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Grey water footprint assessment of geothermal water resources in the southeastern Anatolia region

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Abstract: This paper aimed to determine the grey water footprint (GWF) of geothermal water resources and to investigate the effect of biochar adsorption on grey water footprint in Southeastern Turkey. In this paper, GWF has been calculated in terms of iron (Fe), arsenic (As), manganese (Mn), boron (B), and chrome (Cr) concentrations for fifteen observation geothermal resources located in Southeastern Anatolia Region. In this study, a new approach based on the GWF was developed in order to determine the geothermal water pollution. Grey water footprints related to fifteen geothermal resources were investigated. In the second stage of the study, the effect of biochar adsorption on GWF was estimated using Monte Carlo simulation. The results revealed that arsenic led to higher GWF than other pollutant parameters in geothermal water resources. Biochar application could reduce the GWF according to Monte Carlo simulation. The total average reduction of GWF would be approximately 95, 93.1, 87.5, 96, and 90% respectively for Fe, As, Mn, B and Cr pollution if biochar adsorption is applied for geothermal water treatment.

Key words: Geothermal water, grey water footprint, biochar, Southeastern Anatolia Region, Monte Carlo simulation

1. Introduction

The use of geothermal water is restricted owing to the presence of some toxic materials such as boron, arsenic, manganese, iron, chrome, and the other heavy metals (Derin, 2019; Derin et al., 2020; Ernst et al., 2021). So, geothermal water could be treated properly to remove these pollutant substances using advanced water treatment methods. Some assessment tools have been developed in order to measure and monitor the pollution level of geothermal water. One of these assessment methods is the grey water footprint (GWF) developed by Water Footprint Network (WFN) (WFN, 2014; Yapıcıoğlu, 2020).

The grey water footprint (GWF) is a tool in order to determine the lowest volume of fresh water required diluting contaminant loads with regard to the existing water quality standards (Morera et al., 2016). In this paper, a new approach was developed based on the GWF for the evaluation of geothermal water pollution in terms of heavy metal pollution. Water scarcity has been described as the lack of sufficient accessible freshwater resources to meet the water requirements in a society. The control of water supplies has a critical importance for the countries that have water scarcity such as Turkey (Yapıcıoğlu, 2019a; Yapıcıoğlu, 2020). It is important to preserve the water supplies from pollutions. GWF is an indicator term to monitor the effect of pollutants on the water supplies. From this perspective, GWF of geothermal resources located in the Southeastern Anatolia Region, which contains heavy metals, was investigated in this study.

Turkey, which is located on the Alp-Himalayan orogenic belt, is among the first countries in the world in terms of its geothermal potential because of the widespread formation of geothermal systems. The Southeastern Anatolia Region constitutes a part of this potential with existing resources. The Southeastern Anatolia Region hosts important geothermal systems. Geology, hydrothermal, geophysical, and well information produced in previous studies in the region show that the region has an important geothermal potential (Baba et al., 2019; Derin et al., 2020). From this viewpoint, GWF assessment of geothermal water resources located in Southeastern Anatolia Region has been carried out in this study.

Many researchers focused on grey water footprint of surface water resources. In the literature, the studies related to this topic are very limited. In a study by Serio et al. (2018), they aimed to determine the relationship between groundwater nitrate contamination and agricultural practices, through a similar GWF approach. Miglietta et al. (2017) investigated the grey water footprint of groundwater in Italy for each chemical parameter,

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indicated an extensive pollution 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 goal of this study is to determine the contamination of geothermal water resources and to investigate the effect of biochar adsorption on grey water footprint in Southeastern Turkey. The novelty of this study is that a new estimation model has been adapted for grey water footprint of geothermal water resources. The other originality of this work is biochar application for geothermal water treatment, and this application could be considered as a grey water footprint minimization technique. Biochar application has been carried out to treat geothermal water in order to reduce the GWF. Capsicum annuum (Urfa Isot pepper), which is traditional crop of Turkey, could be used to generate biochar using slow pyrolysis (Qambrani et al., 2017). In the final stage of the study, it has been considered that biochar application could be an alternative to minimize the GWF. The effect of this process on the GWF has been determined using Monte Carlo simulation considering treatment efficiencies and pollutant removal capacities.

2. Materials and methods

2.1. The study area

The Southeastern Anatolia Region contains important geothermal systems. The previous studies carried out by MTA (Mineral Research and Exploration General Directorate) show that it has high geothermal potential (GAP, 2015). Therefore, geothermal water resources located in Diyarbakır, Gaziantep, Mardin, Şanlıurfa, Siirt, and Şırnak provinces were selected as the study areas.

Siirt (Billuris (1), Lif (2), Botan (3)), Şanlıurfa (Karaali (4) and Kabahaydar (5)), Şırnak (Ilıcak (Spring water (6), Zümrüt spa (7), Beytüşşebap drinking water (8), Kaniyagerm (9), Besta (I-II) (10,11), İkizce (12)), Diyarbakır (Çermik (13)), Mardin (Germav (14)), and Gaziantep (Kartalköy (15)) are the observed geothermal water resources for iron (Fe), arsenic (As), manganese (Mn), boron (B), and chrome (Cr) concentrations in the Southeastern Anatolia Region. Figure has demonstrated the location map of study area. The major reasons for selecting these observation resources are that they have high potential of pollution, and they are close to the city centers. In this study, heavy metal analyses have been performed according to standard methods (APHA, 1995) using ICP-MS technique by outsourcing service. Table 1 has demonstrated chemical analyses results of geothermal water resources.

2.2. Estimation of GWF

The grey water footprint calculates the quantity of water required to assimilate a contaminant load generated from general activities (Hoekstra et al., 2011; Yapıcıoğlu, 2019b). The GWF is an indicator of water pollution. The basic calculation term developed by Hoekstra et al. (2011) was given in Eq. (1). In Eq. (1), Lpollution 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 body of water. In Eq. (2), Lpollution was described. "α" means to the leaching-runoff fraction and s indicates the amount of chemical substance used in the soil at a to fertilize, manure, or pesticides (Franke et al., 2013).

$$GWF= \frac{Lpollution}{(Cmax-Cnat)} \tag{1}$$

$$Lpollution = \alpha \times s \tag{2}$$

The recommended estimation term for the GWF in the Water Footprint Assessment (WFA) (Eq. (1)) (Hoekstra et al., 2011) has been modified for geothermal water treatment, in this study. A basic calculation model based on the contaminant mass balance has been developed in order to figure out the GWF in this paper. The modified equation was given in Eq. (3).

$$GWF = \frac{(Q\times Cg)}{(Cmax-Cnat)} \tag{3}$$

At this modified version, treated groundwater volume and the pollutant concentrations were considered. In Eq. (3), Q represents the geothermal water flow rate (volume/time) and Cg means to the concentration of a pollutant in a geothermal water resource. Similarly, with the basic model, Cmax indicates the permissible maximum concentration of pollutant according to the legal standards, and Cnat shows the natural concentration of contaminants in the body of water. Cg could be obtained from the heavy metal analyses in water 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. Cmax values were ensured from World Health Organization (WHO) Guidelines for Drinking-Water Quality (WHO, 2011).

2.3. Effect of biochar adsorption process using Monte Carlo simulation

Biochar has gained the significant importance 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 heavy metals immediately. Biochar could be produced from Capsicum annuum (Locally known name: Urfa Isot peppers) using slow pyrolysis method. In this section, the effect of biochar adsorption process was simulated to this study using Monte

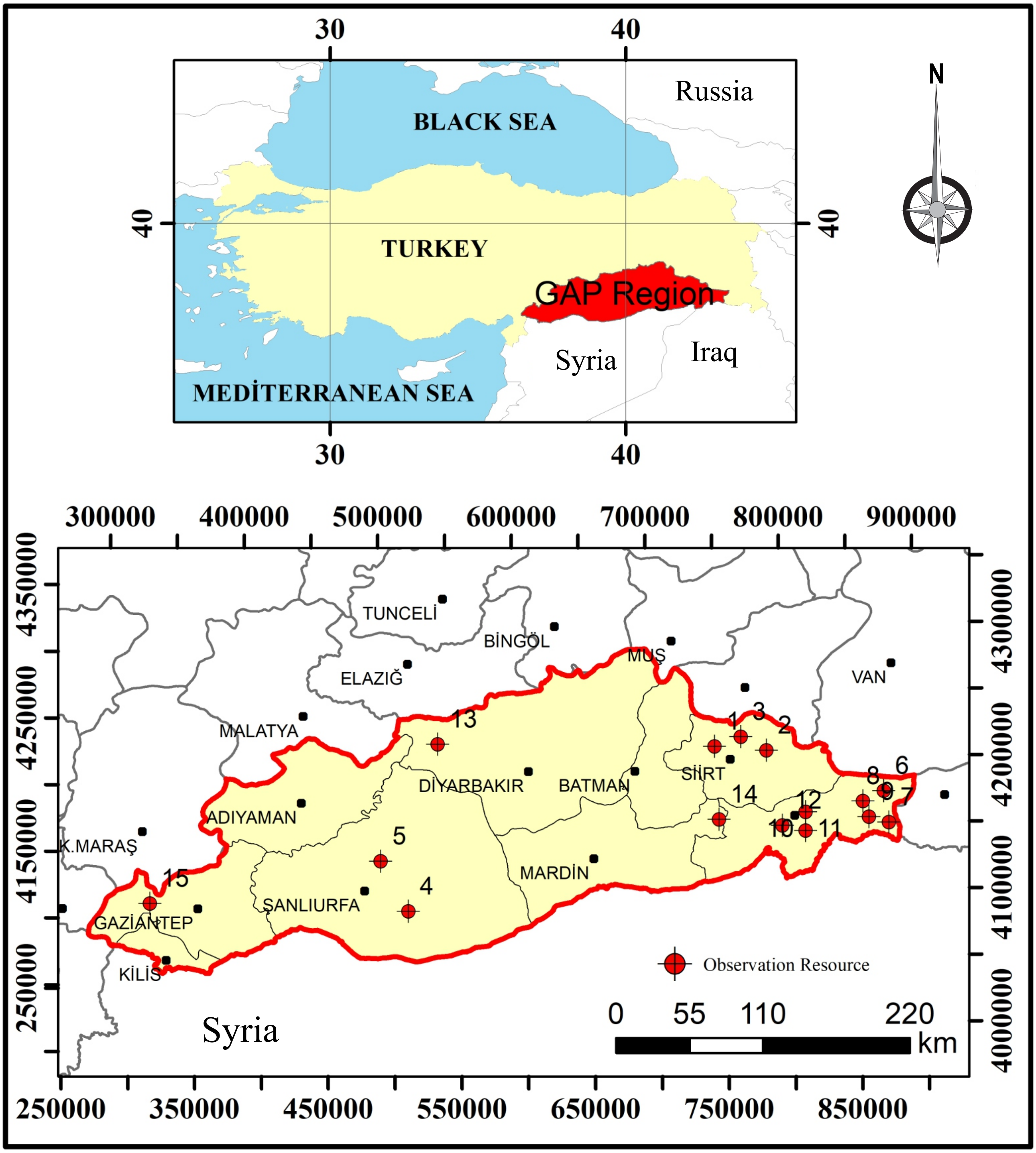

Figure. The location map of the study area.

Carlo simulation methodology. A reduction was estimated using biochar treatment due to adsorption process of pollutant in geothermal water. Monte Carlo simulation is a numerical method which composes random variables for modelling the uncertainty of a system. Various probability distributions have been carried out in order to model

Table 1. Chemical characteristics of geothermal water resources.

Observation Resource	Fe (ppm)	As (ppb)	Mn (ppb)	B (ppb)	Cr (ppb)	Cd (ppb)	Cl (ppb)	Pb (ppb)	pH value
Billuris	9	24.20	14.57	778	8.3	<0.05	200	<0.1	6.40
Lif	8	27.80	13.78	860	9.5	<0.05	223	<0.1	6.50
Botan	105	3.40	16.47	115	3.3	<0.05	26	0.1	7.02
Karaali	39	44.00	3.15	211	0.6	0.18	51	<0.1	8.80
Kabahaydar	79	1.80	24.27	454	5.5	<0.05	132	<0.1	8.90
Ilıcak-Spring Water	9.3	0.60	9.75	11	2	0	<1	0.3	6.90
Ilıcak-Zümrüt Thermal Water	9.5	333.10	21.64	1000	7.4	<0.05	299	<0.1	8.50
Ilıcak-Beytüşşebap Drinking Water	46	0.50	81.22	17	2.7	0	2	<0.1	7.25
Ilıcak-Kaniyagerm	10	335.20	1.95	171	3.2	0	38	<0.1	7.45
Besta-I	9.8	15.30	66.17	432	4.5	<0.05	43	<0.1	7.18
Besta-II	42	13.40	78.62	423	3.7	<0.05	43	<0.1	7.22
İkizce	26	1.50	6.36	3364	16.5	<0.05	167	<0.1	8.01
Çermik	9.6	1.70	2.91	723	0.5	<0.05	129	<0.1	7.27
Germav	10000	3000.00	49	400	300	<700		<4000	10
Kartalköy	9.1	1.10	0.05	101	0.8	<0.05	96	<0.1	6.50

the input variables such as normal, lognormal, uniform, and triangular (Kroese et al., 2014). RISK 7.6 software by Palisade was used to apply Monte Carlo simulation, in this paper. The validation of simulation was performed by the licensed software firm (Palisade). Volumetric Reserves 0-Model with no uncertainty module was selected by implementing 10.000 iterations and 1 simulation.

The iterations (runs) are the tools to carry out the simulation. A simulation contains 10.000 iterations. Probability distribution was decided as lognormal distribution. The uncertain inputs were GWFbiochar values related to biochar adsorption process. The outputs were in the range of 85%–97% of adsorption capacity (AC) of biochar. The adsorption capacities of heavy metals by biochar were ensured from the previous studies in the literature (Qambrani et al., 2017). In the end of the simulation study, minimum GWF was determined with biochar adsorption process. The model related to this simulation was shown in Eq. (4). The minimum GWF is the desired output according to this simulation study.

GWFmin = RiskOutput(“Lognormal”)+RiskLognorm (GWFbiochar; AC) (4)

GWFmin = Minimum grey water footprint

GWFbiochar = Grey water footprint of biochar treatment

AC = Adsorption capacity of biochar

3. Results

3.1. GWF assessment of geothermal water resources

According to the analyses results, heavy metal concentrations were higher than allowable limits (WHO, 2011) in some geothermal water resources. So, the values of GWF were higher in these locations. Table 2 demonstrated the GWF assessment results in details.

The results showed that the GWF values related to arsenic (As) contamination was the highest in this study. The results revealed that the highest GWF corresponded to Germav (Mardin) geothermal resource (181440 m^3/d). It could be resulted from industrial activities in this city. Especially, mineral industries are widespread in Mardin province. Also, this geothermal resource is a hot spring which is an arsenic supply. In Germav (Mardin) geothermal resource, GWF of Fe, Mn, B and Cr were 30240, 592.7, 241.9 and 3628.8 m^3/d, respectively. The lowest GWF corresponded to Mn contamination with the value of 0,6 m^3/d. This GWF was calculated for Kartalköy (Gaziantep) geothermal resource. In Kartalköy geothermal resource, the values of GWF related to Fe, As, B and Cr were figured out as 27.5, 66.5, 61.1, and 9.7 m^3/d, respectively. In Lif and Billuris (Siirt) resources, the highest GWF were related to As contamination. The lowest GWF corresponded to Fe contamination. In contrast, in Botan spring (Siirt), Fe led to the highest GWF (317.5 m^3/d) and Cr led to the lowest GWF (69.5 m^3/d). In Şanlıurfa, Karaali geothermal resource, As has the highest GWF (2661.1 m^3/d) and Cr led to the lowest GWF (7.2 m3/d). Similarly, in Kabahaydar geothermal resource, Cr has the lowest with the value of 66.5 m^3/d. Mn led to the highest GWF in this spring. In Şırnak, (Besta I-II) As and Mn led to the highest GWF, and Cr led to the lowest GWF. In Çermik (Diyarbakır), B led to the highest GWF and Cr led to the lowest GWF.

Table 2. GWF assessment of geothermal water resources.

	Fe					As					Mn				
Observation Resource	Q (m^3/d)	Cg (ppm)	Cnat (ppm)	Cmax (ppm)	$GWF_{,Fe}$ (m^3/d)	Q (m^3/d)	Cg (ppb)	Cnat (ppb)	Cmax (ppb)	$GWF_{,As}$ (m^3/d)	Q (m^3/d)	Cg (ppb)	Cnat (ppb)	Cmax (ppb)	$GWF_{,Mn}$ (m^3/d)
Billuris	604.8	9	0	200	27.22	604.8	24.20	0	10	1463.6	604.8	14.57	0	50	176.24
Lif	604.8	8	0	200	24.19	604.8	27.80	0	10	1681.3	604.8	13.78	0	50	166.68
Botan	604.8	105	0	200	317.52	604.8	3.40	0	10	205.6	604.8	16.47	0	50	199.22
Karaali	604.8	39	0	200	117.94	604.8	44.00	0	10	2661.1	604.8	3.15	0	50	38.10
Kabahaydar	604.8	79	0	200	238.90	604.8	1.80	0	10	108.9	604.8	24.27	0	50	293.57
Ilıcak-Spring Water	604.8	9.3	0	200	28.12	604.8	0.60	0	10	36.3	604.8	9.75	0	50	117.94
Ilıcak-Zümrüt Thermal Water	604.8	9.5	0	200	28.73	604.8	333.10	0	10	20145.9	604.8	21.64	0	50	261.76
Ilıcak-Beytüşşebap Drinking Water	604.8	46	0	200	139.10	604.8	0.50	0	10	30.2	604.8	81.22	0	50	982.44
Ilıcak-Kaniyagerm	604.8	10	0	200	30.24	604.8	335.20	0	10	20272.9	604.8	1.95	0	50	23.59
Besta-I	604.8	9.8	0	200	29.64	604.8	15.30	0	10	925.3	604.8	66.17	0	50	800.39
Besta-II	604.8	42	0	200	127.01	604.8	13.40	0	10	810.4	604.8	78.62	0	50	950.99
İkizce	604.8	26	0	200	78.62	604.8	1.50	0	10	90.7	604.8	6.36	0	50	76.93
Çermik	604.8	9.6	0	200	29.03	604.8	1.70	0	10	102.8	604.8	2.91	0	50	35.20
Germav	604.8	10000	0	200	30240.00	604.8	3000.00	0	10	181440,0	604.8	49	0	50	592.70
Kartalköy	604.8	9.1	0	200	27.52	604.8	1.10	0	10	66.5	604.8	0.05	0	50	0.60

Table 2. GWF assessment of geothermal water resources (continued).

	B					Cr					
Observation Resource	Q (m^3/d)	Cg (ppm)	Cnat (ppm)	Cmax (ppm)	$GWF_{,B}$ (m^3/d)	Q (m^3/d)	Cg (ppb)	Cnat (ppb)	Cmax (ppb)	$GWF_{,Cr}$ (m^3/d)	Total GWF (m^3/d)
Billuris	604.8	778	0	1000	470.53	604.8	8.3	0	50	100.40	2238.0
Lif	604.8	860	0	1000	520.13	604.8	9.5	0	50	114.91	2507.3
Botan	604.8	115	0	1000	69.55	604.8	3.3	0	50	39.92	831.8
Karaali	604.8	211	0	1000	127.61	604.8	0.6	0	50	7.26	2952.0
Kabahaydar	604.8	454	0	1000	274.58	604.8	5.5	0	50	66.53	982.4
Ilıcak-Spring Water	604.8	11	0	1000	6.65	604.8	2	0	50	24.19	213.2
Ilıcak-Zümrüt Thermal Water	604.8	1000	0	1000	604.80	604.8	7.4	0	50	89.51	21130.7
Ilıcak-Beytüşşebap Drinking Water	604.8	17	0	1000	10.28	604.8	2.7	0	50	32.66	1194.7
Ilıcak-Kaniyagerm	604.8	171	0	1000	103.42	604.8	3.2	0	50	38.71	20468.9
Besta-I	604.8	432	0	1000	261.27	604.8	4.5	0	50	54.43	2071.1
Besta-II	604.8	423	0	1000	255.83	604.8	3.7	0	50	44.76	2189.0
İkizce	604.8	3364	0	1000	2034.55	604.8	16.5	0	50	199.58	2480.4
Çermik	604.8	723	0	1000	437.27	604.8	0.5	0	50	6.05	610.4
Germav	604.8	400	0	1000	241.92	604.8	300	0	50	3628.80	216143.4
Kartalköy	604.8	101	0	1000	61.08	604.8	0.8	0	50	9.68	165.4

Table 3. GWF reduction applying biochar adsorption using Monte Carlo simulation.

Location Nos	Observation Point	GWF_{Fe} (m^3/d)	Reduction (%)	GWF_{As} (m^3/d)	Reduction (%)	GWF_{Mn} (m^3/d)	Reduction (%)	GWF_{B} (m^3/d)	Reduction (%)	GWF_{Cr} (m^3/d)	Reduction (%)
1	Billuris	1.1	95.8	102.2	93.0	21.0	88.1	18.8	96.0	10.0	90.0
2	Lif	1.2	95.0	117.9	93.0	19.8	88.1	20.6	96.0	11.5	90.0
3	Botan	15.9	95.0	14.5	92.9	24.0	88.0	2.8	96.0	4.0	90.0
4	Karaali	7.2	93.9	184.5	93.1	4.6	88.0	5.1	96.0	0.7	90.0
5	Kabahaydar	9.2	96.1	6.7	93.9	35.2	88.0	11.0	96.0	6.7	90.0
6	Ilıcak-Spring Water	1.4	94.9	2.5	93.0	13.9	88.2	0.3	95.9	2.4	90.0
7	Ilıcak-Zümrüt Thermal Water	1.4	95.0	1409.2	93.0	30.2	88.4	27.2	95.5	9.0	90.0
8	Ilıcak-Beytüşşebap Drinking Water	7.2	94.8	2.1	93.0	117.8	88.0	0.4	96.2	3.3	90.0
9	Ilıcak-Kaniyagerm	1.5	95.0	1418.3	93.0	2.8	88.0	3.9	96.2	3.9	90.0
10	Besta-I	1.5	95.0	64.7	93.0	96.0	88.0	10.5	96.0	5.4	90.0
11	Besta-II	6.5	94.9	56.2	93.1	114.2	88.0	10.2	96.0	4.5	90.0
12	İkizce	4.1	94.8	6.0	93.3	9.1	88.2	81.6	96.0	20.0	90.0
13	Çermik	1.5	95.0	7,3	92.9	4.2	88.0	17.5	96.0	0.6	90.0
14	Germav	1512.0	95.0	12700.8	93.0	71.1	88.0	9.7	96.0	362.9	90.0
15	Kartalköy	1.4	95.0	4.8	92.7	0.1	80.0	2.4	96.0	1.0	90.0

Considering the total GWF of geothermal water resources, Germav (Mardin) has the highest GWF with the value of 216143.4 m^3/d due to high arsenic contamination and the lowest GWF related to Ilıcak Spring Water (Şırnak) (213.2 m^3/d). As is the main pollutant parameter for GWF assessment. Table 2 shows the values of total GWF on a water resources basis.

3.2. Effect of biochar treatment on grey water footprint

In this study, the effect of biochar adsorption on GWF was determined using Monte Carlo simulation. Table 3 demonstrated the simulation results. The results showed that biochar adsorption could reduce the grey water footprint of all observation resources.

Total average reduction of GWF is 92.3% if biochar adsorption is carried out for geothermal water treatment. The average reduction of GWF corresponded to arsenic was 93.1%. The average reduction of GWF related to Fe contamination is nearly 95% and the minimization of GWF in terms of Mn contamination 87.5%. Reduction of GWF related to B and Cr contamination would be 96 and 90%, respectively. It was obvious that biochar adsorption could reduce the water contaminants. It could dilute the water composition.

4. Discussion

There are limited studies related to grey water footprint of water resources. This study is unique, which investigates the GWF of geothermal resources. Many developed models for the GWF assessment were carried out for surface water 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 using a similar calculation model with this study. The studies related to freshwater 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 developed by Hoekstra et al., 2011 with this study. They investigated the groundwater nitrate contamination and agricultural land use in a GWF approach in Southern Apulia Region (Italy). They reported that higher nitrate GWF values for vineyards than for olive groves, particularly in areas used to produce table grapes. Another study was performed by Miglietta et al. (2017). They reported that an extensive pollution by Mercury (Hg), Vanadium (V), and Ammonium (NH_4^+) with concentrations higher than the limits. They figured out the GWF values for each chemical parameter. They 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. This study confirmed that heavy metal pollution leads to grey water footprint in the geothermal resources. Aldaya et al. (2020) reported that the variation of GWF corresponded to the variation of the nutrient loads, which are the highest in areas of intensive agriculture similarly with this study.

5. Conclusion

This paper shows that the grey water footprint is an important indicator of water pollution. It could be used as the indicator for the sustainability of geothermal water resources.

The results revealed that arsenic led to higher GWF in geothermal water resources in the southeastern Anatolia region in Turkey. Also, biochar adsorption process could reduce the GWF according to the simulation study. Total average minimization of GWF would be approximately 95, 93.1, 87.5, 96, and 90% respectively for Fe, As, Mn, B, and Cr pollution if biochar adsorption is carried out for geothermal water treatment.

It is possible to decrease the grey water footprint using biochar adsorption processes. Nearly, total reduction up to 92.3% has been calculated by applying biochar adsorption in geothermal water resources in the southeastern Anatolia region in Turkey. It was clear that biochar adsorption could decrease the water pollutant materials. It could dilute the water composition. So, biochar treatment could be carried out in order to protect the geothermal water resources.

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