Journal of Geochemical Exploration 148 (2015) 196–205

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

journal homepage: www.elsevier.com/locate/jgeoexp

Determination of natural backgrounds and thresholds of nitrate in South Korean groundwater using model-based statistical approaches

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ARTICLE INFO

Article history:
Received 18 January 2014
Accepted 2 October 2014
Available online 12 October 2014

Keywords:
Background level and threshold of nitrate
Anthropogenic polluted level
Finite normal (Gaussian) mixture model
National Groundwater Monitoring Network of South Korea

ABSTRACT

Increased nitrate loading of groundwater has emerged as a major environmental problem in many countries, including South Korea. This study aims to evaluate the nitrate levels of South Korean groundwater on a regional (national) scale and specifically to demonstrate the procedure to better estimate the natural background level (NBL) and threshold of nitrate as the basis of groundwater management. For this work, nitrate data of groundwater ($n = 8510$) in two major hydrogeologic units (alluvium and bedrock) were collected from the National Groundwater Monitoring Network (NGMN) of South Korea. Four supplementary datasets ($n = 1074$) were also used to test the rationality of estimated thresholds by comparing them with NGMN datasets. Compared with the data reported in many countries, the nitrate concentrations in NGMN groundwater in 2009 are high, with median values of 12.2 and 8.7 mg/L, respectively, for alluvial groundwater and bedrock groundwater. The nitrate levels of South Korean groundwater seem to have been historically steady at these high levels between 1997 and 2009, suggesting widespread diffusive contamination since the 1980s. The NBLs and anthropogenic polluted levels (APLs) of nitrate on a regional (national) scale are statistically established by the model-based approach using a finite normal (Gaussian) two-component mixture model, because (1) the sample size (frequency) of the natural background group is much smaller than that of the polluted group, as a result of widespread nitrate contamination, and (2) nitrate concentrations are more or less affected by natural attenuation processes. Accordingly, thresholds of nitrate (as the concentration level indicating groundwater pollution) are selected as the lower limits (i.e., 10th percentile) of the polluted group, which are 3.0 and 5.5 mg/L NO_3^-, respectively, for bedrock groundwater and alluvial groundwater. This study provides a practical guideline for national groundwater management, based on a heuristic procedure to statistically determine the NBLs and thresholds in the case of groundwater systems with pervasive contamination. Compared with the other classical methods to estimate NBLs, the model-based approach using a finite normal-mixture model can be more effective to reasonably separate the polluted samples from a regional (or national) dataset.

1. Introduction

Approximately 20% of the global water use is groundwater usage, and this share is rapidly increasing (WMO, 1997; Arnell, 1999). However, groundwater quality in many aquifers worldwide has been deteriorating by increased human impact over the past few decades. In particular, groundwater pollution is highly associated with diffusive (nonpoint) sources in relation to agricultural activities in which many types of inorganic and organic fertilizers are used (Burkart and Stoner, 2008; Burow et al., 2010; Scanlon et al., 2007; Sebilo et al., 2013). Thus, nitrate became the most ubiquitous pollutant in groundwater, frequently threatening public water supply sources and human health (Spalding and Exner, 1993). As a common constituent in groundwater, nitrate is the most important indicator of groundwater quality status and, therefore, a practical need exists to precisely assess the nitrate levels in aquifers for better management and regulation of groundwater quality.

In this context, it is essential to determine both the natural background level (NBL) and the threshold value (in general, the upper limit or maximum of NBL) of nitrate to differentiate between natural controls (i.e., geogenic, biological, and atmospheric processes) and anthropogenic impacts on groundwater quality (Corniello and Ducci, 2014; Limbrick, 2003; Panno et al., 2006; Preziosi et al., 2014). The threshold is commonly used as a practical reference value for determining the "good" status of groundwater quality and also serves as the level for an early warning of groundwater pollution, because of the limitations of the existing drinking water standard (DWS) (Edmunds et al., 2003; Langmuir, 1997; Reimann and Garrett, 2005). In recent years,

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http://dx.doi.org/10.1016/j.gexplo.2014.10.001
0375-6742/

EU member states have established threshold values (as the regulatory levels) corresponding to the NBLs of a number of constituents in many aquifers (Edmunds and Shand, 2008; Hinsby et al., 2008; Müller et al., 2006; Preziosi et al., 2010), based on scientific principles established through research projects such as BASELINE and BRIDGE. These studies also used the NBL of nitrate as <10 mg/L NO_3 for a simplified separation approach called preselection.

Many previous studies have published the NBLs of groundwater nitrate based on a number of approaches that were reviewed by Panno et al. (2006). The reported values are low (<5 mg/L NO_3) because natural or geologic sources of nitrate are not abundant and common (Böhlke, 2002; Halberg and Keedny, 1993). Even so, the NBL of nitrate from datasets is still difficult to accurately define because of its ubiquitous occurrence that has resulted from the widespread and/or long-term contamination from diffusive sources (Panno et al., 2006; Reimann and Garrett, 2005). Furthermore, the concentrations of nitrate in groundwater can also depend on redox conditions because anthropogenic nitrate can be naturally attenuated by biogeochemical transformations, such as denitrification (Appelo and Postma, 1999; Langmuir, 1997; Postma et al., 1991). Therefore, a good understanding of biogeochemical processes in the investigated groundwater system is needed to precisely assess the NBL of nitrate. For these reasons, statistical methods, including a model-based approach, were recently used to determine the NBL of nitrate.

Groundwater contamination in South Korea has been an important environmental concern since the 1980s because of rapid industrialization and urbanization. Especially, severe nitrate pollution of groundwater has been reported in many localities with active agricultural practices (e.g., Chae et al., 2004, 2013; Choi et al., 2007, 2014; Joo et al., 2009; Koh et al., 2010). In South Korea, anthropogenic nitrogen inputs from N-fertilizers and manure are much higher than in other countries. The use of synthetic N–P–K-fertilizers in South Korea is the fifth highest among the OECD countries (OECD, 2004). The average application rate of N-fertilizers amounts to 224 kg/ha per year (MOAF, 2001), compared with 128 kg/ha per year in England (Petry et al., 2002) and 27.5 kg/ha per year in the United States (Nolan, 2001). Moreover, the nitrogen efficiency (i.e., balance between inputs and outputs) in the agricultural soils of South Korea is the lowest among the OECD countries (OECD, 2008). These situations indicate that groundwater of South Korea can be highly vulnerable to nitrate pollution without efficient and sustainable measures for nutrient management in agricultural practices. Accordingly, the Korean government recently began to assess the status of nitrate pollution to establish measures for effective groundwater quality management.

As an initial step for groundwater management in South Korea, the current study aims to evaluate the regional status of groundwater quality and to establish the NBL and threshold of groundwater nitrate as the guidelines for management. For these purposes, large datasets collected from the National Groundwater Monitoring Network (NGMN) of South Korea are evaluated. In addition, nitrate datasets obtained from four different hydrochemical surveys are also used to compare with NGMN data. To set the NBL and threshold, the statistical distribution of nitrate concentrations is divided into two groups (natural and anthropogenic) by the model-based clustering approach using a finite normal (Gaussian) mixture model. This study shows the application of a heuristic statistical procedure to determine the NBL and threshold of ubiquitous and widespread aquatic contaminants, such as nitrate. The proposed method can be successfully used for the groundwater systems in which the influence of anthropogenic contamination is prevailing or overwhelming natural processes.

2. Materials and methods

2.1. Usage and hydrogeology of groundwater in South Korea

In South Korea, groundwater is an important resource that accounts for approximately 11% (about 3.7 billion tons per year) of the total water use. The groundwater is largely used for domestic (49%) and agricultural (45%) purposes and comes from two types of aquifers: shallow alluvial aquifer and relatively deep bedrock aquifer (MOCT, 2007). The alluvial aquifers, consisting mainly of sand with subordinate silt or gravel, have thicknesses of 10–50 m and a total areal extent of approximately 27,000 km^2, and commonly occur along rivers and streams. The transmissivity (T) and storage coefficient (S) values of alluvial aquifers are 50–2000 m^2/day and 0.1–0.01, respectively. In rural areas, alluvial aquifers are extensively used for domestic and agricultural water supplies and have potential yields ranging from 30 to 800 m^3/day/well.

Bedrock aquifers represent the typical form of groundwater occurrence in South Korea and are developed in or along weathered zones, faults, fractures, joints, and lithologic boundaries of bedrocks, beneath shallow alluvial aquifers. Groundwater yields from bedrock aquifers vary significantly, from 10 to 5000 m^3 per day, according to the rock type, weathered zone thickness, and topography. For example, groundwater wells in metamorphic rocks in highlands generally have low yields, whereas wells in flat lowlands with sedimentary and volcanic rocks tend to have high yields. Bedrock aquifers in South Korea can be categorized into five major geologic groups (Chae et al., 2007): granitoids, metamorphic rocks, complex (intermixed) rocks, volcanic rocks, and sedimentary rocks. Granitic and metamorphic rocks comprise about 70% of the surface outcrops in South Korea (see Fig. 1B), forming the most important and prevailing lithologic units of fractured bedrock aquifers. The hydraulic conductivity of bedrock aquifers is generally low (average 0.076 m/day) and varies significantly by more than 4 orders of magnitude (Jeon et al., 2005). Even so, bedrock aquifers in South Korea are used for various purposes (i.e., agricultural, industrial, and domestic). More importantly, bedrock aquifers provide the public drinking water supply in rural areas and are also pumped for production of commercial bottled water.

2.2. Nitrate datasets used for this study

The major dataset used for this study is the nitrate concentration data collected from the NGMN (Fig. 1A). The NGMN has been operating since 1995 by the Korea Water Resources Corporation (KOWACO, currently called K-Water) to monitor the overall status of both quantity (by the water level fluctuation) and quality of groundwater (Choi et al., 2014; Lee et al., 2007). A total of 320 monitoring stations are currently assessing bedrock groundwater, at an average depth of 74 m. Among these stations, 158 also have parallel shallow monitoring wells (average depth = 12 m) for monitoring alluvial aquifers. The regular monitoring of water quality at the NGMN stations has been performed twice per year for 15 parameters, including nitrate, chloride, heavy metals, and organic contaminants. In this study, the yearly trend of nitrate concentrations in groundwater is evaluated for the time period between 1997 and 2009 (thus, a total of 24 monitoring times) (Table 1). However, the NGMN's water quality data may not be sufficient to give precise information regarding hydrogeochemical processes and contamination sources, because of the general absence of information on sampling and analysis. Thus, we first investigated the hydrochemistry of NGMN groundwater in the first half of 2009 (Choi et al., 2014). A total of 19 parameters, including field measurements (temperature, pH, Eh, DO, EC), alkalinity, total dissolved solid (TDS), and major cations/anions, were obtained following the standard procedures of sampling and analysis (APHA, 1985). The calculated charge balance errors (C.B.E.) for the analyses were mostly within ±5%, indicating the good quality of the dataset (Hounslow, 1995). The nitrate concentration data obtained from the hydrochemical survey in 2009 (Choi et al., 2014) are also used as the main dataset in this study (Table 1).

Additional datasets are used in this study and they were initially collected from four independent groundwater surveys conducted by the current authors. The nitrate concentration data obtained from the surveys are used as supplementary datasets for comparing and statistically evaluating the nitrate levels according to the locality and scale of groundwater sampling (Table 1). Fig. 1B and C show the sampling localities for the supplementary datasets, together with geologic and