Analysis of hydrochemical time series

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Abstract

Agricultural activity of spreading fertilizers may, in case they are washed away to an aquifer, result in a groundwater contamination. There was a research conducted in Croatia on the lower part of the Danube-Sava canal which is occupied by extensive agricultural production to measure the groundwater pollution by nitrate nitrogen, ammonia nitrogen and phosphate. Amounts of these nutrients were measured six times per year over the period of fifteen years (2004.-2018.) by installed hydrogeological piezometers. The obtained data, given for a relatively long period of time, were analysed by methods of time-series to determine trends. It was established that although concentrations of nitrate and ammonia nitrogen occasionally exceeded the value of maximum allowable concentration, long term trends of all pollutants are still slightly decreasing.

Keywords: groundwater contamination, nitrate and ammonia nitrogen and phosphate concentration, time series analysis

1. Introduction

There is a worldwide concern of groundwater pollution by agricultural activities, mainly by excessive use of inorganic and organic fertilizers (Spain-Villalba et al., 1995, Wales-Halliday et al., 2012, Italy-Matzeu et al., 2017 and Ghilieri et al., 2009). The long term study of underground waters conducted in Croatia (Filipović et al., 2013) was carried out in the area of Biđ field on the lower part of the Danube-Sava canal or more precisely on 6600 ha of mostly agricultural land occupied by extensive animal and crop husbandry. Back in 2002 at 54 locations there were installed pairs of shallow and deep hydropedological piezometers (1m and 4m in depth, respectively) to monitor different groundwater parameters including next nutrients: nitrate nitrogen (NO_3-N), ammonia nitrogen (NH_4-N) and phosphate (PO_4-P). The model of acknowledged methods to assess groundwater nutrient levels given by Eulenstein et al. (2016) defines depth of 4 m as a limit between the drain zone and the groundwater zone and the depth between 3 and 4 meters as ideal for sampling. Water sampling from piezometers was carried out evenly throughout the year in two month periods starting from February to December. After significant pre-processing, we analyzed long term sampling data from 2004 to 2018 by time-series analysis to obtain trends which turned out not to be increasing but on the contrary, decreasing.

2. Data Resources, Pre-Processing and Analysis

The area of Biđ field, an eastward part of continental Croatia, lies on the border between semi-arid to semi-humid continental climate with annual precipitation of approximately 700 mm. Soil types on analysed area were mostly amphigley and hypogley. The data analyzed in this paper were collected during a long term project financed by the state authorities and conducted by the University of Zagreb, Faculty of Agriculture, the Department of Soil Amelioration. The goal of the project was to investigate influence of the irrigation canal to underground water flows and quality of drinking water which is regulated through legislative which transposes the European Commission Nitrate Directive 91/676/EEC. Recommendations for drinking water give maximal allowable concentrations (MAC) which are: for nitrate nitrogen 50 mg/l, for ammonia nitrogen 0.5 mg/l and for phosphate 0.3 mg/l. The concern for the quality of groundwater originates from the fact that in the research area groundwater in different aquifers is used by local inhabitants as the drinking water.

The data set included nutrient values measured six times per year from 2004 to 2018. Originally obtained data set needed pre-processing. Namely, due to lack of water in some piezometers, data for certain periods were missing. It would be wrong to treat them as zero and we did not choose to approximate missing data, therefore we decided to remove such piezometers from further analysis (P4-P7 from Table 1).

Table 1. Part of original data for NO_3-N concentration (mg/l) in 2010

piez.	Feb.	Apr.	Jun.	Aug	Oct.	Dec.
P1	0,45	0,77	0,82	0,77	4,57	1,26
P2	2,27	2,09	0,52	2,33	2,33	0,37
P3	19,49	16,16	0,09	0,08	2,19	2,56
P4	1,78	1,19	2,58			
P5						
P6	1,12	0,66	8,56			0,3
P7	1,93	1,34	0,69			0,23
P8	1	0,86	2,87	1,43	1,86	0,36

Also, due to the existence of outliers which indicate extensive nutrient leaks (values for P3 in first two periods, Table 1), we chose median to represent mean of the respective period. Finally, within the observed time period there were extremely dry periods with no sampling data at all from June to December 2007 and October to December 2016. Also, sampling was not done in October 2008. So, in order not to disturb seasons we reduced time span and therefore time-series analysis given here refers to the period from December 2008 to August 2016. To set data free from seasonal effects, we used the multiplicative time series model, calculated moving averages of length six, obtained seasonal-irregular relatives of original data with centered moving averages to determine seasonal indexes and remove the seasonal component from the original data.

3. Results and Discussion

Graphs of deseasonalized data obtained from the original time-series nutrients data are given on Figure 1. It can be observed that nitrate nitrogen concentration was in all periods more than ten times lower than MAC. Ammonia nitrogen concentrations were mostly above MAC but from 2014 onwards they stayed below 0.5 mg/L. Concentrations of phosphate exceed its MAC only occasionally and stayed below 0.3 mg/L most of the time period. What encourages is that linear trends for all nutrients are decreasing. The linear trend for nitrate nitrogen concentration predicts its decrease by 0.0252 mg/L per season or 0.1512 mg/L per year. The ammonia nitrogen trend suggests the decrease of 0.0195 mg/L per season, which gives the decrease of 0.117 mg/L on the yearly level. The prediction for phosphate is the seasonal decrease of 0.0012 mg/L or 0.0072 mg/L per year. If we take into account mean yearly median of nutrient levels in the observed time range, a relative decrease of a particular nutrient can be calculated. The relative decrease of nitrate nitrogen, ammonia nitrogen and phosphate level turned out to be 7.8%, 19.5% and 4%, respectively. The ammonia nitrogen level, which appears to bring the highest risk of pollution, shows the biggest relative decrease which is encouraging. We can conclude that despite of extensive agricultural production in the Biđ field, trends of observed nutrient levels are decreasing. There is no indication of some serious groundwater pollution.

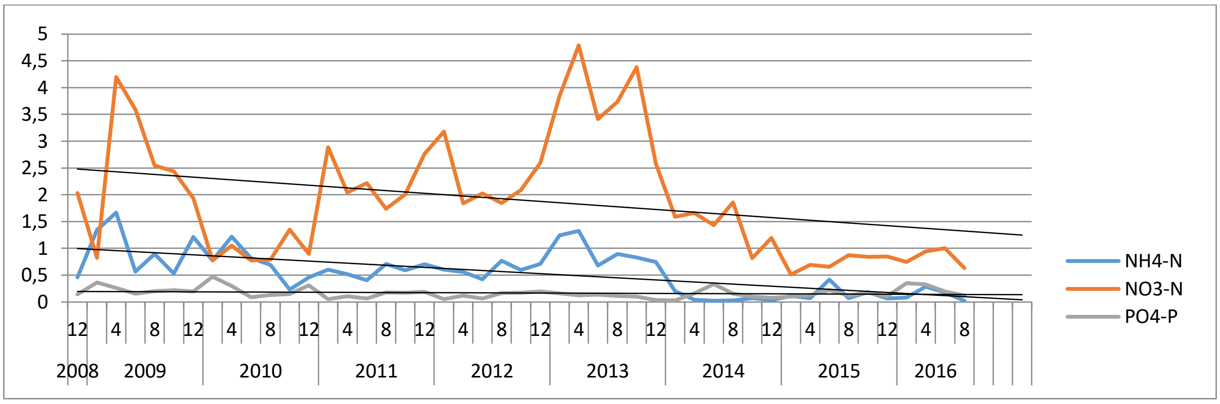

Figure 1. Deseasonalized time series data for nutrients along with trend lines

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