# INFLUENCE OF INDUSTRY POLLUTION ON THE EFFICACY OF COMMON LAMBSQUARTERS (CHENOPODIUM ALBUM L.) CONTROL BY PYRIDATE

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**Abstract:** In the vicinity of copper foundry "Głogów" agricultural farms exist for 35 years. The aim of the work was to determine if biotypes of common lambsquarters (*Chenopodium album* L.) growing for many years in heavy metals polluted environment showed any differences in the efficacy of herbicides' control. Seeds of *C. album* were collected near Głogów, from four cultivated fields with different content of heavy metals in soil (mainly copper). From these seeds experimental plants were grown in greenhouse conditions. In greenhouse experiments the efficacy of control of *C. album* by different pyridate (6-chloro-3-phenylpyridazin-4-yl S-octyl thiocarbonate) doses also in combinations with 0.2% CuSO<sub>4</sub> was compared. Also the efficacy of pyridate in control of *C. album* seedlings which were grown in pots with soils collected from the vicinity of smelter was tested. Additionally, in growth chamber, the effect of increasing copper concentration on shoot and root growth was analyzed. Pyridate showed similar efficacy on tested populations of *C. album* without respect of soil contamination level, seeds' origin and presence of copper ions in spray solution in which herbicide was used in full dose. Statistical differences were observed when herbicide was applied at ½ pyridate full dose, especially in the presence of Cu<sup>2+</sup> ions in spray solution.

Key words: Chenopodium album, copper, herbicide, pyridate, industry pollution

#### INTRODUCTION

Many classes of chemical contaminants are found in aquatic and terrestrial environments. Most of them are generated in large quantities by industrial processes. Smelters have been recognized as important sources of the gaseous and dust pollution. Heavy metals are present in the environment at concentrations that can be hazardous to the biosphere, and Cu<sup>2+</sup> ions are one of the most prevalent and toxic among heavy ones. For all living organisms, Cu<sup>2+</sup> is an essential trace element. None the less, beyond a threshold concentration Cu<sup>2+</sup> can become toxic. The mechanism of

the toxicity mentioned above varies depending on the concentration of this metal ion (Yruela et al. 1996).

Agricultural farms exist on contaminated areas in the vicinity of Copper Foundry "Głogów" for 35 years (Rosada 1996). At the beginning copper smelter emitted large quantities of pollutants causing changes of ecosystem in its surroundings. Thanks to technical progress, from several years Copper Foundry systematically introduced modernizations of technological processes to restrict gaseous and dusty emissions. In 1980 Copper Foundry still emitted in metal containing dusts among other things over 1400 Mg of copper per year. In 1990–1994 emission of copper decreased from 130 to 75 Mg and in 1995–2002 from 35 to about 7.5 Mg of copper per year (Rosada and Urbańczyk 2003). Because all the time heavy metals coexist with herbicides used by farmers, it seems imperative to study the combined effects of these two groups. Particularly, if both i.e. Cu2+ ions and herbicides influencing plant photosynthetic system are involved, it can cause similar damages and changes in metabolic processes and may have synergistic or antagonistic effect (Babu et al. 2001; Teisseire et al. 1991; Teisseire and Vernet 2000). There is a supposition, that biological activity of plant protection products (majority of them are herbicides) may be modified by emitted heavy metals.

This paper reports the results of the study on determination if biotypes of common lambsquarters (*Chenopodium album* L.) which grow for many years in the vicinity of copper foundry "Głogów", therefore in the environment polluted by heavy metals, show any differences in the efficacy of herbicides' control.

## MATERIALS AND METHODS

Seeds of *C. album* were collected from four cultivated fields in the vicinity of copper foundry "Głogów", which differed in heavy metals content in soil (Table 1). Soil samples were taken out from the same localities as the seeds. Comparative seeds were collected from the field at Skórzewo near Poznań (approximately 112km far from Głogów). For measuring the heavy metal concentrations in soil, the atomic spectrophotometrical assay (ASA) was used.

C 11	Total concentration in mg/kg of dry matter						
Soil	Cu	Pb	Zn	Cd	As		
Skórzewo (So)	31.8	37.1	34.8	0.25	3.56		
Żukowice (G-1)	207.2	49.0	50.6	0.37	4.40		
Bogomice (G-2)	224.6	77.5	43.9	0.22	7.02		
Brzeg Głogowski (G-3)	99.4	41.0	26.4	0.42	4.25		
Glinica (G-4)	56.2	38.7	32.4	0.18	3.18		
Standard according to Dz. U. Nr 165, poz. 1359	150	100	300	4	20		

Table 1. Concentration of heavy metals in four samples of soil collected in the areas of Copper Foundry "Głogów" emissions (G-1..G-4) and in soil from Skórzewo

#### Biological tests in growth chamber

Four populations were tested in respect to copper tolerance, using the method of determination of shoot and root elongation (Wilkins 1978). Seeds of three populations collected from fields near Głogów: G-1, G-3 and G-4 and one from Skórzewo (So) were used in experiments. Cultivation was carried out in Petri dishes on Hoagland's diet solution with copper concentrations ranging from 0 to 20 mg/dm<sup>3</sup> (Table 2). After 10 days, the height of hypocotyle and the length of roots of 30 seedlings for each combination of copper concentration were measured. The experiments were repeated three times. Results as average of 90 measurements for each combination were presented. A statistical analysys was made by WinSTAT® for Microsoft® Excel Version 2001.1 R.Fich Software. For tests use one-factor ANOVA (analysis of variance) methods called "multiple comparisons", also known as "a posteriori" or "post hoc" tests. Analysis of variance was made separately for shoots and roots in each population.

 Table 2. The effect of increasing copper concentration [in mg/dm³ of diet] on shoot and root growth of four populations of *Chenopodium album* (three from Głogów and one from Skórzewo)

Dose of	Length of shoots [mm]				Length of roots [mm]			
copper	So	G-1	G-3	G-4	So	G-1	G-3	G-4
0	22.33	22.90	21.47	21.63	24.80	25.67	24.57	23.80
0.5	22.43	23.07	22.50	21.47	27.07	27.70	23.67	23.43
1	21.87	23.07	21.00	21.43	24.23	25.93	24.60	23.27
2.5	20.43	22.63	21.97	21.60	<b>18.93</b> <sup>1</sup>	23.17	21.93	21.83
5	<b>19.37</b> <sup>1</sup>	22.30	20.67	20.50	14.60	17.40 <sup>1</sup>	15.80 <sup>1</sup>	<b>12.77</b> <sup>1</sup>
7.5	18.57	21.23	21.13	<b>19.53</b> <sup>1</sup>	5.23	8.93	7.80	5.73
10	18.10	20.43 <sup>1</sup>	<b>19.57</b> <sup>1</sup>	19.67	3.97	6.10	4.20	3.87
15	17.27	19.33	19.07	18.97	1.93	3.87	3.17	3.40
20	15.67	17.90	17.50	17.90	1.47	2.87	2.57	2.83

<sup>1</sup> with effect from entries in bold, all values below are significantly different from the entry for copper free diet (p < 0.05)

#### **Biological tests in greenhouse conditions**

In first experiment, seedlings gotten from seeds collected near Głogów (G-1, G-3 and G-4) were grown in pots filled with soil originated from the same localizations as the seeds and comparatively in the same soils from Głogów seedlings from Skórzewo (So) were planted. As plants had reached the stage of 4 leaf pyridate (Lentagran 45 WP<sup>1</sup>) was applied in the dose of 1.35 kg/ha and the doses reduced to 1/2 and 1/3 of full dose (0.68 and 0.45 kg/ha respectively) (Table 3).

In the second experiment, all seedlings gotten from seeds collected near Głogów (G-2) and Skórzewo (So) were planted in soil originated from G-2 locality. Combinations with addition of full dose and 1/3 herbicide dose alone or in mixture with 0.2%  $CuSO_4$  v/v in spray solution were compared (Table 4).

In the third experiment, three populations of plants gotten from seeds originated from G-2, G-3 and So were used. These plants were planted in mix of compost and

<sup>&</sup>lt;sup>1</sup> Syngenta Crop Protection

sand (2:1) with addition of solution containing copper ions (as  $CuSO_4 \times 5 H_2O$ ) in concentrations: 0, 200, 400, and 600 mg  $Cu^{2+}/kg$  of dry soil mixture. Pyridate was used only in 1/3 of full dose (Table 5).

	Fresh weight of shoots [g]						
Dose	Source	of soil/Source of	of seeds	Source of soil/Seeds from Skórzewo			
	G-1 / G-1	G-3 / G-3	G-4 / G-4	G-1 / So	G-3 / So	G-4 / So	
1	0.18	0.20	0.19	0.10	0.16	0.14	
1/2	0.35	0.38	0.27	0.15	0.26	0.24	
1/3	2.62 b	3.12 ab	3.67 a	0.88 c	1.35 c	1.35 c	
0	8.06 b	8.75 a	8.23 a	6.03 d	7.63 b	7.09 c	

 Table 3.
 Influence of different pyridate doses on fresh weight of four *Chenopodium album* populations which were grown in soils from Głogów

Significant differences occurred for 0 and 1/3 pyridate dose at p < 0.05 (LSD = 0.589702)

Table 4. Influence of two pyridate doses with or without 0.2% CuSO<sub>4</sub> in spray solution on fresh weight of two *Chenopodium album* populations when seedlings grew in soil from G-2 locality

		Fresh weight of shoots [g]						
	Population	Control without Cu <sup>2+</sup> in spray	Control with Cu <sup>2+</sup> in spray	Dose of pyridate with or without Cu <sup>2+</sup>				
				1	1 + Cu <sup>2+</sup>	1/3	1/3 + Cu <sup>2+</sup>	
	G-2	22.90 a	22.25 a	1.24 f	1.32 f	6.42 d	7.61 c	
	So	17.18 b	17.16 b	0.21 g	0.20 g	4.13 e	1.74 f	

In all experiment values followed by the same letter are not significantly different at p < 0.05 (LSD = 0.98703)

 Table 5.
 Influence of 1/3 pyridate dose on fresh weight of shoots in g when *Chenopodium album* populations grew in mixture of compost and sand (2:1) with addition of Cu<sup>2+</sup>

	Control	1/3 of full pyridate dose						
Population	Level of added Cu <sup>2+</sup> [mg/kg of dry mixture soil]							
		0	200	400	600			
So	6.46 a	0.99 d	1.23 cd	0.99 d	1.69 c			
G-2	6.61 a	1.19 cd	0.89 d	1.10 d	1.72 с			
G-3	6.57 a	1.07 d	1.61 c	1.09 d	2.38 b			

In all experiment values followed by the same letter are not significantly different at p < 0.05 (LSD = 0.55289)

In all experiments herbicide was applied on plants, using a stationary cabin sprayer (type of nozzle: F110/0-6/3110°–LD-015, 200 L/ha, pressure 200 kPa, rotation 400 per min, SPRAY INTERNATIONAL firm). Five seedlings of common lambsquarters (*C. album*) were planted in one pot, each combination was tested in four replications and the experiments were repeated.

The efficacy of pyridate in tested combinations were determined three weeks after the herbicide application by cutting above ground parts of plants *of C. album* and fresh weight for 5 shoots perpot was analysed. Results as average of 8 measurement for each combination were presented.

To determine statistical differences in greenhouse experiments the ANOVA test was also used. A basic individual in analysis of variance was fresh weight of 5 shoots.

## **RESULTS AND DISCUSSION**

Both root length and hypocotyle height of the plants from Głogów and Skórzewo locations changed with the increasing of Cu concentration (Table 2). For plants from Skórzewo significant decrease of shoot length occurred at the level of 5 mg Cu and in case of root length at the level of 2.5 mg Cu in dm<sup>3</sup> of the diet. Three populations from Głogów place showed better tolerance to copper. Significant decrease of shoot length occurred at the level of 10 mg Cu/dm<sup>3</sup> for G-1 and G-3 populations and at the level of 5 mg Cu/dm<sup>3</sup> for G-4 population, whereas root length differed significantly at the level of 5 mg Cu/dm<sup>3</sup> of diet for all three tested populations.

The ability of plant population to tolerate intoxicated substrate depends on their physiological and biochemical adaptation to existent ecological conditions. The basis of this adaptation is avoidance (barrier against ion uptake) or tolerance (accumulation and immobilization of uptaken ions) (Masrovicova and Holubova 1998; Schat and Vooijs 1997).

Plant roots show the ability to retain excessive quantities of cooper, what prevent plants from phytotoxic concentrations of this element. At the moment of too high concentration of cooper in roots plants mobilize defensive mechanisms depending on linking active cooper ions by organic compounds. Organic-mineral compounds which indicate low activity and mobility are formed.

Recently most scientists maintain that the most popular phenomenon of heavy metal ions' detoxificationin plants is formation of phytochelatins (Ruszkowska and Wojcieska-Wyskupajtys 1996). After exceeding of critical concentration of cooper in the diet defensive mechanisms of plant become inefficient, what cause that more and more amounts of cooper migrate to above-ground parts of plant restraining its growth (Brej 1983; Brej 1998; Jasiewicz et al. 2004). Presented results confirmed that tolerance to the copper existing in population of *C. album* from Głogów region is the basis of plant adaptation.

After the application of pyridate at 4-leaf stage seedlings, which grew in soil samples from Głogów location, 100% efficacy of herbicide in full and 1/2 of full dose in all combinations of soils and seeds were observed (Table 3). After application of 1/3 pyridate dose plants were dying slowly and populations from Głogów which grew in soils from the same fields as seeds came from differed significantly from population from Skórzewo which grew in three soils from Głogów. Significant differences were observed between these two groups resulted in weaker growth of above-ground parts of plants from Skórzewo at the moment of pyridate application. Addition of copper to herbicide spray in full dose applied on seedlings in 5/6-leaf stage did not change the pyridate efficacy for G-2 and So tested populations grew in soil from G-2 locality (Table 4). Copper in mixture with 1/3 pyridate dose caused significant decrease of pyridate efficacy in population from Głogów. Instead, in population from Skórzewo in the same experimental combination addition of copper caused significant increase of pyridate efficacy. Addition of copper into the soil in which seedlings of three populations of *C. album* were planted in concentrations: 0 mg, 200 mg and 400 mg Cu<sup>2+</sup>/ kg of dry soil caused similar activity of pyridate used in 1/3 dose (Table 5). Weaker activity of herbicide was noted when 600 mg Cu<sup>2+</sup>/ kg of dry soil was added.

There are not many reports on synergistic or antagonistic effects between heavy metals and plant protection products. Teisseire et al. (1999) investigated the phytotoxicity of diuron alone or in combination with copper on model species – *Lemna minor* L. They found out that growth inhibition of *L. minor* depended on the concentrations of both chemicals. Babu et al. (2000) noted a synergistic effects of photooxidized polycyclic aromatic hydrocarbon (PAH) and copper on photosynthesis and plant growthalso in model species – *L. minor* L.

Generally, tested populations of *C. album* showed similar reaction on pyridate applied in full recommended dose without respect of soil contamination level, seeds' origin or presence of copper' ions in spray solution. Copper can modify action of herbicides mainly in reduced doses (Dopierała 2005a; 2005b). Essential influence on herbicide activity and on plant susceptibility to herbicides may exert mineral compounds existing both in soil and in plants (Sacała et al. 1999).

It is possible that shown in this paper, lower susceptibility to reduced doses of herbicide in presence of cooper, in plants growing in stress conditions on areas contaminated with heavy metals has its foundation in metabolic changes caused by constant stress factor (Grzyś et al. 2004).

## CONCLUSIONS

Populations of *C. album* grown in the contaminated environment of Silesia region, which is polluted by heavy metals show similar reaction to pyridate like those from Wielkopolska region. Continual emission of dust to the air, in the vicinity of Copper Foundry "Głogów" may result in small modification of herbicide action but without changes in their efficacy on condition that herbicide has been used in full recommended dose and in correct term. It does not seem that weed heavy metals tolerance or contaminated soil may change efficacy of herbicide.

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### POLISH SUMMARY

## WPŁYW ZANIECZYSZCZEŃ PRZEMYSŁOWYCH NA SKUTECZNOŚĆ PIRYDATU W ZWALCZANIU KOMOSY BIAŁEJ (CHENOPODIUM ALBUM L.)

W zasięgu emisji przemysłowych działającej od 35 lat Huty Miedzi "Głogów" znajdują się gospodarstwa rolne. Celem pracy było zbadanie, czy biotypy komosy białej (*Chenopodium album* L.), zasiedlające od wielu lat środowisko zanieczyszczone metalami ciężkimi, różnią się w reakcji na ich zwalczanie herbicydami. Skuteczność pirydatu (6-chloro-3-phenylpyridazin-4-yl S-octyl thiocarbonate) badano na czterech populacjach komosy białej, których nasiona zebrano w rejonie oddziaływania emisji przemysłowych Huty Miedzi, z pól różniących się poziomem zanieczyszczenia metalami ciężkimi. W warunkach szklarniowych porównywano skuteczność różnych dawek samego pirydatu oraz w obecności 0,2% CuSO<sub>4</sub> w cieczy opryskowej. Badano

także wpływ zanieczyszczeń glebowych na skuteczność tego herbicydu, szczególnie w odniesieniu do miedzi. W kabinie hodowlanej przeprowadzono testy tolerancji na wzrastające dawki miedzi. Przy stosowaniu zalecanej pełnej dawki polowej pirydatu nie obserwowano zmian w skuteczności działania tego herbicydu, niezależnie od poziomu zanieczyszczenia gleby, pochodzenia nasion oraz obecności jonów miedzi w mieszaninie opryskowej. Przy dawce obniżonej do 1/3 dawki pełnej, w obecności miedzi w mieszaninie opryskowej, wystąpiły istotne statystycznie zmiany skuteczności działania pirydatu.