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Sensitivity of Benzene Natural Attenuation to Variations in Kinetic and Transport Parameters in Liwa Aquifer, UAE

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Abstract Dissolved benzene was detected in the shallow unconfined Liwa aquifer (UAE). This aquifer represents the main freshwater source for a nearby residence camp area. A finite element model is used to simulate the fate, transport, and attenuation of the dissolved benzene plume to help decision makers assess natural attenuation as a viable remediation option. Sensitivity of benzene attenuation to uncertainties in the estimation of some of the kinetic and transport parameters is studied. It was found that natural attenuation is more sensitive to microbial growth rate and half saturation coefficients of both benzene and oxygen than initial biomass concentration and dispersivity coefficients. Increasing microbial growth rate by fourfold increased natural attenuation effectiveness after 40 years by 10%; while decreasing it by fourfold decreased natural attenuation effectiveness by 77%. On the other hand, increasing half saturation coefficient by fourfold decreased natural attenuation effectiveness by 46% in 40 years. Decreasing the same parameter fourfold caused natural attenuation effectiveness to increase by 9%.

Keywords Benzene · Monitored Natural Attenuation · Sensitivity Analysis · UAE

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Groundwater contamination with benzene is a common problem in the Arabian Gulf countries. When released into groundwater systems, benzene causes significant health risk due to its relatively high water solubility and toxicity. Biodegradation could be the only in situ process leading to a decrease of benzene concentrations in groundwater (Rifai and Rittaler 2005). The assessment of in situ biodegradation of benzene is essential for proper implementation of groundwater management strategies. Recently, monitored natural attenuation has become an effective alternative to the more active remediation methods for the in situ treatment of contaminated subsurface environments. However, this low-cost technology requires a high degree of certainty in the conceptual site model and the underlying reactive transport processes including estimation of transport and kinetic parameters. Numerical modeling could be of great assistance in the assessment procedures.

Several studies focusing on the modeling the fate, transport and biodegradation of benzene in field case studies have been reported (e.g. Schafer and Therrien 1995; Parcher 1999; Rifai and Rittaler 2005). Biodegradation of groundwater contamination by redox-sensitive species has been recognized in several other studies (e.g. Guha 2004; Yu et al. 2007; Bauer et al. 2008). The multiple-term Monod expression is used when it is unknown which of the species is rate-limiting (Bauer et al. 2008). An important advantage of Monod kinetics is that the function itself contains regions of zero-order, first-order, and mixed-order. Jean et al. 2002 simulated the transport and biodegradation of benzene-toluene-xylenes (BTX) in an experimental tank in which sand is used to represent a semi-confined aquifer. Comparisons between lab and modeling results showed that Monod kinetics is more accurate than first order kinetics. Rifai and Rittaler (2005) presented procedures for data analysis and interpretation to

reduce model dependency of data when assessing natural attenuation of benzene. They applied their procedures on a contaminated site in central Texas. It was concluded that natural attenuation is an acceptable technology for remediating several benzene contaminated sites. The main objective of this study was to examine the possibility of adopting monitored natural attenuation as a remediation technique for the contaminated Bu Hassa groundwater aquifer.

Materials and Methods

The site under consideration is located 150 km southwest of UAE capital Abu Dhabi (Fig. 1). After benzene contamination was discovered in 2000, soil investigations at the site were performed through 142 organic vapour analysis (OVA) readings from 27 test pits field measurements and hydrocarbons were detected in the soil. Ten test pits were located outside the contamination zone to obtain background concentrations. Soil samples were obtained from each test pit at 1 m depth interval from ground surface to a maximum depth of 5 m (Forrest and Arnell 2001). It was found that contaminated soil had higher concentrations than background OVA measurements. A monitoring wells network was installed to investigate the extent of hydrocarbon plume from the source zone (former warm blow down pit) (Fig. 1). The presence of free phase hydrocarbons floating on the water table was confirmed. The location of the non-aqueous phase liquid (NAPL) measured in the soil is consistent with observations of the distribution of the dissolved hydrocarbons. This suggests that the pure NAPL in the soil migrated downward in the unsaturated zone and, being lighter than water, formed a body floating near the water table. Same wells were used to record depth of the free hydrocarbon pool above the water table and its thickness which is used to estimate its volume. The thickness of free hydrocarbons ranged between 1.00 m and 1.65 m (Fig. 2) and the volume of free phase hydrocarbon was estimated as 2,830 m^3 (Forrest and Arnell 2001). Partial dissolution of benzene in the surrounding groundwater results in the formation of a dissolved plume (Fig. 2). This dissolved benzene plume migrates by advection and dispersion processes and is subjected to natural attenuation. In 2000, it was reported that the concentration of the dissolved benzene in monitoring well 00-8 was 0.03 mg/L (Fig. 2) (Forrest and Arnell 2001). Benzene constitutes the highest dissolved concentration of NAPL constituents at the site. For an ideal NAPL mixture in contact with water, the aqueous phase concentration of a component in NAPL can be calculated using the aqueous analog of Raoult's law as the product of its pure aqueous solubility and its mole fraction. McNab et al. (1997) assumed that the mole fraction of benzene is equal to 0.5% of its weight fraction, the pure benzene solubility is equal to 1,770 mg/L; therefore the aqueous phase concentration of the benzene in NAPL mixture is 8.85 mg/L. However, Johnson et al. (2000) reported that the equilibrium concentration of BETX resulted from typical gasoline mixture in contact with water has a benzene concentration of 18 mg/L. Assuming ideal NAPL mixture, the aqueous phase benzene concentration for this site is estimated to be 8.5 mg/L.

The unconfined Liwa aquifer is the main water supply in the area. Supply wells provide water for irrigation, recreation, and washing for the nearby camp area (Fig. 1) and bottled water is used for drinking. It was indicated from the water elevation data (Woodward 1996) that the regional groundwater flow direction in Liwa aquifer is to the northwest. The hydraulic gradient of the groundwater in the site is variable. The gradient increases towards the pumping wells; therefore, the groundwater velocity also increases in the same area. The hydraulic gradient between the former warm blow down area and the supply water wells is 0.25%. Water depths were recorded in November 2000 using the monitoring network and used to calculate groundwater table elevations. Contour map of groundwater elevation is produced (Fig. 1), based on the records of groundwater levels, and used to estimate groundwater flow direction and horizontal hydraulic gradient. The groundwater flow direction is found to be in agreement with the direction of the regional groundwater flow in Liwa aquifer. Field estimated values for effective porosity of 0.3 and hydraulic conductivity of 1×10^{-4} m/s were used to estimate the average linear groundwater velocity as 25 m/year. It was found that the contamination source is located directly up-gradient of the supply wells; which puts these wells at potential risk of being contaminated. It was reported that the concentration of dissolved oxygen (DO) outside the contaminated area are higher than inside (Forrest and Arnell 2001). This observation suggests that aerobic bacteria are active and are using benzene as their carbon source, thereby contributing to natural attenuation.

Aqueous phase contaminant transport in groundwater is described by the advection–dispersion-reaction equation for an electron donor (benzene) and an electron acceptor (oxygen). The reactive-transport equation for benzene may be written as:

$$R\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C}{\partial x_j}\right) - V_i\frac{\partial C}{\partial x_i} + \frac{-M\,\mu_{\max}}{\theta Y_c}\left(\frac{C}{K_c + C}\right)\left(\frac{O}{K_o + O}\right) \quad (1)$$

where C is the benzene aqueous phase concentration [ML^{-3}], V_i is the average pore water velocity in the i direction [LT^{-1}], x_i is the distance in the i direction ($i = 1$,

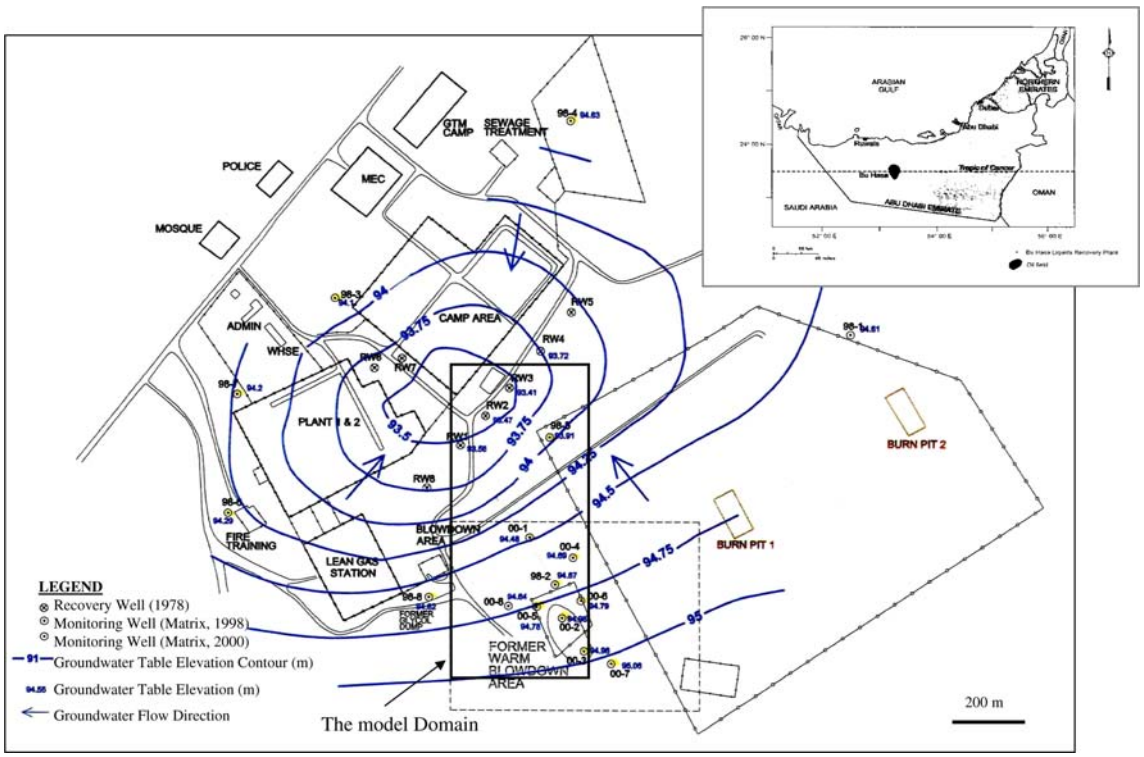

Fig. 1 Site location of Bu Hasa Liquid Recovery Plant, including site plan, water table elevations, and model domain

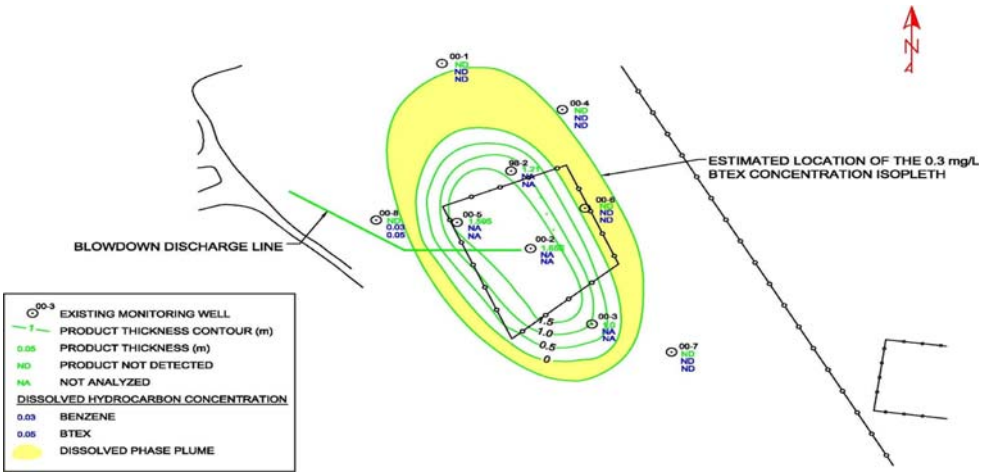

Fig. 2 Estimated location of the dissolved benzene plume in the site

2 or $x_i = x,\ y$) [L], D_{ij} is the 2nd order tensor for hydrodynamic dispersion [L^2T^{-1}], R is the retardation factor [dimensionless], t is time [T], M is the microbial biomass concentration [ML^{-3}], θ is the aquifer porosity [dimensionless], Y_c is the yield coefficient [dimensionless] representing the mass of bacterial species produced per unit mass of benzene utilized, μ_{max} is the microbial maximum specific growth rate [T^{-1}] and K_c, K_o are the half saturation coefficient for benzene and oxygen, respectively [ML^{-3}]. The mass balance equation for growth and death of the microbial population can be written as:

$$\frac{dM}{dt} = M\left(\mu_{max}\left(\frac{C}{K_c + C}\right)\left(\frac{O}{K_o + O}\right) - B\right) \quad (2)$$

where B is the first order decay rate which accounts for cell death.

Results and Discussion

The finite element numerical model METABIOTRANS (Mohamed 2001; Mohamed et al. 2006, 2007) is used to simulate benzene transport in Liwa aquifer. The modeled

Table 1 List of kinetic parameters found in literature and used in this study

Parameter	Value	Reference
Maximum bacterial specific growth rate (μ_{max}) (day^{-1})	0.05–0.96	Kindred and Celia (1989)
	0.96–4.8	Schafer et al. (1998)
	0.05–0.1	Miralles-Wilhelm et al. (1996), Schafer (2001)
	0.05	This study
Benzene half saturation coefficient (K_c) (mg/L)	4.5–270	Kim et al. (2005)
	100–200	Miralles-Wilhelm et al. (1996)
	0.2–70	Schafer (2001)
	125	This study
Oxygen half saturation coefficient (K_o) (mg/L)	0.2	Schafer and Therrien (1995)
	0.1	MacQuarrie et al. (1990), Borden and Bedient (1986), Miralles-Wilhelm et al. (1996)
	0.1	This study
Yield coefficient (Y_s)	1.3E-4–2.0	Salvage and Yeh (1998)
	0.002	Godeke et al. (2008)
	0.02–0.1	Schafer et al. (1998), Schafer (2001)
	0.01	This study
Microbial decay coefficient (B) (day^{-1})	0.1 μ_{max}	Schafer et al. (1998)
	Neglected	Salvage and Yeh (1998), Schirmer et al. (2000)
	0.0	This study

domain covers an area of approximately 292 km; it extends 350 m in x-direction and 850 m in y-direction (Fig. 1). A two dimensional finite element grid of 11,928 elements is used for spatial discretization of the modeled area. The model domain was selected to contain the benzene source area in the southeast corner and the nearest production wells in northwest corner. Values of longitudinal and transverse dispersivities were estimated to be 2.3 and 0.23 m, respectively. These values are average for this type of aquifers (e.g. Weaver and Charbeneau 2000). However, sensitivity of natural attenuation to changes in dispersivities' coefficients will be studied in this paper. It is not known exactly when the release of contaminated water started at the former blow down area. However, knowing that the plant started operation in 1985, it was estimated that NAPL reached water table in Liwa aquifer approximately in 1995; 5 years before contamination was discovered. Therefore, all numerical simulations presented here are assumed to start in 1995. The model is used first to predict the benzene plume migration in a base case considering advection and dispersion and ignoring natural attenuation. This simulation is considered as a reference and all natural attenuation simulations will be compared to this base case. That is, the sensitivity of natural attenuation at any time in any natural attenuation simulation will be represented by the ratio of remaining benzene mass at this time to benzene mass of the base case at the same time. The parameters studied are the maximum specific growth rate (μ_{max}); the initial biomass concentration (M_o); the benzene half saturation coefficient (K_c), the oxygen half saturation coefficient (K_o), the microbial decay factor (B); and the dispersivity coefficient (α). A second base case is simulated in which natural attenuation is considered. Values of the kinetic modeling parameters used in this second base case are carefully selected to represent average values reported in previous similar studies (Table 1). The value of each of the parameters mentioned above is increased two and fourfold, and decreased two and fourfold in a series of simulations to study their effects on natural attenuation. Figure 3a presents the effect of the changes in the estimation of μ_{max} on natural attenuation. The effect of increasing μ_{max} appeared at the earlier times; when μ_{max} value is 0.02 day^{-1}, high attenuation rate occurred. It is very clear from this figure that with higher values of μ_{max}; higher bacterial growth rates are simulated and consequently more attenuation occurs. High attenuation rate is occurred when high amount of benzene mass is reduced. It is observed that less than 50% of the benzene mass was biodegraded after 40 years when μ_{max} value was reduced to its quarter. On the other hand, almost 98% of the benzene mass was reduced when μ_{max} value was increased four times. The slope of the curves in Fig. 3a represents overall attenuation rate. Attenuation rate in the case of μ_{max} equals 0.02 day^{-1} at earlier time was the highest, but decreases after 20 years and stabilizes until the end of the 40 years. Overall attenuation rate in the case of μ_{max} equals

0.0025 day^{-1} was almost zero in the first 15 years, but was increased with time and biodegraded mass ratio reached 70% by the end of 40 years.

Another parameter that affects the attenuation process in the subsurface is the biomass initial concentration (M_o), which represents the population density of the bacteria at the time of benzene release. Figure 3b clarifies the effect of altering the initial biomass concentration on the benzene mass ratio with respect to time. In the case of doubling M_o (0.002 mg/L); benzene mass ratio equaled 0.3 after 20 years; while this values was 0.45 when M_o is decreased to half (0.0005 mg/L). Higher initial biomass concentration led to higher benzene mass reduction. The difference between the values of benzene mass ratio of the same two simulations after 40 years is less than 0.1. This is because the overall attenuation rate increases after 10 years and then slows down gradually after 20 years as shown in Fig. 3b. Natural attenuation did not appear to be much sensitive to changes in M_o compared to changes in μ_{max}.

There is an inverse relationship between K_c and μ_{max} as indicated in Eq. 1. Figure 3c shows that attenuation in the case of using K_c of 31 mg/L started earlier, while in the case of using K_c of 500 mg/L the effect of attenuation on the benzene mass started after 20 years. It is obvious that the lowest half substrate constant caused the highest benzene attenuation; almost 98% of the benzene mass undergoes attenuation after 40 years. When K_c was 62 mg/L, the benzene attenuation started early, but later than the case of K_c equals 31 mg/L. When K_c is assumed 62 mg/L, this resulted in almost 95% benzene mass reduction by the end of 40 years (Fig. 3c). When K_c of 250 mg/L, attenuation becomes effective after 15 years and overall attenuation increased until the end of 40 years. In this case, almost 75% of benzene mass was biodegraded by the end of 40 years (Fig. 3c). When K_c was increased to 500 mg/L, the overall attenuation increased after 20 years and about 50% of the benzene mass is reduced by the end of 40 years. Almost the same behavior is noticed when changing oxygen half saturation coefficient (K_o) (Fig. 3d). However, sensitivity of natural attenuation to changes of K_o was less than changes in K_c.

The effect of the decay rate was neglected in several previous studies and was considered in other studies (Table 1). For the sake of studying the sensitivity of natural attenuation to changes in B, several values were selected; the first of which is 0.0005 day^{-1} which represents 0.1 μ_{max} as previously assumed by Schafer et al. (1998) (Table 1). Another three values of 0.000125, 0.001 and

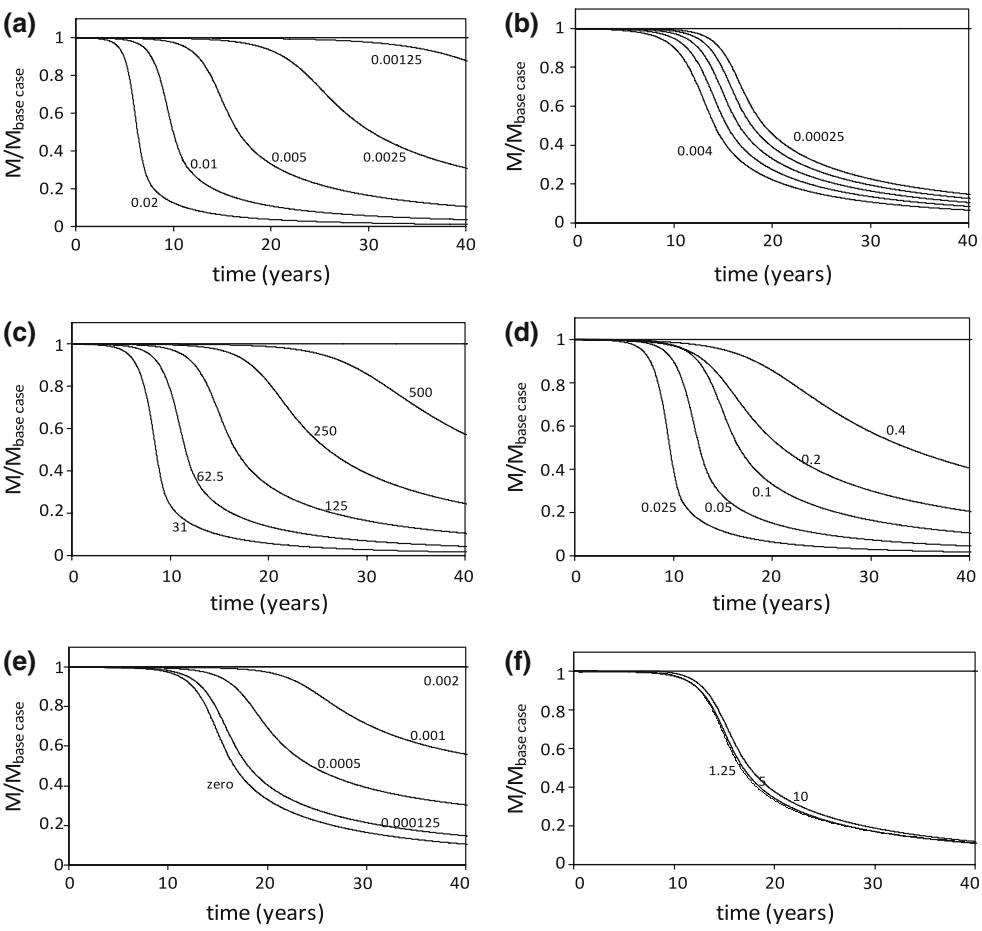

Fig. 3 Sensitivity of benzene mass ratio to changes in **a** μ_{max}, **b** M_o, **c** K_c, **d** K_o, **e** B, and **f** α

0.002 were also tested. The ratio between the benzene mass and the initial mass of the base case with respect to time in the case of using B equals 0.002 day^{-1} is identical to the base case where B was assumed zero (Fig. 3e). when B equaled 0.000125 day^{-1}, the attenuation became effective at earlier time, while in the case of B equals 0.001 day^{-1}, the attenuation started later after 10 years. The attenuation rate when B equals 0.000125 day^{-1} was high after 10 years, then it was decreased gradually and resulted by the end of 40 years in an almost 80% benzene mass reduction. Using B equals 0.0005 day^{-1} resulted in a 60% benzene mass reduction after 40 years, while only 40% of benzene mass is biodegraded in the case of B equals 0.001 day^{-1}. This indicates that natural attenuation is sensitive to changes in B in Bu Hassa field.

The influence of changing the longitudinal dispersivity coefficients of the aquifer on natural attenuation is studied through three additional simulations. The values 2.3 and 0.23 m of α_L and α_T, respectively, were assumed in the base case. The ratio between α_L and α_T is maintained constant in all simulations. Figure 3f shows the effect of changing the dispersivity on the benzene mass. In all simulations, natural attenuation became effective after 10 years. The slope of the mass ratio curve shown in Fig. 3f increased in almost all cases with highest attenuation rate between 10 and 20 years, then attenuation rate decreased after 20 years. The benzene mass reduction was about 85% by the end of 40 years. This figure indicates that natural attenuation of the benzene plume is not sensitive to changes in the dispersivities.

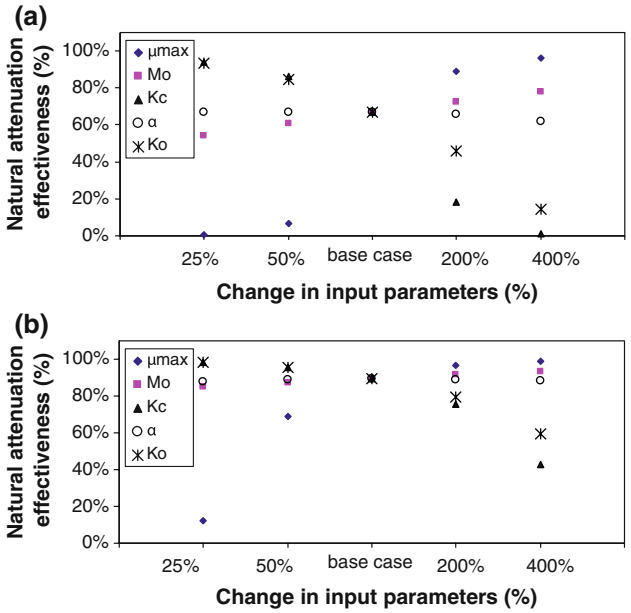

Fig. 4 Sensitivity of benzene natural attenuation effectiveness after **a** 20 years, and **b** 40 years

The natural attenuation effectiveness presented in Fig. 4 represents the biodegraded benzene mass at any time over the benzene mass of the "no attenuation" base case at the same time. This means that at any time the summation of natural attenuation effectiveness plus the mass ratio (presented in Fig. 3) is always one. In general, sensitivity of natural attenuation to changes in all parameters is larger after 20 years (Fig. 4a) than after 40 years (Fig. 4b). Natural attenuation is more sensitive to μ_{max} and K_c than any other parameter at both times. On the other hand, changes in M_o and α showed less influence on natural attenuation effectiveness, especially after 40 years (Fig. 4b). In conclusion, accurate estimation of μ_{max}, K_c, and K_o is essential for the evaluation of monitored natural attenuation to be adopted as a remediation technique in Liwa Aquifer for the first 20 years. Specific attention in the estimation of μ_{max} and K_c must be taken into account if natural attenuation can be considered for up to 40 years.

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