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Pilot application of SVE enhanced bioremediation technology for in situ clean up of light oil contaminated site

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Abstract

Light oil (isooctane) removal using soil vapor extraction (SVE) enhanced bioremediation (BR) was investigated by four steps including (i) amendment of substrates in batches; (ii) continuous induction of contaminants for 15 days; (iii) *in situ* acclimation for 100 days; and (iv) biodegradation assisted with SVE venting for 120 h at 20 m^3 h^{-1}. Results showed that the total removal efficiency was up to 90% after BR-SVE treatments. The contribution of SVE to the overall removal was initially 53% ~ 69% and decreased to 13% ~ 30% after 36 h. This implied that it would be an important strategy to limit water content at the early stage while increase water supply at the end stage during implementation of BR-SVE because water content was a significant factor hindering SVE but favouring BR. Additionally, SVE was observed to increase the bioavailability and biodegradation by one-order of magnitude. The overall results demonstrated a good complementarity between SVE and BR and a potential for their combination in real-world applications.

Keywords: Soil vapor extraction, Bioremediation, Biodegradation, Bioavailability, Isooctane

1. Introduction

Leaking underground storage tank (LUSTs) in the unsaturated zone is extensively present in gas station, chemical plant and dry cleaning laundry, which produces wide-reaching negative environmental impacts and threatens to human health [1, 2]. Bioremediation (BR) and soil vapor extraction (SVE) are effective remediation technologies for treating and disposal of oil contaminated soils [3-5]. Microbial decontamination (or bioremediation) of oil-polluted soils is a versatile alternative to physicochemical treatments [6], which involves microbial decomposition of complex organic or inorganic matter into simple non-toxic compounds such as CO_2 and H_2O by living organisms (both indigenous or extraneous) in the presence of oxygen . It is perceived as an important mechanism in the natural attenuation of oil pollutants and hence a natural or 'green solution' to oil pollution problems because of minimal ecological impacts [7]. However, the rate of microbial degradation of hydrocarbons in soils under natural conditions is usually limited by several physicochemical and biological factors including soil characteristics; abundance and diversity of indigenous microorganisms; conditions for microbial degradation activity (e.g., nutrients, oxygen, pH and temperature); and the quantity, quality and bioavailability of contaminants [7]. In order to augment bioremediation, in situ SVE is an alternative approach, which consists of the installation of vertical and/or horizontal wells in the unsaturated zone and the application of vacuum to increase the air flow through the pore spaces of the soil. The added air flow (oxygen) subsequently stimulates the growth and activity of the indigenous microbes and encourages the desorption of volatile organic contaminants (VOCs) from the soil. In the process, the off-gas is either treated to recover or destroy the VOCs because of its ignitability and toxicity (acute and long-term carcinogenicity). For the treatment of SVE off-gas, active carbon adsorption is currently the most common treatment technology in terms of both cost and waste management [8]. However, the main limitations of carbon adsorption are that (i) it is not effective for treating VOCs with high polarity or high vapour pressures, and (ii) it would suffer from the high operating cost associated with adsorbent replacement or regeneration if the contaminants concentration in off-gas is high.

. BR and SVE were demonstrated to complement each other in terms of the factors (e.g. type of soil and contaminants, moisture, natural organic matter content)

influencing the effectiveness of their performance [9-13]. While SVE is limited to cases involving VOCs in unsaturated zone that is relatively permeable and homogeneous, BR is applicable to a wide range of organics in all environmental media that are prone to degradation by microorganisms. In addition, the high level of moisture is favourable for microbial degradation, but it would reduce the soil permeability, restrict the air flow through soil pores, and lessen the SVE efficiency [9]. The presence of natural organic matter may be a source of nutrients and microbial communities having a great potential in bioremediation [14], but it could also serve as a compartment for strong sorption of contaminants resulting in the decrease of SVE effectiveness [12]. Moreover, SVE has a relatively short treatment time while the period of BR is normally long. Therefore, combination of these two technologies is an attractive approach with the potentials to promote the advantages and circumvent the drawbacks compared to the application of each method individually.

The performance of this combined approach have been currently investigated by Soares et al. [11] in which benzene was removed by SVE followed by BR in *ex situ* column experiments. However, it remains unclear whether this approach would be efficient for *in situ* remediation in which the site disturbance is minimal. Additionally, it is of particular interest to investigate the effectiveness of implementing SVE after BR with the potential to degrade the contaminants to a lower concentration and thereby reduce the cost associated with active carbon replacement during the SVE off-gas treatment. In this work the BR coupled with SVE was proposed for the *in situ* remediation of light oil contaminated soils and the mass distribution of contaminants into soil matrix was evaluated by a simple mathematical fitting. In order to investigate the feasibility of field application, four stages were proposed as follows: (*i*) injection of substrates to the soil in order to induce the real and potential metabolic activity of indigenous microorganisms; (*ii*) addition of contaminants to formulate a simulated contaminated zone; (*iii*) *in situ* acclimation for the adaption of microorganisms to the artificially modified atmosphere; (*iv*) biodegradation assisted with SVE. Isooctane was selected as a representative compound to illustrate the performance of this method. Other contaminants such as cyclohexane, benzene, xylene, biphenyl, perchloroethylene, trichloroethane, and gasoline may be effectively removed in the same way.

2. Materials and methods

2.1 Location of wells

The experimental plot (10 m × 10 m) is located in the east of Tanggu District (Tianjin, China) and soil samples were collected from the perched aquifer where rainfall was the predominant water source. International standard methods were used for the characterization of the soils including pH [15], moisture content [16], soil organic matter [17], particle size [18], particle density [19]. The infiltration property was assessed using drip infiltrometer [20].

The location of wells instrumented in the test field for implementing the BR-SVE treatment is shown in Fig. 1. One vapor extraction well (EW1) was centrally located, screened from 1 to 2 m below ground surface and connected to an air pump. The other two wells (MW1 and MW2) were used as monitoring wells. Three 15 mm diameter PVC wells (N1 to N3) were installed at 1 m intervals for injection of contaminants and nutrients solution. At 11 locations (P1 to P4 and S1 to S7) in the test area, 4 gas sampling wells were installed to sample soil vapor and to measure the pressure drawdown throughout the test plot, and 7 solid sampling wells consisted of 15 mm diameter stainless steel pipes with 20 slots (4 mm diameter) were installed to sample soil and to measure the removal rate of contaminants. The intervals between ground surface and wells were sealed off with bentonite pellets and covered with cement grout.

2.2 Experimental process

The nutrients solutions consisted of $(NH_4)_2SO_4$ (50 g L^{-1}), K_2HPO_4 (5 g L^{-1}) and $MgSO_4$ (0.06 g L^{-1}) were injected from injection wells after 6, 18, 24, 34, 48, 58 and 73 days in the experiments. Total 1.5 L (500 mL × 3 injection wells) nutrients solutions were injected in batch on each injection day. The contaminants isooctane (23 kg) was injected continuously from day 18 to 33. The contaminated zone was then allowed for acclimation for 100 days when the amount of bacteria recovered to the initial order of magnitude (10^7). The dispersion of isooctane underground was calculated using software 'PetraSim' [21]. Briefly, the simulation zone (10 m ×10 m × 3 m) was divided into 9464 (26×26×14) grids. The T2VOC programme was selected as the numerical simulator which is a module designed to simulate 3-phase non-

isothermal flow of water, air and a volatile organic compound in multidimensional heterogeneous porous media [22].

After the 100-day acclimation period, BR enhanced by SVE was performed by venting which last for 120 h until the end of the experiments. The air (viscosity: 1.8×10^{-5} Pa · s) flow was monitored by a flow meter and controlled at 20 ± 1 m^3 h^{-1} as reported in previous studies [23, 24]. The vacuum degree at the intake of air pump and the WE1 well was 17 and 13 kPa, respectively. The pressure drawdown at various monitor wells showed that the radius of influence (ROI) was between 1.2 and 4.0 m [25]. The effective air permeability (k_a) within the range of ROI was estimated to be at the order of magnitude of 10^{-12} m^2 using the model suggested by Johnson et al. [26]. The overall removal of isooctane during this period was determined by the concentration in the soil phase. The isooctane removed by SVE was monitored by measuring the concentration in the gas phase. The contribution of BR to the isooctane loss was identified by the difference between the total isooctane loss in soil phase and the amount removed by SVE.

2.3 Instrument analysis

The concentration of isooctane in gas phase was monitored in an AutoSystem XL Gas Chromatograph (PerkinElmer GC, USA) equipped with a FFAP capillary column (30 m × 0.25 mm × 1.0 μm) and flame ionization detector (FID). Vapor samples (1 mL) were taken at the gas sampling wells (P1~ P4) using syringe (PerkinElmer, USA) and injected into the GC for determinative analysis. Vapor was pumped from each sampling well to reach a steady-state vapor concentration before sampling. The temperature of injector, column and detector were set at 230 °C, 100 °C and 300 °C, respectively. Chromatographic data were collected and handled by the Software Turbochro 4.1.

The concentration of isooctane in soil was determined by HP 5890N GC equipped with Agilent 7694E Headspace Sampler and FID. The soil samples (5 g) were prepared from the sampling points (S1~ S4) to a depth between 1.2 and 1.4 m using standard method [27]. The headspace sample (1 mL) was injected into the GC-FID instrument using splitless injection. The HP-624 capillary column (25 m × 0.2 mm × 1.12 μm) was used for the GC analysis. The injector and detector were set at 250 °C and the column worked isothermally at 100 °C. The isooctane quantification was performed by direct calibration method.

3. Results and discussion

The physicochemical characteristics of the soils are presented in Table 1. The soil texture was recognized as loam, clay, silt clay and silt clay loam at sampling depth from 0.3 to 2.3 m below the surface. Insignificant difference was found in the density, pH and porosity between soils at different depths. The largest difference was observed on the infiltration rate which decreased by 95% at 2.3 m depth compared to the top subsurface. The pH values of the soils were slightly alkaline and within the preferable ranges for bioremediation [28]. The sufficient soil water content (~ 22%) was beneficial to biodegradation [11] but in contrast it may decrease the mass transfer coefficient between the non-aqueous liquid phase and gas phase during the implementation of SVE [9, 10]. Therefore, the relatively high vapor rate (20 m^3 h^{-1}) used in this study was expected to favour SVE as previous study showed that the impact of water content on SVE efficiency could be reduced by increasing the airflow rate [11].

During the acclimation period, the first-order degradation reaction model provided a good fit to the experimental data (R^2 = 0.9937, Fig. 2). At the end of 100-day acclimation, the concentration of isooctane decreased by up to 63%. The estimated areal distribution of the remaining isooctane from a single injection well indicated the contamination was predominantly within the area of 0.5 m from the centre of injection wells (Fig. 3a). Vertical profile of the relative concentration demonstrated that isooctane diminished to undetectable levels within only 0.2 m below the ground water table (1.8 m) during the sampling period (Fig. 3b).

The subsequent BR-SVE treatment resulted in a significant decrease in the concentration of isooctane in both soil and gas phases (Fig. 4). The percentage loss of isooctane resulted from BR was determined using the percentage loss of concentration in soil (Fig. 4a) subtracted by the fractions removed by SVE that was estimated by the area under the venting curve (Fig. 4b). Results demonstrated that SVE dominated the isooctane removal in the first 36 h when its contribution to the overall removal ranged from 53% to 69% (Fig. 5). On the contrary the remaining isooctane was mainly removed by BR which contributed to 70 ~ 87% of the overall efficiency. This finding was partially attributed to the increase of soil water content from 25 to 37% (data not shown) due to the entering into rain season (August - September) in the test site. Therefore, it is an important strategy to control water content at the early stage but

increase water supply at the end stage during the implementation of BR-SVE as water content is a significant factor hindering SVE but enhancing BR.

In order to compare the influence of SVE on BR, the percentage of isooctane removed by BR in absent of SVE (Fig. 5) was predicted using the degradation model developed during the acclimation period (Fig. 2). Results indicated that the presence of SVE significantly increased the biodegradation by one-order of magnitude (Fig. 5). This may be attributed to the fact that the strong airflow accelerates biodegradation by stimulating the transfer of the volatile fractions that was sequestrated in the micro- or nano- pores in the soils from solid phase into aqueous phase, increasing the degree to which the compounds are free to move into or onto microorganisms, and consequently increasing the dissolved mass available for uptake by the indigenous bacterial populations. This finding coupled with the observation of insignificant changes in the number of bacteria during BR-SVE process (Fig. 6) without nutrients amendment suggested that complement of vapor extraction at the final stage of bioremediation was beneficial for shortening the lag phase of biodegradation.

The overall results allowed concluding that the application of SVE would enhance the removal of contaminants in two aspects such as (i) the vapor evaporates and drives out the volatile components and (ii) the high speed air flow greatly increased the bioavailability and biodegradation of the initially adsorbed components. The latter appears predominant in the process. Future works are needed to (i) examine the factors and mechanisms limiting the multiphase distribution of contaminants into soil matrix, and (ii) develop mathematical models simulating the fate of contaminants during the BR-SVE process.

Acknowledgements

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Reference

[1] SIMONS R.A., SAGINOR J. Determining Off-Site Damages to Non-Residential Property from Leaking Underground Storage Tanks Using Contingent Valuation Analysis, International Real Estate Review, **13,** 134, **2010**

[2] UMA S., PHAM H.G. A Review on Petroleum Hydrocarbon Subsurface Contamination and a Guideline toward Thailand Situation, **2010**

[3] HEAD I.M., SWANNELL R.P.J. Bioremediation of petroleum hydrocarbon contaminants in marine habitats, Curr. Opin. Biotech., **10,** 234, **1999**

[4] KHAN F.I., HUSAIN T., HEJAZI R. An overview and analysis of site remediation technologies, J. Environ. Manage., **71,** 95, **2004**

[5] HALMEMIES S., GRONDAHL S., ARFFMAN M., NENONEN K., TUHKANEN T. Vacuum extraction based response equipment for recovery of fresh fuel spills from soil, J. Hazard. Mater., **97,** 127, **2003**

[6] COULON F., POLLARD S.J.T., BRASSINGTON K.J., Weathered Hydrocarbon Biotransformation: Implications for Bioremediation, Analysis, and Risk Assessment. Handbook of Hydrocarbon and Lipid Microbiology pp. 2487-2499, **2010**.

[7] ATLAS R.M., CERNIGLIA C.E. Bioremediation of petroleum pollutants, Bioscience., **45,** 332, **1995**

[8] USEPA EPA-542-R-05-028: Off-Gas Treatment Technologies for Soil Vapor Extraction Systems: State of the Practice, **2006**

[9] ALVIM-FERRAZ M.C.M., ALBERGARIA J.T., DELERUE-MATOS C. Soil remediation time to achieve clean-up goals I: Influence of soil water content, Chemosphere, **62,** 853, **2006**

[10] QIN C.-Y., ZHAO Y.-S., ZHENG W., LI Y.-S. Study on influencing factors on removal of chlorobenzene from unsaturated zone by soil vapor extraction, J. Hazard. Mater., **176,** 294, **2010**

[11] SOARES A.A., ALBERGARIA J.T., DOMINGUES V.F., ALVIM-FERRAZ M.D.C.M., DELERUE-MATOS C. Remediation of soils combining soil vapor extraction and bioremediation: Benzene, Chemosphere, **80,** 823, **2010**

[12] ALVIM-FERRAZ M.D.C.M., TOM S ALBERGARIA J., DELERUE-MATOS C. Soil remediation time to achieve clean-up goals II: Influence of natural organic matter and water contents, Chemosphere, **64,** 817, **2006**

[13] POULSEN T.G., MOLDRUP P., YAMAGUCHI T., HANSEN J.A. VOC vapor sorption in soil: Soil type dependent model and implications for vapor extraction, J. Environ. Engineer, **124,** 146, **1998**

[14] NAMKOONG W., HWANG E.Y., PARK J.S., CHOI J.Y. Bioremediation of diesel-contaminated soil with composting, Environ. Pollut., **119,** 23, **2002**

[15] ISO, BS ISO 10390: Determination of pH., **2010**.

[16] ISO, ISO 11465:1993: Determination of dry matter and water content on a mass basis by a gravimetric method, **1994**.

[17] ISO, BS EN 13039: Determination of the organic matter and ash, **2000**.

[18] ISO, BS ISO 11277:2009: Determination of particle size distribution in mineral soil material- Method by sieving and sedimentation, **2010**.

[19] BSI, BS 7755: Section 5.6: Determination of dry bulk density, **1999**.

[20] BRIDGE B., ROSS P. A portable microcomputer-controlled drip infiltrometer. II. Field measurement of sorptivity, hydraulic conductivity and time to ponding, Aust. J. Soil Res., **23,** 393, **1985**

[21] PRUESS K., OLDENBURG C., MORIDIS G. TOUGH2 User's Guide. Earth Sciences Division, Lawrence Berkeley National Laboratory. Berkeley CA USA. LBNL-43134, **1999**

[22] FALTA R., PRUESS K., FINSTERLE S., BATTISTELLI A. T2VOC User's Guide. Earth Sciences Division. Lawrence Berkeley National Laboratory. Berkeley CA USA. LBNL-36400, **1995**

[23] DUPONT R.R. Fundamentals of bioventing applied to fuel contaminated sites, Environ. Prog., **12,** 45, **1993**

[24] SUI H. Remediation of Organic Contaminants by Bioventing and Cometabolic Bioventing and Mathematic Simulations, Tianjin University (PhD Thesis), **2004** [in Chinese]

[25] WU D., LI X., HUANG G., YANG Y. In-situ venting remediation of light oil polluted surface soil, Chemical industry and engineering **25,** 61, **2008** [in Chinese]

[26] JOHNSON P.C., STANLEY C.C., KEMBLOWSKI M.W., BYERS D.L., COLTHART J.D. Quantitative analysis for the cleanup of hydrocarbon-contaminated soils by in-situ soil venting, Ground Water Monitoring & Remediation, **10,** 159, **1990**

[27] USEPA, EPA method 5021A: Volatile organic compounds in soils and other solid matrices using equilibrium headspace analysis, **2003**.

[28] WILSON S.C., JONES K.C. Bioremediation of soil contaminated with polynuclear aromatic hydrocarbons (PAHs): A review, Environ. Pollut., **81,** 229, **1993**

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295 **Table 1** Physicochemical properties of soils at different depths below the surface

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Depth (m)	Density (g mL^{-3})	Moisture (%)	pH	SOM (%)	Porosity (%)	Infiltration rate (mm min^{-1})	Soil texture (%)		
							Sand	Silt	Clay
0.3 ± 0.1	1.48	22.3	7.8	0.6	45.1	0.63	47	27	26
1.2 ± 0.1	1.48	22.3	8.1	1.2	45.1	0.17	19	31	50
1.8 ± 0.1	1.47	26.4	8.2	1.1	45.4	0.14	0	58	42
2.3 ± 0.1	1.49	24.4	8.2	1.7	44.8	0.03	0	67	33

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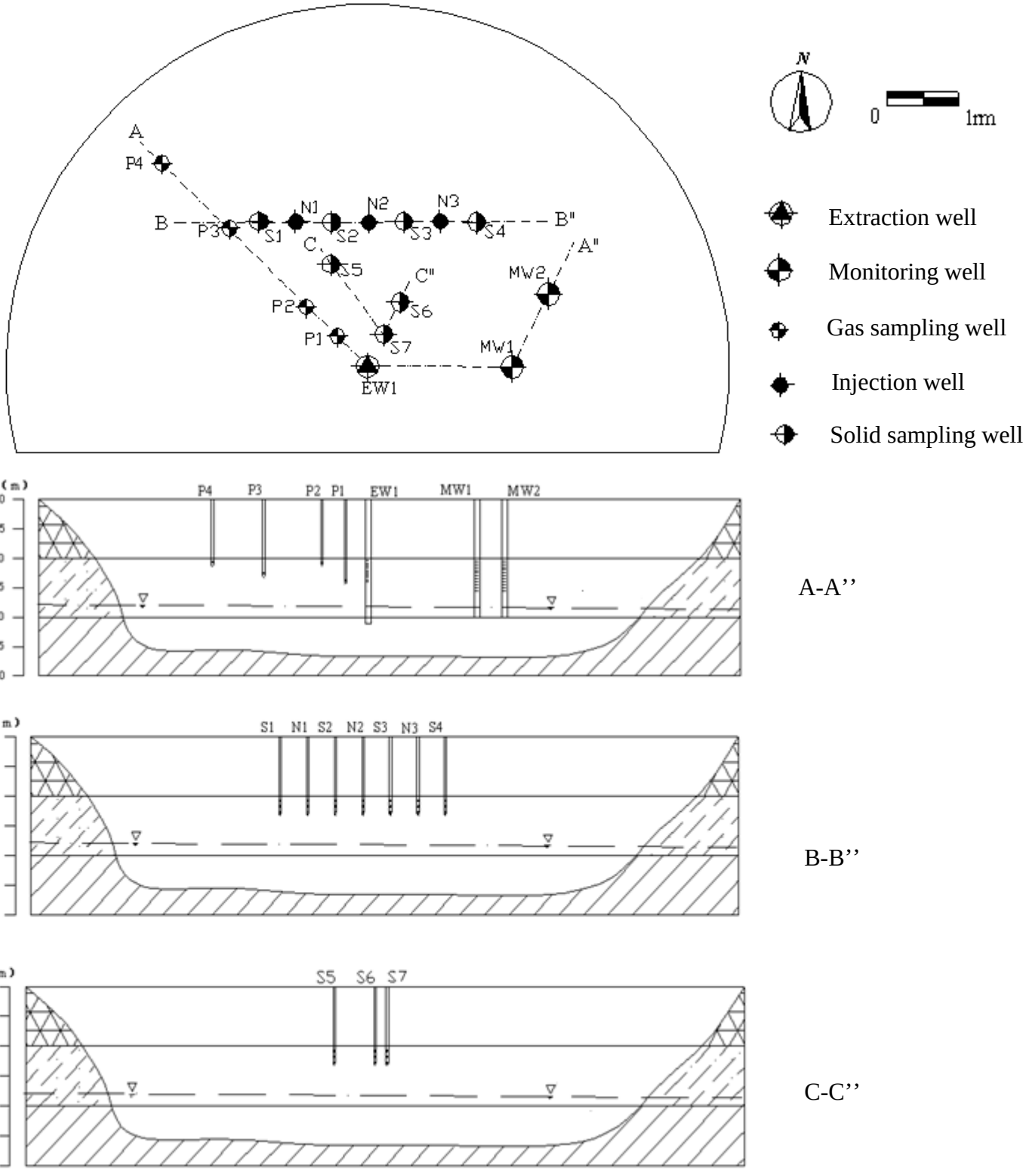


Fig. 1 Schematic of wells location

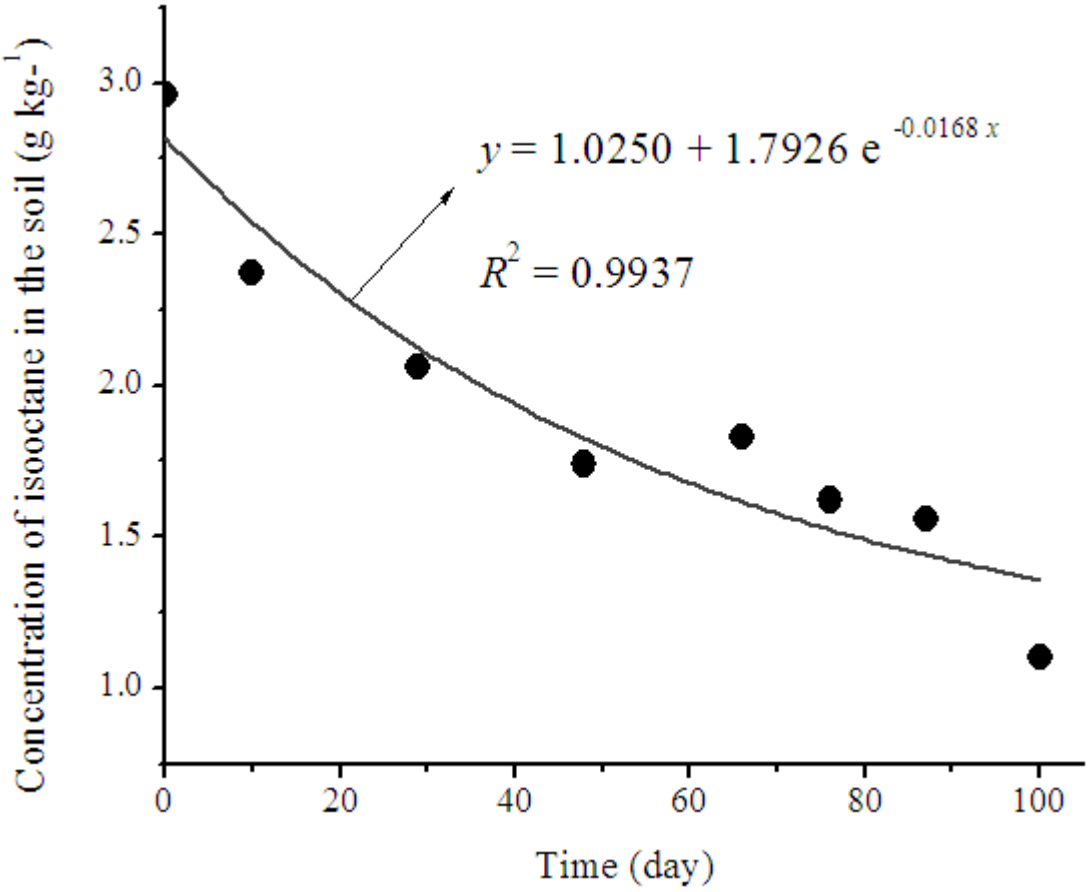


Fig. 2 Concentration of isooctane in the soil during the 100-day acclimation period

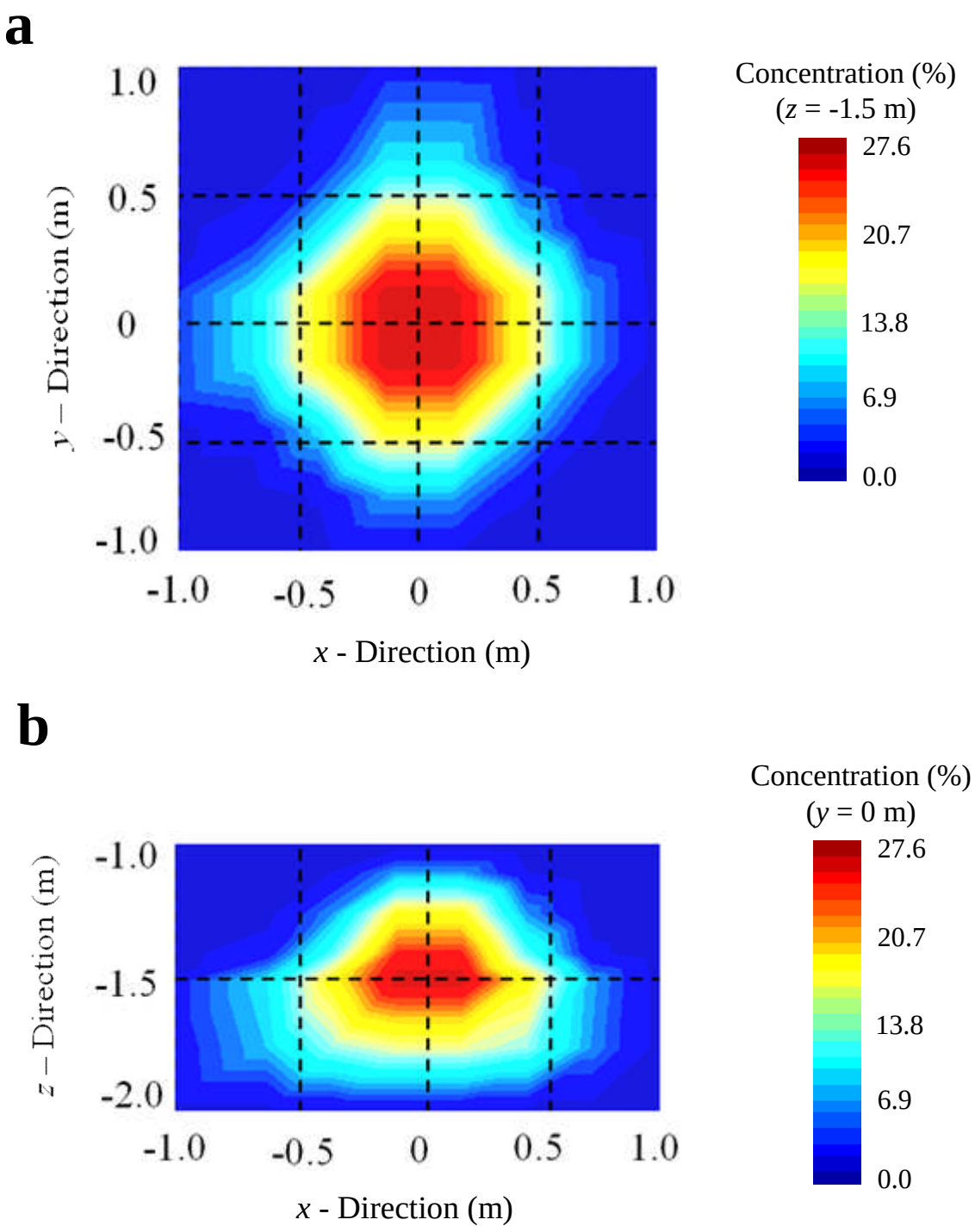


Fig. 3 The estimated (a) horizontal and (b) vertical dispersion of isooctane near the injection well (single well) after 100-day *in situ* acclimation.

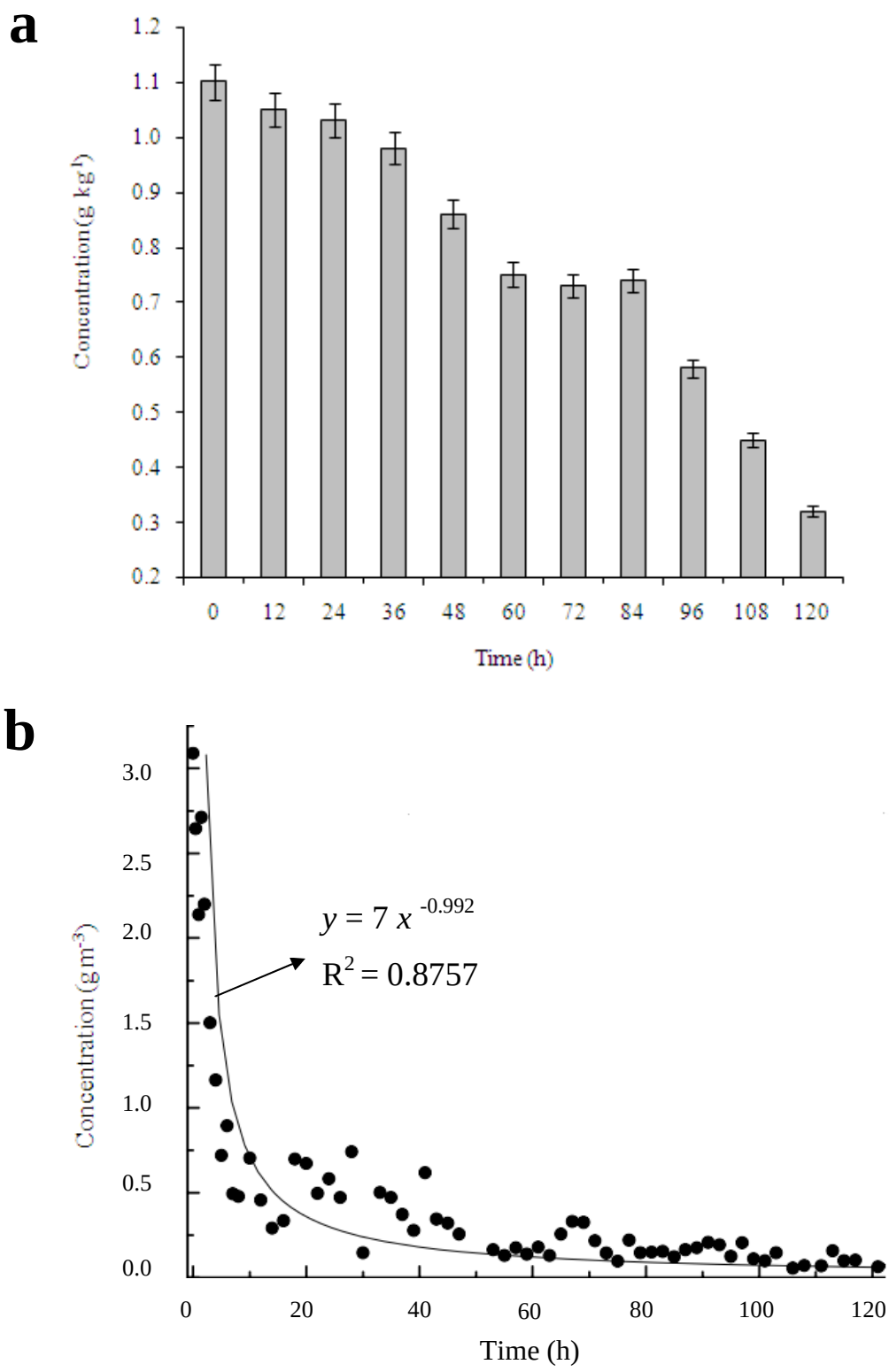


Fig. 4 Concentration of isooctane in the (a) soil and (b) gas phase during the BR-SVE treatment

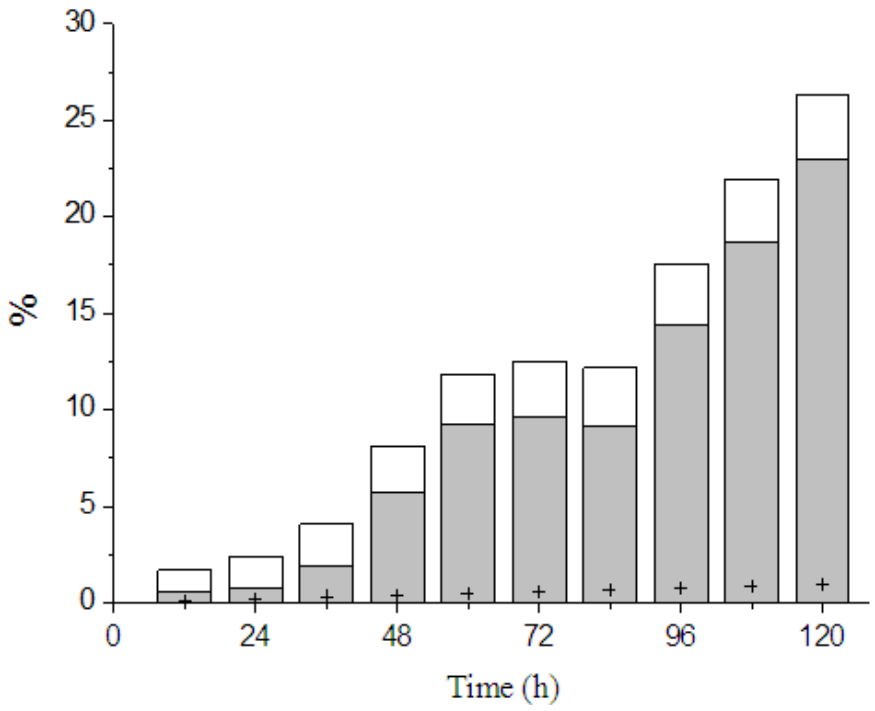
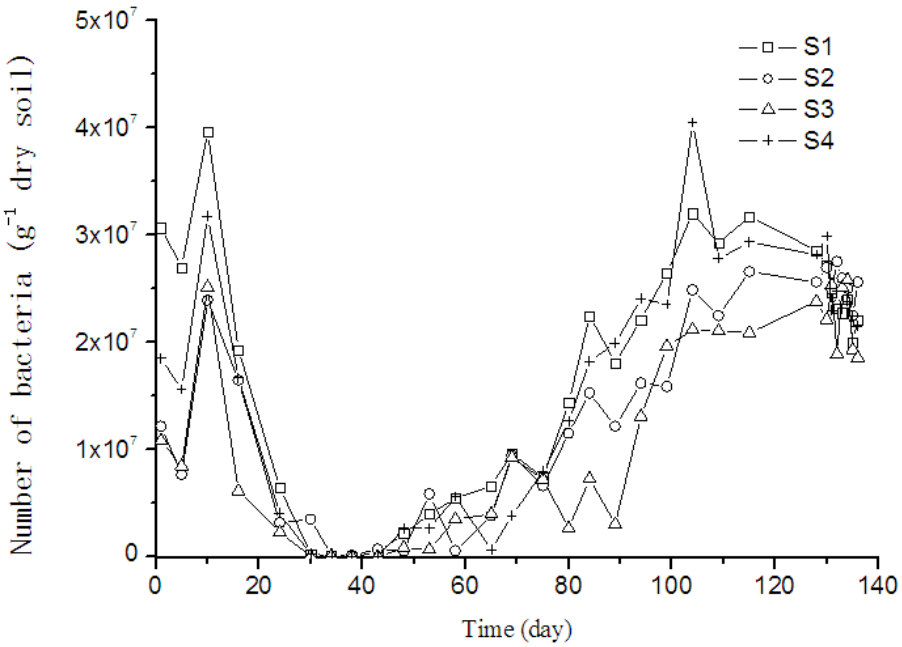


Fig. 5 Percentage of isooctane removed by BR ( ) and SVE ( ) during the BR-SVE treatment. The percentage removal by BR in absent of SVE (+) was estimated by the biodegradation curve during acclimation period.

a



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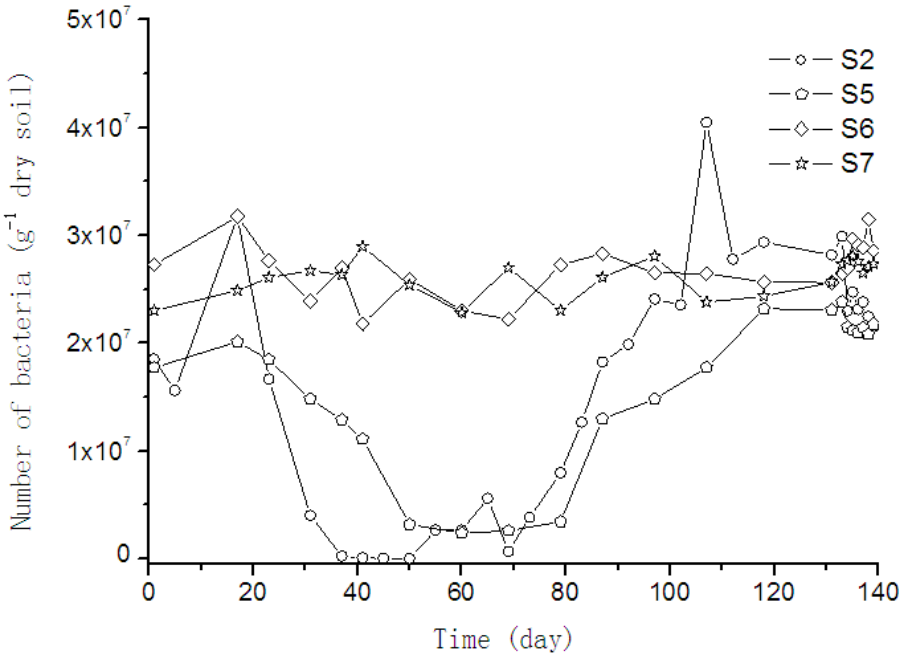

Fig. 6 Number of bacteria around the sampling wells