

Immobilization of heavy metals in the saturated zone by sorption and *in situ* bioprecipitation processes

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Abstract

An ex-mining site located in Katowice, Poland, where silver, zinc and lead mining along with other activities took place for decades is now heavily contaminated with heavy metals. Especially the Quaternary and Triassic aquifers and surface water in the surrounding area are polluted. One serious risk is the threat of the contamination to drinking water, since the Triassic aquifer provides drinking water for more than 300 000 inhabitants. The main pollutants of concern are B, Ba, Zn, Cd, Cu, As and Sr. Remediation measures proposed for the Quaternary aquifer include a combination of natural attenuation, sorption barriers and *in situ* bioprecipitation. Dolomites, fly ash, and peat are considered as suitable adsorbent materials for removing barium and strontium from the contaminated groundwater. However, no adsorbent has been found to efficiently remove B. *In situ* bioprecipitation (ISBP), a process during which sulphate reducing bacteria are stimulated by the addition of various C-sources and sulphate is reduced to sulphides that concomitantly precipitate the heavy metals, has been tested on both clay and sand aquifer taken from the site. Zn and Cu, and sulphate were removed more quickly in the sandy aquifer material than in clay.

In situ bioprecipitation combined with sorption was evaluated over a 150 days time period for the Triassic aquifer. Zeolites in combination with HRC or molasses gave the best results, removing 100 % of Ba and Sr in less than 2 days and 35% of B after 150 days. However, no sulphate was removed under these conditions. In addition, when zeolite was combined with HRC, 100 % Zn was removed in less than 2 days. Zn was also removed using MRC[®], lactate, and diatomic earth in combination with HRC[®] or molasses. A combination of ISBP and sorption offers the potential to contain the metal contamination in this Triassic aquifer.

1. Introduction

Tarnowskie Góry (Katowice, Poland), is a 84 ha ex-mine site which exploited silver, zinc and lead ores for many centuries. Other activities practiced on this site include the production of potassium aluminium sulphate, and sulphuric acid, later on production of oil paint pigments like boric acid (H_3BO_3), barium chloride (BaCl_2) and sodium perborate (NaBO_3). These activities have led to serious contamination of the Quaternary and underlying Triassic aquifer, and surrounding surface waters such as the Stola river. The Triassic aquifer provides drinking water for more than 300 000 inhabitants. Since drinking water standards are under threat from this contamination, the Government has investigated various remediation strategies. So far, 'dig and dump' remediation measures have been undertaken involving the installation of a few controlled landfills. However, these have not provided sufficient guarantee that contamination is under control. The main pollutants are B, Ba, Zn, Cd, Cu, As and Sr and the pollution is located in the unsaturated soil, the saturated soil or aquifer, groundwater and surface water. The Quaternary aquifer is already contaminated and remediation measures proposed include a combination of natural attenuation, sorption barriers and *in situ* bioprecipitation. The Triassic aquifer is not yet fully contaminated and the aim is to prevent further contamination, either by pump and treat or immobilization of the pollutants in the Quaternary aquifer.

In this work, *in situ* bioprecipitation and/or sorption of metals present in groundwater of the Triassic and the Quaternary aquifer were investigated. *In situ* bioprecipitation (ISBP) is a process during which sulphate reducing bacteria are stimulated by the addition of various carbon sources (electron donor) and sulphate is reduced to sulphides that concomitantly precipitate the heavy metals. Different adsorbents were also tested in combination with ISBP with different groundwaters. To obtain information on the precipitates formed during *in situ* bioprecipitation and on the main binding sites, the strength of metal binding to particulates and the phase associations of trace elements in aquifer samples, a sequential extraction of these aquifers was performed. This increased understanding of the geochemical processes governing heavy metal immobilization during *in situ* precipitation (Yuan et al., 2004).



fig1. Map of the Tar-nowskie Góry megasite and relevant concentrations of heavy metals. Blue spheres indicate Zn concentrations above 500 µg/l, green spheres Cu concentrations above 100 µg/l, and purple spheres As concentrations above 40 µg/l.

2. Materials and methods

Aquifer and groundwater samples. Both groundwater and aquifer material from two different geological formations, i.e., Quaternary and Triassic, were used. Four different aquifer samples, either clayly (p8-2 and p28-5) or sandy (p24-6 and p6-4), and corresponding groundwater samples from the quaternary aquifer were used for ISBP experiments while 13 groundwaters were used in sorption experiments. Contaminated (S1) and uncontaminated (S2) Triassic aquifer material were studied using combined sorption/ISBP experiments. All groundwater samples have been summarized in Table 1. All set ups were performed on singular samples.

***In situ* bioprecipitation microcosm experiments.** For the construction of microcosms, 80 g of aquifer was mixed with 186 ml of groundwater in 250 ml serum bottles. Sterile, anoxic solutions that contained either acetate, lactate, molasses or Hydrogen/Metals Release Compound® (HRC®/MRC®, Regenesis) were amended with a final carbon concentration of 0,02% (w/v). In microcosms containing quaternary aquifer samples, the impact of 2 redox manipulating compounds (RMC) on sulphide production and metal precipitation was also examined. Two control experiments were set up, an abiotic control containing 0.0175% (w/v) formaldehyde and a natural attenuation control, which was not amended with an extra C-source.

Table 1 Determination of the parameters in the used groundwater samples.

groundwater	pH	sulfate mg/l	Zn (µg/l)	Cu (µg/l)	Ba (µg/l)	Cd (µg/l)	B (µg/l)	Sr (µg/l)
P28*	6,7	170	56	<10	154	<3	25300	556
P6*	6,6	53	89	19	39	<3	671	72
P24	5,6	36	826	<10	94	8,9	384	86
P24A*	7,3	470	69	<10	55	<3	22000	747
P27A	5,9	580	254000	<10	41	1370	41400	2860
PT8*	7,3	310	55	<10	28	<3	39300	606
PT7	5,6	1200	8070	94800	51	212	40900	6630
PQ1	7	590	596	<10	44	4,7	102000	456
P29	4,9	420	404	95	12	7,8	88100	243
P14	7	<1	1680	33	59400	6,3	6510	9840
P20	6,8	54	66	<10	37	<3	1210	99
P5	5,4	850	404	653	25	6,9	216000	1410
P9	5,2	73	877	118	41	8,4	508	182

Serum bottles were sealed using gas-tight butyl rubber stoppers, incubated statically at room temperature and under a N₂/CO₂/H₂ (87.5/7.5/5 %) atmosphere. Samples were visually examined for blackening, indicative for sulphide precipitation every week. Other parameters like ORP, pH, sulphate content and metal concentration (Zn, Cd, Cu, B, Ba, Sr) were analyzed every 2 weeks. Sulphate analysis indicated the immobilization of heavy metals as sulphides. Furthermore, dissolved organic carbon (DOC) was measured to get an idea about the consumption of electron donor/C-source by sulphate reducing bacteria. Metal removal in Quaternary aquifer samples was studied by *in situ* bioprecipitation only, whereas metal removal in samples from the Triassic formation was studied by ISBP and by ISBP combined with sorption by addition of several adsorbents like zeolites, diatomic earth and dolomites.

Sorption microcosm experiments. Groundwater (20 ml) was mixed with either 0.5 g or 2 g adsorbent in 25 ml serum bottles. Twenty two different adsorbents were used including fly ash (2 types), natural (7 types) and manipulated (7 types) zeolites, granular activated carbon (GAC, 2 types), redox manipulating compounds (RMC, 3 types) and compost. Mixed groundwater samples were incubated during 24 hours with the adsorbents, while groundwater samples containing RMC and compost were sampled after 1 week, 2 weeks and 1 month. Prior to and after incubation, the heavy metals were measured by ICP-AES and pH was measured (Accuracy between 3 and 20 µg/l).

Sequential extraction procedure. A modified model of the extraction method used by Akcay et al. (2003) was applied. One extra step has been added to this protocol, i.e., a leachable fraction was determined prior to the first step. Furthermore, the last extraction step was omitted in the sequential extraction procedure. So, a five step extraction scheme was used including the determination of a leached fraction (1), an exchangeable fraction (2), a carbonate fraction (3), an Fe-Mn oxide fraction (4), and an organic fraction (5).

3. Results and Discussion

Removal of metals in Quaternary groundwater samples by sorption.

In view of using a reactive sorption barrier to contain the metal contamination of the groundwater in the quaternary aquifer, several adsorbents were tested in order to define metal removal capacity from the 13 types of groundwater that were used. Several common conclusions were that the pH increased with 2 to 3 pH units in the conditions containing fly-ash 50/51, zeolite 50/51, zeolite X, Metasorb, calcined magnesite, GACB and GAC1. There was a good removal of Sr in the conditions to which Zeolite X, Zeolite 50/51, Clinoptilolite, Mordenite, PAsXP, PAsEP, PAsX5L and GAC1 were added. The maximum removal percentage of Sr was 86%-98%. B could only be removed with 3 types of manipulated zeolite. However, the maximum percentage removal of B by these three adsorbents varied from 16 to 36%. Zeolite X and GAC1 are the best adsorbents for Ba for each type of groundwater. Fly ash 50/51, zeolite 50/51 and calcined magnesite gave a removal percentage of more than 99% for Cu and Zn. Cd was removed by Zeolite X, Calcined magnesite and GAC1. All these removal capacities are summarized in table 2. Several samples of RMC were used and tested in combination with the groundwater in order to reduce the redox potential and in that way the mobility of some metals. The pH increased by approximately 1 log unit after addition of RMC for 3 types of groundwater, i.e., P28, P6, and P24. Sr and B could not be removed with RMC. The use of RMC gave a good removal for Ba and Cd for almost all groundwaters used except for respectively P14 and P27A groundwater samples. Addition of RMC resulted in a Zn removal of 40 up to 90 % while a removal capacity of 100% Cu was noticed with all types of RMC.

Table2 Representation of removal capacities of heavy metals in different groundwaters using different sorbents. Only the highest removal capacities are presented.

Sorbent/metal	Sr	B	Ba	Cu	Zn	Cd
zeoliteX	98%		>99%			
Zeolite50/51	98%					
clino	92%					
mordenite	98%					
pAsXP	89%	36%				
pAsEP	94%	36%				
pAsX5P	95%	36%				
GAC1	96%		>99%			>99%
Flyash50/51				>99%	>99%	
Calcined magnesite				>99%	>99%	>99%

***In situ* bioprecipitation of elements in microcosm experiments using quaternary aquifer**

The potential for heavy metal immobilization by indirect sulphide precipitation due to sulphate reducing activity was examined by using 4 different aquifer/groundwater samples. Since not only heavy metals were present that are known to precipitate easily with sulphides like Zn and Cd, the impact of *in situ* bioprecipitation on these other elements like B, Ba, Sr was also studied. As shown in fig 2.1, the pH decreased by at least one log unit in the clay-containing microcosms (p8-2cl and p28-5cl) after supplying molasses as C-source. However, in the sand-containing microcosms (p24-6s and p6-4s) no such pH change was observed after the addition of molasses.

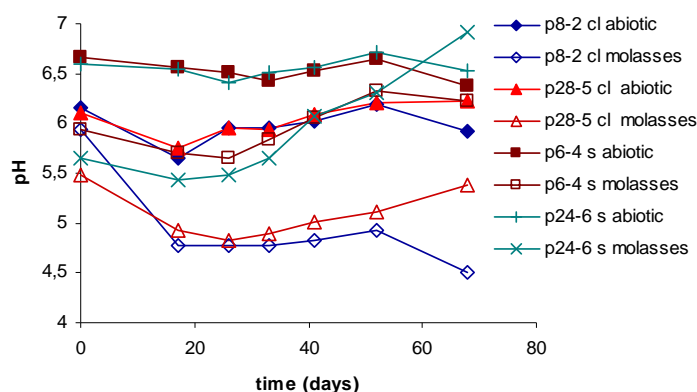


fig 2.1. Effect of the addition of molasses on the pH of the sandy (s) or clayly (c) Quaternary aquifer..

This acidification could be explained by the fact that molasses, contains about 40% glucose that is used as C-6 compound in microbial fermentation and fermented into volatile fatty acids like acetic acid which in turn acidifies the aquifer/groundwater solution. Apparently, this acidification often takes place in experiments where molasses is added and seems crucial for the success of sulphide production and metal precipitation as seen in other experiments performed in our laboratory. Furthermore, it is hypothesized that molasses complexes metals partly and therefore distorts the picture of metal immobilization. Further research is needed to fully understand the mechanisms underlying this observation.

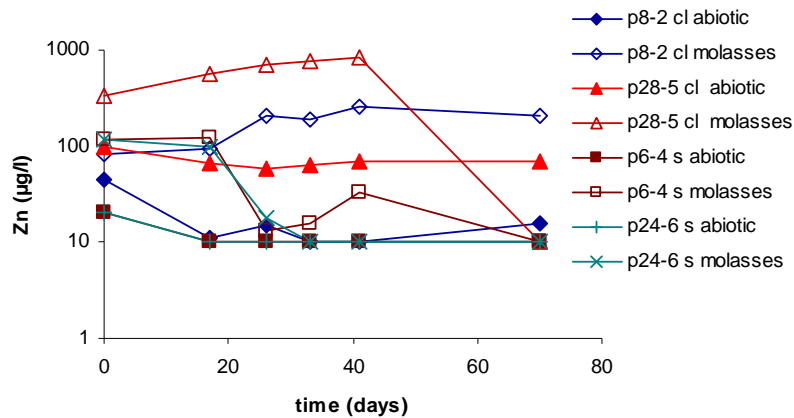


fig 2.2. Evolution of the Zn concentration during *in situ* bioprecipitation in abiotic and stimulated microcosms by addition of molasses.

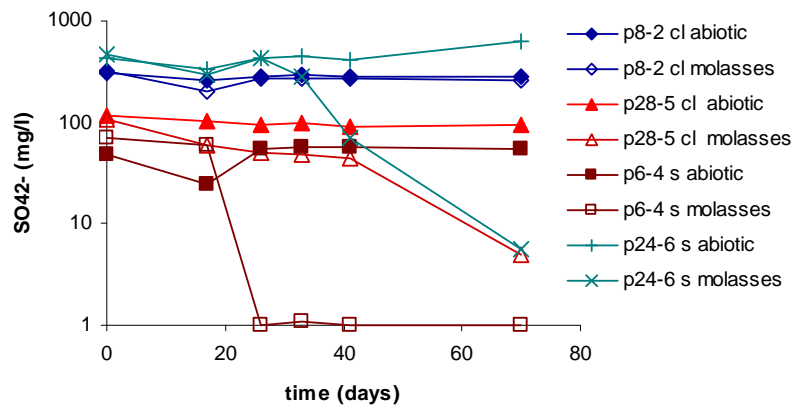


fig 2.3. Evolution of the sulphate concentration during *in situ* bioprecipitation in abiotic and stimulated microcosms by addition of molasses.

As shown in fig 2.2, Zn was first released (approximately 100 µg/l) in microcosms containing sand and supplied by molasses, but after one month the concentration of Zn decreased. In the microcosms containing clay and supplied with molasses, Zn was released with a factor 4.5-8 (about 160µg/l-740µg/l). However, after more than two months incubation Zn was removed in the clay containing condition p28-5cl while in the condition p8-2cl Zn was not removed. Fig 2.3 shows the consumption of sulphate in the conditions where Zn was removed. In the conditions with HRC[®], Zn was also released first but after 1 month incubation Zn was removed (data not shown). In almost all conditions Sr was released except in the sand containing condition p24-6s with RMC where Sr could be removed for 28-33%. Also Ba was released in almost every condition. However, in the condition p8-2cl with molasses, Ba was released first but finally removed for 43%. Also in the condition p24-6s with RMC, Ba was released first but after two months the removal percentage was about 45%.

Sequential extraction was performed on aquifer samples from microcosms studied for natural attenuation and for ISBP after stimulation by acetate and a redox manipulating compound after ISBP had occurred. Our experimental results show that in comparison with the natural attenuation condition (without additional C-source), the Zn, B and Fe concentration in the Fe-Mn-oxide fraction increased in the condition with acetate and RMC (fig 3.1 and fig 3.2). The heavy metals in this fraction are hardly available because they are bound relatively strongly. The metals in this fraction might be derived from metal-sulphides. In comparison with Zn and Fe, low concentrations of Ba, Sr, and B occur in this fraction. Summarized, sequential extraction of the different metals from both clay and sandy aquifer shows very good immobilization of Zn, Cu and Cd. This immobilization as metal-sulphides was however not noticed for Ba, B and Sr (Quevauvillier, 2002).

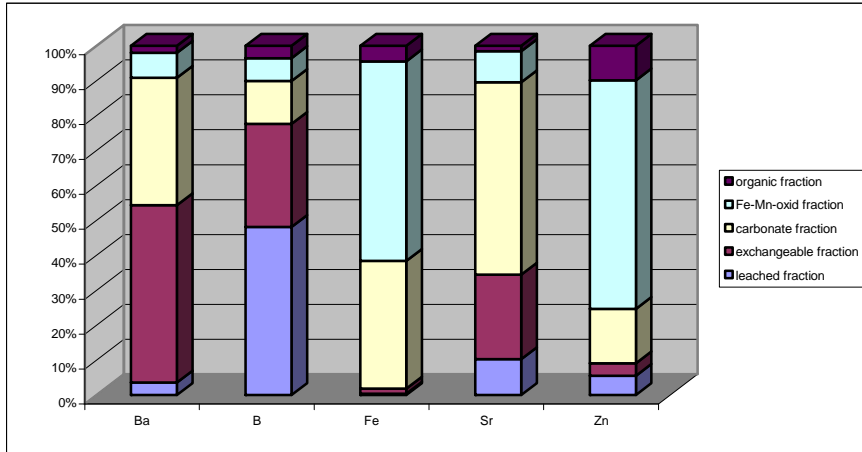


fig 3.1. Distribution of metals in various fractions determined by sequential extraction of aquifer in the natural attenuation microcosm

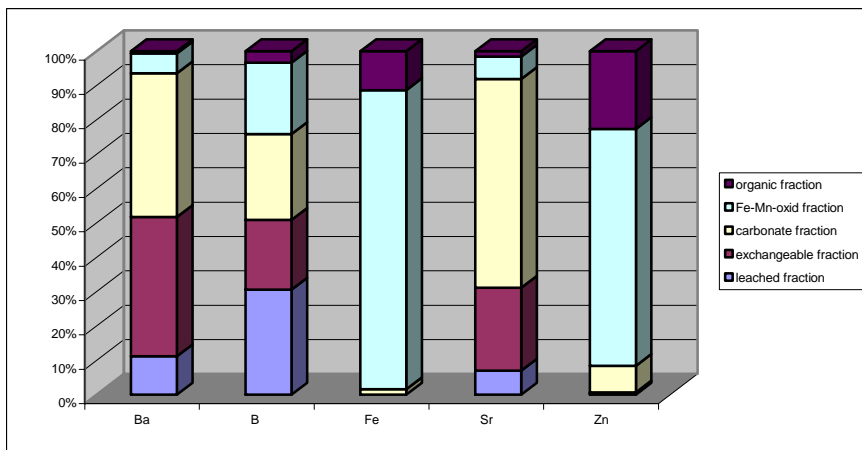


fig 3.2 Distribution of metals in various fractions determined by sequential extraction of aquifer in the microcosm stimulated by acetate and a RMC.

***In situ* bioprecipitation combined with sorption for the removal of elements in microcosms experiments using Triassic aquifer material and groundwater**

For the Triassic aquifer not only *in situ* bioprecipitation was studied but also ISBP combined with sorption to study the impact of sorption on the ISBP

process and vice versa in more detail. Since the Triassic aquifer is a supply for drinkwater, a higher risk reduction than for the Quaternary aquifer is needed. Therefore, 3 different adsorbents, i.e., zeolites, dolomites, and diatomaceous earth were used in combination with different electron donors (HRC[®], lactate, molasses) which were added either individually or combined with the adsorbents. In the conditions where HRC[®] or molasses were supplied simultaneously with zeolite, the removal of Ba, B and Sr was most efficient (fig 4.2, fig 4.3 and fig 4.4). B could be removed for 35%, although sulphate was not removed in these conditions (fig 4.1). Zn removal was efficient (100%) in the condition where molasses was added in combination with diatomaceous earth, and the condition where lactate was supplied. In the condition where zeolite and HRC[®] were added simultaneously, Zn was removed for 100% after 21 days (data not shown). The pH increased with 1-2 log units in the conditions containing zeolite (data not shown). In the condition “HRC in combination with diatomic earth”, Zn removal was initially observed but in a second phase release of Zn was determined.

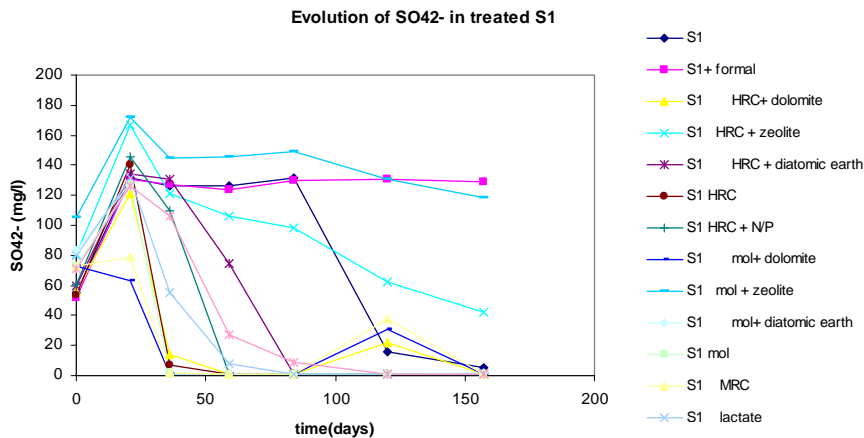


fig 4.1. Evolution of sulphate in treated S1 triassic aquifer

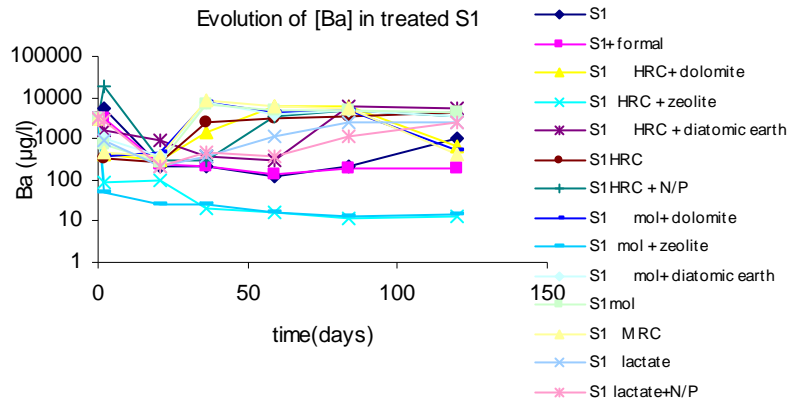


fig 4.2. Evolution of Barium concentration in treated S1 triassic aquifer

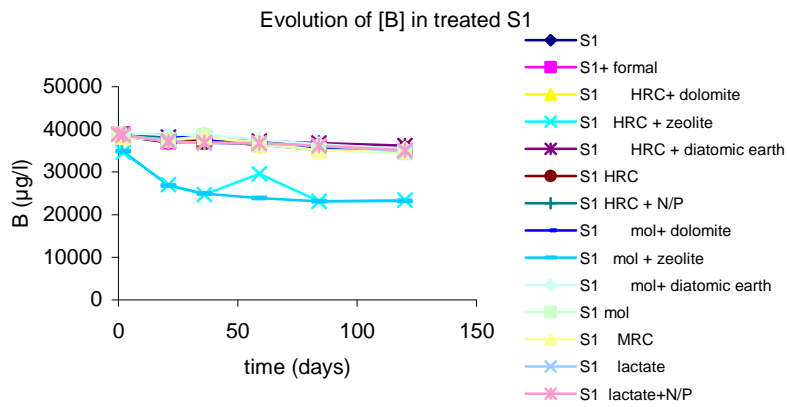


fig 4.3. Evolution of Boron concentration in treated S1 triassic aquifer

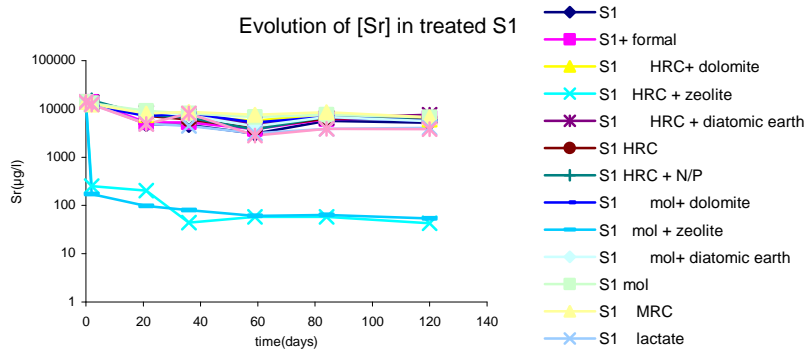


fig 4.4. Evolution of Strontium concentration in treated S1 triassic aquifer

4. Conclusions

ISBP has been shown to have potential to remove the more mobile metals like Zn, but did not efficiently contribute to removal of B, Sr and Ba as shown in the Quaternary aquifer microcosms. However, the combination of *in situ* bio-precipitation with specific adsorbents for the Triassic aquifer samples seems promising to deal with the mixed metal contamination. Because in these conditions there was only a minor decrease of the sulphate concentration and because in the same conditions without adsorbents no such removal of metals was observed, it seems that the heavy metal removal was mainly due to adsorption onto the zeolites. Nevertheless, the impact of adsorbent addition on pH was significant and will probably impact the microbial population. This should be examined in more detail by molecular methods specifically targeting the sulphate reducing bacterial community. Sequential extraction showed that Ba, B and Sr predominantly appeared in the leached, exchangeable and carbonate fractions and more sporadic in the Fe-Mn-oxides and organic fraction. This indicates that these sorbed metals may be easily liberated in the environment. This is contrary with Zn and Fe where the largest fraction appears in the Fe-Mn-oxides and organic fraction. The sorption experiment proved that GAC1 and zeolite X were the best adsorbents for Ba and Sr. No adsorbent has been found to efficiently remove B. The maximum removal percentage of B was only 36%. Fly ash50/51, zeolite 50/51 and calcined magnesite could remove Cu and Zn for 99%. The best adsorbents for Cd were zeolite X, calcined magnesite and GAC1. Further experiments should unravel the impact of ISBP and sorption simultaneously on the stability of metal immobilization and the stability of the precipitates/sorbed metals in the long run.

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