

Assessing Urban Stormwater Runoff Quality and Impact on Shallow Groundwater in Suburb of Urmia City

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Abstract

Rapid expansion of Urmia City in recent decades has caused significant changes in land use and subsequent contamination of water resources. This study aimed to investigate the quality of urban runoff and stormwater from different urban surfaces and assess the impact of stormwater infiltration on groundwater quality in suburban areas. For this purpose, 35 urban stormwater runoff samples and 18 groundwater samples were collected in May 2015 and analyzed for organic matter, nutrients, and heavy metals. Results showed that TSS, COD, BOD, PO₄, Fe, Pb, and Cr concentrations reached 1,100 mg/L, 181 mg/L, 48 mg/L, 3 mg/L, 2,800 µg/L, 50 µg/L, and 240 µg/L, respectively, in parking lot and road runoff—significantly higher than other land uses. Due to sewer overflow, TSS, NO₃, and total coliform increased to 2,050 mg/L, 123 mg/L, and >1,100 per 100 mL in stormwater at the city outlet. Hydrochemical analysis revealed groundwater in suburban areas is hard to very hard (TH: 167–527 mg/L), fresh (TDS: 358–832 mg/L), and of Ca-HCO₃ type, controlled by natural geochemical processes and anthropogenic activities. Ion exchange and reverse ion exchange were identified as dominant mechanisms. Due to shallow groundwater (1–5 m), infiltrated runoff has elevated nitrate concentrations up to 67.3 mg/L, exceeding the WHO guideline of 45 mg/L in 38.8% of samples. Groundwater Quality Index (GWQI) showed 89% of samples were of good quality and 11% poor, with poor-quality samples associated with infiltration areas. Effective urban runoff quality control is essential to protect receiving water resources.

Keywords: Contamination; Groundwater quality; Stormwater; Urban runoff; Urmia City.

Introduction

Population growth and migration towards urban areas in recent decades have caused rapid expansion of cities and led to changes in land use (1, 2). Urbanization brings a range of environmental challenges for local, regional and wider environments as a direct result of biogeochemical and physical changes to hydrological systems (3-6). The development of urban areas and the

proliferation of impervious surfaces have significantly altered natural hydrological cycles, resulting in an increase in stormwater runoff and substantial risks to groundwater quality. In natural landscapes, a substantial portion of precipitation infiltrates into the soil, replenishing groundwater and sustaining baseflow in streams. However, in urban environments, the replacement of permeable surfaces with impervious materials such as asphalt and concrete disrupts this

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balance by reducing infiltration and evapotranspiration while increasing surface runoff (7). These changes include alterations in hydrological flow regimes as well as shifts in the chemical and biological composition of stormwater runoff from these developing areas.

Urban discharges may include stormwater runoff, separate or combined sewer overflows and snowmelt (8). The relative quality and quantity of these discharges vary considerably; in the case of combined sewer overflows, they carry wastewaters whose characteristics represent the combination of different contributions. Runoff pollutant concentrations are more influenced by land use and land cover (LULC) and climate than imperviousness. Differences in LULC significantly affect the generation of metals and nitrogen species; road, city center, and commercial LULCs generally produce the most elevated pollutant concentrations (9). Some of the main factors affecting urban stormwater quality include intensity and duration of precipitation, sewerage system, waste management and disposal practices, urban land use patterns, traffic management, runoff collection infrastructure, population density, living standards, and the geological and topographic setting of the area. Urban stormwater contains a wide range of contaminants, including organic compounds, inorganic substances, nutrients, toxic elements, pathogens, and emerging pollutants such as microplastics and pharmaceuticals (10-16). Heavy metals are of particular concern; they can accumulate up to 100 times higher in urban environments than background levels, posing a significant threat to aquatic ecosystems (17). Trace metals, suspended solids, nutrients, pesticides, petroleum products, *E. coli* and fecal coliform bacteria are generally found at higher concentrations in urbanized and urbanizing areas than in natural systems, due to increased anthropogenic inputs from people, vehicles, roads, and building materials introduced into the environment. High concentrations of heavy metals such as lead, zinc, copper, and cadmium can be generated in surface runoff, particularly after a long dry period, with sources including fossil fuel combustion, tire wear, vehicular abrasion particles, and fertilizers (17, 18).

Currently, it is well known that stormwater transports large quantities of contaminants to receiving waters around cities (8, 19-21), thereby contributing significantly to pollution of receiving waters in many countries (22). Urban stormwater runoff has long been considered a major contributor to non-point source pollution affecting both surface and groundwater resources. The runoff of stormwater in urban areas contributes significantly to the pollution of both groundwater and surface waters (23, 24). These contaminants include toxic elements, nutrients,

pharmaceuticals, and emerging substances of concern such as perfluoroalkyl substances (11). The impact of stormwater pollutants on receiving water bodies depends on the nature of pollutants, their concentration, their mixture, and their total load. The potential for groundwater contamination caused by stormwater infiltration is particularly important in areas with sandy soils and shallow water tables (25). Typically, stormwater runoff reaches groundwater through one of three ways: sedimentation or filtration prior to infiltration into soil, surface infiltration into soil, and direct injection into groundwater (23). Environmental factors such as pollutant concentration in runoff, soil properties, and geological setting influence the contamination potential (25). While most toxic elements in soil are retained in the upper layers through adsorption, nitrates and some pathogens—particularly viruses—can reach groundwater more readily. Most studies conducted in recent years have focused on the quality of urban runoff from different urban surfaces and their contamination levels, with less attention given to the effect of this runoff on groundwater in infiltration basins. In semi-arid regions, this issue is particularly critical because groundwater resources are already under stress from over-extraction and limited recharge (26). Few studies have examined urban runoff contamination and its effect on receiving waters in Iran.

Urmia City is one of the fastest growing cities in Iran, and urban expansion could have a detrimental impact on groundwater quality. Heavy rainfall events have become more frequent and intense in recent years due to the impact of climate change and global warming, underscoring the urgent need to develop robust stormwater management systems (27, 28). Recent studies in Urmia have employed hydrological models such as SWMM and MODFLOW to evaluate stormwater management strategies and artificial recharge potential (27). The objective of this research was to investigate the quality of urban runoff and stormwater and assess the impact of stormwater runoff infiltration on groundwater quality. The results are beneficial for understanding and managing urban non-point source pollution in Urmia City. Novelty of the study: While previous studies have primarily focused on the quality of urban runoff from different land surfaces, the present study provides a comprehensive assessment of both runoff quality and its subsequent impact on shallow groundwater quality in infiltration zones—an aspect that has received limited attention in semi-arid regions, particularly in Iran. Furthermore, this study integrates hydrochemical analysis, heavy metal evaluation indices (HEI), and groundwater quality indices (GWQI) to establish a quantitative link between urban stormwater infiltration and groundwater contamination, offering a novel

framework for managing urban non-point source pollution in rapidly developing cities.

Materials and Methods

Description of the study area

Population and climate

Urmia City, with a population exceeding 0.7 million, is the second largest city in northwestern Iran. The study area covers more than 100 km² and consists of 5 municipal districts (29) (Figure 1). Over the last five decades, the population has more than doubled and urban expansion has increased more than fivefold. Urban development has increased demand on groundwater resources in the study area while exposing these resources to greater contamination risk. Urmia City is situated at an altitude of 1,330 m above sea level and is located along the Shaharchay River on the Urmia Plain (Figure 1). The climate of the study area is cold semi-arid with a mean temperature of 11 °C and mean annual rainfall of about 310 mm, 70% of which falls during spring and winter. Groundwater is an important water resource for drinking, agriculture, and industrial purposes in the study area.

Land use

According to available data, 66.5% of the total 100 km² area of Urmia City is used for residential, transportation and social services, while 33.5% consists of gardens, farms, cemeteries, open areas

and barren lands (29) (Figure 2).

The most common land users in the city are residential areas, transportation networks, green spaces, educational facilities, commercial zones, offices and military installations, urban utilities, industrial zones, sports facilities, healthcare services, and religious, cultural and tourism facilities (Figure 2). According to the data, the major land use across the 5 districts of Urmia City is residential, followed by industrial uses in District 2, commercial uses in District 4, gardens and green spaces in Districts 2 and 4, and military uses in District 5. Between 2005 and 2015, the built-up area increased from about 47% to 66.5% of the total area. Agricultural land decreased from about 24% to 9% over the same period. Most urban expansion has occurred towards the southern and northwestern parts of the city, resulting in the loss of agricultural land.

Surface water drainage system

The surface water drainage system of Urmia City consists of canals, streams and the Shaharchay River, which flows from west to east through the city center with a width of 20 to 150 m. Due to the discontinuity of some canals and streams, reduced riverbed width, and construction of roads and buildings, the system's function is suboptimal. The main problematic district in the surface water drainage system is the central and western parts of the city. The urban sewerage

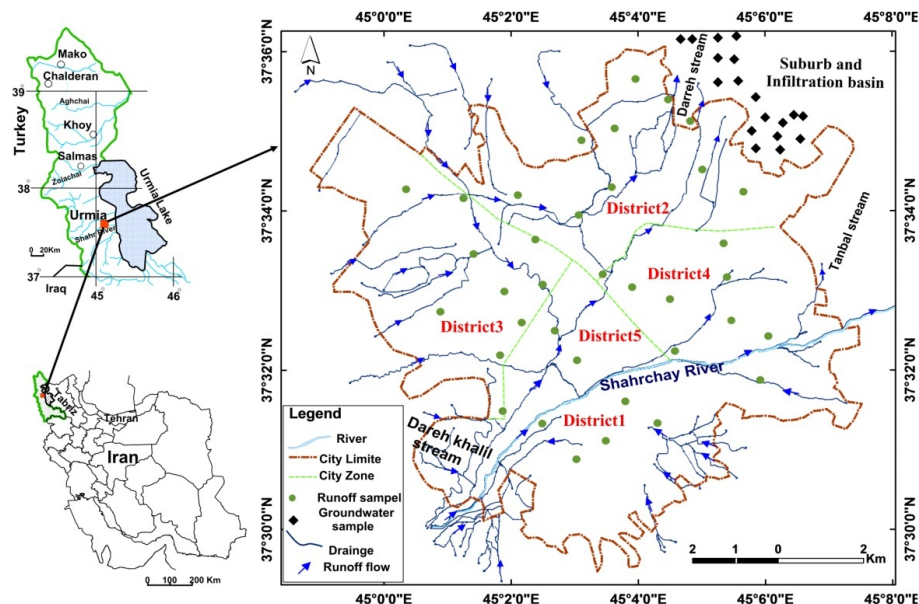


Figure 1. Location and storm runoff, groundwater sampling station within the study area

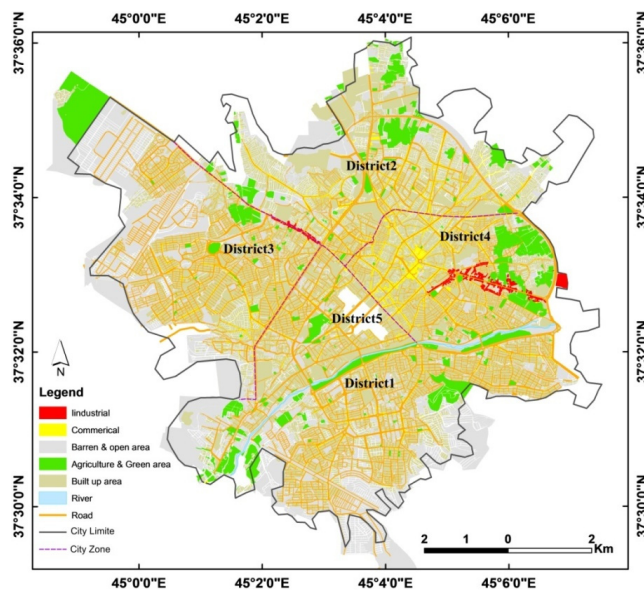


Figure 2. Land use map of the study area

system covers 58% of the city, while the water distribution network covers about 99% of the city (30). Sewer overflow onto streets during heavy rainfall at some points in the urban sewerage network causes recurring problems.

Geology and Hydrogeology

Based on Iran's structural divisions, the study area is located in the Alborz-Azerbaijan zone. The main lithological units around the Urmia Plain include alternating limestone, sandstone, conglomerate and

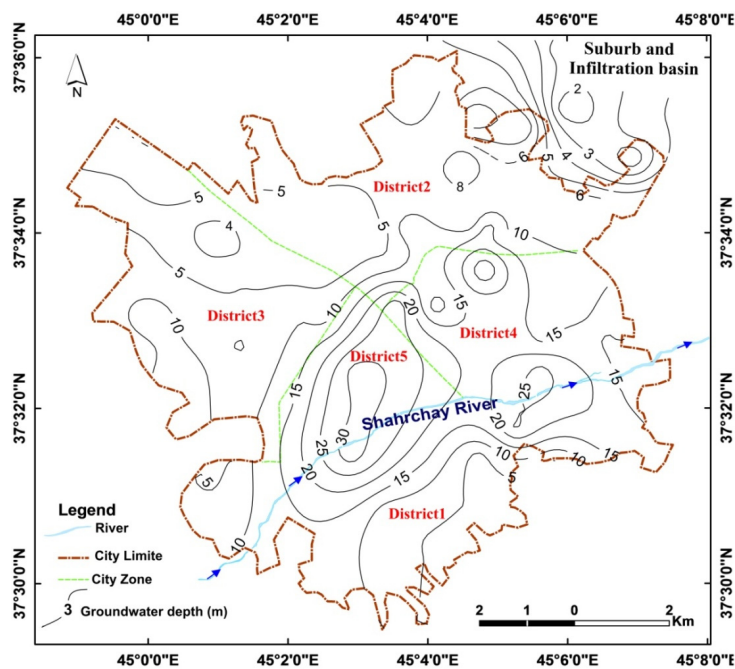


Figure 3. Depth of groundwater map in urban and suburb in study area

marl ranging from Oligocene to Miocene in age (1). Well and borehole logs indicate that the aquifer in the study area is unconfined and composed of gravel, silty sand and clay sediments with medium grain size. The alluvial aquifer thickness is 21-87 m and groundwater depth ranges from 1 to 32 m below ground level (30). The general groundwater flow direction in the urban area is from west to east. In the suburban areas, groundwater depth ranges from 1 to 9 m, with an average of 5 m and a minimum of 1 m in infiltration zones (Figure 3).

Sampling and analysis

In this study, we collected 35 samples from rain water and runoff made in various parts of Urmia city with different land uses; also samples were collected from urban stormwater in exit point of the city and at the areas of spread on the surface and infiltration area during May, 2015. To investigate the effect of infiltration of runoff and urban stormwater on the quality of groundwater at the down streams and suburbs, we collected 18 samples from groundwater in suburb area on 11 June, 2015. The location of sampling points is shown in Figure 1. Groundwater samples collected after 10 minute pumping wells in polyethylene bottles and also 100 ml of water samples separately collected and acidified with ultra pure nitric acid for heavy metal analysis. For microbiological analysis samples collected in sterilized plastic bottles. The samples were stored in a cool box at 4 °C and transferred to laboratory for analysis the physic-chemical and microbiological parameters immediately. The temperature; pH and electrical conductivity (EC) were measured using digital conductivity meters immediately after sampling. Collected samples were analyzed in the laboratory for the total suspended solid (TSS), total dissolved solids (TDS), dissolved oxygen (DO), chemical oxygen demand (COD), biological oxygen demand (BOD), total coli form bacteria, NO₃, NO₂, PO₄, Cl, Ca, Mg, Na and heavy metals (Cu, Cd, Cr, Pb, Ni, Zn, Fe) by COD, BOD measurement instrument, titration, flame photometer, spectrophotometer and ICP-MS methods according standard methods as suggested by the American Public Health association (23). The detection limits (µg/ l) for each heavy metal were as follows, Cu (0.001), Cr (0.001), Zn (0.001), Pb (0.001), Ni (0.001), Cd (0.0001) and Fe (0.01). The analyses were generally carried out according to standard methods (24). Minimum, maximum, and average values of physical and chemical parameters of urban runoff, stormwater and groundwater samples are presented in Table 1, 2.

In this study, we collected 35 samples from rainwater and runoff from various parts of Urmia City with different land uses ; samples were also

collected from urban stormwater at the city outlet and from surface spreading and infiltration areas during May 2015. To investigate the effect of runoff and stormwater infiltration on groundwater quality downstream and in the suburbs, we collected 18 groundwater samples from the suburban area on June 11, 2015. Sampling locations are shown in Figure 1. Groundwater samples were collected after 10 minutes of pumping from wells into polyethylene bottles ; additionally, 100 mL aliquots were acidified with ultrapure nitric acid for heavy metal analysis. For microbiological analysis, samples were collected in sterilized plastic bottles. The samples were stored in cool boxes at 4 °C and immediately transferred to the laboratory for physicochemical and microbiological nalysis. Temperature, pH and electrical conductivity (EC) were measured using digital meters immediately after sampling. Collected samples were analyzed for total suspended solids (TSS), total dissolved solids (TDS), dissolved oxygen (DO), chemical oxygen demand (COD), biological oxygen demand (BOD), total coliform bacteria, NO₃, NO₂, PO₄, Cl, Ca, Mg, Na and heavy metals (Cu, Cd, Cr, Pb, Ni, Zn, Fe) using COD and BOD analyzers, titration, flame photometry, spectrophotometry and ICP-MS according to standard methods recommended by the American Public Health Association (31). The detection limits (µg/L) for each heavy metal were as follows: Cu (0.001), Cr (0.001), Zn (0.001), Pb (0.001), Ni (0.001), Cd (0.0001) and Fe (0.01). All analyses were conducted according to standard methods (32). The statistical summary (minimum, maximum, mean, and standard deviation) of physicochemical parameters for urban runoff, stormwater, and groundwater samples is presented in Tables 1 and 2 in the Results and Discussion section.

Results and Discussion

Urban runoff and stormwater quality

Urban runoff and stormwater transport different pollutants, both organic and inorganic (25, 26). Season and land use are frequently referred to as the most relevant factors affecting stormwater runoff characteristics (27, 28). Therefore, the characterization (qualitative and quantitative) of stormwater runoff should be performed at national and regional bases, with monitoring studies, for it has been proved that site specific, climatic and other local variables play an important role.

Investigation of the acidity (pH), electrical conductivity (EC) and the total dissolved solid (TDS) in the water samples taken from urban runoff shows that pH fluctuates between 7.9 and 9.1, EC 133 to 760 µs/cm² and

Table 1. Average value and range of quality parameter and heavy metals of rainwater, urban runoff and urban stormwater in study area

Parameters	Units	RW	UR			US		
			Min	Max	Mean	Min	Max	Mean
pH	-	8.3	7.9	9.1	8.5	8.2	8.9	8.7
EC	µs/cm	37	133	760	221	143	462	218
TDS	mg/l	18	68	398	116	84	278	135
TSS	mg/l	53	210	1100	596	1080	2050	1368
DO	mg/l	8.5	6.8	7.7	7.3	7.2	7.7	7.4
COD	mg/l	8	38	181	68	107	159	125
BOD	mg/l	-	15	48	31	32	41	37
TC ¹	per/ml	-	-	>1100	-	-	>1100	-
NO ₃	mg/l	3.1	0.3	68	7.6	5	123	21
NO ₂	mg/l	0.04	0.1	2.6	1.4	0.1	2.1	1.48
PO ₄	mg/l	0.3	0.4	3	1.2	<0.01	2.2	-
Fe	µg/l	70	70	2800	450	100	1800	400
Zn	µg/l	<1	<1	0.3	-	<1	-	-
Ni	µg/l	<1	<1	-	-	<1	-	-
Pb	µg/l	10	10	50	18	<1	50	-
Cr	µg/l	<1	<1	240	-	130	280	180
Cd	µg/l	<0.1	<0.1	400	-	<0.1	500	-
Cu	µg/l	<1	<1	38	-	<0.1	47	-

¹Total Coliform per 100 ml, RW(Rainwater), UR (Urban runoff), US (Urban Stormwater)

Detection limits (µg/l) for each heavy metal were as follows, Cu (1), Cr (1), Zn (1), Pb (1), Ni (1), Cd (0. 1) and Fe (10)

Table 2. Summary statistics for concentrations of physicochemical parameters and heavy metals concentration in groundwater with comparison with WHO (2011) standard

Parameters	Units	Groundwater samples			WHO standard (2011)
		Min	Max	Mean	
pH	-	7.03	7.94	7.52	6.5-9.2
EC	µs/cm	551	1600	1058	1500
TDS	mg/l	358	832	582.7	1500
¹ TH	mg/l	167	527	310	500
² CAI 1	meq/l	-1.2	0.57	-0.07	-
CAI 2	meq/l	-0.33	0.17	-0.02	-
TSS	mg/l	1	63	7.3	-
Ca	mg/l	46	146.2	82	200
Mg	mg/l	12	45.7	25.3	150
Na	mg/l	9.2	89	37	200
K	mg/l	0	31.2	4.48	-
HCO ₃	mg/l	225.7	420	293.4	350
SO ₄	mg/l	36.8	133.4	69.41	250
Cl	mg/l	24	99.4	50	250
NO ₃	mg/l	7	67.1	37.45	45
PO ₄	mg/l	0.1	2.88	1.1	10
Fe	µg/l	<10	3280	-	1000
Zn	µg/l	<1	240	-	4000
Ni	µg/l	<1	-	-	20
Pb	µg/l	<1	3	-	10
Cr	µg/l	<1	-	-	50
Cd	µg/l	<0.1	-	-	3
Cu	µg/l	<1	10	-	2000

¹Total Hardness, ²Chloro Alkaline Index

Detection limits (µg/l) for each heavy metal were as follows, Cu (1), Cr (1), Zn (1), Pb (1), Ni (1), Cd (0.1) and Fe (10)

TDS 68 to 398 mg/l (Table 1). The maximum TDS in runoff was in the south east of the city (district 1).

Geological investigations show that some marl and clay sediments which are weak and less resistant to erosion

are outcropped. At the time of torrential rains and stormwater, because of the erosive effect of water, the sediment load of the runoff formed in these areas is high.

Sediment pollutant levels in urban runoff can be measured as Total Suspended Solids (TSS). The TSS is a measure of the total mass of suspended sediment particles in water. The particulates (as a dust or as suspended solids in runoff) are enriched with several types of organic and inorganic pollutants and during wet weather they are washed off along with associated pollutants (16).

The total suspended solids (TSS) in the runoff of different areas of the city show that in all samples, the TSS amount is above standards. The maximum amount of TSS (1100 mg/l) was observed in the runoff of urban areas with transportation use (the runoff of streets and highways). In runoff of other areas of the city with residential, green space and other uses, this parameter was fluctuating between 21 and 650 mg/l. Investigation of the trend of TSS changes shows that the amount of TSS in runoff towards the exit point of the city increases, such that in urban stormwater at the exit points of the city, it reaches beyond 2050 mg/l (Table 1). Result from analysis of samples taken from runoffs show that the dissolved oxygen (DO) is between 6.8 and 7.7 mg/l (Table 1). According to the world health organization's (WHO) standards, DO in drinking water should be more than 5 and for fresh surface waters should be between 10 to 12 mg/l, so the runoff water was not in the acceptable range according to standards and not suitable to support aquatic life in terms of DO levels.

Investigation of chemical oxygen demand (COD) in the runoff of different areas of the city show that the maximum COD which was observed in the runoff of urban areas with transportation use (runoff of streets and highways), was 181 mg/l that is much higher than the surface water standard (40 mg/l). In the runoff of other areas with residential, green space and other uses, the

COD was fluctuating between 38 and 84 mg/l. The amount of COD in urban stormwater runoff at the exit points of the city was 107 to 159 mg/l (Table 1). Biochemical oxygen demand (BOD) is a measure of the amount of oxygen that bacteria will consume while decomposing organic matter under aerobic conditions. The BOD was also higher in the early runoff samples from road and parking lots than that of other land uses, which is consistent with the distribution of COD. Comparison of the BOD and COD of samples with the surface water standards indicate that in most of samples taken from the runoff of streets, roads and also the runoff of city exit points, the amount of these parameters is higher than the standard level.

Nutrients (nitrogen and phosphorus) are essential elements in all aquatic ecosystems and are found in organic and inorganic forms. However, when these nutrients are found at excessive levels, they can have negative impact on aquatic system by promoting the growth of plants and algae. In urban runoff, leakage of sewages is main sources of nitrate. Residential areas and turf areas are major contributors of the nutrients in urban runoff (29, 30). The amount of nitrate in the runoff of different areas of the city is 0.3-68 mg/l. Due to the overflow of sewerage into the streets in some points of urban sewerage network and its flow towards the city exit- point, the amount of nitrate in stormwater runoff is increased. The amount of phosphate in the runoff of different areas of the city is 0.4-3 mg/l (Table 1) and the runoff samples from road and parking lots contained much high phosphate. Figure 4 (a, b) shows the average concentration of total dissolved solid (TDS), chemical oxygen demand (COD), total suspended solids (TSS), nitrate (NO_3) and phosphate (PO_4) in the runoff from different urban land uses.

Total coliform counts in water bodies are an important parameter for checking possible sewage

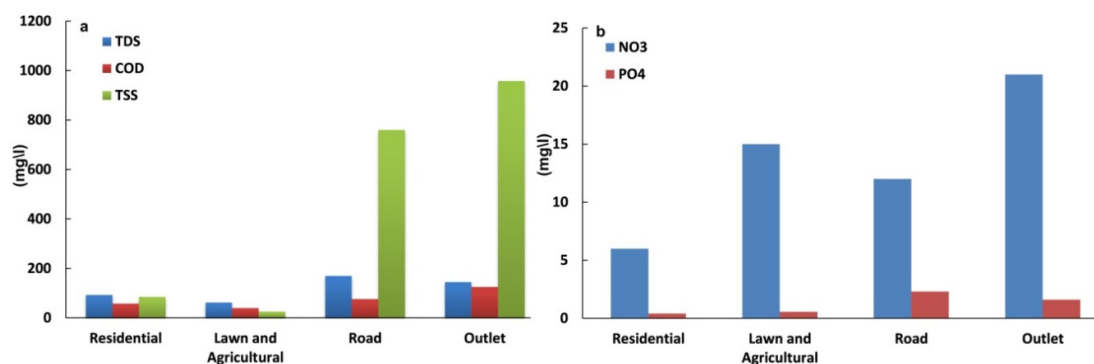


Figure 4. Average concentration of (TDS), (COD), (TSS) (a) and (NO_3) (PO_4) (b) in runoff from different urban land use

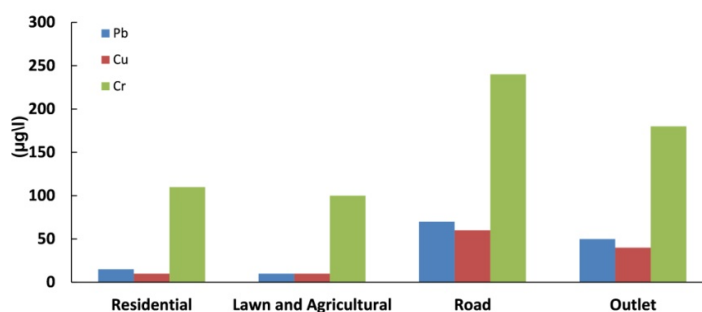


Figure 5. Average concentration of heavy metals (Pb, Cu, Cr) in runoff from different urban land use

contamination. Total coliform include species that may inhabit the intestines of warm-blooded animals or occur naturally in soil, vegetation, and water. They are usually found in water polluted with fecal matter and are often associated with disease outbreaks. In runoffs coming from different areas of the city, the contamination amount was different and the total coliform count was between 6 to more than 1100 (per 100 ml). Due to the type of land use and also surface water collection and urban sewerage systems, in the runoffs of urban area (district 1, 5) the amount of contamination was less and in district 2 and 4 it was more. Due to the overflow of sewerage into the streets in some points of urban sewerage network and its flow towards the city exit point, at the city exit point the amount of contamination in stormwater runoffs is increased, such that in the output runoff of urban areas (district 2), the total coliform count is more than 1100 per 100 ml.

Heavy metals are the most common substances in the urban runoffs. They are of particular interest in stormwater runoff due to their toxicity and the fact that they are not easily chemically transformed and remain in the system for long time threatens in the environment. The most common heavy metals of concern are chromium (Cr), iron (Fe), nickel (Ni), zinc (Zn), copper (Cu), lead (Pb), and cadmium (Cd). Excess levels of these heavy metals can damage human health and ecosystems (31, 32). High concentrations of heavy metals such as lead, zinc, copper, and cadmium can be generated in surface runoff, particularly after a long dry period. The main sources of these metals are the combustion of fossil fuels, tire wear and metal particles abraded from vehicles, and fertilizers (33). The sources of heavy metals in urban runoff vary from location to location and land use as the main contributing factor to this difference.

Results of the investigating the quality of heavy metals show that the most available metal in Urmia runoff is Iron with concentration of 70 to 2800 µg/l (Table

1). The pH of urban runoff has been 7.9 to 9.1 with the mean 8.5. In low temperature and high amounts of pH, the situation for absorption of heavy metals to absorbents is suitable. The investigation of the quality of runoff at the early time of the raining shows that the concentration of contaminants is high. Investigating the Cu amount in runoff of different urban areas shows that the amount of copper in all samples has been less than 40 µg/l. The result show that Ni and Zn were below the detection limit (<1 µg/l) and Pb and Cr concentrations were, 10-50 mg/l and 1-240 µg/l respectively (Table 1). In addition, the amount of Zn (<1 µg/l) show that the runoffs are not contaminated with this element. Investigating the amount of Pb in the studied urban runoff shows that the highest concentration of Pb appeared in the road and parking lot runoffs. Figure 5 shows the average concentration of heavy metals (Pb, Cu and Cr) in runoff from different urban land uses.

Urban runoff stormwater transport various pollutants, both organic and inorganic (33, 34). Season and land use are frequently cited as the most relevant factors affecting stormwater runoff characteristics (35,36).

Therefore, qualitative and quantitative characterization of stormwater runoff should be performed at national and regional levels through monitoring studies, as site-specific, climatic and other local variables have been shown to play important roles. Analysis of pH, EC, and TDS in runoff samples showed values ranging from 7.9 to 9.1 for pH, 133 to 760 µS/cm for EC, and 68 to 398 mg/L for TDS (Table 1).

The maximum TDS in runoff was observed in the southeast of the city (District 1). Geological investigations show that marl and clay sediments, which are weak and susceptible to erosion, outcrop in this area. During torrential rains and storm events, erosive water increases the sediment load of runoff from these areas. Sediment pollutant levels in urban runoff can be measured as Total Suspended Solids (TSS). TSS is a

measure of the total mass of suspended particulate matter in water. Particulates (as dust or suspended solids in runoff) are enriched with several types of organic and inorganic pollutants and are washed off with associated pollutants during wet weather (21).

TSS in runoff from different parts of the city exceeded water quality standards in all samples. The maximum TSS concentration (1,100 mg/L) was observed in runoff from transportation areas (streets and highways). In runoff from other areas with residential, green space and other uses, TSS ranged between 21 and 650 mg/L. TSS concentrations increased towards the city outlet, reaching values beyond 2,050 mg/L in stormwater at the outlet (Table 1). Dissolved oxygen (DO) in runoff samples ranged from 6.8 to 7.7 mg/L (Table 1). According to WHO (2011) guidelines, DO in drinking water should exceed 5 mg/L, and for fresh surface waters it should be between 10 and 12 mg/L; therefore, runoff water did not meet these standards and is unsuitable for supporting aquatic life in terms of DO levels. Chemical oxygen demand (COD) in runoff from transportation areas (streets and highways) was highest at 181 mg/L, significantly higher than the surface water standard (40 mg/L). In runoff from residential, green space and other areas, COD ranged between 38 and 84 mg/L.

COD in stormwater at the city outlet ranged from 107 to 159 mg/L (Table 1). BOD was also higher in road and parking lot runoff than in other land uses, consistent with COD. Comparison of BOD and COD with surface water standards indicates that most runoff samples from streets, roads and city outlet points exceeded permissible levels.

Nutrients (nitrogen and phosphorus) are essential in aquatic ecosystems in organic and inorganic forms. However, excessive nutrient levels can negatively impact aquatic systems by promoting algal growth.

Sewage leakage is a primary source of nitrate in urban runoff; residential and turf areas are also major contributors of nutrients in urban runoff (37,38).

Nitrate concentrations in runoff from different parts of the city ranged from 0.3 to 68 mg/L. Due to sewer overflow at some points in the network and flow towards the city outlet, nitrate concentrations increased in stormwater runoff. Phosphate concentrations in runoff from different parts of the city ranged from 0.4 to 3 mg/L (Table 1), with road and parking lot runoff showing the highest phosphate levels. Figure 4 (a, b) shows mean TDS, COD, TSS, NO₃ and PO₄ concentrations in runoff from different urban land uses.

Total coliform counts are an important indicator of sewage contamination. Total coliforms include species that may inhabit the intestines of warm-blooded animals or occur naturally in soil, vegetation, and water. They are usually found in fecal-contaminated water and are often associated with disease outbreaks. Coliform counts in runoff from different parts of the city ranged from 6 to >1,100 per 100 mL. Counts were lower in Districts 1 and 5 and higher in Districts 2 and 4, due to land use and drainage system differences. At the city outlet, coliform counts increased due to sewer overflow, exceeding 1,100 per 100 mL in District 2. Heavy metals are common constituents of urban runoff and are of particular concern due to their toxicity and persistence in the environment. The most common heavy metals of concern are Cr, Fe, Ni, Zn, Cu, Pb, and Cd; excessive levels of these metals can damage human health and ecosystems (26,39). High concentrations of Pb, Zn, Cu, and Cd in surface runoff are often observed after prolonged dry periods, with sources including fossil fuel combustion, tire wear, vehicular abrasion particles, and fertilizers (18). Heavy metal sources vary by location and land use. The most abundant metal in Urmia runoff was Fe, with concentrations ranging from 70 to 2,800 µg/L (Table 1). Runoff pH ranged from 7.9 to 9.1 (mean: 8.5).

Low temperature and high pH favor heavy metal adsorption. First-flush runoff samples had higher contaminant concentrations. Cu concentrations were <40 µg/L in all samples. Ni and Zn were below the detection limit (<1 µg/L), while Pb and Cr concentrations ranged from 10 to 50 µg/L and 1 to 240 µg/L, respectively (Table 1). The Zn concentrations (<1 µg/L) indicate that runoff is not contaminated with this element. The highest Pb concentrations were in road and parking lot runoff. Figure 5 shows mean Pb, Cu and Cr concentrations in runoff from different urban land uses.

In this study, the Heavy Metal Evaluation Index (HEI) proposed by Edet and Offiong (2002) was used to assess heavy metal contamination. HEI provides an overall water quality rating based on heavy metal content (40). HEI is calculated using Equation (1):

$$HEI = \sum_{i=1}^n Hc/Hmac \quad [1]$$

where Hc is the measured concentration of the i-th parameter, and Hmac is the maximum admissible concentration of the i-th parameter (40).

To calculate HEI for urban runoff and stormwater, concentrations of five heavy metals (Pb, Cr, Cu, Zn, and Ni) were considered. Maximum HEI values for urban runoff and stormwater were 7.7 and

10.6, respectively. HEI values in some samples exceeded the critical threshold, indicating significant heavy metal contamination.

Hydrochemistry and groundwater quality

Results from the chemical analyses were used to identify the geochemical processes and mechanisms in the groundwater aquifer system. In urban area, hydrochemical process and anthropogenic activities such as, industrial and urban runoff can be affected on water quality. Major ion analyses for groundwater samples collected from suburb area shows that pH, EC and TDS values are ranging from 7.03 to 7.94, 551 - 1600 with the mean of 1058 $\mu\text{S}/\text{cm}$ and 358 - 832 with the mean of 582 mg/l respectively. The variation in EC is mainly attributed to geochemical processes prevailing in this region and human activity. These values show that the groundwater in this area is generally neutral to slightly alkaline in nature. According to WHO (2011) standard pH, EC and TDS values of all the samples (except sample No. W17) are within the safe limit (Figure 6a). In this area, the Na and K concentrations in groundwater range from 9 to 89 and 0 to 31.2 mg/l, respectively. The concentrations of Ca and Mg range from 46 to 146 and 12 to 46 mg/l respectively, which Ca is derived from calcium rich minerals. According to the WHO standard, all samples fall within the desirable limits for Mg^{2+} (150 mg/l), Ca^{2+} (200 mg/l) and Na^+ (200 mg/l) (Figure 6b). Values of the total hardness (TH) are varied from 167 to 527 mg/l. All the samples have TH values above the most desirable limit and only one groundwater sample (sample W9) have TH more than permissible limit suggested by WHO (2011) (Table 2). The concentrations of HCO_3^- , SO_4 and Cl are ranges from 225-420, 37-133 and 24-99 mg/l, respectively. The 22 % of groundwater samples

have HCO_3^- more than permissible limit suggested by WHO (2011) (Table 1) (Figure 6c).

The dissolution of calcite and dolomite minerals is the main source of HCO_3^- (35). In this area, the concentrations of nitrate in groundwater samples range 7 to 67.3 mg/l with the mean of 37.5 mg/l. About 38.8 % of groundwater samples have NO_3^- concentration above the tolerance limit of 45 mg/l (Figure 6d) and these samples are located into the infiltration area. The abundance of the major ions is as follows: $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$ and $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$. Based on the analytical results, the groundwater in the area is generally slightly alkaline, hard to very hard and fresh.

The plot of chemical data on Piper diagram (1944)(36) (Figure 7) shows that the major cation is Ca^{2+} and the anion is HCO_3^- . In the study area, the dominant hydrochemical facieses and major groundwater type is Ca- HCO_3 (Figure 7). In groundwater samples alkaline earths (Ca^{2+} and Mg^{2+}) significantly exceed the alkali (Na^+ and K^+) and the weak acids (HCO_3^- and CO_3^{2-}) exceed strong acids (Cl^- and SO_4^{2-}).

Ion exchange is important natural hydrochemical process that can have significant impacts on the evolution of groundwater chemistry(37). Ion exchange can be identified by two chloro-alkaline indices (CAI) (38).

Chemical analysis results were used to identify geochemical processes and mechanisms in the aquifer system.

In urban areas, hydrochemical processes and anthropogenic activities (e.g., industrial and urban runoff) can affect water quality. Major ion analysis of groundwater samples from the suburban area showed pH, EC and TDS ranges of 7.03–7.94, 551–1,600 $\mu\text{S}/\text{cm}$ (mean: 1,058 $\mu\text{S}/\text{cm}$), and 358–832 mg/L (mean: 582 mg/L), respectively. EC variation is mainly attributed to regional geochemical processes

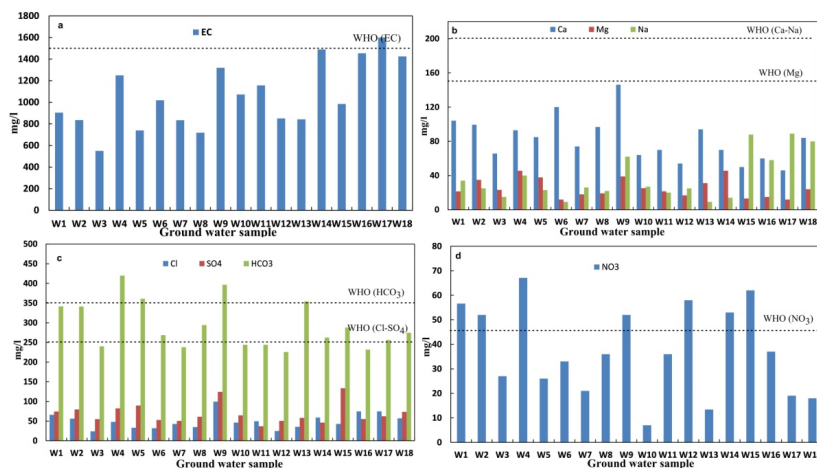


Figure 6. Spatial distribution of EC(a), Ca, Mg, Na(b), Cl, SO_4 , HCO_3 (c) and NO_3 (d) in the groundwater samples

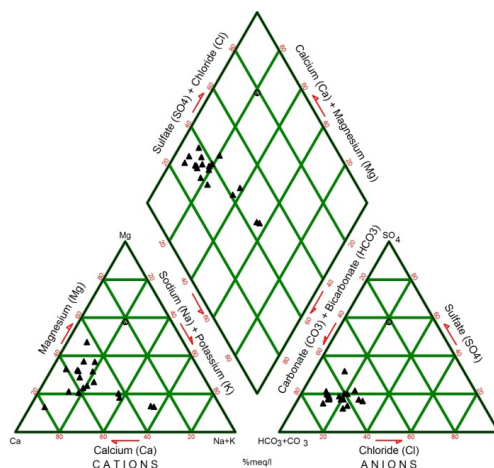


Figure 7. Chemical facies of groundwater of study area in Piper diagram

and anthropogenic activity. These values indicate that groundwater is generally neutral to slightly alkaline. According to WHO (2011) guidelines, pH, EC and TDS values of all samples except W17 are within safe limits (Figure 6a).

In this area, Na^+ and K^+ concentrations range from 9 to 89, and 0 to 31.2 mg/L, respectively. Ca^{2+} and Mg^{2+} concentrations range from 46 to 146, and 12 to 46 mg/L, respectively, with Ca^{2+} derived from calcium-rich minerals. According to WHO guidelines, all samples fall within desirable limits for Mg^{2+} (150 mg/L), Ca^{2+} (200 mg/L) and Na^+ (200 mg/L) (Figure 6b). Total hardness (TH) ranged from 167 to 527 mg/L. All samples had TH above the most desirable limit, and one sample (W9) exceeded the WHO permissible limit (Table 2). HCO_3^- , SO_4^{2-} and Cl^- concentrations ranged from 225–420, 37–133, and 24–99 mg/L, respectively; 22% of samples had HCO_3^- above the WHO permissible limit (Table 2, Figure 6c). Calcite and dolomite dissolution are the primary sources of HCO_3^- (41).

Nitrate concentrations in groundwater ranged from 7 to 67.3 mg/L (mean: 37.5 mg/L). About 38.8% of groundwater samples had NO_3^- concentrations exceeding the WHO guideline of 45 mg/L (Figure 6d); these samples were from infiltration zones. Major ion abundance followed the order $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$ and $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$. Groundwater is generally slightly alkaline, hard to very hard, and fresh.

A Piper diagram (1944) (42) (Figure 7) shows Ca^{2+} and HCO_3^- as the dominant ions, with Ca- HCO_3 as the main groundwater type (Figure 7). Alkaline earths (Ca^{2+}

+ Mg^{2+}) significantly exceed alkalis ($\text{Na}^+ + \text{K}^+$), and weak acids ($\text{HCO}_3^- + \text{CO}_3^{2-}$) exceed strong acids ($\text{Cl}^- + \text{SO}_4^{2-}$). Ion exchange is an important natural hydrochemical process that can significantly influence groundwater chemistry (43). Ion exchange can be assessed by two chloro-alkaline indices (CAI) (44):

$$\text{CAI-1 (meq/L)} = [\text{Cl}^- - (\text{Na}^+ + \text{K}^+)] / \text{Cl}^- \quad [2]$$

$$\text{CAI-2 (meq/L)} = [\text{Cl}^- - (\text{Na}^+ + \text{K}^+)] / (\text{SO}_4^{2-} + \text{HCO}_3^- + \text{CO}_3^{2-} + \text{NO}_3^-) \quad [3]$$

Positive CAI values indicate reverse ion exchange ($\text{Na}^+ + \text{K}^+$ exchanged for $\text{Ca}^{2+} + \text{Mg}^{2+}$ in the aquifer), while negative values indicate cation exchange. CAI values in groundwater from the suburban area ranged from -1.2 to 0.58 (Table 2). About 56% of groundwater samples showed negative CAI values, indicating cation-anion exchange, confirming that host rocks are primary sources of dissolved ions, with ion exchange contributing to higher Na^+ concentrations. Positive values in the remaining samples indicate base-exchange reactions, where Na^+ in groundwater exchanges with Ca^{2+} and Mg^{2+} in aquifer materials. Na-Cl water type in some samples reflects both ion exchange and anthropogenic activity. Groundwater chemistry and hydrochemical processes are controlled by both natural geochemical processes and anthropogenic activities. The statistical summary of groundwater parameters is presented in Table 2.

Effects of the stormwater runoffs on groundwater quality

Urban development has increased water demand and contamination risk for groundwater resources in arid and semi-arid regions (26).

Urban stormwater runoff is a major contributor to non-point source pollution of groundwater. The impact of urban runoff pollutants on groundwater quality in infiltration basins depends on existing water quality and the rate of pollutant introduction. Infiltration of stormwater provides an opportunity for the aquifer to attenuate contaminants (23). Soil composition and aquifer characteristics are critical for sorption capacity and contaminant removal. High-permeability sand and gravel provide ideal infiltration media, while silt-clay soils with low permeability offer higher sorption capacity and pollutant removal.

Borehole data from the suburban infiltration zone indicate that the saturated zone is composed of gravel-sand sediments with silt-clay interbeds. The unsaturated zone is composed of silt (45%), clay (37%), sand (15%) and gravel (3%). The soil plasticity index is 2.9, and the mean hydraulic conductivity of the unsaturated zone is 1.5×10^{-4} cm/s (30). Groundwater depth mapping (Figure 3) in suburban Urmia showed depths ranging from 1 to 9 m. In infiltration areas (suburb of District 2), the average groundwater depth is 5 m, with some areas as shallow as 1 m. Surface water and urban runoff from Districts 1 and 4 drain to the Shaharchay River and ultimately to Urmia Lake; therefore,

stormwater from these areas does not infiltrate or affect groundwater quality. Most runoff and stormwater spread occurs at the outlet of District 2. Due to the shallow groundwater table there, infiltration has altered water quality.

Nitrate (NO_3^-) is an indicator of water pollution, with sources including organic matter decay, sewage waste, septic tank leakage, and fertilizers (45).

Nitrate concentrations in groundwater from infiltration areas (up to 67.3 mg/L) were higher than in other parts of the Urmia aquifer not affected by urban runoff. A comparison of nitrate concentration and groundwater depth shows that shallow groundwater areas have higher nitrate concentrations (Figure 8). In some runoff-affected areas, microbial contamination (coliforms) was observed but limited in extent. Phosphate concentrations in groundwater were generally low (0.1–2.88 mg/L, mean: 1.1 mg/L). Most phosphorus is likely removed by soil adsorption in infiltration areas, although plant uptake may also be an important sink.

The water quality index can be used for evaluating influence of natural and anthropogenic activities on groundwater chemistry. For assessment the variation in groundwater quality and potential effects of urban runoff and storm water infiltration on the groundwater quality, we used groundwater quality index (GWQI). To calculation GWQI was used pH, TDS, TH, Mg^{2+} , Ca^{2+} , Na^+ , HCO_3^- , SO_4^{2-} , Cl^- , PO_4^{3-} and NO_3^- . The GWQI was calculated according to the international formula of WQI

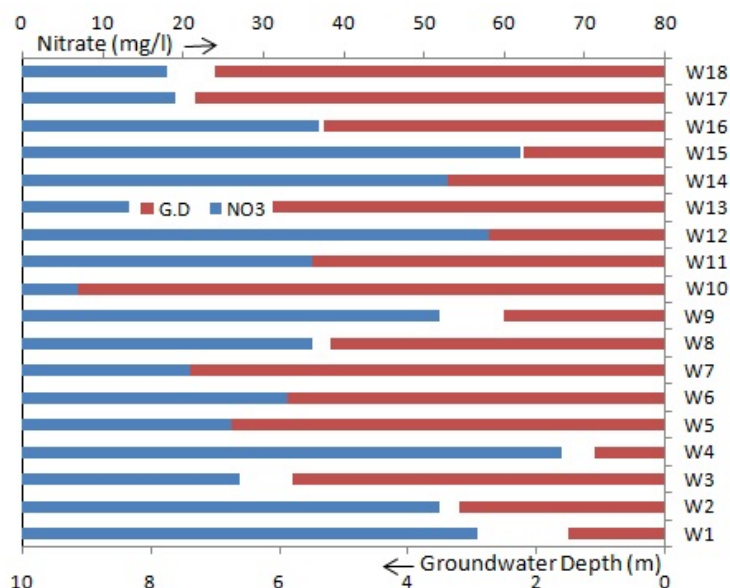


Figure 8. Depth and Nitrate of groundwater samples of study area

computed in four steps, using a weighted arithmetic index method (46):

$$W_i = \frac{w_i}{\sum_{i=1}^n w_i} \quad [4]$$

where, w_i = weight of each parameter (Table 3) and n = number of parameter

$$SI = (w_i \times q_i) \quad [5]$$

where, q_i = quality rating computed according to the formula:

$$q_i = \frac{C_i}{S_i} \times 100 \quad [6]$$

where, C_i = Concentration of each chemical parameter, for each water sample and S_i = WHO standard

$$GWQI = \sum_{i=1}^n SI_i \quad [7]$$

In this formula, SI_i shows the sub index for each parameter. The relative weight (w_i) was assigned for water quality parameters based on their relative

importance on water quality for drinking purposes (Table 3). GWQI values were classified into five categories (Figure 9) (46).

According to GWQI, 89% of groundwater samples from infiltration areas were of good quality, while 11% were poor (Figure 9). Poor-quality samples were affected by runoff and stormwater infiltration.

Heavy metal concentrations in groundwater from infiltration areas (Table 2) were mostly below WHO (2011) drinking water standards, indicating effective metal adsorption by sediments. Only a few samples had Fe concentrations exceeding standards, likely due to runoff infiltration and reduced DO concentrations, which influence iron solubility.

Conclusion

The investigation of organic, inorganic and heavy metal concentrations showed that TSS (1,100 mg/L), COD (181 mg/L), BOD (48 mg/L), PO_4 , Fe (2,800 μ g/L), Pb (50 μ g/L) and Cr (240 μ g/L) were significantly higher

Table 3. Groundwater quality index computation input

Groundwater quality parameter	WHO (2011)	Weight(w_i)	Relative weight(W_i)
Total dissolved solid (TDS)	500	4	0.125
Total hardness (TH)	300	3	0.093
pH	6.5	3	0.093
Phosphates	10	1	0.031
Nitrate	45	5	0.156
Magnesium	50	2	0.062
Bicarbonate	350	3	0.093
Calcium	75	2	0.062
Sodium	200	3	0.093
Chlorides	250	4	0.125
Sulfate	250	2	0.062
		$\sum Gw_i=32$	$\sum GW_i=1.000$

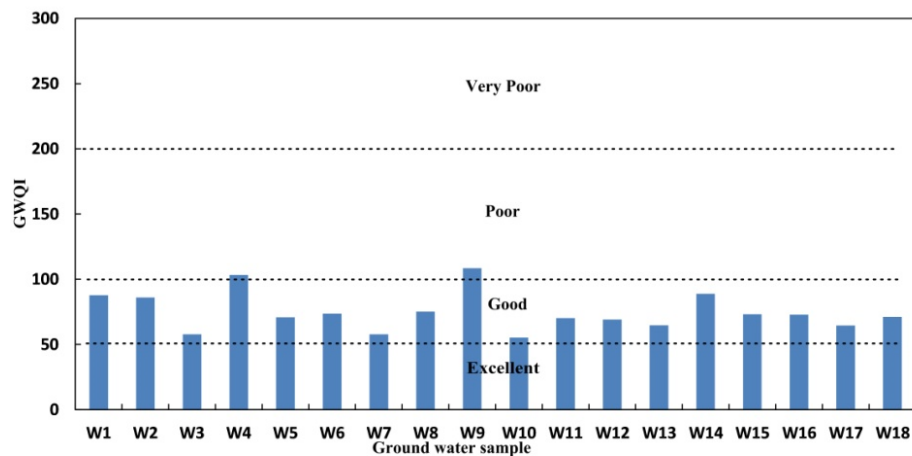


Figure 9. Groundwater quality index (GWQI)

in parking lot and road runoff than in other land uses, indicating that land use type is critical in determining stormwater quality. High TDS in runoff from some urban areas is due to marl and clay sediments. Sewer overflow at several points in the network and flow towards the city outlet increased TSS (2,050 mg/L), NO₃ (123 mg/L) and total coliform counts in stormwater at the outlet, with the highest contamination observed in District 2. Hydrochemical analysis revealed that groundwater is hard to very hard, fresh, and of Ca-HCO₃ type, with chemistry controlled by both natural geochemical processes and anthropogenic activities. Due to the shallow groundwater table (1 m) in some suburban areas, groundwater quality is affected by infiltrated runoff, resulting in elevated nitrate concentrations and localized microbial contamination. GWQI showed that 89% of groundwater samples were of good quality and 11% were poor, with poor-quality samples affected by runoff infiltration. To mitigate the ecological effects of urban stormwater and protect receiving waters, effective quality control of urban runoff in the study area is essential.

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