Agricultural Water Management 96 (2009) 1751–1765

Contents lists available at ScienceDirect

Agricultural Water Management

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

Multi-method assessment of nitrate and pesticide contamination in shallow alluvial groundwater as a function of hydrogeological setting and land use

A.I.A.S.S. Andrade [a,*], T.Y. Stigter [b]

[a] Centro de Geofísica da Universidade de Coimbra, Av. Dias da Silva, 3000-134 Coimbra, Portugal
[b] Geo-Systems Centre/CVRM, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisbon, Portugal

ARTICLE INFO

Article history:
Received 1 April 2009
Accepted 15 July 2009
Available online 18 August 2009

Keywords:
Shallow groundwater
Agricultural contamination
Surface irrigation
Probability maps
Correspondence analysis
Denitrification
Dilution

ABSTRACT

In this study deterministic, multivariate and stochastic methods are applied to a combined temporal and spatial monitoring data set, in order to assess nitrate and pesticide levels and contamination risk in shallow groundwater. The case study involves an area in the Mondego River alluvial body in central Portugal, where agriculture is the main land use, with predominantly maize, rice and some vegetable crops supported by river water irrigation. Factorial correspondence analysis (FCA), reducing the original data matrix to a small number of independent orthogonal factors, is applied to detect associations between nitrate levels, land use (crop type), lithology and groundwater depth. Indicator-geostatistical techniques are used to create maps indicating the probability of nitrate concentrations in groundwater exceeding predetermined threshold values, including the drinking water standard (98/83/EC) and vulnerable zone designation criterion (91/676/EEC) of 50 mg/l NO_3^-. For pesticides the leaching potential is determined by calculating the Groundwater Ubiquity Score (GUS), based on the sorption coefficient and soil half-life for each pesticide compound. Results for nitrate show an overall very low risk of exceeding 50 or 25 mg/l, whereas the risk of exceeding 9.5 mg/l (third data quartile) is particularly high in areas where FCA shows correlation of nitrate contamination with vegetable and maize crops, aerobic conditions, lower groundwater levels and to some extent, coarser grained sediments. On the contrary, nitrate levels under rice are lowest and correlated to a reduced environment, finer-grained sediments and a higher water table. Denitrification is found to be an important attenuation process, as well as dilution by surface water irrigation and precipitation. Crop type and irrigation source are seen to have a large influence on the nitrate contamination potential of groundwater. Total concentrations of the analysed pesticide compounds above the regulatory limit of 0.5 μg/l are observed in 32% of the analysed water samples, with a maximum value of 16.09 μg/l. The probability maps provide a particularly interesting example of how multiple-well monitoring results over a certain period can be condensed into single maps and used by water engineers, managers and policy-makers.

1. Introduction

The leaching of large amounts of nitrate and pesticides from agricultural fields is a serious problem in many countries (Appelo and Postma, 2005). The occurrence in groundwater of high nitrate values (e.g. Hamilton and Helsel, 1995; Causapé et al., 2004; Jalali, 2005; Stigter et al., 2006a,b,c; Lorite-Herrera and Jiménez-Espinosa, 2008), high pesticide values (e.g. Chilton et al., 1998; Batista et al., 2002; Cerejeira et al., 2003; Papadopoulou-Mourkidou et al., 2004a,b; Guzzella et al., 2006; Shomar et al., 2006; Hildebrandt et al., 2008) or both (e.g. Cerejeira et al., 2000; van Maanen et al., 2001; Bouman et al., 2002; Silva et al., 2006) is described in many regions around the world. The relation between nitrate and/or pesticide concentrations in groundwater and agricultural activities is referred in most of these studies. In Europe, pesticide data are often very limited; however, groundwater contamination by nitrates and pesticides is a serious problem. The high nitrate levels are largely caused by man, particularly related to the use of nitrogen fertilizers and manure, which constitutes a diffuse source (EEA, 2000); nitrate in groundwater can also result from point sources, including cattle feed lots, septic tank, sewage discharge and the oxidation of organically bound nitrogen in soils (Appelo and Postma, 2005). At a large scale, agriculture contributes to 50–80% of the total nitrogen load on the aquatic environment in Europe (EEA, 2005).

The problem of groundwater contamination by agricultural practices was considered by the European Environment Agency (EEA, 2003) as an area of no progress in the European Union (EU),

* Corresponding author at: Departamento de Ciências da Terra, Universidade de Coimbra, Largo Marquês de Pombal, 3000-272 Coimbra, Portugal.
Tel.: +351 239860534; fax: +351 239860501.
E-mail address: aandrade@dct.uc.pt (A.I.A.S.S. Andrade).

0378-3774/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.agwat.2009.07.014

despite the adoption of European Council Directive 91/676/EEC in 1991. Known as the Nitrates Directive, its aim was to reduce the nutrient load of agriculture on surface and groundwater, but its implementation by the member states has proven extremely difficult, due to a number of factors, such as: i) the power of the agricultural lobby (e.g. Goodchild, 1998); ii) the lack of cooperation between environmental and agricultural agencies; iii) the complexity of the contamination process, involving other sources of nitrate and iv) the lack of comprehensive monitoring networks (Stigter et al., 2006b).

Nitrate (NO_3^-) is a very soluble anion that does not bind to soils and has a high leaching potential, and can only be removed from groundwater through reduction (Appelo and Postma, 2005). A drinking water guideline value of 50 mg/l is considered by the EU (EC, 1998) and the World Health Organization (WHO, 2006), whereas the Environmental Protection Agency of the USA considers a maximum contaminant level of 10 mg/l of nitrogen N (44 mg/l NO_3^-) as primary drinking water standard (EPA, 2003). Nitrate in drinking water is generally considered to constitute a health hazard for babies and young infants, its toxicity mainly attributable to the reduction to nitrite and associated to methaemoglobinemia. However, several recent studies question the importance of nitrate in drinking water as a risk factor for methaemoglobinemia (e.g. L'hirondel and L'hirondel, 2001; Addiscott, 2006). More consensus exists regarding the environmental problems that stem from enrichment of surface fresh- and saltwaters by nitrates, causing an accelerated growth of algae and ultimately leading to eutrophication (EC, 1991). Elevated levels of nitrate are particularly significant contributors to eutrophication in marine and coastal areas, where nitrogen is the limiting nutrient (Howarth and Marino, 2006).

Groundwater contamination by pesticides can result from incorrect or poor control on their use and application (EEA, 1999), from leaching after application due to subsequent rainfall or from inappropriate disposal methods (WHO, 2006). The properties of the involved substances, their behaviour in the soil environment and the aquifer characteristics and vulnerability are also important factors (Vighi and Funari, 1995). If the pesticide and metabolite degradation rates exceed their percolation rates through the soil, contamination of groundwater is less probable (Guzzella et al., 2006), but the occurrence of preferential flow increases the pesticide contamination risk (Hallberg, 1989). In the USA, pesticide detection in groundwater has a lower frequency than in streams but with similar correspondence to land use (Gilliom, 2007). From all the classes of pesticides, herbicides are the most frequently detected pesticides in groundwater, which is related to their uses and properties (Funari et al., 1995). Groundwater contamination with pesticides is generally not dependent of the season and has a strong inertia (Funari, 1995). The parametric value for each pesticide (including their relevant metabolites, degradation and reaction products) in drinking water in the EU is 0.10 μg/l with a parametric value for total pesticides quantified as 0.50 μg/l (EC, 1998). Guidelines for drinking water from the World Health Organization (WHO, 2006) are generally less restrictive. The greatest risks of pesticides in groundwater supplies occur where: the pesticide is relatively stable, the aquifers are overlain by permeable soils with a short travel time to the water table and the aquifer dilution potential is small (Chilton et al., 1998).

The purpose of the present study is to employ a multi-method approach to the evaluation of nitrate and pesticide contamination levels and risk in shallow groundwater, influenced by lithology, land use (crop type) and irrigation water supply source. In addition to common uni- and bivariate analysis, more advanced tools such as multivariate factorial correspondence analysis (FCA) and indicator kriging are applied as interpretation and visualization tools. Multivariate analysis allows a rapid assessment of multiple correlations among quantitative and qualitative parameters in large data sets, which otherwise would be rather an arduous task. Indicator-kriging tools allow the incorporation of uncertainty in the spatial assessment of a contamination problem.

During FCA, the original variables are reduced to a small number of orthogonal factors that by definition are independent (Pereira and Sousa, 2000). As symmetry is conferred to the data matrix, correlations within and between variables and samples can be studied simultaneously (Benzécri, 1973; Pereira and Sousa, 2000). Moreover, both qualitative and quantitative variables may be used, by dividing them into classes (modalities). Since Benzécri (1973) proposed the FCA methodology, several applications to water quality studies have been published (e.g. Lachance et al., 1979; Usunoff and Guzman-Guzman, 1989; Oleson and Carr, 1990; Johannesson et al., 1996; Pacheco, 1998; Farnham et al., 2003; Pacheco and Landim, 2005; Stigter et al., 2008).

Indicator-geostatistical techniques result in maps that indicate the probability of concentrations in groundwater exceeding predetermined threshold values. According to Ribeiro (1998), such techniques were developed to allow the detection and modelling of so-called spatial dependency patterns of the variables and to evaluate the associated risk. In this non-parametric approach, by using a binary transformation at various cut-off levels and applying the kriging algorithm to these so-called indicator variables, the uncertainty around the unsampled value is modelled in a conditional distribution function (Deutsch and Journel, 1998; Stigter et al., 2005). For (groundwater) management purposes, the existence of a robust tool that specifically incorporates uncertainty into contamination assessment can be extremely useful, as was also concluded by Hu et al. (2005), who used a similar methodology to assess the risk of nitrate contamination in shallow groundwater in Quzhou County in the North China Plain. When the cut-off level corresponds to specific standards such as those defined for drinking water, the resulting maps illustrate the probability of exceeding such standards and are therefore easily interpretable for people outside the scientific domain, such as policy-makers.

For the pesticide compounds, there leaching potential is determined by calculating the Groundwater Ubiquity Score (GUS), created by Gustafson (1989), which is based on the partition coefficient between soil organic carbon and water—sorption coefficient (K_{oc}) and the soil half-life for each pesticide compound. As adsorption is an indicator of the adherence of the pesticide to the soil components while is moving with water and persistence gives a measure of the time the pesticide stays in its original form in soil (Guzzella et al., 2006), the GUS index allows the evaluation of the pesticide leaching potential.

2. Description of the study area

2.1. Geographic location and climate

The study area is located west of Coimbra city and it is part of the Mondego River drainage basin—Central Portugal (Fig. 1). It covers an area approximately 16 km long and 3–4 km wide, totalling nearly 51 km^2. It is a plane region with a maximum elevation of nearly 13 m above mean sea level on the eastern side and a minimum elevation of 4 m on the western side, close to the upper limit of the river estuary.

It is important to emphasize that the study area is strongly affected by anthropogenic changes, namely the construction of: a) an artificial channel for the Mondego River, in all the study area and in the west and b) an irrigation system allowing land irrigation with river water in the main part of the study area; the water for this system is deviated from the river at a place located nearly 3 km east of the study area.