PROBLEMS AND STATE OF THE ART OF WASTE WATERS FROM LEAD & ZINC PRODUCTION IN THE REGION OF PLOVDIV

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Introduction

The scientific technical achievements have often created situations by which the traditional interrelations with the nature turned out insufficient promising.

Recently technical contamination and its reflections are especially tangible on agricultural production. In case of disturbed agricultural background dangerous contamination arouse some troubles in the biological chain. The pollution of a biosphere with its elements is especially topical for a little country like Bulgaria.

The state of contamination with heavy metals of air, water, land and vegetation is anxiously in intensive agricultural regions. It requires new technological solutions and enormous investments.

The Nonferrous Metals Combine-Works near Plovdiv began to work in 1961 with initial project capacity of 40 000 t/year lead and 60 000 t/year Zinc. Since 1970-1975 the ecological failures have started when the real lead output was considerably increased, but the new installation for purification of gases and waste water are enough for the primary project. In this period has begun to increase the range of contamination with heavy nonferrous metals (lead, cadmium, zinc) and in the 80th has already outlined obvious conflict between the output of metals and the environment protection.

The ecological damage of agricultural region, around the Combine Works became evident in 1990. In 1992 lead production was limited by government decree and since then have been done some reconstruction.

The supplementary irrigation of waste water on the soil has caused secondary deterioration.

Methods and materials

The aim of the present study is to establish the concentration of heavy metals in the waste waters of the Combine-Works and their possibility to use for irrigation.

It was carried out pot experiment in five replications with maize, cultivars hybrid Stara and hybrid Helga for investigation of waste water influence on the growth during 1996-1997.

The production of some nonferrous metals and their emissions in waste water are shown in table 1, which quantities are got from lead and zinc production.

Quantities of Zinc, lead and cadmium in 10^{-9} g/hour and concentrations in waste water

Table 1

Production	Zinc 10^{-9} g/h			Lead 10^{-9} g/h			Cadmium 10^{-9} g/h		
	1989	1993	1995	1989	1993	1995	1989	1993	1995
Lead	2.85	-	-	1.75	-	-	0.17	-	-
Zinc	26.8	-	-	1.56	-	-	0.17	-	-
total	29.6	4.38	1.64	3.31	1.3	0.55	0.34	0.08	0.26
Waste water mg/dm^3	14.2	5.90	1.37	1.58	1.8	0.46	0.16	0.11	0.22

According the standard legislative regulations in Bulgaria have been accepted the following recommended concentration of heavy metals in irrigation waters, shown in table 2.

Threshold values for irrigation waters, mg/dm^3

Table 2

N	Heavymetals	II Category	III Category
1	Lead	0.05	0.20
2	Zinc	5.00	10.00
3	Copper	0.10	0.50
4	Arsenic	0.05	0.20
5	Iron	1.50	5.00
6	Manganese	0.30	0.80
7	Cadmium	0.01	0.01
8	Clorine	300	400
9	Sodium and Potassium	-	-
10	Magnesium	-	-
11	Calcium	-	-

Results and discussions

The concentrations of some heavy metal were determined by AAS. Data, obtained for some months in 1996 are shown in table 3.

Concentration of heavy metals in waste water during 1996, mg/dm^3

Table 3

N	Heavy metal	Investigated period				
		February	March	April	May	June
1	Iron	0.3000	0.030	0.642	0.502	0.009
2	Manganese	1.7000	0.105	0.252	0.279	0.150
3	Cadmium	0.1420	0.045	0.358	0.301	0.241
4	Lead	0.3140	0.085	0.728	0.978	0.174
5	Arsenic	0.0003	-	-	-	0.001
6	Copper	0.0800	0.006	0.153	0.098	0.020
7	Zinc	1.5000	0.232	2.890	1.840	0.377

During February-June, 1996 have been observed changeable concentrations of investigated heavy metals in waste water. Their values have exceeded permissible thresholds of trace elements in irrigation waters in many cases.

The maize, grown in pots was irrigated with waste water, which analysis as following:

lead - 1,6 mg/dm^3
cadmium - 0,72 mg/dm^3
zinc - 24,2 mg/dm^3
copper - 0,12 mg/dm^3
pH - 5,72

The results of biometry indeces of the two hybrids are show in table 4. It was measured the height of the stem and the length of the central root the plant, irrigated with waste water and distilled water.

The biometry indeces of maize, hybrid Stara at 14th day in cm

Table 4

N	Treatment	Replications									
		1		2		3		4		5	
		r*	s**	r	s	r	s	r	s	r	s
1	Control (distilled water)	14.0	18.1	16.7	22.5	16.1	23.6	14.2	24.7	17.9	22.6
2	Waste water	15.2	24.9	14.7	22.2	15.5	21.1	15.3	23.6	16.8	21.2

*- root

**- stem

The biometry indeces of maize, hybrid Helga at 14th day in cm

Table 5

N	Treatment	Replications									
		1		2		3		4		5	
		r*	s**	r	s	r	s	r	s	r	s
1	Control (distilled water)	14.8	23.5	17.0	25.1	14.1	24.8	14.8	21.9	13.6	22.7
2	Waste water	12.2	26.3	12.8	25.8	12.9	20.8	14.2	22.4	14.8	21.2

*- root

**- stem

All data are computed by analysis of variance. Statistical data processing of the root length indicated significant differences with $p \leq 0.05$.

It was done an attempt to reduce the contamination of waste water. The water was treated with 8% sodium sulphide with quantity of 0,006 dm^3/m^3.

The treated waste water was analyzed after 24 hours and 48 hours. Table 6 gives trace element analysis for these water samples.

Concentration of heavy metals in treated waste water, mg/dm^3

Table 6

N	Heavy metal	Primary level	After 24^h	After 48^h
1	lead	1.60	0.70	0.60
2	cadmium	0.72	0.24	0.23
3	zinc	24.20	0.12	0.11
4	copper	0.12	0.06	0.02

In this way could be reduced the heavy metal concentration considerably. The quality of water is nearly within the suggested limits in table 2. The greatest percent change is in zinc and copper. The reduction of lead and cadmium is 3 times. In spite of all irrigation with this kind of water is a problem.

Conclusion

From carried out investigation can be drawn the following conclusions:

1. The waste waters of the Nonferrous Metals Combine-Works, hear Plovdiv are significantly contaminated with heavy metals.
2. They are conducted by external open channel to River Tchepelarska, the tributary of River Maritza. The secondary contamination creates ecological problems of rivers.
3. The utilization of waste water for irrigation of maize influences on roots and soil. There are sufficient accumulation of heavy metals in soils.
4. The suggested technological treatment of the waste water with sodium sulplide will improve its quality and became suitable for irrigation.

Bibliography

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Summary

Problems and state of the art of waste waters from lead & zinc production in the region of Plovdiv. The Nonferrous Metals Combine-Works near Plovdiv is an enterprise with 100% state property and is the largest producer of lead and zinc in Bulgaria. In 1961 the Combine was built and began to produce 40 000 t lead and 60 000 t zinc.

Since 1970-1975 the ecological failures have started when the real lead output was considerably increased, but the new installation for purification of gases and waste water are enough for the primary project of 1961. In 1990 there was ecological disaster in the agricultural region around the Combine. Since March, 1992 lead production was limited to 30 000 t yearly by government decree and has began reconstruction of it.

In present study are investigated waste water, which are conducted by external open channel to River Tchepelarska, the tributary of River Maritza. Some indices were estimated. The content of lead and cadmium is over permissible level.

The pot trials were carried out with maize (Hybrid Stara and Hybrid Helga), irrigated with waste waters. The results of biometrics indices are analyzed.

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