Environmental Research 217 (2023) 114827

Contents lists available at ScienceDirect

Environmental Research

journal homepage: www.elsevier.com/locate/envres

# A data-driven modeling approach for the sustainable remediation of persistent arsenic (As) groundwater contamination in a fractured rock aquifer through a groundwater recirculation well (IEG-GCW®)

Paolo Ciampi [a,*], Carlo Esposito [a], Ernst Bartsch [b], Eduard J. Alesi [b], Gert Rehner [b], Piero Morettin [c], Michele Pellegrini [d], Sandro Olivieri [d], Mauro Ranaldo [d], Giovanni Liali [d], Marco Petrangeli Papini [e]

[a] *Department of Earth Sciences, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185, Rome, Italy*
[b] *IEG Technologie GmbH, Hohlbachweg 2, D-73344, Gruibingen, Baden-Württemberg, Germany*
[c] *Enki Ambiente Srl, Via Zandonai 6, 30174, Mestre, Italy*
[d] *Eni Rewind SpA, Via Ribotta 51, 00144, Rome, Italy*
[e] *Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185, Rome, Italy*

ARTICLE INFO

*Keywords:*
Arsenic remediation
Fractured rock
Groundwater circulation wells
3D geological modeling
Multi-source geodatabase
Conceptual site model

ABSTRACT

Persistent arsenic (As) pollution sources from anthropogenic activities pose a serious threat to groundwater quality. This work aims to illustrate the application of an innovative remediation technology to remove As from a heavily contaminated fractured aquifer at a historically polluted industrial site. Groundwater circulation well (GCW) technology was tested to significantly increase and accelerate the mobilization and removal of As in the source area. The GCW extracts and re-injects groundwater at different depths of a vertical circulation well. By pumping out and reinjecting in different screen sections of the well, the resulting vertical hydraulic gradients create recirculation cells and affect and mobilize trapped contaminants that cannot be influenced by traditional pumping systems. The first 45-m deep IEG-GCW® system was installed in 2020, equipped with 4 screen sections at different depths and with an above-ground As removal system by oxidation and filtration on Macrolite (Enki). A geomodeling approach supports both remediation and multi-source data interpretation. The first months of operation demonstrate the hydraulic effectiveness of the IEG-GCW® system in the fractured rock aquifer and the ability to significantly enhance As removal compared to conventional pumping wells currently feeding a centralized treatment system. The recirculation flow rate amounts to about 2 $m^3$/h. Water pumped and treated by the GCW system is reintroduced with As concentrations reduced by an average of 20%–60%. During the pilot test, the recirculating system removed 23 kg As whilst the entire central pump-and-treat (P&T) system removed 129 kg, although it treated 100 times more water volume. The P&T plant removed 259 mg As per $m^3$ of pumped and treated groundwater while the GCW removed 4814 mg As per $m^3$ of the treated groundwater. The results offer the opportunity for a more environmentally sustainable remediation approach by actively attacking the contamination source rather than containing the plume.

## 1. Introduction

Arsenic (As) is among the most toxic groundwater contaminants and is widely distributed worldwide (Adeloju et al., 2021; Armienta and Segovia, 2008; Bretzler et al., 2019; Dalla Libera et al., 2020; Gong et al., 2020; Ghosh et al., 2019; Harvey et al., 2006; Li et al., 2020; Liu et al., 2016; Liang et al., 2019; Litter et al., 2019; Shaji et al., 2021; Singh et al., 2015; Thouin et al., 2016; Zhang et al., 2019; Zuzolo et al., 2020). The occurrence of As in groundwater is associated with both geogenic and anthropogenic processes. Release and dissolution from As-rich minerals

* **Corresponding author.**;
*E-mail addresses:* paolo.ciampi@uniroma1.it (P. Ciampi), carlo.esposito@uniroma1.it (C. Esposito), ernst.bartsch@ieg-technology.com (E. Bartsch), eduard.alesi@ieg-technology.com (E.J. Alesi), gert.rehner@ieg-technology.com (G. Rehner), piero.morettin@enkiambiente.it (P. Morettin), michele.pellegrini@enirewind.com (M. Pellegrini), sandro.olivieri@enirewind.com (S. Olivieri), mauro.ranaldo@enirewind.com (M. Ranaldo), giovanni.liali@enirewind.com (G. Liali), marco.petrangelipapini@uniroma1.it (M.P. Papini).

https://doi.org/10.1016/j.envres.2022.114827
Received 30 May 2022; Received in revised form 12 October 2022; Accepted 14 November 2022
Available online 18 November 2022
0013-9351/© 2022 The Authors. Published by Elsevier Inc. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

represent a source of natural contamination (Zuzolo et al., 2020). On the other hand, human activities related to fertilizer or pesticide use, mining, and industrial production aggravate the As pollution status of environmental matrices (Asere et al., 2019; Maity et al., 2021; Singh et al., 2015; Zhang et al., 2019). The spatial distribution of heavy metals in groundwater in industrial areas and the assessment of risks and impacts on human health are under study (Khan et al., 2022). As exists in groundwater in different oxidation states, of which arsenite [As (III)] and arsenate [As (V)] are the most common (Fazi et al., 2016). The mobility of As species is related to environmental conditions such as pH and redox potential (Adeloju et al., 2021; Liu et al., 2016; Thouin et al., 2016). Great attention is given to the removal of As (III) from groundwater due to its toxicity (Ghosh et al., 2019; Kanel et al., 2016). Also, most treatment systems are more effective in removing the pentavalent species of As rather than the trivalent form (Litter et al., 2019). For this motive, the oxidation of As (III) to As (V) is often a necessary step in groundwater remediation (Fazi et al., 2016). Conventional As remediation techniques involve physical extraction and treatment of groundwater (i.e. Pump & Treat, P&T). These mitigation strategies do not result eco-friendly and sustainable since they require pumping huge amounts of water to achieve a satisfactory As removal rate, take considerable time to fully remediate the aquifer, and are costly (Mondal et al., 2013; Sharma et al., 2014). Traditional and advanced treatment systems for As removal from groundwater include coagulation/flocculation, oxidation/reduction, electrokinetic and membrane processes, adsorption, ion exchange, phytoremediation, and biofiltration (Alka et al., 2021; Asere et al., 2019; Lima et al., 2022; Litter et al., 2019). Recently, new efficient resin-based materials have been synthesized for the adsorption of metal ions from aqueous media (Jalbani et al., 2021). Several studies show that the electrocoagulation (EC) technique, also combined with one or more treatment processes, can efficiently remove As from contaminated water (Al-Qodah et al., 2020; López-Guzmán et al., 2019). Some authors have investigated the possibility of utilizing ultrasound as a powerful oxidation technique in combination with advanced oxidation processes (AOPs) for water decontamination (Al-Bsoul et al., 2020). Irshad et al. (2022) explored the application of goethite-modified biochar (GMBC) to immobilize As and limit its bioavailability in paddy soils. Numerous technological advancements result from literature; however, many are limited to the lab scale. The implementation of field scale As treatment demands extensive attention and is critical for understanding the efficacy, suitability, and sustainability of novel As removal technologies (Yadav et al., 2021).

The design of an effective remediation intervention depends on the site-specific geological and physicochemical characteristics, which define the conceptual site model (CSM) (O'Brien et al., 2021; Dalla Libera et al., 2020; Price et al., 2017; Utom et al., 2019). The construction of a multi-source geodatabase and the realization of a joint model can face the simultaneous integration of data from multiple modalities, measuring diverse properties with varying resolutions (Ciampi et al., 2019a, 2019b, 2021a, 2021b, 2022a; Flores Orozco et al., 2021). A 3D digital CSM put together different sources of knowledge typically found at most contaminated sites, enhancing the exchange of information in the multidisciplinary nature of the elements involved. The hydrogeochemical CSM becomes a multicriterial decision analysis interface for the selection, adaption, and monitoring of an effective and sustainable remediation strategy (Havranek, 2019; Huysegoms and Cappuyns, 2017).

Our paper focuses on an industrial site bordering the Adriatic Sea in southern Italy, where a severe accident in 1976 caused persistent groundwater contamination by As. The explosion of a column for the $CO_2$ removal from the synthesis gas used in the ammonia production caused the release of a huge amount of arsenic compounds into the atmosphere ($As_2O_3$ was used in the washing aqueous solution to enhance $CO_2$ removal) with a consequent fall-out causing contamination of topsoil in a large area. The explosion also resulted in the spillage of high amounts of the aqueous solution containing high concentrations of $As_2O_3$ (Liberti and Polemio, 1981; Gianicolo et al., 2019; Mangia et al., 2018), migrating through the unsaturated zone and reaching the aquifer, characterized by a fractured rock formation. Accumulation, precipitation, and concentration of As oxides into the complex fractured aquifer architecture determine the consolidation of persistent slow-release secondary sources that may explain the occurrence of significant dissolved As concentrations in the aquifer after 45 years since the primary contamination event. A P&T system has been realized as a containment intervention of the plume inside the plant to avoid the migration of dissolved contaminants toward the sea (Mackay and Cherry, 1989) and to progressively reduce the total mass of As still in the aquifer. The intervention applied over the years has been completed by a series of wells, which inject uncontaminated water into the aquifer in the area downstream of the plant. The recharge of the aquifer is aimed at reversing the groundwater flow near the coastline, creating a reverse hydraulic gradient to counteract the intrusion of saltwater deriving from the extraction activities inside the plant (Barlow and Reichard, 2010; Werner et al., 2013). Pump-and-treat (P&T) with down gradient surplus freshwater injection (barrier) has been used for more than 30 years to mitigate off-site migration (Beretta, 2017). Yet a significant mass of As persists in the fractured aquifer.

Groundwater circulation well (GCW) technology was evaluated as an applicable hydraulic system to significantly improve mobilization and acceleration of As removal in the existing fractures of the source area. GCW technology induces groundwater recirculation by extracting and re-injecting groundwater into the same aquifer body at different screens constituting a multi-screened well (Herrling et al., 1991a, 1991b, 1993a, 1993b; Bott-Breuning and Alesi, 1993; Stamm, 1997). The significant vertical hydraulic gradients induce the formation of recirculation cells that potentially mobilize contaminants trapped in fractures of the aquifer that are unaffected by traditional pumping systems (Stamm, 1997; Petrangeli Papini et al., 2016; Pierro et al., 2017; Ciampi et al., 2019a; Ciampi et al., 2021a; Tatti et al., 2019). In previous work, recirculating systems have been applied in porous media. Also, the GCW has been coupled with reagent injection wells to optimize the distribution of chemical solutions in the aquifer and enhance pollutant degradation (Ciampi et al., 2022c). Specifically engineered groundwater recirculation systems may also be advantageously applied in the case of limited saturated thicknesses (Ciampi et al., 2022b). At the highly polluted industrial site, a pilot plant (the first of its kind) consisting of a 45 m deep IEG-GCW®, equipped with 4 screened sections at different depths, direct screen access via peripheral pipes, and a treatment system for the removal of dissolved As by oxidation and filtration on Macrolite (Enki), has been installed and started up in the source area during the sanitary emergency period (September 2020). The first months of operation demonstrated the hydraulic effectiveness of the IEG-GCW® in a fractured rock aquifer, but also the ability to significantly increase As mobilization compared to conventional pumping wells. The encouraging results of the first operational months offer clear insights regarding the efficiency and sustainability of the intervention, providing a technological comparison between a classical plume containment system (P&T) and a strategy that acts on the As contamination source in a deeply fractured aquifer. This can significantly reduce remediation efforts, cost, and remediation time, particularly limiting the consumption of freshwater resources currently used in the groundwater treatment process. Contrary to what has been studied in the literature, the present work aims to study the field application of a GCW for the mobilization of a persistent As source in a fractured aquifer and the As removal by limiting water consumption through groundwater recirculation. To the best of the authors' knowledge and considering the state of the art, such treatment and remediation technology in this geological scenario represents the first of its kind and has not yet been reported in the literature. The pilot application is currently in progress and aims to provide both site-specific hydraulic parameters for the design of the full-scale intervention and valuable indications for the design of similar interventions at industrial sites in coastal areas with fractured rock aquifers. The pilot test has the goals of a) demonstrating the effectiveness of IEG-GCW® in geological contexts characterized by fractured limestone, b) verifying the possibility of recirculating water in the particular hydrogeological context, and evaluating the radius of influence (ROI), c) verifying the Arsenic mobilization induced by recirculation systems, d) evaluating the ability and sustainability of the system to remove As in comparison to traditional physical extraction systems active on-site; (d) defining the optimal conduction parameters to maximize As contaminant mobilization and removal capacity of the system.

## 2. Materials and methods

A conceptual flowchart of the structure of the research approach employed in this study and detailed below is shown in Fig. 1.

The multi-source data acquired since the accidental event in the different phases of site characterization and remediation by geologists, chemists, and engineers have been harmonized in a single big-data package. This multi-temporal geodatabase constituted a simultaneous multi-modality data storage model in the form of a multiple excel worksheet, organized according to the structure of a relational database (Ciampi et al., 2019a, 2019b, 2021a, 2021b, 2022a). The integrated multi-temporal information management platform stored geological-stratigraphic data deduced from 809 surveys, hydrogeological tests, hydrochemical analyses, and piezometric surveys performed on 212 wells and piezometers of the monitoring network. The stratigraphic surveys cover an area of 150 ha and reach depths between 5 and 80 m, while the data of monitored groundwater concentration refer to the period 2006–2020. Besides, the multidisciplinary big-data package contained information on the construction schemes of wells and piezometers and the discharge rates of the active remediation systems on-site.

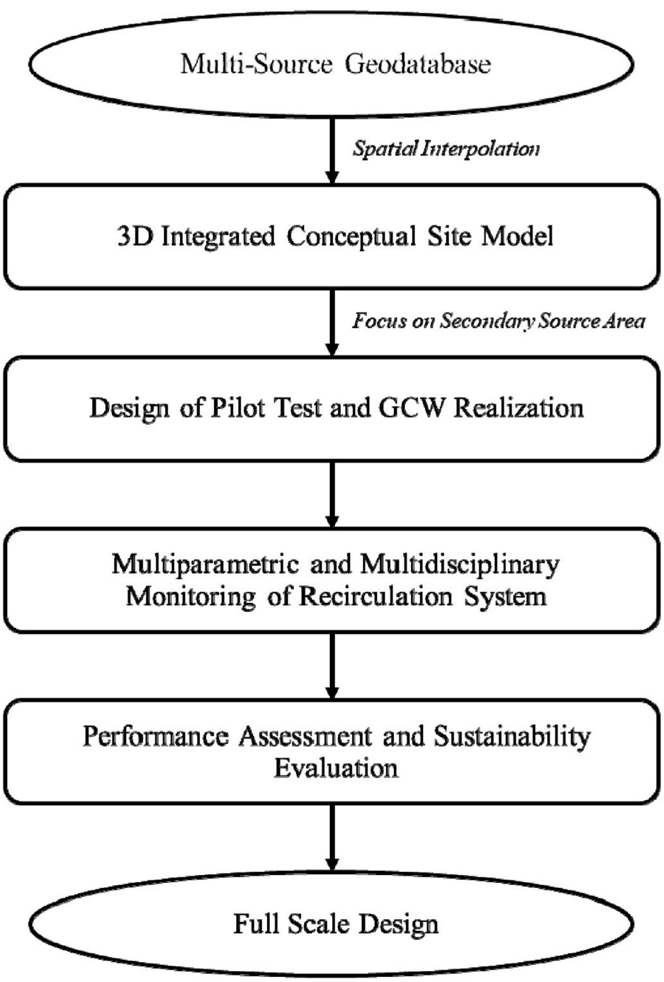


**Fig. 1.** Conceptual flowchart structure of the research approach employed in this study.

Geodatabase-driven interpolation and modeling activities aimed to generate a multi-source hydrochemical conceptual model in which all information acquired during the phases of characterization and remediation converge. The reconstruction of a solid, data-driven model results from spatial interpolation and conjoint analysis of geological and hydrochemical parameters. Such parameters comprise borehole stratigraphic data (depth and lithologic types), groundwater level elevations, hydrogeological investigations (Lugeon and pumping tests), and chemical analysis of the sampled water (contaminant concentration). The inverse distance weighting technique was employed to interpolate geological and hydrochemical parameters, utilizing five neighboring points and a weighting exponent of two. A high-fidelity filter to honor the control point value and smoothing on surfaces were also applied as geoprocessing options. The employed algorithm and adopted interpolation options ensure that the extrapolated value would gradually approach the nearest sampling point data, respecting the value of the measured variables. The hydrogeochemical model was built in the domain of a three-dimensional voxel-based mesh with node resolutions of 5 m $\times$ 5 m x 0.5 m in the x, y, and z dimensions. The solid model featured 299 (x) x 352 (y) x 307 (z) voxels and extended from −89 to 64 m a.s.l. The voxel-based stratigraphic model was constructed by interpolating the upper and lower grid surfaces of each unit itemized in the geodatabase to delineate the volumes of the different geological layers. Spatial interpolation of hydrochemical records led to the generation of 2D contour maps and 3D models to paint the As contamination scenario in the geo-referenced space and identify areas impacted by significant concentrations of pollutants in groundwater. The joint modeling aimed to generate a digital and multi-source CSM that aggregated data-driven hydrogeochemical structures. Fusion and convergence of different types of geomodeling in a data-driven hydrogeochemical interface intended (a) to schematize the geology of the subsurface, delineating the presence of secondary contamination sources, and (b) to unmask the decontamination dynamics affected by hydraulic processes due to the massive P&T system. The extraction of multi-source imaging that overlays the representation of the contamination condition within the hydrogeological patterns for the area close to the primary contamination source was intended to support the design and configurations of an innovative remediation solution that is tailored to the site-specific features, the geological and technical characteristics of the sediments, and those of the contaminants. The multi-source model had the purpose to behave as a tool for multi-criteria decision analysis, guiding the deployment of a targeted, effective, and environmentally sustainable remediation strategy (Havranek, 2019; Huysegoms and Cappuyns, 2017).

Based on the conceptual framework of the site, the applicability of an approach based on the technology of the groundwater recirculation wells (IEG-GCW®), was tested in the field for the acceleration of the mobilization processes and the depletion of As in the portions of the aquifer that present the highest concentrations. The recirculation well, with the option of extraction and re-injection in different screened depth segments, aims to create particularly significant vertical hydraulic gradients to generate recirculation cells of groundwater even in a particularly complex hydrogeological situation (Herrling et al., 1991a, 1991b, 1993a, 1993b; Bott-Breuning and Alesi, 1993; Stamm, 1997). The recirculation induced by a unique well design, and by its adaptable operational management aims to promote the groundwater flow in aquifer areas that cannot be influenced by traditional pumping systems (Petrangeli Papini et al., 2016; Pierro et al., 2017; Ciampi et al., 2019a; Ciampi et al., 2021a; Tatti et al., 2019). The pumped water is sent to an above-ground treatment system before being reintroduced through different vertical screen sections into the aquifer and the saturated zone above groundwater. The treatment system consists of an As removal module, commercially distributed by the company Enki Ambiente, which provides oxidation with sodium perchlorate and ferric chloride, a filtration on Macrolite (ceramic material with filtration capacity up to 2 μm). The realization of the test at the field scale and the variation of the operating conditions of the treatment system had the objective to verify a) the effectiveness of GCW-IEG® in geological contexts characterized by a fractured calcareous rock, b) the possibility to significantly recirculate water in the specific hydrogeological context, c) the ability to mobilize As by accelerating the process of depletion of active secondary sources (also compared to what has been achieved by the system of pumping/reinjection active in the site), d) the possibility of removing As from the extracted water before re-injection to maintain a high concentration gradient necessary for its mobilization, e) the development of the radius of influence of the well, and f) the opportunity of optimizing operating parameters (type of induced recirculation and operating flow rates), to maximize the amount of As removed and obtain useful information for the design of a treatment system of the source area at full scale. Monitoring of GCW pumping rates, As concentrations extracted and re-injected after treatment, estimation of the mobilized and removed mass of As from the recirculation system, and comparison of masses extracted/treated per unit volume from the pilot test and the entire system of pumping wells within the plant offers the evaluation of the performance and sustainability of the technology in removing the target contaminant in the particular geological context.

## 3. Results and discussion

### 3.1. The conceptual site model

The site is in an area characterized by the presence of calcareous rocks of the Mesozoic age, which are covered with gravelly-sandy or silty sediments of alluvial or detrital origin (Masciale et al., 2021). The limestones are well-stratified, fractured, and locally karstified, while the cover soils consist of calcareous pebbles with rounded edges, embedded in a sandy-loamy matrix. The contact with the underlying limestones is marked by a discontinuous and thin reddish level of calcareous breccias with a sandy-loamy matrix. The following geological sequence is observed in the area:

a) filling materials up to depths of about 1.5 m from ground level;
b) conglomerate with calcareous elements embedded in an essentially sandy matrix, at depths between 1.5 m and 8 m from the surface;
c) sandy or silty levels with sharp-edged, rounded calcareous clasts between 8 and 9 m depth (breccia);
d) a whitish-colored calcareous bedrock, found at depths generally between 9 and 55 m (Fig. 2).

The groundwater is hosted in calcareous bedrock. The water table is localized at a depth varying between about 10 and 50 m from SE to NW, influenced by the pumping activities operated by the 48 groundwater extraction wells. The hydraulic gradient inside the plant area is very low (0.03%), locally increased by pumping wells. Given the nearshore location of the site, a freshwater/saltwater interface can be identified, the depth of which increases from seaward toward the inland area of the site. 50 Lugeon tests provide the hydraulic properties of the carbonate aquifer, characterized by an average hydraulic conductivity value of 4.2 $\times 10^{-6}$ m/s 3 pumping tests gave a transmissivity value between 4.8 $\times$ $10^{-4}$ and 2.2 $\times$ $10^{-3}$ $m^2/s$ (Abedian et al., 2019). The presence of high dissolved concentrations of As appears in a well-defined area of the plant. Near the well MW1, the average concentrations observed during the entire monitored period are around 30,000 μg/L. The values are significantly lower in the remaining parts of the site (Fig. 3).

Based on historical monitoring, the distribution of As concentrations shows higher values perennially observed in the area downstream of the former plant, where the primary contamination event occurred (Liberti and Polemio, 1981; Gianicolo et al., 2019; Mangia et al., 2018). In this portion of the site, the highest concentrations of dissolved As in the groundwater were found in 2007, with values locally exceeding 200 mg/L. Since then, a gradual reduction of concentrations is observed, with values currently quite stable in the order of a few thousand μg/l. This trend could be related either to the effectiveness of the implemented extraction system or to the significant drawdown of the groundwater table induced by the pumping activities (Mackay and Cherry, 1989). Accumulations of As inaccessible to conventional pumping procedures could be present in a pumping-induced unsaturated zone. Considering a) the type of subsoil, characterized by the presence of fractured limestone with a significant permeability, b) the type of contaminant (element poorly adsorbed and therefore particularly mobile in an aquifer) (Liu et al., 2016) and c) the primary event of contamination, it is possible to assume the presence of accumulations of aqueous solutions containing high concentrations of As within the

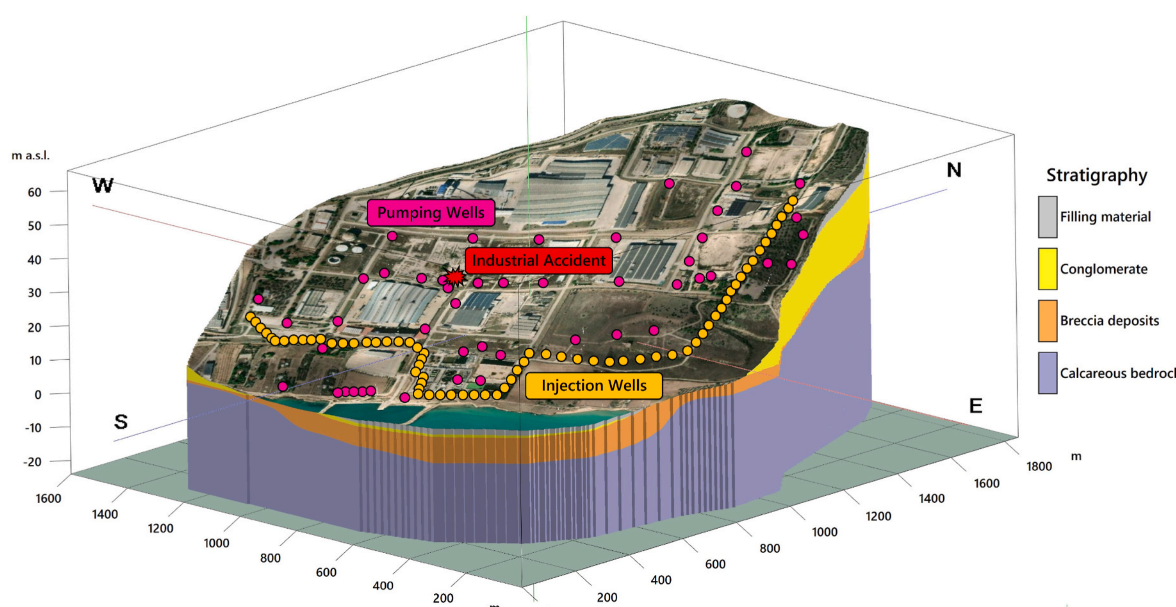


**Fig. 2.** 3D geological site model with location of pumping and injection wells and the area 1976 accident.

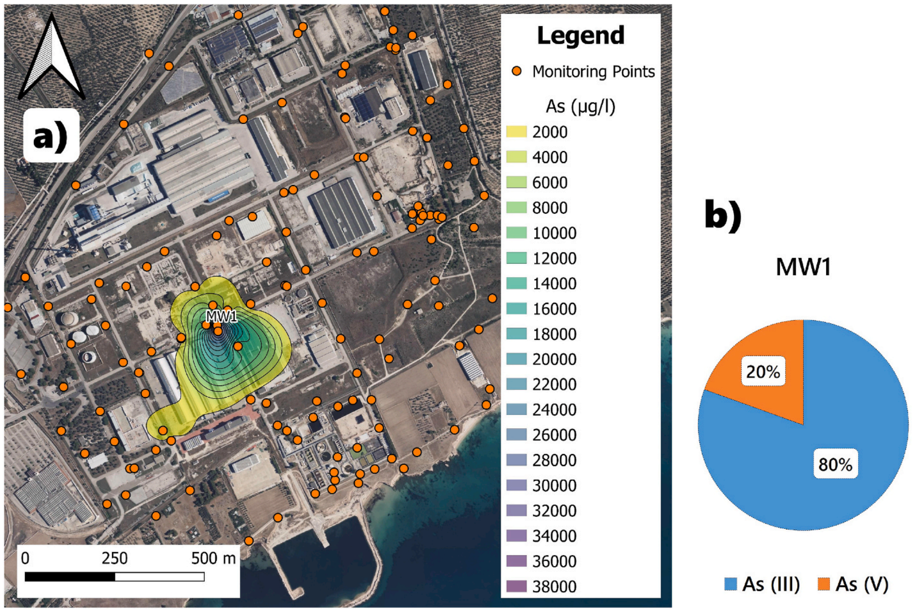


**Fig. 3.** Thematic map illustrating the average As concentrations measured at groundwater monitoring network points from 2006 to 2020 (a). The proportions of As (III) and As (V) in the well MW1 resulting from speciation analysis (b).

non-interconnected fractures that slowly release As in the groundwater. The persistence of high concentrations of dissolved As into groundwater suggests that the secondary contamination source is not affected by pumping activities and that the mass of residual As in the saturated and unsaturated domains is still significant.

### 3.2. The pilot test for arsenic removal

The circulation well is placed in a part of the site where the downstream barrier prevents migration of the mobilized contaminants towards the sea. The pilot plant, consisting of a 45 m deep IEG-GCW® equipped with 4 screen sections at different depths and a treatment system for the removal of dissolved As through oxidation and filtration on Macrolite (Enki) was installed around the piezometers that historically exhibited the highest concentrations of As. The vertical screen positions and the entire construction scheme of the GCW were determined referring to the visible fractures from the core samples, the hydrostratigraphic situation, and the chemical-physical condition of the area. The well construction allows the generation of circulation cells with different flow directions to focus and intercept the secondary source of As contamination (Fig. 4).

The field test in the source area was installed and put in operation in September 2020, employing different pumping/reinjection configurations, flow rates, and flow directions. The variation in operating conditions revealed the possibility of pumping significant volumes of groundwater from the fractured calcareous rock. This accelerated the processes of As mobilization from the aquifer portions characterized by the f significant residual pollution. The field observations from the pilot test show a radius of influence induced by GCW of at least 22.5 m and indicate how the proper design and sizing of a GCW can control and manage the upconig of the saltwater level at a depth of about 50 m below ground. The extrapolation of analytical data from the big-data package and the resulting multi-source model enabled us to evaluate the performance of the technology implemented during the pilot test, in terms of As removal from groundwater. The average recirculation rate was 2 $m^3$/h and As concentrations in the extracted water varied between 10,000 and 25,000 μg/L without a declining trend. This indicates the proper well location, which corresponds with the potential secondary source in groundwater (Shahid et al., 2013). The comparison of the near real-time monitoring data and analyzed and extracted As concentrations reveals a significant mass removal. The treated water is reinjected into the GCW with significantly lower As concentrations. During the first phases of the pilot test, the reduction of As concentrations was recorded between 20% and 60% (Fig. 5).

The possibility of effectively and continuously removing high amounts of As was verified together with the control of the chemical dosages (sodium hypochlorite and ferric chloride) during the back flush process. The set-up of the system can be optimized to a potential efficiency of 100% mass removal, based on experimental observations. However, oxidation, precipitation, and filtration of As on Macrolite, followed by backwashing of the filter media induces sludge production. The sludge generated by the As removal plant requires an eco-friendly disposal strategy. Such poses an issue of threatening concern in the era of sustainable development (Ruj et al., 2021). The information collected through the operation of the system will improve the layout of the intervention, increasing the effectiveness of As removal, in consent with the principles of sustainability and in full accordance with the cost/benefit ratio (Huysegoms and Cappuyns, 2017; Söderqvist et al., 2015). Based on the extracted and re-injected groundwater volumes (4820 $m^3$), the mobilized mass of As with the recirculation system stood at 67 kg. The re-injected mass after treatment amounted to about 44 kg. Thus, a mass of 23 Kg As was directly removed via the treatment system during the pilot test (Fig. 6).

Field experiences in As mitigation options are rather limited (Mondal et al., 2013; Sharma et al., 2014). The field application explores the feasibility and practicality of using advanced technology for As mobilization and removal, offering an innovative solution for the remediation of an As-contaminated aquifer. The GCW experience provides a more geologically chemically appropriate and ecologically sustainable mitigation option than installed groundwater extraction systems. The As contamination source is addressed directly with limited use of groundwater resources. When compared to conventional As treatment methods, the pilot test reveals a relatively fast removal process, employing commercially available chemicals and without the need for external regeneration of adsorbent materials (Yadav et al., 2021).

### 3.3. Performance and sustainability comparison between a GCW and the hydraulic barrier (P&T)

Comparing mass removal data from the active groundwater P&T

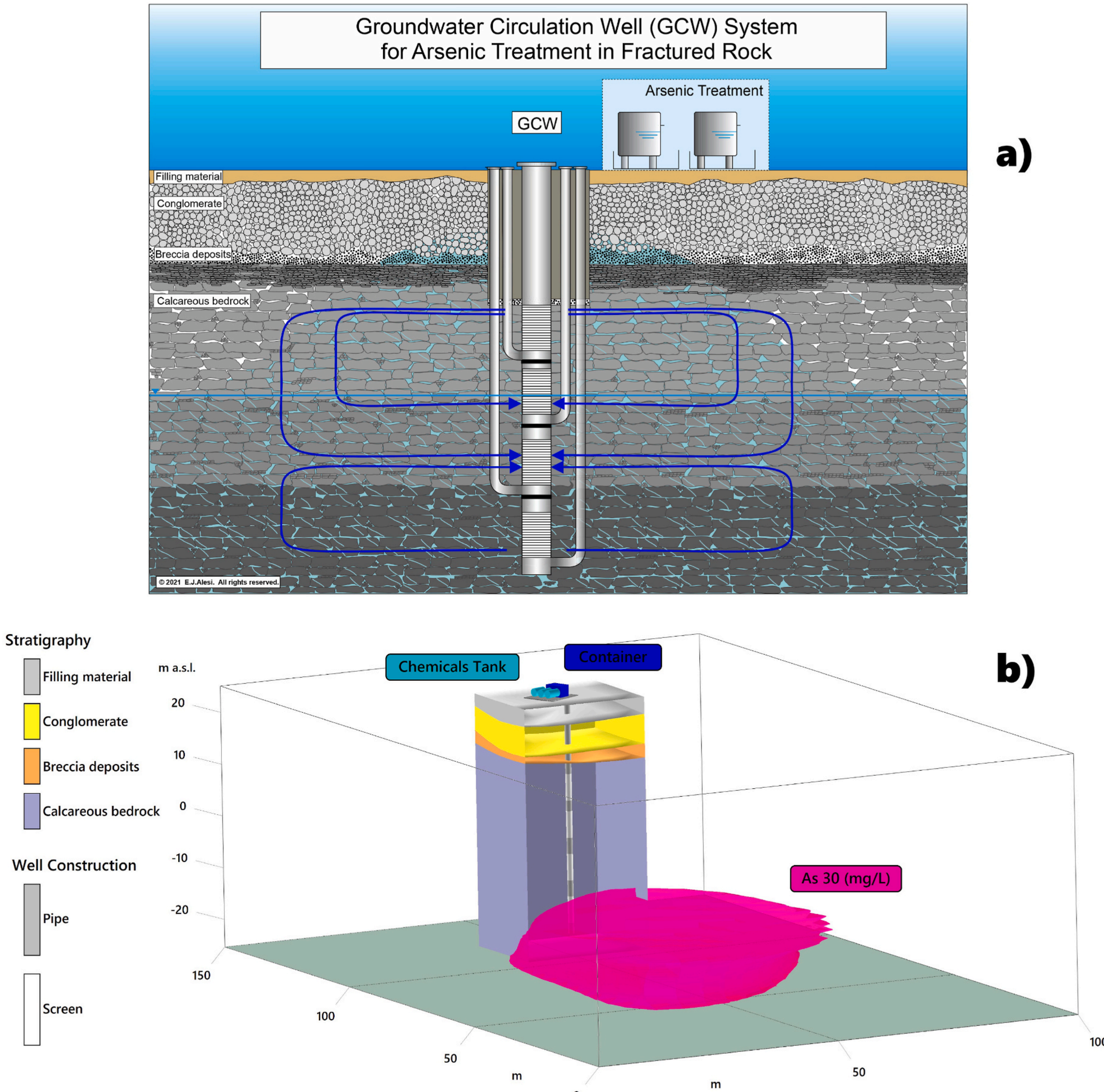


**Fig. 4.** Schematic layout of the IEG-GCW system with stacked circulation and superimposed cells in the fractured rock (a). Geological model of the pilot test area, schematic well design of the GCW field installation, and representation of dissolved As concentrations above 30 mg/L (b).

plant with the GCW system during the pilot test demonstrates that 129 kg of As were removed through the central P&T treatment plant by pumping approximately 500,000 $m^3$ of groundwater. On the other hand, by recirculating about 5000 $m^3$ of groundwater, the GCW extracted 67 kg of As and the treatment system removed 23 kg of As. The comparison between the masses extracted/treated per unit volume via a single GCW (pilot test) and the entire P&T system with 48 pumping wells within the plant exemplifies the much better performance and sustainability, of the GCW technology (Fig. 7).

An average concentration of 4814 mg per $m^3$ of treated groundwater was removed with the GCW system, while the treatment plant removed only 259 mg of As per $m^3$ of pumped and treated groundwater. The recirculation system removed 18% of the As mass in comparison to the entire P&T unit. The P&T system removed only 5% of the As mass per unit volume of water claiming 100 times more groundwater volume compared to a single GCW installed in the source area. This significant lower amount of As removed per unit volume of water is due to the enormous dilution of the As mass mobilized in the overall water volume discharged by the hydraulic system active on the site (Alam et al., 2021; Moeck et al., 2017). However, the application of a single GCW at the pilot scale, located in the area of the site characterized by the highest As concentrations, removed an amount of As corresponding to slightly less than one-fifth of the total mass removed by the entire active hydraulic P&T system and without production of wastewater. This is mainly due to the lack of incisive action of the traditional pumping wells in mobilizing the sources of secondary contamination (Ciampi et al., 2021a) and their inability to act directly on the accumulations of As present in the fractures in the saturated zone. According to the literature, the only alternative to increase the efficiency of conventional physical extraction methods for mobilizing secondary sources of As would be to employ chemical reagents. Although the As contamination has to be in hydraulic contact with the chemical reagent, which is challenging to achieve particularly in fractured rock settings, several authors emphasize that only chemical enhancements can potentially increase the As solubility and P&T applicability (Lookman et al., 2013; Maier et al., 2019; Sun et al., 2016; Wovkulich et al., 2010). Even in challenging geological environments, altering flow vectors and developing groundwater recirculation cells opens up the opportunity to intercept secondary sources and enhance the mobilization, dissolution, and removal of pollutants without the use of chemicals. All these findings attest to the success of

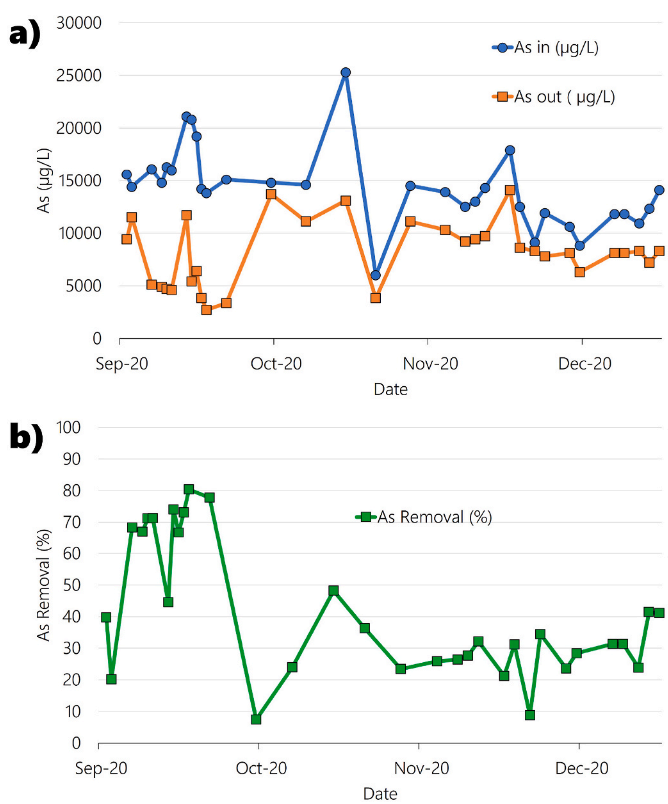


**Fig. 5.** Influent and effluent As concentrations of the GCW (a). Percentage of As removal during the pilot test (b).

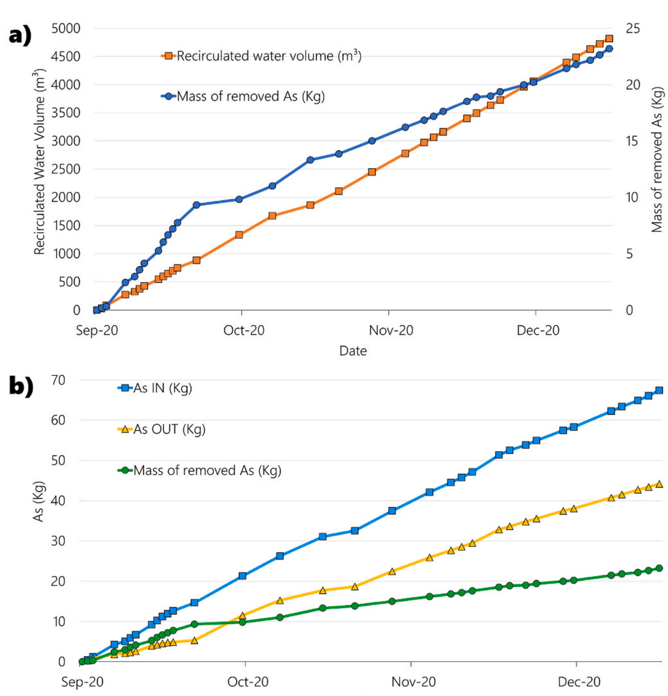


**Fig. 6.** The cumulative mass of As removal (in blue) during the test period at the field scale and volume of water recirculated with the GCW system (in orange) (a). The trend of cumulative mobilized As mass (in blue), re-circulated (in yellow), and removed (in green) from the treatment system during the first few months of the intervention run. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

the intervention adopted in the removal of As and the mobilization of accumulations in a fractured environment, as well as the technical and economic sustainability in the management of water resources and the performance of the technology compared to traditional physical pumping systems. The above points provide relevant insights into the remediation technology implemented in the physicochemical scenario.

Firstly, the pilot test verified the hydraulic efficiency of the GCW system and the possibility of recirculating significant amounts of groundwater in a fractured and karstified rock mass. Hydrochemical monitoring unequivocally testifies to the mobilization of considerable concentrations of As induced by recirculation and the abatement of the contamination load by the treatment system. It is important to emphasize that the mass of As mobilized is attributable to a secondary source of contamination not influenced by traditional extraction techniques (Ciampi et al., 2019a; Tatti et al., 2019). The mobilization of 67 kg of As arose from the development of significant flows of water in portions of the aquifer that present accumulations of As and that are not affected by the pumping activities operated by the wells of the hydraulic barrier. The hydraulic gradients induced by recirculation impact and trigger the mobilization of residual As fractions present in the fractures and porosity of the rock matrix. The latter constitutes an immobile phase whose dissolution is encouraged by the development of forced recirculation cells, which characterize GCWs and are not reproducible by conventional extraction wells (Tatti et al., 2019; Xia et al., 2019). Performing the pumping activity of the hydraulic barrier wells alone, without forcing water channelization in an ellipsoidal configuration and lacking the removal of 23 kg of As, a residual and persistent mass trapped in environmental matrices would have slowly and steadily released significant As concentrations into groundwater due to water table fluctuation. In line with the outcome of Ciampi et al. (2021a), Petrangeli Papini et al. (2016), Pierro et al. (2017), and Tatti et al. (2019), GCW constitutes a powerful tool to accelerate source depletion, pursuing the achievement of remediation objectives.

These considerations are echoed in the analysis of the monitoring data available for well MW1, a pumping well located in the pilot test area. The trend of As concentrations over time illustrates how GCW-induced recirculation mobilized significant pollutant concentrations. Starting from the monitoring campaign of September 2020, when the test was launched, significant concentrations of dissolved As in water are detected, very often in the order of 100 mg/L. On the other hand, until the implementation of the GCW, an average concentration of As in the order of 6000 μg/L was detected. Hydrochemical data highlight the failure of a traditional pumping well to attack the source of secondary contamination, acting only on the dissolved phase, whose mobilization is favored by the development of recirculation cells by the GCW (Fig. 8).

The mobilization of contaminants induced by the recirculation action promotes the removal of As by the pumping wells, otherwise ineffective in acting on a secondary source rather than containing a contamination plume. The trend of As concentrations detected in the first months of pilot testing reveals the mobilization of the contaminant induced by groundwater recirculation near the GCW installation. In particular, since the start-up of the plant and for the following seven months, the collected data do not show a decreasing trend in the measured concentrations, testifying to the significant and effective action of the GCW in mobilizing As in the area where the secondary source of contamination is potentially located. Hydrochemical evidence points to a potential interaction between the drawdown cone induced by pumping activities at MW1 and the recirculation cells developed by the GCW installed at the field scale (Ciampi et al., 2021a; Miller and Elmore, 2005). The latter can significantly accelerate As mobilization and consequently decrease the depletion time of secondary contamination sources.

The findings unequivocally demonstrate the need to employ a geology-focused approach to remediation and site management, which can be defined with a neologism remediation geology. Also, the insights of the research suggest a change of perspective in the approach to

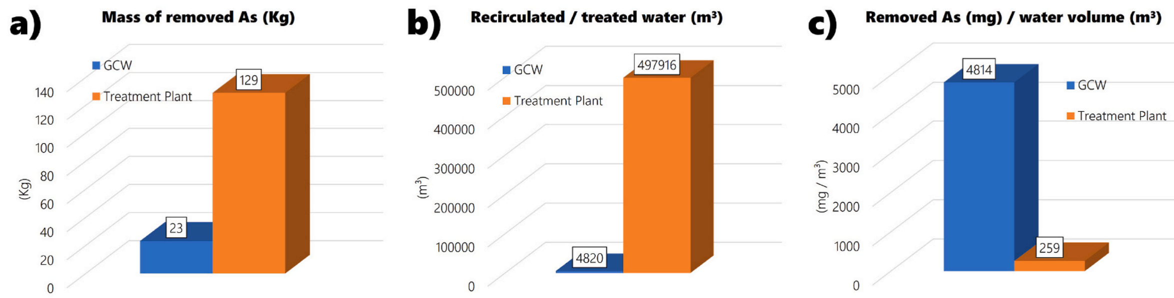


**Fig. 7.** Comparison of P&T and GCW during the pilot test in terms of As mass removal (a), pumped groundwater volumes (b), and removed As per cubic meter of pumped water (c).

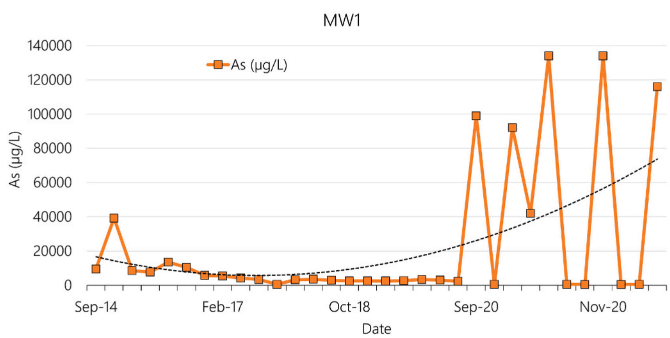


**Fig. 8.** Trend of As concentration at pumping well MW1, located nearby the pilot test area.

remediation of a contaminated site that requires "attacking" the source rather than "chasing" the contamination plume. Without attacking the source of pollution, the persistence of dissolved contamination in groundwater over decades is observed in many studies (Brusseau and Guo, 2014; Li et al., 2021; Mangia et al., 2018; Medunić et al., 2020; Shaji et al., 2021). All these elements driven by geology can lead to the recovery of contaminated industrial sites, reduction of environmental impact, in line with the principles of green and digital transition, and technological eco-sustainability, even in the period of pandemic emergency (Wang e Hang, 2021).

## 4. Conclusions

The pilot test implementation demonstrates the potential of the IEG-GCW® system in developing groundwater recirculation cells in geological settings characterized by fractured calcareous rock. The GCW exhibits the ability to recirculate groundwater with a discharge rate of about 2 $m^3$/h. Modification of flow vectors significantly increases As mobilization from accumulations present in fractures in the saturated horizon. The information acquired through the field scale test provides an estimate of the radius of influence (ROI) of the GCW system in the particular stratigraphic context and defines the optimal operation parameters to maximize the mobilization of the As contaminant and the removal capacity of the system, whose limitation lies in the production of an As sludge. During the pilot test, water treated by the GCW treatment system (Macrolite) was reintroduced into the aquifer with As concentrations reduced by an average of 20%–60%. Optimization of the treatment system will increase the pollutant abatement rate. The results of our work show that the recirculation system removed 18% (23 kg) of the mass of As extracted and treated by the entire P&T plant (129 kg) in the same operation period. Although the P&T unit treated 100 times more volume of water compared to a single recirculation system, it removed only 5% (259 mg/$m^3$) of the As mass per unit volume of water than the GCW (4814 mg/$m^3$) operating in the source area. The findings accentuate the limitations and unsustainability of traditional pumping techniques in the removal of secondary and limited mobility sources of contamination, suggesting a necessary change in the approach to remediation that focuses on attacking the source rather than containing the plume. Multi-source geomodeling and geology-driven approaches determine the success of eco-sustainable remediation, suggesting the leading role of remediation geology. Future studies will address the optimization of the treatment system, together with the proper placement of additional GCWs in the area affected by the presence of active sources in the aquifer, to significantly accelerate the removal of As with a speeding up of the related remediation.

## Author contributions

**Paolo Ciampi:** Writing- Original draft preparation, Software, Conceptualization, Data curation. **Carlo Esposito:** Methodology. **Ernst Bartsch:** Investigation, Data curation, Writing- Reviewing and Editing. **Eduard J. Alesi:** Supervision, Writing- Reviewing and Editing. **Gert Rehner:** Investigation, Data curation. **Piero Morettin:** Data curation, Investigation. **Michele Pellegrini:** Validation. **Sandro Olivieri:** Supervision, Validation. **Mauro Ranaldo:** Validation. **Giovanni Liali:** Supervision, Investigation. **Marco Petrangeli Papini:** Conceptualization, Supervision, Validation, Project administration.

## Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

## Data statement

Due to the sensitive nature of the questions asked in this study, the data that support the findings of this study are available from the Eni Rewind SpA, but restrictions apply to the availability of these data, which were used under license for the current study, and so are not publicly available. Data are however available from the authors upon reasonable request and with permission of the Eni Rewind SpA.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

## References

Abedian, H., Karami, G.H., Karimi, H., 2019. The effect of scale on the water leakage from the reservoir and abutment of Beheshtabad Dam. Bull. Eng. Geol. Environ. 78, 5569–5581. https://doi.org/10.1007/s10064-019-01487-1.

Adeloju, S.B., Khan, S., Patti, A.F., 2021. Arsenic contamination of groundwater and its implications for drinking water quality and human health in under-developed countries and remote communities—a review. Appl. Sci. 11 https://doi.org/10.3390/app11041926, 1926.

Alam, S., Borthakur, A., Ravi, S., Gebremichael, M., Mohanty, S.K., 2021. Managed aquifer recharge implementation criteria to achieve water sustainability. Sci. Total Environ. 768, 144992 https://doi.org/10.1016/j.scitotenv.2021.144992.

Al Bsoul, A., Al-Shannag, M., Tawalbeh, M., Al-Taani, A.A., Lafi, W.K., Al-Othman, A., Alsheyab, M., 2020. Optimal conditions for olive mill wastewater treatment using ultrasound and advanced oxidation processes. Sci. Total Environ. 700, 134576 https://doi.org/10.1016/j.scitotenv.2019.134576.

Alka, S., Shahir, S., Ibrahim, N., Ndejiko, M.J., Vo, D.N., Manan, F.A., 2021. Arsenic removal technologies and future trends: a mini-review. J. Clean. Prod. 278, 123805 https://doi.org/10.1016/j.jclepro.2020.123805.

Al-Qodah, Z., Tawalbeh, M., Al-Shannag, M., Al-Anber, Z., Bani-Melhem, K., 2020. Combined electrocoagulation processes as a novel approach for enhanced pollutants removal: a state-of-the-art review. Sci. Total Environ. 744, 140806 https://doi.org/10.1016/j.scitotenv.2020.140806.

Armienta, M.A., Segovia, N., 2008. Arsenic and fluoride in the groundwater of Mexico. Environ. Geochem. Health 30, 345–353. https://doi.org/10.1007/s10653-008-9167-8.

Asere, T.G., Stevens, C.V., Du Laing, G., 2019. Use of (modified) natural adsorbents for arsenic remediation: a review. Sci. Total Environ. 676, 706–720. https://doi.org/10.1016/j.scitotenv.2019.04.237.

Barlow, P.M., Reichard, E.G., 2010. Saltwater intrusion in coastal regions of North America. Hydrogeol. J. 18, 247–260. https://doi.org/10.1007/s10040-009-0514-3.

Beretta, G.P., 2017. Point and nonpoint pollution and restoring groundwater quality in Italy: 30 years of experience. Rend. Fis. Acc. Lincei 28, 255–264. https://doi.org/10.1007/s12210-016-0594-7.

Bott-Breuning, G., Alesi, E.J., 1993. Biologische In-Situ Sanierung durch Grundwasserzirkulation mit dem Unterdruck Verdampfer Brunnen (UVB). L. Schimmelpfeng (Hrsg.) Altlasten, Deponietechnik, Kompostierung 1993 580–585 (Academia Verlag).

Bretzler, A., Stolze, L., Nikiema, J., Lalanne, F., Ghadiri, E., Brennwald, M.S., Rolle, M., Schirmer, M., 2019. Hydrogeochemical and multi-tracer investigations of arsenic-affected aquifers in semi-arid West Africa. Geosci. Front. Times 10 (5), 1685–1699. https://doi.org/10.1016/j.gsf.2018.06.004.

Brusseau, M.L., Guo, Z., 2014. Assessing contaminant-removal conditions and plume persistence through analysis of data from long-term pump-and-treat operations. J. Contam. Hydrol. 164, 16–24. https://doi.org/10.1016/j.jconhyd.2014.05.004.

Ciampi, P., Esposito, C., Petrangeli Papini, M., 2019a. Hydrogeochemical model supporting the remediation strategy of a highly contaminated industrial site. Water 11 (7), 1371. https://doi.org/10.3390/w11071371.

Ciampi, P., Esposito, C., Viotti, P., Boaga, J., Cassiani, G., Petrangeli Papini, M., 2019b. An integrated approach supporting remediation of an aquifer contaminated with chlorinated solvents by a combination of adsorption and biodegradation. Appl. Sci. 9 (20), 4318. https://doi.org/10.3390/app9204318.

Ciampi, P., Esposito, C., Bartsch, E., Alesi, E.J., Petrangeli Papini, M., 2021a. 3D dynamic model empowering the knowledge of the decontamination mechanisms and controlling the complex remediation strategy of a contaminated industrial site. Sci. Total Environ. https://doi.org/10.1016/j.scitotenv.2021.148649, 148649.

Ciampi, P., Esposito, C., Cassiani, G., Deidda, G.P., Rizzetto, P., Petrangeli Papini, M., 2021b. Field-scale remediation of residual light non-aqueous phase liquid (LNAPL): chemical enhancers for pump and treat. Environ. Sci. Pollut. Res. 28, 35286–35296. https://doi.org/10.1007/s11356-021-14558-2.

Ciampi, P., Esposito, C., Bartsch, E., Alesi, E.J., Rehner, G., Petrangeli Papini, M., 2022c. Remediation of chlorinated aliphatic hydrocarbons (CAHs) contaminated site coupling groundwater recirculation well (IEG-GCW®) with a peripheral injection of soluble nutrient supplement (IEG-C-MIX) via multilevel-injection wells (IEG-MIW). Heliyon 8 (11), e11402. https://doi.org/10.1016/j.heliyon.2022.e11402.

Ciampi, P., Esposito, C., Cassiani, G., Deidda, G.P., Flores-Orozco, A., Rizzetto, P., Chiappa, A., Bernabei, M., Gardon, A., Petrangeli Papini, M., 2022a. Contamination presence and dynamics at a polluted site: spatial analysis of integrated data and joint conceptual modeling approach. J. Contam. Hydrol. 248, 104026 https://doi.org/10.1016/j.jconhyd.2022.104026.

Ciampi, P., Esposito, C., Bartsch, E., Alesi, E.J., Nielsen, C., Ledda, L., Lorini, L., Petrangeli Papini, M., 2022b. Coupled hydrogeochemical approach and sustainable technologies for the remediation of a chlorinated solvent plume in an urban area. Sustainability 14, 10317. https://doi.org/10.3390/su141610317.

Dalla Libera, N., Pedretti, D., Tateo, F., Mason, L., Piccinini, L., Fabbri, P., 2020. Conceptual model of arsenic mobility in the shallow alluvial aquifers near Venice (Italy) elucidated through machine learning and geochemical modeling. Water Resour. Res. 56, e2019WR026234 https://doi.org/10.1029/2019WR026234.

Fazi, S., Amalfitano, S., Casentini, B., Davolos, D., Pietrangeli, B., Crognale, S., Lotti, F., Rossetti, S., 2016. Arsenic removal from naturally contaminated waters: a review of methods combining chemical and biological treatments. Rend. Fis. Acc. Lincei 27, 51–58. https://doi.org/10.1007/s12210-015-0461-y.

Flores Orozco, F., Ciampi, P., Katona, T., Censini, M., Petrangeli Papini, M., Deidda, G.P., Cassiani, G., 2021. Delineation of hydrocarbon contaminants with multi-frequency complex conductivity imaging. Sci. Total Environ. 768, 144997 https://doi.org/10.1016/j.scitotenv.2021.144997.

Gianicolo, E.A.L., Mangia, C., Cervino, M., Bruni, A., Portaluri, M., Comba, P., Pirastu, R., Biggeri, A., Vigotti, M., Blettner, M., 2019. Long-term effect of arsenic exposure: results from an occupational cohort study. Am. J. Ind. Med. 62 (2), 145–155. https://doi.org/10.1002/ajim.22939.

Ghosh, S., Debsarkar, A., Dutta, A., 2019. Technology alternatives for decontamination of arsenic-rich groundwater-A critical review. Environ. Technol. Innovat. 13, 277–303. https://doi.org/10.1016/j.eti.2018.12.003.

Gong, Y., Qu, Y., Yang, S., Tao, S., Shi, T., Liu, Q., Chen, Y., Wu, Y., Ma, J., 2020. Status of arsenic accumulation in agricultural soils across China (1985–2016). Environ. Res. 186, 109525 https://doi.org/10.1016/j.envres.2020.109525.

Harvey, C.F., Ashfaque, K.N., Yu, W., Badruzzaman, A.B.M., Ali, M.A., Oates, P.M., Michael, H.A., Neumann, R.B., Beckie, R., Islam, S., Ahmed, M.F., 2006. Groundwater dynamics and arsenic contamination in Bangladesh. Chem. Geol. 228 (1–3), 112–136. https://doi.org/10.1016/j.chemgeo.2005.11.025.

Havranek, T.J., 2019. Multi-criteria decision analysis for environmental remediation: benefits, challenges, and recommended practices. Remediation 29, 93–108. https://doi.org/10.1002/rem.21589.

Herrling, B., Stamm, J., Buermann, W., 1991a. Hydraulic circulation system for in situ bioreclamation and/or in situ remediation of strippable contamination. In: Hinchee, R.E., Olfenbuttel, R.F. (Eds.), In Situ Bioreclamation. Butterworth-Heinemann, Boston, MA, USA, pp. 173–195.

Herrling, B., Stamm, J., Alesi, E.J., Brinnel, P., Hirschberger, F., Sick, M.R., 1991b. In situ groundwater remediation of strippable contaminants by vacuum vaporizer wells (UVB): operation of the well and report about cleaned industrial sites. Proceedings, Third Forum on Innovative Hazardous Waste Treatment Technologies: Domestic and International. Dallas, TX, USA, June 11–13. EPA/540/2-91/016 1–13.

Herrling, B., Stamm, J., Alesi, E.J., 1993a. Physical and biological in-situ aquifer remediation using vertical circulation flow (UVB technique). Proc. "Environmental Remediation Conference", October 24-28, 1993, Augusta, Georgia, USA.

Herrling, B., Stamm, J., Alesi, E.J., 1993b. In situ Beseitigung flüchtiger und/oder biologisch abbaubarer Schadstoffe aus dem Grundwasserbereich unter Verwendung des UVB-Verfahrens. Grundwassersanierung. H.-P. Lühr, IWS-Schriftreihe. Erich Schmidt Verlag.

Huysegoms, L., Cappuyns, V., 2017. Critical review of decision support tools for sustainability assessment of site remediation options. J. Environ. Manag. 196, 278–296. https://doi.org/10.1016/j.jenvman.2017.03.002.

Irshad, M.K., Ibrahim, M., Noman, A., Shang, J.Y., Mahmood, A., Mubashir, M., Khoo, K. S., Ng, H.S., Show, P.L., 2022. Elucidating the impact of goethite-modified biochar on arsenic mobility, bioaccumulation in paddy rice (Oryza sativa L.) along with soil enzyme activities. Process Saf. Environ. 160, 958–967. https://doi.org/10.1016/j.psep.2022.02.069.

Jalbani, N.S., Solangi, A.R., Memon, S., Junejo, R., Bhatti, A.A., Yola, M.L., Tawalbeh, M., Karimi-Maleh, H., 2021. Synthesis of new functionalized Calix[4] arene modified silica resin for the adsorption of metal ions: equilibrium, thermodynamic and kinetic modeling studies. J. Mol. Liq. 339, 116741 https://doi.org/10.1016/j.molliq.2021.116741.

Kanel, S.R., Ph, D., Asce, A.M., Choi, H., 2016. Removal of arsenic from groundwater by industrial byproducts and its comparison with zero-valent iron removal of arsenic from groundwater by industrial byproducts and its comparison with zero-valent iron. J. Hazard. Toxic Radioact. Waste 7, 10.1061/(ASCE)HZ.2153-5515.0000349.

Khan, R.A., Khan, N.A., El Morabet, R., Alsubih, M., Qadir, A., Bokhari, A., Mubashirg, M., Asiff, S., Cheahh, W.Y., Manickami, S., Klemešf, J.J., Khoo, K.S., 2022. Geospatial distribution and health risk assessment of groundwater contaminated within the industrial areas: an environmental sustainability perspective. Chemosphere 303, 134749. https://doi.org/10.1016/j.chemosphere.2022.134749.

Li, P., Karunanidhi, D., Subramani, T., Srinivasamoorthy, K., 2021. Sources and consequences of groundwater contamination. Arch. Environ. Contam. Toxicol. 80, 1–10. https://doi.org/10.1007/s00244-020-00805-z.

Li, Z., Yang, Q., Yang, Y., Xie, C., Ma, H., 2020. Hydrogeochemical controls on arsenic contamination potential and health threat in an intensive agricultural area, northern China. Environ. Pollut. 256, 113455 https://doi.org/10.1016/j.envpol.2019.113455.

Liang, S., Zhang, W., Zhang, L., Wang, W., Zhang, L., 2019. Remediation of industrial contaminated water with arsenic and nitrate by mass-produced Fe-based metallic glass: toward potential industrial applications. SMT Trends 22, e00126. https://doi.org/10.1016/j.susmat.2019.e00126.

Liberti, L., Polemio, M., 1981. Arsenic accidental soil contamination near Manfredonia. A case history. J. Environ. Sci. Health A16 (3), 297–314. https://doi.org/10.1080/10934528109374983.

Lima, J.Z., Da Silva, E.F., Patinha, C., Durães, N., Vieira, E.M., Rodrigues, V.G.S., 2022. Sorption of arsenic by composts and biochars derived from the organic fraction of municipal solid wastes: kinetic, isotherm and oral bioaccessibility study. Environ. Res. 204 (A) https://doi.org/10.1016/j.envres.2021.111988, 111988.

Litter, M.I., Ingallinella, A.M., Olmos, V., Savio, M., Difeo, G., Botto, L., Torres, E.M.F., Taylor, S., Frangie, S., Herkovits, J., Schalamuk, I., González, M.J., Berardozzi, E., Einschlag, F.S.G., Bhattacharya, P., Ahmad, A., 2019. Arsenic in Argentina: technologies for arsenic removal from groundwater sources, investment costs and waste management practices. Sci. Total Environ. 690, 778–789. https://doi.org/10.1016/j.scitotenv.2019.06.358.

Liu, G.L., Cai, Y., Hernandez, D., Schrlau, J., Allen, M., 2016. Mobility and speciation of arsenic in the coal fly ashes collected from the savannah river site (SRS). Chemosphere 151, 138–144. https://doi.org/10.1016/j.chemosphere.2016.02.071.

Lookman, R., Verbeeck, M., Gemoets, J., Van Roy, S., Crynen, J., Lambié, B., 2013. In-situ zinc bioprecipitation by organic substrate injection in a high-flow, poorly reduced aquifer. J. Contam. Hydrol. 150, 25–34. https://doi.org/10.1016/j.jconhyd.2013.03.009.

López-Guzmán, M., Alarcón-Herrera, M.T., Irigoyen-Campuzano, J.R., Torres-Castañón, L.A., Reynoso-Cuevas, L., 2019. Simultaneous removal of fluoride and

arsenic from well water by electrocoagulation. Sci. Total Environ. 678, 181–187. https://doi.org/10.1016/j.scitotenv.2019.04.400.
Mackay, M.D., Cherry, J.A., 1989. Groundwater contamination: pump-and-treat remediation. Environ. Sci. Technol. 23, 630–636. https://doi.org/10.1021/es00064a001.
Maier, M.V., Wolter, Y., Zentler, D., Scholz, C., Stirn, C.N., Isenbeck-Schröter, M., 2019. Phosphate induced arsenic mobilization as a potentially effective in-situ remediation technique-preliminary column tests. Water 11, 2364. https://doi.org/10.3390/w11112364.
Maity, J.P., Vithanage, M., Kumar, M., Ghosh, A., Mohan, D., Ahmad, A., Bhattacharya, P., 2021. Seven 21st century challenges of arsenic-fluoride contamination and remediation. Groundw. Sustain. Dev. 12, 100538 https://doi.org/10.1016/j.gsd.2020.100538.
Mangia, C., Cervino, M., Gianicolo, E.A.L., 2018. Arsenic contamination assessment 40 years after an industrial disaster: measurements and deposition modeling. Air Qual. Atmos. Health (11), 1081–1089. https://doi.org/10.1007/s11869-018-0610-4.
Masciale, R., Amalfitano, S., Frollini, E., Ghergo, S., Melita, M., Parrone, D., Preziosi, E., Vurro, M., Zoppini, A., Passarella, G., 2021. Assessing natural background levels in the groundwater bodies of the apulia region (southern Italy). Water 13 (7), 958. https://doi.org/10.3390/w13070958.
Medunić, G., Fiket, Ž., Ivanić, M., 2020. Arsenic contamination status in europe, Australia, and other parts of the world. In: Srivastava, S. (Ed.), Arsenic in Drinking Water and Food. Springer, Singapore. https://doi.org/10.1007/978-981-13-8587-2_6.
Miller, G.R., Elmore, A.C., 2005. Modeling of a groundwater circulation well removal action alternative. Pract. Period. Hazard. Toxic, Radioact. Waste Manag. 9, 122–129. https://doi.org/10.1061/~ASCE!1090-025X~2005!9, 2~122.
Moeck, C., Radny, D., Popp, A., Brennwald, M., Stoll, S., Auckenthaler, A., Berg, M., Schirmer, M., 2017. Characterization of a managed aquifer recharge system using multiple tracers. Sci. Total Environ. 609, 701–714. https://doi.org/10.1016/j.scitotenv.2017.07.211.
Mondal, P., Bhowmick, S., Chatterjee, D., Figoli, A., Van der Bruggen, B., 2013. Remediation of inorganic arsenic in groundwater for safe water supply: a critical assessment of technological solutions. Chemosphere 92, 157–170. https://doi.org/10.1016/j.chemosphere.2013.01.097.
O'Brien, R.M., Smits, K.M., Smith, N.M., Schwartz, M.R., Crouse, D.R., Phelan, T.J., 2021. Integrating scientific and local knowledge into pollution remediation planning: an iterative conceptual site model framework. Environ. Dev. 40, 100675 https://doi.org/10.1016/j.envdev.2021.100675.
Petrangeli Papini, M., Majone, M., Arjmand, F., Silvestri, D., Sagliaschi, M., Sucato, S., Alesi, E., 2016. First pilot test on integration of GCW (groundwater circulation well) with ena (enhanced natural attenuation) for chlorinated solvents source remediation. Chem. Eng. Trans. 49, 91–96. https://doi.org/10.3303/CET1649016.
Pierro, L., Matturro, B., Rossetti, S., Sagliaschi, M., Sucato, S., Alesi, E., Bartsch, E., Arjmand, F., Petrangeli Papini, M., 2017. Polyhydroxyalkanoate as a slow-release carbon source for in situ bioremediation of contaminated aquifers: from laboratory investigation to pilot-scale testing in the field. N. Biotech. 37, 60–68. https://doi.org/10.1016/j.nbt.2016.11.004.
Price, J., Spreng, C., Hawley, E.L., Deeb, R., 2017. Remediation management of complex sites using an adaptive site management approach. J. Environ. Manag. 204 (2), 738–747. https://doi.org/10.1016/j.jenvman.2017.04.009.
Ruj, B., Chakrabortty, S., Nayak, J., Chatterjee, R.P., 2021. Treatment of arsenic sludge generated from groundwater treatment plant: a review towards a sustainable solution. S. Afr. J. Chem. Eng. 37, 214–226. https://doi.org/10.1016/j.sajce.2021.06.003.
Shahid, M., Xiong, T., Castrec-Rouelle, M., Leveque, T., Dumat, C., 2013. Water extraction kinetics of metals, arsenic and dissolved organic carbon from industrial contaminated poplar leaves. J. Environ. Sci. 25 (12), 2451–2459. https://doi.org/10.1016/S1001-0742(12)60197-1.
Shaji, E., Santosh, M., Sarath, K.V., Prakash, P., Deepchand, V., Divya, B.V., 2021. Arsenic contamination of groundwater: a global synopsis with focus on the Indian Peninsula. Geosci. Front. 12 (3), 101079 https://doi.org/10.1016/j.gsf.2020.08.015.
Sharma, A.K., Tjell, J.C., Sloth, J.J., Holm, P.E., 2014. Review of arsenic contamination, exposure through water and food and low cost mitigation options for rural areas. Appl. Geochem. 41, 11–33. https://doi.org/10.1016/j.apgeochem.2013.11.012.
Singh, R., Singh, S., Parihar, P., Singh, V.P., Prasad, S.M., 2015. Arsenic contamination, consequences and remediation techniques: a review. Ecotoxicol. Environ. Saf. 112, 247–270. https://doi.org/10.1016/j.ecoenv.2014.10.009.
Söderqvist, T., Brinkhoff, P., Norberg, T., Rosén, L., Back, P.E., Norrman, J., 2015. Cost-benefit analysis as a part of sustainability assessment of remediation alternatives for contaminated land. J. Environ. Manag. 157, 267–278. https://doi.org/10.1016/j.jenvman.2015.04.024.
Stamm, J., 1997. Numerische Berechnung dreidimensionaler Strömungsvorgänge um Grundwasser Zirkulations Brunnen zur In situ Grundwassersanierung. Fortschritt Berichte VDI, Reihe 15. Umwelttechnik Nr. 169.
Sun, J., Bostick, B.C., Mailloux, B.J., Ross, J.M., Chillrud, S.N., 2016. Effect of oxalic acid treatment on sediment arsenic concentrations and lability under reducing conditions. J. Hazard Mater. 311, 125–133. https://doi.org/10.1016/j.jhazmat.2016.02.060.
Tatti, F., Petrangeli Papini, M., Torretta, V., Mancini, G., Boni, M.R., Viotti, P., 2019. Experimental and numerical evaluation of Groundwater Circulation Wells as a remediation technology for persistent, low permeability contaminant source zones. J. Contam. Hydrol. 222, 89–100. https://doi.org/10.1016/j.jconhyd.2019.03.001.
Thouin, H., Le Forestier, L., Gautret, P., Hube, D., Laperche, V., Dupraz, S., Battaglia-Brunet, F., 2016. Characterization and mobility of arsenic and heavy metals in soils polluted by the destruction of arsenic-containing shells from the great war. Sci. Total Environ. 550, 658–669. https://doi.org/10.1016/j.scitotenv.2016.01.111.
Utom, A.U., Werban, U., Leven, C., Müller, C., Dietrich, P., 2019. Adaptive observation-based subsurface conceptual site modeling framework combining interdisciplinary methodologies: a case study on advancing the understanding of a groundwater nitrate plume occurrence. Environ. Sci. Pollut. Res. 26, 15754–15766. https://doi.org/10.1007/s11356-019-05048-7.
Wang, Q., Huang, R., 2021. The impact of COVID-19 pandemic on sustainable development goals – a survey. Environ. Res. 202, 111637 https://doi.org/10.1016/j.envres.2021.111637.
Werner, A.D., Bakker, M., Post, V.E.A., Vandenbohede, A., Lu, C., Ataie-Ashtiani, B., Simmons, C.T., Barry, D.A., 2013. Seawater intrusion processes, investigation, and management: recent advances and future challenges. Adv. Water Resour. 51, 3–26. https://doi.org/10.1016/j.advwatres.2012.03.004.
Wovkulich, K., Mailloux, B.J., Lacko, A., Keimowitz, A.R., Stute, M., Simpson, H.J., Chillrud, S.N., 2010. Chemical treatments for mobilizing arsenic from contaminated aquifer solids to accelerate remediation. Appl. Geochem. 25 (10), 1500–1509. https://doi.org/10.1016/j.apgeochem.2010.08.001.
Xia, Q., Zhang, Q., Xu, M., Tang, Y., Teng, H., 2019. Visualizing hydraulic zones of a vertical circulation well in presence of ambient flow. Desalination Water Treat. 159, 151–160. https://doi.org/10.5004/dwt.2019.24098.
Yadav, M.K., Saidulu, D., Gupta, A.K., Ghosal, P.S., Mukherjee, A., 2021. Status and management of arsenic pollution in groundwater: a comprehensive appraisal of recent global scenario, human health impacts, sustainable field-scale treatment technologies. J. Environ. Chem. Eng. 9, 105203 https://doi.org/10.1016/j.jece.2021.105203.
Zhang, Y., Xu, B., Guo, Z., Han, J., Li, H., Jin, L., Chen, F., Xiong, Y., 2019. Human health risk assessment of groundwater arsenic contamination in Jinghui irrigation district, China. J. Environ. Manag. 237, 163–169. https://doi.org/10.1016/j.jenvman.2019.02.067.
Zuzolo, Z., Cicchella, D., Demetriades, A., Birke, M., Albanese, S., Dinelli, E., Lima, A., Valera, P., De Vivo, B., 2020. Arsenic: geochemical distribution and age-related health risk in Italy. Environ. Res. 182, 109076 https://doi.org/10.1016/j.envres.2019.109076.