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OPINION OF THE SCIENTIFIC COMMITTEE ON PLANTS REGARDING THE INCLUSION OF METSULFURON METHYL IN ANNEX 1 OF COUNCIL DIRECTIVE 91/414/EEC CONCERNING THE PLACING OF PLANT PROTECTION PRODUCTS ON THE MARKET

(Opinion adopted by the Scientific Committee on Plants on 17 March 2000)

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1. TITLE

OPINION OF THE SCIENTIFIC COMMITTEE ON PLANTS REGARDING THE INCLUSION OF METSULFURON METHYL IN ANNEX 1 OF DIRECTIVE 91/414/EEC CONCERNING THE PLACING OF PLANT PROTECTION PRODUCTS ON THE MARKET

2. TERMS OF REFERENCE

The Scientific Committee on Plants (SCP) is requested to respond to the following questions in the context of the Commission's work on the implementation of Directive 91/414/EEC[1] concerning the placing of plant protection products on the market.

(1) Can it be confirmed that use scenarios exist which pose no unacceptable risk to groundwater ?

(2) Can it be confirmed that the uses reviewed are acceptable for the aquatic environment?

3. BACKGROUND

Metsulfuron methyl is an existing active substance in the context of Directive 91/414/EEC concerning the placing of plant protection products on the market and is covered by the first stage of the work programme provide for under the Directive.
The Committee had been supplied with documentation comprising a dossier provided by du Pont de Nemours and Company, a monograph prepared by the French Authorities acting as Rapporteur Member State (RMS) and the recommendations of the ECCO[2] Peer Review Programme which involved contributions from experts of several Member States.

Metsulfuron methyl belongs to the sulfonylurea group of herbicides. It acts on sensitive plants by inhibition of the enzyme acetolactate synthase involved in the synthesis of branched-chain amino acids. It is currently authorised in certain Member States for use as a plant protection product on small grain cereal crops, rice, permanent meadows and linseed. It is effective in controlling a wide spectrum of broad-leaved weed species at rates of application between 4 to 8 g a.s./ ha.

[1] OJ L 230, 19. 08.1991, p.1
[2] European Community Co-ordination

4. OPINION

4.1 Question 1

Can it be confirmed that use scenarios exist which pose no unacceptable risk to groundwater?

Opinion

Use scenarios exist which pose no unacceptable risk to groundwater.

Based on available soil metabolism studies the Committee concludes that the risk to groundwater should include evaluation of the metabolites ester sulfonamide, saccharine, triazine amine, O-demethyl metsulfuron methyl and carbamoyl guanidine. The full results from laboratory studies are not currently available to characterise these metabolites. Therefore the SCP has made its own assessment of leaching potential and concludes that use scenarios exist which pose no unacceptable risk to groundwater. Subject to confirmation by the outstanding laboratory studies on the half-life and adsorption of the metabolites Member States should assess leaching potential in vulnerable locations (e.g. soils with high pH values) to determine whether the GAP[3] can achieve the desired result.

4.1.2 Scientific and Technical Background on Which the Opinion is Based

The assessment of risk to groundwater was based on modelling because no adequate field or lysimeter experiments are available for the soil metabolites of metsulfuron-methyl. Modelling should be based on estimation of the half-life (DT^{4}_{50}) in topsoil at reference conditions of (20^{o}C) and the extent of sorption (quantified as the distribution coefficient over organic-matter and water, K^{5}_{OM}) for the parent compound and for relevant metabolites. For the metabolites the percentage of molecules formed from the parent compound is also needed (this percentage is estimated from the maximum of the percentage from the soil metabolism studies) and also the ratio of the molar masses of parent and metabolite.

For the parent compound twelve sorption studies are available but five of the reported K_{OM} measurements are considered unreliable because the decrease in the concentration in the liquid phase during the adsorption study was too low to be measured accurately. The remaining seven studies results in a median K_{OM} values of about 15 L/kg. The pH of the soil is above 5 for all reliable sorption studies and the pK^{6}_{a} is 3.8. This implies that the K_{OM} applies to the anionic form of metsulfuron-methyl (so the most mobile form). Nine laboratory studies on the transformation rate of metsulfuron-methyl are available. Taking the median DT_{50} and converting for 20^{o}C gives a DT_{50} of about 40 d. This value is reasonably consistent with the available field persistence studies.

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[3] Good Agricultural Practice
[4] Degradation time for first 50% of compound
[5] Organic matter adsorption coefficient
[6] Negative logarithm (to the base 10) of the dissociation constant

For the assessment of the formation of metabolites two types of studies are available: (i) old studies with applied amounts of metsulfuron-methyl of 0.1-4 mg/kg and with uncontrolled or unknown temperature, and (ii) one new study with an applied amount stated to correspond with a normal use rate at 20 ^{o}C. Table 1 gives the seven metabolites which were formed in amounts of substance exceeding 10% in one of these soil metabolism studies. Ester sulfonamide, acid sulfonamide and phenyl urea are all transformed into saccharin. Carbamoyl guanidine is formed out of O-demethyl metsulfuron methyl. Given the results in Table 1 the Committee concludes that assessment of leaching of the following metabolites is needed: ester sulfonamide, saccharine, triazine amine, O-demethyl metsulfuron methyl and carbamoyl guanidine.

No sorption data are available for ester sulfonamide, accordingly its sorption was assumed to be zero. From the new laboratory study referred to in Table 1, a half-life of roughly 25 d at 20 ^{o}C was estimated. The percentage formed was assumed to be 11%.

The sorption of saccharine appeared too low to be measured so its sorption was assumed to be zero. The half-life at 20^{o}C was estimated to be 156 d (conservative estimate based on field dissipation studies). The percentage formed was assumed to be 9%.

The K_{OC}[7] value of triazine amine was assumed to be 155 L/kg (average of studies with four soils). The half-life in soil at 20 ^{o}C was assumed to be 313 d (based on laboratory study giving 210 d at 25 ^{o}C). The percentage formed was assumed to be 33%.

In the absence of sorption data for O-demethyl metsulfuron methyl, its sorption was assumed to be zero. Its half-life in soil at 20 ^{o}C was tentatively estimated at 120 d (in the new metabolism study 11% was detected after 10 d and less than 2% after one year). The percentage formed was assumed to be 10%.

As no sorption data are available for carbamoyl guanidine its sorption was assumed to be zero. Its half-life in soil at 20 ^{o}C was tentatively estimated at 90 d (in the new metabolism study 16% was detected after 3 months and less than 3% after one year). The percentage formed was assumed to be 16%.

The Committee was informed that DuPont is currently conducting laboratory studies on the half-life and adsorption of saccharine, triazine amine, O-demethyl metsulfuron methyl and carbamoyl guanidine but the full results of these studies were not available at the time when preparing this opinion.

Currently no agreed scenarios for assessing pesticide leaching for EU registration are available. So assessment of pesticide leaching was based on a national scenario (i.e. the Dutch standard scenario, published in J. Environ. Qual. 20: 425-435). All

metabolites were treated as if they were parent compounds. The Dutch standard scenario is based on a dose of 1kg/ha. The assessment was based on a metsulfuron-methyl application of 4 g/ha in spring assuming a linear relationship between dose and leaching (a conservative approach). For metsulfuron-methyl an estimated groundwater concentration in the order of 0.01µg/L was found.

[7] Organic carbon adsorption coefficient

This order of magnitude is consistent with measured leaching of metsulfuron-methyl in a Swedish lysimeter study. For the metabolites estimated groundwater concentrations ranged from 0.001 to 0.02 µg/L.

Table 1. Maximum percentages of amounts of substance formed for seven soil metabolites of metsulfuron-methyl. "Old studies" refers to incubations with soils treated with amounts of metsulfuron-methyl corresponding with doses of about 0.1-5 kg/ha, "New study" refers to an incubation with a soil treated at a normal use rate; "n.d." = not detected, "n.a." = not analysed.

Soil metabolite	Old studies	New study
ester sulfonamide	17	11
acid sulfonamide	16	n.d.
phenyl urea	17	3
saccharine	47	9
triazine amine	n.a.	33
O-demethyl metsulfuron methyl	n.a.	11
carbamoyl guanidine	n.a.	16

4.2. Question 2

Can it be confirmed that the uses reviewed are acceptable for the aquatic environment?

Opinion

It is the Committee's opinion that with the employment of appropriate risk mitigation measures e.g. buffer zones the proposed uses of metsulfuron methyl will not pose an unacceptable risk to aquatic algae and plants.

The Committee concludes that whereas metsulfuron methyl does not appear to pose an unacceptable risk to aquatic animals, there is cause for concern with respect to algae and aquatic plants. Toxicity varies widely among algal species, and the species used by the Notifier to estimate risk to algae (*Selenastrum capricornutum*) appears to be relatively insensitive compared to other tested species. Also, whether the TER[8] values for *S. capricornutum* and *Lemna* can be considered acceptable is critically dependent on the assumptions used to estimate both effects and exposure. It is recognised that each of these is associated with a large degree of uncertainty. Exposure assessments which consider all potential routes of entry e.g. drain flow in addition to spray drift and run-off should be made. Metabolites of this pesticide do not appear to cause unacceptable risk to aquatic organisms.

[8] toxicity exposure ration

4.2.1. Scientific Background on Which the Opinion is Based

A wide range of effect concentrations for algae and aquatic plants were provided by the Notifier as well as in an independent study by Blanck & Björnsäter (1988).

The monograph (Volume 1, p. 43) employed a 120h-EC[9]$_{50}$ of 3.5 mg/L and a 120h-NOEC[10] of 10 μg/L for the alga, *Selenastrum capricornutum*, to estimate TER_{acute} and $TER_{long\ term}$, respectively. For *Lemna minor* effect concentrations of 0.36 μg/L (14d-EC_{50}) and 0.16 μg/L (14d-NOEC) were determined. However, in calculating the $TER_{long\ term}$ for this species, rather than using the NOEC, an effect concentration of 0.32 μg/L was employed. This was the highest tested concentration at which the culture showed recovery (defined as an increase in frond number during a subsequent 7-day depuration period). It should be noted that actual concentrations of metsulfuron methyl in the test system were not verified, and the effect concentrations are therefore nominal values. The choice of effect endpoint is critical in this case since use of 0.32 gives a $TER_{long\ term}$ of 13.3 (above the cut-off of 10), whereas use of the NOEC gives a $TER_{long\ term}$ of 6.7 (below the cut-off of 10).

The exposure concentrations used to estimate the TER values in the monograph assumed spray drift from a distance of 5 m + runoff to a water body of 1 m depth (assuming a single application at 8 g a.s./ha). For drift alone from 1 m into a 30 cm deep water body (the standard scenario normally used) the initial PEC[11]$_{SW}$ would be 0.107 μg/L. If this latter PEC_{SW} is used, the TER_{acute} values become: *S. capricornutum*=3500/0.107=3.3 x 10^4; *Lemna minor*=0.36/0.107=3.4. Likewise, the $TER_{long\ term}$ values for the standard scenario are: *S. capricornutum*=10/0.106=94; *Lemna minor*=0.16/0.103=1.6. Drift from a distance of 5 m alone (i.e., without runoff) would give the following: TER_{acute} *S. capricornutum*=3.5/0.016=219; $TER_{long\ term}$ *S. capricornutum*=10/0.016=625; TER_{acute} *Lemna minor*=0.36/0.016=22.5; $TER_{long\ term}$ *Lemna minor*=0.16/0.0151=10.7. Thus whether or not TER estimates indicate acceptable risk is critically dependent on the assumptions used to calculate exposure, as well as effects. The Committee notes that none of the exposure estimates provided in the monograph consider inputs from drain flow. In some situations input from drain flow could increase PEC_{SW}, and this additional source of input should be considered by Member States with respect to local conditions.

Additional tests with two other algal species gave 120h-EC_{50}s > 95.4 μg/L (*Anabaena flos-aquae*) and 93.6 μg /L (*Skeletonema costatum*), but it should be noted that these additional tests used only one exposure concentration. Using the latter two effect endpoints with an initial PEC_{SW} from spray drift of 0.107 g/L (at 1 m) resulted in TER values of >891 and >874.

Additional effects on microalgal species were provided in a study by Blanck & Björnsäter (1988) in which a total of 40 species were tested with the formulated product Ally (20% a.s.). The most sensitive of the 20 freshwater microalgae had an EC_{50} (growth inhibition during 7d) of 0.006 M a.s. (=2.29 g a.s./L). This species was at least 2 orders of magnitude more sensitive than

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[9] Effective concentration 50%

8 No Observed Effect Concentration

[11] Predicted environmental concentration surface water

the other freshwater species tested. The most sensitive of the 20 marine species tested had an EC_{50} <0.0001 M, (i.e., < 0.04 μg /L), but this species was also $\geq$ 2 orders of magnitude more sensitive than the other marine species tested..

Using the most sensitive freshwater alga from Blanck & Björnsäter (1988) gives a TER of 2.29/0.0248 = 92 (or 2.29/0.107=21.4 for the standard scenario); or if we use the EC_{50} for the most sensitive marine species we get TER < 0.04/0.0248=1.6 or 0.04/0.107=0.4). In Blanck & Björnsäter's study, the EC_{50} for *S. capricornutum* was 13 M (=5 mg/L). Thus this species was four orders of magnitude less sensitive than the most sensitive freshwater alga and ranked 13th in sensitivity (from most to least sensitive) of the 20 freshwater species tested.

TER calculations for metsulfuron methyl with respect to aquatic algae and plants indicate that there may be unacceptable risks to these groups. Although there are uncertainties in both exposure and effects estimates, the calculations suggest that risk mitigation, in the form of buffer zones, could be employed to avoid unacceptable risks to the aquatic environment.

With regard to metabolite effects on aquatic organisms, the only metabolite occurring in water (bis-o-demethyl metsulfuron methyl, IN-JX909) showed low toxicity to *Lemna gibba* (14d-EC_{50} = 30-47 mg/L and the freshwater alga, *Selenastrum capricornutum* (120h-EC_{50} = 44-73 mg/L). It also showed low toxicity to fish and *Daphnia*. This metabolite is therefore not expected to cause an unacceptable risk to aquatic organisms. Likewise, the toxicity of metabolite IN-A4098 (triazine amine) to *Lemna gibba* was low (14d-EC_{50} > 10 mg/L nominal concentration), and the TER is well above the cut-off value.

5. REFERENCES

Blanck H, Björnsäter B. 1988. Inhibition of growth of marine and freshwater microalgae by the sulfonylurea herbicides GLEAN and ALLY in the algal microtest battery. Final Report to Nordisk Alkali Biokemi A/S.

6. ACKNOWLEDGEMENTS

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