Environmental Pollution xxx (2016) 1–9

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Influence of 2,4-D and MCPA herbicides on uptake and translocation of heavy metals in wheat (*Triticum aestivum* L.)☆

Elżbieta Skiba*, Joanna Kobyłecka, Wojciech M. Wolf

Institute of General and Ecological Chemistry, Lodz University of Technology, Żeromskiego 116, 90-924 Łódź, Poland

A R T I C L E I N F O

Article history:
Received 30 June 2016
Received in revised form
19 October 2016
Accepted 25 October 2016
Available online xxx

Keywords:
Phenoxyacetic acids herbicides
Wheat
Heavy metals bioaccumulation and translocation
Chemical stress
Farmland soils

A B S T R A C T

The aim of the study was to estimate the influence of the 2,4-dichlorophenoxy acetic acid and 2-methyl-4-chlorophenoxyacetic acid on the uptake and translocation of Cd, Co, Ni, Cu, Zn, Pb and Mn by wheat (*Triticum aestivum* L.). Two farmland soils typical for the central Polish rural environment were used. Studies involved soil analyses, contents of bioavailable, exchangeable and total forms for all investigated metals. Atomic absorption spectrometry was used to determine the concentration of the elements. The best correlation between the herbicide rate and the metal concentration was visibly for the underground part of plants. Analysis of variance proved that herbicide treatment of wheat frequently influences the metal transfer from soil and their concentration in roots and shoots. In particular, higher herbicide rates prompted the significant increase of all metals concentration in roots. Additionally, transfer coefficients depended on the type of soil and the herbicide rate applied. Uptake of metals may be also influenced by the formation of sparingly water-soluble metal-herbicide complexes. Its intensity would then depend on the solubility of particular chemical entity with the low solvable Pb, Cu and Cd complexes being the least mobile.

1. Introduction

Industrial production and agricultural activity often lead to transfer of pesticides and heavy metals into the soil environment (Gall et al., 2015; Nagajyoti et al., 2010; Page et al., 2014; Udeigwe et al., 2015; Wuana and Okieimen, 2011). This issue was recognized widely and prompted numerous studies on the accumulation of metals in plants (Chang et al., 2014; Lee and Sung, 2014; Elekes et al., 2010; Nadgórska-Socha et al., 2013; Wójcik et al., 2014). However, investigations on the concurrent uptake of these elements from soils polluted with pesticides are quite limited indeed (Mattina et al., 2003). In real systems these pollutants rarely appear independently. It is therefore particularly important to understand interactions of these toxic components in soil and plant environment altogether (Gutiérrez-Ginés et al., 2014; Lin et al., 2006; Liu et al., 2015a; Wang and Zhou, 2006).

One of the most popular group of pesticides used throughout the world and especially in Europe are phenoxyacetic herbicides (Eurostat, 2007; Paszko et al., 2016). The total pesticides consumption is continuously increasing, and according to Grube et al. (2011) and Fenner et al. (2013) is approaching 2.5 million metric tonnes. Due to their selective effects on broadleaf plants phenoxyacetic acid herbicides are often used to protect grass and grain crops (Monaco et al., 2002). Low price and high selectivity prompted their wide usage in a modern, highly efficient agriculture. The most common representatives of this group are 2,4-dichlorophenoxyacetic acid (2,4-D) and 2-methyl-4-chlorophenoxyacetic acid (MCPA) (Eurostat, 2007). They are synthetic auxins i.e. phytohormones which are involved in a range of physiological processes essential for the proper plant growth. Their mode of action is based on mimicking indole-3-acetic acid (IAA). The auxins act in plant organisms at low concentrations by specific binding to the AFB and ABP1 receptors located in the lipids cell membrane (Grossmann, 2010; Flasiński et al., 2015). They stimulate plant development by cell division and elongation, vascular differentiation, root formation and apical dominance. On the other hand, high herbicide concentrations significantly disturb the proper plant growth and trigger damage processes leading to the final plant destruction (Grossmann, 2003; Woodward and Bartel, 2005). Auxins are involved in upregulation of genes encoding regulatory enzymes in abscisic acid (ABA) and ethylene biosynthesis and further interfere with stomatal closure and reactive

☆ This paper has been recommended for acceptance by Prof. W. Wen-Xiong.

* Corresponding author.
E-mail address: elzbieta.skiba@p.lodz.pl (E. Skiba).

http://dx.doi.org/10.1016/j.envpol.2016.10.072

oxygen species (ROS) production. Contrary to natural auxins, synthetic formulations are active for a significantly longer time (Grossmann, 2010).

The 2,4-D and MCPA are very often applied to protect wheat which is one of the most widely cultivated crops in Poland and Europe with the domestic production approaching 10 million metric tonnes (Eurostat, 2015). Both compounds are introduced to the environment in the form of suspensions containing their salts, amides or esters (Grabińska-Sota et al., 2003; Moszczyński and Białek, 2016). Their impact on living organisms is limited due to the low toxicity, in particular when compared to the common phosphoroorganic or chloroorganic pesticides (Peterson et al., 1994; Rao, 2007; World Health Organisation, 2010). Despite this fact, they bring considerable environmental risk when applied in excess or without the usual care. To our knowledge concurrent interactions of herbicides and metal ions in soil and plant tissues in connection to their mobility and bioavailability have not been extensively studied so far. In our previous work wheat was cultivated in pots under the laboratory conditions and further sprayed after sprouting with solutions of 2,4-D and MCPA sodium salts. Under these circumstances we firmly observed that wheat shoots accumulated lower levels of metals than the control plants and speculated that this effect resulted from the formation of sparingly soluble metal complexes with phenoxyacetic ligands (Kobyłecka et al., 2003, 2009; Kobyłecka and Skiba, 2008; Kobyłecka et al., 2009). In present paper we extended and revised that work. The number of heavy metals under investigation was significantly increased, their amounts were analyzed either in shoots and roots. Metal migration was evaluated by translocation and bioaccumulation factors.

2. Materials and methods

2.1. Soils

Two representative farmland soils from the central Poland were used in the study. Soil 1 represents the arable land of the typical rural environment in the Skierniewice region, soil 2 was sampled from the meadow which is subjected to lay farming. All samples were collected accordingly to procedure given in the standard PN-ISO 10381-4, 2007.

Soils were air-dried and sifted through a sieve with 2 mm mesh diameter and finally stored in plastic containers. Soil pH was measured by the potentiometric method in 1 mol L^{-1} potassium chloride solution (PN-ISO 10390, 1997). The well-established gravimetric method for the determination of soil organic matter by the mass loss at 550 °C was applied (ASTM D2974-00, 2000; Heiri et al., 2001; Schumacher, 2002). The grain size analysis was performed according to Polish Standard PN-R-04032, 1998 with the dedicated set of sieves. Exchangeable and bioavailable forms of metals were determined in 1 mol L^{-1} solutions of $MgCl_2$ and HCl, respectively (Tessier et al., 1979; Rauret, 1998; Zimmerman and Weindorf, 2010). The total content of metals was evaluated by the well-established soil decomposition method employing mixture of sulphuric(VI) and hydrofluoric acids (Ostrowska et al., 1991). Relevant results of soil analysis are summarized in Tables 1 and 2.

Table 2
Metal concentrations (mg kg^{-1}) in soils used in the experiment (mean value ± SE, n = 3). Concentrations below the detection limit are indicated by the acronym ND.

Metal	Form*	Soil 1 mg kg^{-1}	Soil 2 mg kg^{-1}
Cd	a	0.30 ± 0.02	1.15 ± 0.06
	b	0.14 ± 0.01	0.47 ± 0.03
	c	ND	0.24 ± 0.01
Co	a	0.62 ± 0.06	1.75 ± 0.16
	b	0.49 ± 0.01	0.74 ± 0.02
	c	ND	ND
Ni	a	3.10 ± 0.12	6.63 ± 0.22
	b	0.57 ± 0.01	2.09 ± 0.05
	c	ND	0.20 ± 0.04
Cu	a	9.24 ± 0.13	94.0 ± 2.6
	b	2.60 ± 0.01	28.9 ± 1.8
	c	ND	0.33 ± 0.01
Zn	a	28.3 ± 0.2	167 ± 1
	b	12.0 ± 0.1	49.9 ± 2.8
	c	1.40 ± 0.01	15.5 ± 0.3
Mn	a	195 ± 5	351 ± 9
	b	184 ± 3	208 ± 4
	c	5.28 ± 0.08	6.17 ± 0.44
Pb	a	9.75 ± 0.15	36.9 ± 0.7
	b	8.44 ± 0.15	25.8 ± 1.4
	c	ND	1.07 ± 0.08

(*) a – total content, b – content of bioavailable forms, c – content of exchangeable forms.

2.2. Herbicides

Chemically pure sodium salts of 2,4-dichlorophenoxy acetic acid (Aldrich) and 2-methyl-4-chlorophenoxyacetic acid (Lancaster) were applied in cultivation experiments. Both compounds were additionally purified (99.5%) by recrystallization from toluene or water-ethanol (1:1) mixture, respectively. Concentrations of spraying liquids were adjusted to follow the normal field application rates as recommended for phenoxyacetic herbicides i.e. 2 kg ha^{-1}. Additionally, higher rate of 4 kg ha^{-1} was also tested. The latter is rarely used to fight heavy infestations when weeds are in buds. It is at the verge of wheat resistance limit and occasionally may inflict injures to plants (Różański, 1998). Solutions were prepared by dissolving the respective amounts of 2,4-D or MCPA in 0.1 mol L^{-1} NaOH and subsequent adjustment with 0.1 mol L^{-1} hydrochloric acid to pH 7.0.

2.3. Wheat cultures

Rywalka winter wheat (*Triticum aestivum* L.) seeds (quality class A) from PPH „Rolpuch" Co. LTD Kutno were used in the study. All plants were grown in pot experiments under the laboratory conditions using procedure developed by Kobyłecka and Skiba (2008). Main cultivation experiments were performed in two arrangements, each was related to one type of soil. A single batch consisted of five series of cultures with three pots giving fifteen samples for one arrangement altogether. The fifth series in a batch was cultivated as a reference without addition of herbicides. Sprays were applied in a week after sowing when the plants were in a stage 11 of

Table 1
General properties of soils used in the experiment (mean ± SD, n = 3).

Soil	Reaction		Organic matter content %	Granulometric composition %		
	pH – H_2O	pH - KCl		1.0–0.1 mm	1.1–0.02 mm	<0.02 mm
1	6.15 ± 0.01	4.80 ± 0.01	4.34 ± 0.02	69.61 ± 0.69	20.50 ± 0.60	9.89 ± 0.08
2	6.31 ± 0.02	5.02 ± 0.01	7.63 ± 0.11	90.56 ± 0.81	9.18 ± 0.09	0.25 ± 0.04

Please cite this article in press as: Skiba, E., et al., Influence of 2,4-D and MCPA herbicides on uptake and translocation of heavy metals in wheat (*Triticum aestivum* L.), Environmental Pollution (2016), http://dx.doi.org/10.1016/j.envpol.2016.10.072