important part of air pollutants scavenge due to their bonding by snowflakes, fog or rain droplets. It is calculated that the clearing of the atmosphere goes faster if the droplets/snowflakes have large effective radius and fall with noticeable speed. (Semenchin 1993.)

As such polluting compounds may be dissolved in cloud droplets during the formation of clouds. After pollutants absorption by cloud droplets, these substances can undergo chemical reactions, which are similar to the reaction of sulfur dioxide and ammonia leading to the formation of ammonium sulphate, or other chemical interaction. Cloud droplets with dissolved pollutants are transformed into larger raindrops falling down on the surface of the Earth. The process is known as in-cloud washout or rainout. (Levine, Schwarz 1982; Semenchin 1993; Puttonen 2011.)

During rainout the amount of contaminants entering the liquid phase by diffusion is proportional to their concentration inside the cloud. Since clouds are typically formed at a relatively large distance from the Earth's surface, the process of rainout is effective when meteorological conditions facilitate the vertical mixing of air masses in the lower atmosphere. Therefore, the process of in-cloud washout is most effective at long-range transport of pollutants. Under such conditions, contaminants can enter into the upper atmosphere. (Semenchin 1993.)

The second type of pollutants removal from the atmosphere is the process of below-cloud scavenging. While falling down, raindrops capture pollutants and carry them to the underlying surface. However, this process is generally inefficient because of the low relative density of raindrops in the air mass containing dirt, and a contact time of minor droplets and pollutant compounds. However, in areas with high levels of air pollution and significant rainfall below-cloud washout may play an important role. (Semenchin 1993; Levine, Schwarz 1982.)

In the absence of precipitation pollutants may also fall down on the underlying surface and vegetation. This process of removing pollutants from the atmosphere is called dry precipitation and it is based on gravitational settling of particles. There are a number of important deposition processes that lead to the removal of atmospheric particles and gases. (Semenchin 1993; Puttonen 2011.)

Dry deposition rate depends on the chemical properties of the air pollutants. As such, gaseous compounds with a greater chemical reactivity have a higher deposition rate. Dry deposition takes place mainly due to the fact that in the proximity to the surface there is a boundary air layer with thickness of 10-100 µm. Since this layer is practically stable, particles or gases appearing in it come into direct contact and interact with particles of soil or vegetation due to Brownian motion. As a consequence of these interactions (chemical reactions, physical or chemical sorption), air pollutants are removed from this thin boundary layer. Thus, there is a directed flow of contaminants from the atmosphere into a stable boundary layer and then directly to the underlying surface. (Semenchin 1993.)

3.1.3 Effects of particulate matter

In terms of human health impacts, PM_{10} and $PM_{2,5}$ present a respirable mixture of potentially hazardous chemicals which are so small in a diameter, that can penetrate into the thoracic respiratory system. The negative influence of respirable particulate matter on human health has a full documented acknowledgement. This effect is due to both short (within hours or days), and long-term (months or years) exposure and include (WHO 2013):

- respiratory and cardiovascular morbidity, such as worsening asthma and respiratory symptoms, and increased incidence of hospitalization;

- mortality from cardiovascular and respiratory diseases and lung cancer.

There is sufficient evidence of the impact of short-term exposure of PM_{10} on the respiratory system, but in terms of mortality (especially mortality as a result of long-term exposure) $PM_{2.5}$ becomes a more important risk factor than PM_{10}. It is estimated that with the increase in PM_{10} concentration by 10 mg/m^3, daily all-cause mortality is scaling up by 0.2 - 0.6 %. In conditions of chronic exposure to $PM_{2.5}$, each increase in $PM_{2.5}$ concentration by 10 mg/m^3 is associated with increasing long-term risk of cardiopulmonary mortality by 6 - 13 %. (WHO 2013.)

Especially vulnerable are the sensitive groups of people suffering lung disease or heart disease, as well as the elderly and children. It is stated that particulate exposure adversely affects lung development in children, resulting, in particular, in reversible disturbances in pulmonary function, as well as in chronic slowdown in lungs growth and long-term inefficiency of pulmonary function. There are no evidences that would confirm the existence of any or safe exposure level or threshold below which there is no occurrence of any negative health consequences. In a modern city environment a person can be exposed to negative particulate matter impact everywhere, as it does not depend on the willingness or unwillingness of people in connection with which its importance as determinants of health will be further increased. (WHO 2013.)

A significant influence of particulate matter is observed when the questions of cultural and architectural heritage preservation are discussed. Due to the wet or dry deposition processes, particulate matter covers building surfaces causing their soiling, discoloration, loose salt deposits, and crusts (Fitzner, Heinrichs, Kowatzki 1995). The effect of particulate air pollution becomes visible with surface coverage of 5 %, though it depends on general color of the particles and the relative color of the building surfaces together with their positioning. (Grossi, Esbert et al., 2001.)

According to Grossi C et al., (2001) the greatest visual nuisance is caused by black soiling appearing due to immense vehicle emissions and wood burning. These processes are accompanied by incomplete combustion which produces carbonaceous fine particles. These particles are mainly composed of carbon which has high optical absorptivity affecting the surface darkening. Additionally, traffic exhausts contain numerous other elements which, being deposited, can facilitate other chemical reactions resulting in building surface weathering.

Thick gypsum crust is formed due to the interaction of acidic traffic exhaust elements such as carbon dioxide and sulfur dioxide with stones containing calcite $CaCO_3$. So far, marble, limestone or cement containing buildings are exposed to discoloration, as the gypsum crust often becomes grey or black because of soot and grime which help keeping acidic substances in close contact with stones. (Bortz, Strecich et al., 1993; Nord, Svärdh, Tronner 1994.)

Numerous naturally dispersed particles such as quartz, calcite, kaolinite, feldspar which are inert and harmless to natural stone have a better possibility to stick to building surfaces which are undergoing weathering processes. They are not distinguished from the original stone composition, though they can cause visual hindrances being attached to other materials. (Nord, Svärdh, Tronner 1994.)

Additionally, trace metals such as Pb, Fe, Ni, V and Cr are often determined at different concentration on building surfaces and can facilitate the natural stone decay by catalyzing the oxidation rate of SO_2 causing a synergetic effect. Firstly affecting the visual perception of a building by discoloration these elements damage the natural stone by chemical weathering which are coming with time. (Grossi, Esbert et al., 2001; Nord, Svärdh, Tronner 1994.)

As such, particulate matter directly affects human health increasing the risks of serious diseases and indirectly it damages the architecture of cities reducing its visual and aesthetic value. The historical masterpieces in cities centers are turning into dull dirty pieces of stones negatively influencing the positive perception of the place by the area residents and visitors.

3.2 Chemical composition of dust in Saint Petersburg

A recent investigation of dust in Saint Petersburg which was done in 2011 by a group of researchers from Saint Petersburg State University revealed new information about chemical composition of dust and its origin. The results of the analysis are described in a Master’s degree thesis work named “Ecogeochemical characteristics of dust in Saint Petersburg” by Margarita Kovalenko (2013).

Suspended solids were collected in a form of dust from the asphalt surfaces along the curbside in 13 points basically located near the metro entrances in different parts of the city. Later the dust samples were exposed (1) to panning analysis to identify the mineralogical composition of dust which is based on the samples size fractionation with further definition and description of these fractions; (2) to macroscopic analysis by means of binocular microscope to observe morphological characteristics of dust grains describing their color, shape, degree of abrasion, sphericity and cogenericity;

(3) to raster electronic microscopy to study the dust grains shape; (4) to X-ray fluores-fluorescence analysis to determine the chemical composition of the dust samples.

For this investigation the results of X-ray fluorescence analysis are becoming of the greatest importance. It provides the information on the amount in ppm of different chemicals found in the dust samples which include V, Cr, Co, Ni, Cu, Zn, Sr, Pb, Rb, Ba, La, Y, Zr, Nb, As. The fine and ultrafine particles - less than 2.5 micrometers and less than 0.05 micrometers - were analyzed as they can cause the greatest hazard for human health.

Taking into account that dust represents a mixture of both natural and anthropogenic components, the obtained ppm values are further compared with so-called Clark concentrations or bulk earth values of these elements.

Bulk earth values are used to identify the element concentration found as a ratio of this element to its averaged concentration or percentage abundance in the lithosphere:

$$Kk=C/K \qquad (1)$$

where Kk is bulk earth value, C is the concentration of a chemical element in a particular rock type, and K is percentage abundance of the element in the lithosphere. This procedure of results comparison to the standard is often used for geochemical data interpretation to assess if the component concentration is higher or lower than the averaged. If the value of Kk is > 1, then the element has a tendency to accumulate; and if Kk is < 1, the element is not typical for the studied object. (Panova, Akhmedov 2011,12)

As a result, the following elements were determined which bulk earth values exceeded one: As, Zn, Pb, Zr, V, Cr, La, Y, Ba, Nb, Sr. This can indicate the environmental pollution with toxic heavy metals originated from different anthropogenic sources.

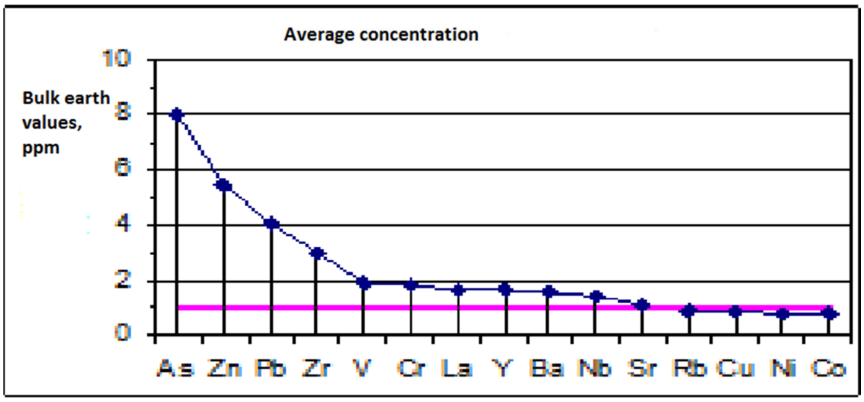

FIGURE 1: The average chemical concentration of elements in dust in Saint Petersburg (Kovalenko 2013, 89)

4 CHEMICAL COMPOSITION VARIATIONS OF RAPAKIVI GRANITE IN SAINT PETERSBURG

Environmental studies show that air pollution is the most powerful and permanent factor that affects negatively the built environment. So far, the urban air is a mixture of gases and aerosols in the atmospheric boundary layer which actively interacts with each other and different building materials. The increased levels of various pollutants including the toxic ones which are found in the modern cities' air definitely leave an unfavorable print on construction surfaces, as corrosive compounds can cause deterioration and weakening of constructions physical properties, while others can deposit on buildings surfaces causing discoloration and diminishing their aesthetic values. Besides, building surfaces seldom go through the maintenance or cleaning works leaving the top soiled layer to accumulate the pollutants which are emitted in the area in the exceeding amount. As such, natural stones and other building materials can be used as passive tracers of air pollution. (Brimblecombe 2003; Rampazzi, Giussani 2010.)

The air quality in Saint Petersburg remains quite far from being good. This fact becomes a direct evidence of a growing urbanization in the area which is accompanied by intensive industrial development, immense traffic load, and crowds of people gathered inside a limited area. Especially high the levels of air pollution are observed in the city center which is a heart of economic, industrial, cultural and scientific life of the whole region. Thus, chemical testing of the most abundant city center building material is undertaken to predict the key pollution sources with their future minimiza-minimization and to analyze the quantitative levels of stone degradation for the purpose of historical preservation.

4.1 Granite as building material in Saint Petersburg

As defined by E. Raguin (1965) granite is an igneous rock “formed essentially of an assemblage of crystalline grains of feldspars and quartz with a small proportion of mica flakes and occasionally hornblende”. These grains are randomly distributed, have different forms and lusters which makes granite architecturally valuable. Granite is a crystalline rock, in which the minerals are tightly bonded together, forming a strong structure (Luodes 2014).

Granite has a long history of being used as a building and ornamental material due to its good mechanical properties, durability and damage resistance. Granite sculptures, columns, pedestals, memorials and bridges can be found in any architectural styles and epoch if a place is located close to a granite quarry. Additionally to its physical properties, chemical and mineralogical composition of the rock affects its colouring which can range from grey to pink with elaborated porphyritic textures giving a certain advantage from the point of view of architectural aesthetics (Pascal 2011).

It is believed that granite can be named as a stone to symbolize Saint Petersburg, as the whole city centre is dressed in this stone: embankments of Neva, Moika and Griboedov Canal, numerous bridges crossing them, the Aleksandrovsky column and the colonnades of Isaakievsky and Kazan cathedrals, pedestals of sculptures in the garden at the Admiralty building, the base of the monument to Nicholas I on St. Isaac’s Square, portals of Marine Crew buildings on the Moika river, the sculptures of lying lions in front of the Laval mansion and other numerous monuments assembling the city’s historical legacy (Bulakh 1993; Panova, Vlasov et al. 2014.).

Geologically Saint Petersburg is located close to the areas rich of granite deposits. Pyterlahti and Monrepo quarries, Sortavala area and Karelian Isthmus (areas Kuznechnoe and Kamennogorsk) produced granite for the growing and developing city since the 18th century. Among them, Vyborg rapakivi granite massif, which nowadays comprises a territory of 18,000 sq. km, is especially famous as it has been widely used for the city’s decoration and ornamentation. The rapakivi granite rocks from this massif are under further analysis. (Panova, Vlasov et al. 2014.)

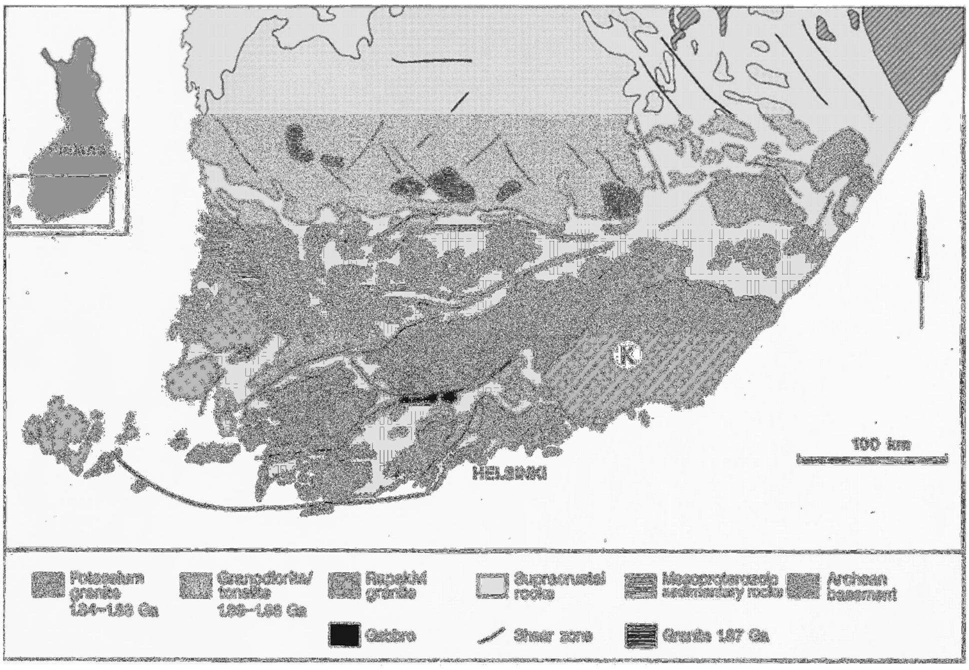

FIGURE 2: Vyborg rapakivi massif (Härmä, Selonen 2008)

There are different kinds of rapakivi granites but generally it can be told that rapakivi granite is a two-feldspar granite with high alkalinity and specific structure determined by the presence of large ovoids of potassium feldspar which can be either surrounded by rims of sodium feldspar or oligoclase, as in the case of the vyborgitic texture or can be un-surrounded in the case of pyterlitic ovoid (Vorma, Atso 1976). From the aesthetic point of view the stone is valuable for the architectural purposes because of these ovoids overfilling the rock as they are cemented by medium-grained mass of pink and white feldspar, grey-black quartz, green- black mica and hornblende. On the contrary, this kind of texture makes the stone to be exposed to a special type of the surface weathering, so-called ‘grusification’. (Härmä, Selonen 2008; Panova, Vlasov, et al. 2014; Bunin 1986.)

4.2 Weathering of granite

Though granite is highly resistant to outside aggressive influence, it is weakened and destroyed with the time, generally undergoing the processes of natural weathering.

Reiche (1950) defines weathering as “the response of materials which were in equilibrium within the lithosphere to conditions at or near its contact with the atmosphere, the hydrosphere, and the biosphere”. In other words, the term “weathering” refers to the processes of rock destruction due to mechanical, chemical and biological activities such as expansion of water freezing, swelling of minerals due to hydration, growth of roots. Generally, the process of weathering includes the stage of rock mineral composition disintegration and decomposition and the stage of decaying products transformations. (Hawkes, Webb 1962.)

Physical or mechanical weathering causes destruction of the rock without changes in chemical or mineralogical composition. The following physical processes initialize and facilitate this type of weathering: erosion, expansion and contraction due to temperature variations, the action of frost, mechanical peeling. As a result, multiple cracks, fissures and joints are formed on the rock surface making it more reactive to the atmospheric water, oxygen and carbon dioxide. (Hawkes, Webb 1962.)

Chemical weathering bears a greater destruction power against the minerals as it results in altering the geochemistry of the rock, as, for example, a coarse silicate rock can turn into a fine dust of clay minerals. The major factor supporting chemical weathering is the solubility of minerals in corrosive natural solutions where rain water is a solvent; and oxygen, carbon dioxide, chlorides and sulphates of both natural and anthropogenic origin are dissolved therein. (Hawkes, Webb 1962.)

Chemical weathering starts at the surface and penetrates into the material over time, forming a rind. There are many chemical processes which take place during weathering, but the major chemical processes altering minerals are hydration and hydrolysis, oxidation and exchange reactions, and hydrogen-ion concentration growth. As minerals disintegrate, some elements leach out. The results of chemical weathering on any particular rock are difficult to predict because the mineralogy of the rock and the conditions to which it was subjected to over time vary greatly. (Hawkes, Webb 1962.)

Hawkes and Webb (1962) consider biological weathering to be a phase of mechanical and chemical weathering, as biologic agents contribute to physical destruction by roots development and moisture generation, while in the course of their own chemical activity, organic acids, nitric acids, ammonia, hydrogen, oxygen and other compounds are produced, which facilitates minerals' degradation and removing. Especially important is plant respiration during which, as a part of the biochemical cycle, oxygen and carbon dioxide are released. Additionally biological tissues, bacteria and fungi produce organic compounds which actually assist many chemical reactions. (Hawkes, Webb 1962.)

Though granite is remarkable for its properties of being very stable and resistant to aggressive environment, it can suffer all types of weathering. The general process of granite degradation includes several stages which can be facilitated by the combinations of weathering activities. Biological weathering takes place basically as mechanical and chemical actions by organic acids. Mechanical weathering facilitates chemical weathering, as it reveals new mineral surfaces to chemical reactions. Biological, mechanical and chemical forces present a cumulative effect and become a natural part of granite surface degradation. (Luodes 2014.)

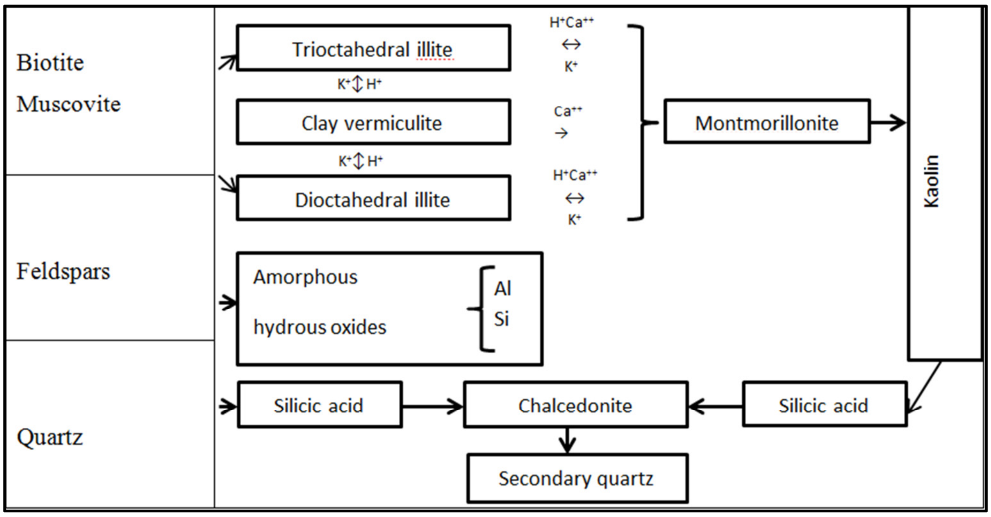

FIGURE 3: Weathering of primary rock-forming minerals. After Fieldes and Swindale (Hawkes, Webb 1962)

Figure 3 represents how the major granite minerals - shown in order of increasing resistance - change to successive secondary minerals during chemical weathering. Thus, potassium leaches first from biotite ($K(Mg,Fe)_3AlSi_3O_{10}(F,OH)_2$) and muscovite ($KAl_2(AlSi_3O_{10})(F,OH)_2$, or $(KF)_2(Al_2O_3)_3(SiO_2)_6(H_2O)$), then K, Na and Ca ions wash out from feldspars ($KAlSi_3O_8$ – $NaAlSi_3O_8$ – $CaAl_2Si_2O_8$). Both processes are resulted in production of kaolin ($Al_2Si_2O_5(OH)_4$) which becomes visible as the stone surface is covered with a white dust. (Hawkes, Webb 1962; Luodes 2014.)

In essence, weathering causes exfoliation joints as weak potassium or sodium feldspars are influenced by hydrolysis producing kaolinite and Na and K ions which are leached from the mineral. They lose their transparency becoming milky, and then powdery with the time. Simultaneously, hydrolysis and oxidation processes affect mica and amphibole which are forming clay and iron oxides. Hornblende becomes green and bleaches, or breaks down into chlorite and epidote. At the same time, quartz remains unchanged keeping all its elements. Quartz is very resistant to weathering, and it is only disintegrated turning into quartz grains or granitic gravel. Though there is a number of research works showing that there is certain leachate of SiO_2 as well. (Hawkes, Webb 1962; Raguin 1965; Luodes 2014.)

4.3 Methods of sampling and analysis

To identify the state of air pollution in Saint Petersburg on the basis of chemical composition variation of granite, 9 sampling points were determined in the city centre and coded by letters A-I. The natural stone used at sampling points was classified as rapakivi granite from Vyborg massif. According to Figure 4 below, sampling point A is located at the spit of Vasilyevsky Island, while sampling points B-D are set along the Moika Embankment and sampling points E-I are set along Griboedov Canal. All the sampling points are bearing a certain value for historical preservation of architectural monuments of the city's centre ensemble, as the objects generally originate to the end of the 17th century - beginning of the 18th century.

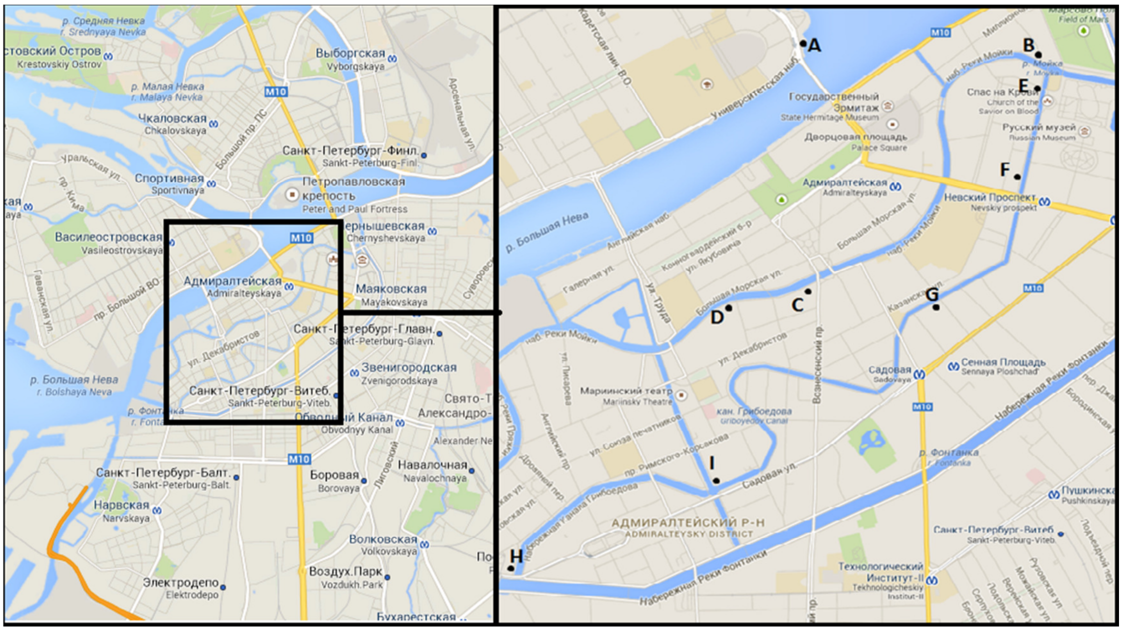

FIGURE 4: Sampling points in Saint Petersburg centre (Google.Maps 2014)

As the sampling material of historical objects, the pieces of dropped or fallen off stone fragments were used. Later the pieces were treated so that the outside and inside parts were prepared for the further chemical analysis. In that case, the outside granite surface represents “crust” which has suffered natural weathering and anthropogenic pollution; while the inside granite material represents a “fresh” part which theoretically is virgin and contains the initial content of elements which have not being influenced by any factor. As such, crust and fresh chemical compositions are statistically compared to describe the air pollution influence and the weathering state.

FIGURE 5: Sampling material (photo by Heikki Pirinen, GTK)

The characteristic of chemical change of a granite crust and not changed granite were analysed by XRF-silicate analysis for macro element composition and ICP MS analysis for micro element composition.

4.3 Chemical composition of granite

To identify the air pollutants which cause a certain hazard for natural stones and to understand their behaviour it becomes essential to describe the chemical composition of rapakivi granite comparing the standard and obtained values and in parallel to determine levels of the chemical weathering by applying specific weathering indices.

4.3.1 Macro chemical composition of rapakivi granite

As a rule, granite is constituted of four minerals: coarse grains of quartz, potassium feldspar or sodium feldspar, mica (muscovite and biotite) and hornblende or amphibole. These minerals can be present in different proportions, but for most types of granite rocks, quartz accounts for 10-60 % of the mass, while the feldspar content basically varies from 65-95 % and biotite levels are around 10-15 %. As such, they determine the chemical composition of a stone which typically consists of macro or rockforming elements (shown in a decreasing order) – SiO_2, Al_2O_3, K_2O,Na_2O, CaO, FeO, Fe_2O_3, MgO, TiO_2, P_2O_5, MnO – and micro or accompanying elements which account for < 0,1 % of the sample mass. (Hawkes, Webb 1986; Panova, Akhmedov 2011.)

In the course of LUKOT project done by GTK according to the standard SFS-EN 12407, the petrographic description of rapakivi content was done based on 5 quarried materials from Vyborg area. As a result, the following minerals in mass percentage (Table 6) are typically constituents of rapakivi granite with the variations appeared by the fact that both brown and red variety of stone are included. (LUKOT project 2005-2007)

TABLE 6: Mineral composition of rapakivi granite (LUKOT project)

Mineral	mass %	Mineral	mass %	Mineral	mass %
Quartz	24-42%	Muscovite	0-0.1 %	Ilmenite	0-0,5%
K-feldspar	28-42 %	Allanite	0-0.2%	Rutile	0-0.1%
Albite	7-13.7 %	Tourmaline	0-0.2%	Apatite	0-0.3%
Andesine	3-27%	Zircon	0.1-0.2%	Pyrite	0.0
Amphibole	0.2-11%	Kaolinite	0-0.1%	Calcite	0.0
Chlorite	0.0-0.2%	Thorite	0-0.1%	Bastnasite	0-0.9%
Biotite	2.9-7.5%	Magnetite	0-0.1%	Fluorite	0.2-1.9%

Through the multi-element XFR determination method, the rock forming oxides of granite samples in mass percentage were defined. For each sample, fresh and crust were analysed and further compared. Additionally all the samples' results for fresh and crust were averaged and then compared to the reference values which present the averaged mass concentrations of rapakivi granite macro elements. Rapakivi granites macro elements have been evaluated averaging 7 sampling points from the Vyborg massif near the area from which the natural stone of Saint Petersburg had been extracted supplemented by the average reference material from 6 quarries of material similar to the one used in Saint Petersburg and from Vyborg massif including red and brown samples. Table 7 shows the results of macro chemical composition analysis of sampled rapakivi granite crust and fresh and further their comparison to the reference data presented in GTK databases.

TABLE 7: The determined values of macro elements mass percentage of sampled rapakivi granite fresh and crust and the comparison of the obtained values and the average macro chemical composition for rapakivi granite, mass %

Sampling point		SiO_2	Al_2O_3	K_2O	Na_2O	CaO	Fe_2O_3	MgO	TiO_2	P_2O_5	MnO	Total
A	**fresh**	69.10	12.40	5.23	2.44	1.92	7.06	0.39	0.760	0.162	0.075	**99.54**
	crust	70.20	14.50	5.31	3.21	2.06	3.54	0.20	0.356	0.106	0.034	**99.52**
B	**fresh**	69.30	14.70	5.60	3.18	1.87	4.11	0.25	0.454	0.104	0.043	**99.61**
	crust	73.10	12.30	4.80	2.64	1.55	4.38	0.24	0.470	0.104	0.042	**99.63**
C	**fresh**	71.30	13.80	5.98	2.71	1.42	3.64	0.20	0.359	0.065	0.032	**99.50**
	crust	71.00	14.10	5.88	2.86	1.21	3.93	0.19	0.378	0.072	0.034	**99.66**
D	**fresh**	71.50	13.70	5.29	3.03	1.79	3.49	0.17	0.344	0.058	0.032	**99.41**
	crust	71.20	13.90	5.48	3.06	1.44	3.83	0.18	0.380	0.063	0.033	**99.57**
E	**fresh**	67.90	13.50	5.11	2.93	2.35	6.39	0.41	0.720	0.193	0.066	**99.57**
	crust	69.00	15.60	5.49	3.60	1.98	3.39	0.21	0.342	0.092	0.032	**99.73**
F	**fresh**	73.70	12.90	6.07	2.65	0.95	2.76	0.13	0.249	0.037	0.021	**99.46**
	crust	71.60	14.00	6.76	2.93	0.82	2.84	0.14	0.220	0.038	0.021	**99.37**
G	**fresh**	75.50	12.40	5.36	2.72	0.80	2.41	0.14	0.211	0.027	0.020	**99.58**
	crust	71.30	14.60	4.78	3.62	1.95	2.82	0.18	0.240	0.041	0.022	**99.55**
H	**fresh**	74.70	12.30	5.58	2.49	1.03	2.97	0.13	0.295	0.042	0.026	**99.57**
	crust	73.80	12.70	5.61	2.62	1.47	2.89	0.13	0.252	0.121	0.023	**99.61**
I	**fresh**	69.90	13.50	5.23	3.02	1.99	4.99	0.28	0.540	0.134	0.056	**99.64**
	crust	70.90	13.40	5.12	3.00	1.93	4.44	0.24	0.451	0.152	0.049	**99.68**
Average fresh		71.43	13.24	5.49	2.80	1.57	4.20	0.23	0.44	0.09	0.04	**99.54**
Average crust		71.34	13.90	5.47	3.06	1.60	3.56	0.19	0.34	0.09	0.03	**99.59**
Reference		**72.55**	**13.05**	**5.53**	**2.88**	**1.43**	**3.39**	**0.21**	**0.33**	**0.07**	**0.04**	**99.48**

The small deviations in mass percentage come from analytical and statistical errors and losses during the analysis procedures. Besides, in the rock there can be minor elements that are not detected in the whole rock analysis and they are not presented in the results. (Luodes 2014.)

The mass percentage of following elements - SiO_2, Al_2O_3 and Na_2O - is slightly higher for crust samples which can be explained through geochemical reactions. As such, the concentration of SiO_2 comes from quartz (SiO_2) which is very resistant to weathering. While the other minerals disappear from the surface, quartz stays and the proportion of SiO_2 increases. The increase of the amount of Al_2O_3 could come from alteration of feldspar into kaolinite (an Al rich clay mineral), which is normal reaction of feldspar weathering in the nature. Most of the other elements of the feldspars are diluted from the surface and that increases the proportion of Al. The increase of Na comes from feldspar that will still stay in the surface as a mineral. It may also come from a Na bearing clay mineral, such as montmorillonite. (Luodes 2014.)

TABLE 8: Petrographic analysis of rapakivi granite from waste areas and freshly excavated (LUKOT project)

Mineral	Mineral Weight (%) waste	Mineral weight (%) fresh	Mineral	Mineral Weight (%) waste	Mineral weight (%) fresh
Quartz	35-46	24-42	Fluorite	0-0.6	0.2-1.9
K_feldspar	28-34	28-42	Fe-oxide	0-0.1	
Plagioclase	20-30	10-41	Rutile	0-0.4	0-0.1
Biotite	1.3-6.6	2.9-7.5	Ilmenite	0-0.2	0-0.5
Muscovite	0.2-1.6	0-0,1	Pyrite	0-0.2	0.0
Berthierine	0-0.2		Kaolinite	0-0.1	0-0.1
Chlorite	0.4-1.6	0,0-0,2	Xeno-time(Y)	0-0.1	
Zircon	0-0.2	0.1-0,2	Amphibole		0.2-11
Västmanland-ite(Ce)	0-0.1		Allanite		0-0.2
Calcite	0-0.2	0,0	Tourmaline		0-0.2
Apatite	0-0.1	0-0.3	Thorite		0-0.1
Monazite	0-0.1		Magnetite		0-0.1

In the table 8 above it is compared the petrographic analysis of the rock collected from the waste areas of active quarries against the petrographic analysis of fresh material to evaluate if there had been formation of minerals by chemical weathering. The material gained from Saint Petersburg had not been analyzed as a thin section making a petrographic description of it, so it is difficult to understand which had been the mineral that had been created and which depleted precisely. Evaluation of the molar balances could help in this understanding, and also a comparison against the average composition of the samples collected from the waste areas of the quarries that excavate similar pyterlite rapakivi from the Vyborg massif could be attempted. (Luodes 2014.)

Quartz, K feldspar and plagioclase are varying, but not clearly diminishing or increasing. The quantity of kaolinite is similar to the fresh material but because of weathering there could be creation of calcite. There is an increase in FeO and a diminishing of biotite but the proportional amount of chlorite (that is a product of biotite alteration) that is higher in the waste because there is less biotite, cannot be related to chemical weathering since formation of chlorite would need magmatic conditions. (Luodes 2014.)

Finally it seems that the material collected from waste of the quarries could present different properties and therefore been excluded from primary production not because of the climatic-chemical weathering conditions but because of the different formation process that determined a different degree of weathering (Luodes 2014). Later on, the macro elements composition data are used for a process of granite chemical weathering characterization through the weathering indices application.

4.3.2 Weathering indices

Chemical weathering indices are a very common and very controversial tool to evaluate the weathering state of natural stones through the quantitative comparison of mobile and immobile rock components usually presented in the scale of depletion levels of the first in relation to the second. The calculations are based on the assumption that during weathering certain major oxides such as Al_2O_3, Fe_2O_3 and TiO_2 remain in the same amount as they are very resistant to leaching, while others such as SiO_2, Na_2O, K_2O and MgO are dissipated. As such, most of the chemical weathering indices present a mass percentage ratio of major oxides. (Price, Velbel 2002.)

In order to use the indices, the weathering mechanism of the material has to be known. For building sites the actions affecting the materials are different from those normally affecting a section of bedrock. The weathering indices have been mainly used for characterization of the weathering level of bedrock. On a building site the chemical actions are important but are added to the physical ones, as wind for example. (Luodes 2014.)

Among the most commonly used indices, the *Chemical index of alteration* (CIA) can be named. The index is based on the idea that chemical weathering of feldspar due to hydrolysis is interconnected to the content changes of the major cations. Thus, it is suggested that Al_2O_3 would remain immobile whereas potassium, calcium and sodium are usually washed out with corrodent soil solutions. CIA considers all kinds of components made out of Al, also secondary weathering formations, but in this case the CIA would be lower compared to the one of Al contained in plagioclase and biotite. The values of CIA differ depending on rock compositions (for certain rocks); The CIA values for kaolinite for example would have been reaching 100, while illite and smectite would have been around 80 (Law, Hesbitt et al. 1991),and for unweathered granites and granodiorites the CIA values are within the range of 50-55 since they are mainly constituted by biotite, plagioclase and quartz. The growing CIA values point to the weathering processes. The CIA is calculated according to the formula (Law, Hesbitt, etc. 1991; Price, Velbel 2002; Bahlburg, Dobrzinski 2009):

$$CIA = \frac{Al2O3}{Al2O3 + Na2O + K2O + CaO} * 100 \qquad (2)$$

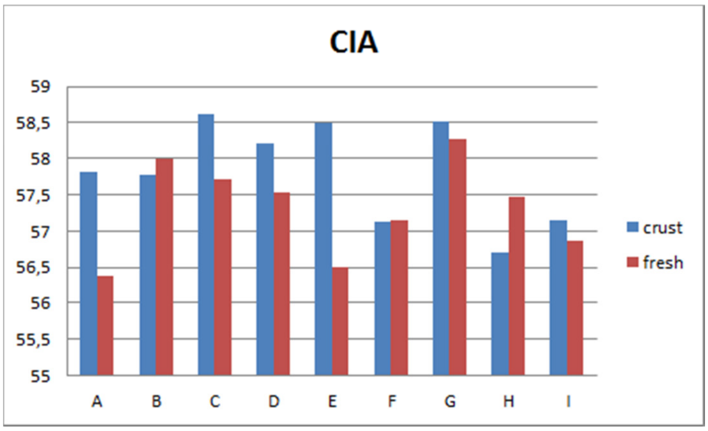

FIGURE 6: The relation of crust CIA and fresh CIA

The CIA values for all sampling points are shown in Table 9. For samples A, C, D, E, G, and I the CIA crust values are higher than the CIA values of fresh (Figure 6). The average crust CIA (57.82) and average fresh CIA (57.32) are exceeding the limits set for this type of rock, as such it gives a reason for suspecting a light chemical weathering activity of the examined granite samples.

All the materials both in their top and base sections have been exceeding the reference CIA values for typical unweathered granite; that would mean that the rapakivi granite examined had certain levels of Al secondary minerals. (Luodes 2014).

Chemical index of weathering (CIW) is very close in its bases to CIA as it evaluates the level of chemical weathering through the relationship of immobile alumina and potassium to other mobile elements. The index value increases with the increasing grade of weathering; for basalt and granites it varies between 76-59. Thus, it can be found (Panova, Akhmedov 2011, 40):

$$CIW = \frac{Al2O3}{Al2O3 + CaO + Na2O} * 100 \qquad (3)$$

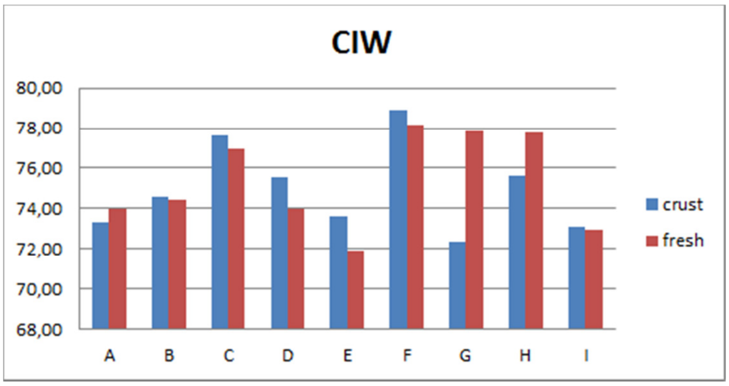

FIGURE 7: The relation of crust CIW and fresh CIW

The CIW values for all sampling points are shown in Table 9. The samples B, C, D, E, F and I (Figure 7) show an increase in crust CIW values in comparison to fresh CIW values pointing to the weathering activities. Additionally, the averaged values for CIW crust (74.97) and CIW fresh (75.33) are in the upper part of the low weathering limit (76-59). (Panova, Akhmedov 2011,40.)

Weathering potential index (WPI) represents the relation of major mobile oxides to the whole rock macro elements composition. As such, no changes between crust and fresh in WPI values provide the information on the stability of mobile cations concentrations and a little level of weathering. The WPI can be presented as the following ratio (Price, Velbel 2002):

$$WPI = \frac{(CaO + Na2O + MgO + K2O - H2O) * 100}{SiO2 + Al2O3 + Fe2O3 + TiO2 + CaO + MgO + Na2O + K2O} \quad (4)$$

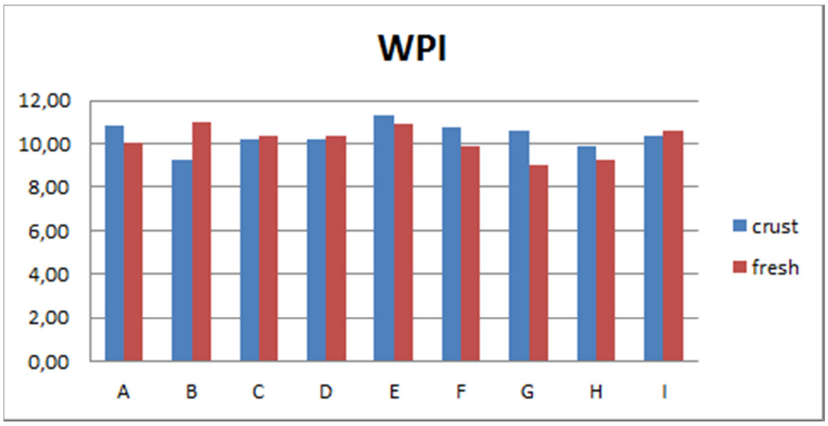

FIGURE 8: The relation of crust WPI and fresh WPI

The WPI values for all sampling points are shown in Table 9. In Figure 8 above it is seen that the modest levels of weathering are observed for samples B, C, D, and I as the crust WPI values are slightly less than the fresh WPI values - the averaged difference for these samples accounts for 0.6 - which reflects the loss of mobile elements.

The Index of compositional variability (ICV) was suggested to determine the weathering state by including total Fe and total Ca into considerations. The average index values for unweathered granite corresponds to 0.95 and they decrease if the level of weathering is boosting. The ICV can be found according to the formula (Panova, Akhmedov 2011):

$$ICV = \frac{CaO + K2O + Na2O + Fe2O3 + MgO + MnO + TiO2}{Al2O3} \quad (5)$$

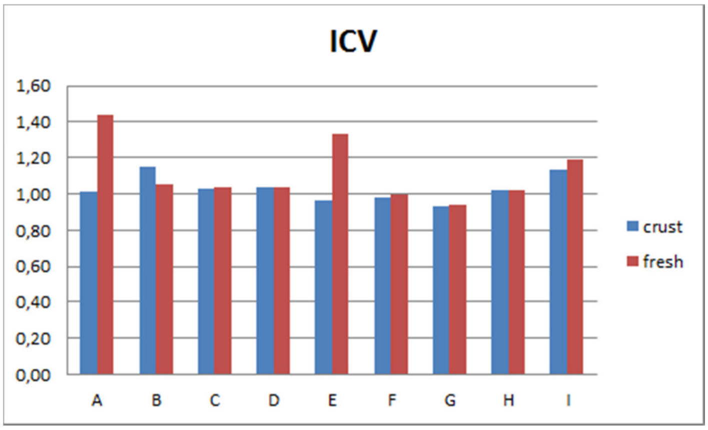

FIGURE 9: The relation of crust ICV and Fresh ICV

The ICV values for all sampling points are shown in Table 9. The comparison of the ICV crust and the ICV fresh gives the reason to observe a certain inconsiderable level of chemical weathering with a special interest paid to samples A and E.

Product Index (PI) has a long history of use, and it is based on the assumption of decreasing silica matter during the weathering processes. PI can be found according to the formula (Price, Velbel 2002):

$$PI = \frac{SiO2 * 100}{SiO2 + TiO2 + Fe2O3 + FeO + Al2O3} \qquad (6)$$

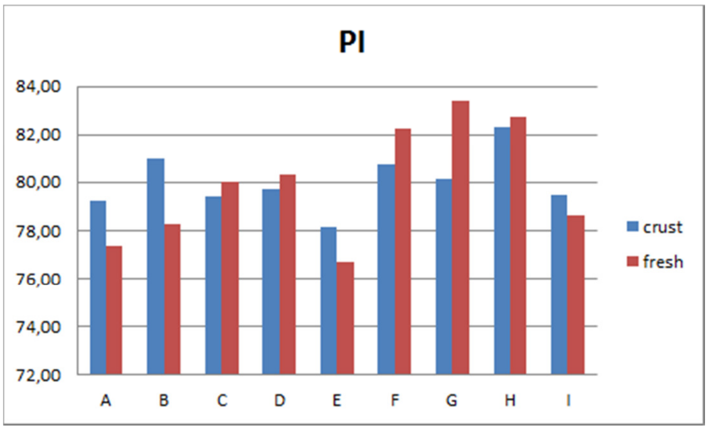

FIGURE 10: The relation of crust PI and fresh PI

The PI values for all sampling points are shown in Table 9. The samples A,B,E and I (Figure 10) show the prevailing amount of silica content in crust PI values while fresh PI values are decreasing. It points out that for these samples the mass percentage of silica is increased while other elements are depleted.

Ruxton's *Silica-Alumina Ratio* is used to assess the total elements depletion expressed through silica content as a ratio to alumina which is accepted to be immobile during weathering. The Ruxton equation has the following form (Price, Velbel 2002):

$$Si - Al = \frac{SiO2}{Al2O3} \qquad (7)$$

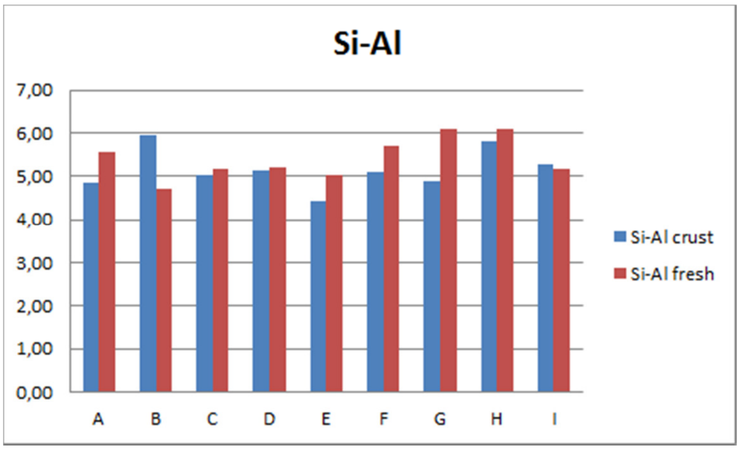

FIGURE 11: The relation of crust Si-Al and fresh Si-Al

The Si-Al Ratio values for all sampling points are shown in Table 9. The decrease in crust Silica-Alumina Ratio values in comparison to fresh values are observed at samples A, C, D, E, F, G and I (Figure 11) indicating a low degree of chemical weathering.

Similarly, *Silica-Titania index* can be applied.

$$Si - Ti = \left[\frac{\frac{SiO2}{TiO2}}{\left(\frac{SiO2}{TiO2}\right) + \left(\frac{SiO2}{Al2O3}\right) + \left(\frac{Al2O3}{TiO2}\right)} \right] * 100 \qquad (8)$$

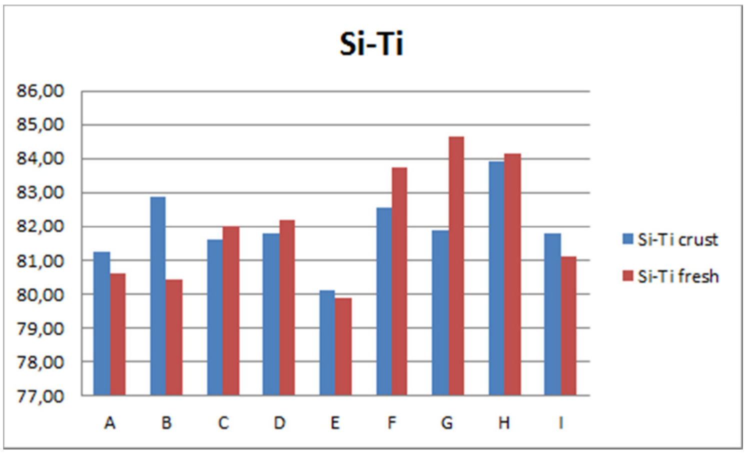

FIGURE 12: The relation of crust Si-Ti and fresh Si-Ti

The Si-Ti Ratio values for all sampling points are shown in Table 9. The decrease in crust Silica-Titanium Ratio values in comparison to fresh values are observed at samples C, D, F,G, H and I (Figure 12) indicating a certain degree of chemical weathering.

Additionally, a new chemical weathering index was suggested by professor Panova based on the idea that natural conditions can affect weathering, e.g. wind took away Al and left SiO_2. Thus, an index called airing coefficient (K) is applied considering immobile/mobile elements. It can be calculated on the basis of the formula (Panova, Vlasov 2014):

$$K = \frac{SiO2 + CaO + Na2O}{Al2O3 + TiO2 + Fe2O3 + MnO + MgO + K2O} \qquad (9)$$

where in numerator symbolizes composition of the steadiest minerals, and a denominator - composition of unstable minerals. Having calculated values K for not changed granite and crust it is possible to estimate degree of weathering of rock as an index of weathering $IW=K_{crust} - K_{granit}$. The larger the value of index the severer the level of chemical weathering is. (Panova, Vlasov 2014.) As a result the average IW for rapakivi granite in Saint Petersburg is equals to 0.1 showing a slight weathering process.

To understand the degree of weathering activity at the sampling points, the calculated values of weathering indices are further compared to the reference (table 9). For the reference, LUKOT project data are used, where the results of 7 sampling points from the Vyborg massif and of red and brown granite material taken from 6 active quarries, similar to the one used in Saint Petersburg and from Vyborg massif, are averaged. (LUKOT project.)

TABLE 9: Summary of chemical weathering index values for granite crust and fresh samples

Sampling point		CIA	CIW	WPI	ICV	PI	Al-Si	Si-Ti
A	**fresh**	56.39	73.99	10.05	1.44	77.36	5.57	80.60
	crust	57.81	73.34	10.85	1.01	79.24	4.84	81.23
B	**fresh**	57.99	74.43	10.96	1.05	78.25	4.71	80.45
	crust	57.77	74.59	9.28	1.15	81.00	5.94	82.89
C	**fresh**	57.72	76.97	10.37	1.04	80.02	5.17	82.00
	crust	58.63	77.60	10.19	1.03	79.41	5.04	81.61
D	**fresh**	57.54	73.97	10.35	1.03	80.31	5.22	82.19
	crust	58.21	75.54	10.22	1.04	79.72	5.12	81.79
E	**fresh**	56.51	71.88	10.87	1.33	76.71	5.03	79.86
	crust	58.49	73.65	11.32	0.96	78.11	4.42	80.13
F	**fresh**	57.16	78.18	9.85	0.99	82.25	5.71	83.73
	crust	57.12	78.87	10.73	0.98	80.76	5.11	82.56
G	**fresh**	58.27	77.89	9.06	0.94	83.41	6.09	84.66
	crust	58.52	72.38	10.58	0.93	80.15	4.88	81.89
H	**fresh**	57.48	77.75	9.28	1.02	82.76	6.07	84.13
	crust	56.70	75.64	9.88	1.02	82.33	5.81	83.90
I	**fresh**	56.87	72.93	10.58	1.19	78.60	5.18	81.09
	crust	57.14	73.10	10.34	1.14	79.49	5.29	81.79
Average fresh		57.32	75.33	10.15	1.12	79.96	5.42	82.08
Average crust		57.82	74.97	10.38	1.03	80.02	5.16	81.97
σ fresh		0.64	2.38	0.66	0.17	2.43	0.47	1.74
σ crust		0.70	2.17	0.59	0.07	1.22	0.47	1.06
Reference		57.00	75.15	10.11	1.06	81.22	5.56	82.96

According to weathering indices applied to the macro elements composition of sampled granite fresh and crust it is evaluated that the level of chemical weathering is probably in its onset and very low though it is noticeable for samples C, I and D. For these sampling points, 7 out of 7 and 6 out of 7 indices indicate loss of mobile elements in relation to immobile components; 4 out of 7 indices demonstrate chemical weathering for sampling points A, E, F and G; at the same time, sampling points B and H are revealing the least signs of elements depletion as only 3 and 2 out of 7 indices signals weathering.

4.3.3 Micro chemical composition

Micro or accompanying elements account only for less than 0,1% of the total mass of the rock. Their composition and quantity depend on the type of the mineral, and the average abundance of micro elements can be found in reference and special literature. The concentration of micro elements is expressed in grams per ton (g/t or ppm), sometimes in grams per a thousand tons (mg/t or ppb). The transition from grams per ton to mass percentage can be applied, so that 1 g/t equals to 0.0001%. (Panova, Akhmedov 2011, 7.)

In the course of ICP MS analysis of micro elements, 37 elements in ppm (mg/kg) were detected in granite crust and fresh samples. The crust and fresh concentrations of micro elements are compared to the values of their percentage abundance in rapakivi granite (Table 10 and 11, Appendix 1). As a reference, the values of the average percentage abundance of rapakivi granite elements based on 5 quarried materials from Vyborg area (LUKOT project) are used; additionally the average percentage abundance of Bi, Ag, Cd, Ce, Sb, Se, Te, Th, U, W in granite suggested by Vinogradov are taken (Voitkevich, Miroshnikov et al. 1977, 47-49).

The procedure of normalization, i.e. the comparison of the fresh and crust elements concentrations to their percentage abundance values, gives a more structural and precise approach; as together with simple comparison of the fresh and crust elements concentrations, it is possible to evaluate the granite composition deviations from the standard values and to ascribe certain variations to elements' accumulation or dissipation.

Thus, the average values of elements concentrations (C) are compared to the reference values (K), and the obtained bulk earth values (Kk) are analysed. If the value of $Kk > 1$, then the element has a tendency to accumulate, and if $Kk < 1$, the element is dissipating from the studied object or is not typical.

The total (averaged) bulk earth values for crust and fresh are shown in Figure 13 below. As a result, it becomes obvious that the granite samples which are used in chemical analysis have a specific element composition, as initially, 26 micro elements, i.e.

Ag, Cd, Ni, As, Pb, Ce, Th, U, Zn, V, La, Ti, Ba, W, Sr, P, K, Al, Na, Be, Li, Sc, Fe, Ca and Mo, are present in the amounts exceeding the bulk earth values (Kk = 1).

Apart from that, the bulk earth values for Se, Bi, Te are not included in the graph below as the averages for 9 samples crust Kk are 70.73/35.56/33.00 correspondently and the averages for 9 samples fresh Kk are 69.13/34.12/36.61 correspondently.

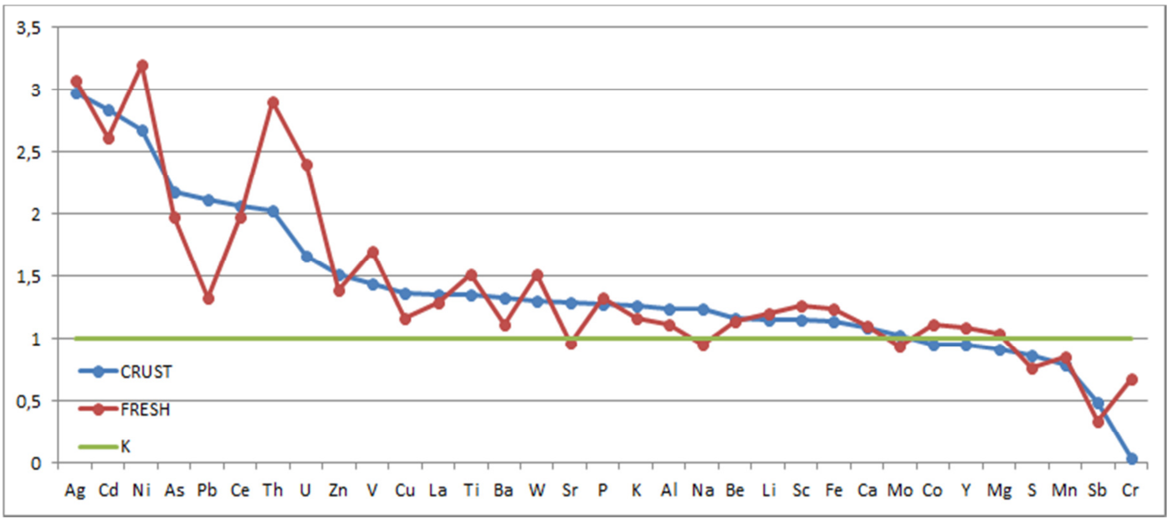

FIGURE 13: The relation of the crust and fresh Kk to the percentage abundance of elements in granite

As the amount of elements makes it indistinct to read the graph correctly it is later divided into three sub-sections based on crust concentrations: A, where the range of elements bulk earth concentrations is between 3.0 and 1.33 ppm; B, where the range is between 1.3 and 1.03 ppm; and C, where the range is between 0.95 and 0.04 ppm.

<table>
<tr><th>Graphs</th><th>Elements accumulated in the crust</th></tr>
<tr><td>

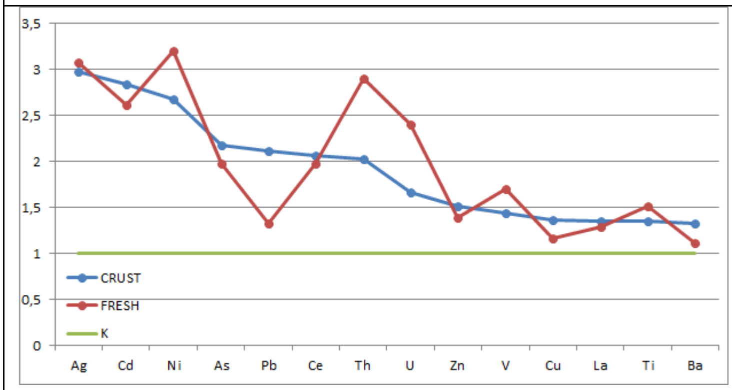

FIGURE 14: Sub-section A (3.0-1.33 ppm)

</td><td>Cd, As, Pb, Ce, Zn, Cu, La, Ba</td></tr>
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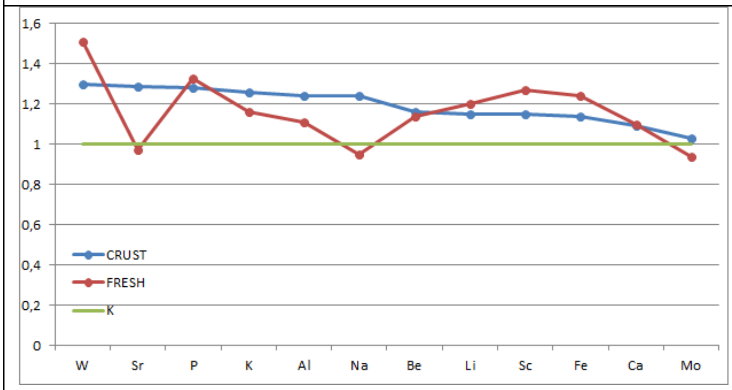

FIGURE 15: Sub-section B (1.3-1.03 ppm)

</td><td>Sr, K, Al, Na, Mo</td></tr>
<tr><td>

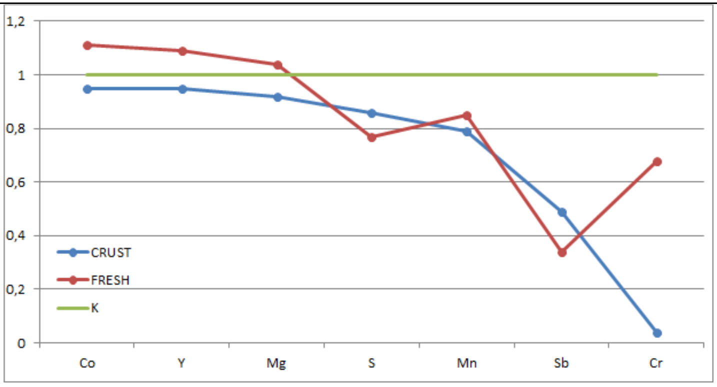

FIGURE 16: Sub-section C (0.95-0.04 ppm)

</td><td>S, Sb</td></tr>
</table>

Consequently, 17 chemical elements have been increased in the amount on the granite surface. Here it should be marked that each chemical analysis gives only relative values, that is why such elements as Al, K, and Na, though they are causing environmental disturbance if they are released in great amounts, will be discriminated from the further analysis, as they are specific for major element granite composition; and two chemical analysis: XRF-silicate analysis for macro element composition and ICP MS for micro elements might interrelate with each results for these particular chemical elements. Thus, based on average basis, 14 elements - Se, Bi, Cd, As, Pb, Ce, Zn, Cu, La, Ba, Sr, Mo, S, Sb - and their origin are further investigated.

Remarkably, the concentration of lead has increased almost at all sampling points except for sampling point H where the crust/fresh Pb concentrations are 18.0/18.2 ppm correspondingly. The greatest increase can be seen at sampling point A.

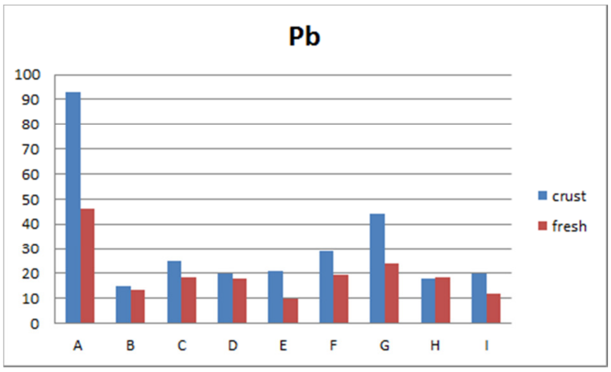

FIGURE 17: The concentrations of Pb at different sampling points

The concentrations of Sb and Sr have increased at all sampling points, except sampling point D. Thus the average increase of Sb and Sr concentration is 60 % and 36 % respectively with almost doubling for some sampling points.

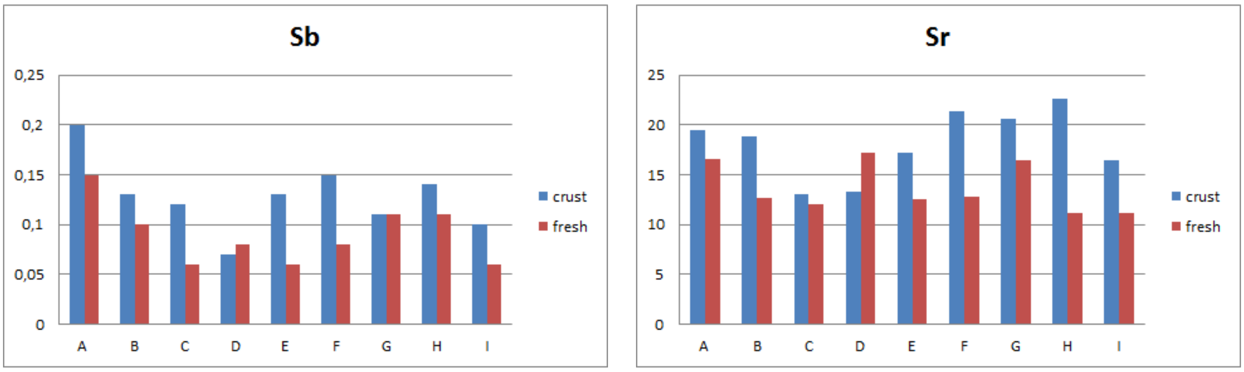

FIGURE 18: The concentrations of Sb and Sr at different sampling points

The concentrations of Ba have increased at 8 sampling points and concentration of S, Zn and Cu have increased at 7 sampling points showing the similar tendency to decrease at sampling point A. Besides, all elements are following the similar distribution pattern at all sampling points showing a good correlation.

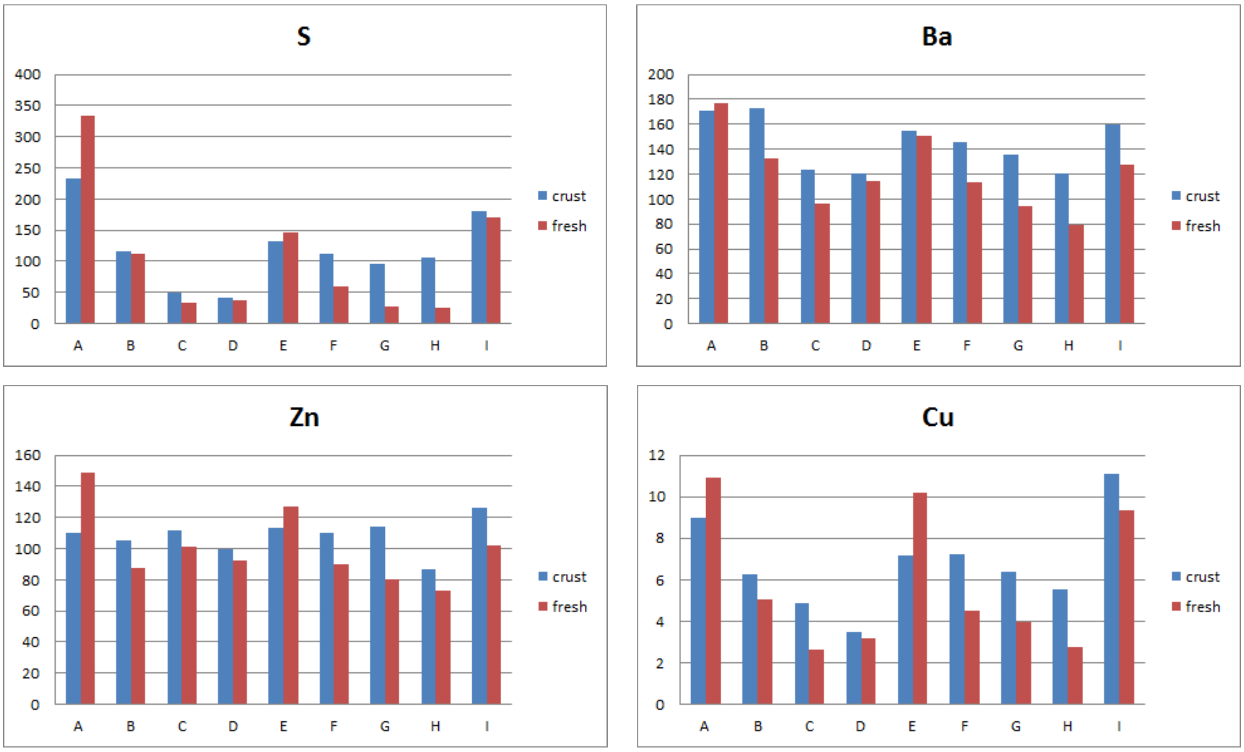

FIGURE 19: The concentrations of S, Ba, Zn and Cu at different sampling points

The concentrations of Ce, La and Se have increased at sampling points C, D and F, being doubled at sampling point F showing a strong interdependence.

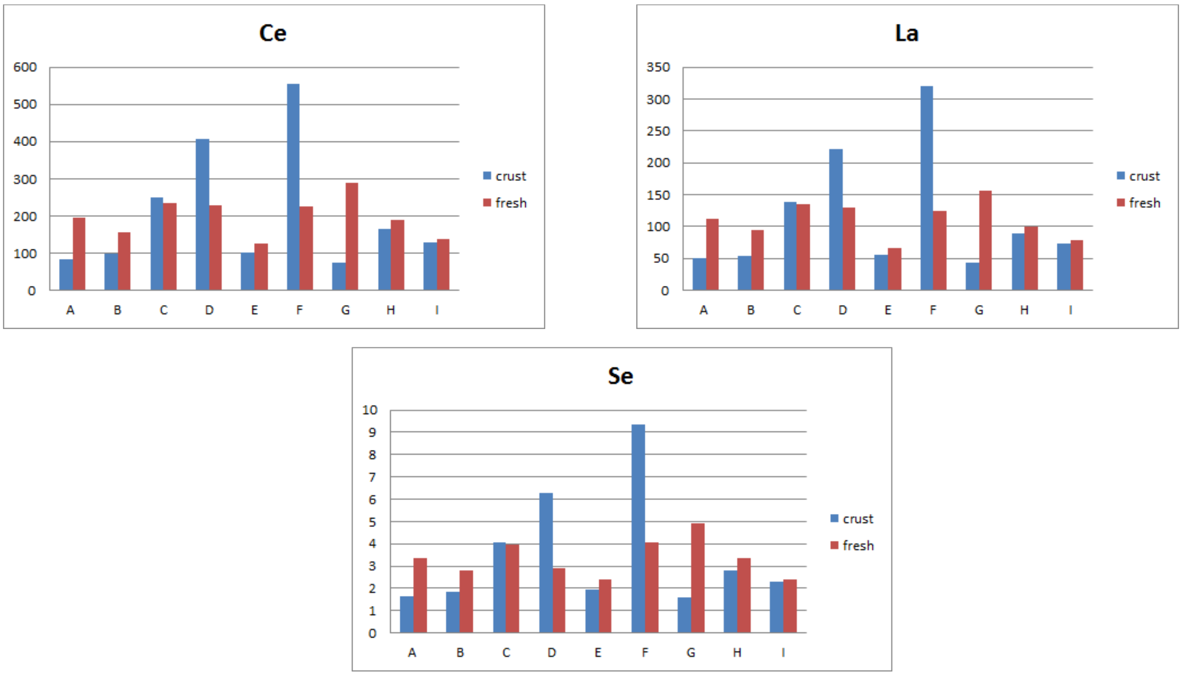

FIGURE 20: The concentrations of Ce, La and Se at different sampling points

The concentrations of Mo and Cd have increased at 4 sampling points. Though according to the graph below there is no distributional correlation between these elements emissions.

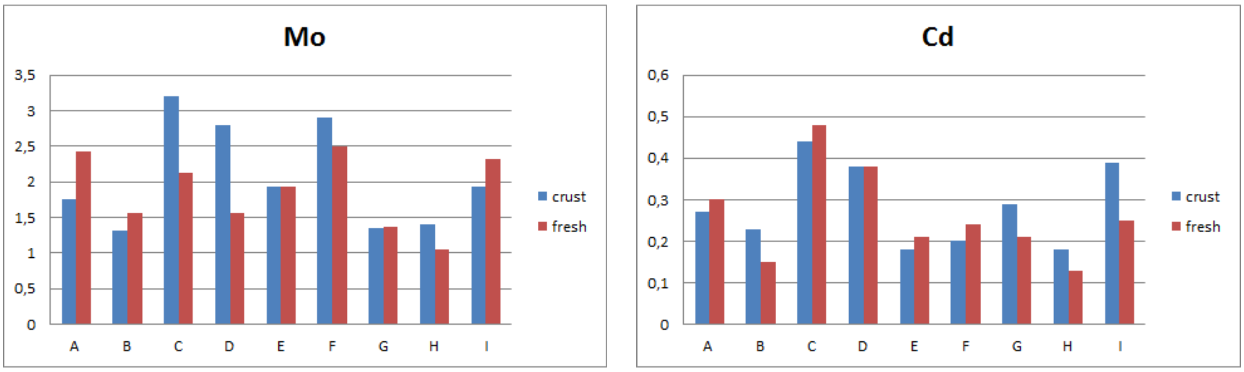

FIGURE 21: The concentrations of Mo and Cd at different sampling points

The graph below shows the gain of As and Bi on the surfaces at 6 sampling points. The gains of the elements do not follow the similar path having low interconnection; the most visible increase of As by 166 % is seen at sampling point F.

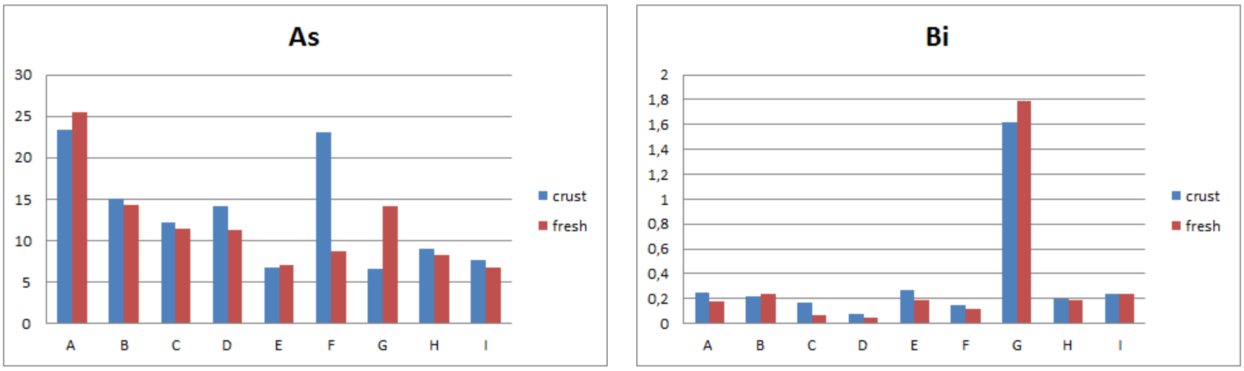

FIGURE 22: The concentrations of As and Bi at different sampling points

So far, 14 chemicals are determined to show a certain gain on the granite surface being accumulated due to urban air pollution. All of them are ascribed to a certain hazardous class as their potential effects on human health and the environment are drastic.

It becomes important to identify the sources of chemicals for the future emission reduction. As such, numerous reports state that Sb, Cd and Pb are resulted from a mixture of industrial emissions; Pb, As, Sr, Ba and La are traffic-related due to brake lining, tire wearing and catalysator utilization. Zn and Mo are a result of road vehicle induced dust resuspension.

4.4 The influence of air pollution on the built environment

The severe air pollution cause a significance influence on buildings and building materials. Mainly, the acidic compounds corrode the structures affecting metal and natural stone materials, while black particulate matter precipitates on different surfaces reducing the aesthetic value. As such, urban air pollution intensifies the natural weathering of building materials. And economically, modern cities are facing a great challenge as the expenses for architectural heritage maintenance and renovation is steadily growing. (Hamilton, Crabbe 2009.)

Saint Petersburg center is a collection of architectural masterpieces presenting a tremendous variety of history, style, art and culture which are recognized by the UNESCO World Heritage Committee since 1988. Unfortunately nowadays, the city center witnesses an enormous anthropogenic pressure due to its versatile political, economic, industrial and entertaining functions. The heavy traffic loads and industrial activities release a great variety of air pollutants which end up in the city environment.

The weathering indices analysis of the granite samples taken from the city center shows that samples C and I are suffering the most. These sampling points are located close to the big traffic arteries: Sadovaya Street and Voznesensky Avenue. Additionally these sampling points display a certain accumulation of micro elements on their surfaces, as sampling point C demonstrates the increase of 13 microelements on the crust while sampling point I shows the gain of 9 underlined micro chemicals. Besides, sample point F is located close to Nevsky Avenue, and the surface of rapakivi granite sample reveals the increase of 13 chemicals. Sampling points B, D and H show the increase of 9 - 10 micro elements at the surface being situated at busy streets. Sampling points A and E show the gain only of 4 elements. At the same time, the chemical weathering indices for these sampling points (except those mentioned before) display a low or negligible levels of natural stone destruction proving the soundness of granite as building material.

Thus, chemical elements which are released into the air and transported together with city dust are deposited on the building surfaces and can facilitate the rock structure damage in a longer term. In a shorter term, the accumulation of traffic induced dust resulted in the formation of black crust deteriorating the aesthetic values of historical masterpieces.

5 CONCLUSIONS

The air pollution in big cities of Russia demands a special attention as the levels of industrialization and urbanization are directly reflecting the amounts of toxic compounds emitted during anthropogenic activities. Numerous studies report that the undertaken monitoring activities are not enough but the certain measures should be taken. The poor urban air quality affects negatively local citizens' health but also biotic life and ecosystems which are located at certain distances from the polluting centres. The air pollutants are spread due to trans-boundary air circulation. Thus, the Russian air quality problems become vital for other countries as well.

Especially hot the topic of air pollution is in Saint Petersburg, the city, which is peculiar for its geographical location, for the multiple functions it bears and for the artistic evaluation as the city centre is remarkable for its magnificent historical monuments and architecture. In spite of all the efforts which the local government and international activists put, the level of air quality remains one of the lowest among Russian cities. According to the governmental reports the total amounts of air pollutants have a steady tendency to grow each year. The specialists explain the situation by the urbanization process which is still going on, as the official statistics prove the increase in industrial enterprises and as a result, increase in air emissions. Additionally to industrial sources of air pollutants, the boost of traffic fleet makes a tremendous contribution to the total environmental burden.

A vehicle pollutes air not only with toxic components of exhaust gases, fuel vapors, but also with the products of tire wear and brake-shoe lining, thus the city's particulate matter is increasing in amounts and becomes more toxic. Traffic-induced dust contains numerous toxic chemicals including Pb, La, Rh, Sb, Sr due to gasoline combustion and catalyst used, Cu, Zn and Sb due to brake lining and tire wear, different VOCs residuals due to gasoline leakage and spills.

All these influence negatively human health affecting the increasing amounts of cancer and respiratory diseases, but additionally these pollutants find their end on building surfaces developing a black crust and causing the greatest visual nuisance. Besides, toxic chemical compounds found in city’s particulate matter enhance the natural weathering of building materials contributing to the overall damage.

So far, Saint Petersburg center which is famous for its granite built environment became an object of the investigation, and the chemical testing of rapakivi granite was undertaken from 9 sampling points to study the composition variations at crust and fresh rapakivi granite parts and to analyze the quantitative levels of stone degradation for the purpose of historical preservation with the help of weathering indices application.

All the sampling points were objects of historical preservation; they all have a history of around 200 years. During the time of their existence, their surfaces have accumulated certain elements which were and/or are abundant in the city’s atmosphere. Besides, for the time passed, granite undergoes natural weathering which cannot be eliminated. For the assessment of the granite status, macro and micro element analyses were undertaken.

The macro element analysis provides data for the following weathering indices analysis showing that granite is very resistant to the aggressive outside influence and the level of weathering is low, though it is developed to a higher degree at sample points C and I.

The micro element composition analysis of granite samples reveals that certain elements have been accumulated on the construction surfaces. However, the comparison of the crust and fresh concentrations to the percentage abundance of elements in rapakivi granite does not provide a stable data for the micro elements attribution to those which are not typical for the rock, as both crust and fresh values exceed the bulk earth value of one. In any case, this comparison gives a ground to identify the acquired elements by the comparison of normalized crust and fresh values. As a result the following 14 elements are determined to be accumulated: Se, Bi, As, Cd, Mo, La, Zn, Pb, Sb, Cu, S, Ba, Ce, Sr.

The results of micro element analysis partly resemble the findings, observed in Saint Petersburg dust examination (Kovalenko 2013), for As, Zn, Pb, La, Ba and Sr, which supports the idea that the elements are transported and deposited on building surface together with urban dust.

All of the defined elements are classified as causing certain harm to the environment. Most of these chemical elements are attributed to the traffic based pollutants. As such, the key source of air pollution in city center is the enormous vehicle fleet.

BIBLIOGRAPHY

Anisimova 2008. Состояние атмосферного воздуха в Санкт-Петербурге. HTML-document. http://www.ecounion.ru/ru/site.php?&blockType=253#start No update information. Read 11.02.2014

Bahlung, Dobrzinski, 2009. A review of the Chemical Index of Alteration (*CIA*) and its application to the study of Neoproterozoic glacial deposits and climate transitions in press (2009), in: Arnaud, E., Halverson, G.P. & Shields, G.A., (eds.), The Geological Record of Neoproterozoic Glaciations. Geological Society, London, Memoir

Bityukova, Kasimov 2012. Atmospheric pollution of Russia's cities: Assessment of emissions and immissions based on statistical data. Geofisica Vol. 29, 2012. PDF-document. http://geofizika-journal.gfz.hr/vol_29/No1/29_1_bityukova_kasimov.pdf No update information. Read 24.02.2014

Brimblecombe P., 2003. The effects of air pollution on the built environment. Air Pollution Reviews - Vol. 2

Bulakh 1993. Абакумова Н. Б. Каменное убранство главных улиц Ленинграда. СПб., 1993

Bunin 1986. Мосты Ленинграда. Очерки истории и архитектуры мостов Петербурга — Петрограда — Ленинграда. Исторические зарисовки. Гранит-рапакиви. HTML-document. http://www.most-spb.ru/stat/stat9.htm No update information. Read 17.03.2014

Cooper, Alley 2002. Air pollution control. A design approach. Waveland Press Inc. 3d ed.

Corbitt 1998. Standard handbook of environmental engineering. McGraw-Hill. 2nd ed.

Dimitrov 2004. Overview of the environmental and health effects of urban transport in the Russian Federation and the other countries in eastern Europe, the Caucasus and central Asia. Ministry of Transport of the Russian Federation. PDF-document. http://www.internationaltransportforum.org/IntOrg/ecmt/urban/Moscow04/Dimitrov.pdf No update information. Read 03.03.2014

Ecologicheskii sojuz 2009. В Петербурге самый высокий рост числа онкологических заболеваний. HTML-document. http://www.ecounion.ru/ru/site.php?content=detailcontent.php&blockType=277&blockID=1199 No update information. Read 24.02.2014

Ecologicheskii sojuz 2010. Жители 67 % городов России дышат опасным воздухом. HTML-document.
http://www.ecounion.ru/ru/site.php?content=detailcontent.php&blockType=196&blockID=1176 No update information. Read 24.02.2014

EEA 2012. Emissions of primary particulate matter and secondary particulate matter precursors (CSI 003 / APE 009) – Assessment published Dec 2012. HTML-document.
http://www.eea.europa.eu/data-and-maps/indicators/emissions-of-primary-particles-and-5/assessment-2 Updated 04.12.2013. Read 28.03.2014

EPA 2012. National Ambient Air Quality Standards (NAAQS). HTML-document.
http://www.epa.gov/air/criteria.html Updated 14.12.2012. Read 28.03.2014

EPA 2013. Particulate Matter (PM). Basic Information. HTML-document.
http://www.epa.gov/pm/basic.html No update information. Read 18.03.2014

Fernandez-Camacho, Rodrigues et al. 2012. Ultrafine particle and fine trace metal (As, Cd, Cu, Pb and Zn) pollution episodes induced by industrial emissions in Huelva, SW Spain. Atmospheric Environment xxx (2012) 1-11. PDF-document.
http://rabida.uhu.es/dspace/bitstream/handle/10272/6015/Ultrafine_particle_and_fine_trace.pdf?sequence=2 No update information. Read 01.03.2014

Fitzner, Heinrichs, Kowatzki 1995. Weathering forms - Classification and mapping, in: Verwitterungsformen - Klassifizierung und Kartierung - Denkmalpflege und Naturwissenschaft, Natursteinkonservierung I, Förderprojekt des Bundesministeriums fur Bildung, Wissenschaft, Forschung und Technologie, Verlag Ernst &Sohn, Berlin

GIBDD 2012. Сведения о количестве транспортных средств и прицепов к ним. PDF-document.
http://www.gibdd.ru/upload/iblock/278/27879c0d1f880b4b7d8008048db42694.pdf
No update information. Read 24.02.2014

Golubeva, Sorokina 2013. Report on Ecological Situation in Saint Petersburg in 2012. ДОКЛАД об экологичской ситуации в Санкт-Петербурге в 2012 году. PDF-document. http://gov.spb.ru/static/writable/ckeditor/uploads/2013/06/19/dok2012.pdf
No update information. Read 25.03.2014

Grossi, Esbert et al. 2001. Soiling of building stones in urban environments. Building and Environment 38 (2003) 147-159

Hamilton, Crabbe 2009. Chapter 1. Environment, Pollution and Effects. J. Watt et al. (eds.), The Effects of Air Pollution on Cultural Heritage, Springer Science Business Media, LLC 2009

Härmä, Selonen 2008. Surface weathering of rapakivi granite outcrops - implications for natural stone exploration and quality evaluation, Estonian Journal of Earth Sciences, 2008, 57, 3, 135-148

Hawkes, Webb 1962. Geochemistry in mineral exploration. Harper & Row, publishers, New York and Evanston, (74-91)

Heck, Wu, Lombardi, Qiu, Meyers , Wilhelm, Cockburn , Ritz 2013. Childhood cancer and traffic-related air pollution exposure in pregnancy and early life. Environ Health Perspect 121:1385–1391. PDF-document. http://ehp.niehs.nih.gov/wp-content/uploads/121/11-12/ehp.1306761.pdf No update information. Read 19.03.2014

Hinds 1998. Aerosol technology: properties, behavior, and measurement of airborne particles/ William C. Hinds. - 2nd ed.

Hjortenkrans, Bergbäck et al. 2007. Metal Emissions from Brake Linings and Tires: Case Studies of Stockholm, Sweden 1995/1998 and 2005, Environmental Science Technology 2007, 41, 5224-5230

Jönsson 2011. Ni, Cu, Zn, Cd and Pb in sediments in the city-center of Stockholm, Sweden. Origins, deposition rates and bioavailability. Swedish Environmental Research Institute. PDF-document. http://www.ivl.se/download/18.3175b46c133e617730d80005564/1350484315220/B2013.pdf No update information. Read 15.02.2014

Kovalenko, 2013. Ecogeochemical characteristics of dust in Saint Petersburg, not published. Degree Programme of Geochemistry. Master's Thesis.

Law, Nesbitt et al 1991. Weathering of granite tills and the genesis of a podzol, American Journal of Science, Vol. 291, December, 1991, p. 940-976

Levine, Schwarz 1982. In-cloud and below-cloud scavenging of nitric acid vapor. Atmospheric Environment Vol. 16, No. 7, pp. 1725-1734. PDF-document. http://www.ecd.bnl.gov/steve/pubs/Levine82InCloudScav.pdf No update information. Read 06.03.2014

LUKOT project (2005-2007). Itä-Suomen luonnonkivialan koulutus- ja tutkimusympäristön kehittäminen, LUKOT-projekti. Geologian tutkimuskeskus 2005-2007

Luodes 2014. An interview on granite geochemistry. 10.04.2014. GTK, Helsinki.

Makarova, Ionov et al. 2011. Characterizing the impact of urban sources in russia on air pollution in Northern Europe. Dept. of Atmospheric Physics, Saint Petersburg State University, Saint Petersburg , Russia. PDF-document. http://www.cmascenter.org/conference/2011/abstracts/makarova_characterizing_impact_2011.pdf No update information. Read 24.02.2014

Maksakovskii 2008.Географическая картина мира. Пособие для вузов. Кн. 1: Общая характеристика мира. Глобальные проблемы человечества. HTML-document. http://www.e-reading.co.uk/chapter.php/127765/36/Maksakovskii_-_Geograficheskaya_kartina_mira_Posobie_dlya_vuzov_Kn._I__Obshchaya_harakteristika_mira._Global'nye_p--chestva.html No update information. Read 24.02.2014

Manta, Angelone et al. 2002. Heavy metals in urban soils: a case study from the city of Palermo (Sicily), Italy. The Science of the Total Environment 300 (2002) 229-243. PDF-document.http://didattica.ambra.unibo.it/didattica/att/d7ef.file.pdf No update information. Read 24.02.2014

Nord, Svärdh, Tronner 1994. Air pollution levels reflected in deposits on building stone. Atmospheric Environment Vol.28, No.16, pp. 2615-2622

Obrazkova 2013. Ten Russian cities that need air-quality clean up. Based on materilas from RIA Novosti and RBK. Russia beyond the headlines. HTML-document.http://rbth.co.uk/society/2013/08/09/ten_russian_cities_that_need_air-quality_clean_up_28801.html No update information. Read 10.02.2014

Panova, Akhmedov 2011. Geochemical indicators of genesis of terrigenous rock. Saint Petersburg, 2011

Panova, Vlasov et al. 2014. Physical, chemical and biological weathering of granite-rapakivi in city environment. Not published

Pascal 2011. The chemical composition of granite. HTML-document. http://www.sciences360.com/index.php/the-chemical-composition-of-granite-5083/ Updated: 13.07.2011. Read 10.03.2014

Price, Velbel 2002. Chemical weathering indices applied to weathering profiles developed on heterogeneous felsic metamorphic parent rocks, Chemical Geology 202 (2003) 397– 416

Puttonen 2011. Energy production and Air Pollution. Lecturing material. PDF-document. https://moodle.mamk.fi/course/view.php?id=949 No update information. Read 18.03.2014

Raaschou-Nielsen, Hertel et al. 2001. Air Pollution from Traffic at the Residence of Children with Cancer, American Journal of Epidemiology, 2001,Vol. 153, No.5 PDF-document. http://aje.oxfordjournals.org/content/153/5/433.full.pdf+html No update information. Read 18.03.2014

Rampazzi, Giusanni et al. 2010. Monuments as sampling surfaces of recent traffic pollution. Research article, Environ Sci Pollut Res (2011) 18:184-191

Roshydromet 2013. Overview of the environmental statement and pollution in Russian Federation in 2012. Federal Service for Hydrometeorology and Environmental Monitoring. Moscow. PDF-document. http://downloads.igce.ru/publications/reviews/review2012.pdf No update information. Read 24.02.2014

Ruguin 1965. Geology of Granite. Interscience Publishers, a division of John Wiley & Sons Ltd. p 312

Segal 1987. Защита воздушного бассейна при сжигании топлива. Л.

Semenchin 1993. Аналитические решения краевых задач в математической модели атмосферной диффузии. - Ставрополь: Изд-во СКИ-УУ, 1993. 141с.

Soubbotina 2004. Beyond Economic Growth. An introduction to Sustainable Development. Second Edition. The World Bank Washington, D.C. PDF-document. http://www.worldbank.org/depweb/english/beyond/beyondco/beg_all.pdf No update information. Read 24.02.2014

Sverlova 2009. Научные основы современного подхода к оценке уровня загрязнения атмосферного воздуха городов // Успехи современного естествознания. – 2009. – № 7 – стр. 20-22. HTML-document. www.rae.ru/use/?section=content&op=show_article&article_id=7783859 ment. www.rae.ru/use/?section=content&op=show_article&article_id=7783859 No update information. Read 28.01.2014

Ufivtseva, Terekhina 2005. Phytoindication of ecological state of urban geosystems in Saint Petersburg. Saint Petersburg “Nauka”, 2005

UNECE 2009. Number of passenger cars per 1000 inhabitants, year 2009. HTML-document. http://w3.unece.org/pxweb/quickstatistics/readtable.asp?qs_id=44 No update information. Read 24.02.2014

UNEP 2010. UNEP Country Questionnaire on Auto Fuel Economy Policies for Russia, 2010. PDF-document.

http://www.unep.org/transport/gfei/autotool/case_studies/europe/russia/Russia%20CASE%20STUDY.pdf No update information. Read 24.02.2014

Voitkevich, Miroshnikov et al. 1977. Kratkii spravochnik po geokhimii, Izdatelstvo "Nedra" pp47-50

Vorma, Atso 1976. On the petrochemistry of rapakivi granites with special reference to the Laitila massif, southwestern Finland. Geological Survey of Finland, Bulletin 28

WHO 2005. Air Quality Guidelines. Global Update 2005. Particulate matter, ozone, nitrogen dioxide and sulfur dioxide. PDF-document. http://www.euro.who.int/__data/assets/pdf_file/0005/78638/E90038.pdf No update information. Read 24.02.2014

WHO 2013. ВоздействВие ВзВешенных частиц на здороВье. PDF-document. http://www.euro.who.int/__data/assets/pdf_file/0007/189052/Health-effects-of-particulate-matter-final-Rus.pdf No update information. Read 25.03.2014

Zereini , Alt et al. 2005. Concentration and distribution of heavy metals in urban airborne particulate matter in Frankfurt am Main, Germany. Environ Sci Technol. 2005 May 1; 39 (9): 2983-9

РД 52.04.186-89 (1991). Руководство По Контролю Загрязнения Атмосферы. HTML-document. http://www.infosait.ru/norma_doc/44/44486/index.htm No update information. Read 24.02.2014

APPENDIX

TABLE 10a: The concentration of micro elements in crust, ppm

Sample	Micro elements, ppm																																			
crust	Al	Ba	Ca	Co	Cr	Cu	Fe	K	La	Li	Mg	Mn	Na	Ni	P	Pb	S	Sc	Sr	Ti	V	Y	Zn	Ag	As	Be	Bi	Cd	Ce	Mo	Sb	Se	Te	Th	U	W
A	9290	171	6450	2,9	0,20	9	23200	5920	50,6	33,6	1120	269	2120	2,68	442	93	232	3,56	19,5	1260	2,53	38,4	110,0	0,09	23,40	0,94	0,25	0,27	83,63	1,76	0,20	1,65	0,021	25,11	5,53	1,49
B	10700	173	5320	3,61	0,13	6,25	29100	7970	54,4	46,5	1380	327	2160	2,10	430	15	117	4,54	18,8	1760	2,59	45,8	105,0	0,09	15,10	1,21	0,22	0,23	99,74	1,31	0,13	1,82	0,027	11,51	4,61	3,53
C	12400	124	3030	3,66	0,12	4,89	29200	10800	138,0	42,7	1290	330	1970	<2	292	25	50	6,53	13,1	2070	5,14	55,5	112,0	0,28	12,20	0,77	0,17	0,44	248,30	3,21	0,12	4,08	0,066	54,93	8,30	1,02
D	12800	121	4420	3,38	0,07	3,47	28500	11100	222,0	41,2	1200	328	2390	<2	236	20	41	4,42	13,3	2090	3,47	57,0	99,6	0,24	14,10	0,83	0,08	0,38	408,10	2,80	0,07	6,29	0,058	85,42	7,32	1,19
E	9830	155	5050	2,93	0,13	7,15	21500	6460	56,3	24,7	1110	241	2600	2,09	380	21	133	3,85	17,2	1230	3,30	34,9	113,0	0,10	6,69	0,91	0,27	0,18	102,10	1,93	0,13	1,95	0,016	16,54	4,32	1,11
F	10900	146	3600	1,84	0,15	7,22	21700	10200	321,0	45,7	874	232	2060	2,29	150	29	112	5,33	21,3	1080	1,10	80,5	110,0	0,12	23,00	1,94	0,15	0,20	555,80	2,90	0,15	9,35	0,020	69,27	5,94	1,17
G	12100	136	6990	1,91	0,11	6,41	21600	8750	42,7	41,8	1150	249	2810	<2	162	44	95	4,36	20,6	1150	1,39	51,6	114,0	0,16	6,56	1,82	1,62	0,29	75,00	1,35	0,11	1,60	0,042	15,34	6,62	2,08
H	8610	121	6720	1,77	0,14	5,55	20600	6830	89,6	39,0	799	219	1760	<2	492	18	105	3,24	22,6	1070	<1	51,2	86,7	0,07	8,99	0,90	0,20	0,18	164,40	1,41	0,14	2,78	0,022	30,33	4,07	4,89
I	10500	160	6760	3,58	0,10	11,10	28200	7410	73,8	27,4	1340	390	2550	2,14	617	20	180	5,67	16,4	1740	3,63	54,4	126,0	0,19	7,71	1,10	0,24	0,39	128,60	1,94	0,10	2,31	0,025	20,36	5,85	1,12
Average	10792	145	5371	2,84	0,13	6,78	24844	8382	116,5	38,1	1140	287	2269	2,26	356	31,7	118,3	4,61	18,	1494	2,89	52,1	108,5	0,15	13,08	1,16	0,36	0,28	207,3	2,07	0,13	3,54	0,03	36,53	5,84	1,96

TABLE 10b: The concentration of micro elements in fresh, ppm

Sample	Micro elements, ppm																																			
fresh	Al	Ba	Ca	Co	Cr	Cu	Fe	K	La	Li	Mg	Mn	Na	Ni	P	Pb	S	Sc	Sr	Ti	V	Y	Zn	Ag	As	Be	Bi	Cd	Ce	Mo	Sb	Se	Te	Th	U	W
A	12000	177	7590	6,10	2,42	10,9	42600	8890	113,0	61,1	2020	485	1780	3,20	649	46,2	334	7,75	16,6	2700	4,3	73,2	149,0	0,16	25,5	1,26	0,18	0,30	196,4	2,43	0,15	3,37	0,031	15,3	29,83	2,62
B	8170	133	4880	3,27	1,93	5,05	24900	5890	94,4	42,3	1320	279	1410	<2	439	13,5	113	3,72	12,7	1410	2,6	43,8	87,3	0,09	14,3	0,96	0,24	0,15	156,2	1,56	0,10	2,78	0,014	23,79	4,15	4,50
C	11100	96	4610	3,34	2,40	2,63	26000	9840	135,0	39,9	1180	295	1670	<2	254	18,6	33	6,06	12,1	1930	4,1	55,1	101,0	0,32	11,4	0,59	0,07	0,48	233,2	2,13	0,06	3,96	0,073	54,18	6,51	1,13
D	12400	114	6470	2,94	2,60	3,18	25700	10300	129,0	38,9	1050	315	2460	<2	225	18,0	37	4,09	17,2	1830	3,0	50,4	92,7	0,26	11,2	0,87	0,05	0,38	229,3	1,57	0,08	2,92	0,066	63,64	9,06	1,15
E	9710	151	7230	5,12	2,46	10,2	33900	6560	67,0	24,5	1930	363	2090	<2	793	9,9	147	6,95	12,6	2030	6,2	50,4	127,0	0,10	7,0	0,89	0,19	0,21	125,4	1,93	0,06	2,39	0,018	13,09	3,04	0,72

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F	8820	113	4290	1,79	1,69	4,53	20100	8370	124,0	36,0	801	218	1610	<2	144	19,3	60	4,18	12,8	1150	<1	69,0	90,0	0,14	8,7	1,54	0,12	0,24	225,7	2,49	0,08	4,04	0,040	45,51	7,64	5,49
G	8110	94	2380	1,48	1,67	3,99	18400	6980	157,0	39,3	845	212	1430	<2	101	24,2	28	2,86	16,4	1000	<1	73,7	80,2	0,12	14,1	2,04	1,79	0,21	289,0	1,36	0,11	4,94	0,035	63,72	7,77	1,77
H	7140	79	4250	1,59	1,07	2,74	20500	5370	100,0	42,0	847	222	1230	<2	168	18,2	25	3,38	11,2	1090	<1	63,4	73,4	0,07	8,3	1,05	0,19	0,13	190,1	1,05	0,11	3,34	0,021	36,47	4,44	1,85
I	9550	128	6780	4,43	2,19	9,32	30300	7060	78,4	33,5	1550	394	1960	<2	559	12,1	171	6,75	11,2	1930	5,5	58,6	102,0	0,13	6,7	1,04	0,24	0,25	137,5	2,32	0,06	2,38	0,029	15,68	3,23	1,16
Average	9667	121	5387	3,34	2,05	5,84	26933	7696	110,9	39,7	1283	309	1738	3,20	370	20,0	105,4	5,08	13,6	1674	4,28	59,7	100,3	0,15	11,9	1,14	0,34	0,26	198,1	1,87	0,09	3,46	0,04	52,12	8,41	2,27

TABLE 11a: The crust micro element concentrations in relation to their percentage abundance in granite, ppm

	Micro elements, ppm																																		
Crust	**Al**	**Ba**	**Ca**	**Co**	**Cr**	**Cu**	**Fe**	**K**	**La**	**Li**	**Mg**	**Mn**	**Na**	**Ni**	**P**	**Pb**	**S**	**Sc**	**Sr**	**Ti**	**V**	**Y**	**Zn**	**Ag**	**As**	**Be**	**Bi**	**Cd**	**Ce**	**Mo**	**Sb**	**Se**	**Te**	**Th**	**U**	**W**
Refer.	8720	109	4908	3	3	5	21780	6660	86	33	1237	363	1834	1	278	15	137	4,0	14,0	1106	2	55	72	0,05	6	1	0,01	0,10	100	2,0	0,26	0,05	0,001	18	3,50	1,50
A	1,07	1,57	1,31	0,97	0,07	1,80	1,07	0,89	0,59	1,02	0,91	0,74	1,16	2,68	1,59	6,20	1,69	0,89	1,39	1,14	1,27	0,70	1,53	1,80	3,90	0,94	25,00	2,70	0,84	0,88	0,77	33,00	21,00	1,40	1,58	0,99
B	1,23	1,59	1,08	1,20	0,04	1,25	1,34	1,20	0,63	1,41	1,12	0,90	1,18	NA	1,55	1,00	0,85	1,14	1,34	1,59	1,30	0,83	1,46	1,80	2,52	1,21	22,00	2,30	1,00	0,66	0,50	36,40	27,00	0,64	1,32	2,35
C	1,42	1,14	0,62	1,22	0,04	0,98	1,34	1,62	1,60	1,29	1,04	0,91	1,07	NA	1,05	1,67	0,36	1,63	0,94	1,87	2,57	1,01	1,56	5,60	2,03	0,77	17,00	4,40	2,48	1,61	0,46	81,60	66,00	3,05	2,37	0,68
D	1,47	1,11	0,90	1,13	0,02	0,69	1,31	1,67	2,58	1,25	0,97	0,90	1,30	NA	0,85	1,33	0,30	1,11	0,95	1,89	1,74	1,04	1,38	4,80	2,35	0,83	8,00	3,80	4,08	1,40	0,27	125,80	58,00	4,75	2,09	0,79
E	1,13	1,42	1,03	0,98	0,04	1,43	0,99	0,97	0,65	0,75	0,90	0,66	1,42	NA	1,37	1,40	0,97	0,96	1,23	1,11	1,65	0,63	1,57	2,00	1,12	0,91	27,00	1,80	1,02	0,97	0,50	39,00	16,00	0,92	1,23	0,74
F	1,25	1,34	0,73	0,61	0,05	1,44	1,00	1,53	3,73	1,38	0,71	0,64	1,12	NA	0,54	1,93	0,82	1,33	1,52	0,98	NA	1,46	1,53	2,40	3,83	1,94	15,00	2,00	5,56	1,45	0,58	187,00	20,00	3,85	1,70	0,78
G	1,39	1,25	1,42	0,64	0,04	1,28	0,99	1,31	0,50	1,27	0,93	0,69	1,53	NA	0,58	2,93	0,69	1,09	1,47	1,04	NA	0,94	1,58	3,20	1,09	1,82	162,00	2,90	0,75	0,68	0,42	32,00	42,00	0,85	1,89	1,39
H	0,99	1,11	1,37	0,59	0,05	1,11	0,95	1,03	1,04	1,18	0,65	0,60	0,96	NA	1,77	1,20	0,77	0,81	1,61	0,97	NA	0,93	1,20	1,40	1,50	0,90	20,00	1,80	1,64	0,71	0,54	55,60	22,00	1,69	1,16	3,26
I	1,20	1,47	1,38	1,19	0,03	2,22	1,29	1,11	0,86	0,83	1,08	1,07	1,39	NA	2,22	1,33	1,31	1,42	1,17	1,57	0,11	0,99	1,75	3,80	1,29	1,10	24,00	3,90	1,29	0,97	0,38	46,20	25,00	1,13	1,67	0,75
Aver.	1,24	1,33	1,09	0,95	0,04	1,36	1,14	1,26	1,35	1,15	0,92	0,79	1,24	2,68	1,28	2,11	0,86	1,15	1,29	1,35	1,44	0,95	1,51	2,98	2,18	1,16	35,56	2,84	2,07	1,03	0,49	70,73	33,00	2,03	1,67	1,30

APPENDIX 1 (1)

TABLE 11ba: The fresh micro element concentrations in relation to their percentage abundance in granite, ppm

	Micro elements, ppm																																			
Fresh	**Al**	**Ba**	**Ca**	**Co**	**Cr**	**Cu**	**Fe**	**K**	**La**	**Li**	**Mg**	**Mn**	**Na**	**Ni**	**P**	**Pb**	**S**	**Sc**	**Sr**	**Ti**	**V**	**Y**	**Zn**	**Ag**	**As**	**Be**	**Bi**	**Cd**	**Ce**	**Mo**	**Sb**	**Se**	**Te**	**Th**	**U**	**W**
Refer.	8720	109	4908	3	3	5	21780	6660	86	33	1237	363	1834	1	278	15	137	4,0	14,0	1106	2	55	72	0,05	6	1	0,01	0,10	100	2,0	0,26	0,05	0,001	18	3,50	1,50
A	1,38	1,62	1,55	2,02	0,81	2,18	1,96	1,33	1,31	1,85	1,63	1,34	0,97	3,20	2,33	3,08	2,44	1,94	1,19	2,44	2,16	1,33	2,07	3,15	4,25	1,26	17,88	3,02	1,96	1,22	0,59	67,46	31,49	8,50	8,52	1,75
B	0,94	1,22	0,99	1,09	0,64	1,01	1,14	0,88	1,10	1,28	1,07	0,77	0,77	NA	1,58	0,90	0,82	0,93	0,91	1,27	1,29	0,80	1,21	1,74	2,38	0,96	24,32	1,50	1,56	0,78	0,37	55,52	14,37	1,32	1,19	3,00
C	1,27	0,88	0,94	1,11	0,80	0,53	1,19	1,48	1,57	1,21	0,95	0,81	0,91	NA	0,91	1,24	0,24	1,52	0,86	1,75	2,05	1,00	1,40	6,43	1,90	0,59	6,58	4,80	2,33	1,07	0,22	79,12	73,31	3,01	1,86	0,75
D	1,42	1,05	1,32	0,98	0,87	0,64	1,18	1,55	1,50	1,18	0,85	0,87	1,34	NA	0,81	1,20	0,27	1,02	1,23	1,65	1,52	0,92	1,29	5,25	1,87	0,87	5,49	3,81	2,29	0,78	0,29	78,30	66,43	3,54	2,59	0,76
E	1,11	1,39	1,47	1,71	0,82	2,04	1,56	0,98	0,78	0,74	1,56	1,00	1,14	NA	2,85	0,66	1,07	1,74	0,90	1,84	3,09	0,92	1,76	1,94	1,17	0,89	18,77	2,13	1,25	0,96	0,24	47,76	18,34	0,73	0,87	0,48
F	1,01	1,04	0,87	0,60	0,56	0,91	0,92	1,26	1,44	1,09	0,65	0,60	0,88	NA	0,52	1,29	0,44	1,05	0,91	1,04	NA	1,25	1,25	2,81	1,44	1,54	11,64	2,35	2,26	1,24	0,31	80,70	40,29	2,53	2,18	3,66
G	0,93	0,86	0,48	0,49	0,56	0,80	0,84	1,05	1,83	1,19	0,68	0,58	0,78	NA	0,36	1,61	0,21	0,72	1,17	0,90	NA	1,34	1,11	2,40	2,35	2,04	178,90	2,12	2,89	0,68	0,41	98,78	34,96	3,54	2,22	1,18
H	0,82	0,73	0,87	0,53	0,35	0,55	0,94	0,81	1,16	1,27	0,68	0,61	0,67	NA	0,60	1,21	0,18	0,85	0,80	0,99	NA	1,15	1,02	1,44	1,39	1,05	19,41	1,33	1,90	0,53	0,42	66,82	21,40	2,03	1,27	1,23
I	1,10	1,17	1,38	1,48	0,73	1,86	1,39	1,06	0,91	1,02	1,25	1,09	1,07	NA	2,01	0,81	1,25	1,69	0,80	1,75	0,11	1,07	1,42	2,52	1,12	1,04	24,13	2,52	1,38	1,16	0,23	47,68	28,88	0,87	0,92	0,78
Aver.	1,11	1,11	1,10	1,11	0,68	1,17	1,24	1,16	1,29	1,20	1,04	0,85	0,95	3,20	1,33	1,33	0,77	1,27	0,97	1,51	1,70	1,09	1,39	3,08	1,98	1,14	34,12	2,62	1,98	0,94	0,34	69,13	36,61	2,90	2,40	1,51