AQUIFER BIOTHERMOREMEDIATION USING HEAT PUMPS: SOUND THEORETICAL BASIS AND RESULTS ON THERMAL, GEOCHEMICAL AND BIOLOGICAL IMPACTS ON AQUIFERS

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ABSTRACT

Geothermal heat pumps have been operated on aquifer over the past thirty years. Currently, these systems constitute a major sector of renewable energy development. However, this development is accompanied by several difficulties at scientific, technical and administrative levels, to describe short and long term interactions with aquifers, at both the local and regional scale, especially close to urbanized or industrialized areas.

As a typical example, the long-term use of groundwater heat pumps for air conditioning of homes or buildings can induce significant increases in temperature of the aquifer, if, for given groundwater flow direction and rate, there is an imbalance between the demands for cooling and heating. Therefore, the aquifer (groundwater and sediments) can be affected. In fact, it is expected that a wide variety of geochemical reactions and microbiological changes with variable intensity should occur which depends on the sediment characteristics and hydrogeological background. The presence of organic pollutants in the aquifer can amplify these phenomena. The predictable results may progressively be: (i) precipitation, which reduces the porosity of the aquifer and/or the well productivity, (ii) an inappropriate temperature for the use of groundwater heat pumps for air conditioning, but also and especially (iii) pollutant bioremediation, which has a beneficial impact on the aquifer. Under certain conditions, this bio-thermo-remediation can be considered as an attractive option for some contaminated aquifers, taking into account the fact that, administratively in European countries, any action is subject to authorization.

Notably in the framework of the collaborative project BIOTHERMEX (French Region Centre, convention n° 200800034163), exploratory studies were focused on three objectives:

i) Improving the understanding of the concept of bio-thermo-remediation of aquifers by using effects induced by geothermal heat pumps.
ii) examining realistic configurations, on a laboratory scale, pilot-scale and *in-situ*, in order to identify the most determining factors for possible (undesirable or helpful) aquifer impacts, e.g. temperature increase, bacterial development, organic pollutants degradation
iii) evaluating if those configurations can present interests for bio-thermo-remediation of polluted aquifers by using heat pumps.

A literature survey led to the consolidation of the basic principles of bio-thermo-remediation of most organic pollutants: increase in volatilization, solubility, degradation kinetics and mobility of the residual pure phases by reduction of their viscosity. The different heat pump systems and processes are discussed in the article, to identify what is suitable for bio-thermo-remediation.

To reproduce the underground thermal conditions encountered in groundwater heat pumps systems (temperature range of water production from 10 to 25 °C, temperature range of water injection between 20 and 35 °C), batch-experiments, at laboratory and pilot scale have been carried out to investigate the impacts of the different parameters on the geochemical equilibrium (solubility, mobility, precipitation, dissolution, volatilization,) on the aquifer inorganic content and organic pollutants as well as on microbial populations activities. Two different sediments were used. Depending on the nature of the sediments and the water composition, the impacts are more significant: (i) thermally, with a low water flow rate, (ii) geochemically, with the high bicarbonate and Ca/Mg contents in water and (iii) biologically, with a organic contaminants contents in water. Some results from *in-situ* measurements (especially with an aquifer polluted by chlorinated solvents) are used to corroborate the conclusions. Even if the most part of the work is still in progress, the obtained results are validated by biogeochemical modelling.

The combination of a low-enthalpy geothermal system using aquifer heat pumps (water pumping and re-injection) and remediation approaches appears to be an appropriate method to treat aquifers polluted by organic contaminants without use of any other way than the thermal energy.

Key words: aquifer heat pumps, remediation, pollution, thermal enhancement, precipitation, biothermoremediation.

1. THEORETICAL AND BIBLIOGRAPHICAL BASIS ON THE REMEDIATION BY THERMAL ENHANCEMENT, PARTICULARLY BY GEOTHERMAL HEAT PUMPS

The use of geothermal energy is today promoted as an alternative and sustainable source of energy. While Geothermal Heat Pumps (GHPs) are operational on aquifers over the past thirty years, today they always constitute a major sector of renewable energy development. However, regarding the authorization, regulation and monitoring of such facilities with respect to possible environmental impacts, a severe lack of knowledge has been identified [1]. Thus, the development of GHPs is accompanied by difficulties in scientific, technical and administrative levels, to describe interactions with aquifers, short and long term as to the local or regional scale, especially close to urban or industrialized areas. Aquifers are not only abiotic reservoirs of water and sediment, but they are complex ecosystems harboring an almost unexploited diversity of microorganisms and fauna. Intrinsic groundwater microorganisms are highly adapted to extremely oligotrophic, but stable conditions including temperature. At the same time, groundwater biotas are the key drivers of important ecosystem services, especially functions connected to water quality.

Examples to demonstrate what was previously presented exist. An example is that the long-term use of GHPs for air conditioning of homes or buildings can induce important increases in temperature of the aquifer, if, for a given groundwater flow direction and rate, there is an imbalance between the demands for cooling and heating. This is the case in the urban and industrialized area of Lyon City (France), where the GHPs density caused a permanent temperature increase sometimes higher than 10°C. Therefore, in such a case the aquifer (groundwater and sediment) can be affected. In fact, it is expected that should occur a wide variety of geochemical reactions and microbiological developments with variable intensity which depends on the groundwater and sediment characteristics and hydrogeological background (type of aquifer, hydraulic conductivity, etc.).

GHPs functioning on aquifer are likely to cause the following predominant problems [1-2-6]:

(i) disturbance of the thermal or hydraulic behaviour of the aquifer which may affect the suitability of groundwater for further use (interference for nearby users)
(ii) precipitation of mineral species, which may reduce the porosity of the aquifer and/or the well productivity (clogging of heat exchangers, scaling on pipes). Dominant scaling product are expected to be calcium carbonate (supersaturation at elevated temperature and/or stripping of carbon dioxide from groundwater) and iron or manganese oxy-hydroxides (microbiological processes, corrosion by-product).
(iii) decrease of dissolved gas saturation (oxygen, carbon dioxide), mobilization of organic matter, silica reactions
(iv) ecological changes in the target groundwater which could lead to detrimental or beneficial effect on activities, diversity, growth and survival of biological species, especially bacterial community. Until now, insufficient data precluded the estimation of the response of an aquatic system to increased water temperature, including study related to health aspects.

In addition, the presence of organic pollutants in the aquifer can amplify these phenomena. This could, in case of appropriate temperature condition, enhance the biodegradation of organic pollutants or pollution bioremediation, which is a beneficial impact for the water quality of the aquifer. Under certain conditions, this bio-thermo-remediation of soils and aquifers, polluted by organic compounds, can be considered an attractive option for some contaminated aquifers, taking into account the fact that, administratively in European countries, any action is subject to authorization [5].

The policy of spreading out of the cities is not any more topicality and the strong current land pressures lead to the rehabilitation of the industrial waste lands, as well as the requirement to give access to clear water and a healthy environment. In order to contribute to the restoration of the industrial waste lands polluted by organic pollutants the use of low enthalpy geothermal energy processes, normally dedicated to the heating and the air-conditioning of the buildings, is often cited in the literature as a key issue.

The main organic pollutant addressed by this “thermally enhanced” remediation are (i) light aliphatic hydrocarbons, Volatile Aromatic compounds (VAC), Volatile Organo-Halogenated Compounds (VOHC), and some dicyclic Aromatic Hydrocarbons (naphthalene and its alkylated derivatives), which are among the most problematic pollutants to manage.

Using, either GHPs directly on aquifers or indirectly with vertical geothermal probes, both in the unsaturated and saturated zone, leads to an increase of the ground temperature. This increase in temperature can enhance the organic compounds recovery and degradation. Thus, for the above mentioned organic compounds (and more specifically for the CAV and COHV), an increase in temperature of the aquifer (groundwater and sediment) can cause [3-4-8-9]:

(i) an increase in volatilization,
(ii) an increase in solubility,
(iii) an increase in degradation kinetics and
(iv) an increase in mobility of residual pure phases by reduction in their viscosity.

The positioning of the bio-thermo-remediation is thus halfway between the traditional *in situ* thermal desorption and the traditional extractive methods used for VOHC (pump and treat, venting, dynamic biostimulation). In addition, the fact to moderately increase the temperature will lead to a biostimulation. Thus, the intermediate positioning of this new *in situ* technology for remediation and reconversion of industrial polluted lands will make it possible to benefit from the advantages of each above-mentioned technique.

If we consider the biothermoremediation as a treatment process, then the temperature increase of the aquifer can cause:

(i) a reduction of treatment duration;
(ii) reduction of the energy impact of the operation of depollution, energy necessary to the thermal increase being provided by a renewable energy to very weak impact in terms of emissions;
(iii) reduction in the treatment costs in comparison to the traditional desorption techniques, because a) of a mutualisation of the material of desorption heating/depollution) and b) of a technique less energy consuming that traditional desorption;
(iv) less impact on the quality of the groundwaters and the micro-organisms that traditional thermal desorption.

A literature survey has led to the consolidation of the basic principles of bio-thermo-remediation mainly known as “thermal enhancement” of most organic pollutants. The different GHPs systems and processes are discussed in this survey, to identify the most suitable for bio-thermo-remediation. A final technical and economical appraisal will enable to rate the technologies on the current remediation market and to determine its optimal range of application with respect to currently used technologies. Through demonstrating the performance of the “thermal treatment”, the expected impacts shall be to promote the implementation of processes coupling remediation and energy taking into account technical, economic and social aspects. This diversion of the traditional use of these renewable energies fits in a "life cycle thinking" approach, which is been developed at the European level, when regarding how we conceive the development, and therefore how to rehabilitate the brownfield sites. The thermal enhancement is trying to gain a sustainable production foothold and it promotes also a minimization of the impacts by using green energy, and thus shows a will to develop the pathway of a "green depollution ".

2. CONTEXT AND OBJECTIVES OF THE PRESENT WORK

Bacterial communities play an essential role in aquatic ecosystems. They are responsible for much of the cycling of both carbon and nutrients. In groundwater, these communities often dominate the biotas, both in biomass and in metabolism. Temperature is known to be a key factor for the growth and the development of microorganisms. More commonly, any species have a range of tolerance on temperature condition, the so-called “cardinal temperature”, with an upper and lower limit for growth and an optimum temperature at some point of these two extremes. Although the effect of temperature on individual taxa is well studied, the effect of temperature on the metabolism of natural bacterial communities is poorly understood in terms of community composition, resources acquisition (metabolism), interaction between species etc. Most of the bacterial species in groundwaters are adapted to a relatively narrow temperature regime and we could ask how the artificial temperature discharge can affect bacterial metabolism.

Notably, in the framework of the collaborative project BIOTHERMEX (French Region Centre, convention n° 200800034163), exploratory studies were focused on two main objectives:

(i) examining realistic configurations, on a laboratory scale, pilot-scale and *in-situ*, in order to identify the most determining factors for possible (undesirable or helpful) aquifer impacts, e.g. temperature increase, bacterial development, organic pollutants degradation
(ii) evaluating if those configurations can present interests for bio-thermo-remediation of polluted aquifers by using GHPs and improve understanding of the concept of bio-thermo-remediation of aquifers by using effects induced by GHPs.

Attempts to attain a metabolism limit by both temperature and substrate is proposed experimentally in this study. Therefore, the main goal of our research is to understand the relationships between temperature, substrate content and microbial activity during Aquifer Thermal Energy Storage (ATES), and quantify the effect on microbial activity of a groundwater used for geothermal applications.

3. MATERIAL AND METHODS

3.1 Groundwater collection

In order to evaluate the metabolic activity, two different sites are used to collect groundwaters. The first site, situated in Balandran (Gard, southern France) is taken for reference. There, non-polluted groundwater is periodically used for cooling or heating of agricultural greenhouses. Three main piezometers surrounding the production and injection wells of this site are equipped with temperature probes in different depths. Their groundwaters are periodically sampled and analyzed during a year. The groundwaters were sampled with a submersible pump from a depth of 12 m and were collected in sterile bottle with aseptic procedure for microbial analysis. The non-conservative water parameters are: pH 6.79 at 16.4°C, electrical conductivity 560µS/cm (at 25°C), pe 7.02, dissolved oxygen 7.24 mg.L^{-1} and alkalinity 3.88 mmol.L^{-1}. The total organic carbon and the dissolved organic carbon (DOC) were both equal to 0.7 mg.L^{-1}. The concentrations of the main inorganic ions (in mM) were: Ca^{2+} 2.76; Na^{+} 0.64; Mg^{2+} 0.32; Cl^{-} 0.82; NO_3^{-} 0.67; SO_4^{2-} 0.79. The second site is situated in the urban and industrialized area of Lyon city (in modern fluviogenic soils), where the GHPs density is so high that groundwater temperature is thermally and quasi-permanently altered. In addition, the site is polluted by organic compounds and there are four GHPs that are using important flow rates (>50 m^3/h) for cooling (reject hot water). The site is monitored over several years. In the field, the main non conservative parameters are measured and after sampling, the main organic pollutants are quantified according to EN ISO 10301 for VOHV, EN ISO 9377-2 for hydrocarbon oil Index; ISO 11423-1 for VAC, and NFT 90-115 for PAH.

3.2. Metabolic activity evaluation

Two approaches are used to examine the temperature effect on bacterial metabolic activity (enzymatic activity) of groundwater from Balandran: the deshydrogenase activity and the carbon source utilization profile.

3.2.1 Deshydrogenase activity approach

The 2-(p-iodophenyl)-3-(p-nitrophenyl)-5-phenyl tetrazolium chloride (INT) was used to measure dehydrogenase activity (respiratory activity). The INT assay is not commonly performed on water as sample, that's why the method has been modified to facilitate the analysis of water. The following steps outline a filtration procedure that traps bacteria on a nylon membrane thereby concentrating them from 100 ml of groundwater. The membrane containing the bacteria is then incubated into a 0.02% INT solution for 4 days in 3 replicates at controlled temperature. Extraction of formazan was made in vials containing 10 ml of acetone. The INT-formazan extract was then measured by spectrophotometry (wavelength adjusted at 480 nm).

3.2.2 Carbon source utilization profile approach

ECOLOG plates (AES Lab, France) were used in order to evaluate the effect of incubation temperature on carbon substrate utilization rate and pattern. Plates were inoculated with 150 µl of whole groundwater samples and incubated in the dark at different temperatures. Each well in these manufactured 96-well microplates contains lyophilized nutrients and a tetrazolium redox dye (triphenyletetrazolium chloride, TTC) as well as one of the 31 carbon source. Oxidation of the carbon source is indicated by colorimetric reduction of the dye. Following incubation, absorbance of the colorimetric reaction was monitored every 24 h for 1 week with a plate spectrometer (Multiskan spectrum, ThermoLab system). Average Well Color Development (AWCD) was calculated and the data was standardized by subtracting the blank control well measure from each substrate. The carbon source utilization profiles were conducted in six replicate samples of each incubation temperature.

Table 1: Substrates in Biolog® Ecoplate

Amines	**Carbohydrates**	**Carboxylic acids**	**Polymers**
Phenyl ethylamine	α-D-lactose	α-Ketobutyric acid	α-Cyclodextrin
Putrecine	β-Methyl D-glucoside	D-Galacturonic acid	Glycogen
	D-Cellobiose	D-Glucosaminic acid	Tween 40
Amino acids	D-Mannitol	D-Malic acid	Tween 80
L-Arginine	I-Erythritol	Itaconic acid	
L-Asparagine	Glucose-1-phosphate	γ-Hydroxybutyric acid	**Phenolic compounds**
L-Phenylalanine	D-Xylose	Pyruvic acid methyl ester	2-Hydroxy benzoic acid
L-Serine	D-Galactonic acid γ-lactone		4-Hydroxy benzoic acid
L-Threonine	N-Acetyl-D-glucosamine		
Glycyl-L-glutamic acid	D,L-α-Glycerol phosphate		

4. RESULTS AND DISCUSSION

4.1. Effect of temperature on groundwater bacterial communities from Balandran

In laboratory conditions, only the metabolic activities of groundwater from Balandran (a reference non-polluted groundwater) were evaluated. The impact of the temperature incubation on substrate degradation could be detected as shown in figures 1 and 2 which present respectively the results of the respiratory activity and ECOLOG approaches.

Results indicate an immediate and significant effect of temperature on GW bacterial communities. As temperature increase, the rate of chemical reactions (carbon mineralization) increases until an optimum temperature is reached.
If the temperature reaches 36°C, there is a sharp decrease in metabolic activities. The low-temperature has the effect of slow down the bacterial activities. The reasons for the upper limit of temperature tolerance are relatively well understood, determined by the denaturation of key cellular components, which disrupt the cellular function.

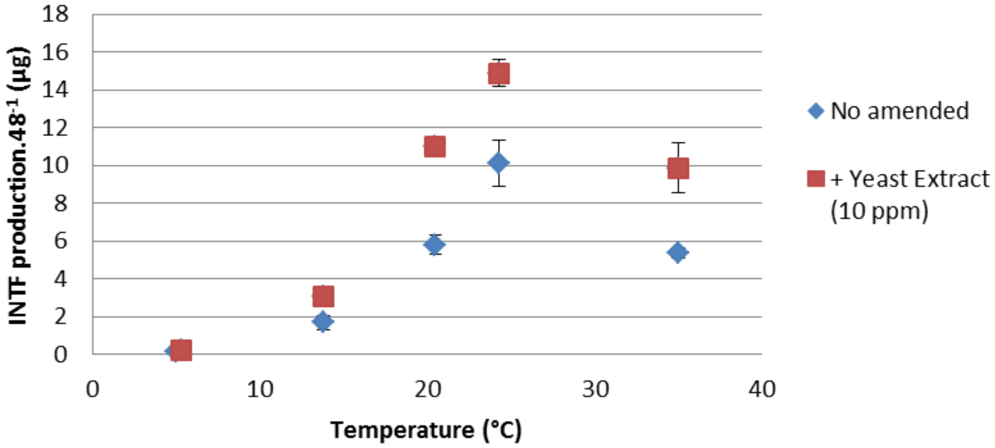

Figure 1: Effect of temperature and substrate addition on deshydrogenase activity of Balandran groundwater.

For the ECOLOG approach (figure 2), there is no further observable effect of temperature on the quality of substrate degradation (data not shown). The presence of substrate seems not to overrides temperatures effect.

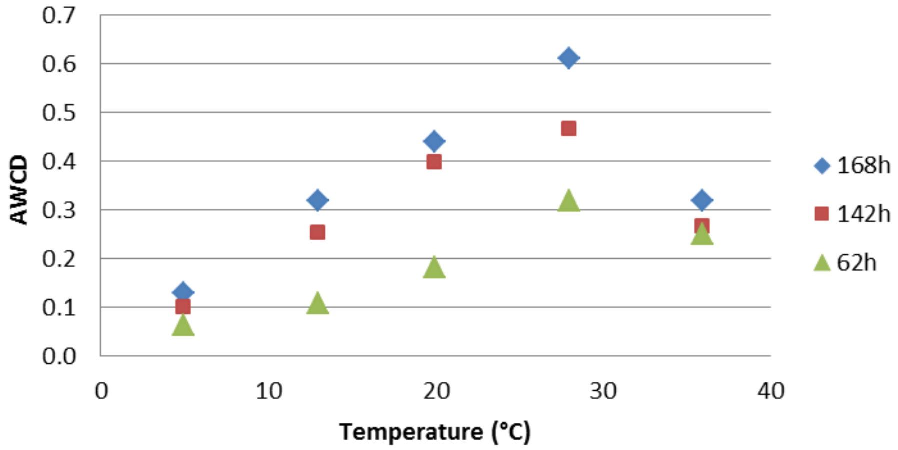

Figure 2: Impact of both temperature and incubation time on substrate mineralization (ECOLOG approach) of Balandran groundwater

4.2. Thermal, geochemical and microbiological perturbations on Balandran site

The non-polluted groundwater of Balandran is periodically extracted for cooling or heating of agricultural greenhouses. Two production-injection wells and three other piezometers, monitored during one entire year, revealed only a slight thermal effect that decreases as a function of the depth and the distance from the injection well (results will be shown in the oral presentation). In addition, no significant geochemical or microbiological disturbance was still evidenced. Nevertheless, in the paragraph 4.1 was demonstrated that the situation will be other and predictable in the longer term, especially if the water table was reached by an organic pollution.

4.3. Thermal and geochemical perturbations on a site in Lyon city

The evolution, over 5 years of monitoring, of the main geochemical parameters and some sensitive ions, and of the organic compounds contents has evidenced that the Lyon site is thermally and geochemically perturbed and partly remediated (results will be shown in the oral presentation). In the groundwater the pH and redox potential were decreased, the dissolved oxygen content was made null; temperature, conductivity and ion chloride content were increased (by reductive dechlorination). Concentrations of all classes of organic compounds (especially those of VOHC and VAC) decline for more than 80 %. Even if the most part of the work is still in progress, the obtained results corroborated the predictable consequences: (i) an inappropriate temperature increase for further use of groundwater by heat pumps for air conditioning and (ii) biodegradation of organic pollutants or pollution bioremediation, which is a beneficial impact for the water quality of the aquifer.

4. CONCLUSIONS AND PERSPECTIVES

Understanding how thermal discharge affects bacterial community processes, and thus ecosystem processes, is one of the challenges of BIOTHERMEX project. The main issue is what happens if groundwater biotas need to cope with sudden temperature dynamics caused by GHPs use. Potential effects of thermal use on groundwater systems already facing enhanced loads of nutrients or contamination require urgent scientific attention.

Within this project, we have assessed, both in the laboratory and in the field, the impacts of temperature discharge and withdrawal on biotic parameters and functional characteristics of exemplary shallow groundwater systems.

We have examined how heterotrophic bacterial communities respond to temperature by two experimental approaches. These preliminary results confirm the predictable effect of temperature on bacterial activities and provide insight into the effect of temperature limitation for bacterial metabolism (loss of biological function represented by carbon mineralization). Temperature is also an important limiting factor for ecological processes. Bacterial communities represent thus sensitive informative indicator to understanding the potential impact of thermal energy discharge in groundwater ecosystem. Additional research is devoted to evaluate how the temperature will affects the population dynamics (e.g. genetic structure and density) and to estimate the degree of adaptation of the communities to higher temperature and the consequence on ecosystem processes.

The combination of a low-enthalpy geothermal system using aquifer heat pumps (water pumping and re-injection) and remediation approaches appears to be an appropriate method to treat aquifers polluted by organic contaminants without use of any other products than the thermal energy.

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