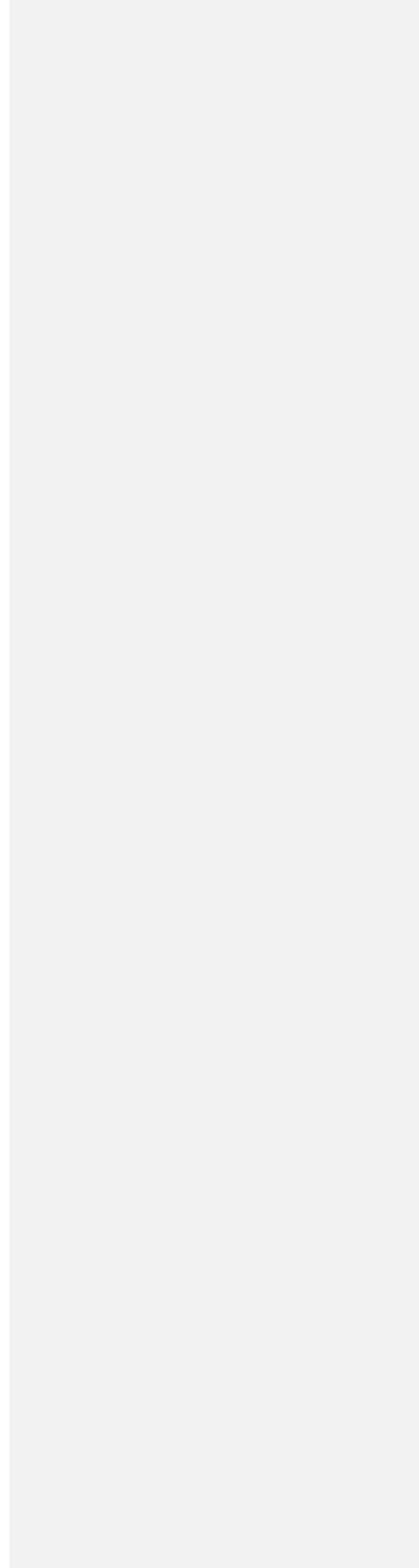


**MOBILITY OF TRACE ELEMENTS DURING REMEDIATION OF OIL POLLUTED
GROUNDWATER: A CASE STUDY**

UNDER PEER REVIEW



ABSTRACT

A study was carried on an area polluted by oil in Oman to determine the mobility of trace elements during each step of an *ex situ* treatment process.

Quality of groundwater following an air flotation treatment was investigated and discussed ~~in the present study~~. About 15

~~Place and Duration of Study: Sultan Qaboos University (Muscat, Oman), 3 months.~~

~~W~~ater samples (~~bout 15~~) were collected from 7 monitoring wells which are under air sparging treatment for remediation of oil contamination. Chemical composition of groundwater during and after the treatment was compared with chemical composition of groundwater before any treatment. Water samples were also collected from different monitoring wells in the same area. The investigated elements consist in Na, Mg, Ca, K, Fe, Cr, Ni, Cu, Zn, Ag, Cd, Sr, Ba, Pb and rare earth elements (REEs).

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Chemical composition of trace and major elements during each step of treatment revealed that Ni, Zn, Cu and Al have been increased relative to untreated water contrary to Ag which decreased. Major elements and Cr, Pb, and Cd remain unchanged during the treatment process. The ~~REES~~ were significantly depleted during the last step of treatment relative to the raw water but their distribution did not reveal any fractionation.

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Trace elements such as Zn, Cu, Ni show an increase and Ag and REES a decrease relative to raw water before any treatment. For treatment of groundwater chemical investigation of different agents used during the treatment and the speciation of each key trace elements should be investigated at each step of treatment procedure.

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Keywords: *trace elements, contamination, groundwater, Oman, treatment*

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1-INTRODUCTION

Groundwater is the primary source of water in arid areas such Oman, and it is a drinking water source. Monitoring these resources of water is necessary in such areas to prevent contamination and depletion. Contamination of groundwater could originate from industry and other anthropogenic sources. The aim of several studies was to determine the risk of waters to pollution [1, 2, 3] and other studies were about the different solutions and methods of remediation of such problems [4, 5, 6, 7].

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The present study is about contamination of groundwater by oil which concentrations in the untreated water samples was less than 0.5mg/l. The origin of this pollution is probably the industry activities developed in the study area many years ago. These activities released waste which could reach groundwater. Ex situ treatment of this groundwater was conducted in the study area. The objective of this paper was to find out the levels of decontamination of metals that have been achieved as the contaminated or raw groundwater have gone through successive purification steps, beginning with the air bubbling process, followed by anthracite filtration, and finally by activated charcoal filtration.

2. DESCRIPTION OF STUDY SITE

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The study area is located in the Batinah Region of the Sultanate of Oman at 23°23'27"N and 57°25'28"E (latitude and longitude coordinates) (Figure 1). It occupies a ~~low lying~~ elevated plateau surrounded by wadis, sloped gently from South to North. Attributed to occasional rainfall, the wadis flow to the North following the topographic pattern. There is no irrigation or any other artificial input to the

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aquifer in the focus study area. The average annual rainfall in the study area is about 60 mm, and the evaporation rate for the existing groundwater depth (>10 m below the ground surface) is negligible. Therefore, natural descending moisture fluxes from the vadose zone can be neglected.

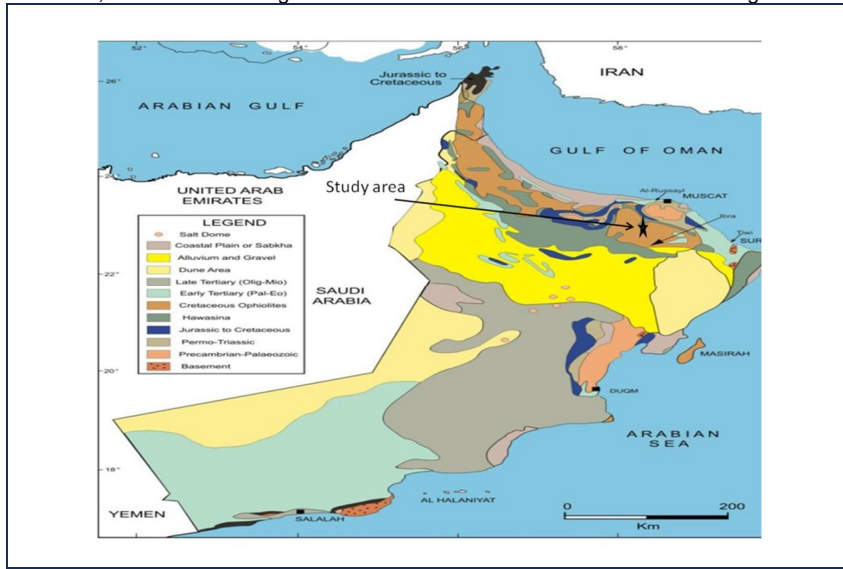


Figure 1: Sampling location

Comment [Garba T.6]: Separate the map of study area and map of sample collection points

The oil contaminated groundwater is first treated at the water treatment site with air flotation technique. Flotation is a process to remove fine suspended solid particles, of both inorganic and organic compositions, from the polluted ground water by passing air bubbles through the water, causing the dissolved air to come out from the water in the form of bubbles. The fine suspended solid particles attach to the surface of the bubbles. The air-floated water is then allowed to pass through an anthracite-filtration system to remove various components that have high affinity for surface reactions and adsorption with this media. The anthracite-filtered water is then introduced into activated carbon system for adsorption-mediated removal of remaining materials from the water. Activated carbon is commonly employed as adsorbent for treatment of wastewater and contaminated groundwater. activated carbon may adsorb contaminants or remove them by air sparging.

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3. MATERIALS AND METHODS

Water samples (about 15) were directly collected from 7 monitoring wells penetrating an alluvium aquifer formed during the Quaternary time. Water samples were also collected from air flotation treatment plant at 4 steps of remediation, 1) raw water (untreated groundwater); 2) water after air flotation (after dissolution of air in the water) 3) water after anthracite filtration and 4) water after adsorption on activated carbon (Figure 2). These water samples have been collected in 500 ml polypropylene containers. Instantaneous site analysis was carried out for pH and conductivity. Every water sample was vacuum filtered through a membrane filter with 0.45 μ m pore size. Laboratory analyses were conducted within 3 days of sample collection.

Comment [Garba T.8]: What is this?

Prior to air flotation step during the treatment, two chemicals were added to the raw water (untreated groundwater) to coagulate the oil droplets. These chemicals consist in PAC (polyaluminum chloride) and an anion polymer (aluminum sulfate).

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Elemental contents in all samples were determined using the ICP-AES for Na, Ca, K, Mg, Al, Fe and the ICP-MS, the latter for Mn, Zn, Ni, Sr, Cr, Ba, Co, Cu, Pb, Ag, Cd and rare-earth elements (REEs). The quality control procedure of the analysis is to run system suitability test mix (provided by the manufacturer) and run a standard calibration across the mass range to check for accuracy and precision. Concentrations of the used calibration standards were 0.1ppt, 1ppt, 5ppt, 50ppt, 100ppt, 500ppt, 1ppb, 5ppb, 10ppb, 50ppb and 100ppb. Blanks run before and after each calibration curve. Repeated analyses carried out in the laboratory on a regular basis yielded analytical precisions that ranged between 5 and 10% with a detection limit of about 1ppt.

4. RESULTS AND DISCUSSION

The chemical composition of groundwater is given in Table 1. Considering usual standard limits [8, 9], water samples of this study do not pose any problem either for major or trace elements in term of quality. Modification in pH is not significant during the different steps of treatment. The chemical composition of raw waters show that the most abundant major elements are Na, Mg, Ca and K while the most abundant trace elements are Zn, Ba, Cu and Ni. Chemical evolution of major elements during the remediation steps does not reveal any modification during the treatment contrary to some trace elements that we will discuss during this study.

Investigations of trace element variations during each step of treatment showed diversities in behaviours of elements.

Relative to the concentrations of elements in raw water before any treatment, the elements which showed an enrichment after air flotation consist in Al, Ni, Pb and Mn (with about 87, 47, 21 and 18% respectively). Other elements such as Ag and the total REEs have been depleted with about 228 and 39% respectively while the elements such as Ba and Cr remain unchanged.

Relative to the first step of treatment (air flotation), waters collected after second step of treatment which consisted in filtration through anthracite, have been enriched in Cd, REEs and Ni with about 64, 29 and 25% respectively. In the opposite, Ag, Al and Pb were depleted with about 250, 34 and 16% while the content of Ba and Cr remain unchanged.

Relative to the second step of treatment, waters collected after the third step of treatment which consisted in filtration through activated carbon were enriched in Zn, Ag and Cr with about (96, 71 and 16%) and depleted in Cd and Ni (with about 100 and 20%). Total of REEs was significantly depleted (more 100%).

Relative to untreated groundwater, the increased elements during the treatment consisted in Al and Zn while the decreased elements were: the total of REEs, Ag, Ba, Pb, Cd and Ni. The elements which remain unchanged were Ca, Cr, K, Mg, Na and Sr (Table 1, Figure 3).

The average total content of REEs in groundwater collected from different wells is about 11.36 ppb. The total REE content in untreated groundwater is about 15.85 ppb. This content decreased significantly from step 1 to step 3 of treatment to reach 0.37 ppb.

The normalization of REE concentrations in waters collected after step 1 (AF) and step 3 (AC) of remediation to REE concentrations in the raw water before any treatment exhibit flat patterns (Figure. 4) with ratios between REEs in samples and those in raw water less than 1 for all REEs. The distribution patterns of REEs in groundwater of step 2 exhibit a slight enrichment in heavy REEs (HREEs) with a slight positive anomaly in Ce and a slight negative anomaly in Eu. The ratio between REEs in samples and those in raw water is about 1 in light and intermediate REEs but higher than one for HREEs.

The normalization of REE distribution in waters treated during the remediation steps to an average distribution in groundwater also showed flat patterns (Figure. 4).

Comparison to uncontaminated groundwater from the same area [10] showed that contaminated groundwater with oil are characterized by low concentrations in major and trace elements.

As it was stated above, evolution of concentration of major elements during air flotation treatment did not reveal any modification except Al which concentration increased in water collected from step1 relative to raw water and exhibit a significant increase in water collected after the last step of treatment relative to raw water. In the opposite, evolution of concentration of trace elements during the treatment showed that after the air flotation step the depletion concerned Ag and Cd relative to raw water. Relative to untreated groundwater the enriched elements in water after air flotation consist in Mn, Ni and Pb (Figure 3).

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Relative to waters collected from step 1, the waters collected after their filtration through sand show an enrichment in Cd and Ni and a depletion in Ag, Cr and Pb. After filtration through anthracite Ag, Cr and Zn increased while Ni and Pb decreased. Relative to untreated groundwater the water collected after the last step of treatment is characterized by an increase of Cu, Ni and Zn and a depletion of Ag, Cd and Ba (Figure 3).

The explanation of the increase of trace elements after filtration through anthracite especially Ni, Zn and Cu relative to untreated groundwater could be that either a large fraction of trace elements in groundwater of this study are carried by organic molecules or released from anthracite during filtration.

Evaporation of organic compounds and their retention on filters released trace elements in groundwater and may explain the peak of Cd and Ni after the second step of treatment because of an effect of concentration. Complexation of trace elements by dissolved organic matter is well known and has been reported in several studies [11, 12, 13] and speciation of trace elements associated with organic matter was the objective of many studies [14, 15; 16].

The last step of treatment consisted in an activated carbon adsorption step. During this step and compared to waters collected after step 2 concentration of elements such as Zn, Cr and Ag are enriched while Ni, Pb, and Cd are depleted. The content of the other elements did not exhibit any change after removal of oil from waters. The only enriched major element is Al because of the agent such as PAC (polyaluminum chloride) and the anion polymer (aluminum sulfate) introduced to groundwater before the remediation in order to coagulate the oil droplets. This increase remains lower than the permissible concentration of Al in drinking waters (Table 1). The decrease of most of trace elements after the last step could be because of their retention on activated carbon.

As it was stated above, relative to REE distribution in raw waters, REE distributions of waters after removal of oil are characterized by flat patterns. There is no significant fractionation of REEs during the treatment process.

The release of REEs at the last step of treatment less important than after the other steps may be due to a fixation of organic molecules on activated carbon. Complexation of REEs in groundwater with organic molecules has been discussed in several studies [17, 18] and it is controlled by pH, alkalinity, and dissolved organic carbon concentration.

5. CONCLUSION

This study showed that in parallel to ~~mobilisation~~ mobilization of oil from groundwater during treatment:

- Little change is observed for most of elements except Zn, Cu, Ni which increased and Ag which decreased relative to untreated groundwater.
- No fractionation of REEs during the treatment but in term of concentration, the waters collected after the last step of remediation are depleted in REEs relative to the untreated and to groundwater collected during the other steps of treatment.

Based on the results of the present study, any study of response of dissolved trace elements in groundwater to a remediation process must include: 1) chemical investigation of different agents used during the treatment and 2) speciation of each trace element in water. The speciation of organic matter may also help to understand the mobility of trace elements.

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Table 1. Average chemical composition of raw groundwater and the waters collected after each step of treatment. Major elements are expressed (in ppm). Trace elements and rare earth elements are expressed (in ppb).

	Groun dwater	Pre-treat water	Air-flotation Water	Anthracite filtration	Activated carbon filtration	WHO DWStd199	Oman (Who, 2006,
pH	8.06	7.97	7.90	8.01	7.91	NG	NG
EC (mS/cm)	1.13	1.13	1.13	1.14	1.14	NG	NG
Elements						mg/l	mg/l
Ca	35.7	36.40	37.20	36.80	37.60	NG	75
K	5.00	5.20	5.20	5.15	5.15	NG	NG
Mg	64.9	61.85	61.75	62.10	61.75	NG	30
Na	95.0	100.00	100.00	100.00	100.00	200	
Sr	0.66	0.66	0.66	0.66	0.65	NG	NG
(in 10 ⁻³ mg/l)							
Ag	0.15	0.23	0.07	0.02	0.07	NG	NG
Al	6.4	17.29	136.65	101.89	108.05	0.2	NG
Ba	56.5	55.65	49.78	52.27	47.87	0,3	NG
Cd	0.09	0.08	0.05	0.14	0.07	0.003	0.003
Cr	2.81	2.98	2.84	2.49	2.98	0.05	0.05
Cu	10.6	1.27	ND	4.49	4.25	2	0.05
Fe	1.39	13.58	ND	ND	ND	NG	0.1

Mn	2.07	0.65	0.79	ND	ND	0.5	0.05
Ni	0.99	0.40	0.75	1.00	0.83	0.02	
Pb	3.66	2.20	2.79	2.40	2.01	0,01	0,01
Zn	7.45	2.40	ND	1.41	32.94	3	5

Nd: not determined

NG. No guideline

Table 1. Continued

	Groun dwater	Pre-treat water	Air-flotation Water	Anthracite filtration	Activated carbon filtration	WHO DWStd199	Oman (Who, 2006,
(in 10 ⁻³ mg/l)							
La	2.87	4.09	3.04	3.96	0.02	NG	NG
Ce	3.76	5.28	3.88	5.50	0.02	NG	NG
Sm	0.99	1.29	0.95	1.30	0.06	NG	NG
Eu	0.48	0.66	0.47	0.64	0.04	NG	NG
Gd	1.09	1.49	1.05	1.50	0.07	NG	NG
Tb	0.20	0.28	0.20	0.30	0.02	NG	NG
Dy	0.79	1.11	0.75	1.17	0.05	NG	NG
Ho	0.24	0.32	0.22	0.35	0.02	NG	NG
Er	0.62	0.88	0.60	0.98	0.04	NG	NG
Tm	0.17	0.23	0.16	0.26	0.02	NG	NG
Lu	0.15	0.20	0.14	0.22	0.01	NG	NG
Total	11.34	15.83	11.44	16.18	0.35	NG	NG

Nd: not determined

NG. No guideline

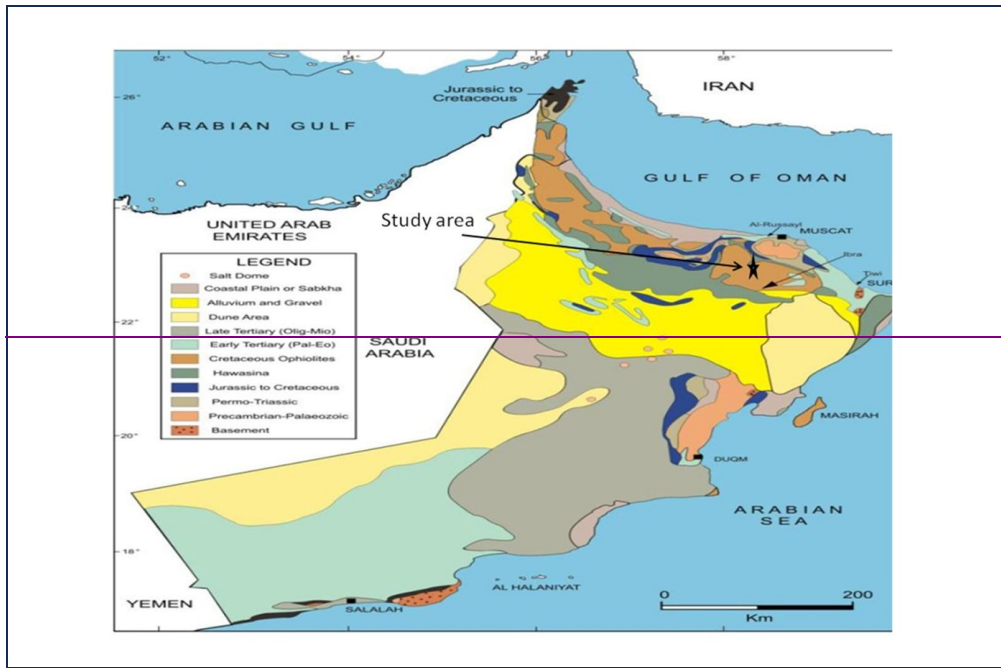


Figure 1: Sampling location

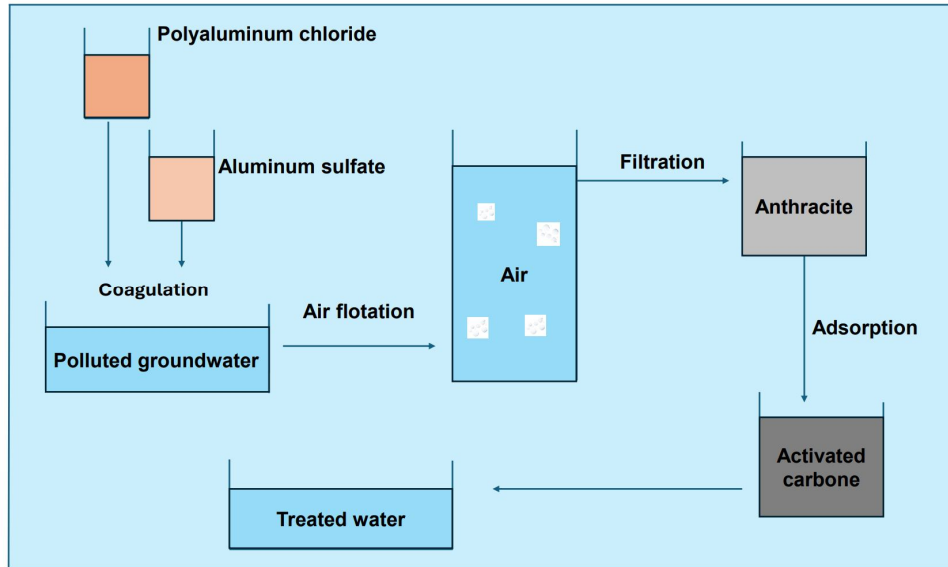


Figure 2: Sketch of the various steps of air flotation treatment

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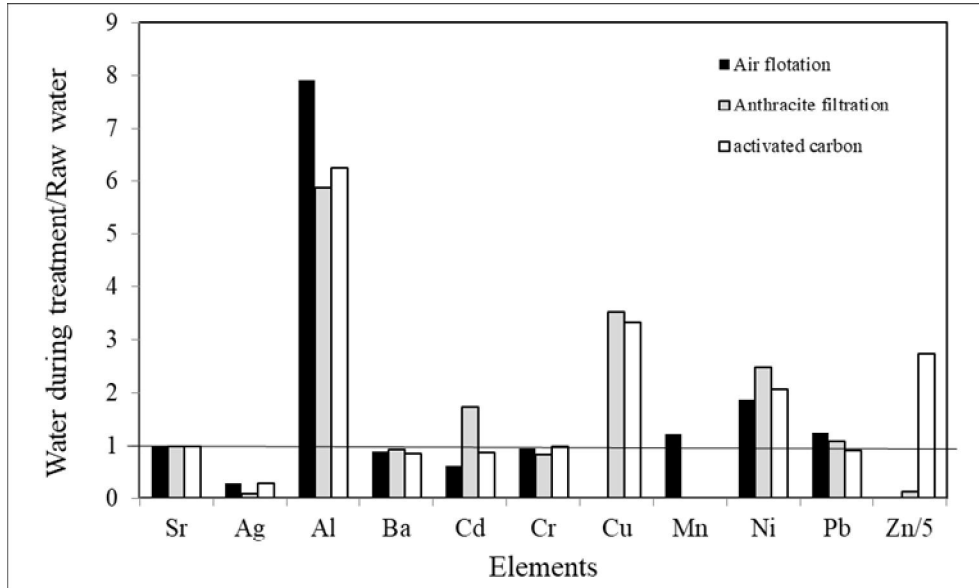


Figure 3. Chemical composition of untreated groundwater and waters after treatment, GW: average composition of groundwater, RW: raw water, AF: air flotation, SF: anthracite filtration, AC: activated carbon adsorption

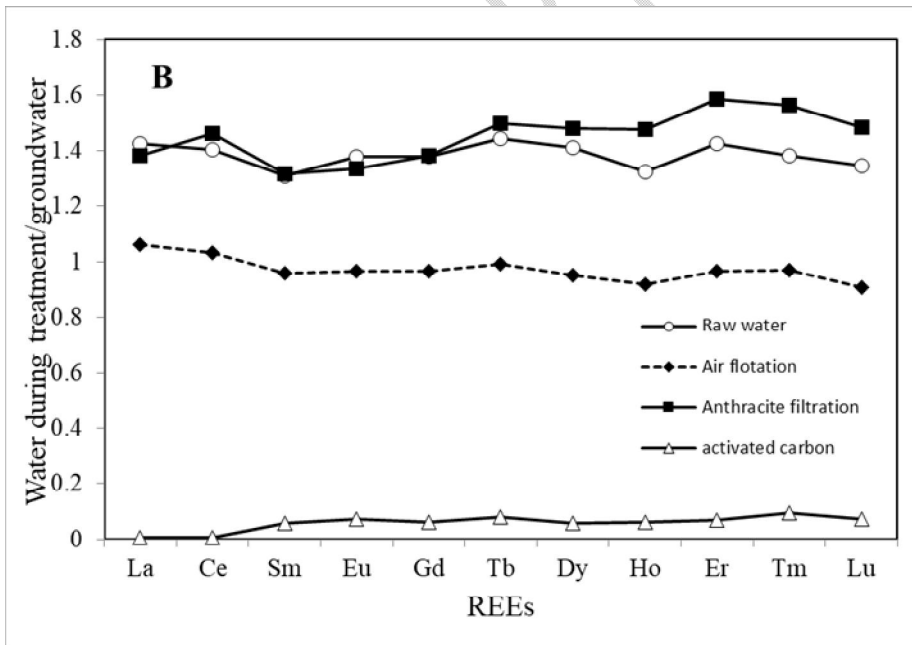
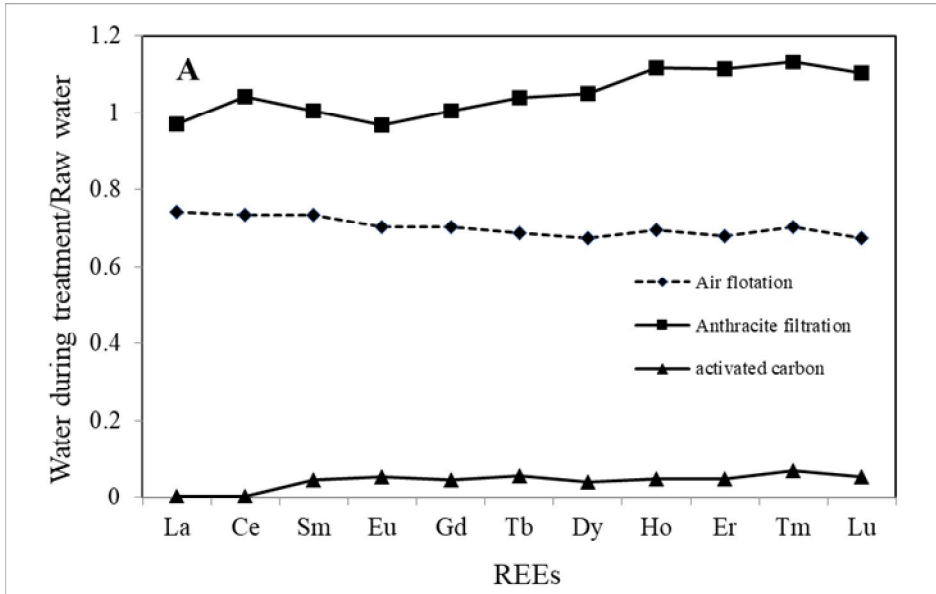


Figure 4. REE distribution patterns in waters collected at every step to a) REE concentrations in raw water before treatment and b) average composition of REEs in different wells.