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Grey water footprint assessment of groundwater resources in southeastern Turkey: effect of recharge

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ABSTRACT

This paper aimed to determine the grey water footprint (GWF) of groundwater resources. The effect of groundwater recharge on grey water footprint was investigated in Southeastern Turkey. In this paper, GWF has been monitored in October and March in terms of nitrate and arsenic concentrations for ten observation wells in the Harran Plain. In this study, a new approach was developed based on the GWF to determine the nitrate and arsenic pollution of groundwater. GWF of coagulation-flocculation and biochar adsorption processes were calculated and benchmarked with each other. In the second stage of the study, the effect of groundwater recharge using reclaimed municipal wastewater on GWF was investigated applying Monte Carlo simulation. The results revealed that nitrate led to higher GWF. According to the results, biochar application could reduce the GWF. Total reduction of GWF would be approximately 64.3% if groundwater recharge using reclaimed wastewater is applied.

Key words: biochar, groundwater, grey water footprint, Harran plain, Monte Carlo simulation, recharge

HIGHLIGHT

- The novelty of this study is that a new estimation model has been adapted for grey water footprint of groundwater resources. The other originality of this work is biochar application for groundwater treatment. Biochar application was carried out to treat groundwater in order to observe the GWF. Urfa Isot pepper, which is a traditional crop of Turkey, was used to generate biochar with slow pyrolysis.

1. INTRODUCTION

The grey water footprint (GWF) is a term to determine the minimum volume of freshwater required for diluting pollutant loading based on the existing water quality standards (Morera *et al.* 2016). Water scarcity is described as the deficiency of adequate available freshwater resources to fulfil water requirements in a region or country. Groundwater resources have a crucial role in water scarcity. Water resources management has a vital importance for countries that have water scarcity problems such as Turkey (Yapıcıoğlu 2019a; Yapıcıoğlu 2020). It is important to protect the water resources from pollution. GWF is an indicator to monitor the effect of pollutants on water supplies. From this perspective, GWF of groundwater resources that nitrate and arsenic located in the Harran Plain was investigated in this study.

The Harran Plain has the largest groundwater resources of the Middle East (Bilgili *et al.* 2018; Yapıcıoğlu *et al.* 2020). In this study, arsenic and nitrate concentrations of ten observation wells have been monitored in October (post irrigation) and March (before irrigation). Nitrate (NO_3^-) has been comprised in the result of nitrification process. NO_3^- in the groundwater is derived from one of the urban, industrial, and agricultural activities. Majorly, it has been estimated that NO_3^- pollution could be originated from agricultural fields at groundwater resources. It is estimated that nitrate leaches from the agricultural fields to the groundwater resources due to using fertilizers that contain nitrogen (Yeşilnacar & Güllüoğlu 2008; Yeşilnacar & Yenigün 2011; Bayhan *et al.* 2020). Another important groundwater pollutant is arsenic. As is a heavy metal that forms in different oxidation states and various forms, which are As(V), As (III), As (0) and As (-III) (Oyem *et al.* 2015; Parviainen *et al.* 2015; Niazi *et al.* 2018; Yapıcıoğlu *et al.* 2020). Arsenic cannot be easily degraded and can only be converted into different forms or transformed into insoluble compounds. Inorganic arsenic generally occurs in two major oxidation states,

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arsenide and arsenate, which are toxic to flora and fauna. Arsenic pollution in groundwater is a worldwide problem and has become an essential environmental issue. Arsenic formation at low concentrations in potable water leads to severe health problems. Also, nitrate is a low toxic compound, but when it is reduced to nitrite, it becomes toxic to human health (Deng *et al.* 2020). Both nitrate and arsenic have led to significant groundwater contamination. The Water Footprint Network (WFN) has developed an estimation model named the grey water footprint (GWF) to determine the water pollution levels of each contaminant parameter (WFN 2014). NO_3^- and As are the main contaminant parameters at the Harran Plain according to the previous analyses (Yeşilnacar & Güllüoğlu 2008; Yeşilnacar & Yenigün 2011; Bayhan *et al.* 2020). The reason for selecting NO_3^- and As is that these pollutants lead to major contamination at the Harran Plain.

Coagulation-flocculation processes and biochar application have been carried out to remove arsenic and nitrate. Then, grey water footprint corresponded to coagulation-flocculation and biochar adsorption process were figured out and benchmarked. In the second stage of the study, the effect of groundwater recharge using reclaimed municipal wastewater on GWF was investigated applying Monte Carlo simulation. Groundwater recharge is one of the reclamation methods in order to feed the groundwater resources. It could be applied in order to increase the water level of the aquifers. Natural replenishment of groundwater forms very slowly (Asano & Cotruvo 2004). This technique can also reduce the water contaminant concentrations. It could dilute the water composition. So, groundwater recharge could be applied to protect the groundwater supplies.

In the literature, previous studies related to this topic are very limited. In a study by Serio *et al.* (2018), they aimed to evaluate the relationship between groundwater nitrate contamination and agricultural activities using a similar GWF approach. Miglietta *et al.* (2017) investigated the grey water footprint of groundwater in Italy for each chemical parameter, which indicated a widespread contamination by mercury, vanadium and ammonium. Aldaya *et al.* (2020) performed a study on the grey water footprint as an indicator for diffuse nitrogen pollution for groundwater and surface water resources. The main aim of this study is to determine the GWF of groundwater resources and to investigate the effect of groundwater recharge on grey water footprint in Southeastern Turkey. The other objective of this study is the confirmation that biochar application could apply for the groundwater treatment. The novelty of this study is that a new estimation model has been adapted for grey water footprint of groundwater resources. Many researchers focused on the grey water footprint of surface water resources. This study concentrated on groundwater resources using a new adapted estimation model. The other originality of this work is that biochar adsorption was applied for groundwater treatment. Biochar application was carried out to treat groundwater in order to observe the GWF. *Capsicum annuum* (Urfa Isot pepper), which is a traditional crop in Turkey, was used to generate biochar using slow pyrolysis. And then, a biochar adsorption column was designed and operated to treat groundwater samples from ten observation wells. On the other hand, the effect of groundwater recharge on the GWF was determined using Monte-Carlo simulation. The study is unique in that it highlights that groundwater recharge could be an alternative to minimize the GWF.

2. MATERIALS AND METHODS

2.1. Description of the study area

The Harran Plain has the biggest irrigation area of southeastern Turkey and the biggest groundwater resources of the Middle East (Baba *et al.* 2019). Harran Plain is in the southeast of Şanlıurfa province. The main products are cotton and corn on the Harran Plain. Drip irrigation is carried out in this region. The drainage, lowland and irrigation areas are 3.700 km², 1.500 km² and 141.500 hectares, respectively in the Harran Plain (Yeşilnacar & Güllüoğlu 2008; Derin *et al.* 2020; Yapıcıoğlu *et al.* 2020).

Çamlıdere (1), Yardımcı (2), Kısas (3), Uğurlu (4), Ozanlar (5), Kızıldoruç (6), Olgunlar (7), Yaygılı (8), Bolatlar (9) and Uğraklı (10) are the observation wells for arsenic and nitrate concentrations in the Harran Plain. Figure 1 demonstrates the location map of the study area. The major reasons for selecting these observation wells are that they are vulnerable, and they are located in the superficial aquifer. Also, they are close to agricultural fields. In this study, arsenic and nitrate analyses have been performed according to the Standard Methods (APHA 1995) using the ICP-MS technique in October and March. October and March were selected as the sampling periods due to the irrigation process in the Harran Plain. The observation wells were monitored in October (post irrigation) and in March (before irrigation). From mid-March to October, the agricultural activities are active in this region. Especially, cotton and corn sowing processes are applied in mid-March. March is the month before irrigation and October is the month of post irrigation. Due to this, water sampling was applied in these

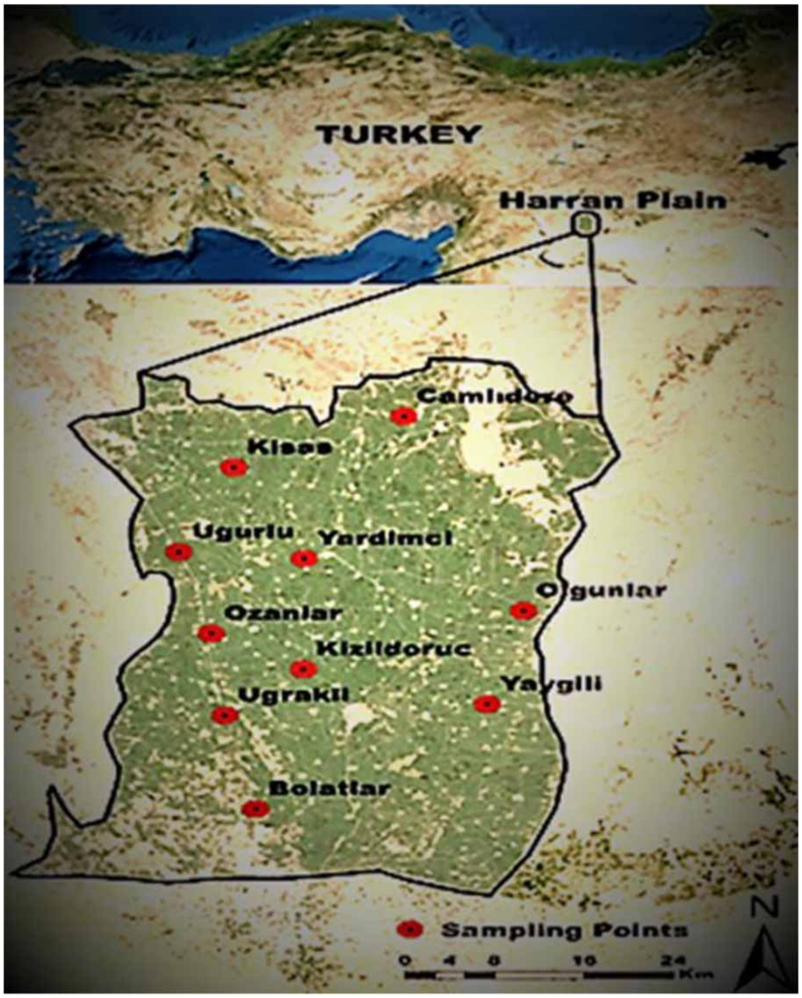

Figure 1 | The location map of the study area.

two months. Water samplings were ensured in earlier March before irrigation. Table 1 shows the analyses results before treatment processes.

Groundwater treatment processes, which were coagulation and flocculation, and a biochar adsorption process were carried out to define the water pollution capacity of arsenic and nitrate. Figure 2 shows the treatment diagrams. The coagulation-flocculation process was applied after the aeration process. This method is a well-known and classical groundwater treatment method. In the coagulation and flocculation process, the optimum concentrations of coagulant and flocculant, which contain polyaluminum chloride (PAC) and cationic polymer (PE) were 20 mg/L and 25 mg/L, respectively. A different treatment technology, which was biochar application, was carried out instead of the coagulation-flocculation process to obtain high treatment and pollutant removal efficiencies. A biochar adsorption column was designed and operated in order to observe the GWF values.

2.2. Biochar production and design of adsorption column

Biochar has gained crucial attention due to its significant role in many environmental issues and challenges, in recent years (Qambrani *et al.* 2017; Yapıcıoğlu *et al.* 2020). It is cheaper than the other treatment methods, and biochar could adsorb arsenic and nitrate immediately. Biochar was produced from *Capsicum annuum* (Urfa Isot peppers) using the slow pyrolysis method.

Capsicum annuum was pulverized. The operational conditions of slow pyrolysis were 5 °C/min of heating rate, 500 °C of temperature, 30 minutes of vapor residence time and 2 hours of heating time. Biochar prepared at various pyrolysis conditions was examined to benchmark adsorption uptake capacity of As and NO_3^- from aqueous solution. Biochar (0.10 g)

Table 1 | Arsenic and nitrate concentrations in March and October before treatment

Well	As concentration in March (ppb)	As concentration in October (ppb)	NO_3^- concentration in March (ppm)	NO_3^- concentration in October (ppm)
Observation Well-1	2.50	2.40	22	7.25
Observation Well-2	1.06	0.85	29	11.95
Observation Well-3	0.60	0.63	51	22.37
Observation Well-4	0.90	0.82	37	27.53
Observation Well-5	0.49	0.47	180	9.32
Observation Well-6	1.30	1.06	45	34.47
Observation Well-7	1.32	1.24	47	5.50
Observation Well-8	4.12	1.20	87	7.99
Observation Well-9	1.07	0.82	526	31.75
Observation Well-10	0.79	0.59	113	34.33

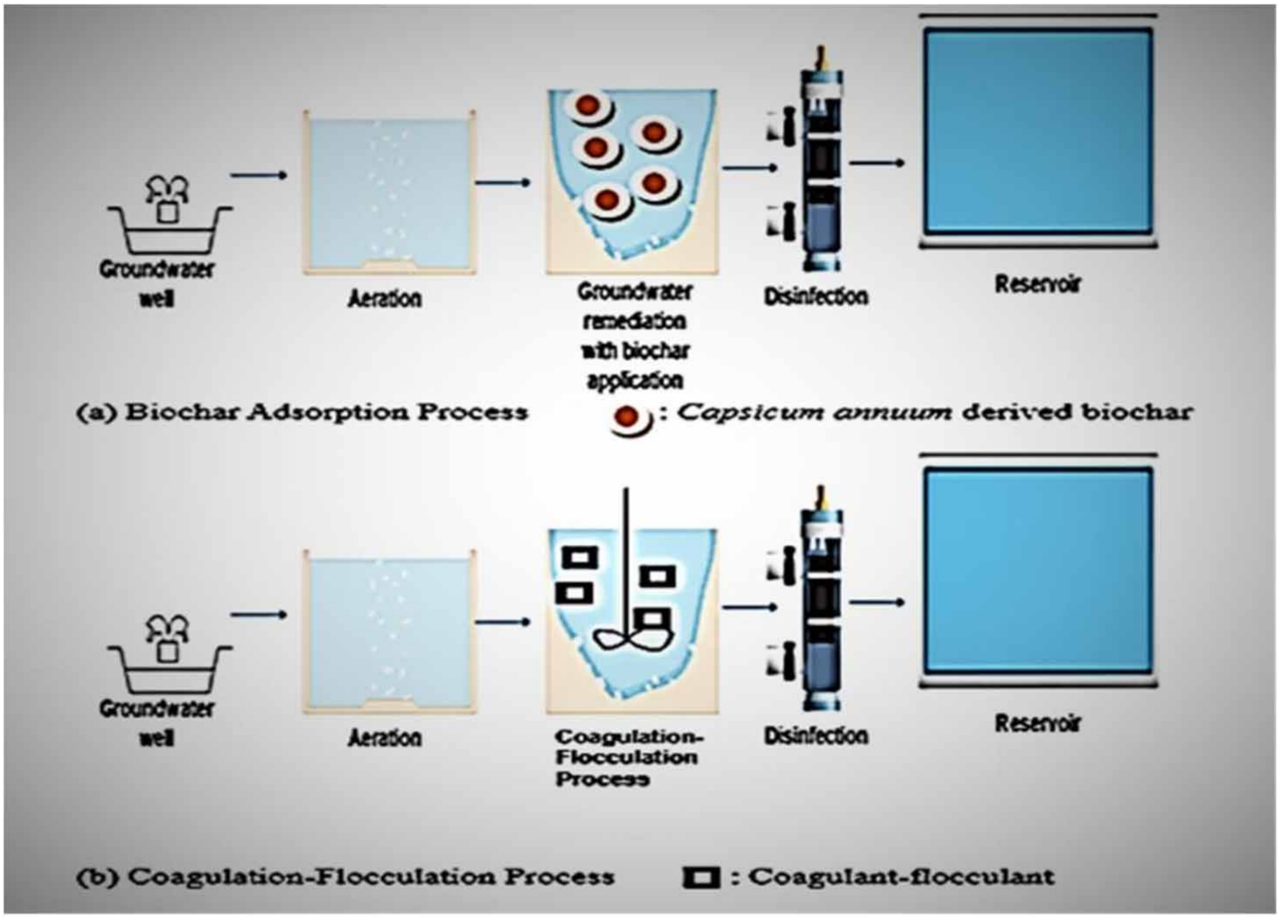

Figure 2 | Groundwater treatment flow schemes.

was mixed with 10 mL of As and NO_3^- solutions in 50 mL glass container. The initial solution pH was adjusted to 6.5 by adding 0.10 M NaOH or HCl. The mixture was shaken using a rotary shaker at 30 rpm for 24 h. Then, the mixture was separated using a 0.45 μm syringe filter. The final concentrations of As and NO_3^- were determined using atomic absorption

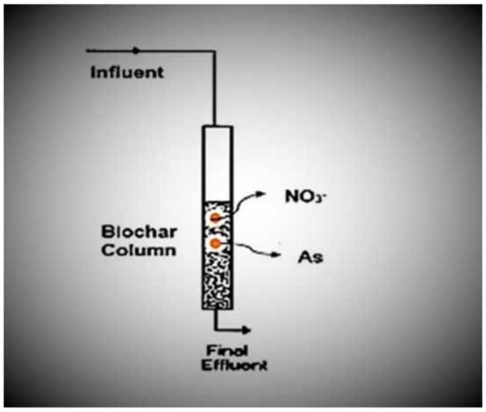

Figure 3 | Biochar adsorption column.

spectroscopy. The amount of As and NO_3^- adsorbed on the biochar (mmol g^{-1}) is determined using Equation (1) (Metcalf & Eddy 2014). Figure 3 shows the schematic diagram of biochar adsorption column.

$$qe = \frac{((Ao - Ae)V)}{W} \tag{1}$$

where Ao is the initial As and NO_3^- concentrations (mM), Ae is the As and NO_3^- concentrations at equilibrium (mM), V is the solution volume (L), and W is the biochar dosage (g).

2.3. Estimation of GWF

The grey water footprint measures the amount of water required to assimilate a polluting load produced from anthropic activity (Hoekstra *et al.* 2011; Yapıcıoğlu 2019b). The GWF is an indicator of water pollution. The main calculation method developed by Hoekstra *et al.* (2011) was given in Equation (2). In Equation (2), Lrunoff indicates the contaminant load observed in water, Cmax shows the allowable maximum concentration of contaminants according to the regulations and Cnat presents the natural concentration of contaminants in the water body. In Equation (3), Lrunoff is described. 'α' means the leaching-runoff fraction and s indicates the amount of chemical substance used in the soil at a in order to fertilize, manure or pesticides (Franke *et al.* 2013).

$$GWF = (Lrunoff)/(Cmax - Cnat) \tag{2}$$

$$(Lrunoff) = \alpha \times s \tag{3}$$

The recommended calculation tool for the GWF in the Water Footprint Assessment (WFA) manual (Equation (2)) (Hoekstra *et al.* 2011) has been modified for groundwater treatment in this study. A simple equation based on the mass balance was developed in order to figure out the GWF in this paper. The modified equation is given in Equation (4).

$$GWF = (Q \times Ce)/(Cmax - Cnat) \tag{4}$$

In this modified version, treated groundwater volume and the pollutant concentrations after treatment were considered. In Equation (4), Q represents the groundwater effluent flow rate (volume/time) and Ce means the concentration of a pollutant after groundwater treatment. Similarly, with the basic model, Cmax represents the allowable maximum concentration of pollutant according to the regulations and Cnat shows the natural concentration of contaminants in the body of water. Cmax are 50 ppm and 10 ppb for NO_3^- and As, respectively (WHO 2011). Ce could be obtained from the water analyses using Standard Methods, directly (APHA 1995). Treated water volume was defined using an automatic flow meter. For Cnat determination, this paper used the values reported by Chapman (1996), which are equal to zero (Cnat = 0) for anthropogenic substances.

2.4. Effect of groundwater recharge using Monte Carlo simulation

In this section, the effect of groundwater recharge was simulated using Monte Carlo (MC) methodology. A reduction has been estimated applying groundwater recharge due to the dilution process of groundwater. MC Simulation is a numerical method that generates random variables in order to model the risk or uncertainty of a certain system. MC Simulation uses probability distribution in order to model a random variable. Various probability distributions are used for modelling input variables such as normal, lognormal, uniform, and triangular (Kroese *et al.* 2014). In this study for MC Simulation, @RISK Trial 7.6 software has been used. Volumetric Reserves 0-Model with No Uncertainty module has been used by applying 10,000 iteration and 1

Table 2 | The reclaimed wastewater characterization

Parameter	Value
TSS	18 mg/L
Turbidity	5 NTU
COD	47 mg/L
BOD	23 mg/L
N-NH_4	6 mg/L
N-NO_3	7 mg/L
P-PO_4	5 mg/L
TCF	3×10^5/100 mL
E.coli	10^5/100 mL

Table 3 | GWF assessment of groundwater resources in March

		NO_3^-					As				
Process	**Observation Well**	**Q (m^3/d)**	**Ce (ppm)**	**Cnat (ppm)**	**Cmax (ppm)**	**GWF,$_{NO3-}$ (m^3/d)**	**Q (m^3/d)**	**Ce (ppb)**	**Cnat (ppb)**	**Cmax (ppb)**	**GWF,$_{As}$ (m^3/d)**
Coagulation-flocculation	Observation Well-1	2,700	4.4	0	50	237.6	2,700	0.50	0	10	135.0
Coagulation-flocculation	Observation Well-2	2,700	5.8	0	50	313.2	2,700	0.21	0	10	57.1
Coagulation-flocculation	Observation Well-3	2,700	10.2	0	50	550.8	2,700	0.12	0	10	32.2
Coagulation-flocculation	Observation Well-4	2,700	7.4	0	50	399.6	2,700	0.18	0	10	48.7
Coagulation-flocculation	Observation Well-5	2,700	36	0	50	1,944	2,700	0.10	0	10	26.5
Coagulation-flocculation	Observation Well-6	2,700	9	0	50	486	2,700	0.26	0	10	70.4
Coagulation-flocculation	Observation Well-7	2,700	9.4	0	50	507.6	2,700	0.264	0	10	71.4
Coagulation-flocculation	Observation Well-8	2,700	17.4	0	50	939.6	2,700	0.82	0	10	222.5
Coagulation-flocculation	Observation Well-9	2,700	105.2	0	50	5,680.8	2,700	0.21	0	10	57.7
Coagulation-flocculation	Observation Well-10	2,700	22.6	0	50	1,220.4	2,700	0.16	0	10	42.5
Biochar treatment	Observation Well-1	2,700	2.2	0	50	118.8	2,700	0.250	0	10	67.5
Biochar treatment	Observation Well-2	2,700	2.9	0	50	156.6	2,700	0.106	0	10	28.5
Biochar treatment	Observation Well-3	2,700	5.1	0	50	275.4	2,700	0.060	0	10	16.1
Biochar treatment	Observation Well-4	2,700	3.7	0	50	199.8	2,700	0.090	0	10	24.3
Biochar treatment	Observation Well-5	2,700	18	0	50	972	2,700	0.049	0	10	13.2
Biochar treatment	Observation Well-6	2,700	4.5	0	50	243	2,700	0.130	0	10	35.2
Biochar treatment	Observation Well-7	2,700	4.7	0	50	253.8	2,700	0.132	0	10	35.7
Biochar treatment	Observation Well-8	2,700	8.7	0	50	469.8	2,700	0.412	0	10	111.3
Biochar treatment	Observation Well-9	2,700	52.6	0	50	2,840.4	2,700	0.107	0	10	28.9
Biochar treatment	Observation Well-10	2,700	11.3	0	50	610.2	2,700	0.079	0	10	21.2

simulation. Probability distribution is selected as the lognormal distributions. The uncertain inputs were $GWF_{biochar}$ values corresponded to without recharge process. The outputs were 90, 80 and 70% of dilution capacity (DC) of recharge water. The characterization of reclaimed wastewater is given in Table 2. The simulation was carried out for both March and October related to biochar treatment. The reason for choosing this treatment method was the lowest GWF values corresponded to biochar adsorption process. In the result of the simulation, minimum GWF has been estimated with groundwater recharge. The model used in this simulation is given in Equation (5). The desired output is the minimum grey water footprint.

$$GWFmin = RiskOutput(``Lognormal'') + RiskLognorm(GWF_{biochar};\ DC) \tag{5}$$

GWFmin = Minimum grey water footprint
$GWF_{biochar}$ = Grey water footprint of biochar treatment
DC = Dilution capacity of groundwater recharge

3. RESULTS AND DISCUSSION

3.1. GWF assessment of groundwater resources

According to the analyses results, arsenic and nitrate concentrations in March (before irrigation) were higher than in October (post irrigation). It is estimated that irrigation could reduce As and NO_3^- concentrations at groundwater. NO_3^- concentrations were higher than As concentrations due to the agricultural activities in this region. As could have resulted from anthropogenic activities. It is estimated that pesticides used in agricultural fields are the main resources of As. The other resource could be the geological structure of the region. According to the analyses results, biochar treatment was more effective

Table 4 | GWF assessment of groundwater resources in October

		NO_3^-					As				
Process	**Observation Well**	**Q (m^3/d)**	**Ce (ppm)**	**Cnat (ppm)**	**Cmax (ppm)**	**$GWF_{,NO_3^-}$ (m^3/d)**	**Q (m^3/d)**	**Ce (ppb)**	**Cnat (ppb)**	**Cmax (ppb)**	**$GWF_{,As}$ (m^3/d)**
Coagulation-flocculation	Observation Well-1	2,750	1.45	0	50	79.75	2,750	0.48	0	10	131,7
Coagulation-flocculation	Observation Well-2	2,750	2.39	0	50	131.45	2,750	0.17	0	10	46,8
Coagulation-flocculation	Observation Well-3	2,750	4.474	0	50	246.07	2,750	0.13	0	10	34,6
Coagulation-flocculation	Observation Well-4	2,750	5.506	0	50	302.83	2,750	0.16	0	10	45,2
Coagulation-flocculation	Observation Well-5	2,750	1.864	0	50	102.52	2,750	0.09	0	10	25,9
Coagulation-flocculation	Observation Well-6	2,750	6.894	0	50	379.17	2,750	0.21	0	10	58,0
Coagulation-flocculation	Observation Well-7	2,750	1,1	0	50	60.5	2,750	0.25	0	10	68,4
Coagulation-flocculation	Observation Well-8	2,750	1.598	0	50	87.89	2,750	0.24	0	10	66,2
Coagulation-flocculation	Observation Well-9	2,750	6.35	0	50	349.25	2,750	0.16	0	10	44,8
Coagulation-flocculation	Observation Well-10	2,750	6.866	0	50	377.63	2,750	0.12	0	10	32,3
Biochar treatment	Observation Well-1	2,750	0.725	0	50	39.875	2,750	0.240	0	10	65,9
Biochar treatment	Observation Well-2	2,750	1.195	0	50	65.725	2,750	0.085	0	10	23,4
Biochar treatment	Observation Well-3	2,750	2.237	0	50	123.035	2,750	0.063	0	10	17,3
Biochar treatment	Observation Well-4	2,750	2.753	0	50	151.415	2,750	0.082	0	10	22,6
Biochar treatment	Observation Well-5	2,750	0.932	0	50	51.26	2,750	0.047	0	10	12,9
Biochar treatment	Observation Well-6	2,750	3.447	0	50	189.585	2,750	0.106	0	10	29,0
Biochar treatment	Observation Well-7	2,750	0.55	0	50	30.25	2,750	0.124	0	10	34,2
Biochar treatment	Observation Well-8	2,750	0.799	0	50	43.945	2,750	0.120	0	10	33,1
Biochar treatment	Observation Well-9	2,750	3.175	0	50	174.625	2,750	0.082	0	10	22,4
Biochar treatment	Observation Well-10	2,750	3.433	0	50	188.815	2,750	0.059	0	10	16,1

than coagulation flocculation process. The removal efficiencies of NO_3^- and As were higher when the biochar adsorption process was applied. The GWF was figured out using pollutant removal efficiencies. From this point of view, the parallel results with pollutant removal efficiencies were achieved for GWF assessment. Tables 3 and 4 demonstrated the GWF assessment results in details.

The results showed that the GWF values related to October were lower than the values in March. This was due to the irrigation process in October. March is the month before irrigation and October is the month post irrigation. Irrigation could dilute the groundwater, so a significant reduction was observed in the GWF values. The results revealed that the highest GWF corresponded to Observation Well-9 (Bolatlar) using coagulation-flocculation process in March. More nitrogen fertilizers are applied after the sowing process in March. So, the peak nitrate leaching was observed in this month. This application could lead to the highest GWF in March. In October, Observation Well-10 (Uğraklı) had the highest GWF. Nitrate led to the

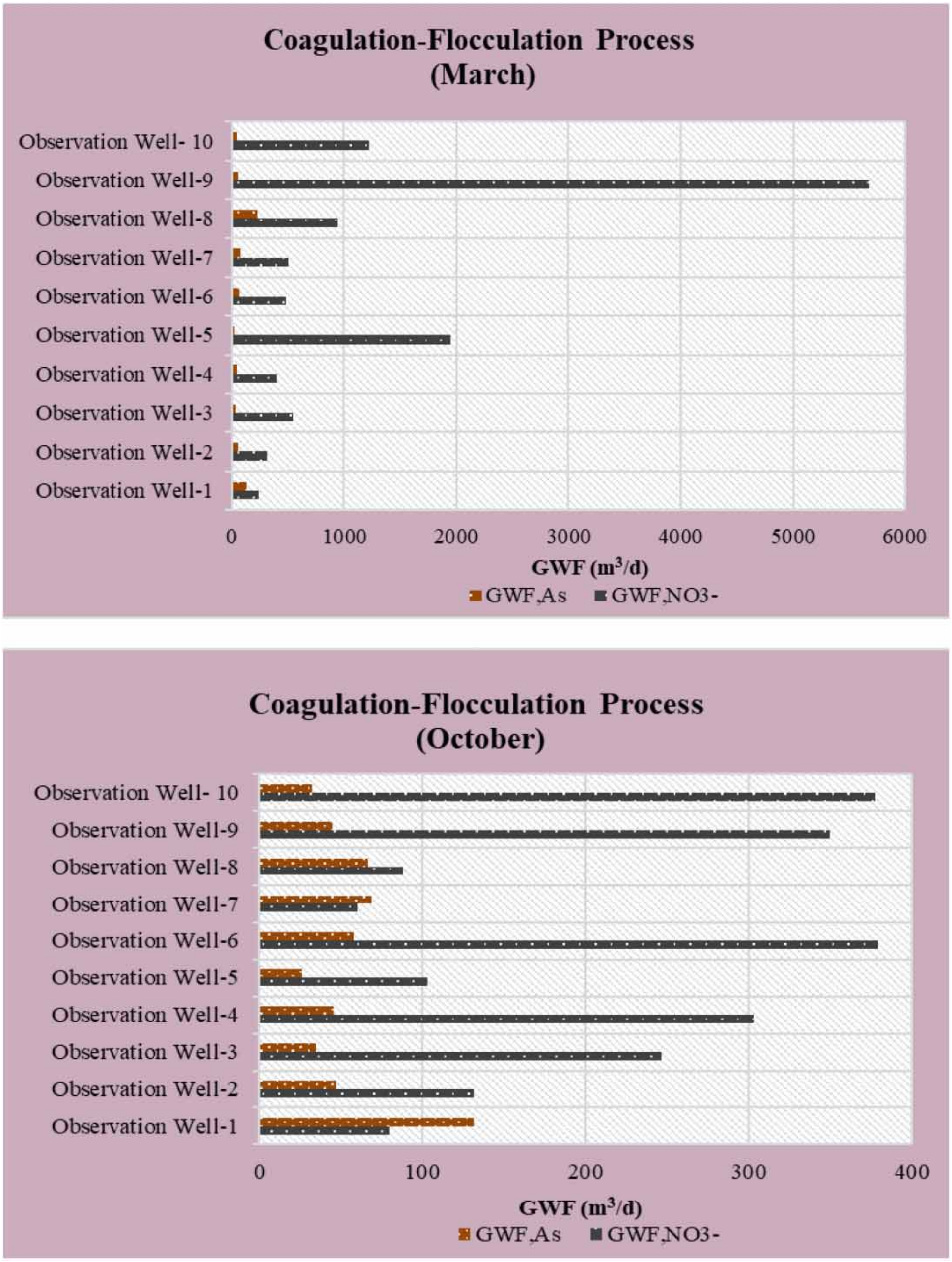

Figure 4 | GWF assessment related to coagulation-flocculation process.

highest GWF with the value of 5,680.8 m^3/d. It could be originated from this well (Bolatlar) being so near to the agricultural fields. The reason for the highest NO_3^- concentrations was fertilizer use in the largest amount in this field in the growing period of cotton and corn. The results demonstrated that nitrate led to higher GWF than the GWF of arsenic. The lowest GWF was observed at Observation Well-5 (Ozanlar) applying biochar treatment in terms of As removal. The lowest GWF was monitored in October with the value of 12.9 m^3/d. The highest GWF due to arsenic treatment corresponded to Observation Well-8 (Yaygılı) in March. In October, the highest GWF related to As removal was observed at Observation Well-1 (Çamlıdere). From this assessment result, it could be considered that the biochar adsorption process led to lower grey water footprint than the coagulation-flocculation process. The coagulation-flocculation process had higher capacity for water pollution Also, this study confirmed that Urfa Isot pepper-derived biochar could adsorb NO_3^- and As, immediately. The results revealed that pollutant removal efficiency is very important to determine the GWF. Figures 4 and 5 show the variation and benchmarking GWF values on a process basis in terms of nitrate and arsenic related to March and October. The calculation of GWF allowed us to ensure a mapping of nitrate and arsenic pollution in the groundwater of the study area. Figure 6 shows the map of GWF related to nitrate and arsenic pollution. According to Figure 6, Kızıldoruç (6), Bolatlar (9) and Uğraklı (10) are in the brown region due to higher GWF values. It could be said that ground water pollution has a high risk in these regions and some preventions should be taken and treatment policies should be developed immediately for these resources. In the grey region, Çamlıdere (1), Yardımcı (2), Olgunlar (7), Yaygılı (8) have been located with medium pollution risk. For these groundwater resources, the treatment and protection policies should be reviewed. Kısas (3), Uğurlu

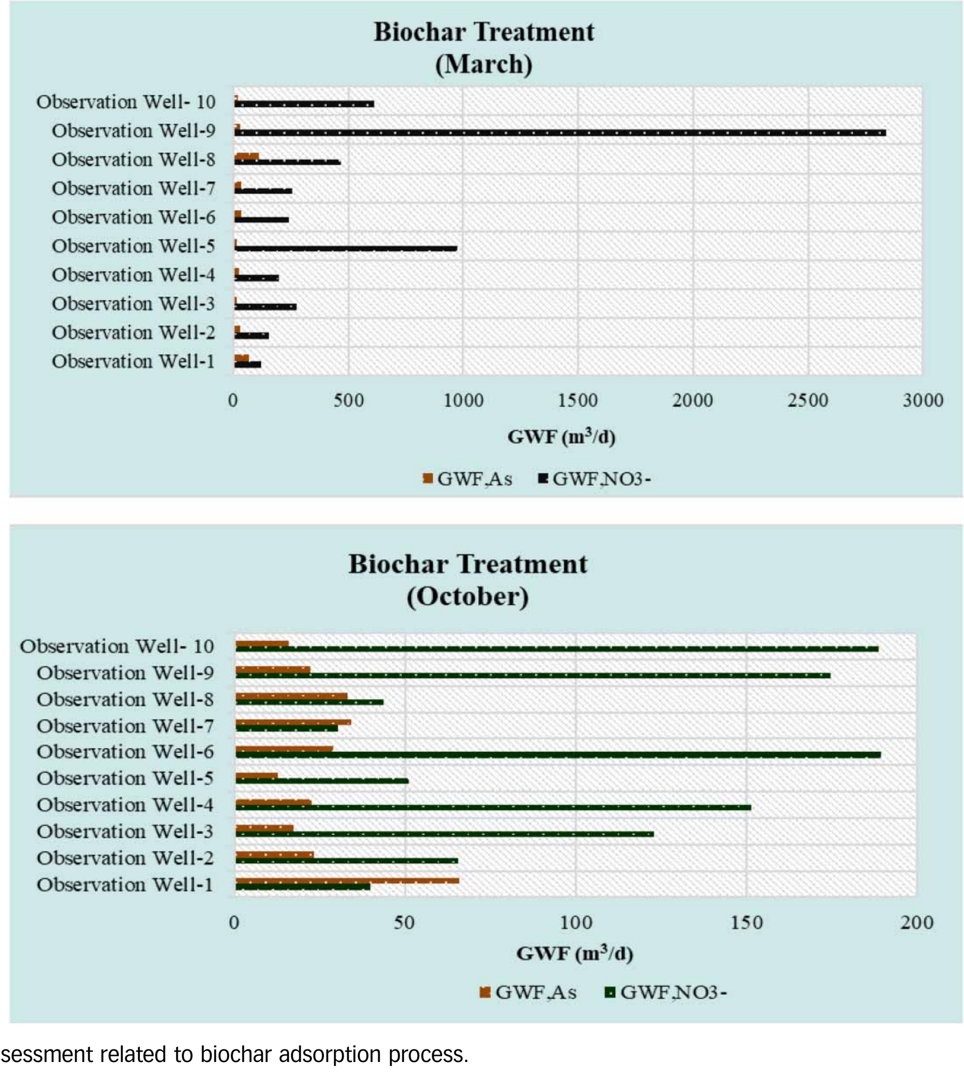

Figure 5 | GWF assessment related to biochar adsorption process.

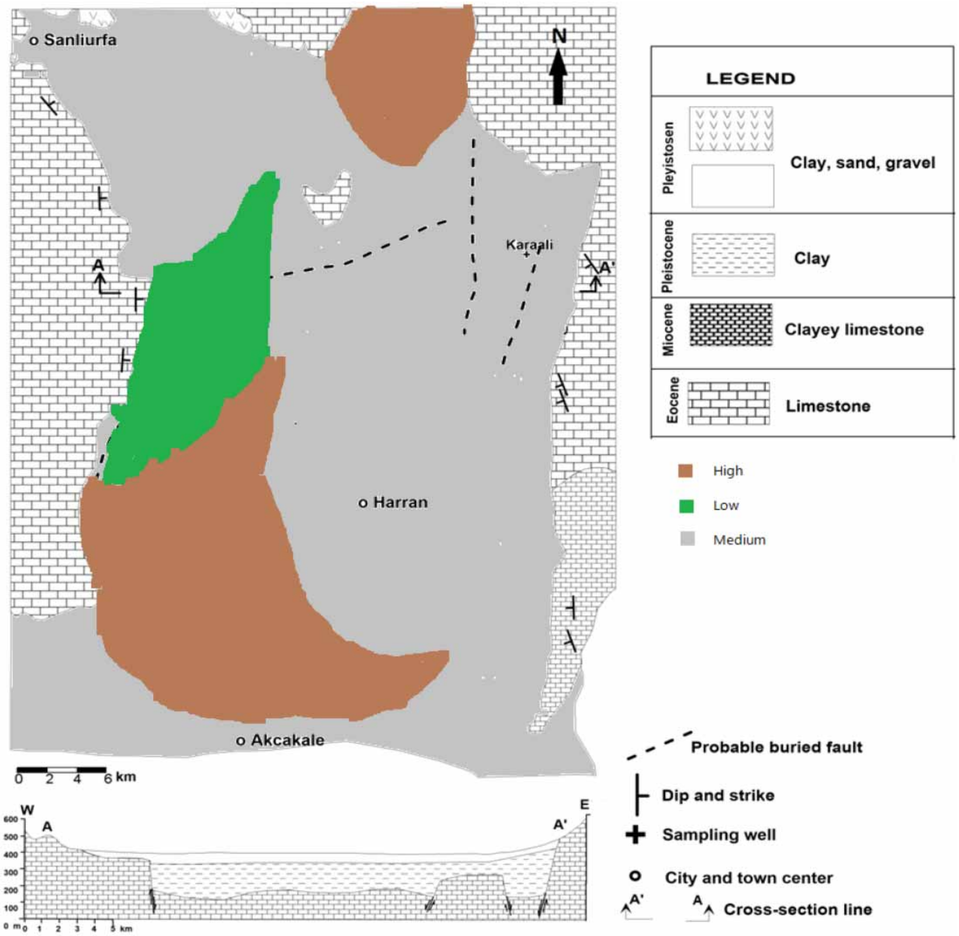

Figure 6 | Map of the GWF in terms of arsenic and nitrate pollution.

(4), Ozanlar (5) are in the green region due to lower GWF levels. The preventions should apply similarly for these wells in the Harran Plain. This assessment using mapping was carried out according to the total GWF values.

There are limited investigations related to this research. Many of the models developed for the GWF assessment were applied to surface freshwater resources and wastewater treatment plants. Many researchers focused on water consumption in terms of water footprint assessment. In a study by Yapıcıoğlu (2020), a new GWF assessment tool was developed for an industrial wastewater treatment plant. Also, Morera *et al.* (2016) observed the GWF for a wastewater treatment plant. The studies related to water treatment plants were limited in the literature. Serio *et al.* (2018) performed a similar study on GWF of groundwater resources. They used a similar methodology based on contaminant mass balance developed by Hoekstra *et al.* (2011). They investigated the groundwater nitrate contamination and agricultural land use in a grey water footprint perspective in Southern Apulia Region (Italy). They carried out their study in April, May and September, October. They reported higher GWF values of nitrate for vineyards than for olive groves, particularly in areas used to produce table grapes. In this study, the GWFs of groundwater were monitored at high values at the wells near the fields in which cotton has been grown. It could be said that more nitrogen fertilizers could be used for growing cotton. They similarly reported that nitrate concentrations are higher due to the agricultural activities. The results of the GWF show high values in these regions. Another study was performed by Miglietta *et al.* (2017). They reported a widespread contamination by mercury (Hg), vanadium (V) and ammonium (NH_4^+) with concentrations that were above the limits. They figured out the GWF values for each chemical parameter. They similarly reported ammonium that was a form of nitrogen such as NO_3^- led to higher GWF than the other heavy metals due to the agricultural activities. They similarly estimated that heavy metals could be the result of anthropogenic activities. They also similarly reported ammonium derived mainly from fertilizers used in agriculture. In this study, NO_3^- is the major pollutant led to the highest GWF. As is the minor contaminant considered in the GWF approach. Aldaya *et al.* (2020) reported that the variation of GWF corresponded to the variation of the nutrient loads, which are highest in areas of intensive

Table 5 | GWF reduction applying groundwater recharge using Monte Carlo simulation

Month	Observation Well	$GWF_{,NO3^-}$ (m^3/d)	Reduction (%)	$GWF_{,As}$ (m^3/d)	Reduction (%)
March	Observation Well-1	110.5	7.0	60	11.1
March	Observation Well-2	146.8	6.3	24	15.9
March	Observation Well-3	235.3	14.6	14	13.0
March	Observation Well-4	185.0	7.4	20	17.8
March	Observation Well-5	900.0	7.3	10	24.4
March	Observation Well-6	221.0	9.1	29	17.6
March	Observation Well-7	200.0	21.2	30	16.0
March	Observation Well-8	414.0	11.9	100	10.1
March	Observation Well-9	2,800.0	1.4	24	16.8
March	Observation Well-10	576.0	5.6	17	19.9
October	Observation Well-1	30.0	24.8	60	8.9
October	Observation Well-2	60.0	8.7	18	23.1
October	Observation Well-3	100.0	18.7	10	42.3
October	Observation Well-4	125.0	17.4	15	33.7
October	Observation Well-5	44.0	14.2	8	38.1
October	Observation Well-6	170.0	10.3	20	31.1
October	Observation Well-7	25.0	17.4	28	18.2
October	Observation Well-8	37.0	15.8	30	9.4
October	Observation Well-9	160.0	8.4	18	19.7
October	Observation Well-10	171.0	9.4	13	19.5

agriculture similarly with this study. They similarly reported a positive significant correlation between nitrogen concentrations and GWF. It is obvious that nitrate leaching from fertilizers in the agricultural fields could increase the GWF values for both of the studies.

3.2. Effect of groundwater recharge on grey water footprint

In this study, the effect of recharge on GWF was investigated using Monte Carlo simulation. Table 5 demonstrated the simulation results. The results showed that groundwater recharge could reduce the grey water footprint of all observation wells for both March and October.

In March, average reduction of GWF corresponded to nitrate was 9.2%. The average reduction of GWF corresponded to arsenic was 16.3%. It could be said that using fertilizers containing nitrogen during the sowing process could increase the NO_3^- leaching to groundwater resources. So, the value of reduction related to nitrate was lower in March. It was obvious that groundwater recharge could reduce the water contaminants. It could dilute the water composition so a reduction would be monitored at pollutant concentrations. From this point of view, groundwater recharge could be applied to preserve the groundwater resources. In October, average reduction of GWF related to nitrate was 14.5%. The average reduction in GWF of arsenic was 24.4%. The reduction of nitrate pollution was lower. It could have originated from agricultural activities and use of nitrogen-based fertilizers. Also, the reclaimed wastewater contains nitrogen. Arsenic could be the result of pesticides used in agriculture to protect crops or the geogenic structure of the region. As reduction was higher due to reclaimed wastewater composition. The reclaimed wastewater contain nitrogen but no arsenic concentration. The dilution with groundwater recharge was higher in October. Total reduction of GWF would be approximately 64.3% if groundwater recharge is carried out.

4. CONCLUSIONS

This paper shows that the grey water footprint is a significant indicator of water pollution. It could be used as the indicator for the sustainability of groundwater resources. The calculation of the grey water footprint allowed us to achieve a mapping of nitrate and arsenic pollution in the groundwater of the study area. The results revealed that nitrate led to higher GWF. NO_3^-

concentrations were higher than As concentrations due to the agricultural activities in this region. Also, the biochar adsorption process reduced the GWF. The GWF in October (post irrigation) was lower than the values observed in March (before irrigation). It could have originated from irrigation reducing As and NO_3^- concentrations at groundwater resources.

It is possible to decrease the grey water footprint by applying the groundwater recharge processes. Approximately, a total reduction of up to 64.3% has been observed by applying the groundwater recharge. It was clear that groundwater recharge could decrease the water pollutant concentrations. It could dilute the water composition. So, this study shows that groundwater recharge could be carried out to protect the groundwater resources. This study especially confirms that groundwater recharge could be an alternative to minimze the GWF.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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