RESEARCHES REGARDING THE INCIDENCE OF LEAD IN GRAINS

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Abstract
Grains are the base of human nutrition and in this way beca,use of large spreding in, diets are, the most dangerous. Assesing the heavy metals must be the carefully and systematicly dome.

The paper present researches results obtained in stationary experiments, carried out at Agricultural Research and Development Station Oradea, regarding the influence of nitrogen, phosphorus and potassium fertilizers. The study was conducted in the frame of project HURO 1001/323/2.2.2 Grains Safety during 2012 in the laboratories of University of Oradea, Faculty of Environmental Protection, Food Engineering Department. There was made the assesment of the lead presence and prospectives about toxicological issues. Lead concentration had the lowest value in the unfertilized variant, the value (wheat grains 0.037 mg/kg and maize grains 0.047 mg/kg) being under the maximum allowed (1.0 mg/kg). In case of the fertilized version with $N_{160}P_{160}$, the lead concentration had the highest value, 0.047 mg/kg in the case of wheat granis, respectively 0.059 mg/kg in the case of maiye grains, but even in this case it was located beneath the maximum limit allowed.

Key words: wheat, maize, grains, lead, fertilizers, stationary experiments.

INTRODUCTION

There is an increasing of the strong demands to provided grains with high inocuity because of the intensive use of chemicals in agriculture and the actual trend that recomand "healty" nutrition (A. Timar, 2010).

In the case of the wheat and maize culture, application of different doses of chemical fertilizers, respectively of different doses of lead increased concentration of lead in grains and straw without exceeding the limit, having negative influence on animals and people (Cataldo D.A. and Wildung R.E., 1978, Turner A.P., 1994, Hough R.L. et al, 2003, Ciobanu G., 2007, Salwa Al., 2009, Samuel A.D., 2009, Orosz F., et al, 2009, Vuşcan A. et al, 2009, Hejcman M. et al, 2013). It has been shown that it is possible to predict the concentrations of cadmium and lead in wheat and maize grains on the soil total content of heavy metals, unlike copper and zinc whose concentrations can not be predicted this indicator (Ross S.M. and Kaye K.J., 1994, Nan Z. et al., 2002, Abd El-Aziz, S.M. et al, 2009, Vuşcan A. et al, 2010, Vuşcan A.N, 2014). Irrigation with wastewater increase the concentration of heavy metals (Cu, Cr, Mn, Ni, Pb and Zn) in roots, stems and seeds of wheat plants, the most significant increase being in

the case of manganese and zinc (M. Karatas et al., 2006, Samuel A.D. et al, 2008, Szabo G. et al, 2008, Shirazi S.M. et al, 2014).

Is important to evaluate if the products are satisfied the consumers demands and food safety requirements (Şandor M. et al, 2008, Hodişan N. and Timar A., 2010, Arapi V et al, 2012). In this way the study propose a the investigation about the wheat and maize quality from toxicological point of view. The parameter taken in to study was lead concentration in different experimental scheme.

Methods used for analysis are according with romanian standards and are quoted in latest studies.

MATERIAL AND METHOD

Taking samples: Samples were taken from the bulk after harvesting. We use to take samples for quality control the cylindrical probe. Procedure was according to Ardelean M. (2008).

Obteining working samples: we form successively elementar, brutto, homogenized, laboratory and work samples according with Timar A. (2008).

There were study first organoleptical parameters in order to eliminate from the study the samples that were not according with specifications. If this parameters was out of normal range, grains samples were considered out of standards, affected by different kind of degradation and study of those samples was ended.

The parameters taken in study were: lead concentration, in this way we use Official Methods of Analysis of AOAC International - 19th Edition, 2012. The study was conducted in 2012 and had the following methodology.

Samples taken in to study were the following:
- winter wheat *NP fertilized*,
- winter wheat *NP and farmyard manure fertilized,*
- maize *NP fertilized*,
- maize *NP and farmyard manure fertilized.*

Number of samples was 5 for each repetition. There were 10 repetitions for each kind of samples.

Grains concentration of heavy metals was determined using the mineralization with sulphuric and perchloric acid mixture method. The results were determined by using the atomic absorption spectrophotometer.

Correlations between doses of mineral fertilizers (N, P, NP + manure) – lead in wheat and maize were calculated using Microsoft Excel; of the 5 types of functions available on the program (linear, exponential,

logarithmic, polynomial and power) was chosen the function with the highest value of R^2.

Research was conducted in the laboratory research and production, the own laboratory of University of Oradea, Faculty of Environmental Protection, Department of Food Engineering. All the data were processed by a i3 Acer Aspire 5733 laptop.

RESULTS AND DISSSIONS

All the samples taken in to study had conform organoleptical properties. Results of the research conducted in the lead analisys were as following.

Table 1

The influence of doses and combinations of NP fertilizers on lead concentration in winter wheat grains, average data, (2010-2012)

Variant	Pb concentration		Difference		Statistical significance
	mg/kg	%	mg/kg	%	
N_0P_0	0.038	100	-	-	Control
$N_{40}P_{40}$	0.042	109.9	0.004	9.9	-
$N_{80}P_{80}$	0.045	117.4	0.007	17.4	-
$N_{160}P_{160}$	0.047	123.5	0.009	23.5	*
		LSD 5%	0.008		
		LSD 1%	0.016		
		LSD 0.1%	0.024		

In the table 1 presented bellow it was shown that the lead percentage had higher levels in the variant fertilised with $N_{160}P_{160}$. This is explained by the higher dosage and high rate of bioacumulation. There was also shown that the values not excede the Maximum limits alowed in this kind of agrifoodstuff.

In the mathematical modeling results show that the type power function $y = 0.037x0.152$, $R^2 = 0.623$ best quantified the link between doses of fertilizers with nitrogen and phosphorus in the lead concentration of wheat grains (Fig. 1).
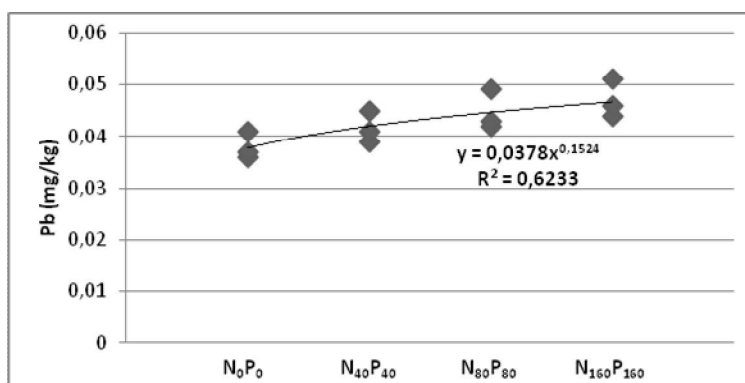

Fig. 1 Correlation between doses of NP fertilizers and lead concentration in wheat grains

Table 2

The influence of NP fertilizers and manure on lead concentration in winter wheat grains, average data, (2010-2012)

Variant	Pb concentration		Difference		Statistical significance
	mg/kg	%	mg/kg	%	
N_0P_0 + 0 t/ha farmyard manure	0.037	100	-	-	Control
$N_{50}P_0$ + 20 t/ha farmyard manure	0.040	108.8	0.003	8.8	-
$N_{50}P_{50}$ + 40 t/ha farmyard manure	0.043	116.2	0.006	16.2	-
$N_{100}P_{100}$ + 60 t/ha farmyard manure	0.045	121.6	0.008	21.6	*
		LSD 5%	0.007		
		LSD 1%	0.013		
		LSD 0.1%	0.021		

The results of the study were very interesting. It is shown that there is a direct corellation betwen the fertilizers doses and the presence of lead in the final product. The level in grains was under the maximum allowed limits in all variants (Table 2).

Mathematical modeling of results of lead concentration in the wheat grains from trial's variants with NP and farmyard manure studied, show that the function type power is best statistically, $y = 0.036x0.141$, $R^2 = 0.745$ (Fig. 2).
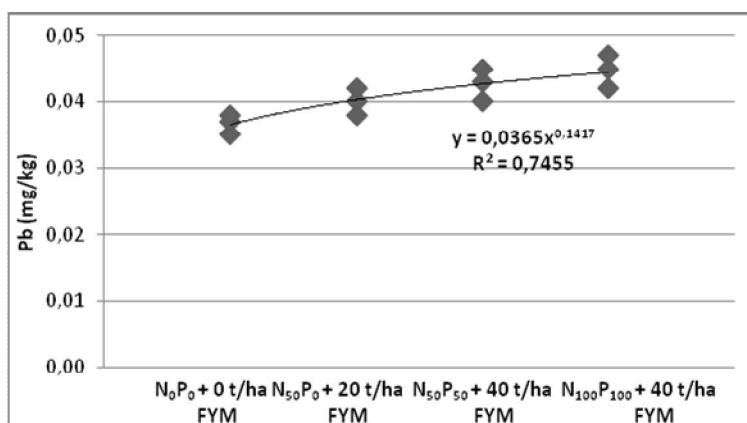

Fig. 2. Correlation between doses of NP fertilizers and farmyard manure and lead concentration in wheat grains

*FYM – farmyard manure

The lead concentrations of the maize grains stored in bulk after harvesting was similar to all samples taken in study before. That suggest a common attitude of maize and winter wheat regarding the biacumulation of lead in the Crisana plane according with the fertilization proposed. Also the values recorded were in the normal range for this kind of agrifoodstuff (Table 3).

Table 3

The influence of doses and combinations of NP fertilizers on lead concentration in maize grains, average data, (2010-2012)

Variant	Pb concentration		Difference		Statistical significance
	mg/kg	%	mg/kg	%	
N_0P_0	0.047	100	-	-	Control
$N_{40}P_{40}$	0.052	111.8	0.006	11.8	-
$N_{80}P_{80}$	0.056	121.0	0.010	21.0	-
$N_{160}P_{160}$	0.058	124.6	0.011	24.6	*
		LSD 5%	0.010		
		LSD 1%	0.023		
		LSD 0.1%	0.035		

Mathematical modeling of results of lead concentration in the maize grains from trial's variants with nitrogen and phosphorus studied, show that the function type power is best quantified the link between doses of fertilizers containing nitrogen and phosphorus and lead concentration in maize grains, $R^2 = 0.741$ (Fig. 3).
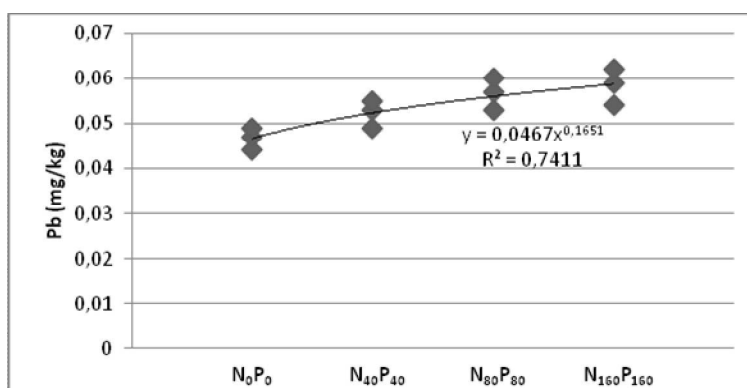

Fig. 3 Correlation between doses of NP fertilizers and lead concentration in maize grains

Table 4

The influence of NP fertilizers and farmyard manure on lead concentration in maize grains, average data, (2010-2012)

Variant	Pb concentration		Difference		Statistical significance
	mg/kg	%	mg/kg	%	
N_0P_0 + 0 t/ha farmyard manure	0.047	100	-	-	Control
$N_{50}P_0$ + 20 t/ha farmyard manure	0.052	110.8	0.005	10.8	-
$N_{50}P_{50}$ + 40 t/ha farmyard manure	0.055	118.5	0.009	18.5	-
$N_{100}P_{100}$ + 60 t/ha farmyard manure	0.056	120.6	0.010	20.6	*
		LSD 5%	0.009		
		LSD 1%	0.016		
		LSD 0.1%	0.024		

Values recorded for maize regarding the lead concentration shown that there is also for maize a direct corelation within the fertilizers dosage and the percentage of lead in grains. The ratio is not so high because of higher production potential of the maize (Table 4).

Mathematical modeling of results of lead concentration in the maize grains from from trial's variants with nitrogen, phosphorus and farmyard manure in the study shows that type polynomial function $y = -0.001x2 + 0.008x + 0.039$, $R^2 = 0.864$, quantified the best relationship between doses of fertilizers and the concentration of lead in the maize grains (Fig. 3).
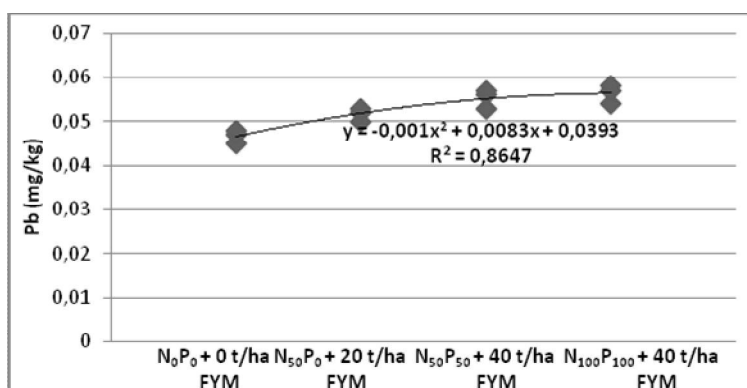

Fig. 4 Correlation between doses of NP fertilizers and farmyard manure and lead concentration in maize grains

*FYM – farmyard manure

CONCLUSIONS

Following the development of the present work there are few conclusions and recommendations:

♣ the concentration of lead in the wheat and maize grains from the mineral or organo-mineral fertilized variants increased compared to the unfertilized control, but the differences are statistically significant only in the variants with the highest doses of mineral and organic-mineral fertilizers, so for wheat variants $N_{160}P_{160}$, respectively $N_{100}P_{100} + 60$ t/ha of farmyard manure the registered concentrations were 0.047 mg/kg and 0.045 mg/kg, and in the case of maize the concentrations were 0.058 mg/kg and 0.056 mg/kg.

♣ cereals have the same attitude - direct correlation - regarding the fertilization and bioaccumulation, our researches highlights that increasing doses of fertilizer, especially those with phosphorus, leads also to the increase of lead concentration.

♣ the maximum allowed limits were never exceeded;

♣ because the cropping was conducted in the same climatic conditions it seems that climate is not very important in bioaccumulation of the lead;

♣ we strongly recommend implementing of traceability regarding fertilizers in order to avoid higher bioaccumulation ratio;

♣ recommended regular training of the staff by enrolling in training courses on good manufacturing practices (GMP) and Good Hygienic Practices (GHP) because the product can be affected by several risk factors on long term cropping.

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