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MONITORING OF HYDROGEN SULFIDE CONTENT IN WINTER IN THE OBSERVATION POINTS OF ATYRAU CITY

The article analyzes the monitoring of hydrogen sulfide content in the air of Atyrau in the winter period of 2021-2022. The purpose of this study is to study the hydrogen sulfide content in the air environment of the city of Atyrau, which has been increasing in recent years as a result of anthropogenic impact. The monitoring results were analyzed according to the data of Kazhydromet observation points, including 15 observation points. Monitoring of the study showed that among 15 observation points, there are exceedances of the maximum permissible concentrations of hydrogen sulfide in all three winter months, but however, it can be observed that the highest concentrations are observed in December and February, whereas in January these data are close to the MPC. Especially high rates are characteristic of points located near the Atyrau Oil Refiner, which is probably the main source of hydrogen sulfide. At the same time, the excess of the MPC for hydrogen sulfide and at points in the territories of the city exceeds more than 5-15 times. An important step towards optimizing the monitoring of the effects of hydrogen sulfide emissions at the Atyrau Refinery is the monitoring of atmospheric air quality and the introduction of modern technologies and dust and gas cleaning equipment. At the same time, it is possible to reduce the emission of hydrogen sulfide as a result of measures aimed at the reconstruction and overhaul of the sewage system in Atyrau.

Key words: hydrogen sulfide in the air, Atyrau, monitoring, winter period, Kazhydromet observation points.

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Атырау қаласының бақылау пункттерінде қысқы кезеңде күкіртсутегі құрамының мониторингісі

Мақалада 2021-2022 жылғы қысқы кезеңде Атырау қаласының ауасындағы күкіртсутектің құрамына мониторинг бойынша талдау жүргізілді. Аталған зерттеудің мақсаты соңғы жылдары антропогендік әсер нәтижесінде артып келе жатқан Атырау қаласының ауа ортасындағы күкіртсутектің құрамын зерттеу болып табылады. Мониторинг нәтижелері Қазгидрометтің бақылау пункттерінің деректері бойынша талданды, оның ішінде 15 бақылау пункті бар. Зерттеу мониторингі 15 бақылау пунктінің арасында барлық үш қыс айында күкіртсутегі құрамының рұқсат етілген шекті шоғырлануының артқаны байқалатынын көрсетті, алайда неғұрлым жоғары құрам желтоқсан және ақпан айларында байқалатынын, ал қаңтарда бұл деректер ШЖК-ға жақын екенін байқауға болады. Әсіресе жоғары көрсеткіштер АМӨЗ-ге жақын орналасқан пункттерге тән, бұл күкіртсутектің негізгі көзі болып табылады. Бұл ретте, күкіртсутегі бойынша ШЖК артуы және қала аумақтарындағы пункттерде 5-15 еседен асады. Атырау мұнай өңдеу зауытында күкіртті сутек шығарындыларының әсер ету мониторингін оңтайландыру жолындағы маңызды қадам атмосфералық ауа сапасына мониторинг жүргізу және қазіргі заманғы технологиялар мен шаң мен газ тазалау жабдықтарын енгізу болып табылады. Сонымен қатар, Атыраудағы кәріз жүйесін қайта жаңартуға және күрделі жөндеуге бағытталған шаралар нәтижесінде күкіртсутектің шығарылуын азайтуға болады.

Түйін сөздер: ауадағы күкіртсутек, Атырау, мониторинг, қысқы кезең, Қазгидрометтің бақылау пункттері.

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Мониторинг содержания сероводорода в зимний период в пунктах наблюдения города Атырау

В статье проведен анализ по мониторингу содержания сероводорода в воздухе города Атырау в зимний период 2021-2022 года. Целью данного исследования является изучение содержания сероводорода в воздушной среде города Атырау, которое за последние годы повышается в результате антропогенного воздействия. Результаты мониторинга проанализированы по данным 15 пунктов наблюдения Казгидромет. Мониторинг исследования показал, что среди 15 пунктов наблюдения отмечаются превышения предельно допустимых концентраций содержания сероводорода во всех трех зимних месяцах, при этом наиболее повышенные содержания отмечаются в декабре и феврале, тогда как в январе эти данные близки к ПДК. Особенно высокие показатели характерны для пунктов, расположенных вблизи АНПЗ, который, возможно, и является основным источником поступления сероводорода. При этом превышение ПДК по сероводороду и на пунктах, расположенных на территории города, составляет 5 – 15 раз. Важным шагом на пути оптимизации мониторинга воздействия выбросов сероводорода на Атырауском нефтеперерабатывающем заводе является проведение мониторинга качества атмосферного воздуха и внедрение современных технологий и пыле- и газоочистных оборудований. В то же время уменьшить выброс сероводорода возможно в результате мер, направленных на реконструкцию и капитальный ремонт канализационной системы в Атырау.

Ключевые слова: сероводород в воздухе, Атырау, мониторинг, зимний период, пункты наблюдения Казгидромет.

Introduction

One of the air pollutants is hydrogen sulfide. Hydrogen sulfide is one of the main compounds involved in the natural sulfur cycle in the environment [1]. It is contained in volcanic gases and is formed by the action of bacteria during the breakdown of both plant and animal protein. Bacteria can also produce it by direct reduction of sulfate. Significant concentrations of hydrogen sulfide are observed in some natural gas fields and in geothermally active areas.

The amount of H_2S emitted into the atmosphere from human activity is difficult to quantify worldwide due to a lack of comprehensive data and/or reporting [2]. Hydrogen sulfide can be formed whenever elemental sulfur or sulfur-containing compounds are exposed to organic materials at high temperatures. In industry, it is usually produced as an undesirable by-product, although it is an important reagent or intermediate in some processes. Hydrogen sulfide is formed as a by-product in the production of coke from sulfur-containing coal, the processing of sulfur-containing crude oil, the production of carbon disulfide, the production of viscose fiber and in the crafting process for the production of wood pulp [3-4]. Although hydrogen sulfide concentrations in urban areas can sometimes reach 0.050 mg/m^3 with an average time of 30 mm/h, they are usually below 0.0015 mg/m^3. Peak concentrations reaching 0.20 mg/m^3 have been recorded near point sources [5].

Therefore, in 2017, 367 cases of high hydrogen sulfide pollution were recorded in Atyrau from 10 to 49 – exceeding the maximum permissible concentration (MPC) and 75 HPs (high pollution) from 20 to 102 – exceeding the maximum permissible concentration. In 2018 – 1102 cases of HP with hydrogen sulfide – from 10 to 68, exceeding the MPC, 177 cases of EHP (extreme high pollution) from 50 to 178 exceeding the MPC, in 2019 – 758 cases of HP from 10 to 49 exceeding the MPC, EHP – 60 cases of EHP from 50 to 178 exceeding the MPC, in 2020 – 161 cases of HP from 10 to 49 exceeding the MPC and 2 cases of EHP from 50 to 178 exceeding the MPC. Most of the facts of HP and EHP with hydrogen sulfide were recorded in the direction of the wind at the ecological post “West Oil”. This station is located in an industrial area near the evaporation fields “Rotten Beam” at a distance of 840 meters [6-9].

Materials and methods

Monitoring of the state of the atmosphere in Atyrau is conducted at 5 stationary posts (three of them are automatic, two are manual). It is carried

out according to 13 indicators: suspended particles (dust), sulfur dioxide, nitrogen oxide and dioxide, hydrogen sulfide, carbon oxide and dioxide, phenol, ammonia, formaldehyde, etc. In addition, Kazhydromet analyzes data from the existing network of observations and posts of NCOC (North Caspian Operating Company N.V.) and AOR LLP. In Atyrau, NCOC has 9 stationary posts and 4 Atyrau Oil Refinery posts. Compared with 2007, when there was a low level of air pollution, there is a high level of pollution for the period 2018 to 2020. The air is polluted with substances such as suspended particles (dust, PM – 10, PM – 2.5), nitrogen oxide and hydrogen sulfide. Meteorologists, according to the Regulations on the procedure of RSE "Kazhydromet", assess the state of the atmosphere according to two criteria: high pollution (HP) and extremely high pollution (EHP) [10]. Now we will give figures and facts on hydrogen sulfide.

Monitoring of hydrogen sulfide content in winter from December 1, 2021 to February 28, 2022 was carried out on 15 points [11]:

Observation point	Location coordinates
Steaming AOR	47.0726660,51.9508610
Himposelok AOR	47.0887220,51.9352780
Mirny AOR	47.0754720,51.9107500
Reshuffling the AOR	47.0685280,51.9052210
POP (Pollution Observation Point) No. 5 (Kursai, Karabau Street, building 12)	47.0668850,51.8864810
POP (Pollution Observation Point) No. 9 (Bereke Industrial Zone area, Gurievsnab Street)	47.1558350,51.9814530
NCOC No.103 (Chagall)	47.1117740,51.9221670
NCOC No. 108 (TKA)	47.1645230,52.0275220
NCOC No. 109 (Vostok)	47.0947250,51.9250130
NCOC No. 110 (Privokzalny)	47.1261730,51.9472360
NCOC No.111 (Zhilgorodok)	47.0988520,51.9006170
NCOC No.112 (Akimat)	47.1050630,51.9164730
NCOC No.113 (Avangard)	47.0930470,51.8869910
NCOC No.114 (Zagorodnaya)	47.1415560,51.8959480
POP (Pollution Observation Point) No. 1 (Zhanbai village, Nysanov Street, plot 96)	47.1394540,51.9646640

Results and discussion

The analyzed area is characterized by a low frequency of calm, weak and comfortable winds. Winds are unpleasantly active most of the time of the year. Wind speeds in the range of 2.6-3.7 m/s are observed in almost 100% of cases. The highest wind speeds are observed in the winter and spring periods of the year, when even the average monthly values of speeds are 3.6 – 4.1 m/s (Table 1). The average annual wind speed is 3.2 m/s [12].

Table 1 – Average repeatability of wind direction and calm (%)

N	NE	E	SE	S	SW	W	NW
11	12	14	17	9	13	10	13

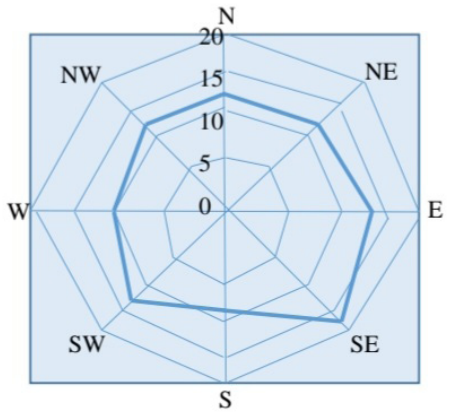

Figure 1 – Wind Rose
In the study area, the prevailing, on average for the year, is the southeasterly wind direction

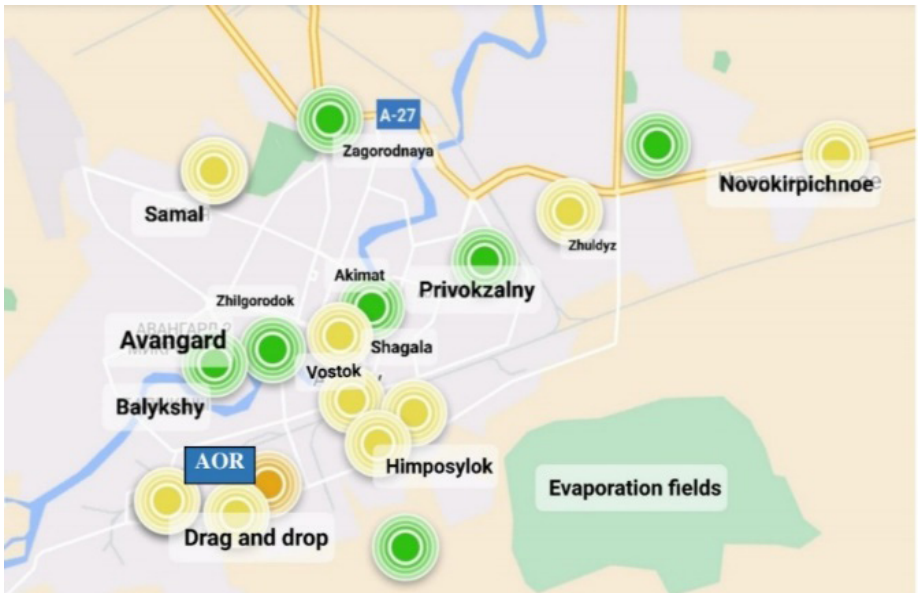

Figure 2 – The Map of Atyrau city

Figure 2 shows a map of the location of observation points and the Atyrau Oil Refinery. Atyrau Oil Refinery is located in the northwestern part of the city. All observation points from the Atyrau oil Refinery are located in the north-western, northern and north-eastern directions, where the average repeatability of the wind direction is from – 11 to 13 m/s. Thus, the emissions of hydrogen sulfide from the Atyrau Oil Refinery are evenly distributed across all observation points within the city.

The results of monitoring the hydrogen sulfide content for three winter months in Atyrau can be viewed in Figures 2-4 and Table 2.

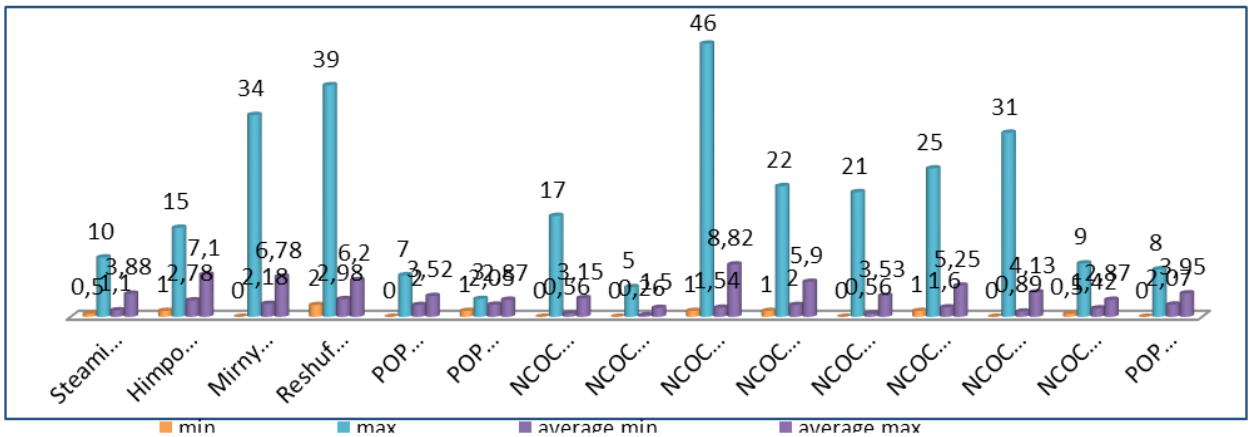

Figure 3 – Monitoring of hydrogen sulfide content in the air of Atyrau in December 2021

Figure 3 shows a diagram of monitoring the hydrogen sulfide content in the air of the city of Atyrau in December 2021. As can be seen from the diagram, the maximum values were observed at NCOC points No.109 (Vostok) – 46 mgm/m^3, Reshuffling the AOR – 39 mgm/m^3, Mirny AOR – 34 mgm/m^3, NCOC No.113 (Avangard) – 31 mgm/m^3, NCOC No.112 (Akimat) – 25 mgm/m^3, NCOC No. 110 (Privokzalny) – 22 mgm/m^3 and at NCOC No. 111 (Zhilgorodok) – 21 mgm/m^3. However, at other points there is an excess of the MPC in terms of hydrogen sulfide content, except

for POP No. 9 (Bereke Industrial Zone area, Gurievnab Street), where the maximum value is 3 mgm/m³.

Figure 4 shows a diagram of monitoring the hydrogen sulfide content in the air of Atyrau in January 2022.

As can be seen from the diagram, the maximum values were observed at the points of Reshuffling the AOR -29 mgm/m³, Himposelok AOR – 27 mgm/m³. Mirny AOR – 21 mgm/m³, NCOC No. 109 (Vostok) – 19 mgm/m³, NCOC No. 110 (Privokzalny) – 17 mgm/m³ and at NCOC No. 112 (Akimat) – 16 mgm/m³. However, at other points there is an excess of the maximum permissible concentration of hydrogen sulfide, except for the POP No. 1 (Zhanbai village, Nysanov Street, plot 96), where the maximum value is 4 mgm/m³.

Figure 5 shows a diagram of monitoring the hydrogen sulfide content in the air of Atyrau in February 2022.

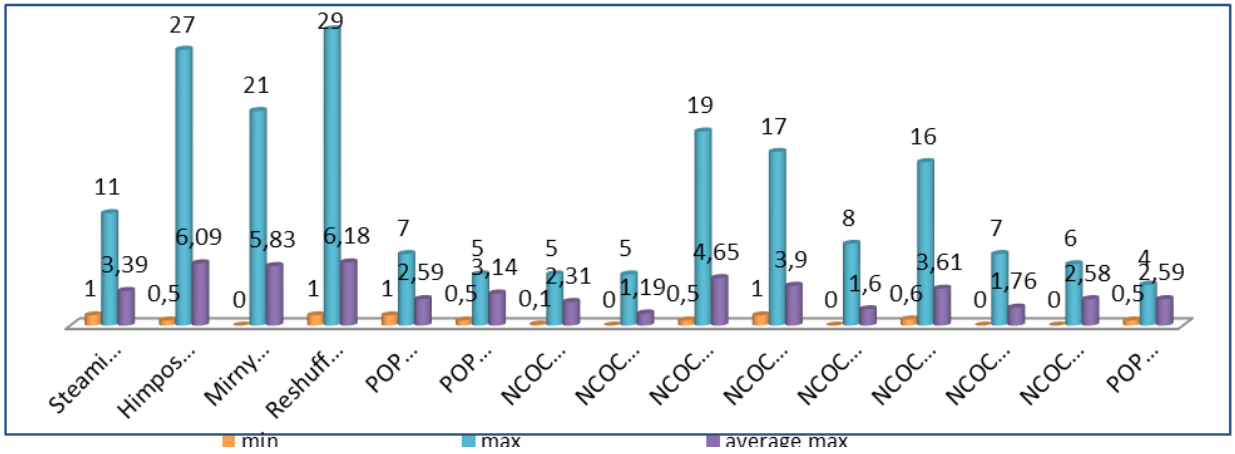

Figure 4 – Monitoring of hydrogen sulfide content in the air of Atyrau in January 2022

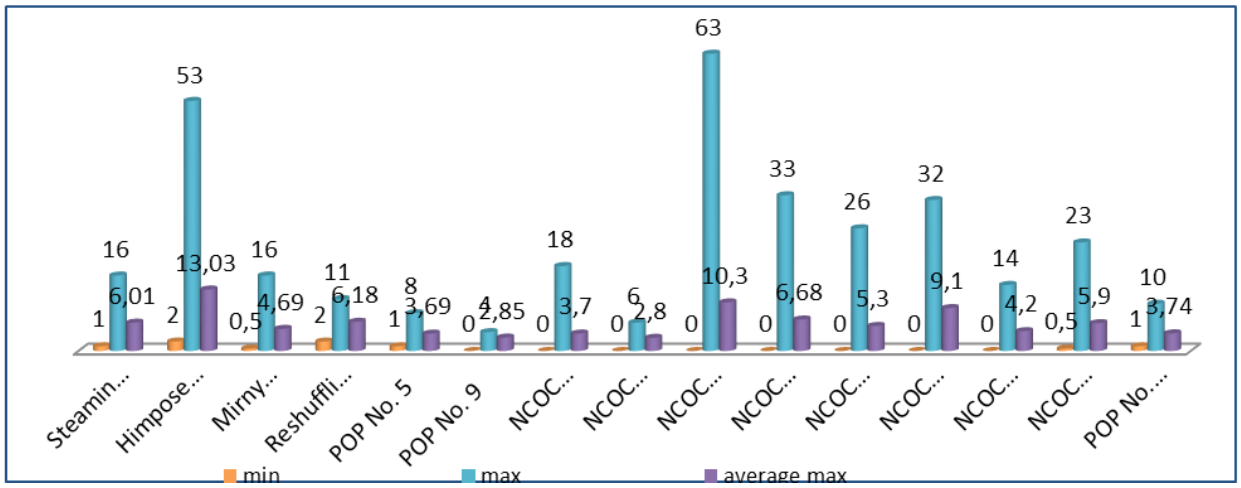

Figure 5 – Monitoring of hydrogen sulfide content in the air of Atyrau in February 2022

As can be seen from the diagram, the maximum values were observed at NCOC points No.109 (East) – 63 mgm/m³, Himposelok AOR – 53 mgm/m³. NCOC No. 110 (Privokzalny) – 33 mgm/m³, NCOC No. 112 (Akimat) – 33 mgm/m³, NCOC No. 111 (Zhilgorodok) – 26 mgm/m³ and at NCOC No.114 (Zagorodnaya) – 23 mgm/m³. However, at other points, there is an excess of the maximum permissible concentration of hydrogen sulfide, except for POP No. 9 (Bereke Industrial Zone area, Gurievsnab Street), where the maximum value is 4 mgm/m³.

Table 2 – Monitoring of hydrogen sulfide content in the air

	Himposelok			Mirny			Reshuffling			POP 109			POP 110			POP 111			POP 112			POP 113			POP 114		
D|M	Dec	Jan	Feb	Dec	Jan	Feb	Dec	Jan	Feb	Dec	Jan	Feb	Dec	Jan	Feb	Dec	Jan	Feb	Dec	Jan	Feb	Dec	Jan	Feb	Dec	Jan	Feb
1	15	7	27	7	4	7	5	3	6	13	11	20	8	2	13	6	1	7	9	5	0	6	1,5	4	6	3	3
2	4	7	8	3	3	16	4	3	10	2	9	7	3	4	7	1	3	4	3	5	0	1	1	8	4	3	2
3	7	3	6	2	3	8	2	3	4	11	1	3	8	3	5	2	1	5	4	2	5	2	1	5	4	3	2
4	3	8		8	3	8	3	x	3	24	3	6	18	3	4	7	3	1	10	3	4	31	2	14	6	3	2
5	5	x	53	7	3	8	2	x	10	3	x	12	15	x	3	12	x	7	2	x	9	10	x	6	3	x	2
6	14	x	8	11	x	1	3	x	5	46	x	6	22	x	3		x	0	25	x	7	9	x	0	9	x	9
7	15	x	5	6	x	3	7	x	6	14	x	10	5	x	3	4	x	0	9	x	7	4	x	0	2	x	3
8	9	x	3	7	x	4	4	x	3	6	x	1	5	x	3	2	x	2	6	x	2	3	x	3	2	x	1
9	4	x	6	8	x	3	4	x	4	2	x	4	6	x	3	1	x	2	4	x	3	4	x	2	3	x	1
10	x	x	3	5	x	1,5	5	x	6	5	x	2	3	x	8	2	x	2	4	x	3,5	2	x	2	2	x	4
11	x	x	4	3	x	3	3	x	5	1	x	2	5	x	0,8	1	x	2	2	x	4	1	x	2	1	x	2
12	x	10	9	4	7	3	8	8	6	1,5	4	2	2	4	4	1	1	3	1	4	22	2	1	3	1	2	3
13	x	2	9	7	8	8	8	5	11	10	1	10	3	4	2,2	3	1	7	4	4	13	1	1	6	1,5	6	4
14	x	4	4	6	0	2	4	4	8	2	4	3	5	4	4	0,5	1	5	4	2	8	2	1	1	2	3	3
15	x	3	8	7	3	2	3	3	3	2	3	30	4	3	27	4	1	3,1	3	2	28	3	2	1	2	3	0
16	x	3	6	4	3	2	4	4	6	17	3	3	8	2	4	3	1	2	5	2	7	5	1	2	3	4	3
17	x	8	6	34	3	2	39	4	4	35	4	6	10	2	4	7	1	3	10	3	4	11	3	2	5	2,5	3
18	x	3	6	7	6	x	11	3	3	14	5	1	4	2,4	3	4	4	2	10	4	6	4	3	1	3	2	2
19	x	3	49	6	7	x	4	4	7	6	4	13	2	2	4	2	1	5	3	3	12	2	2	1	2	2	3
20	x	8	5	7	5	3	4	10	4	5	8	10	4	4	4	1,5	1	3	3	2	6	3	1	3	3	1,3	3
21	5	3	28	7	7	x	5	7	8	3	4	42	4	2	21	4	1,4	4	3	2	32	1,5	2	4	4	2	23
22	13	3	7	1	6	x	19	3	5	7	2	4	6	3	5	4	2	3	6	3	9	4	1	5	4	2	10
23	5	2	14	x	8	x	5	4	6	3	2	3	4	2	3	1	1	3	4	4	4	1	1	4	3	3	9
24	3	4	13	x	7	x	3	7	10	6	1	5	2	3	8	2		13	3	3	10	1,5	1	7	1		9
25	3	3	26	x	7	x	3	7	7	3	2	63	6	3	2	3	2	14	3	3	26	2	3,5	7	1	2	4
26	3		22	x		x	3		4	9		8	3		33	2		6	4		12	3		6	0,5		23
27	7	10	9	5	8	x	5	8	8	6	3	7	4	3	4	1	0	13	3	3	6	2	0,4	6	2	2	20
28	4	6	8	4	8	x	7	10	x	3	6	4	3	3	2	2	0	26	2	3	5	1	2	12	1,5	2	11
29	14	7	x	9	4	x	7	4	x	6	4	x	4	5	x	1,5	0	x	5	3	x	2	1	x	1,5	2	x
30	3	6	x	3	6	x	5	3	x	5	4	x	3	9,4	x	3	1	x	4	2	x	2	1	x	3	2	x
31	6	27	x	5	21	x	3	29	x	3	19	x	3	17	x	1	8	x	5	16	x	2	7	x	3	2	x

Note: x – missing data

The analysis of the observation points shows that on certain days the maximum hydrogen sulfide content in the air was observed. For example:

in the Himposelok point of AOR the maximum values are observed on the 5th of February (53 mgm/m^3), the 19th of February (49 mgm/m^3), the 21st of February (28 mgm/m^3), the 31st of January and the 1st of February (27 mgm/m^3), on the 25th of February (26 mgm/m^3) and the 26th of February (22 mgm/m^3), which, when the MPC is equal to 4 mgm/m^3, exceed by more than 5-13 times;

in the Mirny AOR point the maximum values are observed on the 17th of December – 34 mgm/m^3, the 31st of January – 21 mgm/m^3 and the 2nd of February – 16 mgm/m^3;

in the Reshuffling of AOR point increased contents are observed on the 17th of December – 39 mgm/m^3, the 31st of January – 29 mgm/m^3 and the 22nd of December – 19 mgm/m^3;

in NCOC item No. 109 (Vostok) is characterized by increased contents in December (from 2 mgm/m^3 to 46 mgm/m^3) are observed on the 25th of February – 63 mgm/m^3 (15.75 MPC), the 6th of December – 46 mgm/m^3 (11.2MPC), the 21st of February – 42 mgm/m^3 (10.5 MPC), the 17th of December – 35 mgm/m^3, the 15th of February – 30 mgm/m^3, the 4th of December – 24 mgm/m^3 and the 1st of February – 20 mgm/m^3;

in NCOC point No. 110 (Privokzalny) elevated concentrations were observed on the 26th of February – 33 mgm/m^3 (8.25 MPC), the 15th of February – 27 mgm/m^3 (6.75 MPC), the 21st of February – 21 mgm/m^3 (5.25 MPC) and the 6th of December – 22 mgm/m^3 (5.5 MPC);

in NCOC point No. 111 (Zhilgorodok) elevated contents are observed on the 28th of February – 26 mgm/m^3 (6.5 MPC);

in NCOC point No. 112 (Akimat) elevated contents are observed on the 21st of February – 32 mgm/m^3 (8 MPC), the 15th of February – 28 mgm/m^3 (7 MPC), the 25th of February – 26 mgm/m^3 (6.5 MPC), the 6th of December – 25 mgm/m^3 (6.25 MPC), the 12th of February – 22 mgm/m^3 (5.5 MPC);

in NCOC item No.113 (Avangard) increased contents are observed on the 4th of December – 31 mgm/m^3 (7.75 MPC);

in NCOC item No.114 (Zagorodnaya) elevated contents are observed on the 21st and 26th of February – 23 mgm/m^3 (5.75 MPC) and the 27th of February – 20 mgm/m^3 (5 MPC).

A comparative analysis of the average hydrogen sulfide content in the air of the city of Atyrau from 2020 by 8 points was also carried out, since there were only eight observation points until 2021 (Figure 6).

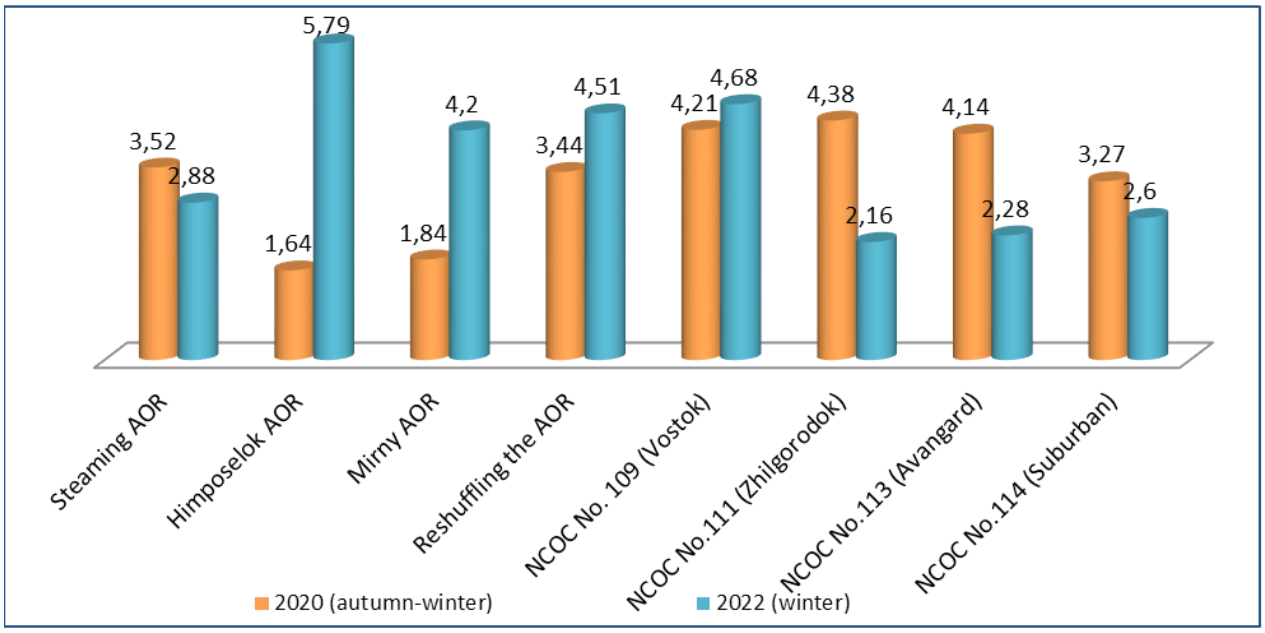

Figure 6 – A comparative analysis of the average hydrogen sulfide content in the air in 2020 and 2022

Overall, it can be seen that the content of the hydrogen sulfide in 2020 is almost similar to the H_2S concentration in 2022, the average levels of which were 1,64-4,38 mgm/m^3 (0,82-2,19 MPC) and 2,16-5,79 mgm/m^3 (1,08-2,89 MPC) respectively. Himposelok AOR and Mirny AOR experienced an increase in the content of the hydrogen sulfide approximately to 2,89 and 2,1 MPC accordingly. Meanwhile in NCOC No.111 and NCOC No. 113 points the H_2S concentration decreased by twice and almost remained within the MPC. As for other points the hydrogen sulfide content was nearly stable in both periods.

One of the most important environmental problems of the region is the pollution of the Atyrau air basin, including intense unpleasant odors that are periodically recorded [13]. There are several potential sources of bad-smelling substances in the city, the main of which are: industry, sewage treatment plants and silt sites [14]. Monitoring of atmospheric air quality in the zone of influence of industrial enterprises located in Atyrau, especially for hydrogen sulfide, which is formed during the processing of oil and petroleum products by the Atyrau Oil Refinery, could be an important step towards optimizing the monitoring of the impact of emissions of industrial enterprises. It is necessary to introduce modern technologies and dust and gas cleaning equipment at all enterprises of the region. First of all, this applies to enterprises that have hydrogen sulfide in their emissions [15-17]. Reduction of hydrogen sulfide emissions can also be expected as a result of measures aimed at the reconstruction and overhaul of the sewerage system in Atyrau, which was launched in 2021 and the project is funded by the European Bank for Reconstruction and Development, with which AOR signed an agreement for $80 million [18].

Conclusion

Monitoring of hydrogen sulfide content in Atyrau in winter showed that the month of February is the most polluted, for example, February 4-6 and especially the end of the month after February 21-27, then December, in which December 4-6 and December 17 can be distinguished, and January is the most unpolluted month, except the 31st of January. The analysis by observation points shows that the most elevated concentrations are observed at points located near the AOR, these are the Himposelok AOR, Mirny AOR and Reshuffling the AOR. Among the observation points in the city itself, one can distinguish such as NCOC No. 109 (East), NCOC No. 110 (Privokzalny) and NCOC No. 112 (Akimat).

The content of hydrogen sulfide in the atmospheric air creates an increased non-carcinogenic risk to public health in acute and chronic admission, which indicates the need for early environmental measures [19-21]. As part of these studies, elevated levels of hydrogen sulfide in the atmosphere were recorded. The greatest danger to the population is represented by oil products processing facilities located in the immediate vicinity of settlements. Thus, the conducted studies indicate that the ecological situation in the settlements in the area of oil production needs improvement [22-25].

Conflict of interest

All authors have read and are familiar with the content of the article and have no conflict of interests.

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