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Risks of Vapour-phase Herbicides in the Atmosphere on Non-target Plants

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Plant Research International B.V., Wageningen
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Table of contents

page

Abstract 1

1. Background 3

2. Approach 5

3. Factors determining risks of vapour-phase herbicides 7

3.1 Use of herbicides in the Netherlands 7
3.2 Herbicidal properties 8
3.3 Plant characteristics 11

4. Atmospheric concentration of herbicides 13

5. Effect concentrations of vapour phase herbicides 17

5.1 Effects of vapour phase herbicides on plants 17
5.2 Derivation of Effect Concentrations 20
5.3 Assessment of risks of vapour phase herbicides 20

6. Conclusions 25

7. References 27

Appendix I. Herbicides used in the Netherlands 2 pp.

Appendix II. Herbicides emitted in the Netherlands 2 pp.

Appendix III. Exposure risk index of herbicides used in the Netherlands 2 pp.

Abstract

The information on atmospheric concentrations, effects and effect concentrations of herbicides available in the literature is very scarce. All of these three types of information were found for only three herbicides used in the Netherlands, i.e. fluorxypyr, ethofumesate and chlorpropham. The maximum monthly mean concentrations measured in the Netherlands during 2000-2001 were 0.6 ng m^{-3} (fluorxypyr), 1.3 ng m^{-3} (ethofumesate) and 25 ng m^{-3} (chlorpropham). In the vicinity of fields on which sprayed herbicides have been applied, peak concentrations can reach a factor 10-100 higher, depending on the distance from the field edge.

Very few data on effect concentrations for herbicides were found and documented information was found for only 2,4-D, ethofumesate, chlorpropham and fluorxypyr. The calculated NOECs for these herbicides were found to be 5 ng m^{-3} (fluorxypyr), 75 ng m^{-3} (ethofumesate) and 77 000 ng m^{-3} (chlorpropham), while that for 2,4-D is 1-100 ng m^{-3}.

When emitted from a sprayed field at a rate of 0.01 g s^{-1}, adverse effects due to these herbicides in vapour phase may be expected to occur on non-target species at distances between 100 m and 3 km from the field edge. Thus, it can be concluded that non-target plant species are at risk from these three vaporised herbicides at distances up to 3 km from sprayed fields, but knowledge on the effects and effect concentrations of many other herbicides is still lacking.

1. Background

There is an increasing amount of concern about the possible side effects of pesticide vapours on non-target organisms. More than half of the amount of pesticides applied as crop protection measures may be volatilised after spraying crops in the Netherlands (De Jong *et al.*, 1995) and an estimated 2% of the recommended herbicide dose is currently being deposited on remote areas in this country (Klepper *et al.*, 1998). Vapours of herbicides may well affect non-target plants, but data on levels of air-borne herbicides and their effect thresholds are generally lacking.

The Health Council of the Netherlands was recently requested to review the current level of knowledge on the atmospheric dispersion of agricultural pesticides and to make recommendations with respect to a risk evaluation of these pesticides. The resulting advisory report concluded that the risks arising from medium-range atmospheric dispersions must be evaluated (Gezondheidsraad, 2000), and be based on a comparison between the anticipated exposure of organisms and their anticipated sensitivity. The report also stated that there is a lack of toxicity data for representative species.

As a direct result of that report, additional financial support was granted for the present evaluation. Within the DLO programme 359 (Emission, emission reduction methods and environmental risks of pesticides), research in 2002 was focussed on two areas: emission during application and emission from plant and soil surfaces after application. This report will focus on the potential risks and effects of vaporised herbicides on non-target plants.

2. Approach

Following the application of herbicides on crops, a portion of the sprayed herbicides will be adsorbed and taken up by the plant (crop) via the cuticle. Another portion of the spray may reach the soil surface where it is bound to the organic matter and broken down in time. Herbicide drift disperses and may be deposited on (non-target) plants at short distances from the spray zone (field edge), or be transported over longer distances depending on the wind speed and spray droplet size (the finer the spray, the larger the distance it will be transported). However, a part of the applied herbicide will evaporate and enter the vapour phase. The fact that herbicides can evaporate and be transported from middle to long-range distances from the site of application (the source) may pose a risk to non-target plants.

Herbicides may enter the vapour phase directly during and immediately following application (spraying) on a targeted crop. Later, herbicides may evaporate from plant leaf surfaces or from the soil into the atmosphere. In all cases, a certain amount of the evaporated active ingredient can affect the targeted species or become a potential risk to non-target plant species.

In the following report, a number of factors will be addressed that determine the potential risk vapour phase herbicides may pose towards plants, i.e. the amount of herbicide applied, herbicide-specific properties and sensitivity of the receptor (plant species). Because insecticides and fungicides are not targeted towards plants, only the effects of herbicides will be examined throughout this report. The effects of herbicides on non-target species will be limited to that of vaporised herbicides. The risks that herbicides in vapour phase may pose for non-target plant species at middle to long-range distances from the source will be addressed. The factors determining the potential risks of vapour phase herbicides to plants will be presented and discussed. The effects of vaporised herbicides found in the literature and through experimental research will be assessed and an inventory of the herbicides used and their atmospheric concentrations in the Netherlands will be given. Finally, the effect concentrations of vapour phase herbicides reported in the literature will be addressed and evaluated with respect to risks for non-target plant species.

3. Factors determining risks of vapour-phase herbicides

3.1 Use of herbicides in the Netherlands

The total amount of chemical pesticides that was used in 2000 on 804,356 ha of agricultural and horticultural land in the Netherlands amounted to 5,346,278 kg (CBS, 1998). The majority of this amount (69%) was used on agricultural soils and 16% on flower bulbs. Herbicides comprise an important part of this amount with 2,294,502 kg being applied to agricultural soil (64%) and flower bulbs (30%). The amounts of individual herbicides used are given in Table 1. The herbicidal nomenclature follows Anon., (1999).

Table 1. *Ranking of the top 20 herbicides used in agriculture and horticulture (kg yr^{-1}) in the Netherlands (CBS, 1998). See also Appendix I for a more extensive list.*

	Herbicide	kg yr^{-1}		Herbicide	kg yr^{-1}
1	MCPA	676 348	11	chloridazon	61 931
2	metamitron	155 099	12	propachlor*	61 721
3	atrazine*	104 748	13	pyridate	58 519
4	glyphosate	104 416	14	bentazone	54 797
5	diquat dibromide	83 738	15	chlorpropham	53 018
6	chlormequat (chloride)	83 117	16	ethofumesate	50 527
7	metolachlor*	82 776	17	sulcotrion	37 653
8	prosulfocarb	76 937	18	phenmedipham	36 248
9	mecoprop-P*	75 244	19	metribuzin	30 848
10	isoproturon	65 966	20	metoxuron*	28 567

* *not approved*

A considerable amount of the herbicides applied to crops in the form of spray are emitted to the atmosphere directly above the crop and from the spray drift carried from the field by the wind. Fine spray droplet and evaporated herbicide may be transported by the wind over middle to long distances. Drift dispersion is deposited nearer to the sprayed field than fine droplets and vaporised herbicides. A list of the top 20 emitted herbicides in the Netherlands in 2000 is given in Table 2. The emissions originate from open field agricultural/horticultural areas (cut flowers, bulbs, grassland, field crops) as well as closed systems like glasshouses in which flowers and vegetables are grown. Relatively large amounts of the herbicides mecoprop-P, propachlor and metoxuron are shown to have been emitted in 2000 (Anon., 2002), but these three herbicides have been since banned from use in the Netherlands.

Table 2. Emission of herbicides (kg yr^{-1}) from open and closed systems calculated for MJPG 2000 (Anon., 2002). A more extensive list is given in Appendix II.

	Herbicide	kg y^{-1}		Herbicide	kg y^{-1}
1	Mecoprop-P*	37951	11	Chlorpropham	8893
2	Propachlor*	31031	12	Metamitron	7063
3	MCPA	29779	13	Ethofumesate	6244
4	Metoxuron*	24411	14	Monolinuron	5743
5	Glyphosate	19320	15	Linuron	5563
6	2,4-D	13708	16	Pendimethalin	5178
7	Bentazone	13361	17	Isoproturon	5021
8	Chlormequat (chloride)	10830	18	Asulam	4856
9	Metam-natrium	9913	19	Glyphosate-trimesium	4678
10	Diquat dibromide	9498	20	Dichlobenil	4537

* *not approved*

The two herbicides with the highest absolute emission in 2000 were mecoprop-P and propachlor, both of which were banned from use in the Netherlands in 2000 and 1999, respectively. The concentrations of these herbicides emitted to the atmosphere can be thus expected to drop drastically in the coming years.

Large amounts of mineral oil are emitted annually as well (75 000 kg), but because it is largely used as an adjuvant and to a lesser extent as an insecticide, it is not included in either list.

3.2 Herbicidal properties

The specific characteristics of each herbicide will influence its dispersion and exposure to plants. Herbicidal properties include, among others, molar mass, solubility in water, and vapour pressure. Another very important characteristic is the adjuvant added to the herbicide to facilitate uptake and effectiveness in the plant. Because all of these properties together determine the exposure of the herbicide to plants and its potential effectiveness, it follows that a ranking of herbicidal toxicity should be possible. However, knowledge about the contribution of each property and their combination is generally lacking.

A very simple relationship for their relative toxicity might be found in the dosage advice of herbicides on crops. The dosage (active ingredient per hectare) recommended for a particular crop (on similar groups of weeds) might be used for a ranking of relative toxicity's with the lowest dosage being relatively the most effective. Because only a limited number of herbicides are used to eradicate weeds in a particular crop, such a list would be relatively short. Thus, a group of target crops were chosen in which a wide range of herbicides is presently used, fodder and forage crops. This example is given in Table 3.

Table 3. Ranking of herbicides according to the amount of active ingredient (a.i.) advised for use on fodder and forage crops.

	Herbicide	kg ha^{-1}		Herbicide	kg ha^{-1}
1	Rimsulfuron	0.01	21	Terbutylazine	1
2	Quizalofop-P-ethyl	0.05	22	2,4-D	1
3	Isoxaflutole	0.1	23	Phenmedipham	1.2
4	Propaquizofop	0.15	24	Cycloxydim	1.2
5	Fluroxypyr	0.18	25	Monolinuron	1.25
6	Bromoxynil	0.28	26	Bentazone	1.44
7	Dicamba	0.288	27	Glyphosate	1.44
8	Fluazifop-P-butyl	0.375	28	MCPA	1.5
9	Sethoxydim*	0.38	29	Pendimethalin	1.6
10	Sulcotrion	0.45	30	Glyphosate-trimesium	1.92
11	Ethofumesate	0.5	31	Carbetamide	2.1
12	Ioxynyl	0.6	32	Metamitron	2.1
13	Tri-allate	0.6	33	Asulam	2.4
14	Metribuzin	0.7	34	Metoxuron*	2.4
15	Glufosinate ammonium	0.75	35	Propachlor*	2.4
16	Lenacil	0.81	36	Chlortoluron	2.5
17	Pyridate	0.9	37	Metolachlor*	2.52
18	Atrazine*	1	38	Aclonifen	3
19	Dinoterb	1	39	Chloridazon	3.87
20	Diquat dibromide	1	40	Dichlobenil	5.4

* *not approved*

However, a ranking of relative toxicity of herbicides in liquid form, even if can be made, cannot be extrapolated to toxicity of herbicides in vapour phase, because to date no relationship has been established between the spray and vapour phase. Either such a relationship would have to be found for most, if not all herbicides, or a comparison of the ranking between herbicides in spray-form and vapour phase would have to be made. Unfortunately, the latter ranking does not exist.

Following application of herbicides to crops, a portion of the sprayed herbicide evaporates and enters the vapour phase. Dispersion via the atmosphere is one of the most important routes in contaminating the environment. The amount of evaporated herbicide depends on climatic conditions, the spray technique (nozzle type, direction of spray), the amount of liquid herbicide deposited on the crop and soil and on the duration of drift. It also depends on a number of physico-chemical characteristics of the herbicide itself and on the adjuvant used. Generally 3% of the total amount of herbicide sprayed evaporates during normal spraying practice (Holterman, 2003).

The largest amount of droplet spray is rapidly deposited, while a part is (re)emitted into the atmosphere and is transported over middle-range distances. Another part of the herbicide spray evaporates and according to Breeze (1993a), one of the most important characteristics in this respect is the vapour pressure. TNO-MEP also used vapour pressure as the best estimate in their evaluation of the MJPG in 1995. Using this characteristic and the amount of herbicide sprayed annually, Wijnands *et al.* (1999) suggested the use of the BRI (Blootstelling Risico Index) for the compartments air, soil and water. With respect tot the air compartment, an emission factor (EF) was defined by dividing vapour pressures of the various herbicides into categories (between 0-100%), indicating the degree to which herbicides will evaporate and disperse. The BRI_{air} is defined as the amount of active ingredient used x the proportional emission factor.

BRI_{air} = kg active ingredient * (EF/100)

This index is not a measure of the toxicity of a herbicide, but a measure of the relative risk that a herbicide will evaporate. The relative toxicity of herbicides in vapour phase influences their risk to non-target organisms because they are not likely to be equally toxic. The BRI for herbicides in the Netherlands are given in Table 4. The BRI does not reflect the relative risk of the herbicides, but incorporates the amounts of active ingredient used (in 1998) and is thus an indication of the risk of emission to the atmosphere above the Netherlands.

Table 4. *Potential risk of the top 20 vapour phase herbicides (BRI_{air}) per year (kg active ingredient), based on their use in 1998. Mechanism indicates the metabolic mode of action in the plant and if it is a systemic (S) or a contact (C) herbicide. See also Appendix III.*

	Herbicide	BRI_{air} (kg a.i.)	Mechanism	Pathway	
				Foliar	Soil
1	Metolachlor*	29799	S, protein synthese	X	X
2	Propachlor*	29317	S, cell division	X	X
3	MCPA	16909	S, growth regulator	X	-
4	Metoxuron*	11427	S, photosynthesis	X	X
5	Chlormequat	9351	S, growth regulator	X	-
6	Mecoprop-P*	6772	S, growth regulator	X	-
7	Daminozide	4747	S, growth regulator	X	X
8	Bentazone	3945	C, photosynthesis	X	-
9	Monolinuron	3671	S, photosynthesis	X	X
10	Metribuzin	3239	S, photosynthesis	X	X
11	Prosulfocarb	3077	S, fatty acid synthese	-	X
12	Tri-allate	2983	S, fatty acid synthese	-	X
13	Atrazine*	2619	S, photosynthesis	X	X
14	Dinoterb	2206	C, membrane disruption	X	-
15	Pendimethalin	1502	S, cell division	-	X
16	2,4-D	1391	S, growth regulator	X	-
17	Dicamba	1193	S, growth regulator	X	-
18	Metamitron	1086	S, photosynthesis	X	X
19	Ethofumesate	970	S, fatty acid synthese	X	X
20	Asulam	847	S, DHP synthase	X	X

* *not approved*

Table 4 indicates that the highest risks of emission hold for metolachlor and propachlor, but that is based on their use in 1998. They have since been banned, and their use should have drastically diminished since. The next group of potential emission risk herbicides are MCPA, metoxuron and chloormequat, used primarily in cereal crops, potatoes and grassland cultures and of these metoxuron has been recently banned as well. Thus, policy makers appear to be effective in reducing the risk of herbicidal emissions.

3.3 Plant characteristics

When considering the influence of plant characteristics on the uptake of herbicides, the role of formulations or adjuvants can not be omitted. Most herbicides are not readily taken up and require an adjuvant for uptake to occur. The following however, will focus on the role of plant characteristics in herbicidal (including adjuvant) uptake.

Uptake via the roots would require deposition to the soil, transition into the liquid phase and eventually uptake via the roots, which can occur, but would likely require larger deposited amounts to be effective. The less lipophilic the herbicide is, the more readily it will be transported through the soil and be taken up by the roots

Vapour phase herbicides deposited on plants are most likely to be taken up via the shoots. Uptake via the shoots or leaves depends on a number of plant characteristics. Herbicides in vapour phase are deposited onto leaf surfaces. The total surface of plant leaves is an important factor, the larger the leaf surface relative to the soil area (leaf area index), the more herbicide can be deposited and adsorbed to the leaf surface. Therefore, broad-leaved species, species with horizontally orientated leaves and vegetation with a high leaf area index (LAI) will run a higher risk than plants with small, vertically orientated leaves.

Plant leaves are often covered with an epicuticular wax layer, the amount and composition of which differs in a species-specific manner. The wax layer gives rise to a microstructure which affects the wettability of the foliage and thus the amount of herbicide in liquid phase taken up and its distribution over the leaf surface. Waxes with granules, rods, plates or crusts give the leaf a rough surface which increases deposition onto the leaf, in contrast to waxes with smooth amorphous surfaces. Lipophilic herbicides are more easily adsorbed and taken up by leaves with epicuticular wax. Also, young leaves on plants with a high growth rate are often more susceptible than older leaves because of their higher physiological activity and higher lipid content.

Dry deposition of herbicides thus increases with increasing leaf roughness (rough structure, hairy leaves, and crinkled leaves), which also affects the uptake via stomata. This also applies in the case of vegetation, so that more vapour phase herbicides will be adsorbed by forest trees (high degree of roughness) than by grassland vegetations. Herbicides taken up via the stomata are potentially more toxic than those taken up via the cuticle. Plants are able to assimilate herbicides at very low concentrations (1-10 pg l^{-1}). The route via the stomata may be less important however, as herbicides are often not very soluble in water Breeze (1993a; 1993b), which is a prerequisite for stomatal uptake and transport into the leaf mesophyll cell layer.

4. Atmospheric concentration of herbicides

The concentrations of herbicides empirically measured in the atmosphere obviously depend on herbicidal properties such as their evaporation rate, on meteorological conditions and distance from the point source of application. Kempenaar *et al.* (1998) presented a list of concentrations of herbicides from the literature (Table 5). The findings are grouped into measurements at distances 100 m - 10 km and more than 10 km from the source.

Peak concentrations up to 10 000 ng m^{-3} were recorded within a distance of 10 km, with 24 h means of a factor 5-10 lower than the peak values. At distances exceeding 10 km from the point source, maximum concentrations up to 10 ng m^{-3} were measured, a factor 10-100 higher than near sprayed fields (Baas & Bakker, 1996) It is important to realise the implications of these observations when examining the commonly presented daily or monthly means. Mean concentrations of herbicides are likely to mask the acute toxic peak concentrations of a factor 10 higher than the 24 h mean and likely even higher than a weekly or monthly mean concentration.

In the past number of years monitoring programs have yielded additional data on the atmospheric concentration of herbicides in the Netherlands as well. TNO-MEP has set up a monitoring campaign in the Netherlands to monitor the atmospheric concentration and deposition of pesticides on a national level. In order to accomplish this, 18 monitoring stations were established throughout the country. The locations were chosen such that they were not in the vicinity of a large (point) source. As a result, these herbicide concentrations can be interpreted as the long-term mean concentration of a herbicide for a particular location or region. Peak concentrations are likely to be masked as mentioned earlier and might well be expected to be 10-100 times higher. Of the total number of pesticides measured on a monthly basis for the period of 2 years (2000-2001), 18 herbicides were included in the campaign, the results of which are given in Table 6.

The 18 monitoring locations were grouped into 4 main regions in the Netherlands, entailing the northern provinces, the central/east area, the western coastal provinces with the intensive open field cultures of bulbs, cut flowers and vegetables, and including 2 locations in the south part of the Netherlands. Table 6 gives the maximum mean monthly concentrations recorded over the 2-year period including the number of locations at which the herbicide was measured. The month(s) in which the herbicide was measured as well as the main crop(s) to which it was applied are given as well. Note that 6 of the herbicides have been banned from use during the past years and are still present in the atmosphere.

Of the 18 herbicides measured, metamitron and MCPP were never found in samples. The highest atmospheric concentrations of chlorpropham were measured in the western provinces during the winter season, reflecting its use on the open fields of bulbs and cut flowers. High concentrations were also recorded in the southern locations during the summer months following applications to potatoes and other field vegetables.
Dichlobenil was measured throughout the whole year, except in the northern provinces. It is used predominantly in fruit tree cultures and on other types of tree farms.
The highest concentrations of propachlor were measured in the central-eastern parts of the Netherlands, likely as a result of application to cut flowers and vegetables in those areas.
Locations in the east and southern provinces also showed increased monthly mean concentrations of triallate following its use on sugar beets and cereal grains.

The differences in the presence of the various herbicides and the season measured obviously reflect their regional use, but is also influenced by their use in surrounding regions. Although a part of the measured concentrations is likely to have been transported over longer distances from other areas including Germany and Belgium, the largest part likely reflects use of the herbicides in that region.

Table 5. Vapour-phase concentrations of herbicides in ambient air, obtained from various monitoring programs. Per measurement, the air sampling period was 24 h, and circa 500 m³ air was sampled (after Kempenaar et al., 1998).

Distance to herbicide treated fields/crops	Herbicide	Concentrations [ng m^{-3} air]		Comments‡
site indicator		maximum	mean	
Distance: 0.1 to 10 km				
1. De Zilk, Naaldwijk, and Noordwijk, the Netherlands	trifluralin	1.6	0.3	Baas & Duyzer, 1997. Weekly observations in the autumn of 1996 on 3 sites in Zuid Holland
	2,4-D	0.8	<0.02*	
	atrazine	0.1	<0.02*	
	simazine	0.1	<0.01*	
	mecoprop	1.3	0.03	
2. Colmar, France	mecoprop-P	60	22	Millet, 1994. 17 Observations per chemical in Jan. - Dec. 1992, detection frequencies > 90%
	isoproturon	9	4	
	atrazine	4	2	
3. California, USA	bromoxynil	37	18	Baker *et al.*, 1996. > 20 Observ. per chemical in certain periods in 1987 to 1995
	DEF	340	68	
	molinate	1200	570	
4. Saskatchewan, Canada	2,4-D	13500	?	Grover, 1989. > 100 Observ. per chemical in certain periods in 1966 to 1982
	tri-allate	198	?	
	trifluralin	62	?	
5. North Dakota, USA	trifluralin	1	?	Hawthorne *et al.*, 1996. > 20 observation
Distance: > 10 km				
6. Vallombrosa, Italy	dichlobenil	3.1	<2.2*	Trevisan *et al.*, 1994. 20 Observations per chemical in April - July 1989
	trifluralin	5.6	<1.2*	
	alachlor	2.0	<1.4*	
7. Kitakyushu, Japan	propyzamide	0.3	0.23	Haraguchi *et al.*, 1994 2 observation dates in July 1991 and April 1992
	trifluralin	0.2	<0.1*	
	pendimethalin	0.3	<0.2*	
	simazine	0.6	0.36	
	atrazine	0.3	0.26	
8. Chesapeake Bay, USA	metolachlor	5	*	McConnell *et al.*, 1995. Data from several stations, spring + autumn
	trifluralin	5	*	measurements in 1993

* *no mean concentrations presented because concentrations were below the detection limit in more than 50% of the air samples analyzed*

? *only peak concentrations were presented by the authors*

‡ *for the references, see Kempenaar et al. (1998)*

Table 6. *Highest mean monthly concentration (ng m^{-3}) of 16 vapour phase herbicides in ambient air recorded in 2000-2001 by TNO-MEP.*

Herbicide	# sites	Monthly high mean (ng m^{-3})	Month(s)	Primary target crop/ remarks	Herbicide	# sites	Monthly high mean (ng m^{-3})	Month(s)	Primary target crop
Region North (4 monitoring sites)					Region East (4 monitoring sites)				
Atrazine*	1	0.1	Aug	corn	Atrazine*	-	-	-	corn
Bentazone	3	0.2	April-July	corn, grass, cereals	Bentazone	4	0.2	July	corn, grass, cereals
Chlorpropham	4	1.8	Oct-June	potato, bulbs, vegetables	Chlorpropham	4	3.5	Oct-March	potato, bulbs, vegetables
Chloridazon	-	-	-	sugarbeet, bulbs	Chloridazon	2	0.2	April	sugarbeet, bulbs
Dichlobenil	4	6.9	Jan-Dec	(fruit)trees	Dichlobenil	4	14.5	Jan-Dec	(fruit)trees
DNOC*	4	3.4	Aug-April	?	DNOC*	4	2.8	Sept-May	?
Ethofumesate	4	0.4	July-Nov	sugarbeet, grass	Ethofumesate	4	0.3	Oct-Nov	sugarbeet, grass
Fluoroxypyr	3	0.6	Sept-Nov	corn, grass, cereals	Fluoroxypyr	3	0.3	Aug-Oct	corn, grass, cereals
Isoxaflutole	-	0	-	corn	Isoxaflutole	-	-	-	corn
MCPA	1	0.1	May	potato, grass, cereals	MCPA	-	-	-	potato, grass, cereals
Metolachlor*	1	0.3	May-June	corn	Metolachlor*	2	0.1	May	corn
Propachlor**	4	4.2	March-Aug	cut flowers, vegetables	Propachlor**	4	13.8	March-Aug	cut flowers, vegetables
Simazine**	4	0.2	March	nursery trees	Simazine**	1	0.4	Aug	nursery trees
Terbutylazine	2	0.5	July	corn	Terbutylazine	3	0.6	June-July	corn
Triallate	4	4.3	Jan-Dec	sugarbeet, cereals	Triallate	4	10.8	Jan-Dec	sugarbeet, cereals
Trifluralin*	4	1.3	April-Aug	?	Trifluralin*	4	0.9	Aug-April	?
Region West (8 monitoring sites)					Region Soutth (2 monitoring sites)				
Atrazine*	2	0.1	March-July	corn	Atrazine*	1	0.3	March	corn
Bentazone	5	0.2	June-July	corn, grass, cereals	Bentazone	2	0.2	June-July	corn, grass, cereals
Chlorpropham	8	24.5	Oct-April	potato, bulbs, vegetables	Chlorpropham	2	9.6	June-July	potato, bulbs, vegetables
Chloridazon	1	0.2	April	sugarbeet, bulbs	Chloridazon	1	0.2	March	sugarbeet, bulbs
Dichlobenil	8	18.2	Jan-Dec	(fruit)trees	Dichlobenil	2	9.8	Jan-Dec	(fruit)trees
DNOC*	8	5.3	July-Dec	?	DNOC*	2	3.1	July-April	?
Ethofumesate	8	0.9	June-Nov	sugarbeet, grass	Ethofumesate	2	1.3	June-Dec	sugarbeet, grass
Fluoroxypyr	6	0.4	Aug-Oct	corn, grass, cereals	Fluoroxypyr	2	0.4	March-July	corn, grass, cereals
Isoxaflutole	1	0.4	June	corn	Isoxaflutole	1	0.2	Oct	corn
MCPA	1	0.4	July	potato, grass, cereals	MCPA	-	-	-	potato, grass, cereals
Metolachlor*	-	-	-	corn	Metolachlor*	2	1.5	May-July	corn
Propachlor**	8	5.5	March-Aug	cut flowers, vegetables	Propachlor**	2	0.7	MarchJune	cut flowers, vegetables
Simazine**	3	0.5	March-April	nursery trees	Simazine**	-	-	-	nursery trees
Terbutylazine	1	0.6	June-July	corn	Terbutylazine	2	1.8	June-July	corn
Triallate	8	2.1	Jan-Dec	sugarbeet, cereals	Triallate	2	11.4	Jan-Dec	sugarbeet, cereals
Trifluralin*	8	2.4	Aug-April	?	Trifluralin*	2	1.7	Jan-Dec	?

** not approved*   *** indicates that the herbicide is still considered necessary in agriculture*

5. Effect concentrations of vapour phase herbicides

5.1 Effects of vapour phase herbicides on plants

There is not a great deal of quantitative data available on effects and effect concentrations of vapour phase herbicides on (non-target) plants. Some experimental results of effects however, published in peer-reviewed literature and in institutional reports are presented here below.

In an experimental study by Kempenaar *et al.* (1999), four common horticultural species (lettuce, kale, tomato and radish) were exposed to 11 herbicides. An equivalent amount of active ingredient of each herbicide in flasks was brought into vapour phase by passing an air stream through the flasks and into fumigation chambers containing the 4 species. It was assumed that similar amounts of each herbicide would evaporate and be brought into contact with the test plants. The plants were simultaneously exposed to each gaseous herbicide for up to 72 h and then transferred to the greenhouse where they were observed for three weeks. The observed plant responses were foliar injury, shoot biomass production, mortality and reduction in light use efficiency (LUE) and are shown in Table 7.

Table 7. Mean foliar injury (%), reduction of shoot biomass (%), mortality (%) and reduction in light use efficiency (%) in four crop species after 72 h of exposure to vapours of eleven herbicides (from Kempenaar et al., 1999).

Herbicide	Injury (%)	Biomass reduction (%)	Mortality (%)	LUE reduction (%)
Asulam	-[1]	-	-	-
Bentazone	-	-	-	-
Glyphosate	-	-	-	-
Metoxuron	0.4	-	-	26
Atrazine	0.2	-	-	-
MCPA	2	-	-	-
Pendimethalin	10	35	-	-
Diquat dibromide	50	31	-	43
Metribuzin	35	72	38	90
Ethofumesate	94	84	38	66
Dichlobenil	88	88	63	-

[1] *indicates no response (injury) or no significant effect*

Although equal amounts of the active ingredient were used, the atmospheric concentrations in the fumigation chambers were not measured, so it is not certain that the experimental concentrations were actually similar in all cases.

The effects of herbicides will increase with increasing concentration and the ranking of toxic effects for these herbicides appears to be similar for each of the chosen endpoints. At the concentrations to which the plants were exposed, visible injury was the most sensitive parameter, followed by biomass reduction and mortality. The LUE reflects the potential biomass per unit assimilated light energy, and can not be considered as an adequate response parameter for all herbicides, as not all affect the photosynthesis process. For those herbicides that do act directly on the photosynthesis process however, the LUE was shown in this experiment to be a good indicator of potentially adverse effects on plants (Kempenaar *et al.*, 1999).

Only few quantitative studies on the effects of vapour phase herbicides have been performed to date. Those published were performed under controlled conditions and are shown in Table 8. Only a few effect concentrations could be derived from these studies. For 2,4-D the concentrations at which an effect was observed ranged from 0.3 – 10 000 ng m^{-3}, depending on exposure duration, plant species and formulation. In three other single experiments, exposures to fluroxypyr, ethofumesate and chlorpropham resulted in visible injury and biomass reduction at varying concentrations. Following 48 h exposure to 5 ng m^{-3} fluoroxypyr, the biomass production of tomato was reduced (Breeze, 1988).

In a subsequent study, Franzaring *et al.* (2001) exposed 14 wild plant species to a range of chlorpropham and ethofumesate concentrations for 48 h. Vapours of ethofumesate caused injury in all higher species, in contrast to chlorpropham despite its higher concentrations in the air. Visible injury and growth reduction was observed only in the species *Agrostemma githago* at 77 000 ng m^{3} (chlorpropham), while ethofumesate caused visible injury in all 14 species at 75 ng ng m^{-3} and biomass reduction at 150 ng m^{-3}. This observation indicates that chlopropham has a higher effect threshold in this experiment with young plants,. The effect threshold for ethofumesate (75 ng m^{-3}) was much lower and is comparable to that for 2,4-D. Ethofumesate adversely affected the growth of one third of the plant species tested. Apparently, herbicidal toxicity is not related to atmospheric concentration, as ethofumesate caused more adverse effects on these plants than chlorpropham did, despite its lower concentration.

The limited amount of data gained from experiments with these herbicides indicate that effect concentrations are in the order of 0.1 to 100 ng m^{-3} and depend on exposure duration, plant species and formulation.

Table 8. *Effects of various herbicides on plants. Effect concentrations reflect LOECs or NOECs.*

Herbicide	Plant species	Exposure (hour)	E.C. (ng m^{-3})	Effect	Reference
2,4-D butyl	Lettuce, tomato	72	5	visible injury	Van Rensburg & Breeze 1990
	Lettuce, tomato	24	± 100	biomass reduction	
2,4-D butyl	Tomato	5	5000	biomass reduction	Breeze & West 1987a
		1-2	10 000	altered physiology	
2,4-D butyl	Tomato	6	120	biomass reduction	Breeze 1988
2,4-D butyl	Lettuce, tomato, cabbage, bean, sunflower	3.5	3000	biomass reduction	Breeze & West 1987b
2,4-D iso-octyl	Lettuce	72	0.3	visible injury	Breeze & Van Rensburg 1992
	Tomato	24	13	visible injury	
2,4-D iso-octyl	Tomato	24	800	altered physiology	Breeze & Fowler 1992
2,4-D (acid)	Lettuce, tomato	72	30	biomass reduction	Breeze & Van Rensburg 1991
fluoxypyr	tomato	48	5	biomass reduction	Breeze 1988
asulam	Lettuce, tomato, kale, radish	72		no effect	Kempenaar *et al.* 1999
bentazone	Lettuce, tomato, kale, radish	72		no effect	Kempenaar *et al.* 1999
glyphosate	Lettuce, tomato, kale, radish	72		no effect	Kempenaar *et al.* 1999
metoxuron	Lettuce, tomato, kale, radish	72		0.4% visible injury	Kempenaar *et al.* 1999
atrazine	Lettuce, tomato, kale, radish	24-72		0.2% visible injury	Kempenaar *et al.* 1999
MCPA	Lettuce, tomato, kale, radish	24-72		0.7-2% visible injury	Kempenaar *et al.* 1999
pendimethalin	Lettuce, tomato, kale, radish	8-72		0.1-10% visible injury	Kempenaar *et al.* 1999
	Lettuce, tomato, kale, radish	48-72		21-35% biomass reduction	
diquat dibromide	Lettuce, tomato, kale, radish	8-72		3-50% visible injury	Kempenaar *et al.* 1999
	Lettuce, tomato, kale, radish	24-72		22-31% biomass reduction	
metribuzin	Lettuce, tomato, kale, radish	8-72		0.6-35% visible injury	Kempenaar *et al.* 1999
	Lettuce, tomato, kale, radish	24-72		21-72% biomass reduction	
	Lettuce, tomato, kale, radish	72		38% mortality	
ethofumesate	Lettuce, tomato, kale, radish	8-72		2-94% visible injury	Kempenaar *et al.* 1999
	Lettuce, tomato, kale, radish	8-72		15-84% biomass reduction	
	Lettuce, tomato, kale, radish	48-72		25-38% mortality	
dichlobenil	Lettuce, tomato, kale, radish	8-72		35-88% visible injury	Kempenaar *et al.* 1999
	Lettuce, tomato, kale, radish	8-72		57-88% biomass reduction	
	Lettuce, tomato, kale, radish	24-72		13-63% mortality	
chloropropham	*Agrostemma githago*	48	77 000	visible effects	Franzaring *et al.* 2001
ethofumesate	14 wild plant species	48	184	visible effects (op 14 sp)	Franzaring *et al.* 2001
	14 wild plant species	48	184	biomass reduction (5 sp)	

5.2 Derivation of Effect Concentrations

If phytotoxic effects occur, dose-response relationships are often performed in order to derive limits to which plants can be safely exposed the chemical component in question. The dose-response relationship is initially used to derive a concentration at which the plant species tested have been found to (adversely) respond to the exposure. The plant's response is influenced by a number of factors (see chapter 3), which determine the potential risk of a herbicide to non-target plants, usually indicated by a (no) effect concentration. This is what we actually wish to derive, the concentration of herbicide at which the target (non-target plant species) undergoes (no) adverse effects. Limitations to the exposure are thus expressed as a concentration, i.e. the lowest observed effective concentration (LOEC) usually for short-term exposures or the no-effect effective concentration (NOEC) for longer-term exposures. Limits should address exposure to key plant species. Usually weed species are the targeted species, but in this case may include non-targeted weed and crop species as well.

As mentioned earlier, the only herbicide for which a number of experimental studies have been performed that have derived effect concentrations is 2,4-D (Breeze and co-workers from 1987-1992). For the references see Kempenaar *et al.* 1998. The lowest-observed-effect concentrations derived from the various experiments by Breeze *et al.* (Table 5) are shown in Figure 1. A power trend line was drawn to indicate the expected borderline between effective and non-effective exposure concentrations. Two additional points are shown indicating the atmospheric concentration of 2,4-D of 13 500 ng m^{-3} measured by Grover (1989), which far exceeds the effect concentration and a concentration of 0.8 ng m^{-3} measured by Baas & Duyzer (1997), which would not be expected to cause negatives effects. Clearly, more data is required to establish a more reliable effect concentration line.

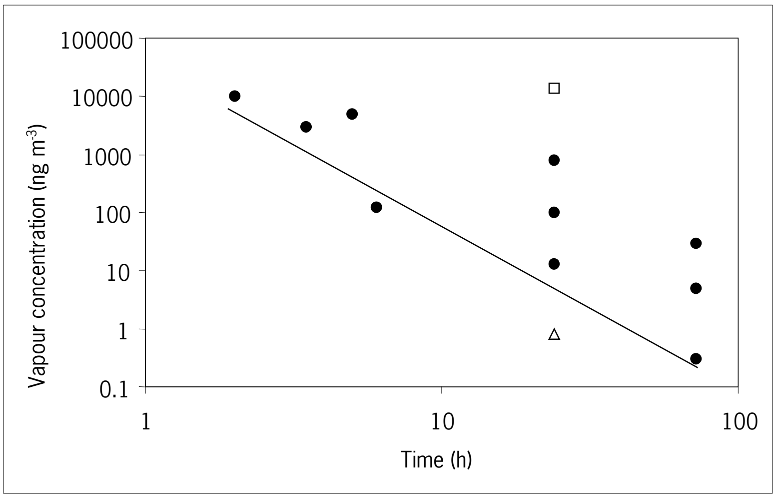

Figure 1. Lowest observable effect concentrations (LOEC) for vaporised 2,4-D (from Kempenaar et al., 1998). A power trend line indicates the relationship between exposure duration and LOEC. The two extreme 24 h mean concentrations taken from Table 5 are indicated by □ (from Grover, 1989) and Δ (from Baas & Duyzer, 1997).

5.3 Assessment of risks of vapour phase herbicides

Similar trend lines for other herbicides, even if no more reliable than that for 2,4-D, would provide more insight into vapour phase herbicidal toxicity and the assessment of risks to non-target plants. However, as they are not available, the highest observed 24 h means vapour concentrations of the various herbicides in Table 5 were plotted against the trend line for 2,4-D and are shown in Figure 2. The concentrations all refer to 24 h mean values and indicate that the large majority of measurements taken within 10 km from the source field sprayed remain above the trendline, meaning that they exceed the effective concentration. In the case of measured herbicide at more than 10 km from the point source, three of the six observed herbicide concentrations exceed

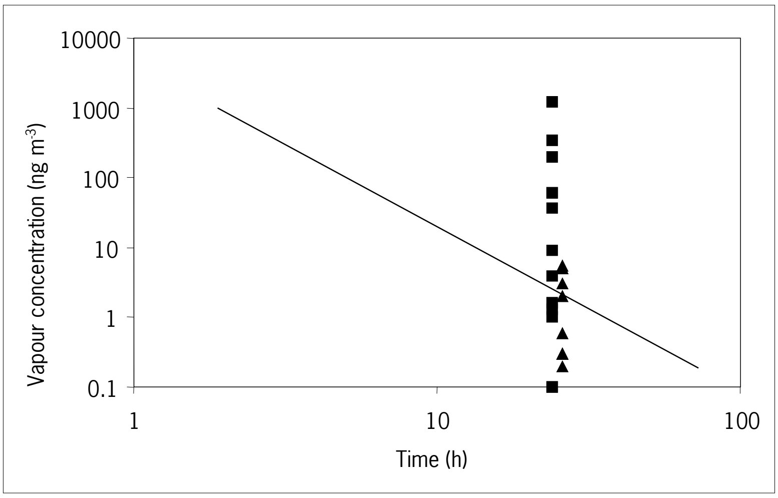

Figure 2. The highest observed 24 h mean concentrations of various herbicides (from Table 5) on sites 0.1 – 10 km (■) or more than 10 km (▲) from sprayed fields. The power trend line indicates the relationship between exposure duration and the LOEC for 2,4-D. The different symbols are shown next to each other for clarity sake. (from Kempenaar et al. 1998).

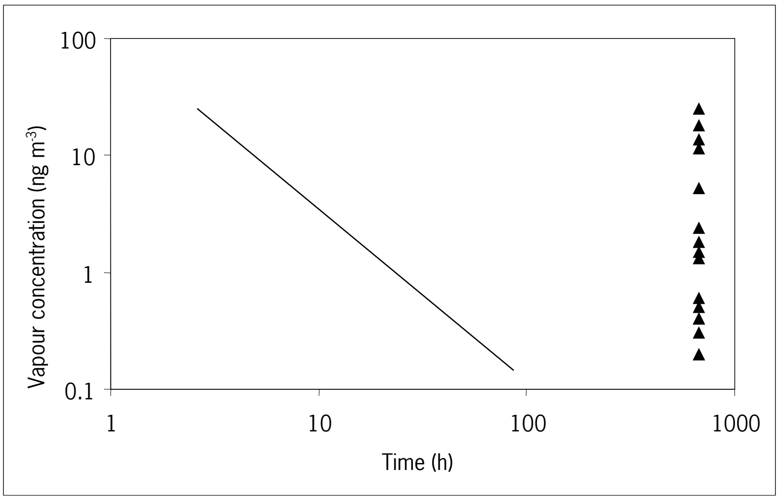

Figure 3. The maximum monthly mean concentrations of herbicides measured in the Netherlands in 2000-2001 (Table 6) in relation to the effect concentration for 2,4-D. The power trend line indicates the relationship between exposure duration and the LOEC for 2,4-D.

the effect concentration as well. Thus, at considerable distances from fields sprayed with herbicides, a potential risk to plants is suggested.

If the effect concentration for 2,4-D can be considered as an indication of general herbicide toxicity, then the limited amount of data on herbicidal vapours in general suggest a risk for plants.

During the years 2000 and 2001, the maximum monthly concentrations measured in the Netherlands by TNO-MEP (see also Table 6) were plotted against the expected borderline between effective and non-effective concentrations for 2,4-D (Fig. 3). They are given as mean monthly concentrations and fall above the effect concentration for 2,4-D and thus suggest a risk for plants. The monthly concentrations under-estimate the toxicity of the herbicide vapour phase concentrations. During a month of cumulative sampling, the peak concentrations are averaged out and the effects of short-term (hours to days) exposures are masked. However, even these maximum monthly means are well above the effective concentration for 2,4-D, again, given that the toxicity of 2,4-D is representative for the toxicity of other herbicides.
The use of the trendline for 2,4-D for other herbicides is debatable of course, but it does provide some idea of the potential toxicity of these herbicides.

When more data on effect concentrations and long-term mean atmospheric concentrations become available, another approach might be used to assess risks for plants. Given both effect concentrations and mean atmospheric concentrations, the distance from a point source of herbicide emission (sprayed field) might be estimated with the following principles.

Concentrations of emitted gaseous components at increasing distances from the source follow a similar general pattern, and this pattern is applicable to most gaseous emissions (J. Duyzer, pers. comm.). This relationship holds for a known source concentration, which diminishes with increasing distance from the source. Figure 4 shows a hypothetical example given of a field (1 ha) from which a gaseous component (herbicide) is emitted at a rate of 0.01 g s^{-1}. This emission rate may be viewed as a worst case example in which the total amount of evaporated herbicide is emitted at one time.

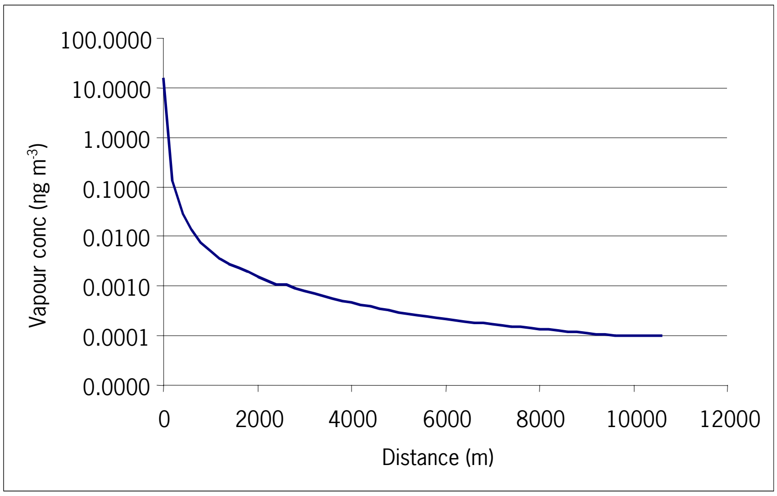

Figure 4. *Atmospheric concentration of a chemical component (herbicide) emitted at 0.01 g s^{-1} from a 1 ha source in relation to distance from the source.*

The exposure of a herbicide in vapour phase is determined by its concentration and the duration plants are exposed to it (exposure = c x t). Thus plants closer to the source (highest concentration) are likely to experience the highest exposure, as can be seen in Figure 4. The concentration diminishes rapidly at first, and then more gradually until it reaches a long-term mean concentration. Because the emission rates of vaporised herbicides at a point source (considering a field of 1 to possibly 10 ha as a point source) are often unknown, the calculation might be attempted in the other direction. As the emission pattern is generally applicable to gaseous compounds, one might thus begin from a long-term mean concentration and proceed towards the source. A realistic NOEC must be known in order to estimate the distance from the source at which non-target plants are exposed to a risk of the vapour phase herbicide and for a few herbicides is an (no) effect concentration known. Assuming the background concentration to have been reached at a distance of 10 km from the source, the distance at which the NOEC would be reached can be estimated from Figure 4. The results are given in Table 9.

Table 9. The distance from a source of herbicide emission (a sprayed field) at which plants might be adversely affected.

Herbicide	NOEC (ng m^{-3})	Background concentration (ng m^{-3})	Distance from source (m)
chlorpropham	77000	25	<100
ethofumesate	75	1	400
2,4-D	0.1-100	0.8	500
fluroxypyr	5	0.6	3000

From the scarce amount of data available it can be concluded that for the 4 herbicides given, their potential for adversely affecting non-target plants varies in distance from the source (a sprayed field) from less than 100 m to 3 km (Table 9). Given more data on effective concentrations and measured atmospheric concentrations, more accurate estimations of the distance from a sprayed field at which non-target plant species may be at risk of injury from vapour phase herbicides may be be realised.

6. Conclusions

1. The toxicity of vapour phase herbicides cannot be directly related to their toxicity in liquid phase, nor can it be related to their rate of vaporisation.

2. Data on atmospheric concentrations, effects and effect concentrations of herbicides is very scarce and was found for only three herbicides used in the Netherlands, i.e. fluorxypyr, ethofumesate and chlorpropham.

3. NOECs have been calculated for fluorxypyr (5 ng m^{-3}), ethofumesate (75 ng m^{-3}) and chlorpropham (77 000 ng m^{-3}), while that for 2,4-D ranges from 1-100 ng m^{-3}.

4. Non-target plant species are expected to be at risk from vaporised herbicides at distances up to 3 km from sprayed fields.

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Appendix I.

Herbicides used in the Netherlands in 1998 (CTB, 2001)

	Herbicide	kg y^{-1}		Herbicide	kg y^{-1}
1	MCPA	676348	51	trinexapac-ethyl	2354
2	metamitron	155099	52	lenacil	1737
3	atrazine*	104748	53	haloxyfop-P-methylester	1602
4	glyphosate	104416	54	triflusulfrron-methyl	1466
5	diquat dibromide	83738	55	ethephon	1360
6	chlormequat (chloride)	83117	56	cycloxydim	1313
7	metolachlor*	82776	57	chlorbromuron	1256
8	prosulfocarb	76937	58	clopyralid	1243
9	mecoprop-P*	75244	59	sethoxydim*	1214
10	isoproturon	65966	60	diflufenican	1180
11	chloridazon	61931	61	fluazifop-P-butyl	1142
12	propachlor*	61721	62	mineraal oil	1098
13	pyridate	58519	63	isoxaflutole	1095
14	bentazone	54797	64	EPTC	1081
15	chlorpropham	53018	65	fenoxaprop-P-ethyl	713
16	ethofumesate	50527	66	prometryn	711
17	sulcotrion	37653	67	dichlorprop-P	701
18	phenmedipham	36248	68	dichlobenil	678
19	metribuzin	30848	69	rimsulfuron	642
20	metoxuron*	28567	70	quizalofop-P-ethyl	612
21	maleine hydrazide	20983	71	amidosulfuron	600
22	bifenox	19072	72	clodinafop-propargyl	493
23	buminafos	17734	73	desmetryn	493
24	DNOC*	17592	74	benazoline	274
25	paraquat-dichloride	17124	75	gibberellic acid A3	211
26	linuron	17023	76	cloquintocet-mexyl	123
27	monolinuron	14684	77	1-nafthaleneacetic acid	92
28	asulam	14121	78	gibberellic acid A4+A7	68
29	fluroxypyr	14118	79	indol-3-butyric acid	30
30	glyphosate-trimesium	12089	80	borax	27
31	metobromuron	12085	81	3-indolylacetic acid	24
32	dinoterb	11612	82	triclopyr	17
33	diuron	10002	83	propaquizofop	11
34	simazine*	9833	84	paclobutrazol	6
35	tri-allate	7851	85	bromacil	0
36	daminozide	7807	86	chlortoluron	0
37	pendimethalin	7512	87	cinidon-ethyl	0
38	propyzamide	6542	88	clomazone	0
39	ioxynyl	6396	89	cresoot/cresol	0
40	glufosinate-ammonium	5962	90	dimethenamide	0
41	bromoxynil	5179	91	ferri-phosphate	0
42	dicamba	4969	92	ferrosulphate	0
43	aclonifen	4062	93	florasulam	0
44	carbetamide	3670	94	imazamethabenz-methyl	0
45	metsulfuron-methyl	3575	95	mesotrione	0
46	terbutylazine	3305	96	metam-natrium	0
47	metazachlor	3115	97	nicosulfuron	0
48	2,4-D	2929	98	paraffine oil	0
49	amitrol	2911	99	quinmerac	0
50	desmedipham	2760	100	S-metolachlor	0

* *not approved*

Appendix II.

Herbicides emitted in the Netherlands (Anon., 2002)

	Herbicide	kg y^{-1}		Herbicide	kg y^{-1}
1	mineral oil	75024	51	glufosinate-ammonium	338
2	mecoprop-P*	37951	52	cresoot/cresol	324
3	propachlor*	31031	53	triclopyr	306
4	MCPA	29779	54	dimethenamide	273
5	metoxuron*	24411	55	carbetamide	219
6	glyphosate	19320	56	nicosulfuron	216
7	2,4-D	13708	57	S-metolachlor	187
8	bentazone	13361	58	haloxyfop-P-methylester	124
9	chlormequat (chloride)	10830	59	desmedipham	120
10	metam-natrium	9913	60	fenoxaprop-P-ethyl	79
11	diquat dibromide	9498	61	clodinafop-propargyl	56
12	chlorpropham	8893	62	quizalofop-P-ethyl	34
13	metamitron	7063	63	isoxaflutole	28
14	ethofumesate	6244	64	triflusulfuron-methyl	26
15	monolinuron	5743	65	rimsulfuron	21
16	linuron	5563	66	cinidon-ethyl	15
17	pendimethalin	5178	67	metsulfuron-methyl	12
18	isoproturon	5021	68	amidosulfuron	10.6
19	asulam	4856	69	1-naftyaleneacetic acid	10.4
20	glyphosate-trimesium	4678	70	indol-3-butyric acid	1.4
21	dichlobenil	4537	71	gibberellic acid A3	1
22	prosulfocarb	4392	72	paclobutrazol	1
23	bifenox	3785	73	3-indolylacetic acid	0.04
24	bromoxynil	3727	74	atrazine*	0
25	metolachlor*	3548	75	benazoline	0
26	chloridazon	3459	76	bromacil	0
27	terbutylazine	3038	77	buminafos	0
28	cycloxydim	2842	78	chlorbromuron	0
29	dicamba	2718	79	chlortoluron	0
30	pyridate	2354	80	clomazone	0
31	sulcotrion	1882	81	desmetryn	0
32	maleine hydrazide	1807	82	dichlorprop-P	0
33	trinexapac-ethyl	1765	83	dinoterb	0
34	paraquat-dichloride	1763	84	diuron	0
35	simazine*	1607	85	DNOC*	0
36	ioxynyl	1567	86	EPTC	0
37	phenmedipham	1564	87	ferri-phosphate	0
38	fluroxypyr	1553	88	ferrosulphate	0
39	metribuzin	1285	89	gibberelllic acid A4+A7	0
40	amitrol	1160	90	lenacil	0
41	metazachlor	957	91	prometryn	0
42	metobromuron	920	92	propaquizofop	0
43	fluazifop-P-butyl	708	93	quinmerac	0
44	tri-allate	700	94	sethoxydim*	0
45	daminozide	646	95	borax	
46	ethephon	639	96	cloquintocet-mexyl	
47	clopyralid	601	97	florasulam	
48	propyzamide	510	98	imazamethabenz-methyl	
49	aclonifen	453	99	mesotrione	
50	diflufenican	412	100	paraffine oil	

* *not approved*

Appendix III.

Exposure risk index (Blootstelling risico index, BRI) based on the amounts of herbicides used in the Netherlands in 1998

	Herbicide	kg y^{-1}		Herbicide	kg y^{-1}
1	metolachlor*	29799	51	sethoxydim*	12
2	propachlor*	29317	52	carbetamide	11
3	MCPA	16909	53	amitrol	7
4	metoxuron*	11427	54	metsulfuron-methyl	7
5	chlormequat (chloride)	9351	55	ethephon	7
6	mecoprop-P*	6772	56	dichlorprop-P	4
7	daminozide	4747	57	diflufenican	4
8	bentazone	3945	58	haloxyfop-P-methylester	2
9	monolinuron	3671	59	rimsulfuron	2
10	metribuzin	3239	60	cycloxydim	1
11	prosulfocarb	3077	61	triclopyr	1
12	tri-allate	2983	62	clodinafop-propargyl	1
13	atrazine*	2619	63	fenoxaprop-P-ethyl	0.5
14	dinoterb	2206	64	desmedipham	0.4
15	pendimethalin	1502	65	quizalofop-P-ethyl	0.3
16	2,4-D	1391	66	cloquintocet-mexyl	0.1
17	dicamba	1193	67	benazolin	0.1
18	metamitron	1086	68	propaquizofop	0.0
19	ethofumesate	970	69	paclobutrazol	0.0
20	asulam	847	70	1-naftylaleneacetic acid	0
21	diquat dibromide	837	71	3-indolylacetic acid	0
22	bifenox	475	72	indol-3-butyric acid	0
23	linuron	426	73	amidosulfuron	0
24	metobromuron	302	74	borax	0
25	glyphosate-trimesium	290	75	bromacil	0
26	chloridazon	266	76	buminafos	0
27	terbutylazine	248	77	chlorpropham	0
28	ioxynyl	192	78	chlortoluron	0
29	glyphosate	188	79	cinidon-ethyl	0
30	pyridate	176	80	clomazone	0
31	paraquat-dichloride	171	81	cresoot/cresol	0
32	isoproturon	165	82	dimethenamide	0
33	propyzamide	164	83	DNOC*	0
34	aclonifen	122	84	ferri-fosphate	0
35	diuron	80	85	ferrosulphate	0
36	metazachlor	78	86	florasulam	0
37	bromoxynil	78	87	gibberellic acid A3	0
38	clopyralid	62	88	gibberellic acid A4+A7	0
39	simazine*	49	89	imazamethabenz-methyl	0
40	maleine hydrazide	47	90	isoxaflutole	0
41	glufosinate-ammonium	45	91	mesotrione	0
42	dichlobenil	43	92	metam-natrium	0
43	prometryn	37	93	mineraal oil	0
44	chlorbromuron	31	94	nicosulfuron	0
45	fluroxypyr	28	95	paraffine oil	0
46	phenmedipham	22	96	quinmerac	0
47	fluazifop-P-butyl	21	97	S-metolachlor	0
48	EPTC	19	98	sulcotrion	0
49	desmetryn	18	99	triflusulfuron-methyl	0
50	lenacil	14	100	trinexapac-ethyl	0

* *not approved*