



Temperature change affected groundwater quality in a confined marine aquifer during long-term heating and cooling



Takeshi Saito ^{a,*}, Shoichiro Hamamoto ^b, Takashi Ueki ^a, Satoshi Ohkubo ^a, Per Moldrup ^c, Ken Kawamoto ^a, Toshiko Komatsu ^a

^a Graduate School of Science and Engineering, Saitama University, 255 Shimo-Okubo, Sakura-ku, Saitama, 338-8570, Japan

^b Graduate School of Agricultural and Life Sciences, The University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo, 113-8567, Japan

^c Department of Civil Engineering, Aalborg University, Sofiendalsvej 11, 9200, Aalborg SV, Denmark

ARTICLE INFO

Article history:

Received 22 July 2015

Received in revised form

14 January 2016

Accepted 19 January 2016

Available online 21 January 2016

Keywords:

Subsurface thermal pollution
Ground Source Heat Pump (GSHP) systems
Long-term heating and cooling
Confined marine aquifer
Dual-Well Analysis (DWA)
Groundwater quality

ABSTRACT

Global warming and urbanization together with development of subsurface infrastructures (e.g. subways, shopping complexes, sewage systems, and Ground Source Heat Pump (GSHP) systems) will likely cause a rapid increase in the temperature of relatively shallow groundwater reservoirs (subsurface thermal pollution). However, potential effects of a subsurface temperature change on groundwater quality due to changed physical, chemical, and microbial processes have received little attention. We therefore investigated changes in 34 groundwater quality parameters during a 13-month enhanced-heating period, followed by 14 months of natural or enhanced cooling in a confined marine aquifer at around 17 m depth on the Saitama University campus, Japan. A full-scale GSHP test facility consisting of a 50 m deep U-tube for circulating the heat-carrying fluid and four monitoring wells at 1, 2, 5, and 10 m from the U-tube were installed, and groundwater quality was monitored every 1–2 weeks. Rapid changes in the groundwater level in the area, especially during the summer, prevented accurate analyses of temperature effects using a single-well time series. Instead, Dual-Well Analysis (DWA) was applied, comparing variations in subsurface temperature and groundwater chemical concentrations between the thermally-disturbed well and a non-affected reference well. Using the 1 m distant well (temperature increase up to 7 °C) and the 10 m distant well (non-temperature-affected), the DWA showed an approximately linear relationships for eight components (B, Si, Li, dissolved organic carbon (DOC), Mg²⁺, NH₄⁺, Na⁺, and K⁺) during the combined 27 months of heating and cooling, suggesting changes in concentration between 4% and 31% for a temperature change of 7 °C.

© 2017 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

1. Introduction

An increase in subsurface temperature (subsurface thermal pollution) has been recognized below several large cities worldwide (Harris and Chapman, 1997; Pollack et al., 1998; Huang et al., 2000; Taniguchi et al., 2003; Perrier et al., 2005; Taniguchi et al., 2007; Kooi, 2008). For example, a study in the Netherlands showed an approximately 0.8 °C increase at 20 m depth over the last three decades (Kooi, 2008). The temperature changes are strongly associated with surface warming effects such as global warming and urbanization (Huang et al., 2000; Taniguchi et al., 2003). Thus, a rapid increase in temperature in the subsurface

can be expected due to the combined effects of surface warming and subsurface infrastructures (including subways, shopping complexes, sewage systems, and Ground Source Heat Pump (GSHP) systems). Among these subsurface infrastructures, GSHP systems have gained popularity recently in many parts of the world as a highly promising renewable energy technology for cooling and heating buildings (Sanner et al., 2003; Spitler, 2005; Banks, 2008; Yang et al., 2010; Dinçer and Rosen, 2011; Lund et al., 2011; Bayer et al., 2012). Subsurface temperatures may decrease during GSHP heating, while GSHP systems used for cooling discharge waste heat into the subsurface environment, which could induce a subsurface temperature increase in the vicinity of the system (Sowers et al., 2006; Rybach and Eugster, 2010; Haehnlein et al., 2010; Bonte et al., 2011; Hähnlein et al., 2013). The degree of subsurface temperature change and the area of impact will depend on numerous factors including the configuration and scale, operational

* Corresponding author.

E-mail address: saitou@mail.saitama-u.ac.jp (T. Saito).

conditions of the GSHP system, and hydrogeological conditions at the installation location.

Temperature changes could trigger changes in physical, chemical, and microbial processes in the subsurface environment, resulting in groundwater quality changes (Banks, 2008; Bonte et al., 2011; Hähnlein et al., 2013). Previous studies have mainly investigated the impacts of temperature increase on subsurface processes including water flow, mineral weathering, chemical adsorption and desorption, gas solubility, and microbial redox processes. Based on several laboratory experiments using aquifer materials, carbonate precipitation, silicate dissolution, and mobilization of cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+}), heavy metals and trace elements (B, Si, P, V, Fe, As, and Mo), and dissolved organic carbon (DOC) as well as progression to strongly reductive conditions, such as sulfate reducing and methanogenic conditions, were observed (Brons et al., 1991; Griffioen and Appelo, 1993; Bonte et al., 2013a, 2013b, 2013c; Jesuþek et al., 2013).

However, the potentially negative impacts on the subsurface environment during artificially induced thermal pollution (heat discharge) or cooling and their temperature-dependent effects on groundwater quality during temperature fluctuations have not been sufficiently studied and clarified. In particular, there are virtually no studies representing field-scale conditions. Full-scale in-situ experiments during controlled temperature loading (heating and cooling) of the subsurface environment are therefore essential to investigate potentially harmful impacts of changes in groundwater quality during subsurface temperature changes and fluctuations.

The main objectives of this study were: (i) to mimic GSHP system operation and its effects in a shallow marine groundwater aquifer during full-scale, in-situ, and long-term heating and cooling experiments by establishing a closely controlled GSHP heating and cooling test site on the campus of Saitama University near the Tokyo metropolitan area of Japan, (ii) to monitor spatial and

temporal changes in the subsurface temperature and temporal changes in as many as 34 groundwater quality parameters during long-term thermal experiments, and (iii) to apply Dual-Well Analysis (DWA) to better quantify the effects of subsurface temperature changes on groundwater quality in a confined marine aquifer in order to evaluate the temperature dependence during subsequent heating and cooling periods.

2. Materials and methods

2.1. Site description

The experimental site was established at the Saitama University campus ($35^\circ 51' 44.146''$ N, $139^\circ 36' 34.034''$ E) in the Arakawa Lowland near the Tokyo metropolitan area of Japan (Fig. 1a). At this site, a full-scale GSHP test facility consisting of a 50 m deep heat exchanger (double U-tubes) was installed with silica sand (mined from the Kashima district, Ibaraki, Japan) as backfill material. Platinum resistance temperature detectors (R36, Nihondensoku Co., Ltd.) were placed at the inlet and outlet of the U-tube heat exchanger to measure the heat-carrying fluid temperature (Fig. 1b). Four groundwater monitoring wells were installed at 1 m (W1), 2 m (W2), 5 m (W5), and 10 m (W10) distance from the U-tube as the heat source. Strainer screens were situated at depths corresponding to the two confined groundwater aquifers at the study site, the upper marine aquifer (Holocene) (strainer depth: 15.51–18.36 m below the surface) and lower non-marine aquifer (Pleistocene) (strainer depth: 37.70–40.01 m). R36 platinum resistance temperature detectors were also placed at five depths (10, 20, 30, 40, and 50 m) near the U-tube heat exchanger and at 10 depths (approximately 5, 10, 17, 23, 27, 31, 36, 39.5, 44, and 49 m) outside the walls of all four monitoring wells to measure subsurface temperatures.

The hydrogeological conditions of the upper and lower aquifers are markedly different (Table 1 and Fig. 2). A previous study carried

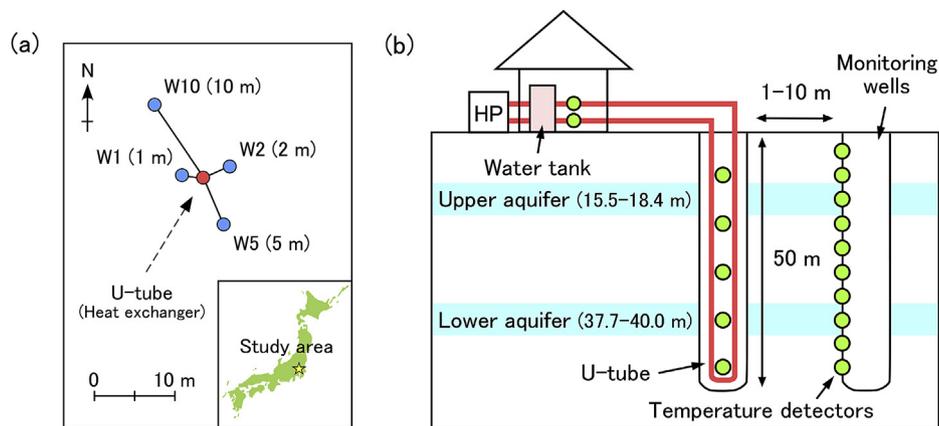


Fig. 1. (a) Location of the experimental site on the Saitama University campus in the Arakawa Lowland near the Tokyo metropolitan area of Japan, and (b) schematic of the in-situ experimental set-up for the long term enhanced heating and natural and enhanced cooling test.

Table 1

Hydrogeological properties of sediments from upper (marine) and lower (non-marine) groundwater aquifers: particle size (%), BET surface area (m^2/g), total carbon (%), electric conductivity: EC ($\mu\text{S}/\text{cm}$), pH, and saturated hydraulic conductivity (m/s).

Hydrogeological properties	Upper aquifer (marine)	Lower aquifer (non-marine)
Particle size (%)	Gravel (0), Sand (84.3), Silt (12.4), Clay (3.1)	Gravel (81.0), Sand (16.9), Silt (1.7), Clay (0.4)
BET surface area (m^2/g)	18.2	7.1
Total carbon (%)	0.6	0.4
EC ($\mu\text{S}/\text{cm}$)	283.7	43.7
pH	7.1	7.2
Saturated hydraulic conductivity (m/s)	3.0×10^{-7}	4.3×10^{-6}

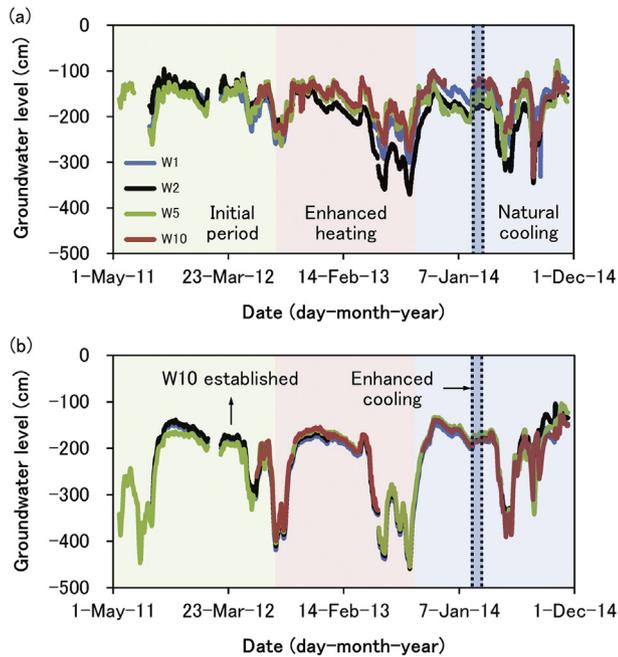


Fig. 2. Temporal variations of groundwater level in the (a) upper and (b) lower aquifers.

out at very close proximity to the experimental site (Komatsubara et al., 2010) revealed that the upper aquifer consists of marine sediment, while the lower aquifer consists of non-marine sediment. Generally, marine sediment contains higher concentrations of chemical components than non-marine sediment. Further, the sediment texture (based on the International Society of Soil Science classification) was finer in the boring core obtained from the upper aquifer (silty to sandy texture) than that of the lower aquifer (sandy to gravelly texture), giving sediment from the upper aquifer a larger specific surface area (Table 1). The larger surface area would also imply that higher amounts of absorbed chemical components are present in the sediment. In agreement with this, the total carbon in the sediment from the upper aquifer and electric conductivity (EC) of water extracted from the upper aquifer sediment were markedly higher than those from the lower aquifer sediment. Based on monitoring of continuous groundwater levels in the upper and lower aquifers since May 2011 (Fig. 2), the groundwater demonstrated variable flow directions for both aquifers. Additional information on the hydrogeological conditions including the ground thermal properties at the site is presented in Saito et al. (2014).

2.2. Field experiments

At the experimental site, in-situ subsurface heating was performed. Approximately 40 °C water was used as the heat carrier. The water was sequentially heated by using an installed air source heat pump system, and circulated inside the U-tube heat exchanger at flow rate of approximately 40 L/min for 13 months (from August 10, 2012 to September 10, 2013). After the heating period, the site was maintained under natural cooling conditions for 14 months (from September 10, 2013 to November 10, 2014), with the exception of one month (from February, 2014 to March, 2014). During this one month period, in-situ enhanced cooling was carried out for rapid temperature decrease by circulating approximately 10 °C water at the same flow rate as used during thermal loading (approximately 40 L/min). The heat-carrying fluid temperatures at the inlet and outlet of the U-tube and the subsurface temperature

were monitored at all measurement locations (described in Section 2.1) at 10-min intervals using a data logger (LR8400, HIOKI E. E. CORPORATION).

Groundwater was sampled from all four monitoring wells with two aquifers using a sampling bailer (custom-made by ASANO TAISEIKISO ENGINEERING Co., Ltd.). Sampling was carried out every 1–2 weeks from May 2011, purging the groundwater of at least two well volumes before each sampling event. On-site measurements of groundwater temperature, pH, EC, dissolved oxygen (DO), and oxidation-reduction potential (ORP) were immediately carried out using portable analyzers calibrated at each sampling time. Further, hydrogen sulfide (H₂S) in the groundwater was measured at selected times using a simplified colorimetric method (Packtest, KYORITSU CHEMICAL-CHECK Lab., Corp.). Groundwater for the quantification of dissolved methane (CH₄) was sampled separately, directly into an analytical amber glass vacuum vial using a custom-made sampling tool (ASANO TAISEIKISO ENGINEERING Co., Ltd.), making it possible to sample groundwater without exposing it to air.

2.3. Laboratory analyses

The sampled groundwater was immediately filtered using a 0.20 μm membrane filter (DISMIC-25CS, Toyo Roshi Kaisha, Ltd.). Major inorganic ions (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, NO₂⁻, Br⁻, NO₃⁻, and SO₄²⁻), dissolved inorganic and organic carbon (DIC and DOC), and heavy metals and trace elements (Li, B, Al, Si, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Sr, Cd, Sb, and Pb) were analyzed using an ion chromatograph (HIC-NS), TOC analyzer (TOC-V CSH), and ICP-MS (ICPM-8500, all SHIMADZU CORPORATION), respectively. The dissolved CH₄ concentration in the groundwater was measured by the head-space method using a gas chromatograph (GC-2014, SHIMADZU CORPORATION) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID).

3. Results and discussion

3.1. Subsurface temperature change

Fig. 3 illustrates depth profiles of subsurface temperatures (°C) at all four monitoring wells (W1, W2, W5, and W10) during the heating (13 months) and cooling (14 months) tests. During heating, the 40 °C water injected as the heat carrier came back to the outlet of the U-tube heat exchanger with a temperature of around 39 °C. Thus, the actual thermal loading into the subsurface was constantly around 1 °C, corresponding to 2.8 kW over totally 50 m depth (i.e., on average 56 W/m).

Based on the one-year observation, the subsurface temperature was almost constant up to 10 m depth throughout the year before the heating test. Once the heating test started (August 10, 2012), the subsurface temperature increased steeply at the closest monitoring well, W1, during the first four months (Fig. 3). The increase in the temperature was less and more gradual at both W2 and W5, while there was a minor change in the subsurface temperature at the most remote monitoring well, W10, during the entire heating period. During the subsequent cooling period, decreases in temperature were observed at wells W1, W2, and W5. The elevated subsurface temperature was still decreasing towards the original (natural) temperature levels throughout all monitoring depths at wells W1, W2, and W5 even after 14 months cooling. After the 14-month cooling period, the subsurface temperature was still higher than the original temperatures (see Figs. 3 and 4a). Thus, it will take markedly longer to reach the original (natural) subsurface temperature levels during cooling.

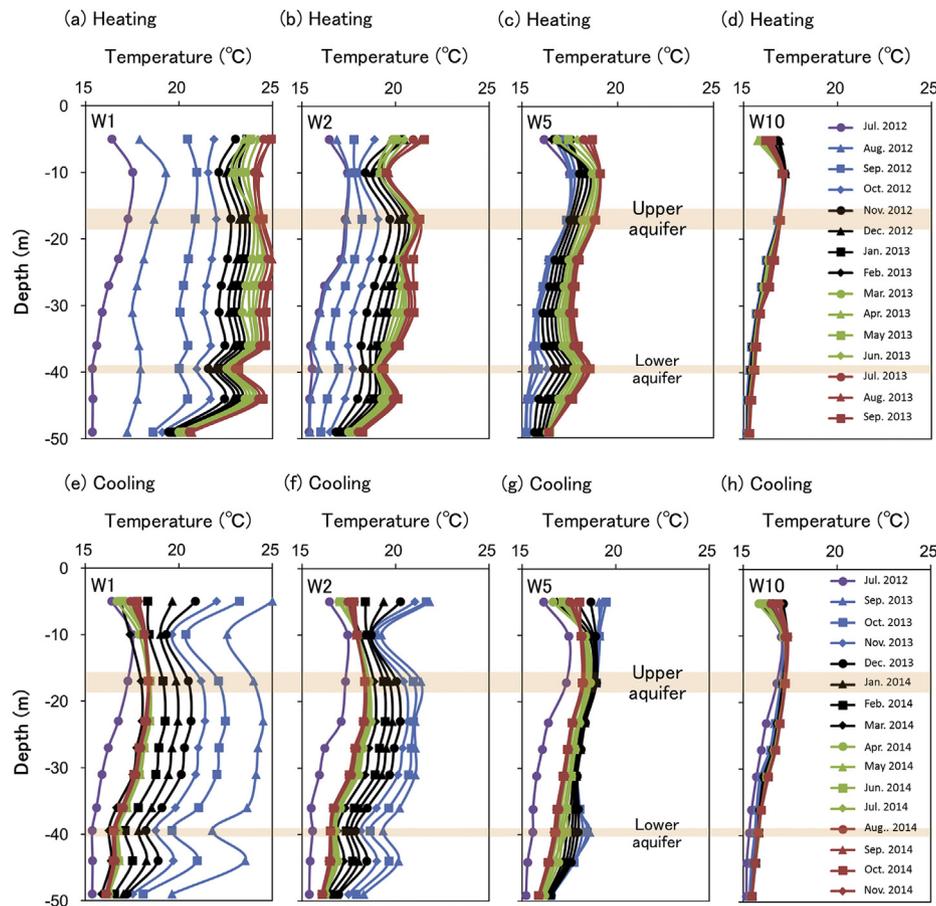


Fig. 3. Depth profiles of subsurface temperature ($^{\circ}\text{C}$) at all four monitoring wells (W1, W2, W5, and W10) during the enhanced heating ((a)–(d)) and natural and enhanced cooling ((e)–(h)) test.

3.2. Groundwater quality changes

Because data for the lower, non-marine aquifer at present do not suffice for detailed analyses of temperature effects on groundwater quality (on-going experiments), we will consider only the data for the upper, marine aquifer in this study. Temporal variations of subsurface temperature ($^{\circ}\text{C}$) and concentrations of B, As, and Se at all four monitoring wells in the upper aquifer from May 2011 to November 2014 are presented in Fig. 4. During the continuous thermal loading for 13 months, the increase in the subsurface temperature was clearly larger at the closer monitoring wells, with final temperature increases of 7.2°C , 4.0°C , 1.5°C , and 0.2°C for wells W1, W2, W5, and W10, respectively. The subsurface temperature changed slightly at W10 throughout this field experiment but because the change was within 0.2 – 0.5°C , the W10 monitoring well is assumed to represent a non-temperature-affected (reference) well in this study.

In the upper aquifer, the concentrations of almost all groundwater quality parameters including B showed minor seasonal changes (Fig. 4). A few chemical components such as As and Se, however, showed clear seasonal changes, especially during the summer. This period corresponded closely to the period where the groundwater level fluctuated strongly (Fig. 2), likely due to abstraction of groundwater for field irrigation in the area. Because this phenomenon prevented accurate analyses of temperature effects on groundwater quality from the time series of measured chemical concentrations in the individual wells and the fluctuations of groundwater level were highly similar in the four wells (separated by only a few meters), we decided to base our general

evaluation of temperature effects on groundwater quality by always comparing data sets for two wells, a highly-temperature-affected well (e.g., W1) and the presumably non-affected well (reference well, W10).

Fig. 5 illustrates the temporal variations of concentrations of B, Mg^{2+} , Si, Na^{+} , Li, K^{+} , and DOC together with changes in the subsurface temperature at the monitoring wells W1 (temperature increase and subsequent decrease of up to around 7°C) and W10 (temperature-affected) in the upper marine aquifer. For comparison, the K^{+} concentration monitored at W2 (temperature increase or decrease of up to around 4°C) together with data for the W10 reference well is also shown in Fig. 5 (see Fig. 5h). Fig. 5 shows that the concentrations of B, Mg^{2+} , Si, Na^{+} , Li, K^{+} , and DOC increased or decreased more at W1 (or W2) than at W10. Thus, comparing temperature-affected and non-affected data for chemical concentrations in wells undergoing similar fluctuations in groundwater level (Fig. 5), implies that some chemicals were affected by the temperature of groundwater. To further quantify this therefore requires analyzing data based on simultaneous temperature and concentration differences in the two wells.

3.3. Dual-Well Analysis (DWA) for relating changes in subsurface temperature and groundwater quality

A DWA was applied to analyze the temperature effects on groundwater quality during the in-situ heating (13 months) and cooling (14 months) periods, based on differences between the subsurface temperature (ΔT , $^{\circ}\text{C}$) and in chemical concentration (ΔC , $\mu\text{g/L}$ or mg/L) in a set of wells. The ΔT and ΔC values were calculated

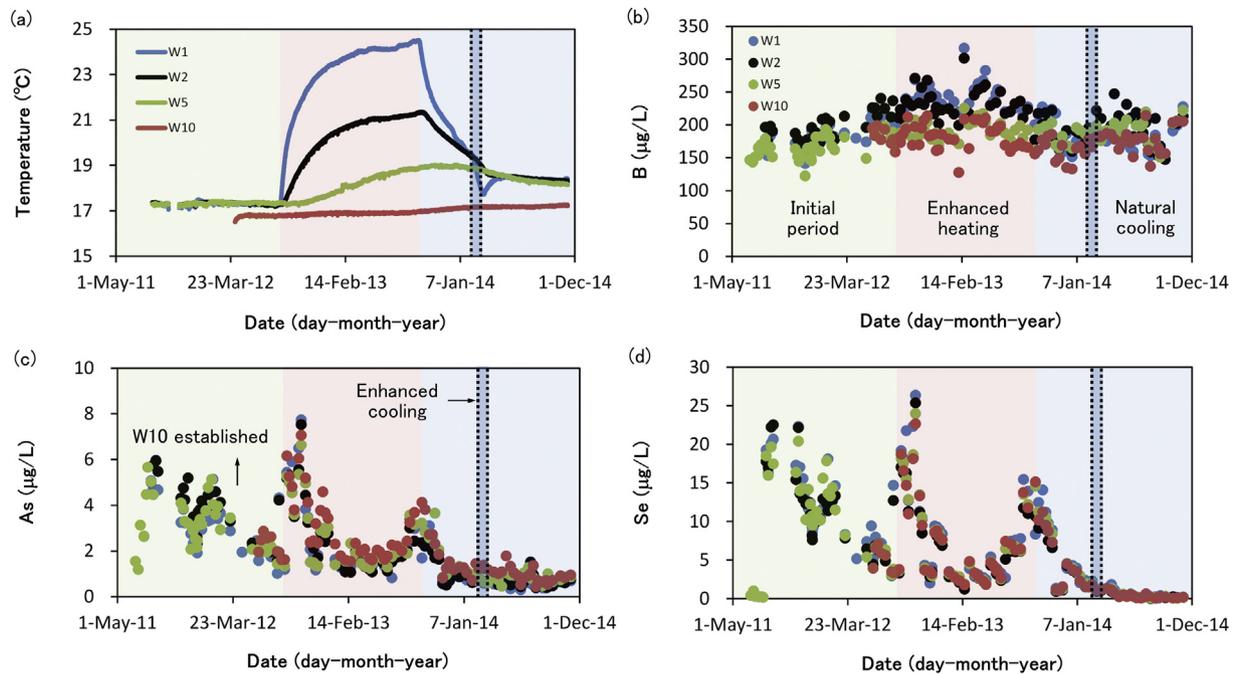


Fig. 4. Temporal variations of (a) subsurface temperature ($^{\circ}\text{C}$) and (b) B, (c) As, and (d) Se concentrations ($\mu\text{g/L}$) at all four monitoring wells for the upper aquifer.

by subtracting the data values for a given time at W10 (representing the reference, temperature-unaaffected well) from the data at W1 (or W2; representing the thermally-disturbed well).

Fig. 6 presents ΔT and ΔC relationships for B, Mg^{2+} , Si, Na^+ , K^+ , Li, and DOC in the upper aquifer. The result of the DWA application in Fig. 6 shows approximate linear trends between ΔT and ΔC , hereby representing the pure effect of temperature on groundwater quality, filtering out all other effects including groundwater level fluctuations that affect individual well data. Because the ΔT - ΔC relationships were similar for heating and cooling periods, the DWA suggests a temperature dependence of groundwater chemical concentrations on heating and cooling (Fig. 6). Confirmation of this result at other sites under different hydrogeological conditions is essential to evaluate the environmental risks of subsurface thermal pollution as well as the application of GSHP systems.

The results of DWA are summarized in Table 2. Both Si and K^+ showed increasing trends, which might be explained by dissolution of silicate (potassium feldspar) as an irreversible process (Bonte et al., 2013b). As reversible processes, K^+ and Si can be mobilized by cation exchange with Mg^{2+} and by desorption from iron oxides, respectively (Bonte, 2013). The mechanism controlling DOC behavior may be mobilization from sediment at increased temperatures (Brons et al., 1991). In this study, DOC could be also mobilized from aquifer sediment with an increase in temperature. Boron occurring in oxyanion form is adsorbed to iron (hydrrous) oxides, suggesting mobilization by desorption from or reductive dissolution of iron (hydrrous) oxides with temperature increase, as discussed in Bonte et al. (2013b). At the study site, NO_3^- and SO_4^{2-} were not detected, while CH_4 was clearly detected. These phenomena imply a strongly reductive environment, such as a methanogenic condition. Boron, therefore, can be mobilized by desorption from and/or reductive dissolution of iron (hydrrous) oxides. Only Mg^{2+} demonstrated a decreasing trend, possibly due to cation exchange with K^+ (Bonte, 2013). Another possibility is carbonate precipitation with increased temperature. Because the mechanisms of temperature effects on groundwater quality are complex (reversible and/or irreversible processes), further research

is needed to clarify them.

As shown in Table 2, the average changes in chemical concentrations (ΔC , $\mu\text{g/L}$ or mg/L) for a reference ΔT of 7°C were calculated by multiplying the slopes of the regression lines in Fig. 6 (corresponding to a unit temperature response in chemical concentration) by 7°C . Based on this, the percentage increases in concentration for a ΔT of 7°C were calculated using the initial concentration of each chemical component before the start of the thermal loading experiment. Estimated concentration changes for the eight chemicals in Table 2 varied from 4% to 31%. For only one of the eight components, a small decrease in concentration (Mg^{2+} , around 4% decrease), was observed due to a subsurface temperature increase, while for all seven remaining components a temperature increase caused an increase in concentration (between 9% and 31%). Using well W2 (temperature variations of up to around 4°C) as the temperature-affected well, the effect of temperature on chemical concentration could be recognized for one of these eight chemicals (K^+) (Fig. 6h). The slope of the regression line for K^+ shows almost the same gradient as that of K^+ with DWA application using W1 and W10 data. Also as shown in Table 2, the coefficient of determination (R^2) had relatively higher values for B and K^+ (more than $R^2 = 0.6$).

Besides the eight chemicals shown in Table 2, the more harmful chemical components defined in environmental quality standards for groundwater pollution (Ministry of the Environment, Government of Japan) including NO_3^- , Cr, Cu, As, Se, Cd, and Pb were not likely affected by temperature during the thermal loading and subsequent cooling test. Even for the eight less harmful chemicals shown in Table 2, the absolute temperature effects are not dramatic with regard to environmental regulations. Boron, for example, showed a maximum increase in the concentration (ΔC) of $62.9 \mu\text{g/L}$ (corresponding to a 31% increase) with a 7°C temperature increase in the upper marine aquifer from an original (natural) B concentration of around $203 \mu\text{g/L}$. In Japan, the environmental quality standard established by Ministry of the Environment for this element in water as well as for groundwater is $1000 \mu\text{g/L}$. The standard for drinking water is also $1000 \mu\text{g/L}$ (Ministry of Health,

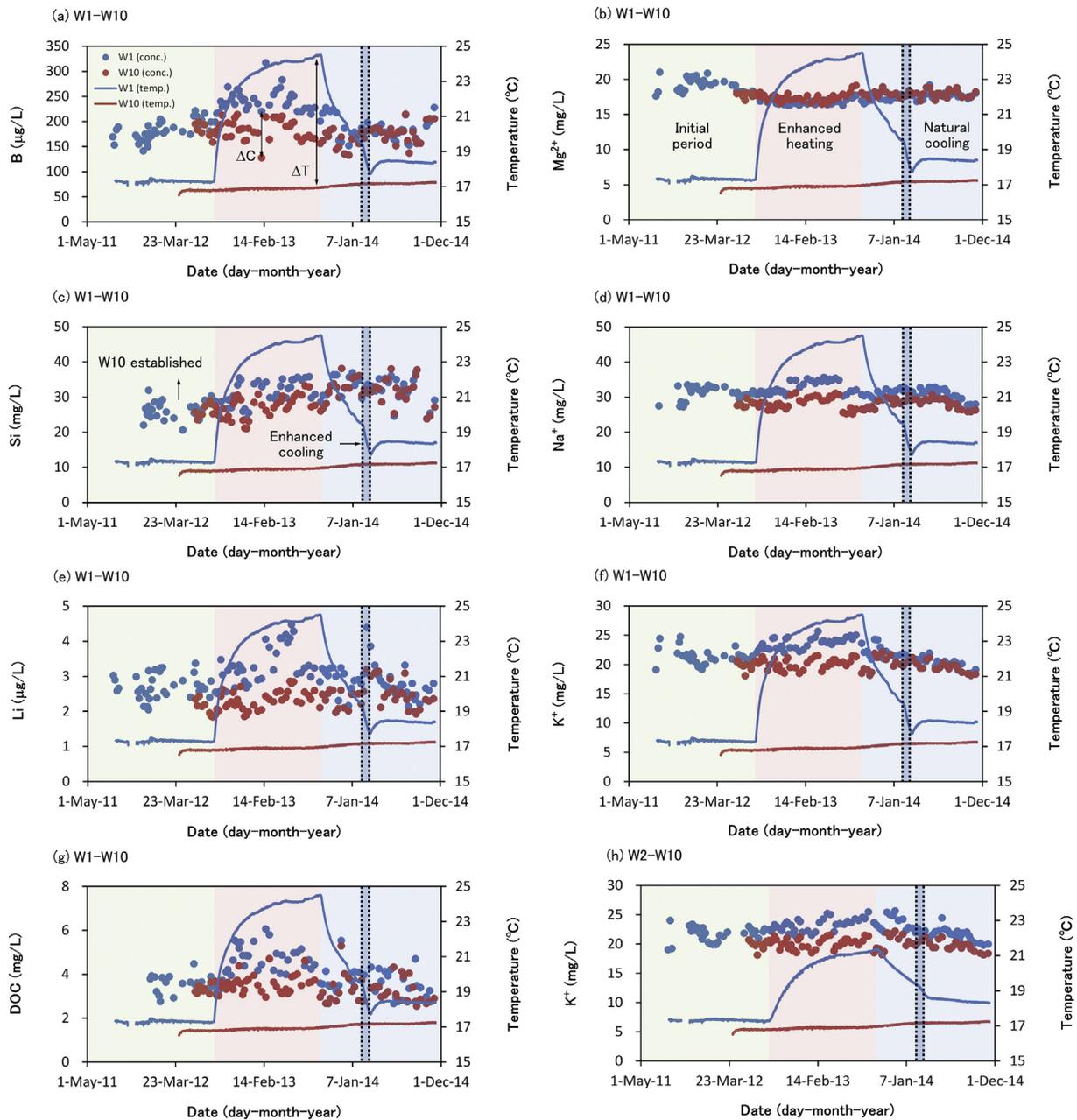


Fig. 5. Temporal variations of the concentration of (a) B, (b) Mg^{2+} , (c) Si, (d) Na^+ , (e) Li, (f) K^+ , (g) DOC, and (h) K^+ in the groundwater at monitoring wells W1 (note: W2 in (h)) and W10 (non-affected) for the upper aquifer, shown together with the concurrent variations in subsurface temperature. Concentrations on the y-axes are expressed as mg/L or $\mu g/L$ depending on the chemical component.

Labour and Welfare). Moreover, the drinking water quality committee of the World Health Organization (WHO) recommends a guideline value of 2400 $\mu g/L$ for B. Thus, the additional temperature effects would be of high and immediate environmental concern only in aquifers with B concentrations already close to the limit. In summary, we documented the effects of temperature on groundwater quality using DWA, with changes up to around 30% in chemical concentration for a 7 °C temperature change, but the absolute effects of temperature changes up to 7 °C in this marine aquifer seemed minor as compared with Japanese water quality standards and international drinking water quality standards.

4. Conclusions

A full-scale GSHP test facility consisting of a 50 m deep U-tube

for conducting heating or cooling into the subsurface was established on the Saitama University campus of Japan and operated for 27 months under enhanced heating and natural or enhanced cooling conditions. Subsurface temperatures and 34 groundwater quality parameters were near-continuously monitored in a confined marine aquifer at around 17 m depth.

Close spatial and temporal subsurface temperature measurements in the four surrounding monitoring wells revealed minor temperature changes at the most remote well (10 m distance from the U-tube), while a temperature increase and subsequent decrease of up to 7 °C was observed at the closest well (1 m distance from the U-tube). Using the 10 m distant well as the reference (non-temperature-affected well), DWA applied to the data showed temperature effects on groundwater quality for eight chemicals (B, Si, Li, DOC, Mg^{2+} , NH_4^+ , Na^+ , and K^+) when using the 1 m distant well as

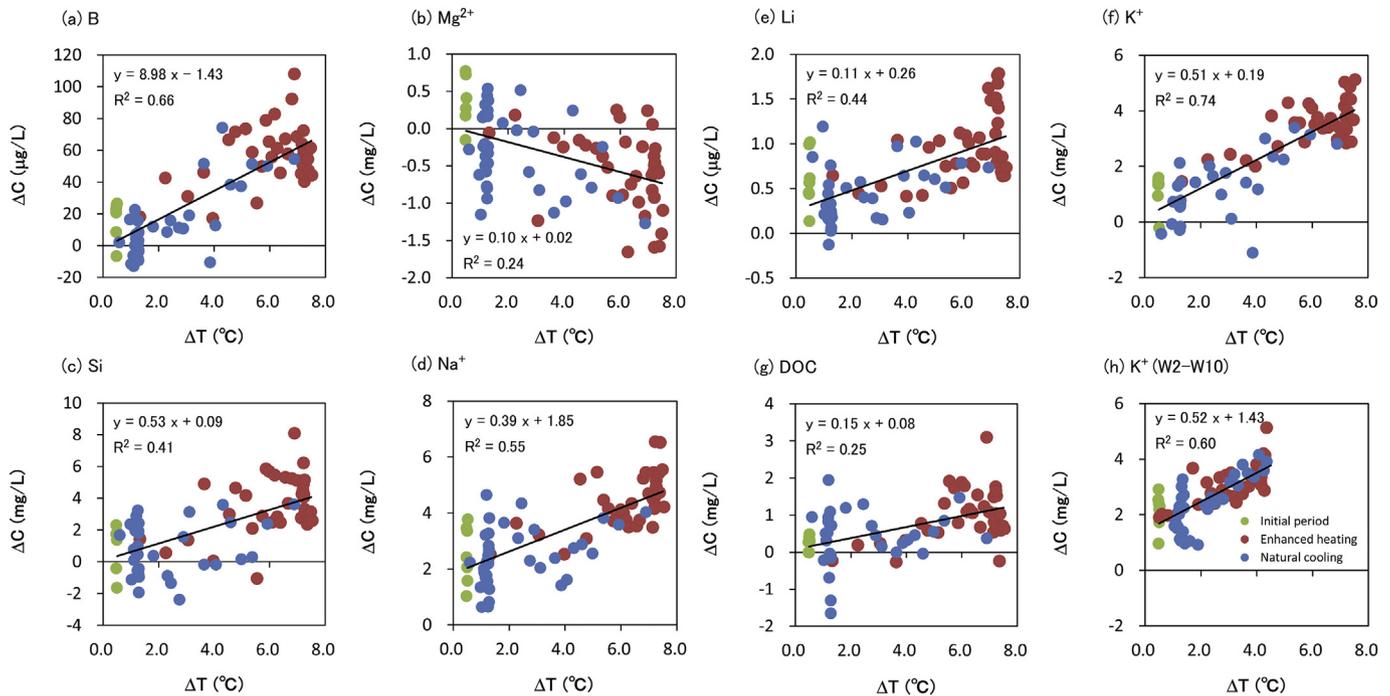


Fig. 6. Dual-Well Analysis (DWA) to determine the difference between subsurface temperatures in wells W10 (non-affected) and W1 (Note: between W10 and W2 in (h)) (ΔT) and the analogous difference in chemical concentration (ΔC) of (a) B, (b) Mg^{2+} , (c) Si, (d) Na^+ , (e) Li, (f) K^+ , (g) DOC, and (h) K^+ (comparing Wells 2 and 10) in the groundwater of the upper, marine aquifer.

Table 2
Overall results of DWA for eight selected chemical components with coefficient of determination (R^2). The ΔC values corresponding to a 7 °C increase in the subsurface temperature were calculated using the best-fit ΔC - ΔT relations given in Fig. 6.

Component	Initial concentration	ΔT of 7 °C		Coefficient of determination (R^2)
		ΔC (absolute)	ΔC (%)	
B	202.9 $\mu g/L$	62.9	31	0.66
Si	27.2 mg/L	3.7	14	0.41
Li	2.8 $\mu g/L$	0.8	28	0.44
DOC	3.6 mg/L	1.1	30	0.25
Mg^{2+}	18.2 mg/L	-0.7	-4	0.24
NH_4^+	11.2 mg/L	1.6	14	0.46
Na^+	30.7 mg/L	2.7	9	0.55
K^+	21.1 mg/L	3.6	17	0.74
K^+ (W2-W10)	22.1 mg/L	3.6	16	0.60

the temperature-affected well. Using the 2 m distant well (maximum subsurface temperature change of 4 °C), the effect was recognized for one of these eight chemicals (K^+). The DWA showed approximately linear relationships in the shallow confined marine aquifer, suggesting changes in concentration between 4% and up to 31% for the given temperature change of 7 °C. For one of the eight chemicals, this subsurface temperature increase caused a small decrease in concentration (Mg^{2+} , around 4% decrease), while for all the remaining seven chemicals the temperature increase caused an increase in concentration (between 9% and 31%). The largest effect of the temperature increase was observed in the B concentration (31%).

The present experiments are being continued with a new long-term period of heating and subsequent cooling to obtain sufficient data to also analyze subsurface temperature change effects on groundwater quality in a deeper and confined non-marine aquifer (located at around 39 m depth) and also to evaluate whether a higher temperature change (planned up to 10 °C) in the most temperature-affected W1 well would demonstrate a larger linear or non-linear change in concentration as a result of the DWA. We

recommend that the same kind of full-scale, long-term site investigations and method application should be established at experimental sites worldwide under different hydrogeological conditions to create the necessary information for environmental risk assessment of subsurface thermal pollution as well as optimal design and planning for minimal subsurface environmental impact of GSHP systems.

Acknowledgments

This study was supported from Core Research for Evolutionary Science and Technology (CREST) by Japan Science and Technology Agency (JST) and partly supported by a Grant-in Aid for Scientific Research (no. 26889015) by the Japan Society for the Promotion of Science (JSPS). The authors deeply appreciate Dr. Iwao Sakaguchi, Dr. Kazuno Arai, Mr. Shigeo Matsukura, Mr. Keisuke Tateishi, Mr. Masato Kenmochi, and Mr. Tatsuya Nakayama all of Saitama University (CREST, JST) for helping us collect and analyze the groundwater.

References

- Banks, D., 2008. *An Introduction to Thermogeology: Ground Source Heating and Cooling*. Blackwell Publishing Ltd., Oxford, UK.
- Bayer, P., Saner, D., Bolay, S., Rybach, L., Blum, P., 2012. Greenhouse gas emission savings of ground source heat pump systems in Europe: a review. *Renew. Sustain. Energy Rev.* 16 (2), 1256–1267.
- Bonte, M., 2013. *Impacts of Shallow Geothermal Energy on Groundwater Quality*. PhD thesis. VU University, 175pp.
- Bonte, M., Stuyfzand, P.J., Hulsmann, A., van Beelen, P., 2011. Underground thermal energy storage: environmental risks and policy developments in the Netherlands and European Union. *Ecol. Soc.* 16 (1), 22.
- Bonte, M., Röling, W.F.M., Zaura, E., van der Wielen, P.W.J.J., Stuyfzand, P.J., van Breukelen, B.M., 2013a. Impacts of shallow geothermal energy production on redox processes and microbial communities. *Environ. Sci. Technol.* 47 (24), 14476–14484.
- Bonte, M., van Breukelen, B.M., Stuyfzand, P.J., 2013b. Temperature-induced impacts on groundwater quality and arsenic mobility in anoxic aquifer sediments used for both drinking water and shallow geothermal energy production. *Water Res.* 47 (14), 5088–5100.
- Bonte, M., van Breukelen, B.M., Stuyfzand, P.J., 2013c. Environmental impacts of aquifer thermal energy storage investigated by field and laboratory experiments. *J. Water Clim. Change* 4 (2), 77–89.
- Brons, H.J., Griffioen, J., Appelo, C.A.J., Zehnder, A.J.B., 1991. (Bio) geochemical reactions in aquifer material from a thermal energy storage site. *Water Res.* 25 (6), 729–736.
- Dinçer, I., Rosen, M.A., 2011. *Thermal Energy Storage: Systems and Applications*, second ed. John Wiley & Sons Ltd., Chichester, UK.
- Griffioen, J., Appelo, C.A.J., 1993. Nature and extent of carbonate precipitation during aquifer thermal energy storage. *Appl. Geochem.* 8 (2), 161–176.
- Haehnlein, S., Bayer, P., Blum, P., 2010. International legal status of the use of shallow geothermal energy. *Renew. Sustain. Energy Rev.* 14 (9), 2611–2625.
- Hähnlein, S., Bayer, P., Ferguson, G., Blum, P., 2013. Sustainability and policy for the thermal use of shallow geothermal energy. *Energy Policy* 59, 914–925.
- Harris, R.N., Chapman, D.S., 1997. Borehole temperatures and a baseline for 20th-century global warming estimates. *Science* 275, 1618–1621.
- Huang, S., Pollack, H.N., Shen, P.-Y., 2000. Temperature trends over the past five centuries reconstructed from borehole temperatures. *Nature* 403, 756–758.
- Jesušek, A., Köber, R., Grandel, S., Dahmke, A., 2013. Aquifer heat storage: sulphate reduction with acetate at increased temperatures. *Environ. Earth Sci.* 69 (5), 1763–1771.
- Komatsubara, J., Kimura, K., Fukuoka, S., Ishihara, Y., 2010. Sedimentary facies and physical properties of the latest Pleistocene to Holocene sediment core (GS-SSS-1) in the Arakawa Lowland, Saitama City, central Japan. *J. Sedimentol. Soc. Jpn.* 69 (1), 3–15 (in Japanese with English abstract).
- Kooi, H., 2008. Spatial variability in subsurface warming over the last three decades; insight from repeated borehole temperature measurements in The Netherlands. *Earth Planet. Sci. Lett.* 270 (1–2), 86–94.
- Lund, J.W., Freeston, D.H., Boyd, T.L., 2011. Direct utilization of geothermal energy 2010 worldwide review. *Geothermics* 40 (3), 159–180.
- Perrier, F., Le Mouel, J.-L., Poirier, J.-P., Shnirman, M.G., 2005. Long-term climate change and surface versus underground temperature measurement in Paris. *Int. J. Climatol.* 25 (12), 1619–1631.
- Pollack, H.N., Huang, S., Shen, P.-Y., 1998. Climate change record in subsurface temperatures: a global perspective. *Science* 282, 279–281.
- Rybach, L., Eugster, W.J., 2010. Sustainability aspects of geothermal heat pump operation, with experience from Switzerland. *Geothermics* 39 (4), 365–369.
- Saito, T., Hamamoto, S., Mon, E.E., Takemura, T., Saito, H., Komatsu, T., Moldrup, P., 2014. Thermal properties of boring core samples from the Kanto area, Japan: development of predictive models for thermal conductivity and diffusivity. *Soils Found.* 54 (2), 116–125.
- Sanner, B., Karytsas, C., Mendrinós, D., Rybach, L., 2003. Current status of ground source heat pumps and underground thermal energy storage in Europe. *Geothermics* 32 (4–6), 579–588.
- Sowers, L., York, K.P., Stiles, L., 2006. Impact of thermal buildup on groundwater chemistry and aquifer microbes. In: *Proceedings of the Tenth International Conference on Thermal Energy Storage (ECOSTOCK 2006 Conference)*. Galloway, USA, 7pp.
- Spitler, J.D., 2005. Ground-source heat pump system research-past, present and future. *HVAC&R Res.* 11 (2), 165–167.
- Taniguchi, M., Shimada, J., Uemura, T., 2003. Transient effects of surface temperature and groundwater flow on subsurface temperature in Kumamoto Plain, Japan. *Phys. Chem. Earth A/B/C* 28 (9–11), 477–486.
- Taniguchi, M., Uemura, T., Jago-on, K., 2007. Combined effects of urbanization and global warming on subsurface temperature in four Asian cities. *Vadose Zone J.* 6 (3), 591–596.
- Yang, H., Cui, P., Fang, Z., 2010. Vertical-borehole ground-coupled heat pumps: a review of models and systems. *Appl. Energy* 87 (1), 16–27.