DETERMINATION OF LEAD METAL POLLUTION ALONG THE TRANS EUROPEAN MOTORWAY AGRICULTURAL SOILS BY ICP-OE SPECTROMETERS

ADILOGLU S.[1] and SAGLAM M.T.[1]

[1] Namık Kemal University Agricultural Faculty, Department of Soil Science and Plant Nutrition,59030 Tekirdağ, Turkey
E-mail: sadiloglu@hotmail.com

ABSTRACT

Environment pollution is a big problem for our country and all over the world, nowadays. Heavy metal pollution is very important in environmental pollution. It was investigated lead pollution of near the motorway agricultural lands in this research. For this purpose, 25 different agricultural areas for each edge of motorway and total 50 soil samples were taken from research areas in Tekirdağ. Then extractable lead contents of soil samples were determined. According to the results, lead contents of soil samples were determined between 1,346 and 6,546 mg kg^{-1}. These results were compared with critical values of this heavy metal. Lead pollution was obtained in research area soils. Lead pollution ratio was 60 % in the research are soils. According to the research results it should be recommended phytoremediation methods application in the research are lands for the improvement of lead pollution.

Keywords: Agricultural soils, pollution, Lead, motorway, ICP-OES.

1. Introductıon

Problems, resulting from human activities, such as fast and in an unbalanced way growing world population, undernourishment, unplanned urbanization, adverse land usage, dangerous and harmful wastes, fast receding green areas and forests, unconscious energy consumption, heavy metal loaded products created by the industrial sites and ore beds are the most important reasons of environmental pollution. It is a widely accepted fact that environmental pollution is the result of our modern life style. Heavy metal resulted soil pollution is one of the important issue that is given particular attention throughout the world. The sources of heavy metals and their impact on public health and environment, study and analysis of contaminated/polluted areas, improvement management techniques, and risk analysis are the main issues on which researches on heavy metal pollution/contamination in soil focused on. While studying the soil contamination, it must be bore in mind that the existing soil cannot be replaced by any means or increased in terms of surface area. Soil pollution is caused by a number of agents such as chemical fertilizers used to increase the annual agricultural output, pesticides, using of soil improvers and growing medias, discharging of solid and liquid pollutants and sludge, using polluted water in agricultural irrigation, atmospheric precipitations and radioactive fallouts. As a result of this, the limits of the ability of productive and trouble-free use the soil shrinks and this is continuing every day as a problem. With its 4 Organized Industrial Sites and European Free Zone, transportation facilities and high quality human resources, fast growing industrial investments and having natural resources like coal, natural gas, and ground water reserves that attract these investments, its proximity to Istanbul, and its being at the junction of the railways, motorways, airways, and sea route to Europe and other parts of the world, Tekirdağ, where this research has been conducted, is a strategic and attractive place for investments. As a result of extensively used motorways in the province, due to the above mentioned factors, a biological, physical, and chemical pollution in environmental components such as soil, air, and water has started. In the soil samples taken from the forest areas, and areas with heavy traffic, in Mexico City in Mexico, total concentrations of some heavy metals have respectively been measured as

followed; Zn concentration 195.8 mg/kg, 335.5 mg/kg, and 741.7 mg/kg; Pb concentration 49.7 mg/kg, 354.1 mg/kg, 1188.9 mg/kg; Cu concentration 43.5 mg/kg, 61.7 mg/kg, 98.2 mg/kg; Cd concentration 1.1 mg/kg, 1.4 mg/kg, 1.6 mg/kg. As it can be understood from the concentration rates, all the areas the samples taken from have been contaminated. According to the researchers, the high Pb concentration is caused by the traffic and the highest concentrations have been measured in the soils where the traffic is the heaviest (Morto-Bermea *et al*. 2002).
In a research, conducted in Istanbul, in the soil along the 18 km route of E-5 motorway between Topkapı and Avcılar Pb, Cu, Zn, and Cd concentrations have been measured. According to the results, the Pb, Cu, Zn, and Cd concentrations are at the maximum level in the mentioned area. It is observed that the soil in the areas with heavy traffic is contaminated by heavy metals (Sezgin *et al*. 2003). Lead, which is used in automobile batteries, in printing press, and in the industry, spread around and if it is exposed to, it causes poisoning and it ruins the central nerve system and inhibits the absorption of nutrients (Karatepe 2006). The limit value of lead concentration in drinking water has been declared as 0,05 mg/L by the WHO. Lead is used in batteries, petrol and paint industries, ceramics and porcelain production, as additive in gasoline, in printing press, glass industry, for insecticide production, and in polishing some pipes and cutlery. (Beliles 1975; Klassen *et al*. 1986).

Most of the Pb is the result of the tetraetil Pb which comes from the combustion of the fuel by the motor vehicle. Pb pollution is also seen in the sea as a result of carried industrial wastes through water in those areas (Yiğit *et al*. 1979; Güneş 1984; Abu-Hilal and Bardan 1990). Lead is a widely used metal in a great many of countries. It causes environmental pollution during the mining, processing, and using of Pb based productions. Pb can be seen in the air, food, water, soil and dust. It is generally found as inorganic forms in environment. However, through the usage of gasoline containing Pb and through the processes used to produce methyl Pb compounds, a small amount organic Pb arises. It is usually accumulated on the surface soil. This accumulated Pb compounds turn into carbonate, phosphate, and sulfate, which are difficult to dissolve (Ward *et al*. 1977). Soil, which is one of the most important components of the environment, is infected with Pb mainly through the industry and motorway vehicles. High level of lead in soil has a toxic influence. 4 mg/kg of a lead in soil solution does not create any toxicity problems for the plants (Chapman 1971).

A study, in which the lead contamination in agricultural land has been aimed to be researched into, has been conducted in the province of Edirne. 56 samples, which were searched in this study, revealed a minimum of 1.212 mg/kg and a maximum of 5.560 mg/kg lead content that could penetrate into the solution (Sarı 2009). When interpreted according to the limit values, 42, and 85 % of the soil in the area where this study conducted identified to contain lead contamination. The lead contamination along the motorway diminishes as you get further away from the motorway. This case has been explained with the low quality fuel used by the vehicles. In a similar research carried out in China, a correlation between the distance of the agricultural fields to the motorway and the lead concentration in the soil identified. Thus, the further away the land from the motorway the lower is the lead concentration in the soil (Ke- Lin *et al*. 2006).

2. Materials and methods

Çorlu, Çerkezköy, and Saray were the area of research and the soil samples, studied into, were taken from 50 different sample areas and from a depth of 0-20 centimeters from the wheat, sunflower, canola, and barley fields of 13 different villages along the motorway. The soil samples were taken from the villages of Pınarbaşı, İğneler, Ahimehmet, Bakırca, Karamehmet, Yulaflı, Seymen in Velimeşe and Ulaş districts, from Veliköy and Kızılpınar in Çerkezköy district, and from the villages of Beyazköy, and Göçerler in Saray district. The geographical location of the villages, from where the samples were taken is given in Figure 1 below. The ph values of the soil samples taken from the agricultural land are specified as 1: 2, 5 soils: water/ph meter. The lime content of the sample soils has been measured in calcimeter (Sağlam 2012). The organic substance content of the samples has been identified with Smith-Weldon technique suggested by Sağlam (2012). Phosphorus content has been measured whereby the soil phosphorus in ICP-OES mg/kg taken into solution with $NaHCO_3$ method. The alterable

potassium content in the samples was measured with the NH_4-OAc method suggested by Sağlam (2012). The salt content of the samples has been measured with EC-meter as it is suggested by the U.S. Soil Survey Staff (1951). The clay, silt and sand contents of the samples have been measured with the method suggested by Bouyoucos (Tuncay 1994). The extractable lead heavy metal contents of the samples have been measured by a buffer solution method suggested by Lindsay and Norvel (1978) and the amount penetrated from the soil into the chemical solution has been measured with the ICP-OES device in mg/kg.

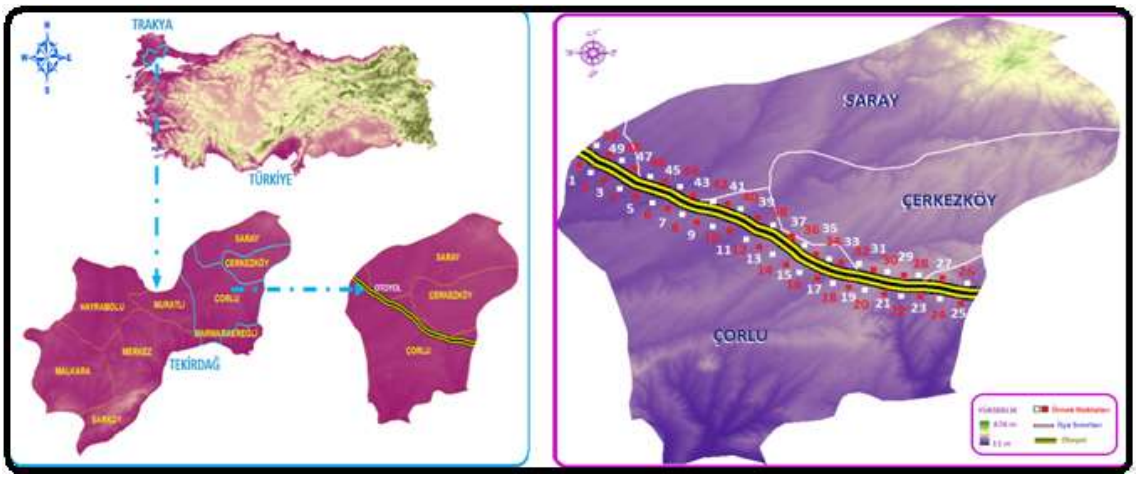

Figure 1. Soil samples geographical location

3. Results and dıscussıon

Soil reaction (pH) rates of 50 samples used in this research have been measured between a minimum of 5. 60 and a maximum of 7.20. The organic substance rate of the soils has reached to 3.01 % as a maximum. The minimum organic substance rate has been measured as 0.53%. When evaluated in terms of organic content, 84 % of the samples lack the sufficient level of organic substances. This result indicates the deficiency of organic substance which was shown in the researches carried out in the agricultural fields in Tekirdağ before (Eyüpoğlu 2002; Adiloğlu *et al*. 2011) once more.

According to the laboratory analysis, the lime content of the samples used in the research has increased to 2.80 % as a maximum. The minimum level of lime in the same research on the other hand has been identified as trace amount. With $NaHCO_3$ method, useful phosphorus analysis of the samples for the vegetation has been done. According to the results of the study, the useful phosphorus content of the samples has been measured between 8.87 mg/kg and 36.17 mg/kg. According to the results of the analysis of the soil samples, the alterable potassium content has been measured between the maximum and minimum rates of 102 mg/kg and 392 mg/kg. The potassium content of the soil in the research area has been measured as sufficient for the vegetation. The clay, silt and sand rates of the soil taken from the research areas have been identified with the Bouyoucos method. When evaluated by the texture triangle, it is identified that the rates of the soil textures changes from clay category (C) to clay loam (CL). More than half of the texture (56 %) category of the soil has been identified as sand clay loam (SLC) category.

According to the findings of the research, the extractable and soluble lead amount in the soil along the motorway in Tekirdağ has been measured between the minimum of 1.346 mg/kg and the maximum 6.546 mg/kg (Table 1)(Figure 2). The fact that there is a correlation between the lead contamination along the motorways and the motor vehicles has been identified by a series of researches throughout the world. The researchers have pointed the low quality fuel as the cause of the increasing lead contamination. According to great many researchers, the lead contamination in agricultural fields further away from the motorways decreases (Abu-Hilal and Bardan 1990; Kim *et al*. 2003; Nabulo *et al*. 2006; Ke- Lin *et al*. 2006; Wei and Yang 2010).

In a heavy metal research carried out in Iran, the industrial effects and extend of heavy metal contamination has been studied. In this study in Zanjan region, it has been found out that the level of Pb and Cd contamination in agricultural soil is high enough to endanger human health (Parizanganeh *et al*. 2010).

Table 1. Lead content in soil samples, mg kg^{-1}

Number	Lead (Pb)	Number	Lead (Pb)
1	4.250	26	2.349
2	5.627	27	4.660
3	6.546	28	5.363
4	3.287	29	4.239
5	4.575	30	3.051
6	2.507	31	6.240
7	3.292	32	3.554
8	4.541	33	3.730
9	4.544	34	2.635
10	5.733	35	1.998
11	4.143	36	2.526
12	4.309	37	2.218
13	3.581	38	2.005
14	3.840	39	3.400
15	2.100	40	2.812
16	1.346	41	1.460
17	2.334	42	2.127
18	2.889	43	4.370
19	4.676	44	2.246
20	3.344	45	4.322
21	4.265	46	2.297
22	2.713	47	4.456
23	3.428	48	3.565
24	4.160	49	3.352
25	4.787	50	3.734
Min.		1.346	
Max		6.546	

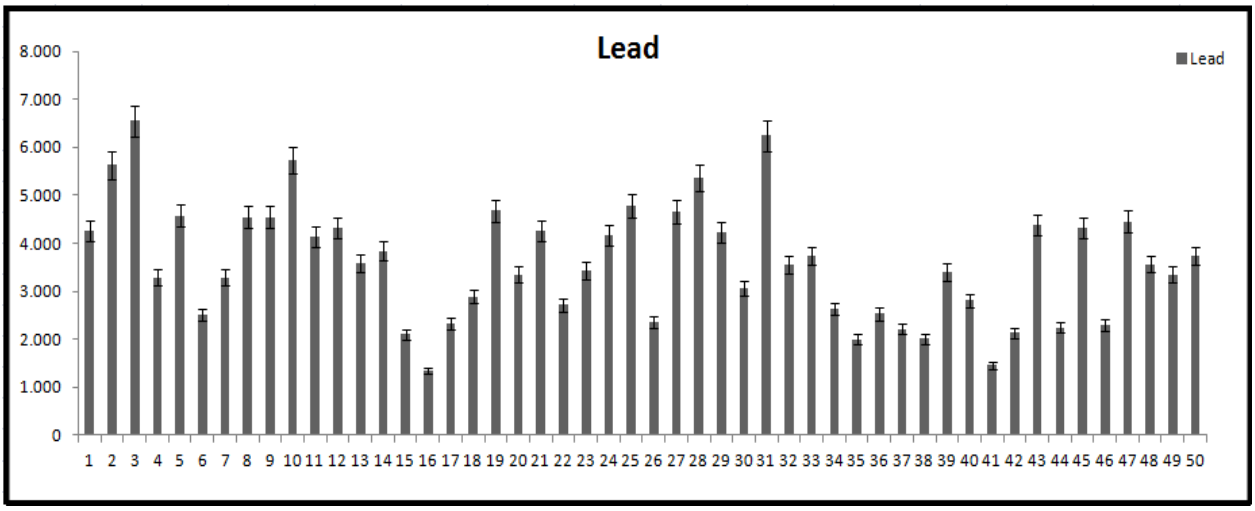

Figure 2. Change of lead content in soil samples, mg kg^{-1}

Aforementioned research revealed that the lead contamination in the soil in the above mentioned area is as high as 60%. The lead contamination can be seen in figure 3. The micro mobility of the lead amount in the soil of the research area has been displayed in figure 4. In a study carried out by Adiloğlu *et al*. (2011) in the coastal area of Tekirdağ province, namely in M. Ereğlisi, Çorlu, Şarköy and in the center to research into heavy metal contamination, samples from 25 different agricultural fields have been taken and extractable Cr,Cd, Ni, and Pb content detected. According to the findings, while the Cr, Cd, and Ni contents in the agricultural land along the coastal area have been detected in the permissible limits, Pb contamination has been detected as 24% and it is emphisized that the lead contamination must be more seriously observed. In another research into Pb contamination, carried out in Tracian Region, in 56 samples taken from the agricultural fields along the motorway in Edirne soluble lead has been detected (Sarı 2009). The results indicate that there is a considerable amount of lead contamination in the soil, and 43 % of the soil has been contaminated. The researcher has emphasized that immediate precautions should be taken.

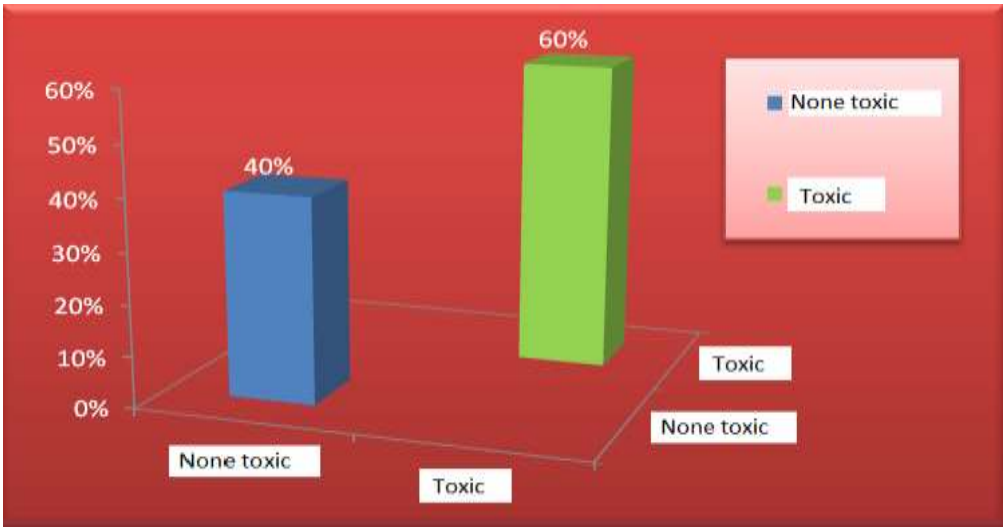

Figure 3. Heavy metal shows the case of the lead in research area.

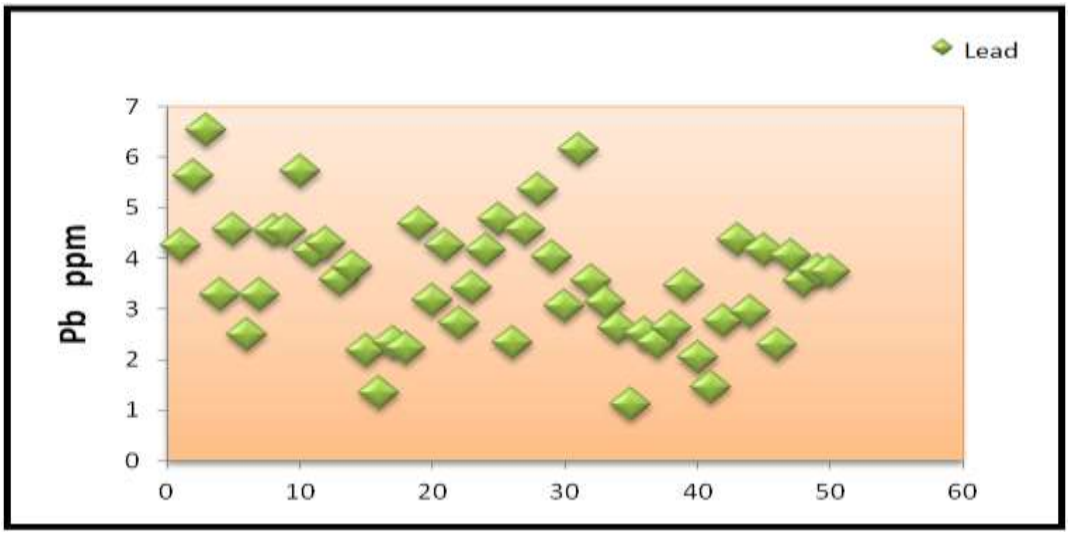

Figure 4. The micro mobility of Pb heavy metal in the soil

The lead pollution caused by the motorway traffic contaminates the cultivated plants in the fields around also. Another research into the lead contamination has been made along Kırıkkale – Kırşehir motorway (Çavuşoğlu *et al* 2008). Samples from *Sinapis arvensis* L plant have been

taken and looked into the amount of lead in plant leaves and it has been found out those plants further away from the motorway contain 5 % less lead than those closer to the motorway.

Another research into lead contamination has been done along the motorway of Giresun-Ordu. Along the 40 kilometers motorway, samples from lichen plant (*peltigera praetextata*) have been collected. The samples have been taken with 10 kilometers intervals both among the plants along the motorway and from the plants 100 meters away from the motorway. The findings revealed that the further away you go from the motorway absorbed lead amount in the plants decreased considerably. The researchers suggested that lichen plant could be used as an indicator in detecting lead contamination caused by the motor vehicle traffic (Çavuşoğlu *et al*. 2009).

Fitoremeditation is an environmentally friendly technique, which is widely and successfully used in a number of countries in order to regenerate heavy metal contaminated soil. And the pollutant heavy metals removed from the soil by using this method. In this method, the heavy metals causing the pollution are removed from the soil by using hyper accumulator plants. In one of the research into fitoremeditation, canola plant has been used as the hyper accumulator plant (Esringü 2012). At the end of a field test, researcher showed that it could be possible to remove lead contamination through using the canola plant

The correlation coefficient (r) between the clay content and lead in the soil samples used in the research and significance tests have been done. And the correlation coefficient between the clay content and the amount of lead has been r: 0.36, the level 5% has been considered as significant statisticaly. The correlation coefficient between the lime content of sample soils and the heavy metal Pb is r: 0.24. The correlation coefficient of lead, chrome and nickel was found significant with 5%. The correlation coefficient between pH rates of the soils and heavy metal lead has been found as (r) 0.14. The correlation coefficient between the pH rates of the soils and heavy metals like cobalt, chrome and nickel has been found significant with 5%.

Between the heavy metals and the organic contents of the soil significant correlation coefficients have been found. These coefficient for lead is -0.28 and it has been found with 5% as significant.

4. Conclusıon

The increasing amount of motorway transportation in the world, and cicculation of the agricultural products via motorways cause serious damages to the agricultural fields along the motorways. The most important one of these damages is heavy metal pollution and toxicity in the soil. The most important adverse effect of the environmental pollution caused by these heavy metals is that the possibility of reaching these heavy metals to the human body either through direct consumption of the plants that absorb these metals from the soil or consuming the animals that are fed with these contaminated plants. The problem of heavy metal contamination in the soil inThracian region, especially in the province of Tekirdağ, is higher than the other regions of Turkey. The reason of this is the relatively high human and industry caused heavy metal pollution in this region. The aim of this research is to specify the amount of heavy metal in the soil and the possible level of the contamination. With this object in mind, samples from 50 different points along the motorways have been taken and the soluble amount of lead has been analysed. According to the findings, the heavy metal contents of the soils for Pb have been measured between 1.346 and 6.546 mg/kg^{-1}. When compared to the critical limit values, these given findings indicates a serious level of pollution in the research area. The level of lead contamination is 60%.The cultivated land of Tekirdağ is one of the most fertile lands of Turkey. However, increasing number of motor vehicles and the industrial plants result in increasing amount of lead and other heavy metals in the soil and this poses a threat for the life of any kind in the region. The findings of this research indicate a high amount of Pb pollution in the agricultural land in this region. According to the results of this research, the Pb pollution in the depth of 0-20 cm in the agricultural land along the motorways in the region should be treated through the use of hyperacumulator plants and fitoremeditation technique in order to reduce this pollution under the limits of toxicity that would allow the cultivation of plants. Fiteromeditation metdod should be developed and its use should be widened to reduce the heavy metal

accumulation in the fields specified in this research.It is especially vital to treat the soils through fitoremeditation method in the research area, especially in the fields near to the industrial sites and along the motorways so that the heavy metal pollution doesn't endanger human and plant life.

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