

Article

Relation of Hydrogeology and Contaminant Sources to Drinking Water Quality in Southern Kazakhstan

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Abstract: Southern Kazakhstan is one of the fastest-growing regions of this country and continued development depends on a sustainable supply of freshwater for multiple purposes. Groundwater in Southern Kazakhstan occurs in a wide variety of hydrogeological conditions with varying levels of quality and vulnerability to contamination. The aim of this paper is to investigate the present groundwater quality through sampling and laboratory analysis of source water from public supply wells, compare results to hydrogeology and known contaminant sources, and indicate where future protections may be needed. Protection from surface-borne contaminants is mainly determined by the thickness of the vadose zone, depth of the groundwater level, presence, thickness and composition of aquifers, and mobility of pollutants. Forty-five wells were sampled, yielding 106 samples of groundwater presently used for drinking water, which were evaluated to investigate the occurrence of potential pollutants and hydrogeology of the region. Of the samples collected, 46 samples were used for analysis of inorganic water chemistry, 30 for individual indicators including metals, and 31 samples for determination of petroleum products. A contaminant inventory database and geospatial database aided the interpretation of the results and allowed the prediction of future water issues. Kazakhstan's maximum permissible concentrations (MPCs) for metals were exceeded in areas associated with industrial enterprises, while fluoride and nitrate were more closely associated with mining and agricultural sources. Groundwater quality is dependent on hydrogeology and environmental contaminants resulting from historical land uses and must be regularly monitored for drinking water safety. Petroleum hydrocarbons were not detected in any of the drinking water sources.

Keywords: Kazakhstan; hydrogeology; groundwater quality; land use; pollutant inventory; hazardous chemicals



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1. Introduction

Southern Kazakhstan is an important economic and geographic region within the Republic of Kazakhstan. From 1992 until 2018, this region's population grew very rapidly, making it one of the most populated regions of the country [1]. The largest cities of Kazakhstan, Almaty and Shymkent, are located in this region, and after the administrative-territorial reform of 1997, Southern Kazakhstan includes regions designated as Almaty, Zhambyl, Turkestan (formerly South Kazakhstan), and Kyzylorda. The economy of Southern Kazakhstan is largely based on mining, light and heavy industries, and agriculture. Due to the milder winters compared to northern Kazakhstan, agriculture is well developed, and annual crops of cotton, rice, wool, grain, fruits, vegetables, tobacco, apples, grapes, and hemp are grown here. Industrial sectors include nonferrous metallurgy, mechanical engineering, the chemical industry, instrument making, light and food industries, fish and forestry, and animal husbandry. The climate of this region is mostly arid, with cold winters

at $-30\text{ }^{\circ}\text{C}$ and hot summers at $+40\text{ }^{\circ}\text{C}$, and the landscape is sparsely populated steppes and deserts, high snow-capped mountains with humid and densely populated foothills. Agricultural and industrial development follows along the banks of rivers and large lakes including Balkhash and previously the Aral Sea. Major surface water features include the transboundary Karatal, Ili, Syr Darya, and Talas–Shu river basins (Figure 1).

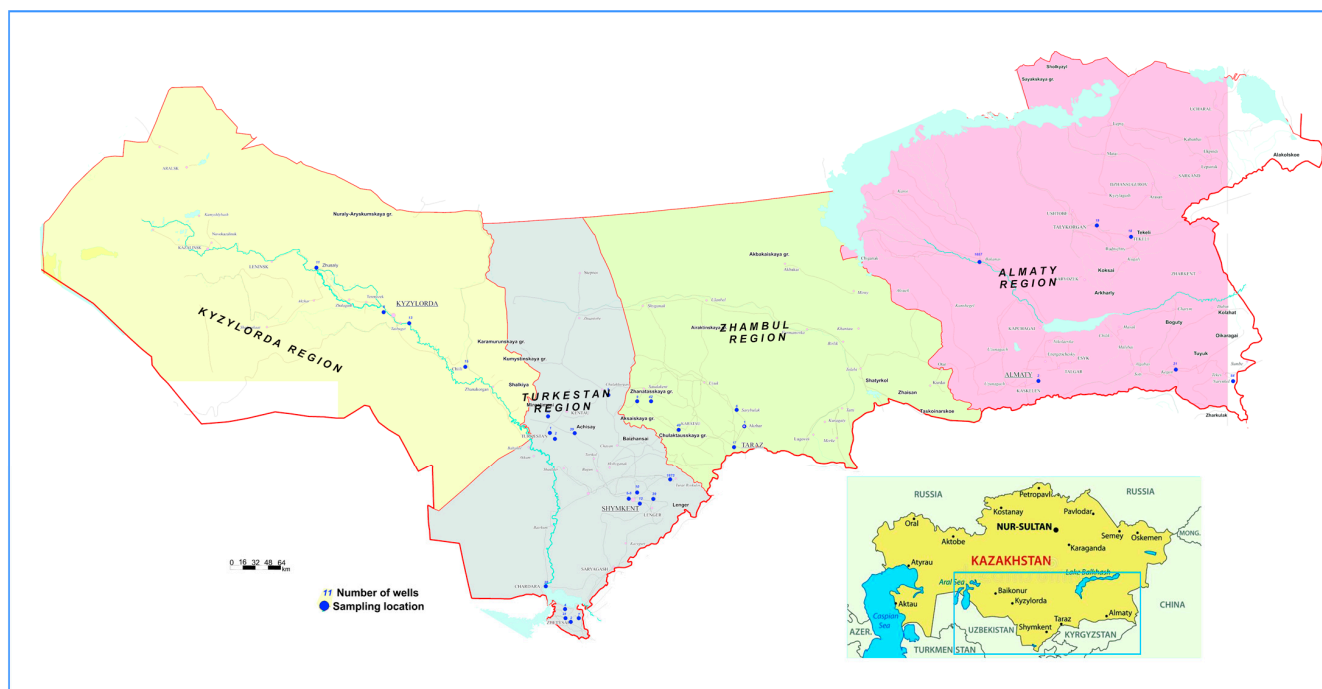


Figure 1. Groundwater sampling locations in Southern Kazakhstan.

Groundwater in Southern Kazakhstan occurs under a variety of hydrogeological conditions, with variable vulnerability to contamination [2]. Protection from surface pollution is mainly determined by the thickness and composition of the vadose (unsaturated) zone, the presence, capacity, and composition of confining layers, the mobility of surface contaminants, as well as the proximity of pollutant sources. Sources of groundwater pollution include industrial, mining, and oil and gas production complexes; agricultural activities and storage facilities; and accumulation of industrial, household, and radioactive waste [3,4]. In recent years, the inventory of pollutant sources has remained practically unchanged due to the economic recession [5,6]. The processes of controlling the discharge of pollutants and treatment of wastewater have not kept pace with the growth of industrial and agricultural production in the region [7,8]. At the same time, there appears to be an increase in pollution of surface water likely due to the increase in runoff from diffuse sources of nonpoint pollution and a lack of systematic efforts to control these sources [9,10].

The most important source of information on the availability of groundwater is from observations and control surveys conducted by the groundwater monitoring services of the Committee for Geology and Subsoil Protection of the Republic of Kazakhstan. The Ministry of Ecology, Geology, and Natural Resources of the Republic of Kazakhstan is the central executive body of the Republic of Kazakhstan. This committee leads the formation and implementation of state policy, coordination of management processes in the fields of environmental protection, development of the “green economy”, waste management (excluding municipal, medical, and radioactive waste, which are under the control of the Ministry of Healthcare of the Republic of Kazakhstan), control and supervision of the rational use of natural resources, and geological surveys [11]. This committee is responsible for monitoring and reporting on the mineral resource base, use, and protection of the water fund, water supply, sanitation, forestry, conservation, and the management of wildlife and specially protected natural territories, or regulated areas. Records from this committee

include observations of groundwater level changes and trends in the chemical composition of groundwater, groundwater use, and especially critical use of groundwater for domestic and public drinking water supplies.

Because few published studies have described the present condition of groundwater quality in Southern Kazakhstan, the purpose of this paper is to summarize the quality and availability of groundwater used for municipal drinking water sources in this important region. Sampling and laboratory results are compared with the State Standards of the Republic of Kazakhstan Water for drinking water [12], as well as the World Health Organization and United States Environmental Protection Agency drinking water standards. Trends regarding the chemical composition are evaluated in terms of hydrogeology, arid climate, industrial and agricultural land use, and related distribution of contaminant sources. Our overall objective is to provide a complete assessment of Southern Kazakhstan groundwater quality through the systematic analysis of its chemical composition and to predict sustainable uses for domestic drinking water supply. Our two research hypotheses are to test whether or not there are relationships between current groundwater quality and surface contaminant sources, and between groundwater composition and aquifer composition. This study will help guide future monitoring of these groundwater supplies for the protection of public drinking water in southern Kazakhstan.

2. Materials and Methods

2.1. Water Sampling

Groundwater wells (45 in total) were selected from water intakes and distribution systems located in the settlements and towns with the aim of identifying contamination and characterizing the quality of drinking groundwater. One hundred and six (106) samples were collected from these observation points and tested for determination of chemical pollutants from the Almaty, Zhambyl, and Turkestan regions in the summer of 2019. The following route was used: Almaty–Taraz–Zhetysay–Arys–Ordabasy–Shymkent–Sholakkorgan–Turkestan–Kantau–Shardara–Karatau–Zhanatas–Almaty (Figure 1). Details of the wells sampled are in the Supplementary Materials (S4). One hundred and six (106) samples were taken, of which 45 samples were used for inorganic chemical composition, 30 samples for individual indicators including metals, and 31 samples were preserved for determination of petroleum products. Protocols for sampling followed the guidelines published by the State Standard of the Republic of Kazakhstan Water for drinking water [12]. Samples were collected in 1 L glass containers for trace metals, anions, cations, and alkalinity; and in 0.5 L glass containers preserved with 10 mL hexane per 500 mL sample of hydrocarbon screening. Samples were stored on ice for transport to the laboratory. Testing for the determination of organic pollutants, including oil products, was carried out in accordance with ST RK SS R 51592-2003 [12]. Samples for the determination of organic pollutants in the Shymkent and Zhambyl regions were taken in glass containers of 1 L and preserved with 10 mL hexane per 500 mL sample. The Supplementary Materials summarize the results for these 106 sampling sites, including sampling site name, depth of dug well, pH, hardness, alkalinity (CO_3 , HCO_3), anions (Cl , SO_4), cations (Ca , Mg , Na , K), salinity, Kurlov's formula, metals (Cu , Zn , Ni , Cd , Pb , Co , Mn , Sr , Hg , Cr , Se , As), and the route taken for collection of samples.

2.2. Chemical Analysis

The laboratory methods used are listed in Table 1 [13]. General requirements for methods for determining oil products in natural and wastewater are defined according to [14] and details are provided in Supplementary Materials, Section S1. All samples were taken from the water intake nearest the wellhead for general chemical analysis and for the determination of oil products. In the course of early studies at the sites of oil deposits and near oil product plants, traces of oil products were found in groundwater, which indicates that the groundwater is not sufficiently protected during the extraction and processing of

oil and gas [15]. This part of the sampling campaign is a follow-up to evaluate whether or not petroleum contamination was still a problem.

Table 1. Laboratory method details used for well-water testing [14,16,17].

Parameters	Detection Limits (mg/L) Li Limit	Instrument	Description of Methods
Dry residues, total solids		OHAUS Adventurer Balance	Gravimetry (0.00001 g)
pH		Mettler Toledo pH meter	Potentiometry
Ammonia	0.1	KFK-2MP Photocolorimeter	Photometric method for ammonia and ammonium ions (in total) with Nessler reagent calibration from 0.1 to 3.0 mg/L.
Nitrite	0.003	KFK-2MP Photocolorimeter KFK-2	Photometric method for nitrites using sulfanilic acid. Calibration range from 0.003 to 0.3 mg/L.
Nitrate content using sodium salicylic acid	0.1	KFK-2MP Photocolorimeter	Photometric method for determining the nitrate using sodium salicylic acid. Calibration range from 0.1 to 2.0 mg/L.
Ferrum (iron)	0.01–0.03	KFK-2MP Photocolorimeter	Photometric method in an alkaline medium with sulfosalicylic acid to form a yellow-colored complex (400–430 nm). Calibration range is 0.10–2.00 mg/L [11].
Metals: Cd, Co, Mn, Cu, As, Ni, Hg, Pb, Cr, Zn	0.00001	ICPE-9820 Atomic Emission Plasma Spectrophotometer.	ICPE-9820 Atomic Emission Plasma Spectrophotometer. Calibration range is 0.00001–10.0.
Alkalinity CO ₃ , HCO ₃	10	Automatic titrator	Titration: HCl volume consumption per 100 mL sample using phenolphthalein indicator.
Ca, Mg	10	Automatic titrator	Titration: consumption of Triton B per 100 mL sample using an indicator.
Chloride	10	Automatic titrator	Titration: mercurimetry by Hg(NO ₃) ₂ per 50 mL sample and indicator.
Sulfate	30	OHAUS Adventurer Balance	Gravimetric method using precipitation of sulfate ions in a hydrochloric acid medium with barium chloride. Range is 30–300 mg/L [12].
Total Petroleum Hydrocarbons	0.0001	Bruker SCION SQ 456-Gas Chromatograph with Flame ionization Detector)	Chromatography (Bruker SCION SQ 456-GC) (description of method is provided in Supplemental Materials Section S1).

3. Results and Discussion

3.1. Hydrogeology

The vast territory of Southern Kazakhstan is located at the junction of two large geological structures (“rock-laid” and “platform” regions), which differ sharply in hydrogeological properties [18]. Southern Kazakhstan, which includes four administrative regions (Almaty, Zhambyl, Turkestan, and Kyzylorda), has large water resources that have an extremely uneven distribution over the territory. The presence of mountain ranges, powerful intermountain depressions, and large and small river valleys contributed to the formation of significant reserves of fresh groundwater [7]. There are large artesian basins of non-pressurized pores and pressure-stratified groundwater—Syrdarya, Shu-Sarysu, Shu-Ileysky, Ileysky, and Balkhash-Alakolsky. The main reserves of fresh groundwater are confined to aquifers of Quaternary, Neogene, Paleogene, and Cretaceous deposits, common in intermountain depressions. Overall, these units provide groundwater for this region

for drinking water, especially for large water consumers, industrial and technical water supply, land irrigation, balneological purposes, and also a heat source [10,19]. Groundwater quality is controlled to a large extent by aquifer materials and water residence time [20]. Southern Kazakhstan occupies a vast territory, but a generalized stratigraphic column of the Almaty region (Figure 2) provides a good overview of the water-bearing units. Various rock complexes of the Silurian, Permian, Triassic, Cretaceous, Neogene, and Quaternary ages comprise the geological structure of the region, and important freshwater-bearing units are described below [21,22].

Quaternary deposits of the western part of the Ili Basin are widely developed and are represented by various genetic types of continental deposits. Among them are alluvial, alluvial–proluvial, deluvial–proluvial, proluvial, eolian, and lacustrine deposits. Recent and Upper Quaternary lacustrine sediments spread over an area of 15 km² in the drainless Sorbulak depression located in the central part of the study area on the border of the Ili depression and the Karoy plateau, provide some confining layers. Well flow rates range from 0.15 to 0.37 L/s with drawdowns of 7.1 and 10.2 m, respectively, in interbedded alluvial sands.

Previous surveys [23] indicate that groundwater from the Middle Quaternary alluvial deposits is generally fresh, with a mineralization range of 0.24 to 2.0 g/L, and it is the most common yield water with a mineralization of 0.5–0.9 g/L. To the northwest of the city of Almaty, in the valleys of the rivers Kaskelen, Big Almaty and others, groundwaters of the Middle Quaternary deposits are characterized by a significant diversity of mineralization. Here, waters with mineralization from 0.3 to 2.1 g/L are common, which is likely explained by the close hydraulic connection with surface water. Groundwater sources in this region are mainly classified as sulfate–hydrocarbonate calcium–sodium. Near Sorbulak, the middle Quaternary lacustrine sediments beneath the Upper Quaternary and the modern clay, sand, and silt groundwater confined to them have a small head, reaching 24 m. The water content of the sands is low due to the fine-grained composition of the water-bearing sands. Well flow rates vary from 0.9 to 0.32 L/s with depressions of 32.5 and 1.4 m, respectively. The composition of the waters is most often mixed hydrocarbonate–sulfate magnesium–calcium–sodium. In the area of the Sorbulak depression groundwater is generally classified as sodium chloride or sulfate.

The Lower Quaternary Koturbulak Formation deposits are widespread and have been noted over a large area located between the Chemolgan and Zhirenaigyr rivers. This territory has a hilly relief of the adyr type and is dissected by a relatively dense hydrographic network. In the river valleys, there are above-floodplain terraces nested in the rocks of the described suite, which lay mainly on the loams of the Ili Formation. Lithologically, the formation is represented mainly by loams and loess-like loams with thin lenses and horizons of pebbles and sands. Their thickness varies from 10 to 450 m (wells 1, 2, 3, 17, 18, etc.). By genesis, these are predominantly lacustrine deposits, but in their water flows, other factors took part in the formation. The Koturbulak deposits are widely developed in the south and southeast of the area of the characterized sheet. The thickness of the lower horizon is 62 m, and the upper one is 28.5 m. Between the loams and the boulder–pebble horizon lies a layer of coarse-grained brownish-gray sands, 8 m thick. The upper boulder–pebble horizon is overlaid by brownish-gray loess-like loams. The fragments are comparatively well rounded, and their dimensions vary from 0.2 to 5–10 cm in diameter. The thickness of the deposits of the Koturbulak suite in this area reaches 98.5 m. Microchemical analyses of loess-like loams show the presence of the following rare and trace elements: strontium, about 0.1%; vanadium, about 0.1%; copper, 0.001 to 0.03%; nickel, less than 0.1%; lead, up to 0.001%; gallium 0, 01%; tin, 0.001%; molybdenum and cerium, traces. Trace elements such as cobalt, cadmium, chromium, zinc, and gold are generally absent.

STRATIGRAPHIC COLUMN

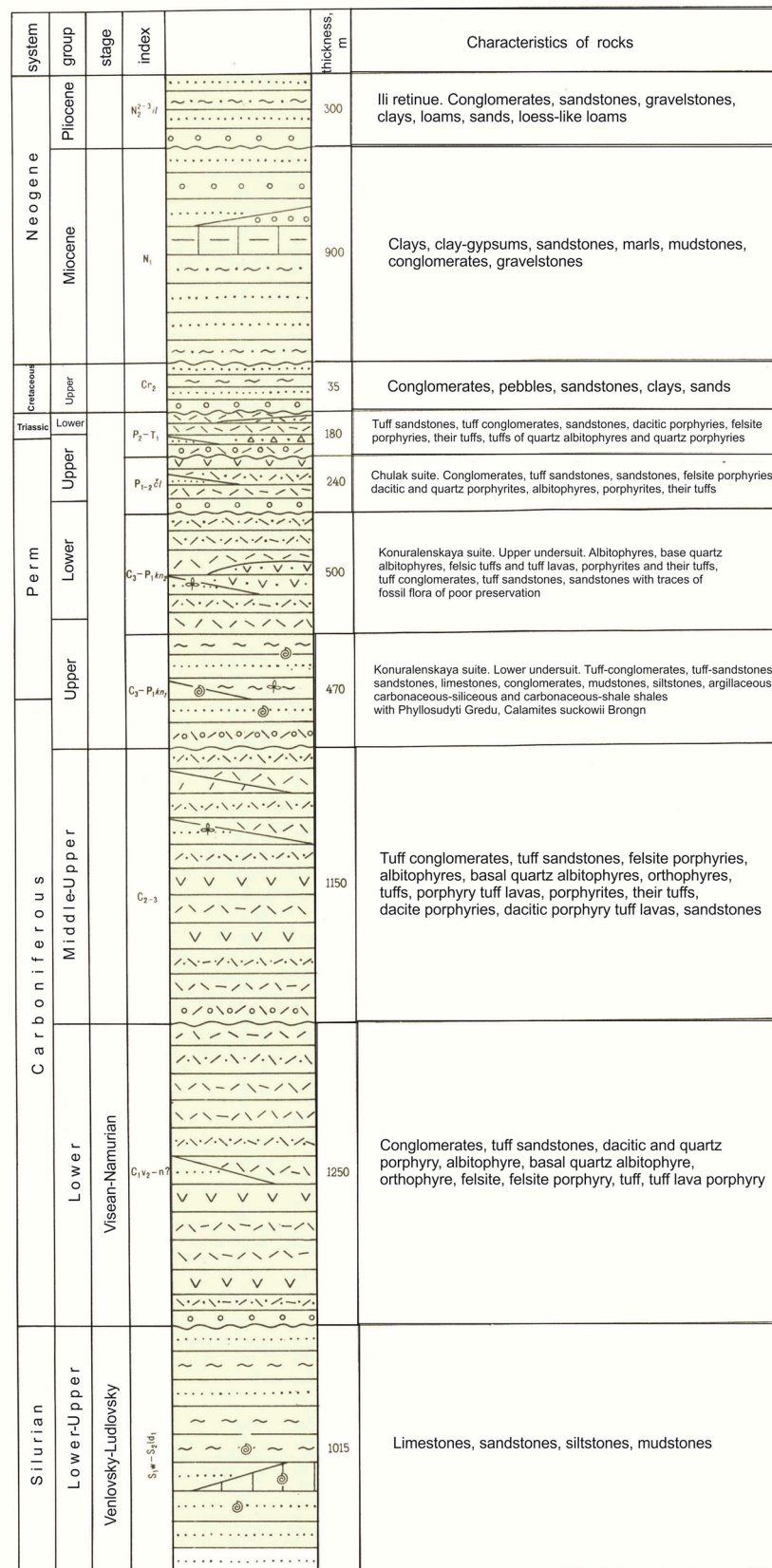


Figure 2. Stratigraphic column of sheet K-43-V—Almaty composition [22].

Deposits of Middle Quaternary are widely developed and are represented by various genetic types: alluvial, alluvial–proluvial, eolian, lacustrine, and deluvial–proluvial formations. According to the lithological composition, these are pebbles, crushed stone, sands, clays, sandy loams, loams, and loess-like loams. According to the age of sedimentation, the characterized deposits mainly correspond to the time of formation of the third terrace above the floodplain. The third terrace above the floodplain is fixed in the valleys of the Zhirenaigyr and Aksengir rivers in Uzynkargaly, Kaskelen, and Almatinka. The height of its ledge ranges from 2 to 5 m. The Moyunkum sands, developed in the form of a wide strip up to 10 km long and traced from west to northeast for up to 55 km, are attributed to the same age. Moyunkum sands are fine-grained, consisting of particles with a diameter of more than 0.05 mm, the amount of which varies from 90 to 99%, and the clay fraction is almost absent. The content of the silty fraction is very small and varies from 0.21% to 5.72%. The almost complete absence of silty and clay fractions in the composition indicates a strong wind force and repeated winding of these sands [24].

Upper Quaternary deposits are widely developed at the confluence of the Zhirenaigyr, Aksengir, and Uzynkargaly rivers in the Kaskelen river valley and in the Sorbulak lake area. Genetically, they are represented by alluvial deposits and compose the first and second floodplain terraces of the rivers Kaskelen, Almatinka, Aksengir, Zhirenaigyr, Uzynkargaly, Kurty, Aksai, etc. They are characterized by a variegated and variable lithological composition. They are represented by loams, loess-like loams, clays, sands, rubble, and pebbles. In the section of the ledge of the second floodplain terrace of the Kurta and Kaskelen rivers, Aksengir and others note three horizons of buried soils and humus. The thickness of these deposits ranges from 3 to 25 m.

Recent Quaternary deposits are genetically represented by alluvial lacustrine and eolian formations. In the floodplains of the rivers Kaskelen, Kurta, Aksengir, Zhirenaigyr, Uzynkargaly, and others, pebbles, sandy loams, loams, solonchaks, crushed stone, and sand are noted. Lacustrine deposits are developed in the Sorbulak lake basin. Eolian deposits in the form of gray, loosely cemented sands are noted to the northwest and northeast of Lake Sorbulak and the left bank of the Kurta River, west of the village of Akchi. All river terraces of the characterized region are nested [25].

Deluvial–proluvial Middle Quaternary deposits have developed significantly in the northwestern part of the described region. The depth of groundwater levels varies from 1.6 to 7–8 m. The water content of the rocks is low. The waters are slightly brackish with a dry residue of 2.1–2.7 g/L. The composition of the waters is sodium sulfate–chloride and calcium–sodium sulfate–chloride. Lower Quaternary lacustrine sediments contain mainly fresh and slightly brackish waters. The salt content in the waters of the described deposits ranges from 0.3 to 3 g/L. Most often, there are waters with a mineralization of 0.3–1.0 g/L. The composition of these waters is mainly sodium hydrocarbonate–sulfate–chloride. Workings with groundwater salinity from 1 to 6–7 g/L are characterized by a predominantly magnesium–sodium sulfate–chloride composition [22].

Miocene deposits are developed along the left bank of the Kurta River, in the upper reaches of the Zharkara and Kantarbay rivers, and to the west of the Taskotan hills containing the lowest Miocene horizons corresponding to the Saryozek Formation. This lithological suite is represented by weakly cemented sandstones, gravels, clays, loams, sands, and loess-like loams. The water abundance of the Pliocene deposits is very diverse and depends on the lithological composition of the water-bearing rocks and the thickness of the aquifers. The flow rates of wells that have exposed sands vary from 0.75 to 1.3–1.4 L/s with decreases from 1.3–15.2 to 2.4 reaching 2–5 L/s in some areas. The waters are mostly fresh and slightly brackish, ranging from 1 to 3 g/L in salinity. Classification is mainly chloride–sulfate calcium–sodium. The water yield is often low and ranges from 0.04 to 0.6 L/s at depressions from 3 to 10 m. Less common are fresh waters containing bicarbonate sodium–calcium with a dry residue of about 0.3 g/L. The waters of this deposit are considered brackish and often not suitable for drinking, but they can be used for irrigation purposes.

3.2. Contaminant Inventory

A contaminant inventory map was prepared for the Almaty, Turkestan, Zhambyl, and Kyzylorda regions starting with a database of potential sources of contamination, such as oil products, uranium deposits, and industrial facilities and heavy metals (Figure 3). Contaminant source inventories and geospatial mapping of surface activities are useful in predicting areas for future monitoring and protection of groundwater [26,27]. All information was taken from a physiographic information database maintained by Kazhydromet [28]. A geoinformation database was created for understanding the potential contaminant sources to groundwater in Kazakhstan, including natural and anthropogenic factors that can have negative impacts [29]. General information semantic databases contain primary materials, geo-filtration parameters, and industries/activities that may contribute contaminants. Geo-filtration parameters are represented by tables containing information about the location of the corresponding graphic object, parameter values, and intervals of their change. These tables are used as attribute information for graphical database objects. The objects of economic activity are presented in the information system from the point of view of their influence on the regime and qualitative composition of groundwater. General information includes topographic data, objects of economic activity, and schemes of territorial division. A block termed “Groundwater deposits” is represented by tables with descriptions of local aquifers and water intake structures (boreholes or wells). All data are represented by three classes of objects—polygons, points, and polylines. Attribution data are associated with each graphic object, which may belong to a semantic database [30]. The semantic database is organized, and data checked using Microsoft Excel, while the graphical database and maps were created using ArcGIS version 10.8 and MapInfo Professional version 12.5 (ESRI, Redlands, CA, USA).

The public water supply monitoring system in Kazakhstan is an extensive network of regulatory, organizational, and material programs [31]. Monitoring is often performed by various services and there are difficulties in collecting and receiving all monitoring data in one place. Results provided through the Kazhydromet network have declined sharply in the last 5 years, now serving only one-third of the former state surveillance network [28]. Previous monitoring in the areas of large cities has suggested that local areas of groundwater pollution occur from industrial activities [32,33]. Hydrochemical indicators used for comparison with previous monitoring are the values of maximum permissible concentrations (MPCs) of pollutants for the sources of fishery, domestic drinking, and municipal water. According to the degree of danger to human health, pollutants are generally divided into four classes (Table 2). This classification is based on indicators that characterize the degree of hazard from chemicals that pollute drinking water, depending on their toxicity, persistence, and ability to cause long-term effects [34,35].

Table 2. Pollutants in groundwater by hazard classes.

Risk Category	Chemical Elements
Extremely hazardous	mercury, beryllium, carbon tetrachloride
Highly hazardous	lead, cadmium, aluminum, silicon, cobalt, barium, arsenic, lithium, cyanides, rhodanides, nitrites
Hazardous	nitrites, ammonia, iron, manganese, nickel, chromium, zinc, copper, phosphates, acetone, chlorobenzene, nitrobenzene, synthetic surfactants
Moderately hazardous	chlorides, sulfates, phenols, oil products, boron, fluoride

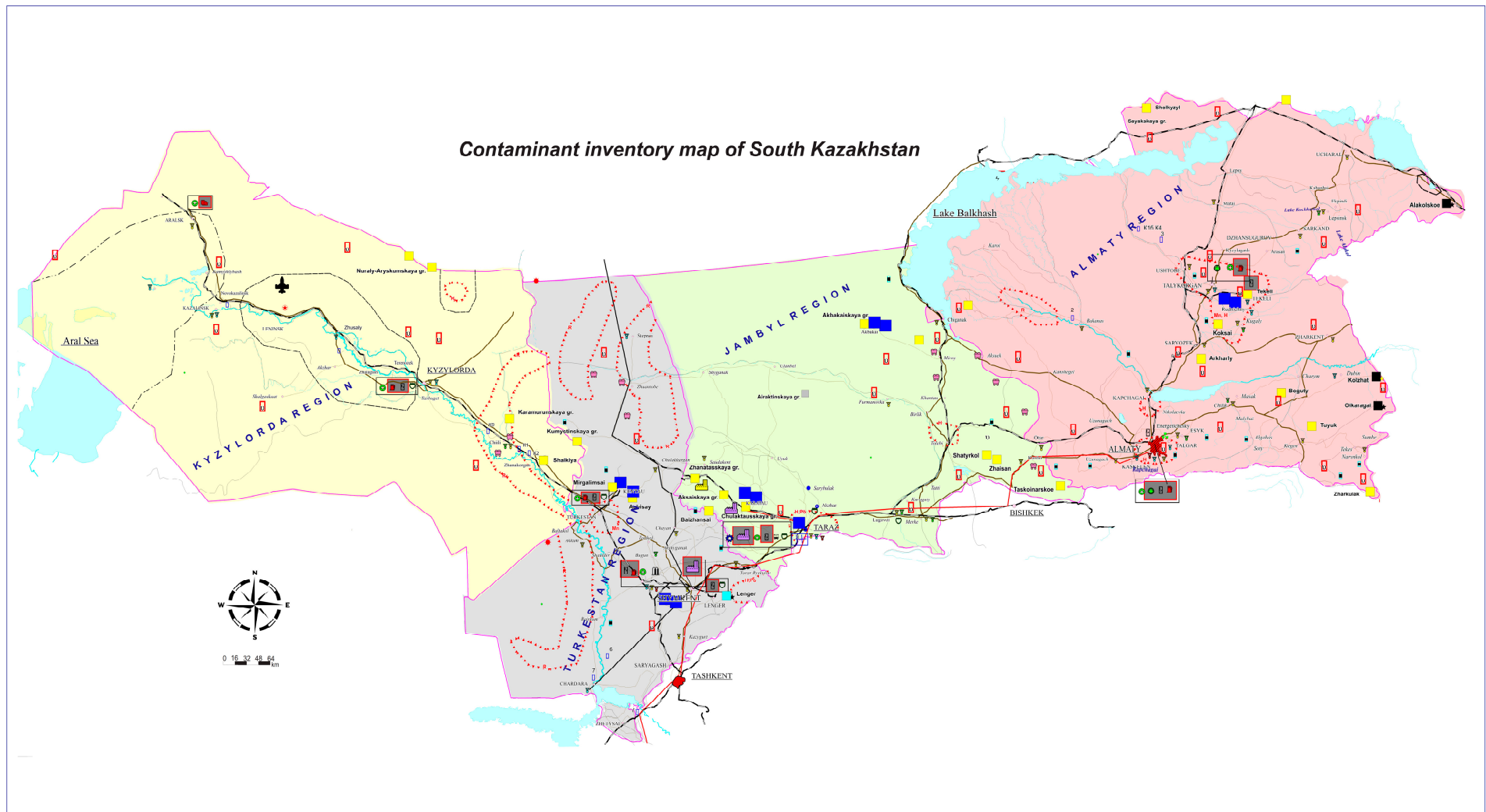
Figure 3. *Cont.*



Figure 3. Contaminant inventory map of Southern Kazakhstan prepared for this study.

3.2.1. Almaty Region

A previous survey reported that the frequency of tap water samples with deviations from the standard for sanitary, chemical, and microbiological indicators was 0.07% and 1.7% for centralized water supply systems and, respectively, 0.2% and 0.37% for decentralized water supply systems [36]. The reported discrepancy in the quality of the supplied water according to sanitary and chemical indicators is often associated with elevated iron or water hardness. The number of incidences where sanitary standards were not met in the Enbekshikazakh district amounted to 7.7–7.8%, and 8.1–8.3% in the Almaty region. The distribution of pollutants, intensity, and area is shown in Tables 2 and 3.

Table 3. Distribution of groundwater pollution sites by hazard classes of pollutants by administrative regions of the Republic of Kazakhstan.

Administrative Region	Total Number of Observed Contamination Sites	Number of Ground Water Contamination Sites by Hazard Class of Identified Pollutants			
		Extremely Hazardous	Highly Hazardous	Hazardous	Moderately Hazardous
Almaty	10 (21.4%)	1	-	-	9
Zhambyl	16 (34.2%)	-	-	4	12
Turkestan	17 (36.3%)	-	-	-	17
Total for the RK:	214	15	34	51	114

Based on prior investigations [17], 10 areas of groundwater pollution have been identified (Table 4). Contamination of groundwater in the Almaty region was characterized as extremely hazardous (1) and moderately hazardous—9 (Table 5).

Table 4. Distribution of sources and sites of groundwater pollution and their provision with an observation network in Southern Kazakhstan.

Administrative Area	Number of Pollution Sources	Number of Identified Areas of Groundwater Pollution		
		Total Identified	Surveyed	Having an Observation Network
Almaty	103	10	10	10
Zhambyl	19	16	15	16
Turkestan	29	17	3	17
Kyzylorda	11	3	2	2
Total	162	46	30	45

Out of 24 groundwater deposits in the Almaty region, 10 are subject to hazardous and moderately hazardous levels of contamination. Almaty groundwater used for domestic water supply may contain cadmium (ten times the MPC), manganese (seven to fourteen times the MPC), mercury (one to two times the MPC), phenols (six times the MPC), bromide (two to five times the MPC), oil products (three to five times the MPC), nitrates (up to four times the MPC). Shallower aquifers, with the water table close to the surface, are more frequently polluted, though contaminants may be found up to a depth of 100 m. Contamination of shallow groundwater has been reported at the Almaty wastewater treatment facilities [37].

The Commission on Reserves recommends [19] using shallow groundwater to a depth of 150 m for industrial and technical water uses, and for economic and drinking water supply, the lower horizons in the range of 300–500 m. The main sources of pollution within this groundwater deposit are industrial enterprises within the city of Almaty, including

CHPP-1, CHPP-2, filtration fields, settling tanks, and wastewater storage [38]. Groundwaters from the Pokrovsky and Nikolaevsky deposits were found with an increased content of fluoride (up to eight times the MPC), while the Taldykorgan groundwater is reported to contain lead at two to three times the MPC and nitrate at three to fifteen times the MPC [39].

Table 5. Groundwater contamination sites by pollutants, number exceeding MPC, and estimated areas (km²).

Administrative Region	Total Number of Contamination Sites	Number of Sites where Groundwater Contamination Was Detected								Number of Sites with Pollution above MPC			Number of Polluted Areas, km ²				
		Sulfates, Chlorides, Mineralization	Nitrogen Compounds	Oil Products	Phenols	Other Organic Compounds	Ferrum Compounds	Heavy Metal	Other Inorganic Compounds	Up to 10	10–100	More than 100	Less than 10	10–20	20–100	More than 100	Not Installed
Almaty	10 (21.4%)	9	-	7	-	-	-	-	9	9	-	-	-	-	-	-	-
Zhambyl	16 (34.2%)	-	14	3	-	-	-	-	12	3	-	-	-	-	-	-	15
Turkestan	17 (36.3%)	5	-	2	-	3	-	-	10	-	-	-	5	5	-	-	13
Total:	214	95	55	37	15	4	35	24	92	82	39	21	87	13	20	12	75

3.2.2. Zhambyl Region

In the Zhambyl region, we identified 19 sites with contaminant sources, including 16 sites with evidence of contamination (Table 4). This region has the country's largest Karatau phosphorite-bearing formation, as well as a large industrial complex for the production of phosphorous products: the Novozhambyl phosphorous plant, the Zhambyl production Association “Khimprom”, and the Zhambyl superphosphate plant. These enterprises are located in the valley of the Talas and Asa rivers on the foothill plain. Common to these industries is the composition of industrial effluents, which contain the main pollutants, fluoride and phosphorus. In general, the region is already characterized by elevated concentrations of fluoride in surface and groundwaters [36].

Thirty-two aquifers in the Zhambyl region are for economic, drinking, and complex purposes, six of which are vulnerable to pollution. The most noticeable pollution of groundwater is observed in the territory of the Talas–Assinsky interfluvium, where industrial enterprises are concentrated, and the largest groundwater reserves have already been explored and exploited. The Talas–Assinsky in the southern part, and the northern Talas–Assinsky, Zhualynsky, Predeskov, and Bijlikolsky aquifers have a high density of water intakes. Fluoride concentrations exceed 3–8.2 times the MPC in these groundwater supplies. In addition, a number of components in high concentrations have been established: sulfates (1.5–3 times the MPC), ammonium (3–5 times the MPC), and mineralization (2–2.5 times the MPC). In some places, groundwater also contains nitrates and nitrites exceeding 1.7 times the MPC, while chlorides approach 1.7–2 times the MPC near filtration fields and sugar factories. Synthetic surfactants are measured at levels up to four times the MPC. Groundwater contamination of these deposits is moderately hazardous and, in places, hazardous (Table 2). Potential surface sources of groundwater pollution are silt reservoirs, evaporation ponds, and storage tanks discharging more than 2 million m³/year of industrial water with a high content of fluorine and phosphates.

3.2.3. Turkestan Region

In the Turkestan region, 29 potential sites of groundwater contamination were identified, of which 17 sites of contamination are characterized by hazard classes as moderately hazardous (Table 3). The expeditions “Volkovgeology” and “Krasnoyarskgeologiya” also revealed the number of activities potentially resulting in groundwater contamination. The development of uranium deposits in the Chu-Sarysu Artesian basin led to the contamination of the groundwaters of Paleogene and Cretaceous aquifers with radionuclides [34]. It is noted here that laboratory work was carried out to determine radioactivity safety since there are some isotopes in the sample, and the results are shown here—Pb-210 < 0.1 Bq/L, Po-210 < 0.1 Bq/L, Rn-222 < 0.1 Bq/L [40]. Groundwater intakes of the Badam–Sairam interfluvium are reportedly contaminated with NO₃ (up to 1.1X), Fe (4.2X), Hg (3X), and PO₄ (2.5X). About 140 thousand m³/day is taken at water intakes with pollution for household drinking purposes, which is 31.4% of the total amount of the extracted groundwater for drinking [34].

In the industrial region of Shymkent, chemical analyses revealed that groundwater may contain excessive Mn (4.1 times MPC); SO₄ (1.22 times MPC), and NO₃ (1.18 times the MPC). Lead, zinc, oil products, phosphates, and copper are all below the MPCs. The mineralization of groundwater in the industrial zone wells ranges from 2 to 4 mg/L [35]. The Mirgalimsay–Turkestan landfill is located in the territory of the Turkestan region, 180 km from Shymkent, in the foothills of the southwestern slope of the Big Karatau and is associated with the Mirgalimsay lead–silver–barite deposit. The total number of observation points is 69. Among them: wells—46, springs—14, surface runoff—9 points. Sulfate, sodium, and chloride contamination and increased mineralization noted at the beginning of the study are present in the wells, although some of the wells show a decrease in their concentrations. The main heavy metal contamination that occurs periodically is associated with the operation of the Bayaldyr tailings dump. The MPC for lead was exceeded 2.86 times, and the tailings dump runoff exceeded it 1.6 times. For the wells of Mirgalimsay–Turkestan region (Figure 1), the strontium and the manganese content exceeded maximum permissible levels. The quality of groundwater in all operated fields generally meets sanitary and epidemiological standards [25,41].

3.2.4. Kyzylorda Region

In the Kyzylorda region, out of 11 potential sources of pollution, 3 areas have been found in groundwater (Table 3). In the Kyzylorda region, 18 groundwater deposits have been explored for economic and drinking purposes, and 14 are used for drinking or other purposes [42]. According to regime observations, there is an overall increase in water mineralization. For instance, in the Terenozek groundwater deposit, the mineralization of groundwater has increased from 1.3 to 1.43 g/L. In Kyzylorda, it has risen from 1.1 to 1.5 g/L, while in the Karmakchinsky area, it has gone up from 1.53–1.6 to 1.65–1.8 g/L. Similarly, at Shalkiya, the mineralization has increased from 0.6–1 to 0.7–1.1 g/L, from 1.5–3 to 2–3.3 g/L at Sarybulak, and from 1.2–1.4 to 1.45–1.6 g/L at Kuvandarya during the summer period. Groundwater in these aquifers is moderately hazardous.

Contamination was reported in the upper aquifers of the Torangylsai Field, which are not used as a drinking water source, while the developed Kyzylorda aquifer is also of low quality near this deposit [42,43]. Other possible sources include the influence of irrigation and salination of soils in the Syrdarya river basin [44,45]. Groundwater at the Kumkol oil field is contaminated with organic substances, surfactants, sulfates, nitrates, nitrites, sodium and potassium salts, phosphorus, petroleum products, and chemical reagents used for drilling fluids and for water injected into wells. Groundwater in the Badam–Sairam field continues in the Turkestan region, and its quality is affected by the discharge of wastewater from a number of chemical plants located in the Badam river valley. Discharge contains arsenic at 10X MPC, phosphorus at 5X MPC, fluoride at 13X MPC, and lead. The Badam–Sairam water intake, the main source of water supply in the city of Shymkent, is located in the pollution zone. Large pockets of groundwater pollution are also associated

with the activities of chemical enterprises in the Zhambyl industrial district. So, at the site of the settling tanks of the phosphorus plant and the Khimprom plant, the content of fluoride in some places was three to six times higher than the norm. The groundwater in the northeastern part of Taraz, near the filtration fields, exhibits high mineralization levels, along with elevated concentrations of chromium and synthetic surfactants [25]. About 640 million m³/year of industrial wastewater is discharged in the Zhambyl region to surface water, filtration fields, and evaporation ponds. Municipal wastewater is not discharged to surface sources, but in Taraz City, raw sewage is collected in seepage ponds and recharging local groundwater. Due to infrastructure age of the Shymkent wastewater treatment plant, insufficiently treated wastewater is currently diverted to storage tanks and used to irrigate crops, creating a risk of infection in the population. Household and industrial effluents from the city of Kyzylorda, totaling 33,670 m³/day, are fed through a pressure pipeline without treatment to existing storage facilities and discharged to filtration fields. Irrigation return waters are also a major source of surface water pollution. Evidence of surface-borne deep groundwater contamination has been reported in nearby Kyrgyzstan [46,47] and Uzbekistan [48].

The majority of the urban population of the Zhambyl region (up to 98.9%) receives water of good quality from groundwater sources. In contrast, in the cities of Kyzylorda, Aralsk, Saryagash, Shardara, and Lenger, surface water is used for drinking supplies and the quality does not meet regulatory requirements. Villages using groundwater for drinking generally receive good-quality drinking water, but the system infrastructure is aging. Depreciation and aging of equipment of central water supply in cities and towns ranged from 40 to 80%, and in the city of Saryagash and three settlements of Zhambyl region—100%. The situation for providing good-quality drinking water supplies to the rural population is much worse. Only 32.6% had access to the centralized water supply. Only 512 out of 1508 rural settlements have a centralized water supply. The quality of tap water taken from surface sources, as a rule, does not meet standards for drinking. The level of provision of the population with sanitary conditions is insufficient; even in regional centers, only 54–65% of their residents use centralized sewerage systems, and in rural settlements and small towns of the Southern Kazakhstan region, it is practically absent [40].

4. Present Study

To facilitate a greater understanding regarding groundwater quality, all results of this study were compared with worldwide standards as in related studies of drinking water supplies [49]. According to Table 6, concentrations of some physicochemical parameters do not meet water quality standards. Overall sodium exceeds worldwide drinking water standards in 1.5%, sulfate in 3%, total iron in 1.2%, nitrates in 1.9%, lead in 1.8%, cadmium in 1.4%, nitrate in 1.9%, and ammonia in 3.3% of the supplies sampled in the present study. Based on our assessment, the drinking water of Southern Kazakhstan may exceed the recommended health levels for sulfate, sodium, nitrate, cadmium, lead, and ammonia. In the present study, 46% of samples had fluoride levels beyond the suggested levels of the WHO for ingestion. The water type of these supplies was generally a Ca-HCO₃ type, which can be attributed to freshly recharged water. Rock–water interaction controls the hydrochemistry of groundwater, and the aquifers likely contribute fluoride during weathering. A previous analysis demonstrated that geological and anthropogenic activity contaminated the studied area's groundwater resources [50].

General water chemistry. The major ion composition of groundwater determines the requirements for treatment methods and also affects the toxicity of hazardous elements. A Piper diagram (Figure 4) shows that groundwater used for municipal drinking supplies in the Almaty region is a calcium–magnesium bicarbonate type, some samples are a mixed calcium–magnesium–sulfate–chloride type, and only one sample is a sodium–potassium chloride–sulfate type, that is the groundwater of the Middle-Quaternary sediments. Water intakes of the Almaty region are calcium type, some samples are a sodium and potassium type, some have no dominant type, and the groundwater of this region is a water bicarbon-

ate type. In comparison, groundwater in the Zhambyl region is mostly calcium–magnesium bicarbonate type, calcium type, and bicarbonate, which are groundwater characteristic of alluvial and alluvial–proluvial sediments of the Talas–Assay interfluvium. The Turkestan region groundwater used for municipal supplies is a calcium–magnesium bicarbonate type; some samples are a mixed type, a calcium–magnesium–sulfate–chloride type, and some samples are a sodium–potassium chloride–sulfate type and mainly include locally aquiferous Pliocene–Quaternary terrigenous complexes. The Piper diagram (Figure 4) shows that groundwaters in the Turkestan region are a calcium and sodium and potassium type, while many have no dominant type.

Table 6. Comparison of assessed parameters with Kazakhstan [13], WHO [51], and USA [52] standards.

Parameters	Standards (mg/L)			Current Samples from Southern Kazakhstan (mg/L)		
	Kazakhstan	WHO	USA	Max	Min	Percent above WHO Standard
pH	6–9	6.5–8.5	6.5–8.5	8.18	6.58	0
TDS	1000–1500	200–2500	500	285	198	0
Sodium	200	200	200	298	3	1.5
Sulfate	300	250	250	753.2	11.5	3
Chloride	350	250	250	248.2	3.5	0
Fluoride	1.5	1.5	4	1.4	0.08	0
Total Iron	0.3	0.2–2	0.3	2.45	<0.1	1.2
Nickel	0.1	0.07	0.1	0.02	0.01	0
Lead (Pb)	0.03	0.01	0.015	0.018	0.009	1.8
Cadmium	0.001	0.003	0.005	0.0042	0.001	1.4
Nitrate	45	50	10	98.9	<0.2	1.9
Nitrite	3	3	1	0.43	<0.01	0
Ammonia	2	3	--	10	<0.05	3.3
Petroleum hydrocarbons	0.1	0.3	0.1	>0.005	>0.008	0

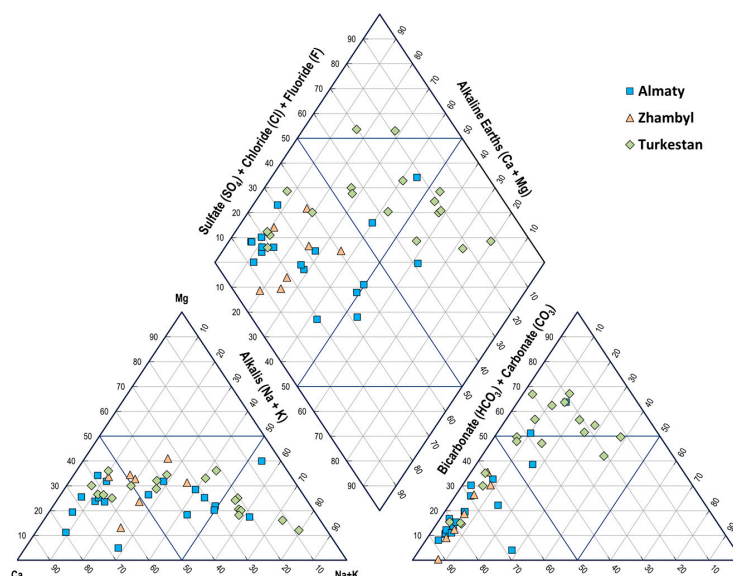


Figure 4. Piper diagram of groundwater type in Southern Kazakhstan by region.

Among the 106 samples collected, 45 underwent general chemical analysis, 30 were designated for specific indicators and metals, and 31 were utilized for determining petroleum product levels from the Almaty, Zhambyl, and Turkestan regions. Petroleum hydrocarbons were not detected in these 31 samples, though previous sampling suggested that there may have been hydrocarbon contamination [15]. Based on the contaminant inventory map (Figure 3), the Almaty region's groundwater pollutant sources include oil pipelines, municipal effluent and solid waste, as well as mining waste sources. Public water systems do not reflect an influence from these sources, but because local groundwater has been obviously contaminated, it should be monitored regularly. For example, a tailing dump of the Koksuy mine likely resulted in the release of oil products, aluminum, and cyanides to local groundwater; however, the municipal drinking water sources do not presently exceed permissible concentrations. Mine tailing drainage water is discharged near Ushtobe and Bakanas, thus groundwater near these sites should also be carefully monitored. In the Almaty region, there are such mineral deposits as the Boguty tungsten deposit, the Tuyuk deposit of barite–polymetallic ores and silver, the Zharkulak gold deposit, and the Koldzhat uranium coal deposit extraction. The vulnerability of local groundwater used for drinking must be continuously evaluated in these processing areas.

In the territory of the Zhambyl region, pollution may originate from industrial facilities. Major industries include the Karatau phosphorite-bearing formation, the Novozhambyl phosphorus plant, the Zhambyl production association “Khimprom,” and the Zhambyl superphosphate plant. Common to these industries is the composition of industrial effluents, which contain the main pollutants of fluorine and phosphorus. In the eastern part of the Zhambyl region, groundwater influenced by uranium mining must be protected. In the Turkestan region, noticeable pollution is detected in the cities of Shymkent and Mirgalimsay. The Mirgalimsay–Turkestan test site is located on the territory of the Turkestan region, 180 km from the city of Shymkent, in the foothills of the southwestern slope of the Greater Karatau, and is confined to the Mirgalimsay lead–silver–barite deposit. In the Kyzylorda region, groundwater pollution of the upper aquifer was noted within the Torangylsai field and the developed Kyzylorda field. Groundwater pollution from irrigated cropland may also contaminate shallow aquifers in this region [53,54].

Future monitoring will be important around the cities of Taraz and Shymkent, where copper, phosphorites, and lead are actively extracted. Though the current quality of groundwater in southern Kazakhstan allows for safe consumption in nearby industrial regions, continued extraction will undoubtedly contribute to local groundwater quality. Some of these underground reservoirs pose challenges in accessibility for research, as they fall under the jurisdiction of industrial sectors, without state-level documentation of their metrics. Neglecting the monitoring could result in the contamination of drinking water across populated areas in Taraz and Shymkent.

5. Conclusions

In general, both hydrogeochemical analyses of water were taken during fieldwork and evaluation of contaminant sources provide useful knowledge for the protection of these important resources in southern Kazakhstan. Results were compared to aquifer characteristics and a contaminant source inventory prepared from a recently compiled database. Chemical pollutants including sodium, nitrates, sulfates, and cadmium were found in excess of MPCs in some drinking water supplies, though most appear to be unaffected by local activities at present. In the areas of the mining, oil and gas, and chemical industries, groundwater may be influenced by industrial, municipal, and agricultural sources.

Proposed measures to address water supply issues and reduce pollution and negative impact on groundwater in southern Kazakhstan's water-deficient regions include: *Almaty region*: compliance with rules for sanitary protection zones of water sources, elimination of pollution foci, increasing wastewater treatment, monitoring of groundwater, introduction of water-saving technologies, strict compliance with water limits. *Zhambyl region*: compliance with rules for sanitary protection zones of water sources, elimination of pollution foci,

increasing wastewater treatment, monitoring of groundwater, introduction of water-saving technologies, strict accounting of water extraction, and control over depletion. *Turkestan region*: compliance with rules for sanitary protection zones of water sources, elimination of pollution foci, increasing wastewater treatment, monitoring of groundwater, and studying the water–salt balance in irrigation areas. *Kyzylorda region*: compliance with rules for sanitary protection zones of water sources, elimination of pollution foci, increasing wastewater treatment, monitoring of groundwater, introduction of water-saving technologies, accounting for water extraction, development of desalination technologies, control over depletion.

6. Future Directions and Research

Our research findings strongly suggests that future monitoring studies continue to investigate heavy metals and petroleum products in groundwater supplies, especially in regions with local contaminant sources identified with an inventory database and map. While we found that most groundwater used for drinking in Southern Kazakhstan complies with the established standards, this conclusion is based on a single sampling campaign. Recharge and groundwater movement may introduce these same contaminants into wells where they were previously undetected. While the chemical analysis from these 45 wells included many regularly measured contaminants, there is a wide variety of other contaminants originating from the sources identified. While hydrogeology and aquifer characteristics affect source water composition, the relatively small number of wells sampled limits the statistical power in evaluating trends between these regions, and trends with other regions throughout Central Asia. More intensive monitoring of supply wells close to industrial, municipal, mining, and agricultural sources is urgently needed to protect public drinking water quality in this region. Other research directions may focus on impacts on domestic well water quality, another important source of drinking water for this region. Finally, the effectiveness and safety of water system infrastructure and treatment technologies employed should be regularly evaluated to ensure adequate measures are taken to protect public health.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w15244240/s1>.

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