ORIGINAL ARTICLE

Chemometric analysis of groundwater quality data around municipal landfill and paper factory and their potential influence on population's health

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ABSTRACT

Aim To assess the level of 15 groundwater quality parameters in groundwater samples collected around municipal landfill and paper factory in order to evaluate usefulness of the groundwater and its possible implication on the human health.

Methods Obtained data have been analyzed by principal component analysis (PCA) technique, in order to differentiate the groundwater samples on the basis of their compositional differences and origin.

Results Wastes and effluents from municipal landfill did not contribute significantly to the pollution of the aquatic medium. Groundwater degradation caused by high contents of nitrate, mineral oils, organic and inorganic matters was particularly expressed in the narrow area of the city centre, near the paper factory and most likely it has occurred over a long period of time. The results have shown that the concentrations of the most measured parameters (NO_3-N, NH_4-N, oils, organic matter, Fe, Pb, Ni and Cr) were above allowed limits for drinking and domestic purposes.

Conclusion This study has provided important information on ecological status of the groundwater systems and for identification of groundwater quality parameters with concentrations above allowable limits for human consumption. The results generally revealed that groundwater assessed in this study mainly does not satisfy safe limits for drinking water and domestic use. As a consequence, contaminated groundwater becomes a large hygienic and toxicological problem, since it considerably impedes groundwater utilization. Even though, all of these contaminants have not yet reached toxic levels, they still represent long term risk for health of the population.

Key words: ground water, quality, pollution, Principal Component Analysis

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INTRODUCTION

The surface and groundwater contamination have become one of the main sources of health related problems (1, 2). The results of investigation of the appearance of diseases linked to contaminated water in Croatia since 1981 have shown that gastroenterocollitis, bacillary dysentery, hepatitis and gastroenteritis predominated; while leptospirosis and Legionnaire's disease were less present (1,3). The recent studies indicate that the water of the Lower Drava River meet only the standards for the Class III and as such is not suitable raw material for production of drinking water (4). Unfortunately, ground waters in eastern Croatia are troubled with As, Fe, Mn, ammonia and natural organic material (5, 6). Despite the well known fact that chronic arsenic exposure has been associated with a variety of cancers as well as skin changes and high iron content in water is related with higher risk of developing inflammatory bowel disease, ground waters are still the main sources of drinking water in the area of eastern Croatia (7, 8). Beside arsenic contamination, long-term exposure to other chemical contaminants such as nitrate, Cr, Pb, Cd and polyaromatic hydrocarbons (PAHs), may also lead to environmental and health problems (9-14). Since food chain contamination is one of the major routes for entrance for various contaminants into the human system, groundwater monitoring and assessment always generate a lot of interest. (15-18). In the long run, chemical and microbial pollution can contaminate the groundwater, soil, crops, food, vegetables and fruits and may cause considerable adverse impact on health of the local population and final consumers (19-24). The purpose of the present study was to evaluate variables/sources responsible for groundwater quality in samples collected at different distances from the landfill and paper mill through the application of principal component methods (PCA) technique (25). Further, the objective of this study was to assess possible groundwater pollution due to landfill and paper mill in urban and suburban area in order to prevent and avoid health risks.

MATERIALS AND METHODS

Study area

The industrial town of Belišće in eastern Croatia is located at 45.68ºN and 18.41ºE at the right bank of the Drava river at latitude of 92m with a population of about 7200. The municipal landfill covers the area of 32 000 m^2 and it has been active since 1980; paper mill since 1960. Agricultural (vegetable gardens, orchards and meadows), cattle farming and industrial activities (paper industry) are carried out in the area. Map of investigated area with locations of thirteen sampling sites (hand pumps) is shown in Fig.1.

Sampling and chemical analysis

The water samples were selected in such a manner as to represent the whole study area around the landfill and paper mill. The ground water samples were taken by means of hand pumps (from the depth of 15-20 metres) after a pumping period of at least 15 minutes in order to remove stagnant water. Analyses were performed immediately after sample collection, using atomic absorption spectrometry methods to determine the concentrations of Cd, Cr, Cu, Fe, Pb, Ni and Zn. Chemical oxygen demand (COD) was measured by titration method while electrical conductivity and pH by electrochemical method. NH_4-N, NO_2-N and NO_3-N were determined spectrophotometrically, total organic carbon (TOC) and oils (Oils) by using TOC analyser and IR-spectroscopy method respectively. All the groundwater quality parameters are expressed in mgL^{-1}, except pH, EC (μScm^{-1}) and COD (mgO_2L^{-1}). The analysis of various water samples from different locations were carried out, according to the standards of the International Organization for Standardization (ISO) (26). Today's legislation in the Republic of Croatia regulates standards for drinking water quality, maximum allowed concentrations for some toxic substances, water use and protection (27).

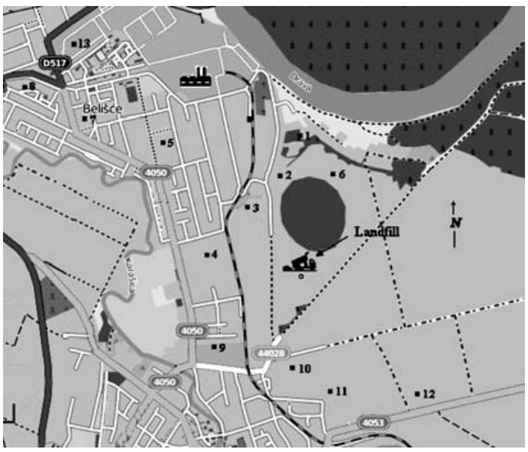

Figure 1. Map of Belišće area with locations of 13 measurement places

Statistical procedures

Besides standard descriptive statistics, PCA was performed. The data contain 15 groundwater quality parameters but 12 of them were selected for PCA because of their higher concentrations in groundwater samples.

RESULTS

Groundwater chemistry

Results for NO_3-N, NO_2-N and NH_4-N are converted and reported in Table 1 as NO_3^- (nitrate), NH_4^+ (ammonia) and NO_2^- (nitrite). Table 1 contains some descriptive statistics for fifteen groundwater chemical variables. Highest variability was noted for NO_3^- and EC. In addition, the obtained maximum EC and NO_3^- values were above the maximum allowed value for drinking water. The maximum values of oils, EC, COD, NH_4^+, Ni, Fe, Cr and Pb were also above the maximum allowed concentrations determined by Croatian standards. The concentrations of remaining variables (pH, NO_2, Cd, Cu and Zn) were within normal range of values and have shown little variations. Groundwater samples were circumneutral, with pH ranging from 7.02 to 7.85. The approximate location of the source of organic waste inputs and the extent of ground-water degradation were delineated by the TOC values. The TOC values showed high variability and deviations from median values.

Principal Component Analysis

The obtained data were subjected to the PCA in order to define virtual variables which will describe their interdependence. PCA, followed by varimax rotation method, provides the results given in Fig. 2 (so-called biplot).

Table 1.Descriptive statistics of the 15 groundwater quality parameters measured at 13 measurement sites located in the Belišće area

Variables	M.A.C.	Mean	Minimum	Maximum	S.D.
pH	6.5-9.5	7.311	7.020	7.850	0.211
Oils	0.02	0.899	0.3392	3.478	0,835
NH_4^+	0.50	3.321	0.0058	16.872	5.629
NO_2^-	0.50	0.054	0.0039	0.331	0.086
NO_3^-	50.0	38.504	0.0199	232.999	75.41
EC	2500	1257.077	517.000	2879.000	715.0
Cd	0.005	0.001	0.001	0.002	0.000
Cr	0.05	0.021	0.0010	0.057	0.020
Ni	0.02	0.005	0.0009	0.027	0.007
Pb	0.01	0.018	0.0045	0.039	0.013
Cu	2	0.008	0.0009	0.051	0.013
Zn	3	0.114	0.0060	0.434	0135
Fe	0.2	1.443	0.0190	7.325	2.097
TOC	*	2.727	1.2100	10.120	2.415
COD	5	3.077	1	9	2.46

S.D., standard deviation; M.A.C., maximum allowed concentrations; *values should not significantly deviate from the mean values

Three main clusters of samples could be distinguished: a rather compact cluster in the left portion of Fig. 2 which contains most samples (zone 3). It therefore defines the most common conditions, i.e. determines situations that are more frequent. Since the variables that point toward certain objects are more important for those objects, it is obvious that variables NH_4^+ and NO_2^- are important for these measuring sites. While the measuring sites 2 and 6 in the right portion of Fig. 2 display the sites with highest variations in EC and metal concentrations (zone 2), central cluster (zone1) contains TOC, COD, Fe, oils, pH and NO_3^-, and groundwater samples: 3,4,5 and 7. Consequently, these two clusters represented less frequent cases.

DISCUSSION

The three zones were identified using principal component analysis technique. Zone 1 consisted of highly polluted sites which were restricted to the places in the vicinity of paper factory and city centre area. In these samples a considerable amount of mineral oils, nitrate and Fe were found, even 170, 5 and 37 times grater than maximum allowable concentrations regulated by Croatian regulative for drinking waters. It is notable that samples in this zone were polluted with chemical contami-

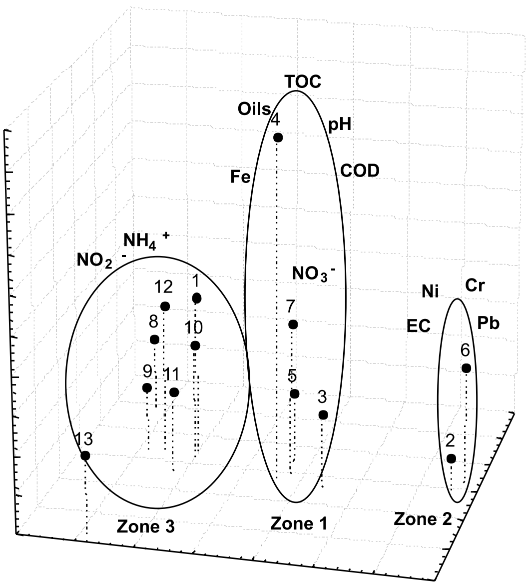

Figure 2. Plot of scores and loadings of 13 groundwater samples characterized by 12 chemical parameters (EC, pH, TOC, Oils, COD, NH_4^+, NO_3^-, NO_2^-, Ni, Fe, Cr, Pb). Numbered points refer to the corresponding measurement sites distributed in three different clusters (zones)

nants of industrial origin and results demonstrate a significant influence of anthropogenic activities on the aquatic media. Further, results have shown that significant organic and oil groundwater contamination did occur at distance of about 500 m from the paper mill plants. Vegetable growing on soil contaminated by gasoline or diesel fuel may contain carcinogenic chlorinated or hydrocarbon pollutants in their tissues at significant concentrations (10, 28). Irrigation with such degraded water might result in build-up of the elevated concentrations especially due to long-term use. Elevated concentrations of other relevant chemical pollutants such as nitrate, also lead to pollution problems (23). Based on methaemoglobinaemia in infants (an acute effect), the WHO has established a guideline value for nitrate ion of 50 mgL^{-1} as NO_3^- (29). The nitrate concentration higher than 10 mgL^{-1} may cause nitrate poisoning of infants during the first months of life (blue-baby syndrome) but chronic ingestion of smaller doses can contribute to the risk of non-Hodgkin's lymphoma, colon cancer, dyspepsia and mental depression (24, 30,31). Recent studies showed that higher levels of the nitrate and nitrite in edible portions of some leafy vegetables are indicators of possible pollution as a result of excessive usage of fertilizers and irrigation with polluted water (16, 32). The levels of pollutants (other than heavy metals) measured in less populated zone 2 located in the vicinity of landfill were low in comparison to levels on other two zones, which is to some extent related to the dilution effect of the Drava River water.

However, the heavy metal values observed in samples from this study were much higher in comparison with their typical concentrations in natural groundwater (33). Heavy metals are very harmful because of their non-biodegradable nature, and they have potential to accumulate in different body parts and even low concentrations have damaging effects to people and animals. (12). Heavy metals often form a part of the active compounds of pesticides and superphosphate fertilizers (32). Approximately 20% of human exposure to lead is attributable to lead in water, which is cumulative poison, initiating irritability, anaemia and tiredness (9).

The most of the samples in this study with elevated ammonia concentrations were located in suburban parts of the observed area where septic tanks and manure storages are situated and poultry farming is still a common practice. Ammonia in the environment mainly results from on-site sanitation (septic tanks or primitive toilets) and leaking sewers, thus concentrations higher than 0.2 mgL^{-1} in groundwater are mostly indicators of sewage pollution (29, 33,34). In some samples the maximum values for ammonia were even thirty times more than prescribed by the permitted values of Croatian standard for drinking water. Although ammonia in drinking water is not of direct health relevance, bacteria and viruses from human and animal wastes carried to groundwater can cause disease (33,35,36). The results generally revealed that groundwater assessed in this study mainly does not satisfy safe limits for drinking and domestic use.

It would be desirable to obtain some other data for groundwater in the wider area of eastern part of Croatia, but there are either no data or the existing data are not comparable because in this pioneering study the samples were collected in completely different ways and in different locations. Further extended studies are certainly needed to estimate possible occurrence of any adverse health effects in the populations.

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TRANSPARENCY DECLARATIONS

Competing interests: none to declare.

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Kemometrijska analiza kvalitete podzemne vode na području odlagališta komunalnog otpada i tvornice papira, te njihov mogući utjecaj na zdravlje stanovništva

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SAŽETAK

Cilj Utvrditi vrijednosti 15 parametara kakvoće u uzorcima podzemnih voda, prikupljenim oko komunalnog odlagališta otpada i tvornice papira, kako bi se procijenio stupanj zagađenja i moguće posljedice na ljudsko zdravlje.

Metode Dobiveni podaci su analizirani metodom analize glavnih komponenata (PCA), kako bi diferencirali podzemne uzorke na temelju njihovog sastava i podrijetla.

Rezultati Otpad i otpadne vode iz odlagališta komunalnog otpada nisu značajno doprinosili zagađenju vodenih medija. Podzemno onečišćenje, uzrokovano visokim sadržajem nitrata, mineralnih ulja, organskim i anorganskim spojevima, osobito je bilo izraženo u uskom području centra grada, u blizini tvornice papira, a vjerojatno je posljedica onečišćenja koje se dogodilo tijekom dužeg vremenskog razdoblja. Koncentracije većine mjerenih parametara (NO_3-N, NH_4-N, ulja, organska tvar, Fe, Pb, Ni i Cr) bile su iznad dopuštene granice za humanu uporabu.

Zaključak Ova studija je poslužila za stjecanje važnih informacija o stanju eko sustava podzemnih voda i za određivanja parametara kvalitete podzemnih voda (u ovom slučaju, s koncentracijama iznad dopuštene granice za ljudsku uporabu). Rezultati su općenito pokazali da podzemne vode u ovom istraživanju, uglavnom nisu zadovoljavale kriterije ispravnosti za pitku vodu i korištenje u kućanstvima. Kao posljedica toga, kontaminirane podzemne vode postaju veliki ekološki i toksikološki problem. Iako onečišćenje nije dostiglo toksičnu razinu, ono ipak predstavlja trajnu opasnost za zdravlje populacije.

Ključne riječi: podzemne vode, kvaliteta, zagađenje, analiza glavnih komponenata