Eurasian J Soil Sci 2020, 9 (3) 194 - 201

Eurasian Journal of Soil Science

Journal homepage : http://ejss.fesss.org

Assessment of potential ecological risk index based on heavy metal elements for organic farming in micro catchments under humid ecological condition

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Article Info
Received : 11.10.2019
Accepted : 10.04.2020

Abstract

Soil pollution, influenced by both the natural and anthropogenic factors, significantly reduces environmental quality. This research was carried out in some micro catchments located on Ordu province of Black Sea Region-Turkey in order to determine potential ecological risk index based on heavy metal elements (HMs) for organic farming. For this purpose, 166 soil samples (0-20 cm) were taken from the study area and some physical and chemical and HM concentrations (Cd, Cu, Cr, Ni, Pb and Zn) analysis were done. In this study, it was determined; i-) some physical and chemical properties of catchments' soils, ii-) HM contents and the correlation relation between physico-chemical properties of soil and HM concentrations and iii-) potential ecological risk index (PERI). PERI was calculated using the data obtained to evaluate the environmental risks of HMs in the region. The results showed that Cu concentration in 3%, Cr in 0.6% and Ni in 4.8% of the soil samples exceeded the threshold levels whereas, the concentrations of other HMs were lower than the critical values. Statistically, it was also found significantly positive relationships between sand content and Cu of soils whereas, it was determined significantly negative relationships between EC and Cu. In addition, according to the obtained PERI results, while 54% of total soil samples were low while, 42% of them were moderate class. Only 4% of them were classified as significant ecological risk level. Moreover, according to mean potential ecological risk index of these HMs, it can be ordered as Cd>Pb>Cu>Ni> Zn>Cr.

Keywords: Heavy metal, potential ecological risk, micro catchment, humid ecological condition, Black Sea Region.

Introduction

Nowadays, contamination of heavy metal elements has become an environmental issue in both developed and developing countries throughout the World (Tam and Wong, 2000; Sun et al., 2010). Natural toxicities of heavy metals, having a large number of sources, not being biodegraded and being able to survive for a long time; It has increased the importance of ecological and environmental studies on metal accumulation (Gao et al., 2016). Rapid urbanization, industrialization, agricultural practices and the use of fossil fuels are the main causes of heavy metal accumulation in soil, especially in water resources, street dust, sediment, aquatic organisms consumed by humans and in the food chain (El Nemr, 2011; Chaudhari et al., 2012; Yang et al., 2014; Cheng et al., 2015). Under certain environmental conditions, heavy metals might accumulate up to toxic concentration levels, and cause ecological damage (Bai et al., 2011; El Nemr et al., 2012).

An important problem is how to assess heavy metal deposits and how to distinguish man-made contribution from natural concentrations (Bing et al., 2013). Many indexes have been developed to evaluate the accumulation of heavy metals and the environmental problems they create. For example, in order to

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e-ISSN : 2147-4249 DOI : https://doi.org/10.18393/ejss.719167

determine the accumulations of anthropogenic origin and to identify possible ecological risks; Enrichment factor, contamination factor, geo-accumulation index, potential ecological risk index are frequently used indices (Rashed, 2010; Yang et al., 2011; Bing et al., 2013; Islam et al., 2015; Kükrer et al., 2015).

Structural and textural properties of the soil, cation exchange capacity (CEC), pH and amount of organic matter have an effective role in the retention of heavy metals in the soil. Especially due to the high CEC of clay, soils hold heavy metals more than other soils with higher clay and organic matter content hold difficult metals and form strong soluble compounds. Variation of these elements or compounds deposited in the soil along the soil profile, it depends on the characteristics of the soils and the intensity of agricultural activities, and the distribution of metals in the soil profile is indicative of air pollution, soil genesis and anthropogenic pollution (Wilcke et al., 2000; Cemek and Kızılkaya, 2006).

The objectives of this present study was (i) to determine some physico-chemical soil properties of some micro catchment in Ordu province, (ii) to determine the correlation between heavy metal (HM) contents and physico-chemical properties of soil, (iii) to assess the environmental risks of heavy metals in the micro catchments.

Material and Methods

Study area

The study area chosen as Ordu, Turkey's eastern Black Sea region, is located between 40º 18'-41º 08' north parallel 36º 52'-38º 12' eastern meridians (Figure 1). Ordu is surrounded by the Black Sea from the north, Giresun from the east, Sivas and Tokat from the south, and Samsun from the west. The total area of Ordu is approximately 6141 km^2. About 10.2% of the province consists of meadow and pasture areas, while about 28.7% of it has forest areas. In addition, the area where have been used agricultural activities are carried out covers approximately 52.0% (DOKAP, 2018).

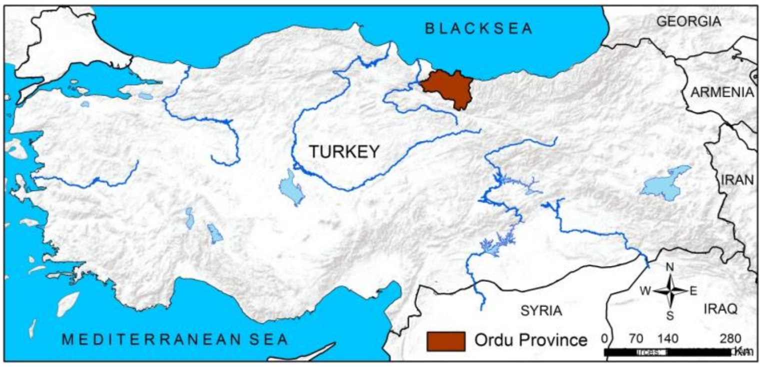

Figure 1. Location map of the study area

Ordu has a typical Black Sea climate which means that winters are mild and cool summers and shows humid ecological conditions. According to long-term climate data (1959-2018) the average annual rainfall and annual average temperature are 1038.4 mm, 14.4°C, respectively (TMS, 2015). An insight into climatic conditions of the Black Sea Region can be found in the study (Mihálikova et al., 2016). These steep slopes play an important role in growing hazelnut and tea. The study area is located at an altitude of 0-3082 m above sea level. In the majority of the northern part of the region has a mountainous and rugged topography with steep and very steep slopes (>50% slope) (Figure 2).

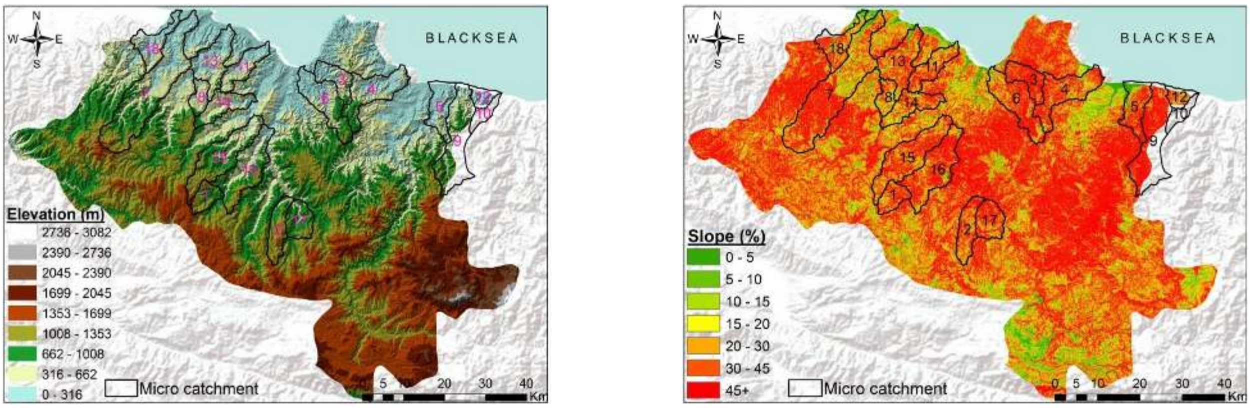

Figure 2. Elevation and slope maps of the Ordu Province

Soil Sampling and analysis

Field study was conducted in 2017. Soil samples which were classified as gray brown podzolic, brown forest, Non-calcerious brown forest, redish yellow podzolic, alluvial, high mountain meadow and colluvial great soil group according to old American soil classification system (GDRS, 1984) were taken from 166 soil in total agricultural lands (Figure 3). Sampling was carried out after autumn harvest and before the crop growing season. In addition, the coordinates were recorded using global positioning system (GPS) device.

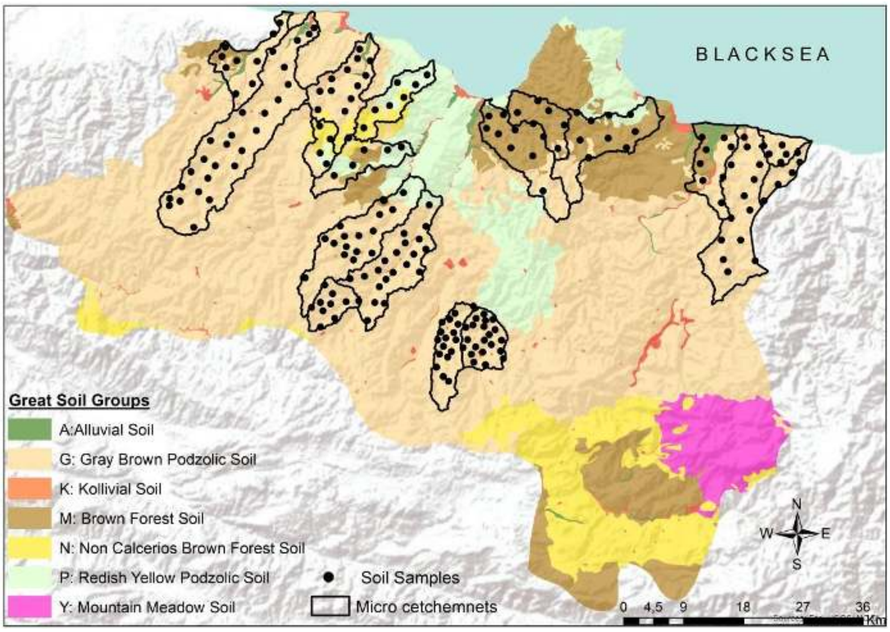

Figure 3. Soil samples pattern in great soil group map of the study area

Soil samples taken from the field were air dried and sieved from a screen with 2 mm opening size to prepare for analysis. Sand, silt, clay contents of the soil samples were determined by Hydrometer method (Bouyoucos, 1962). Soil pH values were measured in soil suspension (1:1, w:v) by glass electrode pH meter and EC values were determined in the same soil suspension (1:1, w:v) by EC meter (Rowell, 1996). Soil organic matter (OM) contents were determined by modified Walkley-Black method (Walkley and Black, 1934). Lime ($CaCO_3$) contents of soils were determined by Scheibler calcimeter (Nelson, 1982). Total heavy metal (Cu, Cd, Cr, Pb, Ni, Zn) contents were determined by EPA 3051 using ICP-OES (Kloke, 1980)

Potential ecological risk assessment of heavy metals referred to Hakanson (1980) method with the following formula:

$$CF = \frac{C_s^i}{C_r^i} \qquad (1)$$

$$PER = TRF \times CF \qquad (2)$$

$$PERI = \sum PER \qquad (3)$$

Where; C_s^i: is the measured concentration of heavy metal in each soil sample; C_r^i: is reference value, here the background value of each heavy metal in soil is used (Taylor, 1964; Hasan et al., 2013) , CF is the pollution of a single element factor (contamination factor); PER is the potential ecological risk index of a single element; PERI is a comprehensive potential ecological risk index; and TRF is the toxic response factor of a single element (Kloke, 1980), which is determined for Zn = 1, Cr = 2, Cu = Pb = Ni= 5 and Cd = 30. The terminology used to describe the risk PERI was suggested by (Kloke, 1980; Long et al., 1995), where: PERI < 95 indicates a low potential ecological risk; 95 < PERI < 190 is a moderate ecological risk; 190 < PERI < 380 is a considerable ecological risk and PERI >380 is a very high ecological risk.

Results and Discussion

Soil physical and chemical properties and heavy metals

Some researchers indicated that some chemical such as pH, CEC, organic matter contents and physical such as clay content are the essential soil characteristics that designate the capacity to hold heavy metal pollutants (Omran, 2016; Gabrielyan et al., 2018). The descriptive statistical parameters (mean, maximum, minimum, and coefficients of variation) of the some physical, chemical properties and heavy metals related to 166 soil samples taken from surface (0-20 cm) of the crop lands in 18 micro catchments of the Ordu province were presented in Table 1. The average clay content of the micro catchments' soils was 23.31%, and 55% are slightly coarse soils. The pH values of soil samples varied between 68% strong-medium-light acid, while soil samples; It has 99% salt-free, 88% lime-free, 38% medium and 32% high organic matter content. When the heavy metal contents in the research area are examined, it is seen that Cu, Cr and Ni elements are above the limit values in the surface soil in some micro catchments (Table 1). The statistics results showed that the mean value of soil Cu, Cd, Cr, Pb, Ni and Zn concentrations was 39.99, 0.54, 15.36, 11.83, 14.86 and 30.46 mg kg^{-1}, respectively. Especially Ni and Cu were determined in micro catchments coded as 7 in Akkuş and Çaybaşı district boundaries and micro catchments coded as 2 and as 17 in Aybastı, Gölköy and Kabataş district boundaries. Grouping of heavy metal concentrations was detected in all catchments except the southern parts of the Çarşıbaşı district. Although not dense, Cu, Cr and Ni may be caused by the increase in solubility of soils due to acidification process, and Cu may be caused by pesticides containing copper element in the active substance especially in areas where intensive hazelnut cultivation is carried out. There was high variations and great skewness for Cr (117.26% and 4.76). Coefficients of variation (CV) % values show the mean variation of each sampling site in the population. In this current study, it was found that the order of the CV % for heavy metal element from high to low was Cr > Ni > Pb > Cd > Cu > Zn. In some researches, it has been shown that high Ni level is caused by parent material and Pb content is caused by particle from surrounding lead acid battery factory (Pesantes et al., 2019). In addition, mean value of PERI was found 90.91 which indicate as low potential ecological risk in general for all soil samples. However, it should be evaluated each soil samples taken from each individual micro catchment.

Table 1. Descriptive statistical analysis of physical and chemical properties and heavy metal of soil samples

Parameters	Min.	Max.	Mean	SD	CV, %	Skewness	Kurtosis
Physical and chemical properties							
Sand, %	22.31	84.62	51.11	12.84	25.12	0.01	-0.47
Clay, %	5.57	56.02	23.58	10.74	45.54	0.55	-0.31
Silt, %	2.35	40.86	25.31	5.50	21.73	-0.41	1.73
pH, 1:2.5	4.24	8.10	6.02	0.92	15.28	0.25	-0.98
EC, dS m^{-1}	0.06	1.22	0.33	0.21	63.63	1.15	1.54
$CaCO_3$, %	0.00	39.25	1.50	5.48	365.33	4.72	23.38
OM, %	0.31	5.99	2.98	1.44	48.32	0.43	-0.87
Heavy metals							
Cu (0-100)#	8.19	164.26	39.99	24.47	61.19	1.73	4.46
Cd (0-3) #	0.00	2.42	0.54	0.39	71.46	1.46	4.67
Cr (0-100)#	1.20	166.04	15.36	18.01	117.26	4.76	31.87
Pb (0-100)#	2.20	96.24	11.83	8.85	74.78	6.34	53.78
Ni (0-50)#	3.54	120.13	14.86	14.76	99.33	4.10	20.88
Zn (0-300)#	10.52	91.23	30.46	12.77	41.91	1.65	3.90
PERI	6.80	373.66	90.91	2.89	3.18	1.50	4.71

SD: Standard deviation, Min.: Minimum, Max.: Maximum, n: sample number, EC: Electric conductivity, OM: Organic matter. EC: Electrical conductivity, pH: soil reaction, *CV (Coefficient of Variation), **skewness:< │∓0.5 │= Normal distribution, 0.5- 1.0 = Application of character changing for dataset, and > 1.0 → application of Logarithmic change, #: Maximum permissible concentration (mg kg^{-1})

Correlation Analysis

Correlation analysis of some physical and chemical properties and heavy metal content of micro-catchment soils were performed (Table 2). Heavy metals have a significantly relationships organic content, clay and fine silt particles because of their high CEC (Tjahjono and Suwarno, 2018). A positive correlation was determined between sand content and Cu ($p<0.01$) and Zn ($p<0.01$) whereas, a negative correlation was detected between clay content and Cu ($p<0.01$) and Zn ($p<0.01$). In addition, there was a negative relationship between the EC value and Cu content of the soils whereas, a positive correlation between lime value and Cd content as well as a positive relationship between OM value and Cd content. Moreover, it was found that a significant negative correlation was found between the total copper content and the Cd concentrations, whereas a positive correlation was determined between the Cu content and Cr ($p<0.01$) and Zn ($p<0.01$) contents. There was a positive correlation between Cd content and Pb ($p<0.01$) content and a negative correlation with Cr content ($p<0.01$). In addition, positive relationships were found between both Cr content and Ni ($p<0.01$) concentration and between Pb content and Zn ($p<0.01$) concentration. Many researchers have obtained similar results in correlation analysis between OM, pH, lime and soil particle distribution with heavy metal content of soils (Demir et al., 2016; Özyazıcı et al, 2017; Tang et al., 2018). On the other hand, some researchers (Tume et al., 2006; Nizami and Rehman, 2018) reported that there was no relationship between pH and OM content of soils and heavy metal contents. Potential ecological risk index was calculated and evaluated both separately for each metal and to reveal the total potential impact of all metals.

Table 2. Correlation relationships between some physical and chemical properties of the soils and the heavy metals in the surface

Parameters	Sand, %	Clay, %	Silt, %	pH	EC, dS m^{-1}	$CaCO_3$, %	OM, %	tCu, mg kg^{-1}	tCd, mg kg^{-1}	tCr, mg kg^{-1}	tPb, mg kg^{-1}	tNi, mg kg^{-1}	tZn, mg kg^{-1}	PERI
Sand, %	1													
Clay, %	-0.906**	1												
Silt, %	-0.564**	0.161*	1											
pH	-0.087	0.203**	-0.195*	1										
EC, dS m^{-1}	-0.138	0.217**	-0.102	0.400**	1									
$CaCO_3$, %	-0.247**	0.255**	0.078	0.421**	0.016	1								
OM, %	-0.045	-0.022	0.148	-0.052	0.175*	0.107	1							
tCu, mg kg^{-1}	0.222**	-0.253**	-0.026	-0.042	-0.235**	-0.188*	-0.055	1						
tCd, mg kg^{-1}	-0.143	0.152	0.037	0.057	0.118	0.233**	0.244**	-0.231**	1					
tCr, mg kg^{-1}	-0.100	0.064	0.109	-0.013	-0.097	-0.057	0.102	0.209**	-0.210**	1				
tPb, mg kg^{-1}	-0.116	0.122	0.033	-0.196*	-0.033	-0.051	0.054	0.193*	0.272**	-0.011	1			
tNi, mg kg^{-1}	-0.054	0.068	-0.008	0.069	-0.017	-0.010	0.091	0.177*	-0.149	0.817**	-0.031	1		
tZn, mg kg^{-1}	0.200**	-0.245**	0.013	0.086	-0.143	-0.126	0.142	0.504**	0.006	0.100	0.230**	0.129	1	
PERI	-0.141	0.149	0.039	0.067	0.105	0.221**	0.246**	-0.174*	0.997**	-0.180*	0.336**	-0.120	0.046	1

**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed).

Assessment of PERI for soil samples

Among investigated heavy metals (Cu, Cd, Cr, Pb, Ni and Zn), only cadmium and lead significantly correlated with the PERI (Table 2). According to researcher, this case shows that the possibility of both heavy metals in the micro catchments located inducing ecological risks was quite high (Effendi et al., 2016). Distribution map of soil samples for PERI classes was given in Figure 4. It was not detected high PERI classes in the micro catchments of Ordu province. In addition, PERI results, it was detected that while 54% of total soil samples were low while, 42% of them were moderate class. According to the potential ecological risk index results, 54% of the catchment soils was low; 42% was moderate; 4% was at significant ecological risk level. Moreover, it can be seen that almost all micro catchments have moderate classes whereas some micro catchments coded 11, 13, 16, 6 and 12 have considerable class. On the other hand, two micro catchments coded 3 and 4 have no potential ecological risk.

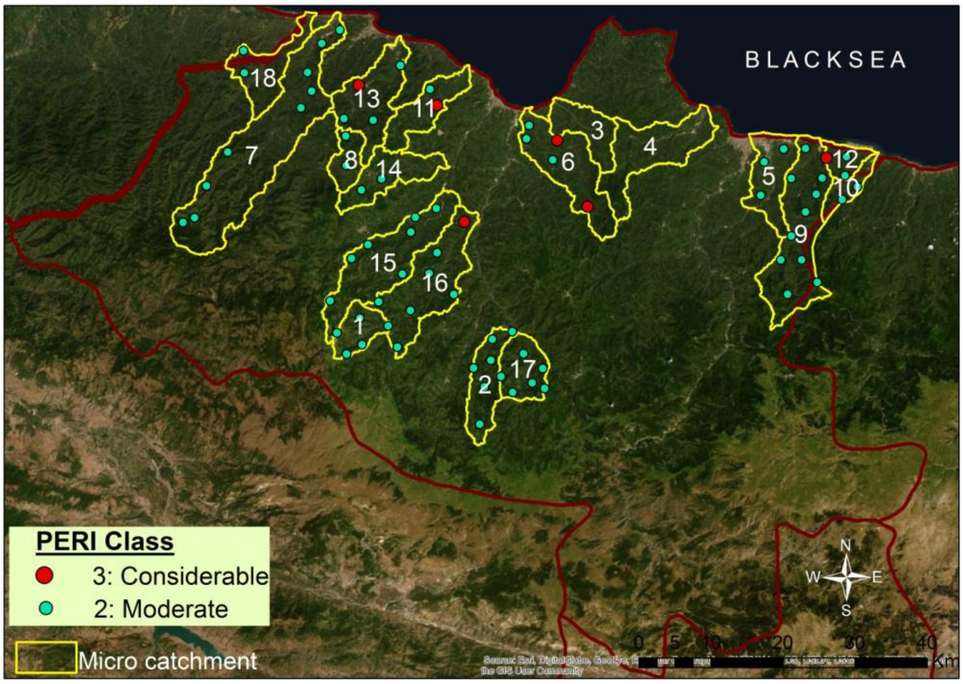

Figure 4. Distribution map of soil samples for PERI classes

In this present study, the greatest contribution to PERI comes from the Cd element. Accordingly, the ranking of heavy metals according to calculated average potential ecological risk indexes is Cd> Pb> Cu> Ni> Zn> Cr. In a study conducted by Islam et al (2015), considering the seriousness of potential ecological risks for single metal (PER), the decreasing order of pollutants Cd>As> Cu> Pb>Ni>Cr. Given the potential ecological risk (PERI), it has shown that all land soils are important for a very high potential ecological risk.

Conclusion

In addition to fossil fuels, chemical fertilizers, pesticides, fungicides and similar pesticide residues used in industrial applications and agricultural activities are pollutants that result from human activity. Heavy metals contaminated and accumulated in soils can cause many environmental, plant and human health problems, such as microbial activity, soil fertility, biodiversity and yield losses, and food chain poisoning. In this present study, heavy metal element contents for organic agriculture and their potential ecological risks were determined in some micro catchment soils of Ordu province. According to the Potential Ecological Risk Index (PERI), cadmium is the highest risk posing the toxic metals, whereas the other elements have low risk.

DAP, TSP and compound fertilizers consumed in agricultural soils to increase the yield, especially the Cd content is quite high and affect the many metabolic activities such as photosynthesis, respiration, ion uptake, growth and development by passing into the plant structure. That's why; the fact that Cd, which has the highest ecological risk value, is not associated with other elements suggests that it reaches the ecosystem in different ways. The anthropogenic and geogenic elements were considered for the enrichment of metals in soil. The average of ecological risk potential was classified as moderate and low risk in this current study. Moreover, the soil pH decreases with the use of acidic fertilizers and causes the activity of heavy metals to increase. We all have various responsibilities for the protection of our land and water resources. Nowadays, it is seen that there is not enough precautions for soil pollution which is a universal problem in our country and there is not enough studies about polluted soils. Therefore, chemical fertilizers should be applied with a fertilization program based on analysis results under expert control.

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