

Assessment of Pollution of the Atmospheric Air in the Cities of Azerbaijan

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Abstract

The article is devoted to the results of monitoring of the pollution of the atmospheric air by 26 observation points based in 8 large industrial cities of Azerbaijan. The observations were carried out by 18 harmful substances, including dust, sulfur dioxide, soluble sulfates, carbon dioxide, nitrogen oxide (IV), nitric oxide (II), hydrogen sulfide, soot, solid fluorides, hydrogen fluoride, mercury, ammonia, sulfuric acid, formaldehyde, phenols, furfural in the atmospheric air. On the basis of the monitoring, concentrations of these substances are being defined.

Key words: ingredient, pollutant, concentration, substances, precipitation

The observations on the pollution of the atmospheric air were made by the observation points based in eight largest cities of the Republic of Azerbaijan, including Baku, Sumgait, Ganja, Mingachevir, Nakhchivan, Sheki, and Shirvan, and Lankaran. At observation points, the overall number of which is 26, 102796 analyses have been implemented by 100434 samples during a year. The amount of dust, sulfur dioxide, soluble sulfates, carbon dioxide, nitrogen dioxide, nitric oxide, hydrogen sulfide, soot, solid fluorides, hydrogen fluoride, mercury, ammonia, sulfuric acid, formaldehyde, phenols and furfural per unit volume have been defined with different ways. The results allow to identify the definite concentrations of the harmful substances in the atmospheric air of cities.

Determination of the amount of dust in the air is based on the definition of mass of dust particles absorbed by special filter. Dust concentration is determined by the weight method. Identification of sulfur dioxide in the air is based on the capture of sulfur dioxide by hemosorbent membrane composed of tetrachloride mercurite, and later photometric determination of compounds formed by sulfur dioxide with magenta. Samples of sulfur dioxide are being taken with absorbent pipes.

Determination of nitrogen oxide (IV) is being done with capture of nitrogen oxide (IV) in the air by hemosorbent membrane, and later photometric measuring of optical density of liquid of azo dye formed as a result of combination of nitrite ion with sulfonylureas acid and alphanaphthylamine. Samples of nitrogen oxide (IV) are being taken with absorbent pipes.

Determination of nitrogen oxide (II) in the air is being carried out firstly on the basis of oxidization of nitrogen oxide (II), and then based on capture of derived nitrogen oxide (IV) by hemosorbent membrane with photometric measuring of optical density of liquid of azo dye formed after combination of nitrite ion with sulfonylureas acid and alphanaphthylamine as well. Samples of nitrogen oxide (II) are being taken with absorbent pipes. Determination of soot in the air is based on capture of it by membrane filters, and comparison of the color of the dimming filter with the colors of scale of filter made from clean soot slurry.

Identification of solid fluorides is based on capture of these solid fluorides by AΦA-B10 filter-attached device which allows (after converting them to liquid) to analogically carry out analysis of hydrogen fluoride with defining concentration of the ions of fluoride. Hydrogen fluoride is being captured by hemosorbent membrane. Color of compound formed after amalgamation of zirconium and xylenol orange is being weakened as a result of influence of fluoride ions. Photometrical measurement of this process allows to determine concentration of hydrogen fluoride in the air. Samples of hydrogen fluoride are being taken with absorbent pipes, too.

For determining concentration of chlorine in the air, firstly it is being captured with liquid of methyl orange. Then depending on amount of chlorine, weakening of this liquid as a result of reaction is being measured with photometrical method.

For the purpose of defining concentration of ammonia, the studied air is being absorbed with acid liquid. With using influence of sodium nitroprusside, photometrical determination of indophenol derived after interaction of ammonia with hydrochloride and phenol, is being carried out.

In order to determine hydrogen sulfide in the air, this compound is being captured by hemosorbent membrane after which photometrical measurement of optical density of methylene blue derived after mixture of sulfide ion N, Dimethyl-4-phenylenediamine N and iron chloride, is carried out. For the purpose of disposable determination of concentration of hydrogen sulfide, the air is being absorbed through sorption tubes at speed of 4 liter/minute within 20 minutes.

Determination of soluble sulfates is being carried out in accordance with infusing sediments formed as a result of amalgamation of sulfate ions and chloride of barium.

The mass of sulfate ions is being defined with turbidimetric method. Aerosol of sulfate acid is being determined with the capture of it in the air by filter after which the liquid is being extracted via aerosol filter, and then the concentration of hydrogen ions in its composition is being measured with potentiometric method. In order to define concentration of aerosol of sulfate ion, the sample of air is being absorbed via aerosol filter (filter-keeping device attached with aspirator) at speed of 10 l/min within 20 minutes.

Determination of formaldehyde is being started with capture of it with sulfate ion. The mixture of formaldehyde with phenylhydrazine hydrochloride and chloramine B in the acidic condition creates colored liquid, optical density of which is being measured with photometric method. In order to determine concentration of formaldehyde, the studied air is being absorbed via absorbent device of Richter with using 6 ml of absorbent liquid at 1 l/min within 20 minutes. Determination of phenol in the air is being implemented after capture of phenol by hemosorbent membrane, and photometric determination of compound made by mixture of phenol with 4 of aminoantipyrine and potassium iron cyanide. In order to determine the concentration of phenol, the air is being absorbed through sorption tube with aspirator at speed of 10 l/min within 20 minutes.

Determination of furfural in the air is based on measurement of optical density of oxyglutaconic aldehyde dianilide. With the purpose of deriving this pink-colored liquid, interaction of furfural and aniline is being subjected in the acidic condition. In order to take the needed sample, the air is being absorbed through absorbent device with one-numbered porosity, into which 5 ml of absorbent liquid is poured. The process of absorption is being carried at speed of 0,5 l/min within 20 minutes.

Determination of the concentration of carbon dioxide is carried out with using gas analyzer.

Working principle of gas analyzer is based on electrochemical method. Consisting of potentiostatic amperometry, the mentioned method is being applied on the basis of measurement of current that arises due to electrochemical oxidation of carbon dioxide on working electrode.

In order to define mercury in the atmospheric air, firstly mercury vapors are being captured by hemosorbent membrane from chromium trioxide. Then mercury with tin 2-chloride is being reduced to elementary condition, and the concentration of mercury is being determined with atomic absorption method.

As for determination of hydrogen chloride in the air, it is based on absorption of the atmospheric air through glass beads-composed sphere soaked with soda solution. The concentration of hydrogen chloride is being determined on the basis of reaction of mercury (II) thiocyanate and 3-valent iron. In order to determine disposable hydrogen chloride, the studied air is being absorbed through absorbent tube at speed of 5 l/min within 20 minutes.

In accordance with sanitary and hygienic requirements, the disposable (1) and the average daily (2) Allowed Concentration Limit (ACL) is considered to be one of main peculiarities of harmful substances. The disposable ACL includes taking of samples within 20 minutes after which the disposable concentration of mixtures is being compared. The average daily ACL includes long-term effect on the basis of which the average daily and annual concentrations are being compared.

Air Pollution Index (API) is being defined for specific mixture. For substance, API is calculated as the following formula:

$$J_i = \left(\frac{c_{ave}}{ACL_i} \right)^{C_i},$$

where, c_{ave} is medium daily concentration of a substance;

ACL_i is the daily average of allowed concentration limit;

C_i is the stable measure that allows to equalize the harmfulness degree of a substance to the harmfulness degree of sulfur dioxide; the four classes of riskiness of C_i for harmful substances is accepted as follows: 1.7, 1.3, 1.0 and 0.9.

The summative pollution degree of the atmospheric air is calculated with complex ACL. The calculation of 'm'-named substance in the air is carried out as the following:

$$J_m = \sum_{i=1}^m J_i = \sum_{i=1}^m \left(\frac{c_{ave}}{ACL_{c_i}} \right)^{C_i}$$

Depending on the API, the level of air pollution are graded as the following:

1) <5 – low pollution; 2) 5-6 – medium pollution; 3) 7-13 – high pollution; 4) ≤ 14 – very high pollution.

According to the results of analyses carried out in the territory of the Republic of Azerbaijan, the highest grade of contamination with basic and specific mixtures is being observed in the air of Sumgait, Baku and Shirvan cities. Among pollutant ingredients, the highest average annual concentration in the air was fixed by the air of Sumgait city where concentration of chlorine exceeded the ACL by 2,7 times as well as hydrogen fluoride by 2,0 times and nitrogen dioxide by 2,2 times as much. These indicators are dated to 2004-2008. The API in Sumgait was 5,1 or at medium grade in 2010.

The higher grade of contamination of the air in Sumgait is related to location of chemical, petrochemical and other industries in the relatively small industrial area where wastes arise in organized and non-organized forms. The city of Sumgait is situated in non-wide coastal plain of the Absheron peninsula. The city is covered by the Caspian Sea in north as well as the southern lower foothills of Greater Caucasus Mountains on the opposite side. The dominant winds are from the north, the north-west and the south.

The physically and geographically favorable peculiarities of Sumgait create aerodynamic effect of pipe, playing a role of natural regulator of the air. The industrial zone is situated to the north-west and west of the compact residential area. Therefore, the blowing north-western and western winds partially bring harmful wastes to the residential part of Sumgait. The highest grade of pollution takes place in warmer period of year. This is particularly connected with domination of anticyclone and the condition when winds blow weakly.

Baku city situates in the south of the Absheron peninsula, on the shore of the Caspian Sea. Its position of location looks like amphitheatre due to the terraces descending towards the bay of Baku. The territory of Baku city is chiefly dominated by north-, north-western-, south-western- and south winds.

The repeating of quiet air condition is 51,4, and the average amount of annual precipitation makes 18,25 mm. By the harmful wastes, the highest average annual concentration were observed at 19th station located in the Binagadi district of Baku where hydrogen fluoride was 1,2 times more than the ACL. This was related to proximity of the Binagadi district to Sumgait city where the concentration of the mentioned compound were fixed at higher grade. Compared with 2009, the average annual concentration of hydrogen fluoride were increased by 1,2 times as much in Baku.

Ganja city is situated at the foothill valley, to the north and north-east of the Lesser Caucasus Mountains. The city is surrounded by mountain ranges on the south and south-west. Ganja-located area is dominated by winds blowing from the south-west, the north-west and the south-east. The repeating of low-speed winds (0-1 m/sec) is 64,3%, and the quiet air condition makes 50,4%. The average amount of annual precipitation is 8,8 mm. The repeating of hazy days is 1,2%. Among pollutants in the air of Ganja city, only the annual average concentration of dust was observed as 1,3 times more than the ACL. Other indicators did not exceeded the ACL, being at the same level compared to 2008.

Mingachevir city is located on the plain territory of Kur-Araz, near the Mingachevir water storage. The city is surrounded by Bozdag Mountain Range to the north and north-east. The dominant winds blow from the south, the north, the north-west and the west. The repeating of winds with 0-1 m/sec of speed is 53,6% whereas the repeating of quiet air makes 33%. The average amount of annual precipitation is 5,9 mm. The concentration of pollutants in the city remained at the same level compared to 2008.

According to the results of analyses, the average annual concentration of nitrogen oxide (IV) in the air of Shirvan city does not exceed the ACL.

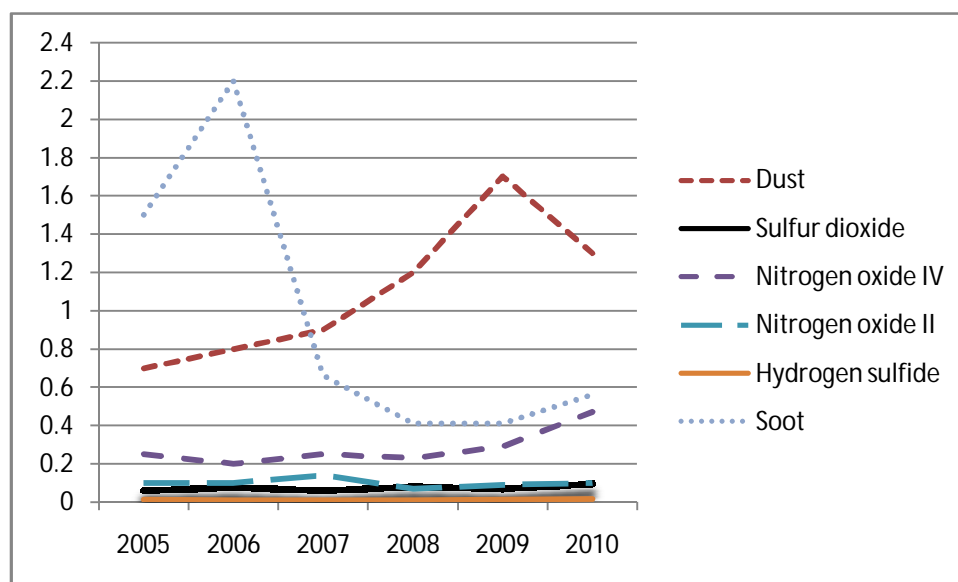
The fixed API is 0,43 by the air of Shirvan city equated 0,43 or at weak contamination grade. The repeating of winds with 0-1 m/sec of speed is 7,4% whereas the repeating of hazy days is only 0,5%. The average annual amount of precipitation is 8,1 mm. The average annual concentration of pollutants fixed by the air of Nakhchivan, Sheki and Lankaran cities do not exceed the ACL as well. The fixed API by these cities is 0,7, 1,03 and 0,4 respectively, showing the medium level of air pollution.

The following tables and pictures reflect the change of average and maximal concentrations of harmful substances in the air of the largest cities of Azerbaijan. Observations on air pollution are carried out by dust, sulfur dioxide, soluble sulfates, carbon dioxide, nitrogen oxide II, nitrogen oxide IV, hydrogen sulfide, soot, solid fluorides, hydrogen fluoride, chlorine, ammonia, sulfuric acid, formaldehyde, and furfural.

Table1
The average concentration of harmful substances in the air of Baku city (mg/m³)

Ingredients	ACL	Years						
		2004	2005	2006	2007	2008	2009	2010
Dust	0,15	0,2	0,1	0,2	0,2	0,2	0,3	0,3
Sulfur dioxide	0,05	0,025	0,019	0,020	0,015	0,014	0,015	0,015
Carbon dioxide	3	2	2	2	2	2	2	3
Nitrogen oxide IV	0,04	0,06	0,05	0,04	0,05	0,05	0,05	0,08
Nitrogen oxide II	0,06	0,03	0,03	0,02	0,02	0,02	0,02	0,04
Hydrogen sulfide		0,002	0,002	0,002	0,002	0,002	0,002	0,003
Soot	0,05	0,05	0,04	0,02	0,02	0,01	0,01	0,01
Solid fluorides	0,03	0,00	0,00	0,00	0,00	0,00	0,00	0,01
Hydrogen fluoride	0,005	0,005	0,003	0,003	0,003	0,007	0,006	0,006
Chlorine	0,03	0,03	0,03	0,03	0,03	0,03	0,01	0,03
Sulfuric acid	0,1	0,01		0,01	0,01	0,01	0,01	0,01
Ammonia	0,04	0,00	0,00	0,00	0,00	0,00	0,01	0,02
Formaldehyde	0,003	0,004	0,003	0,003	0,002	0,003	0,004	0,004
Furfural	0,05	0,05	0,03	0,03	0,02	0,01	0,01	0,02

The changes of concentrations of dust, sulfur dioxide, nitrogen oxide IV, nitrogen oxide II, hydrogen sulfide and soot in the air of Baku were obvious in 2005-2010 (pic. 1).



Picture 1. The change of maximal concentration of main harmful substances in the air of Baku city by years (mg/m³)

The change of the concentration of other substances is given on the following table 2. Overconcentration of carbon dioxide is particularly should be noted.

Table 2

The maximal concentration of some harmful substances in the air of Baku city (mg/m³)

Ingredients	Years						
	ACL	2005	2006	2007	2008	2009	2010
Carbon dioxide	5	11	13	14	18	12	12
Solid fluorides	0,2	0,01	0,01	0,01	0,01	0,02	0,03
Hydrogen fluoride	0,02	0,019	0,018	0,024	0,025	0,022	0,021
Chlorine	0,1	0,11	0,10	0,10	0,12	0,08	0,11
Sulfuric acid	0,3	0,03	0,02	0,02	0,02	0,02	0,02
Ammonia	0,2	0,01	0,01	0,01	0,01	0,05	0,04
Formaldehyde	0,035	0,011	0,015	0,012	0,034	0,032	0,028
Furfural	0,05	0,15	0,17	0,17	0,11	0,13	0,13

In 2010, 41273 examples were taken and 42071 analyses were carried out by the observation stations. The annual amount of sulfur dioxide, carbon dioxide, nitrogen oxide (II), soot, solid fluorides, ammonia, sulfuric acid and furfural in the air was less than the ACL. The average annual amount of chlorine and formaldehyde was in accordance with the ACL.

Among main pollutants, the amount of nitrogen dioxide (IV) was higher in the air of administrative districts of Baku as it was in the previous year. By Khatai, Yasamal and Narimanov districts, this indicator was 2,8-5,5 times much more than the allowed disposable maximal concentration. The high concentration of contaminants was observed at stations situated in the vicinity of the oil-refining facilities, and highways.

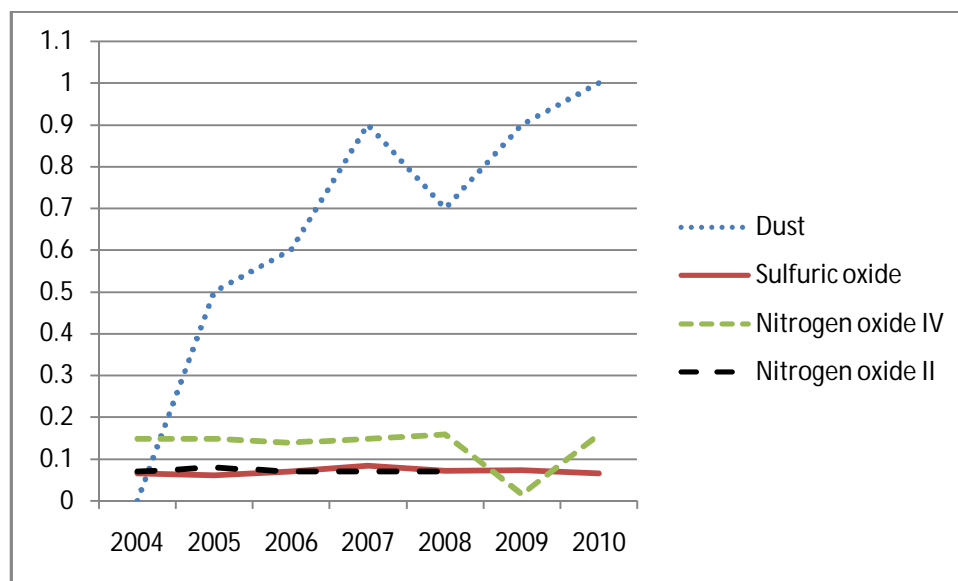
The analysis of the following table shows that some ingredients exceed the ACL in Sumgait city as well.

Table 3
The average concentration of harmful substances in the air of Sumgait city (mg/m³)

Ingredients	ACL	Years						
		2004	2005	2006	2007	2008	2009	2010
Dust	0,15	0	0,1	0,1	0,1	0,1	0,1	0,2
Sulfur dioxide	0,05	0,023	0,024	0,024	0,025	0,025	0,025	0,026
Carbon dioxide	3	1	1	1	1			
Nitrogen oxide (IV)	0,04	0,08	0,08	0,08	0,09	0,08	0,08	0,09
Nitrogen oxide (II)	0,06	0,03	0,03	0,04	0,04	0,04		0,04
Hydrogen sulfide		0,08	-	-	-	-		0,08
Soot	0,03	-	-	0,01	0,01	0,01	0,01	0,01
Solid fluorides	0,005	0,010	0,010	0,010	0,011	0,011	0,027	0,011
Hydrogen fluoride	0,03	0,08	0,07	0,08	0,08	0,08	0,07	0,08
Chlorine	0,04	0,02	0,02	0,02	0,02	0,02	0,02	0,02

In particular, the concentration of dust, solid fluorides and hydrogen fluoride is much more than the ACL in Sumgait.

The change of maximal concentration of harmful substances in the air of Sumgait was more obvious by the four ingredients: dust, sulfuric acid, nitrogen oxide-4 and nitrogen oxide-2 (pic. 2).



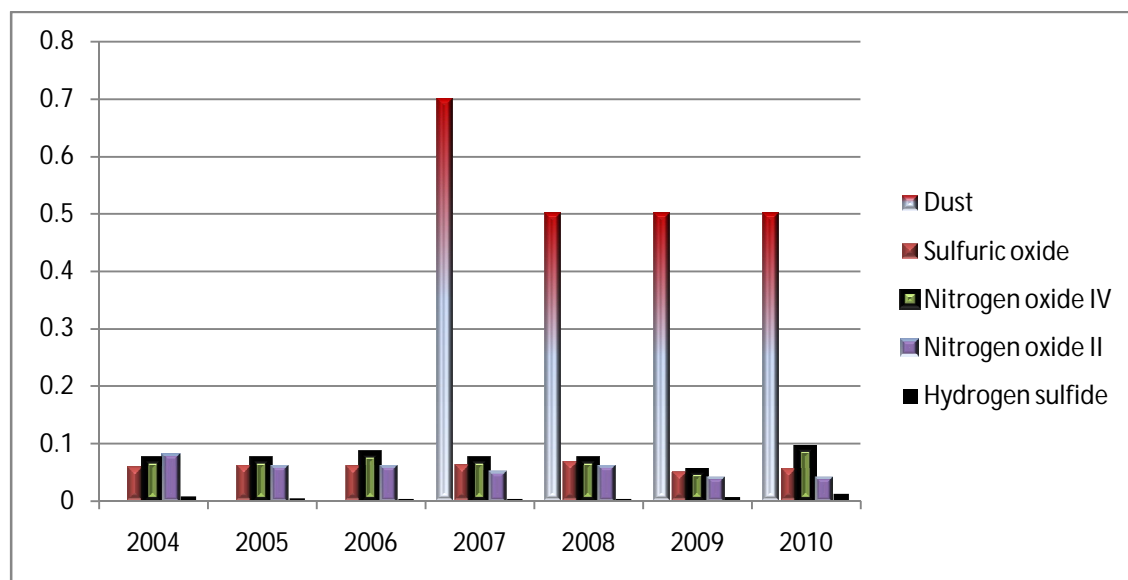
Picture 2. The change of maximal concentration of harmful substances in the air of Sumgait city by years (mg/m³)

The observations on pollution of the air in Ganja have been carried out at 5 observation stations by dust, sulfuric dioxide, nitrogen oxide (IV), nitrogen oxide (II) and hydrogen sulfide. In 2009, 17055 samples were taken and 17924 analyses were carried out at these observation stations.

According to the analysis, the average annual concentrations of the sulfuric dioxide, nitrogen oxide (IV), nitrogen oxide (II) and hydrogen sulfide were less compared to the ACL. The maximal concentrations of each of these ingredients were fixed as within the ACL. The API by the air of Ganja made 2,7.

Table 4
The average concentration of harmful substances in the air of Ganja city (mg/m³)

Ingredients	ACL	Years						
		2004	2005	2006	2007	2008	2009	2010
Dust	0,15	-	-	-	0,2	0,2	0,1	0,2
Sulfur dioxide	0,05	0,032	0,032	0,036	0,034	0,037	0,034	0,037
Nitrogen oxide (IV)	0,04	0,04	0,03	0,03	0,03	0,03	0,03	0,02
Nitrogen oxide (II)	0,06	0,03	0,03	0,03	0,03	0,02	0,02	0,02
Hydrogen sulfide		0,003	0,003	0,003	0,002	0,002	0,002	0,002
Hydrogen fluoride	0,005	0,005	0,006	0,006	0,009	0,006	0,006	0,004



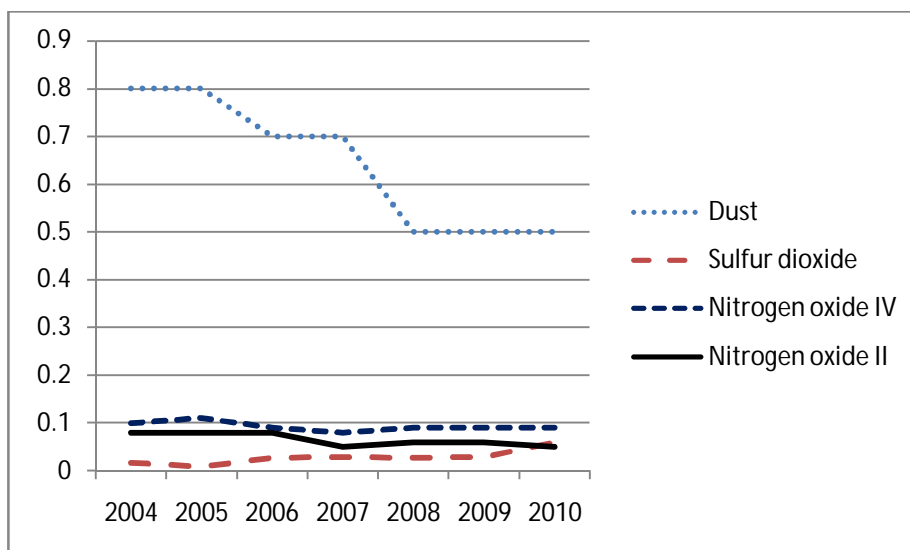
Picture 3. The maximal concentration of harmful substances in the air of Ganja city (mg/m³)

In Mingachevir city, the observations on air pollution were carried out at 4 stations where 15897 samples were taken in the air, on the basis of which 16683 analyses were carried out.

According to these analyses, the concentrations of sulfur oxide, carbon dioxide, nitrogen oxide (IV) and nitrogen oxide (II) were fixed as within the ACL. In the air of Mingachevir, the API was equal to 3,4 or at low level of pollution.

Table 5
The average concentration of harmful substances in the air of Mingachevir city (mg/m³)

Ingredients	ACL	Years						
		2004	2005	2006	2007	2008	2009	2010
Dust	0,15	0,4	0,4	0,2	0,2	0,2	0,2	0,2
Sulfuric dioxide	0,05	0,005	0,8	0,007	0,012	0,011	0,009	0,011
Carbon dioxide	3	2	3	2	2	2	2	2
Nitrogen oxide (IV)	0,04	0,06	0,05	0,05	0,04	0,04	0,04	0,03
Nitrogen oxide (II)	0,06	0,04	0,04	0,03	0,02	0,02	0,02	0,03
Hydrogen sulfide		-	-	-	-	-		
Hydrogen fluoride	0,03	-	-	-	-	-		
Phenol	0,003	0,005	0,005	0,005	0,004	0,004	0,004	0,005



Picture 4. The change of maximal concentration of harmful substances in the air of Mingachevir city (mg/m³)

The observations on air pollution of Shirvan city is carried out at one station. 1407 analyses on the basis of 1407 samples were carried out within a year.

According to the results of observations, the average annual concentration of nitrogen oxide (IV) was much more by 1,5 times compared to the ACL. In 2005-2008, the concentration of nitrogen oxide (IV) was increased from 0,04 mg/m³ to 0,07 mg/m³. The API made 0,43.

Table 6
The average concentration of harmful substances in the air of Shirvan city (mg/m³)

Ingredients	ACL	Years						
		2004	2005	2006	2007	2008	2009	2010
Dust	0,15	-	0,1	-	-	-		
Sulfuric dioxide	0,05	0,030	0,038	-	-	-		0,041
Nitrogen oxide (IV)	0,04	0,04	0,04	0,06	0,06	0,07	0,06	0,06

Table 7
The maximal concentration of harmful substances in the air of Shirvan city (mg/m³)

Ingredients	ACL	Years						
		2004	2005	2006	2007	2008	2009	2010
Dust	0,5	0	0,1	-	-	-		
Sulfuric dioxide	0,5	0,148	0,050	-	-	-		0,091
Nitrogen oxide (IV)	0,085	0,06	0,08	0,12	0,09	0,09	0,14	0,10

In Nakhchivan city, the observations on air pollution were carried by three pollutants (dust, sulfuric dioxide and carbon dioxide) based on analyzing 4395 samples at two stations.

According to observations, the average annual concentrations of dust, sulfuric dioxide and carbon dioxide were fixed as within the ACL. By the air of Nakhchivan, the API was 0,7.

Table 8
The average concentration of harmful substances in the air of Nakhchivan city (mg/m³)

Ingredients	ACL	Years						
		2004	2005	2006	2007	2008	2009	2010
Dust	0,15	0,1	0,1	0,1	0,1	0,1	0,1	0,1
Sulfuric dioxide	0,05	0,039	0,042	0,044	0,050	0,052	0,053	0,044
Nitrogen oxide (IV)	0,04	0,03	0,03	0,03	0,03	0,03	0,03	0,03

Table 9
The maximal concentration of harmful substances in the air of Nakhchivan city (mg/m³)

Ingredients	ACL	Years						
		2004	2005	2006	2007	2008	2009	2010
Dust	0,5	0,3	0,2	0,3	0,2	0,3	0,3	0,03
Sulfuric dioxide	0,5	0,096	0,098	0,074	0,078	0,079	0,080	0,080
Nitrogen oxide (IV)	0,085	0,09	0,06	0,06	0,05	0,07	0,06	0,06

In Sheki and Lankaran cities where industries are less-developed, observations on air pollution were carried out at one station for each.

In Sheki city, 1758 analyses were carried out within a year concerning sulfuric dioxide and nitrogen oxide (IV). The concentration of these substances were observed as within the ACL.

In Lankaran, in order to define the concentration of dust, 2240 samples were analyzed. The analyses found that the average annual and maximal concentrations of dust were within the ACL. The API was 0,4.

Analysis of the results of the observations shows also that in some years, excluding

Sumgait city, amount of wastes emitted by vehicles considerably changed. Thus, in 2000, the amount of pollutants of the mentioned group in the air of Baku city was 229,9 thousand tons whereas in 2007, it made 410,7 thousand tons. In 2000-2007, the corresponding indicators were fixed as from 20,8 to 37,2 thousand tons. For Sumgait city, the data made 14,3 and 8,2 thousand tons respectively.

Conclusion

1. The carried studies show that the chemical composition of rains seasonally change and therefore the amount of concentrations of mixtures are averagely calculated by the current year.
2. According to the observation and studies, chemical composition of atmospheric precipitations consist of sulfate (19,5%), nitrate (9,5%), ammonia (1,0%), chloride (11,0%), hydrocarbonate (20,5%), phosphate (0,02%), calcium (8,73%) and magnesium ions (3,75%).

More than half of the defined wastes falls to the share of vehicle transport. In particular, density of vehicles affects the composition of harmful rains in Baku, and there are differences between this city and the others for this feature.

3. The studies also show that the reason of high amount of carbon dioxide and nitrogen compounds among harmful ingredients of anthropogenic origin in the air of cities of Azerbaijan during warmer period is related to vehicles. 65-70% of the pollutant ingredients were emitted by vehicles in the industrial cities of the country.

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