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«ҚАЗАҚСТАН РЕСПУБЛИКАСЫ ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫ» РҚБ «ХАЛЫҚ» ЖҚ

ХАБАРЛАРЫ

ИЗВЕСТИЯ

РОО «НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК РЕСПУБЛИКИ КАЗАХСТАН» ЧФ «Халык»

NEWS

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NAS RK is pleased to announce that News of NAS RK. Series of geology and technical sciences scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of geology and technical sciences in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of geology and engineering sciences to our community.

Қазақстан Республикасы Ұлттық ғылым академиясы «ҚР ҰҒА Хабарлары. Геология және техникалық ғылымдар сериясы» ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Webof Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Геология және техникалық ғылымдар сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді геология және техникалық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАНРК сообщает, что научный журнал «Известия НАНРК. Серия геологии и технических наук» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК. Серия геологии и технических наук в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по геологии и техническим наукам для нашего сообщества.



ЧФ «ХАЛЫК»

В 2016 году для развития и улучшения качества жизни казахстанцев был создан частный Благотворительный фонд «Халык». За годы своей деятельности на реализацию благотворительных проектов в областях образования и науки, социальной защиты, культуры, здравоохранения и спорта, Фонд выделил более 45 миллиардов тенге.

Особое внимание Благотворительный фонд «Халык» уделяет образовательным программам, считая это направление одним из ключевых в своей деятельности. Оказывая поддержку отечественному образованию, Фонд вносит свой посильный вклад в развитие качественного образования в Казахстане. Тем самым способствуя росту числа людей, способных менять жизнь в стране к лучшему – профессионалов в различных сферах, потенциальных лидеров и «великих умов». Одной из значимых инициатив фонда «Халык» в образовательной сфере стал проект Ozgeris powered by Halyk Fund – первый в стране бизнес-инкубатор для учащихся 9-11 классов, который помогает развивать необходимые в современном мире предпринимательские навыки. Так, на содействие малому бизнесу школьников было выделено более 200 грантов. Для поддержки талантливых и мотивированных детей Фонд неоднократно выделял гранты на обучение в Международной школе «Мирас» и в Astana IT University, а также помог казахстанским школьникам принять участие в престижном конкурсе «USTEM Robotics» в США. Авторские работы в рамках проекта «Тәлімгер», которому Фонд оказал поддержку, легли в основу учебной программы, учебников и учебно-методических книг по предмету «Основы предпринимательства и бизнеса», преподаваемого в 10-11 классах казахстанских школ и колледжей.

Помимо помощи школьникам, учащимся колледжей и студентам Фонд считает важным внести свой вклад в повышение квалификации педагогов, совершенствование их знаний и навыков, поскольку именно они являются проводниками знаний будущих поколений казахстанцев. При поддержке Фонда «Халык» в южной столице был организован ежегодный городской конкурс педагогов «Almaty Digital Ustaz.

Важной инициативой стал реализуемый проект по обучению основам финансовой грамотности преподавателей из восьми областей Казахстана, что должно оказать существенное влияние на воспитание финансовой грамотности и предпринимательского мышления у нового поколения граждан страны.

Необходимую помощь Фонд «Халык» оказывает и тем, кто особенно остро в ней нуждается. В рамках социальной защиты населения активно проводится

работа по поддержке детей, оставшихся без родителей, детей и взрослых из социально уязвимых слоев населения, людей с ограниченными возможностями, а также обеспечению нуждающихся социальным жильем, строительству социально важных объектов, таких как детские сады, детские площадки и физкультурно-оздоровительные комплексы.

В копилку добрых дел Фонда «Халык» можно добавить оказание помощи детскому спорту, куда относится поддержка в развитии детского футбола и карате в нашей стране. Жизненно важную помощь Благотворительный фонд «Халык» оказал нашим соотечественникам во время недавней пандемии COVID-19. Тогда, в разгар тяжелой борьбы с коронавирусной инфекцией Фонд выделил свыше 11 миллиардов тенге на приобретение необходимого медицинского оборудования и дорогостоящих медицинских препаратов, автомобилей скорой медицинской помощи и средств защиты, адресную материальную помощь социально уязвимым слоям населения и денежные выплаты медицинским работникам.

В 2023 году наряду с другими проектами, нацеленными на повышение благосостояния казахстанских граждан Фонд решил уделить особое внимание науке, поскольку она является частью общественной культуры, а уровень ее развития определяет уровень развития государства.

Поддержка Фондом выпуска журналов Национальной Академии наук Республики Казахстан, которые входят в международные фонды Scopus и Wos и в которых публикуются статьи отечественных ученых, докторантов и магистрантов, а также научных сотрудников высших учебных заведений и научно-исследовательских институтов нашей страны является не менее значимым вкладом Фонда в развитие казахстанского общества.

С уважением, Благотворительный Фонд «Халык»!

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ЖҰРЫНОВ Мұрат Жұрынұлы, химия ғылымдарының докторы, профессор, ҚР ҰҒА академигі, «Қазақстан Республикасы Ұлттық ғылым академиясы» РҚБ-нің президенті, АҚ «Д.В. Сокольский атындағы отын, катализ және электрохимия институтының» бас директоры (Алматы, Қазақстан) $\mathbf{H} = \mathbf{4}$

Ғылыми хатшы

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DEPENDENCE OF MOBILE SULFUR ACCUMULATION IN SOILS AND HYDROGEN SULFIDE EMISSIONS ON THE TERRITORY OF ATYRAU

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Abstract The article analyzes the dependence of the accumulation of mobile sulfur in the soil and hydrogen sulfide in the air of the city of Atyrau. Atyrau city is located in the western part of the Republic of Kazakhstan. In the city of Atyrau, the main source of air pollution with hydrogen sulfide is the Atyrau Oil Refinery. Hydrogen sulfide is a toxic gas whose pollution contributes to the accumulation of sulfur in the soil. The analysis of the hydrogen sulfide content in the atmosphere was carried out on the basis of Kazhydromet data, according to the AirKz application at 15 observation points and on the device with GANK-4 Argus analyzers. The content of mobile sulfur in the soil was determined by photometric method in the Testing Laboratory of Analytical Laboratory for Environmental Protection LLP. The results were analyzed taking into account the correlation coefficient. The dependence of the accumulation of sulfur in the soil on hydrogen sulfide in the air is associated with observation points located near the Atyrau oil refinery, for example, at the observation point of Himposylok, Mirny, Steaming. There is no such pattern in the observation points located in settlements, for

example, at the points of NCOC No. 110 (Privokzalny), NCOC No. 111 (Zhilgorodok) and NCOC No. 112 (Akimat). At points No. 1 (Samal) and No. 5 (Kursai), an increased content of sulfur is observed in the soil, while in the air the content of hydrogen sulfide is in an acceptable concentration. According to the correlation coefficient, there is a weak positive relationship only in the spring of 2022 between the sulfur content in the soil on the Earth's surface and hydrogen sulfide in the air. In the same period between the sulfur content in the soil at a depth of 50 cm and in the autumn period of 2021, the correlation coefficient is negative, which indicates that there is no connection between the accumulation of sulfur in the soil from incoming hydrogen sulfide from the air.

Keywords: Atyrau city, mobile sulfur in the soil, hydrogen sulfide in the air, correlation coefficient, Atyrau oil refinery, observation points

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АТЫРАУ ҚАЛАСЫНЫҢ АУМАҒЫНДА ТОПЫРАҚТА ЖЫЛЖЫМАЛЫ КҮКІРТТІҢ ЖИНАҚТАЛУЫНЫҢ ЖӘНЕ КҮКІРТСУТЕГІ ШЫҒАРЫНДЫЛАРЫНЫҢ ТӘУЕЛДІЛІГІ

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Аннотация. Мақалада Атырау қаласының топырақтағы жылжымалы күкірттің және ауасында күкіртті сутектің жинақталу тәуелділігіне талдау жүргізілді. Атырау қаласы Қазақстан Республикасының батыс бөлігінде орналасқан. Атырау қаласында ауа ортасын күкіртсутегімен ластаудың негізгі көзі Атырау мұнай өңдеу зауыты болып табылады. Күкіртсутек-улы газ, оның ластануы топырақта күкірттің жиналуына ықпал етеді. Атмосферадағы күкіртсутектің құрамы бойынша талдау Қазгидромет деректері негізінде, АігКz қосымшасына сәйкес 15

бакылау пунктінде және аспапта GANK-4 Argus анализаторларымен жургізілді. Топырақтағы жылжымалы күкірттің құрамы "Қоршаған ортаны қорғау бойынша аналитикалық зертхана"ЖШС сынақ зертханасында фотометриялық әдіспен аныкталды. Нәтижелер корреляция коэффициентін ескере отырып талданды. Топырақтағы күкірттің ауадағы күкіртсутекке тәуелділігі Атырау мұнай өңдеу зауытының жанында орналасқан бақылау пункттерінде, мысалы, химиялық кенттерді. Мирный, булауды бақылау пунктінде байланысты. Елді мекендерде орналасқан бақылау пункттерінде мұндай заңдылық байқалмайды, мысалы НКОК № 110 (Вокзал маңы), НКОК № 111 (Жилгородок) және НКОК № 112 (әкімдік) пункттерінде. № 1 (Самал) және № 5 (Курсай) пункттерде топырақта күкірттің жоғары мөлшері байқалады, ал ауада күкіртсутектің мөлшері рұқсат етілген концентрациядан аспайды. Корреляция коэффициентіне сәйкес тек 2022 жылдың көктемінде жер бетіндегі топырақтағы күкірт пен ауадағы күкіртсутек арасында элсіз оң байланыс бар. Дэл осы кезеңде топырақтағы күкірт мөлшері 50 см тереңдікте және 2021 жылдың күзгі кезеңінде корреляция коэффициенті теріс мәнге тең болады, бұл топырақтағы күкірттің ауа ортасынан келетін күкіртсутектен жиналуы арасында байланыс жоқ екенін көрсетеді.

Түйін сөздер: экологиялық-биологиялық зерттеулер; Индер көлінің тұрақтылығы; гидрохимиялық құрамы; ауыр металдардың құрамы; хлор аниондары; натрий катиондары

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ЗАВИСИМОСТЬ НАКОПЛЕНИЯ ПОДВИЖНОЙ СЕРЫ В ПОЧВАХ И ВЫБРОСОВ СЕРОВОДОРОДА НА ТЕРРИТОРИИ ГОРОДА АТЫРАУ

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Аннотация. В статье проведен анализ зависимости накопления подвижной серы впочве и сероводорода в воздухе города Атырау. Город Атырау расположен в западной части Республики Казахстан. В городе Атырау основным источником загрязнения воздушной среды сероводородом является Атырауский нефтеперерабатывающий завод. Сероводород является токсичным газом, загрязнение которым способствует накоплению серы в почве. Анализ по содержанию сероводорода в атмосфере проводился на основе данных Казгидромет, согласно приложению AirKz на 15 пунктах наблюдения и на приборе анализаторами GANK-4 Argus. Содержание подвижной серы в почве определяли фотометрическим методом в Испытательной лаборатории ТОО «Аналитическая лаборатория по охране окружающей среды». Результаты были проанализированы с учетом коэффициента корреляции. Зависимость накопления серы в почве от сероводорода в воздухе связана на пунктах наблюдений, расположенных возле Атырауского нефтеперерабатывающего, например в пункте наблюдения Химпоселок, Мирный, Пропарка. В пунктах наблюдения, расположенных в населенных пунктах такой закономерности, не отмечается, например на пунктах НКОК № 110 (Привокзальный), НКОК № 111 (Жилгородок) и НКОК № 112 (Акимат). На пунктах № 1 (Самал) и № 5 (Курсай) в почве наблюдается повышенное содержание серы, тогда как в воздухе содержание сероводорода находится в допустимой концентрации. Согласно коэффициенту корреляции отмечается слабая положительная зависимость только весной 2022 года между содержанием серы в почве на поверхности земли и сероводородом в воздухе. В этот же период между содержанием серы в почве на глубине 50 см и в осенний период 2021 года коэффициент корреляции равен отрицательному значению, что говорит о том, что отсутствует связь между накоплением серы в почве от поступающего сероводорода из воздушной среды.

Ключевые слова: город Атырау, подвижная сера в почве, сероводород в воздухе, коэффициент корреляции, Атырауский нефтеперерабатывающий завод, пункты наблюдения

Introduction

The Earth's crust contains about 0.06% sulfur, and the total supply of the element in the soil is determined by the soil-forming rocks and the content of organic matter in them. 70–90 % of sulfur from its gross reserves is associated with the organic matter of the soil (Kolbe, 2022). According to the soil profile, sulfur is distributed along with humus. A linear relationship has been established between humus carbon and sulfur, and as the degree of dispersion of soil fractions increases, sulfur and carbon increase (Sangadzhieva, 2004).

Sulfur is a widespread element in nature, which is important for the functioning of both plant and animal organisms (Cherkasov et.al., 2018). Hydrocarbon minerals contain sulfur, since sulfur was part of the organic compounds from which these fossils were formed. Sulfur is extracted as a by-product from fossil fuels such as oil, gas, tar sands and coal (Nadirov et al., 2018). Sulfur is a necessary element for most plants and the total sulfur content in different soils ranges from 20 to 35 mg per 1 kg of soil. The

maximum permissible concentration of sulfur content in the soil is 160 mg/kg. In the works on the study of sulfur content in the soil, it is shown that in most works the sulfur content is minimal, especially in the soils of agricultural lands (Lukin et al., 2021).

In a number of foreign countries, another grouping based on the determination of sulphate sulfur in acetic acid extract is more often used to assess the sulfur content in soils (Table. 1) (Sainova et al., 2019; Likus-Cieślik et al., 2017).

Soil group	Element content level	Sulfur content (S)		
		mg/kg	kg/ha	
1	Very low	<5	<15	
2	Low	5-10	15-30	
3	Average	10-35	30-105	
4	Tall	35-90	105-270	
5	Very high	>90	>270	

Table 1 - Grouping of soils by mobile sulfur content abroad

The lack or excess of sulfur is primarily manifested on young leaves and growth points. Its reverse movement is very insignificant and therefore it belongs to the elements that are difficult to reutilize. In this, sulfur is very different from phosphorus. Excess sulfur in the soil leads to excessive absorption of iron and other trace elements, resulting in the appearance of necrotic areas. With an overabundance of sulfur, the leaves gradually turn yellow from the edges and shrink, turning inside. Then they turn brown and die. Sometimes the leaves take not yellow, but a lilac-brown shade. There is a general coarsening of plants, the leaves are getting smaller. Excess sulfur lowers the pH of the soil, making the soil more acidic. Since H ions can be released by the reaction of sulfur, oxygen, CO₂ and H₂O, a reaction carried by microorganisms. The more H ions there are, the more acidic it will be (Zenda et al., 2021; Mamedova, 2019).

The source of sulfur is the intake of sulfates and sulfuric acid into the soil of natural and man-made origin with atmospheric precipitation. Sulfur oxides enter the atmosphere with combustion products of various types of sulfur-containing fuels. In addition, natural sources of sulfur are also important: volcanic emissions, emanation from swampy soils, etc. All these sources supply about 200 million tons of sulfur to the atmosphere annually. In the atmosphere, the interaction of sulfur oxides with water leads to the formation of sulfuric acid, which, together with atmospheric precipitation, enters the soil, causing an undesirable increase in soil acidity in humid areas. In the northern hemisphere, sulfur precipitation averages 11–20 kg/ha per year, in industrial areas – up to 100–150 kg/ha per year (Kalimanova et al., 2019).

Some sulfur compounds are pollutants of the natural environment. These include, as the most dangerous, sulfur dioxide and hydrogen sulfide. It has been established that the ability of plants to assimilate sulfur from the atmosphere is directly dependent on the level of root nutrition (Yessenamanova et al., 2020). Assimilation increases with an increase in the content of sulfates in the soil and reaches a maximum with optimal availability of sulfur in the soil (Mustafaev et al., 2019). Plants can absorb up to half of the required amount of sulfur from the atmosphere. The most common anthropogenic

sources of H₂S emissions are the extraction and processing of oil and natural gas. It is also formed during bacterial decomposition of human and animal waste and is present in the emissions of sewage treatment plants and landfills (Zuo et al., 2019).

Hydrogen sulfide can also be released from industrial sources such as oil refineries, natural gas plants, paper mills, manure processing plants, sewage treatment plants and tanneries (Ausma et al., 2019; Habeeb et al., 2018).

Hydrogen sulfide can get into the soil as a result of atmospheric precipitation or spills. In the soil, hydrogen sulfide is consumed by bacteria, which turn it into sulfur (Malone et al., 2017; Vasilakos et al., 2005).

Research on the accumulation of sulfur in the soil and the dependence of this accumulation on hydrogen sulfide in the air is currently relevant for the city of Atyrau. Atyrau in Kazakhstan, the administrative center of Atyrau region. It is located in the western part of the country, on the banks of the Ural River (Tauova et al., 2022). In recent years, in the city of Atyrau, where the Atyrau oil Refinery is located, the content of hydrogen sulfide in the air exceeds the maximum permissible concentrations, there is a need for the relationship between the accumulation of sulfur in the soil from the incoming hydrogen sulfide from the air (Yessenamanova et al., 2021).

The Earth's crust contains about 0.06% sulfur, and the total supply of the element in the soil is determined by the soil-forming rocks and the content of organic matter in them. 70–90 % of sulfur from its gross reserves is associated with the organic matter of the soil. According to the soil profile, sulfur is distributed along with humus. A linear relationship has been established between humus carbon and sulfur, and as the degree of dispersion of soil fractions increases, sulfur and carbon increase (Kanbetov et al., 2023).

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The lack or excess of sulfur is primarily manifested on young leaves and growth points. Its reverse movement is very insignificant and therefore it belongs to the elements that are difficult to reutilize. In this, sulfur is very different from phosphorus. Excess sulfur in the soil leads to excessive absorption of iron and other trace elements, resulting in the appearance of necrotic areas. With an overabundance of sulfur, the leaves gradually turn yellow from the edges and shrink, turning inside. Then they turn brown and die. Sometimes the leaves take not yellow, but a lilac-brown shade. There is a general coarsening of plants, the leaves are getting smaller. Excess sulfur lowers the pH of the soil, making the soil more acidic. Since H ions can be released by the reaction of sulfur, oxygen, CO₂ and H₂O, a reaction carried by microorganisms. The more H ions there are, the more acidic it will be (Yessenamanova et al., 2023).

The source of sulfur is the intake of sulfates and sulfuric acid into the soil of natural and man-made origin with atmospheric precipitation. Sulfur oxides enter the atmosphere with combustion products of various types of sulfur-containing fuels. In addition, natural sources of sulfur are also important: volcanic emissions, emanation from swampy soils, etc. All these sources supply about 200 million tons of sulfur to the atmosphere annually. In the atmosphere, the interaction of sulfur oxides with water leads to the formation of sulfuric acid, which, together with atmospheric precipitation, enters the soil, causing an undesirable increase in soil acidity in humid areas. In the northern hemisphere, sulfur precipitation averages 11–20 kg/ha per year, in industrial areas – up to 100–150 kg/ha per year (Ryskalieva et al., 2023).

Some sulfur compounds are pollutants of the natural environment. These include, as the most dangerous, sulfur dioxide and hydrogen sulfide. It has been established that the ability of plants to assimilate sulfur from the atmosphere is directly dependent on the level of root nutrition. Assimilation increases with an increase in the content of sulfates in the soil and reaches a maximum with optimal availability of sulfur in the soil. Plants can absorb up to half of the required amount of sulfur from the atmosphere. The most common anthropogenic sources of H₂S emissions are the extraction and processing of oil and natural gas. It is also formed during bacterial decomposition of human and animal waste and is present in the emissions of sewage treatment plants and landfills.

Hydrogen sulfide can also be released from industrial sources such as oil refineries, natural gas plants, paper mills, manure processing plants, sewage treatment plants and tanneries.

Hydrogen sulfide can get into the soil as a result of atmospheric precipitation or spills. In the soil, hydrogen sulfide is consumed by bacteria, which turn it into sulfur.

Research on the accumulation of sulfur in the soil and the dependence of this accumulation on hydrogen sulfide in the air is currently relevant for the city of Atyrau. Atyrau in Kazakhstan, the administrative center of Atyrau region. It is located in the western part of the country, on the banks of the Ural River. In recent years, in the city of Atyrau, where the Atyrau oil Refinery is located, the content of hydrogen sulfide in the air exceeds the maximum permissible concentrations, there is a need for the relationship between the accumulation of sulfur in the soil from the incoming hydrogen sulfide from the air (Nursaule et al., 2022).

Materials and methods

Atyrau Oil Refinery is located in close proximity to a residential area about 450 meters to the west and 730 meters to the northwest.

On the map (Fig. 1) we can see the points of 15 points of observation of the state of atmospheric air in the city of Atyrau, which can be seen in Table 2.



Figure 1 - The map of Atyrau city

All 15 points are located on the territory of the main microdistricts of the city, where the urban population lives, and the territory near the refinery, which makes it possible to determine the influence of the plant and the wastewater basin on the hydrogen sulfide content in the air and the accumulation of sulfur in the soil.

Table 3 - Locations of observation Point for the state of atmospheric air in the city of Atyrau,
Republic of Kazakhstan

Point title	Point address	The location
Steaming AOR	Atyrau, Steaming AOR	47.0726660,51.9508610
Himposylok AOR	Atyrau, Himposylok AOR	47.0887220,51.9352780
Mirny AOR	Atyrau, Mirny AOR	47.0754720,51.9107500
Drag and drop AOR	Atyrau, Drag and drop AOR	47.0685280,51.9052210
POP (Pollution Observation	Atyrau, Samal microdistrict, A. Kekilbayev	47.1261210,51.8708850
Point) No. 1 (manual Point)	Street No. 15	
POP (Pollution Observation	Atyrau, Kursay, Karabau Street, building 12	47.0668460,51.8864240
Point) No. 5 (manual Point)		
POP (Pollution Observation	Atyrau, Zhuldyz microdistrict, 6th street, 29	47.1558350,51.9814530
Point) No. 6 (manual Point)		
POP NCOC No. 103	Atyrau, Shagala	47.1117740,51.9221670
POP NCOC No. 108	Atyrau, TKA	47.1645230,52.0275220
POP NCOC No. 109	Atyrau, Vostok	47.0947250,51.9250130
POP NCOC No. 110	Atyrau, Privokzalny	47.1261730,51.9472360
POP NCOC No. 111	Atyrau, Zhilgorodok	47.0988520,51.9006170
POP NCOC No. 112	Atyrau, Akimat	47.1050630,51.9164730
POP NCOC No. 113	Atyrau, Avangard	47.0930470,51.8869910
POP NCOC No. 114	Atyrau, Zagorodnaya	47.1415560,51.8959480

Measurements of atmospheric air pollution were carried out by the GANK-4AR gas analyzer (NPO Pribor Russia, Head No. 1566, inv. No. 000000962 - 02/21/2018 Self-adhesive label HMS No. 5405921 1 time per year) designed for continuous automatic measurement of concentrations of pollutants in atmospheric air and in the air of the working area and and according to the results of round-the-clock monitoring of the Republican State Enterprise "Kazhydromet" through the mobile application "Air Kz" (Kazhydromet, 2022).

The soil samples were collected (according to the standards) in two different depth: 0 cm and 50 cm. The content of mobile sulfur in the soil at 15 observation points was carried out in accordance with GOST 26490–85 "SOILS. Determination of mobile sulfur by the CIASA (Central Institute of Agrochemical Services of Agriculture) method" in the Testing Laboratory of Analytical Laboratory for Environmental Protection LLP. The sulfur content in soil was determined by the photometric method (GOST, 1985).

A special case of the statistical dependence between X and Y is the correlation dependence, when each value of X corresponds to the mathematical expectation (arithmetic mean) of the distribution of another value Y. When establishing the correlation dependence, the corresponding pairs of values of X and Y are obtained experimentally for each object under study. The correlation dependence can be described using the equation of the form:

$$M(Y_x) = f(x) \tag{1}$$

where $M(Y_x)$ is the conditional mathematical expectation of the value Y corresponding to a given value x;

x is the individual values of the value X;

f(x) is some function.

The closeness of the connection (the degree of dispersion of points) is estimated using the correlation coefficient r:

$$r = \frac{\overline{x \cdot y} - \bar{x} \cdot \bar{y}}{\sigma_x \sigma_y} \tag{2}$$

In practice, we do not have data on the entire population, but only on those values that are obtained from the experiment (sample). Therefore, a sample correlation coefficient r_s is determined, approximately equal to the general correlation coefficient r. Denoting the mean square deviations for the sample s_r and s_r obtain:

$$r_{s} = \frac{\sum_{i=1}^{n} (x_{i} - \bar{x})(y_{i} - \bar{y})}{s_{x}s_{y}} = \frac{\bar{x}\bar{y} - \bar{x}\cdot\bar{y}}{\sqrt{\bar{x}^{2} - (\bar{x})^{2}}\sqrt{\bar{y}^{2} - (\bar{y})^{2}}}$$
(3)

where
$$s_x = \sqrt{\bar{x}^2 - (\bar{x})^2}$$
, $s_x = \sqrt{\bar{y}^2 - (\bar{y})^2}$, $\bar{x}^2 = \frac{\sum_{i=1}^n x_2^i}{n}$, $\bar{y}^2 = \frac{\sum_{i=1}^n y_2^i}{n}$.

By its nature, the correlation can be direct and inverse, and by strength – strong, medium, weak. In addition, there may be no connection or it may be complete (functional) (Table 3).

The strength of the connection	The nature of the connection	
	Forward (+)	Reverse (–)
Full (functional)	1	-1
Strong	from 0.7 to 1	from -0.7 to -1
Average (moderate)	from 0.3 to 0.7	from -0.3 to -0.7
Weak	from 0.3 to 0	from -0.3 to 0
There is no connection	0	0

Table 4 - The strength and nature of the relationship between the parameters

Results

In the autumn period of 2021 and the spring period of 2022, a study was conducted on the content of hydrogen sulfide in the air and mobile sulfur in the soil at the main 15 observation points of the city of Atyrau. For the analysis, the average values for the maximum and minimum indicators for hydrogen sulfide in the air and the content of mobile sulfur on the surface (0 cm) and deeper at a depth of 50 cm, where the accumulation of sulfur can affect the root system of plants, were taken. In the figures, these data on the content of hydrogen sulfide in the air and mobile sulfur in the soil were studied in interdependence in Figures 2–15.

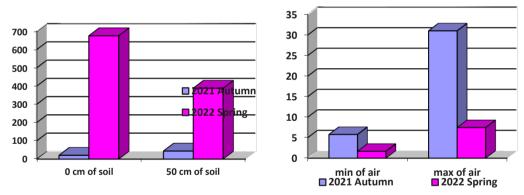


Figure 2 - The content of sulfur in the soil and hydrogen sulfide of the air on the Steaming AOR point

The bar charts of Figure 2 provide information on the content of sulfur in soil and hydrogen sulfide of the air on the Steaming AOR point for autumn 2021 and spring 2022. Overall, the hydrogen sulfide level in the air was higher in 2021, meanwhile the exceeded sulfur content in the soil was recorded in 2022.

According to the Hygienic standards for the safety of the environment of the Republic of Kazakhstan the maximum permissible concentrations of elemental sulfur in the soil is 160 mg/kg. As a result, in autumn 2021 in both 0 cm and 50 cm depth no exceedance of chemical substance was conducted (20.78 mg/kg and 44.04 mg/kg respectively). However, in spring time period of 2022 the sulfur content in soil increased dramatically to 676.1 mg/kg in the surface and to 388.2 in the depth.

According to the Hygienic standards for atmospheric air in urban and rural

settlements, on the territories of industrial organizations of the Republic of Kazakhstan the maximum single value of the maximum permissible concentrations is 8 mcg/m³, while the average daily MPC is not set. However, in accordance with the Kazhydromet data, the concentration of the H₂S above 2 mcg/m³ is considered as increased.

In terms of air condition, in autumn 2021 there was a significant excess of the maximum average values of H_2S by almost 4 times of MPC (31.03 mcg/m³). In the following season the hydrogen sulfide level dropped remarkably to 7.48 mcg/m³.

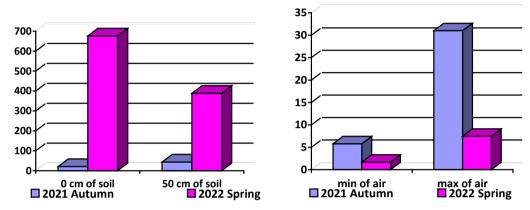


Figure 3 - The content of sulfur in the soil and hydrogen sulfide of the air on Himposylok AOR point

As it can be seen from the charts on the Figure 3 the sulfur concentration in the soil as well as the air pollution with the hydrogen sulfide is significantly high in both periods considered. One of the reasons of high indicators could be the close location of the point to Atvrau Oil Refinery.

In autumn 2021 the content of sulfur on the surface was 4 times higher than MPC (640.8 mg/kg), whereas the sulfur contamination of the soil in 50 cm depth was not observed. However next season these indicators changed markedly. The sulfur content rose sharply to 944.8 mg/kg which is 6 times more than the maximum permissible concentration of elemental sulfur in the soil. The sulfur content in deep soil increased by almost 4 times in spring 2022 and reached 336.8 mg/kg.

In terms of air pollution, the maximum average hydrogen sulfide level was nearly 20 mcg/m 3 or 2.5 MPC. In spring 2022 the $\rm H_2S$ maximum level decreased considerably to 7.26 mcg/m 3 . The minimum hydrogen sulfide level generally followed the same pattern in both seasons.

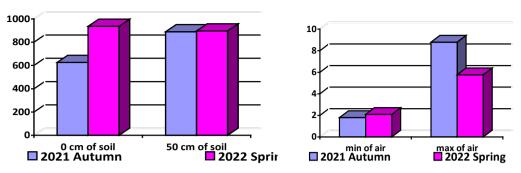


Figure 4 - The content of sulfur in the soil and hydrogen sulfide of the air on Mirny AOR point

In the Figure 4 was an apparent excess of the sulfur in the soil and a slight increase of the hydrogen sulfide in the air for both periods considered.

Being the closest point to the Atyrau Oil Refinery Mirny AOR point soil is the most contaminated with the mobile sulfur on the surface as well as in depth. So, in autumn 2021 the content of the chemical element in the soil exceeded the MPC almost 4 times on the ground and 5.5 times in 50 cm. Next season the figure for the surface increased drastically to 936.8 mg/kg or 6 MPC, while the soil in 50 cm remained relatively unchanged.

In the periods given, the maximum hydrogen sulfide concentration in the air was approximately 9 mcg/m³ and 6 mcg/m³ in autumn 2021 and spring 2022 respectively. As for the minimum concentrations no excess was observed over the periods.

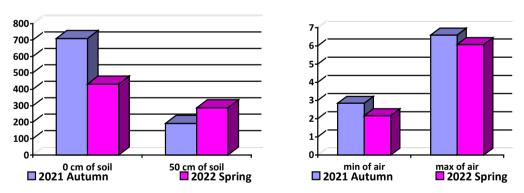


Figure 5 - The content of sulfur in the soil and hydrogen sulfide of the air on the Drag and drop AOR point

According to the Figure 5, the Drag and drop AOR point shows some mixed results in the content of sulfur in the soil and the stable indicators for the air condition in the periods given.

In autumn 2021 the soil contained over 700 mg/kg (4.4 MPC) of sulfur on the surface and just under 200 mg/kg under the ground. In spring 2022 the sulfur content on the ground decreased considerably to 432.3 mg/kg (2.7 MPC), meanwhile in depth the chemical concentration slightly grew to about 290 mg/kg.

In terms of air pollution, the figures remained relatively steady in both periods: the maximum hydrogen sulfide concentration varied between 6 and 6.6 mcg/m³, whereas the minimum $\rm H_2S$ content fluctuated between 2 and 2.85 mcg/m³, which is within the maximum permissible concentration.

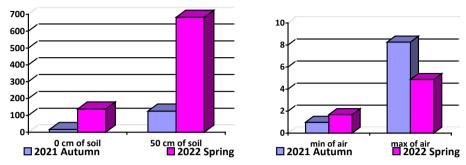


Figure 6 - The content of sulfur in the soil and hydrogen sulfide of the air on the NCOC No. 103 (Shagala) point

The Figure 6 gives quite ambiguous results on the Shagala point for periods considered. In autumn 2021 the sulfur content in the soil was within the maximum permissible concentration both on the surface and under the ground – approximately 16 and 125 mg/kg. However, in spring 2022 the indicators increased dramatically by almost 8.5 and 5 times respectively. These changes could be affected by the exceedance of the hydrogen sulfide in the air in autumn 2021. The maximum concentration of the gas reached 8 mcg/m³ or 1 MPC. In spring 2022 the figure decreased by twice to 4.8 mcg/m³. The minimum levels of the H₂S did not exceed the MPC in both seasons.

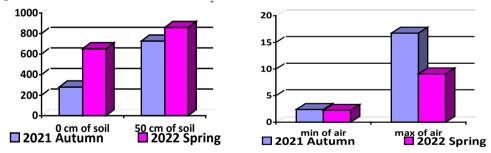


Figure 7 - The content of sulfur in the soil and hydrogen sulfide of the air on the NCOC No. 109 (Vostok) point

The NCOC No.109 point (Figure 7) is the closest residential area to the oil refinery and accordingly more prone to the exceedance of the hydrogen sulfide in the air than the other points. Due to the residents' frequent complaints on the odor of "rotten eggs", given location is particularly significant to explore.

The maximum average level of the hydrogen sulfide in the air in 2021 exceeded the MPC 2 times (16.74 mcg/m³). Next season the indicator decreased considerably to 9 mcg/m³, however the H₂S pollution still remained increased. As for the minimum concentration there was no limit excess of the hydrogen sulfide.

There is an apparent correlation between the $\rm H_2S$ concentration in the air and the sulfur content in the soil. So, in autumn 2021 the sulfur content on the surface exceeded the MPC just over 1.5 times (279.5 mg/kg). However, in spring 2022 this figure reached 651.3 mg/kg which prevails the MPC 4 times. The high content of the sulfur was observed under the ground as well. In autumn 2021 the chemical element contained in the soil was over 725 mg/kg that is 4.5 times more than MPC. In spring the sulfur concentration in 50 cm depth was almost 860 mg/kg or 5.3 MPC.

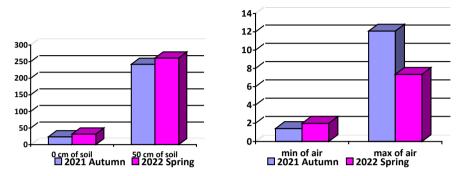


Figure 8 - The content of sulfur in the soil and hydrogen sulfide of the air on the NCOC No. 110 (Privokzalny) point

The NCOC No. 110 (Figure 8) is a relatively new point that located in the residential area. According to the laboratory results, the sulfur accumulation in the soil was within the maximum permissible concentration on the surface and fluctuated between 240–260 mg/kg under the ground. In general, the sulfur content in the soil was fairly stable for period given. In contrast, the hydrogen sulfide concentration showed some excessive levels. In autumn 2021 the maximum average content of H_2S was about 12 mcg/m³ or 1,5 MPC. In spring 2022 the figure dropped noticeably to 9 mcg/m³, however the hydrogen sulfide exceedance still remained.

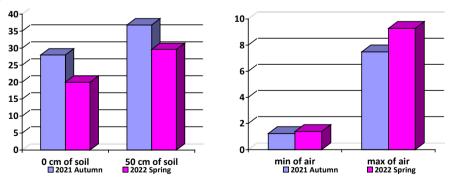


Figure 9 - The content of sulfur in the soil and hydrogen sulfide of the air on the NCOC No. 111 (Zhilgorodok) point

Across the period considered no exceedance of the sulfur in the soil was observed and the content of the chemical element fluctuated between 20 and 36 mg/kg in both depths (Figure 9). On the contrast, there was a significant increase in the hydrogen

sulfide concentration in the air: in autumn 2021 the average level of the substance was nearly 8 mcg/m³, which means the maximum permissible concentration was reached, while spring 2022 the figure went up almost to 10 mcg/m³. The minimum concentration was within the standards. It should be noted that 8 mcg/m³ is one time concentration, while the figures provided in the charts illustrate the average daily H₂S levels.

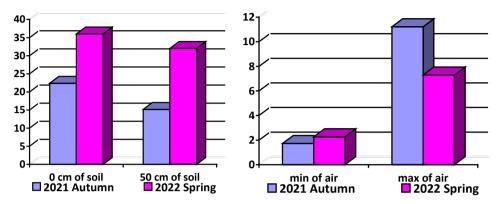


Figure 10 - The content of sulfur in the soil and hydrogen sulfide of the air on the NCOC No. 112 (Akimat) point

The figure 10 illustrates the content of sulfur in the soil and the hydrogen sulfide in the air for two seasons. Overall, it should be noted that the correlation between the indicators monitored is weak, however there might be some effect by the hydrogen sulfide level in autumn 2021 on the sulfur in the soil in spring 2022 which needs to be observed in the future.

It can be seen in the first chart that the sulfur content was within the MPC in all groups given – between 25–36 mg/kg. However, there is a pattern for increase of the sulfur contained in the soil in the following season for both depths.

As for the $\rm H_2S$ content, the maximum average concentration in autumn 2021 prevailed the MPC almost 1,5 times. In spring 2022 the maximum level decreased slightly to 7.35 mcg/m³. The rest of indicators did not exceed the MPC.

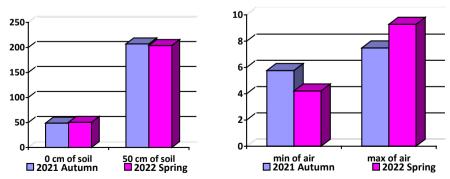


Figure 11 - The content of sulfur in the soil and hydrogen sulfide of the air on the NCOC No. 113 (Avangard) point

It can be noted that the content of the sulfur in the soil remained stable across the periods and there was insignificant exceedance (about 200 mg/kg) of the chemical element under the depth of 50 cm in both seasons (Figure 11). Unlike the sulfur, the hydrogen sulfide concentration prevailed the MPC several times in both years. So, in autumn 2021 the minimum and the maximum average H₂S levels were almost equal at about 6–7 mcg/m³. Next season the minimum average hydrogen sulfide concentration decreased to about 4 mcg/m³, while the maximum level hit a high of 9 mcg/m³ or 1.1 MPC.

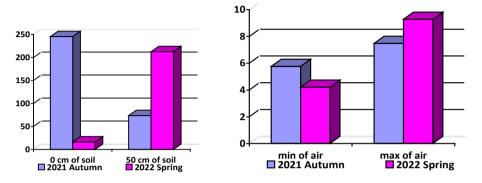


Figure 12 - The content of sulfur in the soil and hydrogen sulfide of the air on the NCOC No. 114 (Zagorodnaya) point

According to the NCOC No. 114 point results (Figure 12), there was an excessive amount of sulfur compounds in all groups observed. Thus, in autumn 2021 the sulfur content on the surface was around 250 mg/kg, which is more than the MPC only by 90 mg/kg. However, there is a pattern for accumulation of the substance under the ground as in spring 2022 the level of the sulfur content in 50 cm increased almost by three times: from 73 mg/kg in autumn to 212 mg/kg in spring. Moreover, one of the reasons of the accumulation could be the high level of the hydrogen sulfide in the air. Over the periods considered the minimum H₂S concentration fluctuated between 4–6 mcg/m³, while the maximum concentrations were even worse at about 8 and 10 mcg/m³ in autumn 2021 and spring 2022 respectively.

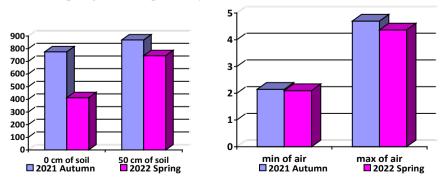


Figure 13 - The content of sulfur in the soil and hydrogen sulfide of the air on the POP No. 1 (Samal) point

It is obvious from the charts that there is weak correlation between the content of the sulfur in the soil and the hydrogen sulfide concentration in the air for both periods on the Figure 13. According to the laboratory results the soil in Samal point is significantly contaminated with the sulfur. In autumn the content of the substance was over 775 mg/kg on the surface and 870 mg/kg under the ground, that is almost 5 and 5.5 times more than the maximum permissible concentration of the sulfur in the soil. In spring the level of the sulfur on the ground declined twice, whereas the soil in 50 cm did not experience significant changes and remained at the level of 5 MPC. In terms of the hydrogen sulfide pollution the maximum average H_2S concentration was under 5 mcg/m³ and the minimum level was about 2 mcg/m³ which did not exceed the norm for both seasons explored.

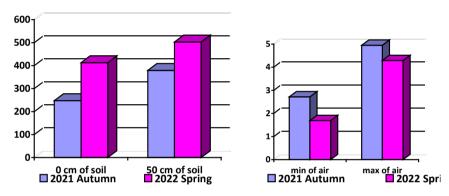


Figure 14 - The content of sulfur in the soil and hydrogen sulfide of the air on the POP No. 5 (Kursay) point

The content of the sulfur in the considered point has a pattern to increase in the Figure 14. In autumn 2021 the sulfur concentration on the surface was around 250 mg/kg and under the ground about 380 mg/kg. However, the following year the figures changed to 415 and 500 respectively. The air pollution is quite similar to the previous point analyzed. The maximum concentration reached 5 mcg/m³, while the minimum level was around 1.5 mcg/m³.

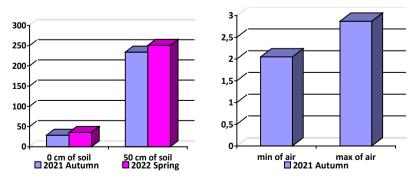


Figure 15 - The content of sulfur in the soil and hydrogen sulfide of the air on the POP No. 6 (Zhuldyz) point

Figure 15 illustrates the content of the sulfur in the soil and incomplete results of the H₂S in the air due to the closure of the point. Overall, there is no obvious contamination of the area among all groups. The autumn and spring measurements have similar results with 28–35 mg/kg of sulfur on the surface and 235–250 mg/kg under the ground. Also, in autumn 2021 the hydrogen sulfide concentration was under 3 mcg/m³.

Discussion

The results of the analyses allow us to unequivocally state that there is a change in the content of sulfur in the soil and hydrogen sulfide in the air.

It can be assumed that an increase in the concentration of hydrogen sulfide in the air during the Steaming AOR point in the fall of 2021 significantly affected the composition of the soil and the growth of mobile sulfur in it in the spring of 2022.

In general, it is noticeable that the sulfur content in the soil at the Himposylok AOR point tends to increase as a result of the high concentration of hydrogen sulfide in the air.

According to the charts there might be some correlation between the content of sulfur in the soil and hydrogen sulfide of the air on Mirny AOR point. Among the reasons of the sulfur accumulation in the soil could be the close location to the industrial zone, and subsequently that it is mostly prone to one-time emissions.

Overall, it can be assumed that the hydrogen sulfide levels of autumn 2021 in the Drag and drop AOR point might have some effects on the content of sulfur in the soil of spring 2022, however the indicators vary within the norm (1.1 MPC).

At the NCOC No. 109 (Vostok) point, there is an increased content of sulfur in the soil, which indicates its accumulation as a result of its intake from the air as hydrogen sulfide pollution occurs, since this particular point is located near the source of pollution.

Overall, it can be assumed that there is weak correlation between the indicators considered on the NCOC No. 110 (Privokzalny), NCOC No. 111 (Zhilgorodok) and NCOC No. 112 (Akimat) points.

At points NCOC No. 113 (Avangard), NCOC No. 114 (Zagorodnaya) and the POP No. 6 (Zhuldyz) point the sulfur content in the soil and the hydrogen sulfide content in the air did not exceed the permissible concentrations. Overall, there is an assumption that the level of the hydrogen sulfide could affect the content of the sulfur in the soil.

At the POP No. 1 (Samal) and POP No. 5 (Kursay) points, there are an increased sulfur content in the soil, while the sulfur content does not exceed the permissible concentrations. Probably the reasons for the accumulation of sulfur in the soil are different, not related to the intake of sulfur from the air.

The calculation of the relationship between the content of sulfur in the soil and hydrogen sulfide in the air for the autumn period of 2021 and the spring period of 2022 was carried out on the basis of average indicators and the sum of indicators. At the same time, for 2021, the average sulfur content in the soil on the surface is 265.17 mg/kg, and the sum is 3712.44 mg/kg; in the atmosphere, the average hydrogen sulfide content is 10.57 mcg/m³, and the sum is 148.01 mcg/m³. At the same time, according to formula (3), the correlation coefficient is equal to (-0.000059), which, according to the data in Table 3, indicates a weak negative relationship between the accumulation of sulfur in the soil from incoming hydrogen sulfide from the air. For the same year, the average sulfur content in the soil at a depth of 50 cm is 337.5 mg/kg and the sum is

4725.1 mg/kg. The correlation calculation shows that the data (-0.035) also indicate a weak negative correlation between the sulfur content in the soil and hydrogen sulfide in the atmosphere. In the spring period of 2022, the average sulfur content in the soil on the surface is 366.1 mg/kg, the sum is 5125.59 mg/kg. At the same time, the average hydrogen sulfide content is 6.51 mcg/m³, with a total of 84.6 mcg/m³. According to formula 3, the correlation value is (+0.036), which indicates a weak positive relationship. The same calculation at a depth of 50 cm shows that the average sulfur content in the soil is 406.27 mg/kg, and the sum is 5687.7 mg/kg, while the correlation coefficient is (-0.1145), which indicates a weak negative correlation.

Conclusion

In conclusion, it can be concluded that out of 15 observation points in the city of Atyrau, at points located near the Atyrau oil refinery, there is a direct dependence of sulfur accumulation in the soil on hydrogen sulfide emissions, for example, such as at the Himposylok AOR poin, NCOC No. 109 (Vostok) point. In the settlements of NCOC No. 113 (Avangard), NCOC No. 114 (Zagorodnaya) and the POP No. 6 (Zhuldyz), there is a possibility of accumulation of sulfur in the soil from hydrogen sulfide emissions. Whereas there is no such dependence in the points of the exchange rate. If we consider the correlation between the sulfur content in the soil at different depths from the maximum content of hydrogen sulfide in the air in the whole city during these periods, then calculations show that only in the eternal 2022 the correlation coefficient between the accumulation of sulfur on the earth's surface and hydrogen sulfide has a positive insignificant effect, which suggests that hydrogen sulfide emissions in the spring the period can settle on the surface of the earth. In 2021, in the autumn at any depth and in the spring of 2022 at a depth of 50 cm, the accumulation of sulfur is not associated with hydrogen sulfide emissions, since the correlation coefficient has negative values.

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