

HYGIENIC REGLAMENTATION OF 2,4-D GROUP HERBICIDES AND LIMITATION OF THEIR APPLICATION IN UKRAINE

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Abstract

The 2,4-D group herbicides are well known as cheap and effective pesticides. They are very stable in the environment. Physical, chemical properties and toxicological assessment including different delayed effects of 2,4-D exposure is given. Behavior in environment is discussed, including monitoring of 2,4-D in food stuffs on the territory of the former USSR. Operator risk assessment of 2,4-D by different models was performed. Hygienic standards, harvesting intervals and re-entry periods for 2,4-D and its derivatives were introduced and adopted. Application of 2,4-D group herbicides has been reduced in Ukraine since 1998 for 25 % under our recommendations. 2,4-D group herbicides are prohibited for use by plane, helicopters and private owners of small farms.

Introduction

2,4-dichlorophenoxyacetic acid /2,4-D/ and her salts and esters are used as herbicides on different agricultural plants, especially cereals for more than 40 years all over the world. Volumes of 2,4-D application are still big due to the cost of formulations which is relatively to other herbicides cheap and several new formulations which appear on Ukrainian market every year.

Scope of investigations was to minimize adverse influence of 2,4-D on environmental and human health. The above mentioned scope was achieved by fulfilling such aims:

- assessment of physical, chemical and toxicological properties of 2,4-D;
- evaluation of 2,4-D behavior in environment;
- operator risk assessment of 2,4-D;
- 2,4-D hygienic reglamentation;
- limitation of herbicide's application in Ukraine.

Assessment of Physical, Chemical and Toxicological Properties of 2,4-D

2,4-D is colourless powder with a slight phenolic odour. Its molecular weight is 221.0, molecular formula - $C_8H_6Cl_2O_3$. 2,4-D vapour pressure is $1.86 \cdot 10^{-12}$ mPa at 25 °C, octanol-water coefficient - $\log P = 2.58-2.83$ at pH 1, 0.04-0.33 at pH 5. Its solubility: in water at 25 °C is 311 mg/l at pH 5, 20031 mg/l at pH 5, 23180 mg/l at pH 7, 34196 mg/l at pH 9; in ethanol – 1250 g/kg at 20 °C, diethyl ether – 243 g/kg at 20 °C, heptane – 1.1 g/kg at 20 °C.

2,4-D is used in different agricultural sectors and in forestry as active ingredient in form of acid, its dimethylammonium salt or different ethers.

Properties of 2,4-D and its formulations are given as literature review (1, 2, 3, 4, 5) and results of own investigations in this and next section.

Among impurities of technical substance important toxicological role belongs to dioxins.

International standards for presence of polychlorinated dibenzodioxins and dibenzofurans in 2,4-D are established as I-TEQ since the end of 80th on the level smaller than 0.001 mg/kg in calculation on 2,3,7,8-tetrachlorodibenso-para-dioxin.

Toxicological properties of 2,4-D are given in Table 1.

The main limiting criterion in assessment after acute inhalation toxicity is cancerogenicity. Experimental investigations showed astrocytomas in male rats with number of discussion points, epidemiological - connection between no-Hojskin lymphomas and exposure to 2,4-D.

Table 1. Toxicological properties of 2,4-D

Criterion of HC	Value of effect, assessment (Class by HC)
LD ₅₀ per oral	375 mg/kg (III)
LD ₅₀ dermal	> 2000 mg/kg (IV)
LC ₅₀ inhalation	1790 mg/m ³ (II)
Skin irritation	no irritation (IV)
Sensitization	no sensitization (IV)
Cancerogenity	2B - IARC, C - EPA, (III)
Other delayed effects (embryotoxicity, teratogenic and mutagenic activity, reproductive toxicity)	are not limiting in assessment (III-IV)

* - HC – Ukrainian Hygienic Classification of pesticides by Hazard (6)

JARC experts classified 2,4-D to 2B group - probably carcinogenic to humans, but having (usually) no human evidence (7). EPA experts analyzed mentioned above epidemiological and experimental data and classified substance to group C - possible human carcinogen, with limited evidence from animal studies in the absence of human data (8), saying that epidemiological investigations not evaluated exposure of another factors, which acted together with 2,4-D. That's why real contribution of 2,4-D was not evaluated. And astrocytomas are not comparable with no-Hojskin lymphomas. Thus, estimation of 2,4-D cancerogenity remains open.

Evaluation of 2,4-D Behavior in Environment

All 2,4-D derivatives - salts and esters are quickly transform into 2,4-D acid.

2,4-D dimethylammonium decays in plants within 3-6 weeks. In steady cultures, i.e. cereals are formed water-soluble conjugates with sugars. Investigations of 2,4-D residues done during last 7 years in Ukraine show, that 2,4-D residues are on level of detection limit of chemical analytical method in green plants of cereals on the 30-45 day after herbicide's application. 2,4-D is not detected in straw and grain during harvesting. This is explained by the presence of enzymes in cereals which actively metabolize 2,4-D. Broad-leaved plants don't have such enzymes. So 2,4-D is phytotoxic to most broad-leaved crops, especially cotton, vines, tomatoes, fruit trees, oilseed rape and beet.

Researches of 2,4-D behavior in soils have shown, that organic substances, soil of superficial horizons ?? and exchanging aluminium (clay subhorizons) are the major factors determining percentage of adsorbed 2,4-D. The basic mechanism influencing availability, mobility and disintegration of herbicide in soil is the ratio of processes of adsorption and desorption. 2,4-D communicates in soil with the high contents of organic substances more strongly, than in soil with their low contents. 2,4-D deposit on ground is rather quickly accompanied by hydrolysis. Soil microorganisms destroy 2,4-D and its derivatives rather quickly with practically full destruction of molecules. Full destruction in soil occurs faster if application rate of formulation decreases.

Warm, moist conditions and addition of organic matter stimulate degradation.

Autoclaving the soil and inhibiting bacterial metabolism reduce degradation. The kinetics of 2,4-D disappearance suggests that microorganism are responsible. Some microorganisms are capable of using 2,4-D as their single carbon source. More often 2,4-D is co-metabolized with another carbon source. Regular treatment of soil with 2,4-D stimulates the number of organisms which are capable of degrading the compound.

In laboratory conditions in soils of different types the half-life period of 2,4-D is 14-41 days. 2,4-D acid and its salts are kept in soil during 1-2 months at application rate 1-3 l/hectare and during near four months at application rate of 2-6 l/hectare. 2,4-D dimethylammonium decays in ground within one month.

Naturally 2,4-D and its derivatives easily sorbed from water by various clays. Photolysis is the important way of destruction 2,4-D in water ecological systems. The ambient temperature and intensity of illumination can also influence on speed of destruction and distribution of the residues between water and deposits. Anaerobic conditions can promote microbic destruction. 2,4-D acid and its salts are kept in water from 10-15 days till 4-6 months.

2,4-D group formulations were found not only in superficial, but also in subsurface water.

Results of All-Union automatic control system of pesticides' residues in food stuffs done on ECOHYNTOX base (9) are given in Table 2.

Table 2. 2,4-D residues detected in different types of food stuffs

Year	Number of types with 2,4-D detection	Number of types with 2,4-D detection higher than MRL	Mean values of residues in food stuffs, mg/kg
1990	12	11	0.49
1991	17	16	0.47
1992	8	6	0.25

Data from Table 2 show severe pollution of food stuffs in 1990-1991.

In some areas of Ukraine 2,4-D is found out also in blood of countrymen (10) .

The analysis of ethiology of acute poisonings with pesticides of agricultural workers has shown, that the application of organochlorine and organophosphorus substances was main source of poisonings in 70-80-th years, Nowadays acute intoxications of agricultural workers caused by 2,4-D group herbicides, pyrethroids, carbamates are registered more often, organophosphorus substances, which were the main source of poisonings in 70-80-th. 346 patients in 6 cases of acute group poisonings with the given herbicide were observed in Institute's hospital for last 5 years.

Herbicide's behavior in environment and its assessment is given in Table 3.

Table 3. 2,4-D behavior in environment and its assessment

Criterion of HC	Value, assessment (Class by HC)
Stability in soil (T_{50})	5-41 days (II-III)
Stability in water (T_{50})	22-60 days (I)
Vertical migration into soil depth	20-30 cm /sometimes up to 50 cm/ (II)
Stability in vegetating agricultural plants	residues up to 30-45 days (III)

Operator Risk Assessment of 2,4-D

Studying of working conditions, formed during use of different 2,4-D formulations has shown, that concentration of substance in air of working zone of tractor operator and during mixing the formulation was below suggested and adopted hygienic standards.

Professional risk assessment of formulations was done by two alternative models. The first model suggested by Sergejev, represents modification of model of pesticide's operator risk assessment accepted in European Union - so-called German model (11). The second, suggested by Spynu E.I. (12), is based on comparison of an actual doze of the substance acting on working organism with pesticide's acceptable daily intake (ADI). Results of estimation on two models are submitted in Table 4.

Table 4. Operator risk assessment of 2,4-D

Occupation	Risk values of complex exposure of substance ¹	Values of Real Pesticide Pressure Index ² at ADI figure, adopted	
		in Ukraine	by FAO/WHO
Worker for mixing the product	0.012	3	0.03
Tractor operator	0.032	14	0.14
Mechanized work after application since			
1 day	0.003	0.3	0.003
3 days	0.003	0.3	0.003
7 days	0.001	0.1	0.001

1. Risk is acceptable at value of ≤ 1 .

2. Hazard classes according to Classification of Real Pesticide Pressure Index: acceptable class – Index is not higher than 1; moderately hazardous class – Index is from 1.1 to 2; slightly hazardous class – Index is from 2.1 to 3; highly hazardous class – Index is more than 3.1.

Data given in Table 4 show, that operator risk of pesticide is assessed as acceptable. ADI value, adopted in the USSR and now in Ukraine (13) is in 100 times lower than adopted by FAO/WHO (14). It is due to not revised ADI for 20 years. Such low ADI value is connected with delayed effects of dioxins, which were present in 2,4-D formulations in 70-80th and remains unchangeable till terminal 2,4-D cancerogenicity assessment.

2,4-D Hygienic Reglamentation

Analysis of 2,4-D properties and own hygienic investigations allowed to recommend and adopt or confirm for use hygienic standards (13), which are given in Table 5.

Table 5. Hygienic standards of 2,4-D group herbicides in Ukraine

Active ingredient	ADI, mg/kg	MRL ^a in food stuffs, mg/kg	MAC ^b /TSEL ^c in working zone air, mg/m ³	TSEL in ambient air, mg/m ^d	MAC in water of reservoirs, mg/dm ³	MAQ ^e in soil, mg/kg
2,4-D acid	0.0001	NA ⁵	1.0/	0.0002	0.002	0.1
2,4-D dimethyl-ammonium	0.0001	NA ⁵	1.0/	0.0003	0.002	0.25
2,4-D butyl, octyl esters	0.0001	NA ⁵	/0.5	0.006	0.002	0.15
2,4-D ethylhexil ester	0.0001	NA ⁵	/0.5	0.0005	0.002	0.1

^a – maximum residual level;

^b – maximum allowable concentration;

^c – tentative self exposure level;

^d - maximum allowable quantity;

^e - not accepted (limit of method detection in cereals – 0.02 mg/kg).

In connection with fact that 2,4-D derivates are quickly metabolised up to equivalent on toxicity, more mobile and more stable in ground and water 2,4-D, standards of them in plant food stuffs, water and soil were accepted on 2,4-D. Such periods and intervals were recommended and adopted: re-entry period for mechanized work after application for formulations with 2,4-D – 3 days, harvesting interval is not limited due to application of 2,4-D at early stages of cereals vegetation.

Limitation of Herbicide's Application in Ukraine

Steps to decrease 2,4-D pressure on environment of Ukraine, which were introduced and realized:

1) application of 2,4-D is reduced for 25 % since 1998; 2) 2,4-D herbicides are prohibited for application: by private owners of small farms; by planes and helicopters and in forestry; 3) recommendations to the Ministry of Agriculture are given to use 2,4-D mainly in mixture formulations and to change gradually 2,4-D with herbicides of another chemical group.

Main step was to reduce the volume of herbicide's application. In 1998 Ministry of Agriculture planned to apply 6688 tones of 2,4-D formulations on 5129.33 thousands hectares. Volumes of 2,4-D for application in 1999 were reduced for 25 % – 5016 tones on 3847 hectares under our recommendations given by Ministry of Health to Ministry of Agriculture. In further years adopted 2,4-D volumes remains on the same reduced level.

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