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EFFECT OF IRRIGATION WITH MARITZA AND ERGENE RIVERS WATER ON SOIL CONTAMINATION AND HEAVY METAL ACCUMULATION IN RICE CROP

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Abstract

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This research was conducted to investigate the level of contamination in the soil and rice plants irrigated with Maritza and Ergene Rivers' water contaminated by industrial and domestic wastewater. Whether heavy metal concentrations in the water, soil and plant reached to critical levels was examined. Waters from Maritza River, Ergene River and mixed of Maritza and Ergene Rivers were qualified as the 1st, 4th and 3rd class, respectively, according to the inland water quality classification in terms of heavy metal loads. While Cr, Cu, Fe, Mn, Pb and Zn concentrations of the soils of all research area were below the critical limit, Ni concentrations of the soil were found to be above the critical limit with the values between 32.1 and 43.8 ppm. Cadmium and Co contents of the soil were very small. As for the plants, heavy metals were mainly concentrated in the roots. Lead concentrations of the rice irrigated by Ergene and mixed of Maritza and Ergene rivers' water changed between 0.25 and 0.35 ppm, which was above the critical level of 0.2 ppm suggested by Turkish Food Codex.

Key words: heavy metal contamination, Maritza and Ergene Rivers, rice, soil, water

Introduction

Rapid population growth and industrial development in order to maintain food supply for this population and keep well being of people lead to increases in industrial investments. The same situation is true for the Thrace Region, the European part of Turkey. The considerable part of the region has been occupied by industrial infrastructures. This has brought environmental problems, particularly soil and water pollution. As well known, water on the earth is in a continuous cycle by energy from the sun, which is defined as hydrologic cycle. Human being withdraws this water from the cycle for economical and vital requirement reasons and disposes into the same cycle after using. Mixing materials during this process change the physical, chemical and biological properties of the water, which is defined as pollution (Anonymous, 1991). While excessive pollution causes the loss of self-cleaning capacity of waters, it harms all water-related ecosystems.

Commercial fertilizers, pesticides, soil conditioners and hormones used to improve the quality and quantity of agricultural production can cause pollution of the soils at different levels. In addition, discharge of waste water from various industrial activities into the streams or water bodies without treating and then using this contaminated water for irrigation accelerates the process of soil pollution. Accumulated heavy metals in the soil such as Cd, Ag, Pb and Cr may have toxic effects since they are not disposed out of human body by natural physiological mechanisms. They tend to accumulate to a critical level when they enter into the food chain. This is considered the most important impact of soil pollution. Wang et al. (2003) reported that the dynamics of soil metal contamination of plants and the onward movement of metals should be elucidated. Their results indicated that the consumption of rice grown in paddy soils contaminated with Cd, Cr, or Zn may pose a serious risk to human health, because from 22 to 24% of the total metal concentration in the rice biomass was concentrated in the rice grain.

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Bahmanyar (2008) studied Cd, Ni, Cr and Pb levels in soils, vegetables and rice under long-term irrigation with industrial wastewater. They found that the concentration of these heavy metals were more in subsoil (15-30 cm) than in the surface soil (0-15 cm). The accumulation of heavy metals was higher in the roots of rice than in shoot and rice grain. Gupta et al. (2010) investigated the trend of metal accumulation in wastewater irrigated soil, which was in the order: Fe > Pb > Mn > Cr > Cd. Similarly, Mendez –Romero et al. (2003) reported this order as: Fe > Mn > Zn > Cu > Cr > Pb > Ni >Mo > Cd. It is widely accepted that there is nothing to do with a polluted soil other than abandoning it. Many factors and parameters should be considered in the investigation and evaluation of soil pollution. The reason for this is that among the complex physical, chemical, physicochemical, biochemical and biological processes in the soil, there is a natural balance.

Approximately, half of the rice production of Turkey is obtained from the Maritza and Ergene rivers basin, located in the European part of Turkey, known as Thrace, with very productive arable lands. However, Maritza and Ergene rivers, collecting surface water of the basin and used for rice irrigation, has been extensively polluted due to intensive industrialisation and urbanisation. The observations have revealed that the use of this contaminated water causes decreases in the yield of rice and destruction of the rice fields, contamination of underground water resources and soils. The objectives of this research are to assess the level of contamination in the soil and rice plants irrigated with Maritza and Ergene Rivers' water contaminated by industrial and domestic wastewater and provide practical measures to be taken.

Materials

The research area is located in the Maritza-Ergene River basin in the Thrace part of Turkey, between the 40° 35' and 41° 10' North Latitudes and 26° 00' and 26° 45' East Longitudes. The climate of the basin is completely characterised by the Mediterranean type with hot and dry summers and cool and rainy winters. According to the long-term meteorological data, annual average temperature is 14°C, annual average precipitation is 627.3 mm and annual average evaporation is 922.5 mm (Anonymous, 2009). Thrace region is about 2.37 million hectares and the research area covers about 1.37% of it, 32000 hectares. Alluvial great soil group is prevalent in the research area. This soil was carried and deposited by Maritza River and its branches. While no horizons exist, there are mineral stratums in different characteristics in the soil profile. Mineral compounds are heterogenic. They are mainly wet and continuously under the impact of groundwater.

Almost all research area is under irrigation and irrigated by Maritza River. Maritza River has been intensively polluted by Ergene River as well as its own pollution. Because, Ergene is an extensively contaminated river since it functions as a waste water canal carrying all waste water from industrial and settlement areas of all Thrace region. Ergene River joints into the Maritza River then it reaches to the research area and threats human and environmental health (Anonymous, 2000; Baser et al., 2007). Rice is the predominant crop in the research area. It is irrigated by waters from Ergene River, Maritza River and mixed of Ergene and Maritza rivers, depending on the location of rice fields. Rice variety of Osmancık-97, breed of Thrace Agricultural Research Institute, is generally sawn (Anonymous, 1997).

Methods

Since the research area is very large, the research was conducted at three locations according to the randomised complete block design with three replications. The treatments of the research were formed considering the source of water. The three locations formed according the three water resources were:

MAR: Area irrigated with water from Maritza River; ER: Area irrigated with water from Ergene River;

MARER: Area irrigated with water from mix of Maritza and Ergene rivers.

Three similar sizes (about 0.5 ha) and shapes of farmers' fields at each location were chosen as research plots. Therefore, there were 9 different farmers' fields or plots. Soil samples from 0-20 cm and 20-40 cm depths of three locations of each plot were collected to determine their physical and chemical properties. The analysis of pH, electrical conductivity (EC), $CaCO_3$, organic matter, available phosphor (P_2O_5) and potassium (K_2O), Exchangeable Sodium Percentage (ESP) and Boron (B) were done on the samples (Page, 1982; Klute, 1986). Infiltration characteristics of the soil were investigated in a plot representative for each research area.

Irrigation water samples were collected from each source at five different times representing different phonological stages of the crop between the first and the last irrigation. These five specified times of water sampling were: a) just before the sawing during the first irrigation, b) tillering stage, c) heading formation stage, d) flowering stage, e) grain filling stage. Analysis were done on the samples for pH, EC, residue sodium carbonate (RSC), sodium adsorption rate (SAR), total hardness (German), organic matter, NH4, NO3, PO4, chemical oxygen demand, biological oxygen demand, heavy metal (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) concentrations as described in APHA (2010). ICP-OES (TERKIN ELMER 5300DW) device was used for heavy metal analysis. As for the plants, heavy metal contents of roots, stems and grain were obtained on the samples collected from each plot during the harvest time.

Results and Discussion

Properties and heavy metal load of the soils in the research area

Soil textures of the three locations were different from each other. The textures for MAR, ER and MARER locations were sandy loam, clayey and sandy loam whereas their bulk density varied between 1.37 and 1.53 g/cm^3, 1.21 and 1.35 g/cm^3 and 1.39 and 1.57 g/cm^3, respectively. The plant-available water holding capacity of the soil for sandy loam texture was around 100 mm per 1.0 m soil profile while it was about 215 mm per 1.0 m soil profile for clayey soil texture. The water intake rates of the soils for MAR, ER and MARER locations were high, medium and very high respectively. In general, soils contain small amount lime, increasing form the upper part of the basin to the lower part.

The highest Boron concentration of the was observed in ER location with about 1.55 to 2.89 ppm, followed by MARER location with 0.58 to 2.42 ppm and MAR location with 0.34 to 1.20 ppm. This is seen as a serious problem that should be death with since it may be toxic affect on the crops. Similarly, ESP values were higher than 15% in ER area, which may cause problematic soils it the near future. Heavy metals concentrations of the investigated soils are also important issues since accumulated heavy metals can cause certain environmental and human health problems. For instance, it may cause decreases in the microbiological activities and productivity of the soils, lessen the biodiversity and even case of poisoning of living beings in the food chain. The heavy metal concentrations of the soils for the research area are presented in Table 1.

When the concentration of heavy metal in Table 1 are compared with the limit values of Turkish Soil Pollution Control Regulation (2001), only Ni concentrations in the sites of MAR and ER were higher that the suggested limit of 30 ppm (Anonymous, 2005). Ni can be easily uptake by the crops if it exists in the soil and cause phytotoxicity. Normally, Ni concentration of the plants varied between 0.1 and 5.0 ppm and it is 8 times more toxic than Zn to the plants (Tok et al., 2005). As for the other heavy metals listed in Table 1, none of their concentrations was above the limit values. No Cd was detected in the collected soil samples. It is highly soluble elements in the water and therefore rapidly spread in the nature. It is not necessary for human life.

Living organisms need some heavy metals, such as Co, Cr, Cu, Fe, Mn and Zn, in trace amounts but after a certain limits they may have toxic effect on the plant. However, some other heavy metals such as Cd, Ni and Pb are known useless to the plants and tend to accumulate in the body and cause serious health problems in the mammals. When the research sites were compared with each other in terms of heavy metal concentrations of their soil, similar results were obtained for the sites of MAR and ER. However, Cu, Mn and Ni concentrations of the soils in MARER area were found to be smaller than that of other sites.

Characteristics of irrigation water and their heavy metal loads

As explained in Materials and Methods section, there were three water sources (MAR, ER and MARER) and five sampling times. The analysis of MAR water provided information both about the suitability of this water for irrigation and the quality of water entering from Bulgaria. Electrical conductivity (EC) of MAR water varied between 0.45 and 0.55 dS/m during the irrigation season. Hardness (German Hardness, i.e. 10 mg/ l) changed between 9.3 and 13.8 SAR values were 0.51-1.05 whereas RSC value was around 0.15. There was no problem with quality of MAR water in terms of these EC, hardness, SAR and RSC parameters. The biological analyses of MAR water at five specified times are summarised in Table 2.

In terms of biological properties presented in Table 2, MAR water is classified as the 2nd class according to the inland water classification system as described in Anonymous (2004). The second class is considered "little contaminated"

Table 1
The heavy metal concentrations of the soils for the research area

Locations	Soil depth, cm	Heavy metal concentration, ppm								
		Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
MAR	0-20	-	3.8	49.5	29.8	20821	781.4	35.0	39.2	83.9
	20-40	-	4.9	51.8	18.6	20264	870.5	32.1	20.4	53.6
ER	0-20	-	4.0	48.0	30.4	24843	777.7	41.4	34.0	76.1
	20-40	-	5.3	58.4	29.8	25893	608.2	43.8	30.0	72.4
MARER	0-20	-	1.6	27.8	18.3	15563	380.2	21.1	24.0	50.0
	20-40	-	1.6	28.3	19.1	17012	441.4	23.2	24.1	55.0

and no problem when using for irrigation purposes. Heavy metal concentrations of the MAR water at five different times during the irrigation season are presented in Table 3. This table reveals that only Mn concentration values in heading formation, flowering and grain filling stages were above the suggested limits of 0.2 ppm (Anonymous, 2004) whereas concentrations of Mn in other stages and other heavy metals during the whole irrigation season are below the suggested limits in terms of suitability for irrigation. Ca and Co, which was thought to be in trace amounts, could not be detected by the method used in the research due to low concentrations. Therefore MAR water falls into the 1st class irrigation water (Anonymous, 2004). Table 3 reveals also that heavy metal concentration of MAR increase with the decrease in the amount of water flow in the river gradually from April to September and peak in grain filling stage.

As for ER water, EC increased from 2.5 to 4.5 dS/m from April to September, which fall into very highly saline water class and was not suitable for irrigation (APHA, 2005). SAR values were 10.3 in April and increased up to 19.2 in September, being above the upper limit of 15 towards the end of irrigation season. There was no problem in terms of hardness of water, ranged from 17.9 to 40.0 and in terms of RSC values changed between 0.82 and 6.6. The biological analyses of ER water at five specified times are summarised in Table 4. The ER water is classified as the 4th class, "highly polluted water", (Anonymous, 2004) in terms of biological properties during the whole irrigation season. Therefore it is not suggested for irrigation in plant

Table 2
The biological analysis of MAR water at five specified times

Biologic analysis parameters	Times of water sampling representing development stage of rice				
	Before sawing	Tillering	Heading formation	Flowering	Grain filling
BOI (Biolog. Oxygen Demand)	10.0	11.0	21.0	25.0	13.0
COI (Chem. Oxygen Demand)	-	-	3.46	-	-
OM (Organic Matter)	3.5	2.0	1.6	5.6	3.3
NH_4	0.19	0.45	-	0.24	0.34
NO_3	-	-	1.10	0.37	1.86
PO_4	1.55	-	1.00	1.30	1.00

Table 3
Heavy metal concentrations (ppm) of the MAR water at five different times during the irrigation season

Heavy metals, ppm	Times of water sampling representing development stages of rice				
	Before sawing	Tillering	Heading formation	Flowering	Grain filling
Cd	-	-	-	-	-
Co	-	-	-	-	-
Cr	-	-	-	-	0.002
Cu	0.002	0.003	-	-	-
Fe	-	-	0.854	0.742	0.535
Mn	-	-	0.191	0.436	0.205
Ni	0.001	0.001	-	-	-
Pb	-	-	0.003	0.002	0.015
Zn	-	-	-	-	0.320

Table 4
The biological analysis of ER water at five specified times

Biologic analysis parameters	Times of water sampling representing development stage of rice				
	Before sawing	Tillering	Heading formation	Flowering	Grain filling
BOI (Biolog. Oxygen Demand)	78.0	41.0	58.0	55.0	28.0
COI (Chem. Oxygen Demand)	21.3	-	43.3	45.5	58.0
OM (Organic Matter)	14.1	12.6	7.8	23.9	25.0
NH_4	5.04	7.27	8.00	9.13	9.75
NO_3	-	5.22	2.64	1.14	4.29
PO_4	5.15	2.60	4.80	4.84	6.13

and environmental health point of view. Heavy metal concentrations of this source, ER water, at five different times during the irrigation season are presented in Table 5.

When the heavy metal concentrations of ER water are compared with the inland water quality classes, it is defined as the 3rd class, "polluted", and irrigation water. AS expected, heavy metal concentrations increased with the decrease in flow rate gradually from April to September. Cd and Co concentration remained in the trace amount during whole growing season. As for the MARER water, samples were collected from the downstream about 5 km blow the junction where Ergene River Joint into Maritza River. The pH of it was around neutral, EC varied between 0.5 and 1.2 dS/m, hardness changed from 9.5 to 15.9, SAR was around 3.0 and RSC was about 0.5 during the irrigation season. Except EC values (the 3rd class), there is not any significant problem with the other parameters. Biological analysis results of MARER are given in Table 6.

MARER water can be categorised as the 3rd class "polluted" water according to inland water quality classification in terms of biological properties. Drainage conditions should be improved. Otherwise, it may cause environmental problems shortly. Heavy metal contents of the MARER water, at five different times during the irrigation season are presented in Table 7. As expected, the heavy metal concentrations of MARER water, mixed of MAR and ER water were between

Table 5
Heavy metal contents (ppm) of the ER water at five different times during the irrigation season

Heavy metals, ppm	Times of water sampling representing development stages of rice				
	Before sawing	Tillering	Heading formation	Flowering	Grain filling
Cd	-	-	-	-	-
Co	-	-	-	-	-
Cr	-	0.011	0.012	0.021	0.019
Cu	0.001	0.003	0.0035	0.0037	0.0040
Fe	0.021	0.032	0.625	0.206	0.505
Mn	0.15	0.20	0.374	0.590	0.615
Ni	0.001	0.001	0.001	0.0013	0,0015
Pb	-	0.010	0.012	0.020	0.035
Zn	0.10	0.114	0.235	0.425	0.775

Table 6
Biological analysis results of MARER at five specified times during the growth season

Biologic analysis parameters	Times of water sampling representing development stages of rice				
	Before sawing	Tillering	Heading formation	Flowering	Grain filling
BOI (Biolog. Oxygen Demand)	34.0	16.0	33.0	30.0	13.0
COI (Chem. Oxygen Demand)	-	-	20.6	-	-
OM (Organic Matter)	6.5	4.0	2.4	7.5	5.8
NH_4	1.77	0.92	-	1.84	0.39
NO_3	1.08	0.22	1.93	0.80	2.96
PO_4	2.88	-	-	1.60	1.00

Table 7
Heavy metal contents (ppm) of the MARER water at five different times during the irrigation season

Heavy metals, ppm	Times of water sampling representing development stages of rice				
	Before sawing	Tillering	Heading formation	Flowering	Grain filling
Cd	-	-	-	-	-
Co	-	-	-	-	-
Cr	-	-	0.048	0.011	0.061
Cu	-	0.002	0.006	0.007	0.005
Fe	2.453	3.564	4.986	0.730	0.610
Mn	0.258	0.325	0.540	0.504	0.050
Ni	0.001	0.001	0.001	0.0012	0.001
Pb	-	0.013	0.022	0.003	0.004
Zn	-	-	0.224	0.251	0.750

the two rivers, being the 2nd class, "little contaminated". Similarly, the quality of water decreased with the decrease in flow rate. No Cd and Co were detected in MARER water.

Heavy metal analysis done on rice plants

Heavy metal analyses were done on the grains (with and without husk), stems and roots of rice plant collected in three locations, representing the areas irrigated with MAR, ER and MARER water at harvest time and the average values are presented in Table 8. The highest heavy metal concentrations were obtained in the plants irrigated with ER water, followed by MARER and MAR water (Table 8). This reveals that heavy metal contents of the plants directly reflect the quality of irrigation water. The heavy metals reached to grain. As for the plant parts, the highest concentrations were found in the roots, which were followed by stems, grain with husk and grain without husk.

Cd and Co accumulated only in the roots. Fe and Mn were the most accumulated elements in all parts of the plants. These were followed by Zn and Cu. Ni accumulated in all parts of the plants from ER area while it accumulated only in roots, stems and grain with husk in the other locations. Although, Pb accumulated in all parts of the plants from all locations, it was above the allowable maximum limit of 0.2 ppm defined by Turkish Food Codex (Anonymous, 2008) in the grains without husk in ER and MARER locations.

Conclusions and Suggestions

Recently, rapid population growth, received migration, urbanisation and industrialization have led to significant environmental problems in Thrace region of Turkey. Ergene and Maritza River, being important fresh water sources of the region and used for irrigation, particularly irrigation of region's traditional crop of rice, have been affected by this problem seriously. This research was conducted to investigate the level of contamination in the soil and rice plants irrigated with Maritza and Ergene Rivers' water contaminated by industrial and domestic wastewater. The following conclusions are drawn:

- When the heavy metal concentrations of the rice cultivated soils are compared with the Soil Pollution Prevention Regulations of Turkey, only Ni concentrations of the soils in MAR and ER area are above the critical suggested limit.
- MAR water was medium saline, in the 2nd class in terms of biological parameters (slightly polluted) and the 1st class in terms of heavy metal concentrations. ER water has salinity and sodicity problem, is classified as the 4th class (highly polluted) and 3rd class (polluted) irrigation biological properties and heavy metal contents, respectively. MARER water is highly saline and sodic, polluted (the 3rd class) regarding biological analysis results and slightly polluted (the 2nd class) water according to the heavy metal contents.

Table 8
Average heavy metal concentrations of rice plants in three locations at harvest time (MAR: Maritza River, ER: Ergene River and MARER: Mixed of Maritza and Ergene River)

Location	Plant parts	Heavy metal concentrations, ppm								
		Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
MAR	Grain	-	-	0.60	2.14	42.6	3.7	-	0.16	8.11
	Grain with husk	-	-	5.92	2.05	57.3	44.8	0.02	0.12	9.78
	Stem	-	-	2.96	1.11	105.3	337.6	0.44	0.28	10.11
	Root	0.001	2.32	8.02	52.99	6530.0	545.4	4.81	15.56	20.71
ER	Grain	-	-	0.83	2.25	70.0	5.8	0.03	0.35	12.28
	Grain with husk	-	-	6.27	2.91	66.1	65.3	0.06	0.01	13.38
	Stem	-	-	2.90	3.36	287.7	422.1	0.97	0.39	18.77
	Root	0.24	3.19	14.23	40.31	7239.0	379.8	6.83	11.86	31.92
MARER	Grain	-	-	0.72	0.29	64.9	4.9	-	0.25	9.57
	Grain with husk	-	-	5.40	1.21	60.8	46.7	0.03	0.14	10.26
	Stem	-	-	2.63	2.31	252.7	359.4	0.78	0.52	12.54
	Root	0.10	2.97	13.05	11.85	7069.0	323.5	4.25	11.98	24.04

- The highest heavy metal concentrations are found in the plants irrigated with ER water, followed by MARER and MAR water.
- Pb concentrations of the crops are above the allowable maximum limit of 0.2 ppm defined by Turkish Food Codex (Anonymous, 2008) in the grains without husk in ER and MARER locations.
- The obtained results on heavy metal concentrations of grain reveals that there are serious risks of soil contamination and food toxicity if contaminated water is used for irrigation purposes.
- To control the pollution and minimize the possible risks, all relevant geographical and environmental data for the river basin should be collected and interpreted for the future countryside, urban and industrial settlement plan. Particularly, disorganised industrialisation in Maritza-Ergene River basin should be prevented and wastes should be managed carefully.
- Water quality should be continuously monitored.

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