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Quantitative evaluation of specific vulnerability to nitrate for groundwater resource protection based on process-based simulation model

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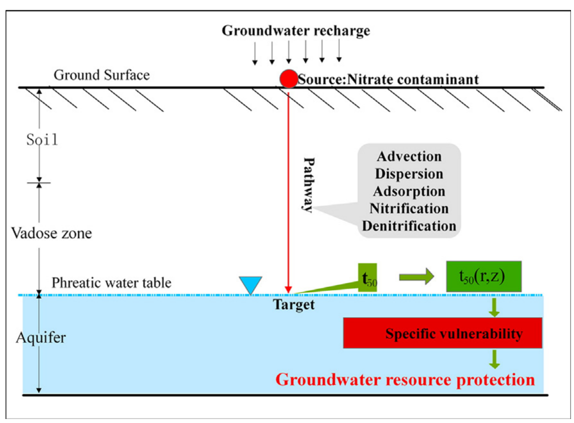
HIGHLIGHTS

- A quantitative method to assess the specific vulnerability to nitrate is proposed.
- Rate constants of nitrate in the vadose zone are acquired by laboratory tests.
- The most vulnerable areas are distributed in the floodplain of the rivers.
- Three types of parameters are the most sensitive for specific vulnerability.
- The method is verified to be suitable by a group of integrated indicators.

GRAPHICAL ABSTRACT



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ABSTRACT

It has been proved that groundwater vulnerability assessment is an effective tool for groundwater protection. Nowadays, quantitative assessment methods for specific vulnerability are scarce due to limited cognition of complicated contaminant fate and transport processes in the groundwater system. In this paper, process-based simulation model for specific vulnerability to nitrate using 1D flow and solute transport model in the unsaturated vadose zone is presented for groundwater resource protection. For this case study in Jilin City of northeast China, rate constants of denitrification and nitrification as well as adsorption constants of ammonium and nitrate in the vadose zone were acquired by laboratory experiments. The transfer time at the groundwater table t_{50} was taken as the specific vulnerability indicator. Finally, overall vulnerability was assessed by establishing the relationship between groundwater net recharge, layer thickness and t_{50}. The results suggested that the most vulnerable regions of Jilin City were mainly distributed in the floodplain of Songhua River and Mangniu River. The least vulnerable areas mostly appear in the second terrace and back of the first terrace. The overall area of low, relatively low and moderate vulnerability accounted for 76% of the study area, suggesting the relatively low possibility of suffering nitrate contamination. In addition, the sensitivity analysis showed that the most sensitive factors of specific vulnerability in the vadose zone included the groundwater net recharge rate, physical properties of soil

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medium and rate constants of nitrate denitrification. By validating the suitability of the process-based simulation model for specific vulnerability and comparing with index-based method by a group of integrated indicators, more realistic and accurate specific vulnerability mapping could be acquired by the process-based simulation model acquiring. In addition, the advantages, disadvantages, constraint conditions and applying prospects of the quantitative approach for specific vulnerability assessment were discussed.

1. Introduction

Groundwater is one of the most important water resources in China, especially in the North China (Ministry of Environmental Protection of the People's Republic of China's, 2011). As an increasingly useful tool for groundwater sustainable development (Gogu and Dassargues, 2000), groundwater vulnerability mapping can evaluate the possibility of groundwater pollution under natural conditions or under the influence of human activity (National Research Council, 1993). It can indicate which regions are more vulnerable to contamination than others and give proposals to resolve of key issues and regional pollution combined with the distribution of contaminant sources.

Stephen Foster gave a detailed review about the concept of groundwater vulnerability (Foster et al., 2013). It is generally accepted that groundwater vulnerability can be divided into intrinsic vulnerability and specific vulnerability (National Research Council, 1993). Intrinsic vulnerability takes into account the inherent geological, hydrological and hydrogeological characteristics, but it does not count on the nature of the contaminants, while specific vulnerability also considers the behaviors of the contaminants and the groundwater vulnerability to a specific contaminant or a group of contaminants (Vrba and Zaporozec, 1994). Besides, the European approach of vulnerability assessment is based on hazard–pathway–target model, making a distinction between groundwater resource (the aquifer) and groundwater source (the well) (Brouye're et al., 2001). The groundwater table or the top of the aquifer is the target in the scheme of groundwater resource vulnerability assessment and its pathway is vertically distributed through the overlying layers (Frind et al., 2006). The resource vulnerability can be represented by both intrinsic and specific vulnerability.

At present, a great deal of attention has been gradually paid due to increasing effect of human activities. Specific vulnerability assessment aims at composite pollutants characterized by different features (Mair and El-Kadi, 2013). In addition, a type of particular contaminant or a group of contaminants can be taken as a target in the specific vulnerability assessment. Several substances are often taken as the objective, including pesticide (Di Guardo and Finizio, 2015; Jackson et al., 2007; Karimova, 2003), heavy metals, such as arsenic (Guo and Wang, 2007; Hinkle et al., 2009), radioactive substance. Such as uranium (Hinkle et al., 2009), and other organic matters, such as Halogenated Volatile Organic Compounds (Deeds et al., 2012). Therefore, nitrate is often selected for consideration during the assessment of vulnerability and pollution risks (Assaf and Saadeh, 2009; Lake et al., 2003; Nobre et al., 2007; Nolan and Hitt, 2006; Pisciotta et al., 2015; Rodriguez-Galiano et al., 2014; Stigter et al., 2006).

Among all the assessment methods for groundwater vulnerability, three types of techniques are mainly used in the creation of vulnerability mapping, including statistical techniques, process-based simulation model and index-based model (Kumar et al., 2015). Index-based model, especially DRASTIC model (Aller et al., 1987) is the most preferred method for the groundwater vulnerability assessment (Gogu and Dassargues, 2000). However, index-based model has received much criticism due to its strong subjectivity, lack of proper validation, inability to reflect the physical processes of contaminants and incapacity of assessing the dynamic characteristics of groundwater vulnerability (National Research Council, 1993). Therefore, it is necessary to quantitatively assess the groundwater vulnerability based on the physical processes. As a quantitative assessment approach, process-based simulation model relies on groundwater flow and pollutant transport to determine the quantitative indexes reflecting groundwater vulnerability in spite of the drawbacks, such as restriction to converge of good geologic and geochemical database and uncertainty of results (Huan et al., 2012a; Huan et al., 2012b). However, few studies have been conducted on the quantitative index to indicate groundwater vulnerability based on groundwater flow and pollutant transport model (Frind et al., 2006). Some approaches can assess intrinsic groundwater vulnerability based on mean transit time of percolation water from the source to the target (Connell and Van Den Daele, 2003; Ross et al., 2004; Schwartz, 2006; Voigt et al., 2004; Witkowski and Kowalczk, 2003). However, mean transit time cannot reflect the distribution of transit time when preferential flow, dual domain or long tailing appears in the vadose zone (Neukum and Azzam, 2009). Besides, some approaches are based on the ratio between the maximum concentration at the target to the released concentration at the contamination source (C/C_0), transit time of 50% solute mass breakthrough at groundwater table, duration of breakthrough defined by the difference in 75% and 25% solute mass breakthrough at groundwater table and temporal shape of the breakthrough curve expressed with the quotient $(t_{25\%} - t_{50\%})/(t_{25\%} - t_{75\%})$ (Brouye're et al., 2001; Butscher and Huggenberger, 2009; Neukum and Azzam, 2009). The quantitative indexes were abstracted from the concentration cumulative curve based on analytical solution or numerical simulation of transport models. Until now, most of the studies are aimed to assess intrinsic vulnerability based on process-based simulation model by which the advection and dispersion processes are barely considered.

Overall, specific vulnerability assessed by index-based models and intrinsic vulnerability assessed by process-based simulation models have been investigated to a relatively abundant extent. Comparatively, few investigations of specific vulnerability have been carried out by process-based simulation models due to limited cognition of complicated contaminant fate and transport processes in the vadose zone. To fill in this methodological gap, the paper selects nitrate as the typical pollutant followed the fundamental idea of Neukum and Azzam's (Neukum and Azzam, 2009) method to assess the groundwater intrinsic vulnerability. Moreover, the further objectives of the paper are: (1) to acquire the parameters indicating the fate and transport processes of nitrate; (2) to demonstrate a process-based simulation model to assess the specific vulnerability to nitrate for groundwater resource protection; (3) to discuss the factors playing important roles in the specific vulnerability; and (4) to validate the feasibility and the accuracy of groundwater specific vulnerability. The application of the proposed framework was selected in Jilin city of northeast China in order to test its flexibility and evaluate whether the proposed framework can provide an effective support in the groundwater management.

2. Methods

2.1. Study area

The study region is located across the floodplain, the first terrace and the second terrace of Jilin City in Northeast China with an area of 104.5 km^2 (Fig. 1). The average annual rainfall and evaporation from 1981 to 2005 were 645.5 mm and 1506 mm, respectively. Surface waters mainly include Songhua River and Mangniu River. Songhua River