Integrating biological degradation potential into ecological risk assessment

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Abstract: Expanding agricultural activities and industrial operations have resulted in the accumulation of toxic chemicals in our environment, and have become a potential threat to human health as well as to the flora and fauna in our ecosystems. The assessment of contamination risk to our environment mainly relies on mathematical models that estimate the contaminant concentrations and the leaching rates into aquifers. The contaminant level is commonly determined by comparing the concentrations predicted by models against a threshold concentration, and the ecosystem is considered at risk if the predicted contaminant concentration is above a threshold value. Although environmental models can describe contaminant transport and adsorption processes relatively well, most of these models do not take into account the capability of microorganisms to degrade toxic contaminants into less toxic or non-toxic molecules. Many experimental and in-situ studies have shown that soil microbial activity can result in a relatively fast rate of contaminant degradation, therefore implying that the time required to "clean-up" a contaminated site may be substantially shorter in the presence of receptive microorganisms. Hence, ecological risk assessments not accounting for microbial load and specific catabolic processes can overstate the risks and lead to the making of policies and management strategies only partly suitable to specific contaminated ecosystems.

In this study, we integrated the biodegradation potential ψ_B of a contaminant into ecological risk assessment index through the specific biomass affinity ϕ. We focused on atrazine (ATZ), one of the most extensively used herbicides in Australia, as the model contaminant using data from la Cecilia and Maggi (2017), and the Hazard Quotient as the modeled ecological risk index (Suter II, 2007). Model parameters were estimated from laboratory experiments, while simulations were extended to a 60-year time scale to analyze the Hazard Quotient of ATZ contamination in groundwater with the inclusion of ATZ biodegradation potential under scenarios of different ATZ application rates. These analyses demonstrated that ATZ contamination level can be overestimated if the biodegradation potential were not taken into account. The use of contaminant biodegradation potential in ecological risk assessments can improve information for optimum decision making in environment and resources management.

Keywords: *Atrazine, agrochemicals, contamination, ecological risk index, specific biomass affinity*

1. INTRODUCTION

Although government agencies and industry organizations have invested a great effort in developing best management practices for handling chemical wastes and minimizing their impacts on ecosystems, traces of industrial and agricultural chemicals have been detected in the surface and ground water over the last few decades. For example, high concentrations of organochlorine compounds including dichloro-diphenyl-trichloroethane (DDT), polychlorinated biphenyl (PCB), and hexachlorocyclohexane (HCH) have been detected in the Sydney Harbour catchment (Birch and Taylor, 2000), while atrazine (ATZ) concentrations above the Australian Drinking Water Guidelines threshold (i.e., 20 μg/L; NRMMC, 2011) have been measured in groundwater in residential areas of Perth (Appleyard, 1995). These observations give rise to public concerns regarding the potential threat contaminants can impose on ecosystem and human health.

Many environmental risk assessment indices (e.g., Ecological Risk Index (ERI) and Hazard Quotient (HQ); Suter II, 2007) have been developed to quantify and predict the potential contamination risks on ecosystems. The majority of these indices consolidated the idea that the ecosystem health is at risk if the monitored or predicted contaminant concentrations are above a threshold concentration. The prediction of contaminant concentrations in decadal to centennial time scales often relies on mathematical models, which are expected to capture the dynamics of all physical, chemical, and biological processes in an ecosystem. However, most of the models include only contaminant transport and adsorption-desorption processes without accounting for biological processes. Many studies have documented the ability of microorganisms to change the information content, structure, properties, and chemical contents of geophysical systems (e.g., Jones *et al.*, 1994; Eldridge and Greene, 1994; Tang and Maggi, 2017). Many experimental studies have shown that microorganisms can degrade contaminants into less toxic molecules (e.g., Leahy and Colwell, 1990; Coleman *et al.*, 2002), and therefore models not accounting for biodegradation may overestimate the contamination level.

In this study, we described the biodegradation potential ψ_B of a contaminant, and we incorporated its effect into an environmental risk assessment index. The parameter ψ_B allows users to account for biodegradation without having to run a full biodegradation mechanistic model. The application of ψ_B was then tested in a case study of atrazine (ATZ) contamination in West Wyalong, which is located in the "cereal belt" of New South Wales. Details of the site and model descriptions are presented in the following sections.

2. METHODS OF PARAMETER ESTIMATION

All model parameters were calibrated against existing experiments reported in the literature. Calibration was conducted with PEST (Doherty, 2005), which minimizes errors between model and experimental observations. The goodness-of-fit was measured using the R-squared $R^2 = [\mathrm{cov}(x,y)/(\sigma_x\sigma_y)]^2$ and normalized root mean squared error $\mathrm{NRMSE} = \left\{\sqrt{1/n\sum_{i=1}^{n}(x_i - y_i)^2}/[\max(y) - \min(y)]\right\}\times 100$, where x and y are the modeled and experimental values, respectively, n is the total number of observations, whereas, σ_x and σ_y are the standard deviation of x and y, respectively.

3. THE BIODEGRADATION POTENTIAL

Using Michaelis-Menten-Monod kinetics, the capability of a specific microbial functional group B with biomass concentration $[B]^*$ to degrade a substrate S at low concentration can be expressed by the specific biomass affinity ϕ [T^{-1}] (la Cecilia and Maggi, 2016)

$$\phi = \lim_{\substack{[S]\to 0 \\ [B]\to[B]^*}} \frac{\mu[B]}{Y([S]+K_S)} = \frac{\mu[B]^*}{YK_S}, \tag{1}$$

where μ [T^{-1}] is the maximum specific biomass growth rate, K_S [ML^{-3}] is the Michaelis-Menten half-saturation concentration, and Y [MM^{-1}] is the biomass yield per mole of consumed S. High values of ϕ indicate a rapid S degradation and a shorter half time $t_{1/2}$ for S; that is, $1/\phi \propto t_{1/2}$ as illustrated in Figure 1 (third column).

A sensitivity analysis of the effects of μ and Y on ϕ and $t_{1/2}$ is presented in Figure 1. The values of ϕ increased with increasing μ and decreasing Y for unchanged K_S and $[B]^*$. In a kinetic modeling framework that assumes stationary biomass content (i.e., $\mathrm{d}[B]/\mathrm{d}t \approx 0$), $1/\phi$ and $t_{1/2}$ are strongly correlated with R^2 =1.00 (Figure 1, first row), whereas when biomass undergoes growth $\mathrm{d}[B]/\mathrm{d}t = -Y\mathrm{d}S/\mathrm{d}t$ and mortality $\mathrm{d}[B]/\mathrm{d}t = -\delta[B]$, the correlation between $1/\phi$ and $t_{1/2}$ is weaker, i.e., $R^2 \approx 0.66$ (Figure 1, second and third row). If microbial ecology and its dynamics in a natural environment were hypothesized to not dramatically vary over time, the specific biomass affinity ϕ can be used as a proxy to the biodegradation strength; hence, the

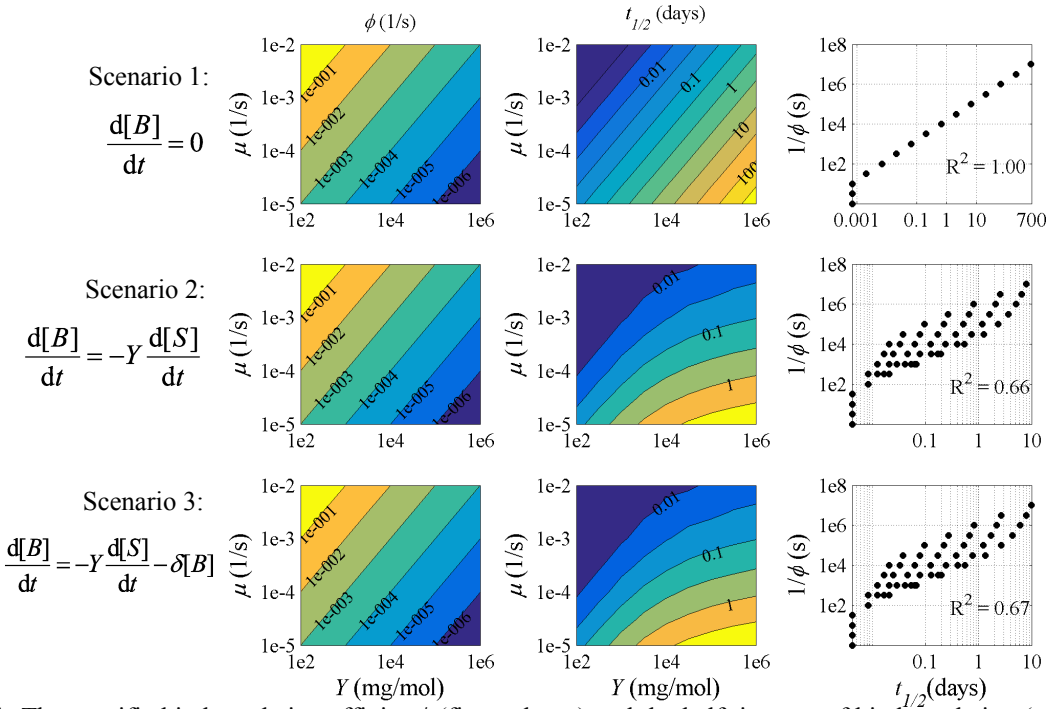

Figure 1. The specific biodegradation affinity ϕ (first column) and the half time $t_{1/2}$ of biodegradation (second column) at various values of specific growth rate μ and biomass yield Y with the half-saturation concentration K_S = 1×10^{-4} mol/L and $[B]^*$ = 1 mg/L. Panels in the third column show the relationship between $1/\phi$ and $t_{1/2}$. First row shows scenarios that consider no change in biomass over time. Second row represents scenarios considering biomass growth. Third row shows scenarios accounting for biomass growth and mortality.

biodegradation potential ψ_B of S by n microbial functional groups can be expressed as,

$$\psi_B = \frac{\sum_{i=1}^{n} \phi_{S,i}}{\phi_{ref}}, \quad (2)$$

where ϕ_{ref} is the reference specific biomass affinity that would result in a complete degradation of S. Note that, ψ_B ranges between 0 and 1, where $\psi_B \rightarrow 0$ indicates S cannot be biodegraded and $\psi_B \rightarrow 1$ indicates S can be fully biodegraded. Here, we propose to use the specific biomass affinity of glucose as the ϕ_{ref} because glucose is the preferred carbon source for most heterotrophic microorganisms. Michaelis-Menten-Monod kinetic parameters of aerobic glucose consumption (μ = 1.71×10^{-4} s^{-1}, K_S = 8.15×10^{-5} mol L^{-1}, Y = 147580 mg-wet mol^{-1}) were estimated from experiments in Kremling *et al.* (2001).

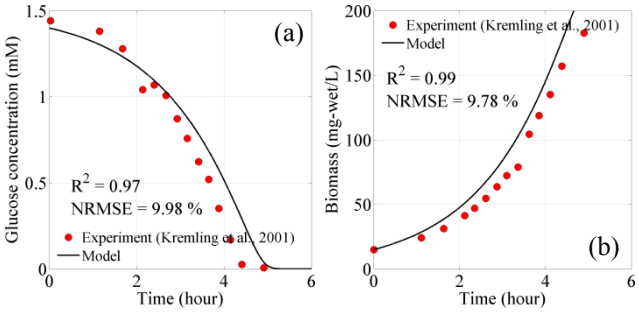

Figure 2. Kinetics of aerobic glucose consumption: (a) glucose concentration and (b) biomass concentration. Experimental data obtained from Kremling *et al.* (2001).

The parameter ψ_B in Eq. (2) can then be incorporated into ecological risk assessment indices to account for biodegradation. In this work, we used the Hazard Quotient HQ (Suter II, 2007) defined as

$$\mathrm{HQ} = \frac{(1-\psi_B)C_{predicted}}{C_{threshold}}, \quad (3)$$

where $C_{predicted}$ is the predicted environmental concentration of a contaminant in the absence of biodegradation and $C_{threshold}$ is the threshold concentration for no adverse effect.

4. CASE STUDY OF ATRAZINE CONTAMINATION

4.1. Site description and application scenarios

The use of ψ_B to assess atrazine (ATZ) contamination was numerically tested in an agricultural site at West Wyalong (about 470 km West of Sydney, 33º55'0''S; 147º13'0''E), NSW, Australia. The test site is classified as clay in the top 1.5 m, loamy sand from 1.5 to 5 m depth, and shale below 5 m depth (JRC, 2012), with soil properties and hydraulic parameters summarized in Table 1.

Table 1. Soil properties and hydraulic parameters at West Wyalong, NSW, Australia. *Data obtained from the Harmonized World Soil Database (JRC, 2012). **Estimated using van Genuchten (1980). ***Estimated as in Maggi (2015).

***Depth (m)**	0 – 1.5	1.5 – 5
***Soil texture**	Clay	Loamy sand
***Sand-silt-clay fraction**	15%–28%–57%	80%–10%–10%
***Bulk density (kg/m^3)**	1370	1350
***Porosity**	0.47	0.50
****m**	1.43	1.74
****α (1/Pa)**	2.14×10^{-4}	2.37×10^{-4}
*****Permeability (m^2)**	0.16×10^{-12}	1.58×10^{-12}

The precipitation and potential evapotranspiration rates in the period between 1990 and 2015 obtained from the Bureau of Meteorology (2016) were used to construct time sequences that extended for 60 years. Precipitation events that exceeded 15 years return time were substituted with the mean value to avoid repetition of unlikely events. The actual crop evapotranspiration during the growing season was determined by multiplying the time-varying crop coefficient of wheat (K_C = 0.5 – 0.6) by the potential evapotranspiration, while K_C = 0.3 was used in the absence of crops. The root density distribution was assumed to be a negative exponential function down to 1.5 m with an average depth at 0.3 m. In the model, ATZ was applied yearly at application rates r_{ATZ} ranging between 0.5 and 8.0 kg/ha for 60 years. ATZ leaching to an intermittent shallow groundwater (1.0 m thickness) at 4 m depth at the end of the 60-year application was analyzed.

4.2. Model description

The model was solved in the general-purpose multiphase and multicomponent bio-reactive transport solver BRTSim-v2.2 (Maggi, 2015). The model considers only the ATZ vertical transport and its adsorption-desorption processes. Weekly-averaged precipitation, wheat actual evapotranspiration, and irrigation were applied as the upper boundary conditions. Water flow in the vertical direction was solved with the Richards equation, while ATZ transport was modeled by Darcy's advection and Fick's diffusion (e.g., Maggi, 2015; Tang and Maggi, 2016). The adsorption-desorption processes were modeled using Langmuir kinetics (Atkins and De Paula, 2005), such that

$$\frac{\mathrm{d}[\mathrm{ATZ}]_{ad}}{\mathrm{d}t} = k_a[\mathrm{ATZ}]_{aq}(Q_m - [\mathrm{ATZ}]_{ad}) - k_d[\mathrm{ATZ}]_{ad}, \quad (4)$$

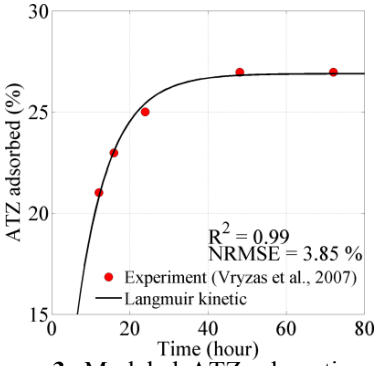

Figure 3. Modeled ATZ adsorption on soil (64% clay, 17% silt, 19% sand) using Langmuir kinetics. Experimental data obtained from Vryzas *et al.* (2007).

where $[\mathrm{ATZ}]_{ad}$ and $[\mathrm{ATZ}]_{aq}$ are atrazine concentrations in adsorbed and aqueous phases, respectively, k_a [$\mathrm{L^3M^{-1}T^{-1}}$] and k_d [$\mathrm{T^{-1}}$] are the adsorption and desorption rate constants, respectively, and $Q_m = q_m C_{soil}$ with q_m [$\mathrm{MM^{-1}}$] the maximum adsorption per unit mass and C_{soil} the soil concentration. At equilibrium ($\mathrm{d}[\mathrm{ATZ}]_{ad}/\mathrm{d}t = 0$), $K_L = k_a/k_d$ is the Langmuir equilibrium constant [$\mathrm{L^3M^{-1}}$]. The model considered only ATZ adsorption to clay and silt fractions, assuming that adsorption to sand was negligible.

Langmuir kinetics parameters k_a, k_d, and q_m in Eq. (4) for ATZ were calibrated against experiments in Vryzas *et al.* (2007) for a soil consisting of 64% clay, 17% silt, and 19% sand monitored over time at 22ºC. The estimated parameters were k_a = 4.02 L mol^{-1} s^{-1}, $k_d = 1.98\times10^{-5}$ s^{-1}, $K_L = 2.03\times10^5$ L mol^{-1}, and $q_m = 5.79\times10^{-9}$ mol g^{-1} (Figure 3).

4.3. Biodegradation potential of ATZ

Experiments showed that ATZ can be degraded by two soil microbial functional groups, i.e., the hydrolytic B_{ATZhyd} and oxidative ATZ degraders B_{ATZoxi} (la Cecilia and Maggi, 2017). B_{ATZhyd} (e.g., *Pseudomonas* sp. ADP and *Nocardia* sp.) can hydrolyze ATZ to hydroxyatrazine (HOATZ) under both aerobic and anaerobic conditions (e.g., Mandelbaum *et al.,* 1995; Smith *et al.,* 2005; Katz *et al*., 2000). B_{ATZoxi} (e.g., *Rhodococcus*, *Enterobacter cloacae* strain JS08.Deg01) can catabolize ATZ via two different pathways to either deisopropylatrazine (DIATZ) or deethylatrazine (DEATZ) in aerobic condition (e.g., Shao *et al.*, 1995; Soloman *et al.*, 2013). A comprehensive ATZ biodegradation network with Michaelis-Menten-Monod kinetic parameters calibrated against laboratory experiments was reported in la Cecilia and Maggi (2017), while a summary of the parameters is presented in Table 2.

Table 2. Michaelis-Menten-Monod kinetic parameters of ATZ biodegradation (la Cecilia and Maggi, 2017).

Microbial functional group	End-product	Respiration	μ (s^{-1})	K_S (mol L^{-1})	Y (mg-wet mol^{-1})	$\phi' = \mu/(K_S \times Y)$ (L mg^{-1} s^{-1})	Average ϕ' (L mg^{-1} s^{-1})
B_{ATZhyd}	HOATZ	Aerobic	3.67×10^{-5}	3.89×10^{-4}	2.98×10^{5}	3.17×10^{-7}	1.12×10^{-5}
		Anaerobic	2.31×10^{-6}	3.43×10^{-6}	3.06×10^{4}	2.20×10^{-5}	
B_{ATZoxi}	DIATZ	Aerobic	1.61×10^{-4}	2.25×10^{-3}	7.22×10^{4}	9.91×10^{-7}	1.21×10^{-6}
	DEATZ	Aerobic	1.51×10^{-4}	2.09×10^{-3}	5.06×10^{4}	1.43×10^{-6}	

By using the ATZ kinetic parameters in Table 2 and the specific biomass affinity of glucose as ϕ_{ref}, the effect of B_{ATZhyd} and B_{ATZoxi} concentrations on ATZ biodegradation potential ψ_B was analyzed and depicted in Figure 5. The analysis was conducted by assuming that the total biomass in soil is capable of degrading ATZ, i.e., $[B_{Total}] = [B_{ATZ}] = [B_{ATZhyd}] + [B_{ATZoxi}] = 100$ mg-wet/kg-soil, which is the biomass concentration typically found in soil (Raynaud and Nunan, 2014). Figure 4 shows that ψ_B increased with increasing $[B_{ATZhyd}]$ and decreasing $[B_{ATZoxi}]$ because B_{ATZhyd} has significantly higher ϕ' [i.e., $\phi' = \mu/(K_S \times Y)$] than B_{ATZoxi}; this therefore suggests that the ecology of soil microorganisms can affect the biodegradation potential of a contaminant.

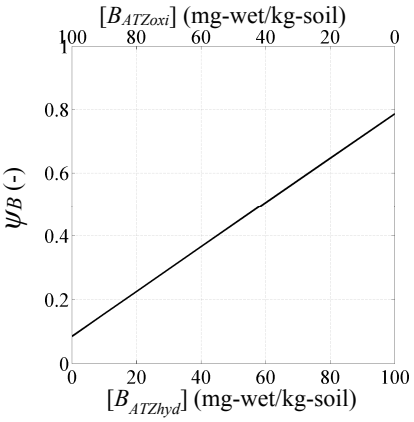

Figure 4. ATZ biodegradation potential ψ_B at various concentrations of B_{ATZhyd} and B_{ATZoxi}.

4.4. Analyses of ATZ leaching

ATZ leaching to the shallow groundwater at 4 m depth after 60 years of applications at different rates was analyzed using the model without biodegradation described in Section 4.2. At the lowest application rate (i.e., r_{ATZ} = 0.5 kg ha^{-1} $year^{-1}$), approximately 58% of ATZ applied was immobilized by adsorption onto soil, whereas, the fraction of applied ATZ that could be immobilized decreased exponentially with increasing r_{ATZ} (Figure 5a). ATZ was found to be mainly adsorbed in the top 1.5 m of the soil column, which was rich in silt and clay (Figure 5b). A portion of ATZ in the aqueous phase leached into the aquifer at the end of the 60-year simulation period. ATZ concentrations in the shallow groundwater increased with increasing r_{ATZ} (Figure 5c). ATZ found in groundwater exceeded $C_{threshold}$ suggested by Australian drinking water guidelines (i.e., 0.02 mg/L; NRMMC, 2011) when r_{ATZ} > 2 kg ha^{-1} $year^{-1}$, an application rate commonly used in agriculture.

The Hazard Quotient (HQ) for ATZ contamination in the groundwater after 60-year ATZ applications was determined using Eq. (3), where ATZ biodegradation potential ψ_B was incorporated into the risk assessment index. Here, $C_{threshold}$ = 0.02 mg/L was used as per the Australian drinking water guidelines (NRMMC, 2011), and the total biomass concentration in soil $[B_{Total}]$ was assumed to be 100 mg-wet/kg-soil after Raynaud and Nunan (2014). We assumed that all B_{Total} can degrade glucose, but only a fraction γ of B_{Total} are ATZ degraders, i.e., $[B_{ATZ}] = \gamma\,[B_{Total}] = [B_{ATZhyd}] + [B_{ATZoxi}]$. Note that, $\psi_B = 0$ when $[B_{ATZ}] = 0$, signifying that ATZ cannot be biodegraded.

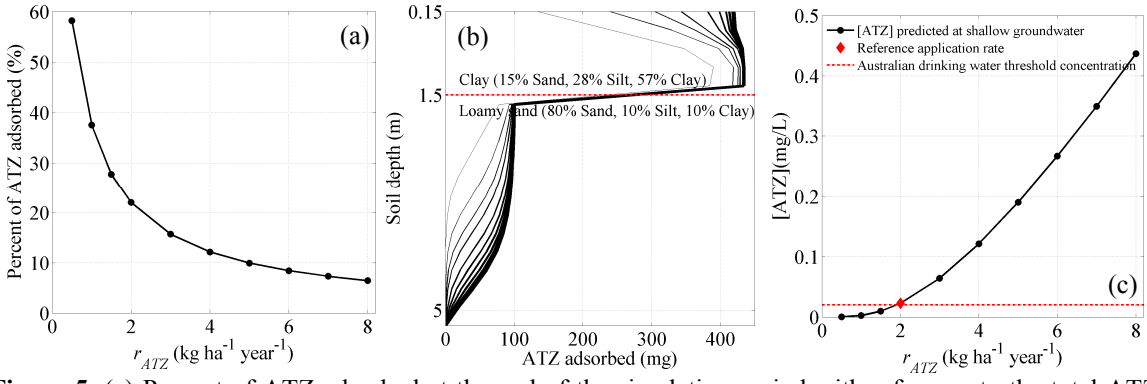

Figure 5. (a) Percent of ATZ adsorbed at the end of the simulation period with reference to the total ATZ applied in 60 years, (b) ATZ adsorbed mass at different soil depth at the end of the 60-year simulation for different ATZ application rates r_{ATZ} (i.e., r_{ATZ} increased with increasing line thickness), and (c) predicted ATZ concentration in the shallow groundwater after 60 years of ATZ application.

In general, HQ decreased with increasing $[B_{ATZ}]$ (Figure 6). The decrease in HQ values was especially remarkable in the case where all ATZ degraders were hydrolytic (Figure 6a), while HQ values were not significantly decreased when B_{ATZhyd} were not present in the microbial community even though B_{ATZoxi} existed (Figure 6b). These results show that the index HQ after the incorporation of parameter ψ_B as in Eq. (3) can capture the biodegradation capacity of a microbial population with different ecology.

The uncertainties associated with HQ may arise from several aspects, including kinetic parameters estimation, the choice of ϕ_{ref}, soil properties measurement, variations in hydrometeorological characteristics, and the estimation of degrader concentrations. For example, the kinetic parameters of ATZ biodegradation used in this study had standard deviations of about 50% (la Cecilia and Maggi, 2017), while variations in soil properties and hydrometeorological characteristics of a test site can affect the prediction of contaminant transport and immobilization. Although concentration of degraders can be laboratory estimated from field samples, its spatial heterogeneity may cause uncertainty in the prediction using HQ. These uncertainties can be quantified through stochastic global analysis, which is not presented in this work.

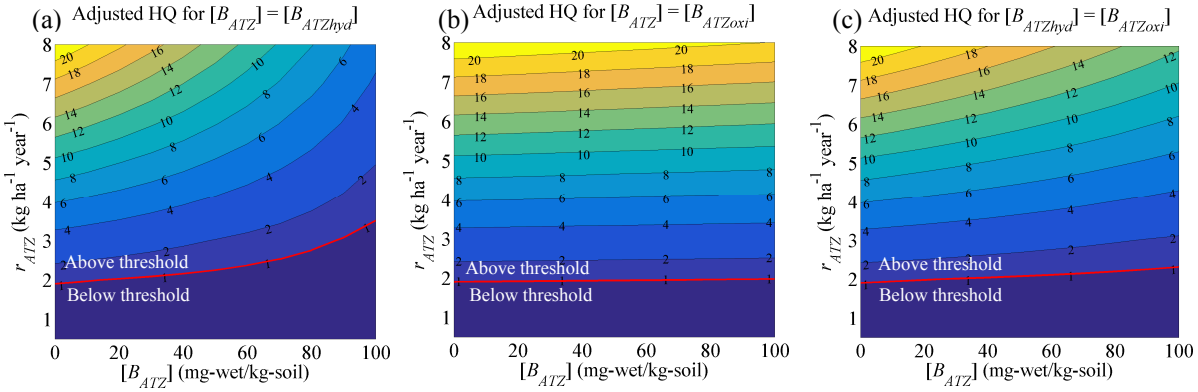

Figure 6. The Hazard Quotient HQ of Eq. (3) for ATZ contamination at 4 m shallow groundwater in West Wyalong, NSW after 60 years of ATZ application with scenarios where (a) all ATZ degraders are hydrolytic, (b) all ATZ degraders are oxidative, and (3) the ratio of hydrolytic to oxidative degraders was 1:1. Note, $[B_{ATZ}] = \gamma\,[B_{Total}]$ with $[B_{Total}]$ = 100 mg-wet/kg-soil and γ ranged between 0 and 1.The red solid line represents HQ = 1.

5. CONCLUSIONS

In this study, we proposed to incorporate a parameter that accounts for contaminant biodegradation potential into the risk assessment indices. The biodegradation potential ψ_B parameter is defined based on the specific biomass affinity ϕ of the contaminant, which relates the specific growth rate μ and Michaelis-Menten half saturation concentration K_S of a biochemical reaction to the biomass yield Y and biomass concentration of the microbial functional groups that carry out the reaction. In this study, we used atrazine as the model contaminant, West Wyalong, NSW, as the test site, and the Hazard Quotient (HQ) as the modeled ecological risk assessment index to test the applicability of ψ_B on the assessment of ATZ contamination level in groundwater after 60 years of ATZ application at different rates. We demonstrated that ϕ is inversely proportion to the half time of a contaminant and therefore, it can be used to describe the contaminant biodegradation potential ψ_B. We also showed that HQ is sensitive to biomass concentrations and the dynamics of the microbial ecology when it accounts for ψ_B. HQ generally decreased with the increase in the concentrations of the degraders.

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