ISBN 978-81-934174-2-3
6th International Conference on Healthcare, Environment, Food and Biological Sciences (HEFBS-17)
Istanbul (Turkey) Sept. 8-10, 2017

Nitrate and Heavy Metal Contamination of Grounwater under the Greenhouse Cultivation

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Abstract: *A survey study was conducted in groundwater and soils of intensive agricultural areas of Kaş, one of the major greenhouse production region of Antalya, Turkey to assess the nitrate and heavy metal pollution and their relationships with soil nitrate and metal parameters..*

All physico-chemical characteristics except NO_3 and electrical conductivity values of groundwater in the majority of greenhouse areas were within the acceptable limit values and differences in water characteristics among the regions were found statistically important. Groundwater have high electrical conductivity, slightly alkaline reaction, high and moderate alkalinity. Dissolved oxygen (DO), biological oxygen demand (BOD), chemical oxygen demand (COD) and total dissolved solids (TDS) were detected in acceptable ranges. Total NO_3^- values of groundwater were generally exceeded permissible safe limits for drinking waters. Nitrate pollution evaluation values of groundwater were indicated that due to higher NO_3^- contents of groundwater, there are a possible health risks for the consumptions of groundwater as drinking water in a short and moderate-term in the greenhouse regions.

Total As and Fe contents of almost all ground waters were above the permissible pollution limits. All other heavy metal concentrations of groundwater were below the limits. According to evaluation parameters, generally, it can be concluded that all ground waters in regional size may be considered less contaminated, and in point of heavy metals and pollutants is in acceptable limits. Groundwater NO_3 concentrations were positively correlated with soil NO_3 concentrations. Most of groundwater metals were positively correlated soil F1 and F2 metal fractions, and Zn and Ni in groundwater were positively correlated with soil Zn and Ni mobility factors.

Keywords: *Groundwater, Greenhouse Soil, Nitrate, Heavy Metals*

1. Introduction

Mediterranean region has an important agricultural potential especially greenhouse cultivation with its special climate and geographical characteristics in Turkey. Greenhouse cultivation has resulted in increasing usage of nitrogenous fertilizers and in recent years, many research findings have indicated that an extreme fertilizer and pesticide applications in the greenhouse soils of Mediterranean region. Crop plants which are cultivated in contaminated soils can accumulate contaminants and transfer them to animals and human beings via food chain which are eventually result in various health problems.

Due to intensive use of agrochemicals in greenhouse soils, nitrate nitrogen and heavy metals is become to common pollutant in ground waters of greenhouse soils and adjacent environment. Especially, high concentration of nitrate nitrogen in groundwater is accepted as an important indicator of agricultural pollution. Nitrate pollution in intensive greenhouse areas is an important environmental problem that threats sustainable production and national economy and interests particularly for public health. In addition, low level exposure to nitrate over many years, possibly could cause certain types of cancer such as digestive system cancer, stomach, esophagus, lungs, colon, bladder, ovaries, testicles, urogenital tract and non-hodgkins lymphoma [1]. Additionally, nitrate was more affects the ground water rather than phosphates in which related to agricultural activities and animal farming [2].

Repeated amendments of organic matter and intensive use of fertilizers, and other agrochemicals may cause soil, ground water and environmental pollution in greenhouses. Although greenhouse areas a have great impact on environment due to intensive use of agrochemicals, little attention has been paid to nitrate and metal accumulation of groundwater around greenhouses and environmental pollution assessment in ground waters with respect to comprehensive and integrated environmental evaluation.

The impact of agricultural activity on water sources has been widely acknowledged and its impact on surface water of nitrogen) and anthropogenic sources (i.e., industrial residue, intensive agriculture and septic tanks). Among them, heavy used of nitrogenous fertilizers in agricultural activities were the largest contribution of systems has been described in numerous studies [3]. Especially, the relationship between agricultural practices and the dissolution of nitrate in groundwater, as well as other pollutants have been studied in a number of case studies [4]. Nitrate in ground water accumulating from both natural (i.e., soil mineralization and atmospheric deposition nitrate in ground water [5].

Assessment the extent of pollution in groundwater comes into prominence with regard to prevention of possible risks. The aim of this study was to provide information on the nitrate and heavy metal levels in groundwater and to assess the groundwater pollution by using soil parameters in the greenhouse regions

2. Material and Methods

***Geography of study region*:** The experiment was conducted on the major greenhouse vegetable growing area located at Kaş in the western part of Antalya, Turkey. The site studied is intensively cultivated and is not industrialized area. The experiment was carried out at greenhouse region and water samples were taken from 2 sub-region and 10 sampling points (Fig. 1).

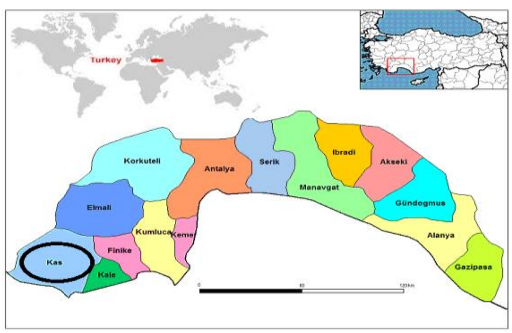

Fig. 1: Map of greenhouse regions of Kaş, Antalya

The geological materials of greenhouse area are mainly of calcareous nature and adjacent to Mediterranean sea with average 9-10 m altitude. The land is influenced by a Mediterranean climate with a high average annual rainfall (782,9 mm/year), the annual average temperature being around 19,6 °C, 54 % average humidity and 8,11 hours average sunshine duration. As for greenhouses, the annual temperature is higher inside than outside, and most of them are watered by sprinklers with ground water source at the same point. All greenhouses have passive ventilation to control temperature and humidity inside. A great number of greenhouse soils is artificially built up with a different layer of sand, organic matter and other soil source.

***Groundwater Sampling and Analysis*:** Water samples taken for metal analysis were collected in polyethylene (HDPE) bottles (washed with detergent then with double-distilled water followed by 2 M nitric acid, then double-distilled water again and finally with sampled water). Water samples were acidified with 10% HNO_3 for metal analysis, samples were stored in an ice-box and brought to the laboratory and kept refrigerated and analyzed immediately within 24 h.

Water samples taken for nitrate and other physiochemical analysis were collected in polyethylene bottles of 1 liter. Before sampling, the recipient was cleaned several times using the pumped water. Water samples were gradually filled to avoid turbulences and aeration during the sampling. To avoid sampling artifacts and analytical artifacts, in particular the gain of dissolved gas and microbiological activity, water samples were immediately

https://doi.org/10.17758/URST.U0917227

cooled at 4 °C using portable icebox. Analysis was further performed as fast as possible and this within 24 h after sampling.

Groundwater samples were analyzed for nitrate as NO3-N by the Cadmium Reduction Flow Injection Method, [6]. Other routine analysis in water samples were analysed according to Standard methods recommended by APHA [7]. pH was measured by digital pH meter, electrical conductivity was measured by conductometry. Alkalinity was determined by titration with 0.01N H_2SO_4, Total dissolved solids (TDS) was measured by TDS meter. Dissolved oxygen (DO), biological oxygen demand (BOD) was measured by Wrinkler's method and chemical oxygen demand (COD) by Reflux method [7]. pH, electrical conductivity (EC), DO and nitrate were measured on site.

To determine heavy metals in water samples, 10 ml of aqua regia and 1 ml of perchloric acid added to 100 ml of water samples in a culture test tube, then incubated at 80°C in a water bath, after total digestion and subsequent cooling, the solution was diluted to 50ml and analyzed for heavy metals. For the determination of 'total' heavy metal concentrations, water samples were digested in aqua regia (1:3 HNO_3/HCl) and $HClO_4$ according to the international standard [8].

***Soil Sampling and Analysis*:** Greenhouse soil samples were taken at a depth of 0-30 cm and these were air-dried, sieved (< 2 mm) and stored in polyethylene bags sealed awaiting analysis.

Soil samples were analyzed for nitrate as NO3-N by the Cadmium Reduction Flow Injection Method, [6]. For the determination of 'total' heavy metal concentrations, soil samples were digested in aqua regia (1:3 HNO_3/HCl) and $HClO_4$ according to the international standard [8]. Sequental extraction method [9] was applied to soil samples to identify metal fractions. The heavy metal sequential extraction procedure had the following steps:

- F1. 1 M $MgCl_2$ (1:8 w/v, pH 7) for 1 h at room temperature; metals in soil solution and in exchangeable forms.
- F2. 1 M NaOAc (1:8 w/v, pH 5) for 5 h at room temperature; metals mainly in the carbonate fraction.
- F3. 0,04M NH_2OH/HCl in 25 % (v/v)HOAc (1: 20 w/v) for 6 h at 96 °C ; metals associated with Fe and Mn oxides.
- F4. 3 ml 0,02 M HNO_3+5 ml 30 % H_2O_2 (pH 2) for 3 h at 85 °C; metals associated with organic matter.
- F5. HNO_3-HCl digestion; residual fraction.

Fe, Zn, Mn, Cu, Cd, Ni, Cr, Pb and As concentrations of groundwater and greenhouse soil samples were analyzed using ICP-MS under optimized measurement conditions and values were adjusted for oven dried (12 h at 105 °C) material.

Due to some metal forms are strongly bound to soil components than those extracted in F1 and F2, the mobility of metals in soil samples may be evaluated on the basis of absolute and relative content of fractions weakly bound to soil component. Relative index of metal mobility was calculated as a 'mobility factor' (MF) [10] on the basis of the following equation:

$$MF: \frac{(F_1+F_2+F_3)}{(F_1+F_2+F_3+F_4+F_5)} x100 \qquad (1)$$

***Pollution Evaluations*:** Selected environmental pollution indexes for water samples were used for comprehensive and integrated evaluation of heavy metal pollution. In this study several evaluation methods developed for heavy metal pollution were modified for assessment of nitrate pollution in groundwater.

***HPI index*:** was developed by assigning a rating or weightage (*Wi*) for each chosen parameter. In computing the HPI for the present water quality data, the concentration limits i.e. the standard permissible value (*Si*) and highest desirable value (*Ii*) for each parameter were taken from the WHO standards.

The HPI is determined by using the expression below [11]:

$$HPI = \frac{\sum_{i=1}^{n} WiQi}{\sum_{i=1}^{n} Wi} \tag{2}$$

Where *Qi* is the sub-index of the ith parameter. *W*i is the unit weightage of the ith parameter and n is the number of parameters considered. The sub-index (*Qi*) is calculated by

$$Qi = \sum_{i=1}^{n} \frac{\{Mi(-)Ii\}}{Si-Ii} \times 100 \tag{3}$$

where, *Mi*, *Ii* and *Si* are the monitored value of heavy metal, ideal and standard values of the ith parameter, respectively. The sign (-) indicates numerical differences of the two values, ignoring the algebraic sign.

Pollution Evaluation Index (PEI): PEI, gives an overall quality of the water with respect to heavy metals, and is computed as:

$$PEI = \sum_{i=1}^{n} \frac{H_c}{H_{mac}} \tag{4}$$

Where, Hc and Hmac are the monitored value and maximum admissible concentration (mac) of its parameter, respectively [11]. In this study, PEI was used for both nitrate and heavy metals pollution.

Degree of contamination (Cd): The contamination factor (Cfi) is defined as the ratio of heavy metal concentration in the soil to the background value:

The contamination index (Cd) summarizes the combined effects of several quality parameters considered harmful to household water, and is calculated as follows:

$$C_d = \sum_{i=1}^{n} Cfi$$
$$Cfi = \frac{CAi}{CNi} - 1 \tag{5}$$

where C*fi*, C_{Ai} and C_{Ni} represent contamination factor, analytical value and upper permissible concentration of the ith component, respectively, and N denotes the normative value. Here, C_{Ni} is taken as MAC. The contamination levels were classified by their intensities, ranging from 1 to 3 ($C_d < 1$: low, $1 < C_d < 3$ = medium, $3 < C_d$ = high) [12].

Target hazard quotient (THQ): The methodology for estimation of target hazard quotient (THQ) although does not provide a quantitative estimate on the probability of an exposed population experiencing a reverse health effect, but it offers an indication of the risk level due to pollutant exposure. This method was available in US EPA Region III Risk based concentration table and it is described by the following equation [13]:

$$THQ = \frac{E_{Fr} \times E_D \times F_{IR} \times C_m \times 10^{-3}}{R_{fD} \times B_w \times A_T} \tag{6}$$

Where E_{Fr} is exposure frequency (365 days/year); E_D is the exposure duration (70 years), equivalent to the average lifetime; F_{IR} is the food ingestion rate (2000 g/person/day (FAO, 2005); Cm is the contaminant concentration in water (μg g_1); R_{fD} is the oral reference dose of contaminant (US EPA, 1997, 2000); Bw is the average body weight (70 kg), and A_T is the averaging exposure time for non-carcinogens (365 days/ year x E_D).

Hazard Index (HI): For carcinogenic health effects posed by contaminant in drinking water, the Hazard index (HI) was calculated using the following equation [14]. A HI value more than 1 (HI>1) shows a significant risk level. The higher the value, the greater the likelihood of adverse non-carcinogenic health effect.

$$HI = \sum_{n=1}^{i} THQn \tag{7}$$

Potential ecological risk index (RI) : Potential ecological risk index (RI), which was developed to scree sediment contamination degree caused by heavy metals was introduced to assess the ecological risk degree of heavy metals in present water, soil and sediments [15]. The value of RI can be calculated by the following formulas:

$$RI = \sum_{i=1}^{n} E_r^i \quad ; \quad E_r^i = T_r^i \times C_f^i$$

$$C_f^i = \frac{C_D^i}{C_B^i} \tag{8}$$

where RI is the sum of the potential risk of individual heavy metal, Er i is the potential risk of individual heavy metal, Tr is the toxic-response factor for a given contaminant, Cfi is the contamination factor, C_D i is the present concentration of heavy metals, and C_B i is the maximum permissible concentration of contaminant.

Statistical analyses were performed by using SPSS-16 for Windows program.

3. Result and Discussion

Land altitude and groundwater table in greenhouse areas: Land Altitude and groundwater table in greenhouse regions of Antalya are given in Figure 2. Land altitude of greenhouse regions are varied in a wide range and groundwater table that below the sea level is changed depending on the regions.

The study area, Kaş has average 10 m altitude and depending on the sampling points about 5-10 m water table, those below the sea level. This means that there is a possibility of seawater intrusion to aquifers in these regions. Land altitude, water table properties, and differences of agricultural practices among the greenhouse regions may be affective on pollution and contamination characteristics of groundwater.

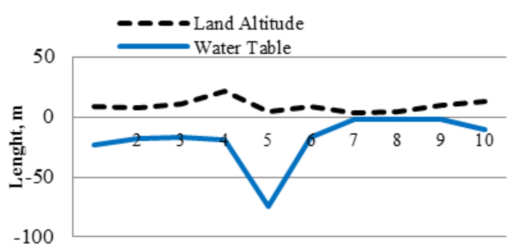

Fig. 2. Altitude and groundwater table of greenhouse regions in the greenhouse regions of Antalya, Turkey

General Groundwater Properties: The mean physico-chemical characteristics of groundwater in the majority of greenhouse areas were within the acceptable limit values [16]. with the exception of electrical conductivity and NO_3 parameters. Differences in characteristics among the sampling points were found statistically important (Table 1). Groundwater temperatures were detected in acceptable ranges. Groundwater in sampling points have ranged slightly alkaline reaction, and generally high electrical conductivity. Also water characteritics with regard to irrigation water quality were found high and in inacceptable level. Due to high water salinity there was a possibility of seawater intrusion to groundwater in these sampling sites. Dissolved oxygen (DO), biological oxygen demand (BOD), chemical oxygen demand (COD) and total dissolved solids (TDS) were detected in acceptable ranges. These values indicate that groundwater in greenhouse regions were not polluted by organic solids, and physiochemically may be accepted clean.

Nitrate Pollution Evaluations in Groundwater: Total NO_3^- values of groundwater in sampling sites were generally exceeded permissible safe limits [16] for drinking waters. High concentration of NO_3^- in these areas is of course may be due to highly intensive agricultural practices for all season. Mineralized nitrogen fertilizers such as ammonium nitrate and urea applied in greenhouses appeared to be the dominant source of NO_3^- in the groundwater, with contributions from native soil organic matter, and organic amendments. Leaching of nitrates into shallow groundwater under greenhouse agriculture may be accepted high because of the relatively large irrigation density and fast chemical and microbial degradation and nitrification processes under the greenhouse conditions.

Nitrate C_d values of groundwater were generally found in low levels. However, C_d was found in medium contamination levels in sampling site 1 and site 2 (Figure 3). Nitrate pollution evaluation values (PEIN) of groundwater are indicated in Figure 4. PEIN values of groundwater were below the referenced limit value (40). THQ values in the groundwater of Kaş region was mostly exceeded limit value 1 (Figure 5). These evaluations show that due to high contents of NO_3^- there are a possible health risks for the consumptions of groundwater as drinking water in a moderate and long-term in the greenhouse regions.

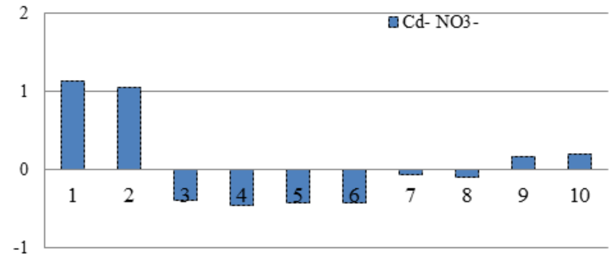

Fig. 3. Contamination degree values of NO_3^- in the groundwater.

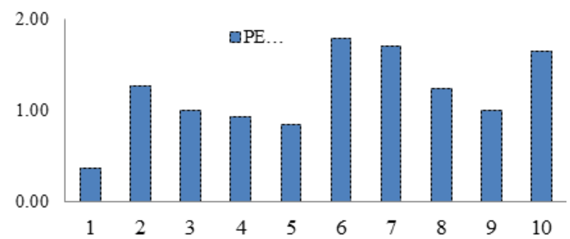

Fig. 4. Pollution evaluation index values of NO_3^- in the groundwater.

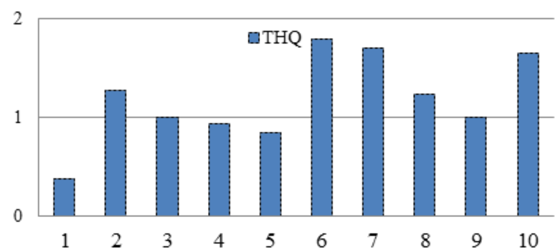

Fig. 5. Target hazard quotient values of NO_3^- in the groundwater.

In Table 2 Pearson's correlation cofficients showing relationship between water physico-chemical parameters and groundwater geographic parameters were presented. Positive correlations were recorded between NO_3 content and EC value and also NO_3 content and alkalinity value. Low altitude of sampling sites and swallow water table may be main cause of NO_3 leaching possibility to groundwater.

TABLE II. Pearson's correlation cofficients showing relationship among the water physico-chemical parameters

	EC	pH	Alkalinity	Nitrate
EC	1,000			
pH	-0,597	1,000		
Alkalinity	-0,503	0,563	1,000	
Nitrate	0,876**	-0,398	-0,632*	1,000

[1]: Values were computed for 30 samples.

Groundwater and Soil Heavy Metal Characteristics: The mean Fe, Zn and As contents of groundwater were above the permissible pollution limits (Table 3). Although average contents of other metals were below the limits, in some sampling sites Cu, Pb and Ni contents of groundwater were exceeded referenced toxicity limit values for drinking waters. Total metal concentration of groundwater was significantly varied in sampling sites.

Soil total metal concentrations were significantly varied in sampling sites (Table 4). All average total metal concentrations except Ni were belove the limits of European Union (86/278/EEC) [16] directive to agricultural soils with pH>7. Ni concentrations in most of soil samples were higher than limit values. Based on the greenhouse soil metal concentrations, it can be assumed that no contamination possibility risk with the exception of Ni will recorded.

In Table 5, Pearson's correlation coefficients showing relationship between soil and groundwater parameters were presented. Groundwater nitrate concentrations were positively correlated with soil nitrate concentrations. But no correlations were recorded between water and soil metals. High concentration of nitrate values are of course may be due to highly intensive agricultural practices for all season in this region.

In Table 6, Pearson's correlation coefficients between groundwater metal concentration and soil metal fractions and metal mobility factor were presented. According to correlation table, Zn and As metals were positively correlated soil F2 fraction that represents soil exchangeable and plant available metals. Also soil metal mobility factor that represents mostly water soluble, exchangeable fractions was correlated with groundwater Zn and Ni metals. These data shows us the importance of soil metal fractions and metal mobility on groundwater metal characteristics.

Soil Metal Speciation and Metal Mobility: Concentrations of Fe, Zn, Mn, Cu, Cd, Ni, Pb and As in soil fractions and metal mobility factor values were given in Figure 6 and Figure 7, respectively. Irrespective of sampling sites, the distribution of metals in greenhouse soil samples generally followed the order below for the metals studied.

Fe: F1<F2≤F3<F4<F5
Zn: F3<F1<F4<F2<F5
Mn: F2<F1<F3<F4<F5
Cu: F3<F1<F4<F2<F5
Cd: F1<F2<F4<F3<F5
Ni: F3<F2<F1<F4<F5
Pb: F2<F3<F1<F4<F5
As: F3<F4<F2<F1<F5

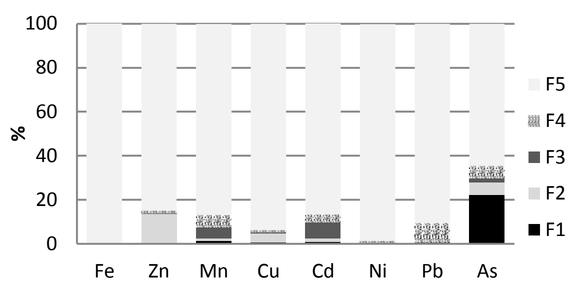

Fig. 6. Concentrations of Zn, Cd, Ni, Pb and As in soil fractions

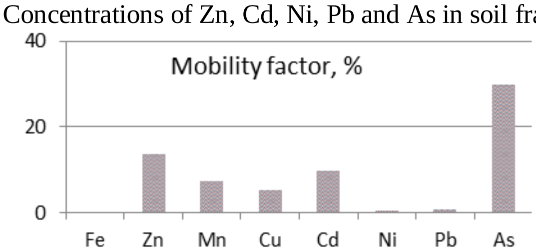

Fig. 7. Average metal mobility of greenhouse soils

The study of the distribution of metals showed that the greatest percentage of all metals was present in the residual fraction. However, F1, F2 and F3 fractions of Zn, Cu, Cd and As metals were higher than other metals.

This property possibly gives these metals a high mobility. The most mobile metal fraction was detected in As and the most immobile metal fraction was detected in Ni. Iron and Ni largely (99,75 % and 98,45 %, respectively) associated with residual phase. The MF values were considerably higher for As, Zn and Cd (Figure 4). The high MF values refer to relatively high metal lability and biological availability of heavy metals to plant and organisms in soils system. The results of the present study suggest that the mobility of the metals declines in the following order: As>Zn>Cd>Mn>Cu>Pb>Ni>Fe (Figure 4).

Groundwater Pollution Evaluation: HPI values of groundwater are shown in Figure 8. HPI values of Fe, Cu, Cd and Cr metals and the mean HPI value including all metals were above the referenced limit value 100. According to this evaluation parameter, groundwater in Kaş region could be accepted in risky group in view of metal concentrations.

Heavy metal contamination factor (Cfi) values for all metals were presented in Table 7. The mean Cfi values of Fe were exceeded critical value 1. Although the mean Cfi values of Zn and Cu were recorded high level, these values were possibly arised from some sampling sitess those have extreme Cfi values. Totally, average metal contamination degree (C_d) values of groundwater in the greenhouse sites were below the critical value 1. According to this parameter some of groundwater samples may be considered as highly contaminated.

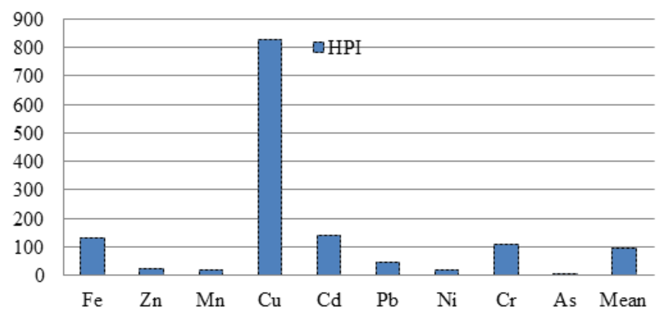

Fig. 8. Heavy metal pollution index (HPI) values of groundwater in the greenhouse areas.

HEI values for all of metals in groundwater of all sites were below the critical value 40 (Table 8). Thus, all of groundwater samples may be considered as less contaminated and may be acceptable clean with regard to this evaluation parameter.

Er and RI values of heavy metals in the groundwater are shown in Table 9. Er values of individual metals in all sites were below the minimum referenced value 40. RI values that represent the potential ecological risks of all metals in groundwater of all sites were below the minimum referenced value 150. Er and RI values have not set for Fe and Mn elements. According to these results, there cannot be expected an ecoloogical risk in a short and medium term.

The heavy metal contamination of groundwater and the potential health risk were evaluated by THQ and HI parameters (Table 10). THQ values of individual heavy metals were all lower than 1. The cumulative risk of all heavy metals (HI) through the drinking of groundwater also has not exceeded limit value 1. This indicated that the daily intake of individual metals through the drinking of groundwater was unlikely to cause an adverse health risk.

Variation in metal concentrations, HPI, HEI, Er, RI, THQ and HI values of groundwater, Cfi values of Fe, Mn, Cd, Pb and Ni metals among the sites were found statistically significant. Land altitude, water table properties, and differences of agricultural practices among the greenhouse regions may be affected on pollution and contamination characteristics of groundwater.

4. Conclusion

Results showed us that land altitude, water table properties, and differences of agricultural practices among the greenhouse regions may be affective on contamination characteristics of groundwater.

Physico-chemical characteristics except EC values of groundwater in the majority of greenhouse areas were within the acceptable limit values and differences in characteristics among the regions were found statistically important. High nitrate contents of groundwater due to agricultural activities all season in greenhouse regions seem the main threats for public health. According to this, control of nitrate pollution in groundwater especially in greenhouse areas requires a holistic approach to climate land, aquifer and land use factors.

According to metal evaluation parameters, generally, it can be concluded that most of groundwater in Kaş region may be considered less contaminated. However, data also showed that there was an alarming rate of NO_3 and heavy metal pollution risks in some sampling sites. Results showed us that soil metal fractions and soil metal mobility factor were also effective on groundwater metal contamination.

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