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

Pelin Yapıcıoğlu and Mehmet İrfan Yeşilnacar
College of Civil Engineering and Architecture, Zhejiang University, Anzhong Building, Zijingang Campus, 866 Yuhangtang Road, Hangzhou, Zhejiang 310058, China
*Corresponding author. E-mail: pyapicioglu@harran.edu.tr

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 traditional crop of Turkey was used to generate biochar with slow pyrolysis.

1. INTRODUCTION

The GWF is a term to determine the minimum volume of freshwater required 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 fulfill water requirements in a region or country. Groundwater resources have a crucial role on water scarcity. Water resources management has a vital importance for the countries that have water scarcity problem such as Turkey (Yapıcıoğlu 2019a; Yapıcıoğlu 2020). It is important to protect the water resources from pollutions. GWF is an indicator to monitor the effect of pollutants on the water supplies. From this perspective, GWF of groundwater resources which contain 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 (NO₃⁻) has been comprised in the result of nitrification process. NO₃⁻ is derived from one of the urban, industrial, and agricultural activities in the groundwater. Majorly, it has been estimated that NO₃⁻ 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 the 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 degrading and can only be converted into different forms or transformed into insoluble compounds. Inorganic arsenic generally occurs in two major...
oxidation states which are arsenide and arsenate 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 the significant groundwater contamination. Water Footprint Network (WFN) has developed an estimation model named as the grey water footprint (GWF) to determine the water pollution levels of each contaminant parameters (WFN 2014). NO₃ 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 of selecting NO₃ and As is that these pollutants lead to major contaminations at the Harran Plain.

Coagulation-flocculation process 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 on 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 similar GWF approach. Miglietta et al. (2017) investigated the grey water footprint of groundwater in Italy for each chemical parameter indicated a widespread contamination by Mercury, Vanadium and Ammonium. Aldaya et al. (2020) performed a study on 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 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 annum um (Urfa Isot pepper) which is traditional crop of Turkey was used to generate biochar using slow pyrolysis. And then, 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 the 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 at 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 Harran Plain (Yeşilnacar & Güllüoğlu 2008; Derin et al. 2020; Yapıcıoğlu et al. 2020).

Çamlıdere (1), Yardımcı (2), Kisas (3), Uğurlu (4), Ozanlar (5), Kızılıdorucu (6), Olgunlar (7), Yaygılı (8), Bolatlar (9) and Uğrafı (10) are the observation wells of arsenic and nitrate concentration in Harran Plain. Figure 1 has demonstrated the location map of study area. The major reasons of selecting these observation wells are that they are vulnerable, and they locate 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 ICP-MS technique in October and March. October and March were selected as the sampling periods due to 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 reason, water sampling was applied in these 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 biochar adsorption process were carried out to define the water pollution capacity of arsenic and nitrate. Figure 2 shows the treatment diagrams. Coagulation-flocculation process was applied after aeration process. This method is well-known and classical groundwater treatment method. At coagulation and flocculation process, the optimum concentrations of coagulant and flocculant that contain Polyaluminum Chloride (PAC) and Cationic Polymer (PE) were 20 mg/L and 25 mg/L, respectively. Different treatment technology which was biochar application was carried out instead of coagulation-flocculation process to obtain high treatment and pollutant removal efficiencies. 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 the 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 from the other treatment methods, and biochar could adsorb arsenic and nitrate immediately. Biochar was produced from *Capsicum annuum* (Urfa Isot peppers) using slow pyrolysis method.

*Capsicus 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)
was mixed with 10 mL of As and NO₃ solutions in a 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 NO₃ were determined using atomic absorption.

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

| Well             | As concentration in March (ppb) | As concentration in October (ppb) | NO₃ concentration in March (ppm) | NO₃ 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                             | 0.65                             | 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.
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.

$$\text{qe} = \frac{(\text{Ao} - \text{Ae})V}{W}$$  \hspace{1cm} (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 was described. ‘$\alpha$’ means to 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).

$$\text{GWF} = \frac{(\text{Lrunoff})}{(\text{Cmax} - \text{Cnat})}$$  \hspace{1cm} (2)
$$\text{Lrunoff} = \alpha \times s$$  \hspace{1cm} (3)

The recommended calculation tool for the GWF at 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 was given in Equation (4).

$$\text{GWF} = \frac{(\text{Q} \times \text{Ce})}{(\text{Cmax} - \text{Cnat})}$$  \hspace{1cm} (4)

At 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 to 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 Standards 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-NH₄       | 6 mg/L  |
| N-NO₃       | 7 mg/L  |
| P-PO₄       | 5 mg/L  |
| TCF         | $3 \times 10^5$ /100 mL |
| E.coli      | $10^5$ /100 mL |

Table 3 | GWF assessment of groundwater resources in March

| Process          | Observation Well | NO₃ | As |
|------------------|------------------|-----|----|
| Coagulation-Flocculation | Observation Well-1 | 2,700 | 2,700 |
| Coagulation-Flocculation | Observation Well-2 | 2,700 | 2,700 |
| Coagulation-Flocculation | Observation Well-3 | 2,700 | 2,700 |
| Coagulation-Flocculation | Observation Well-4 | 2,700 | 2,700 |
| Coagulation-Flocculation | Observation Well-5 | 2,700 | 2,700 |
| Coagulation-Flocculation | Observation Well-6 | 2,700 | 2,700 |
| Coagulation-Flocculation | Observation Well-7 | 2,700 | 2,700 |
| Coagulation-Flocculation | Observation Well-8 | 2,700 | 2,700 |
| Coagulation-Flocculation | Observation Well-9 | 2,700 | 2,700 |
| Coagulation-Flocculation | Observation Well-10 | 2,700 | 2,700 |
| Biochar Treatment | Observation Well-1 | 2,700 | 2,700 |
| Biochar Treatment | Observation Well-2 | 2,700 | 2,700 |
| Biochar Treatment | Observation Well-3 | 2,700 | 2,700 |
| Biochar Treatment | Observation Well-4 | 2,700 | 2,700 |
| Biochar Treatment | Observation Well-5 | 2,700 | 2,700 |
| Biochar Treatment | Observation Well-6 | 2,700 | 2,700 |
| Biochar Treatment | Observation Well-7 | 2,700 | 2,700 |
| Biochar Treatment | Observation Well-8 | 2,700 | 2,700 |
| Biochar Treatment | Observation Well-9 | 2,700 | 2,700 |
| Biochar Treatment | Observation Well-10 | 2,700 | 2,700 |
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 was given in Table 2. The simulation was carried out for both March and October related to biochar treatment. The reason of 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 used model in this simulation is given in Equation (5). The desired output is the minimum grey water footprint.

$$GWF_{min} = \text{RiskOutput(Lognormal)} + \text{RiskLognorm}(GWF_{biochar}, DC)$$  \hspace{1cm} (5)

$GWF_{min} = \text{Minimum grey water footprint}$

$GWF_{biochar} = \text{Grey water footprint of biochar treatment}$

$DC = \text{Dilution capacity of groundwater recharge}$

### 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 be resulted from anthropogenic activities. It is estimated that pesticides used in agricultural fields are the main resources of As. The other resource could be geological structure of the region. According to the analyses results, biochar treatment was more effective than coagulation

| Process              | Observation Well | $NO_3^-$ | $As$  |
|----------------------|-----------------|---------|-------|
|                      |                 | $Q$ (m$^3$/d) | $Ce$ (ppm) | $C_{nat}$ (ppm) | $C_{max}$ (ppm) | $GWF_{NO_3}$ (m$^3$/d) | $Q$ (m$^3$/d) | $Ce$ (ppb) | $C_{nat}$ (ppb) | $C_{max}$ (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 | 131.14 | 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 | 0.24 | 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 |
floculation process. The removal efficiencies of NO₃ and As were higher when 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 of March. It was due to irrigation process in October. March is the month before irrigation and October is the month of post irrigation. Irrigation could dilute the groundwater, so a significant reduction was observed on the GWF values. The results revealed that the highest GWF corresponded to Observation Well-9 (Bolatlar) using coagulation-floculation process in March. More nitrogen fertilizers are applied after 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 highest GWF with the value of 5,680.8 m³/d. It could be originated from this well (Bolatlar) is so nearby with the agricultural fields.

![Coagulation-Flocculation Process](image)

**Figure 4** | GWF assessment related to coagulation-floculation process.
The reason of highest NO$_3$ concentrations was fertilizer use in largest amount in this field at 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 results, it could be considered that biochar adsorption process led to lower grey water footprint than coagulation-flocculation process. Coagulation-flocculation process had higher capacity of 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 showed 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, Kızıldorucu (6), Bolatlar (9) and Uğrankılı (10) are at 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 take and immediately treatment policies should be developed for these resources. At 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. Kısıas (3), Uğurlu (4), Ozanlar (5) are at green region due to lower

![Figure 5](image-url) | GWF assessment related to biochar adsorption process.
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 developed models 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 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 that higher GWF values of nitrate for vineyards than for olive groves, particularly in areas used to produce table grapes. In this study, the GWF of groundwater were monitored at high values at the wells nearby the fields which cotton has been grown up. It could be said that more nitrogen fertilizers could use for growing up of 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 that a widespread contamination by Mercury (Hg), Vanadium (V) and Ammonium (NH₄⁺) with concentrations 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 NO₃⁻/CO₂ led to higher GWF than the other heavy metals due to the agricultural activities. They similarly estimated that heavy metals could be resulted from anthropogenic activities. They also similarly reported ammonium derived mainly from fertilizers used in agriculture. In this study, NO₃⁻ is the major pollutant led to the highest GWF. As is the minor contaminant considering 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.
agriculture similarly with this study. They similarly reported that a positive significant correlation between nitrogen concentrations and GWF. It is obvious that nitrate leaching from fertilizers at the agricultural fields could increase the GWF values for each two 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 contain nitrogen during 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 on GWF of arsenic was 24.4%. The reduction of nitrate pollution was lower. It could be originated from agricultural activities and using nitrogen-based fertilizers. Also, the reclaimed wastewater contains nitrogen. Arsenic could be resulted from pesticides used in the agriculture to protect the crops or 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 lower than As concentrations due to the agricultural activities in this region. Also, biochar adsorption process has reduced the GWF. The GWF in October (post irrigation) was lower than the values observed in March (before irrigation). It could be originated from that irrigation could reduce As and NO$_3^-$ concentrations at groundwater resources.

It is possible to decrease the grey water footprint by applying groundwater recharge processes. Approximately, a total reduction up to 64.3% has been observed by applying 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 an alternative to minimize the GWF.

**DATA AVAILABILITY STATEMENT**

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

**REFERENCES**

Aldaya, M. M., Rodriguez, C. I., Fernandez-Poulussen, A., Merchán, D., Beriaín, M. J. & Llamas, R. 2020 Grey water footprint as an indicator for diffuse nitrogen pollution: the case of Navarra, Spain. *Science of the Total Environment* **698**, 134338.

American Public Health Association (APHA), American Water Works Association 1995 *Standard Methods for the Examination of Water and Wastewater*. USA.

Asano, T. & Cotruvo, J. A. 2004 Groundwater recharge with reclaimed municipal wastewater: health and regulatory considerations. *Water Research* **38**(8), 1941–1951.

Baba, A., Saroğlu, F., Akkuş, İ., Özel, N., Yeşilmacular, M. İ., Nalbantçılär, M. T. et al. 2019 Geological and hydrogeochemical properties of geothermal systems in the southeastern region of Turkey. *Geothermics* **78**, 255–271.

Bayhan, I., Yeşilmacular, M. İ., Yetiş, A. D. & Tutkun, E. 2020 An evaluation of drinking-usage water quality in terms of environmental health: a case study of Siverek (Sanliurfa), Turkey. *The Turkish Bulletin of Hygiene and Experimental Biology* **77**(4), 107–120.

Bilgili, A. V., Yeşilmacular, I., Akhiiko, K., Nagano, T., Aydemir, A., Hzlh, H. S. & Bilgili, A. 2018 Post-irrigation degradation of land and environmental resources in the Harran plain, southeastern Turkey. *Environmental Monitoring and Assessment* **190**(11), 1–14.

Chapman, D. 1996 *Water Quality Assessments-A Guide to Use of Biota, Sediments and Water in Environmental Monitoring*, 2nd edn. CRC Press, Boca Raton, FL, USA.

Deng, S., Peng, S., Xie, B., Yang, X., Sun, S., Yao, H. & Li, D. 2020 Influence characteristics and mechanism of organic carbon on denitrification, N$_2$O emission and NO$_3^-$ accumulation in the iron [Fe (0)]-oxidizing supported autotrophic denitrification process. *Chemical Engineering Journal* **393**, 124736.

Derin, P., Yetiş, A. D., Yeşilmacular, M. İ. & Yapoçoğlu, P. 2020 Investigation of potential heavy metal pollution caused by geothermal waters in GAP’s largest irrigation area. *Geological Bulletin of Turkey* **63**(1), 125–136.

Franke, N. A., Bovaciu, H. & Hoekstra, A. Y. 2013 *Grey Water Footprint Accounting: Tier 1 Supporting Guidelines – Value of Water Research Report Series No 65*. UNESCO-IHE, Delft, The Netherlands.

Hoekstra, A. Y., Chapagain, A. K., Aldaya, M. M. & Mekonnen, M. M. 2011 *The Water Footprint Assessment Manual*. Earthscan, London-Washington, DC.

Kroese, D. P. et al. 2014 Why the Monte Carlo method is so important today. *WIREs Computational Statistics* **6**(6), 386–392.

Metcalf & Eddy. 2014 *Wastewater Engineering: Treatment and Resource Recovery*, 5th edn. McGraw-Hill, Boston, USA.

Migliaetta, P. P., Toma, P., Fanizzi, F. P., De Donno, A., Coluccia, B., Migoni, D. & Serio, F. 2017 A grey water footprint assessment of groundwater chemical pollution: case study in Salento (southern Italy). *Sustainability* **9**(5), 799.

Morera, S., Corominas, L., Poch, M., Aldaya, M. M. & Comas, J. 2016 Water footprint assessment in wastewater treatment plants. *Journal of Cleaner Production* **112**, 4741–4748.

Niazi, N. K., Bibi, I. & Shahid, M. 2018 Arsenic removal by perilla leaf biochar in aqueous solutions and groundwater: an integrated spectroscopic and microscopic examination. *Environmental Pollution* **232**, 51–41.

Oyem, H. H., Oyem, I. M. & Usse, A. I. 2015 Iron, manganese, cadmium, chromium, zinc and arsenic groundwater contents of Agbor and Owa communities of Nigeria. *SpringerPlus* **4**(1), 1–10.

Parviainen, A., Loukola-Ruskeeniemi, K., Tarvainen, T., Hatakka, T., Härmai, P., Backman, B. et al. 2015 Arsenic in bedrock, soil and groundwater – the first arsenic guidelines for aggregate production established in Finland. *Earth-Science Reviews* **150**, 709–723.

Qambrani, N. A., Rahman, M. M. & Won, S. 2017 Biochar properties and eco-friendly applications for climate change mitigation, waste management, and wastewater treatment: a review. *Renewable and Sustainable Energy Reviews* **79**, 255–273.

Serio, F., Miglietta, P. P., Lamastra, L., Ficocelli, S., Intini, F., De Leo, F. & De Donno, A. 2018 Groundwater nitrate contamination and agricultural land use: a grey water footprint perspective in Southern Apulia Region (Italy). *Science of the Total Environment* **645**, 1425–1431.

Water Footprint Network, WFN 2014 Available from: http://http://waterfootprint.org/ (accessed 01 Jan 2021).

World Health Organization (WHO) 2011 *WHO Guidelines for Drinking-Water Quality*. Washington, DC.
Yapıcıoğlu, P. 2019a Grey water footprint of a dairy industry wastewater treatment plant: a comparative study. Water Practice and Technology 14 (1), 137–144.
Yapıcıoğlu, P. 2019b Seasonal water footprint assessment for a paint industry wastewater treatment plant. Sakarya University Journal of Science 23 (2), 175–183.
Yapıcıoğlu, P. 2020 Grey water footprint assessment for a dye industry wastewater treatment plant using Monte Carlo simulation: influence of reuse on minimisation of the GWF. International Journal of Global Warming 21 (2), 199–213.
Yapıcıoğlu, P., Derin, P. & Yeşilınacar, M. I. 2020 Assessment of Harran plain groundwater in terms of arsenic contamination. Geological Bulletin of Turkey 63 (1), 137–144.
Yeşilınacar, M. I. & Güllüoğlu, M. S. 2008 Hydrochemical characteristics and the effects of irrigation on groundwater quality in Harran Plain, GAP Project, Turkey. Environmental Geology 54, 183–196.
Yeşilınacar, M. I. & Yenigün, I. 2011 Effect of irrigation on a deep aquifer: a case study from semi-arid Harran Plain, GAP Project, Turkey. Bulletin of Engineering Geology and the Environment 70, 213–221.

First received 10 February 2021; accepted in revised form 22 July 2021. Available online 5 August 2021