

**MON 52276**  
**(360 g/L glyphosate acid)**

**Herbicide**

**Application for Renewal of Approval (AIR 2) according  
to Commission Regulation (EC) N° 1141/2010**

**ANNEX III**

**Document M:**

**Point 9: Fate and behaviour in the environment**

**Monsanto Europe S.A.**  
**on behalf of the 'Glyphosate Task Force'**  
**Avenue de Tervuren 270-272**  
**B-1150 Brussels**  
**Belgium**



## Table of contents

<b>IIIA 9</b>	<b>Fate and behaviour in the environment .....</b>	<b>4</b>
<b>IIIA 9.1</b>	<b>Rate of degradation in soil.....</b>	<b>4</b>
<b>IIIA 9.1.1</b>	<b>Aerobic degradation of the preparation in soil .....</b>	<b>4</b>
<b>IIIA 9.1.2</b>	<b>Anaerobic degradation of the preparation in soil .....</b>	<b>12</b>
<b>IIIA 9.2</b>	<b>Field studies .....</b>	<b>13</b>
<b>IIIA 9.2.1</b>	<b>Soil dissipation testing on a range of representative soils .....</b>	<b>13</b>
<b>IIIA 9.2.2</b>	<b>Soil residue testing.....</b>	<b>18</b>
<b>IIIA 9.2.3</b>	<b>Soil accumulation testing.....</b>	<b>18</b>
<b>IIIA 9.2.4</b>	<b>Aquatic (sediment) field dissipation .....</b>	<b>18</b>
<b>IIIA 9.2.5</b>	<b>Forestry field dissipation .....</b>	<b>18</b>
<b>IIIA 9.3</b>	<b>Mobility of the plant protection product in soil .....</b>	<b>18</b>
<b>IIIA 9.3.1</b>	<b>Column leaching.....</b>	<b>20</b>
<b>IIIA 9.3.2</b>	<b>Lysimeter studies.....</b>	<b>20</b>
<b>IIIA 9.3.3</b>	<b>Field leaching studies .....</b>	<b>21</b>
<b>IIIA 9.3.4</b>	<b>Volatility – laboratory study .....</b>	<b>21</b>
<b>IIIA 9.3.5</b>	<b>Volatility – field study.....</b>	<b>21</b>
<b>IIIA 9.4</b>	<b>Predicted environmental concentrations in soil (PEC<sub>s</sub>).....</b>	<b>22</b>
<b>IIIA 9.4.1</b>	<b>Initial PEC<sub>s</sub> value.....</b>	<b>27</b>
<b>IIIA 9.4.2</b>	<b>Short-term PEC<sub>s</sub>.....</b>	<b>27</b>
<b>IIIA 9.4.3</b>	<b>Long-term PEC<sub>s</sub>.....</b>	<b>28</b>
<b>IIIA 9.5</b>	<b>Predicted environmental concentration in soil (PEC<sub>s</sub>) for relevant metabolites .....</b>	<b>28</b>
<b>IIIA 9.5.1</b>	<b>Initial PEC<sub>s</sub> value .....</b>	<b>28</b>
<b>IIIA 9.5.2</b>	<b>Short-term PEC<sub>s</sub> values .....</b>	<b>28</b>
<b>IIIA 9.5.3</b>	<b>Long-term PEC<sub>s</sub> values.....</b>	<b>29</b>
<b>IIIA 9.6</b>	<b>Predicted environmental concentration in ground water (PEC<sub>gw</sub>).....</b>	<b>30</b>
<b>IIIA 9.6.1</b>	<b>Active substance PEC<sub>gw</sub> value.....</b>	<b>36</b>
<b>IIIA 9.6.2</b>	<b>Relevant metabolites, PEC<sub>gw</sub> values .....</b>	<b>36</b>
<b>IIIA 9.6.3</b>	<b>Additional field testing.....</b>	<b>36</b>
<b>IIIA 9.6.4</b>	<b>Information on the impact on water treatment procedures.....</b>	<b>36</b>
<b>IIIA 9.7</b>	<b>Predicted environmental concentration in surface water (PEC<sub>sw</sub>).....</b>	<b>43</b>
<b>IIIA 9.7.1</b>	<b>Initial PEC<sub>sw</sub> value for static water bodies .....</b>	<b>49</b>
<b>IIIA 9.7.2</b>	<b>Initial PEC<sub>sw</sub> value for slow moving water bodies .....</b>	<b>57</b>
<b>IIIA 9.7.3</b>	<b>Short-term PEC<sub>sw</sub> values for static water bodies .....</b>	<b>58</b>
<b>IIIA 9.7.4</b>	<b>Short-term PEC<sub>sw</sub> values for slow moving water bodies .....</b>	<b>58</b>

IIIA 9.7.5	Long-term $PEC_{sw}$ values for static water bodies .....	58
IIIA 9.7.6	Long-term $PEC_{sw}$ values for slow moving water bodies .....	59
IIIA 9.8	Predicted environmental concentration in surface water ( $PEC_{sw}$ ) for the relevant metabolites .....	59
IIIA 9.8.1	Initial $PEC_{sw}$ value for static water bodies .....	59
IIIA 9.8.2	Initial $PEC_{sw}$ value for slow moving water bodies .....	59
IIIA 9.8.3	Short-term $PEC_{sw}$ values for static water bodies .....	59
IIIA 9.8.4	Short-term $PEC_{sw}$ values for slow moving water bodies .....	59
IIIA 9.8.5	Long-term $PEC_{sw}$ values for static water bodies .....	59
IIIA 9.8.6	Long-term $PEC_{sw}$ values for slow moving water bodies .....	60
IIIA 9.8.7	Additional field testing .....	60
IIIA 9.9	Fate and behaviour in the air .....	60
IIIA 9.9.1	Spray droplet size spectrum – laboratory studies .....	60
IIIA 9.9.2	Drift – field evaluation .....	60
IIIA 9.10	Other/special studies .....	61
IIIA 9.10.1	Other/special studies – laboratory studies .....	61
IIIA 9.10.2	Other/special studies – field studies .....	61

This document is retrieved from the Bayer Transparency website. Please note that its content could be subject to copy-right and other IP-rights. Any use for commercial purposes is prohibited.

## IIIA 9 Fate and behaviour in the environment

MON 52276, the lead formulation of the Glyphosate Task Force (GTF) submission, was one of the representative formulations supporting the 2001 Annex 1 inclusion of glyphosate. This formulation is still registered in Europe and its composition has not changed. This document reviews the environmental fate studies and exposure assessment for the product MON 52276 containing 360 g glyphosate acid/L (486 g/L glyphosate isopropylamine salt) and a surfactant blend. The environmental fate of glyphosate from application of the formulation is determined by the properties of the active substance therefore the exposure assessment associated with the use of MON 52276 is relying on the information on fate and behaviour of the active substance only.

Concentrations of glyphosate in various environmental compartments are predicted following the proposed use pattern. The predicted environmental concentrations (PEC values) in soil, surface water, sediment, and groundwater following the proposed use pattern are provided. In the EU the representative use of glyphosate for the renewal of the authorisation is control of annual, perennial and biennial weeds. The representative uses supported in the GTF submission for the renewal of the authorization of glyphosate include:

- pre-emergent use of glyphosate in all crops
- pre-harvest uses in cereals and oilseeds
- orchards and vines (around the base of the trunk and as a spot treatment)

The representative GAP defines a maximum (cumulative) annual application rate of 4320 g glyphosate acid/ha in 1-3 applications, the maximum individual application rate in row crops is 2160 g glyphosate acid/ha (pre-emergent and pre-harvest use) and is 2880 g glyphosate acid/ha for spot-treatment applications in orchards. The exposure assessments in this dossier section were designed in a way that they cover all intended uses of glyphosate. The application scenarios selected for modelling purposes are specified in the respective chapters of this section.

### IIIA 9.1 Rate of degradation in soil

Additional data with the formulated product was not generated. The fate and behaviour of glyphosate in soil is discussed in detail in the Annex II dossier where the study references can be found. For a detailed presentation of data on the active substance glyphosate acid, please refer to AII annex point 7.1-7.2.

Studies show that chemical degradation, photo-decomposition and volatilisation are, at most, very minor pathways for the dissipation of glyphosate in soil. However, studies have conclusively demonstrated that glyphosate is rapidly degraded in soil, under both aerobic and slightly anaerobic conditions, by indigenous soil micro-flora. The metabolite distribution resulting from the degradation of glyphosate in soil is similar under both aerobic and anaerobic conditions. The principal soil metabolite is aminomethylphosphonic acid (AMPA). These studies also established that AMPA is further degraded by soil micro-flora,

#### IIIA 9.1.1 Aerobic degradation of the preparation in soil

Studies on aerobic degradation in soil with the formulation were not performed, since it is possible to extrapolate from data obtained with the active substance.

The results of the aerobic laboratory degradation studies (see section 5, AII annex point 7.1-7.2) have consistently demonstrated that glyphosate is degraded in soil over time to a single major metabolite aminomethylphosphonic acid (AMPA). Several other minor components were also detected but none were present in amounts greater than 3% of the applied glyphosate. The aerobic soil metabolism studies indicate that 14.7 to 50.1% of applied glyphosate degraded to AMPA. These studies clearly demonstrate that AMPA is further degraded by soil micro-flora, although at a slower rate than glyphosate. They also show that 23.6 to 79.6% of the applied glyphosate is mineralised to carbon dioxide.

The procedures for deriving degradation rates have not been standardised globally and the assumptions made when implementing kinetic models can significantly affect the results. The endpoints reported in the reports of all available glyphosate laboratory aerobic degradation studies are not appropriate for risk-assessment and exposure modelling of the environmental fate of glyphosate and AMPA in the EU. Therefore, the aerobic degradation half-lives from all available route and rate of degradation studies from the GTF member companies (including 15 data sets from nine independent aerobic soil degradation studies of glyphosate) were re-calculated in accordance with the kinetic approaches recommended in the latest guidance (FOCUS, 2006<sup>1</sup>, 2011a<sup>2</sup>). The kinetic evaluation of all laboratory soil degradation studies of glyphosate have been performed by [REDACTED] 2012 (IIIA 9.1.1/01) in a special report and a tier II summary of the report is presented below.

Updated kinetic endpoints were derived following the recommendations of FOCUS (2006, 2011a), using the modelling software, KINGUI v1.1 in the framework of MatLab 7.0.4.365 ([REDACTED], 2006<sup>3</sup>; [REDACTED], 2005<sup>4</sup>) which simulates the simultaneous degradation of glyphosate and the subsequent formation and decline of the major metabolite AMPA. Kinetic evaluation was conducted in order to derive “persistence” DegT<sub>50</sub> and DegT<sub>90</sub> values for use as a trigger for higher-tier environmental fate studies and “modelling” DegT<sub>50</sub> values for use in models for calculation of Predicted Environmental Concentrations (PECs) for ground and surface water. Four kinetic models were evaluated to provide an assessment of the kinetic behaviour of glyphosate in soil for use in subsequent risk assessments: the single first-order (SFO), the first-order multi-compartment (FOMC), the double first-order in parallel (DFOP) and the hockey-stick (HS) model.

FOCUS (2006, 2011a) guidance for deriving kinetic endpoints provides a logical stepwise assessment to derive DegT<sub>50</sub> values for pesticides and associated metabolites. According to FOCUS guidance the model that fits the experimental data best should be used to derive “persistence” endpoints. In all cases, datasets were initially evaluated by comparing SFO and FOMC kinetic models. If the degradation curve was better described by the FOMC model, then DFOP and HS were evaluated as additional bi-phasic models. “Persistence” DegT<sub>50</sub> and DegT<sub>90</sub> values were then calculated from the best-fit model in accordance with the recommendations of the FOCUS (2006, 2011a).

FOCUS guidance for deriving “modelling” endpoints (FOCUS, 2006, 2011a) is somewhat different from the guidance provided for the “persistence” endpoints. FOCUS versions of environmental fate models, which simulate the degradation of molecules in environmental compartments, usually rely on SFO kinetics to describe degradation rates in soil. Degradation parameters from alternative kinetics cannot generally be used as input data for these models, using FOCUS recommended (first-tier) approaches. Additional higher-tier approaches are available in cases that SFO fit is not acceptable. As a consequence, the guidance states that no further action is required where the SFO model fit is visually and statistically acceptable in accordance with the detailed guidance provided by FOCUS (2006, 2011a). As a first step, the degradation rates of glyphosate and AMPA in each soil were evaluated using KINGUI and SFO kinetics. If the model conformed to the acceptance criteria then no further modelling was done. If the model did not conform then additional modelling was conducted using a bi-phasic model for the parent only. The three bi-phasic models then were evaluated which were comprised of the FOMC model, the HS model, and the DFOP model. Modelling half-lives for the degradation of AMPA were calculated based on data from glyphosate aerobic degradation studies but AMPA was evaluated as an SFO model in all cases. For use in environmental fate models, modelling endpoints derived from the kinetic analysis were then

<sup>1</sup> FOCUS (2006): Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration. Report of the Work Group on Degradation Kinetics of FOCUS. EC Document Reference SANCO/10058/2005 version 2.0, June 2006.

<sup>2</sup> FOCUS (2011a): Generic Guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration, version 1.0.

<sup>3</sup> [REDACTED] (2006): Kinetic Evaluation with MATLAB: Introduction to the Use of KINGUI Version 1.1. Bayer CropScience AG.

<sup>4</sup> [REDACTED] (2005): MatLab Version 7.0.4.365 (R14) Service Pack 2, Optimisation Toolbox, Statistics Toolbox, MATLAB Compiler, January 29, 2005, The Mathworks, Inc., USA.

acorrected for soil moisture content (EU reference temperature and moisture conditions) at field capacity (pF2) and temperature (20°C), in accordance with the guidance, if necessary.

Table 9.1-1 and Table 9.1-2 summarise the “persistence” DegT<sub>50</sub> values and the “modelling” DegT<sub>50</sub> values before and after correction for moisture content of the test soils for glyphosate and AMPA, respectively. The “persistence” endpoints were not used for exposure modelling; they are only calculated for use as a “trigger” for higher-tier environmental fate studies. The normalised “modelling” DegT<sub>50</sub> values for glyphosate for use in models for calculation of PECs for ground and surface water are in the range of 2.1 to 92.7 days. The normalised DegT<sub>50</sub> values for the AMPA metabolite are in the range of 25.6 to 110.3 days.

FOCUS (2006, 2011a) recommends that “the geometric mean be used when averages of degradation rates are desired. The recommendation to use a geometric mean applies only to degradation rates, half-lives, and trigger values. Averages of other kinetic parameters such as formation fractions and fractions of starting materials applied to compartment in the DFOP model should be arithmetic means.”

The geometric mean values for the “modelling” DT<sub>50</sub> values for glyphosate and AMPA used for input to the FOCUS models in subsequent exposure modelling are 12.8 and 55.7 days, respectively. Table 9.1-3 shows the range of AMPA formation fraction calculated from the model and the arithmetic mean of AMPA formation fraction, used for input to the FOCUS groundwater models is 0.34.

Prior to kinetic evaluation all available studies were checked for their suitability and acceptability according to FOCUS (2006, 2011a) and OECD no. 307 (OECD, 2002<sup>5</sup>). A new study (██████ 2010a) was conducted since the existing studies were considered not sufficient to fulfil the required range of pH and organic matter content as required by OECD no. 307 (OECD, 2002). The kinetic evaluation was based on residue data from nine independent aerobic soil degradation studies, including 15 independent data sets. Other data set were considered not suitable. For details, please refer to AII Table 7.2-2.

<sup>5</sup> OECD (2002): Guideline for the Testing of Chemicals. Aerobic and anaerobic transformation in soil. OECD 307.



## I. MATERIALS AND METHODS

### A. MATERIALS

Not applicable, no materials were used as this study is a computer simulation.

KINGUI v1.1 in the framework of MatLab 7.0.4.365 (██████████, 2006; ██████████, 2005) was used as fitting software. Microsoft Excel™ 2003 was used for statistical evaluation of the optimised parameters.

### B. STUDY DESIGN AND METHODS

The evaluation was based on residue data from nine independent aerobic soil degradation studies, including 15 independent data sets. [ $C^{14}$ ] radiolabelled glyphosate was applied as test substance, formulated as free acid or salt, on each of the evaluated soils with a range of application rates and under varying study conditions.

The studies were conducted under laboratory conditions at a range of incubation temperatures (10°C, 20°C and 25 °C) and moisture contents as well as varying application rates (██████████ 2010a; ██████████ 1995; ██████████ 1996; ██████████ 1993; ██████████ 1996; ██████████ 1993; ██████████ 2010b; ██████████ 1993 / ██████████ 2002; ██████████ 1996). For details on the experimental conditions of the studies, please refer to AII Annex point 7.1-7.2.

According to OECD guideline 307 (OECD, 2002) sampling points should not be considered for which the overall mass balance is <90% AR. Following this guidance principle a few data points from several studies were excluded for kinetic analysis. Data points beyond the typical study duration were excluded as well. The exclusion of sampling intervals beyond the typical duration of 120 days is justified considering that the viability of soil microbes may suffer during prolonged storage of soils under laboratory conditions (SETAC, 1995<sup>6</sup>). The experimental data were adjusted for the kinetic modelling as recommended by FOCUS (2006, 2011a).

The evaluation was conducted following the guidance of FOCUS (2006, 2011a) as explained above (see Annex point IIIA 9.1.1). Persistence and modelling endpoints for glyphosate and AMPA were derived. The modelling endpoints were normalised to reference conditions (20°C, pF2). Additionally, formation fractions for AMPA were determined.

The goodness of fit of the estimated data points to the measured residue data was evaluated visually (concentration vs. time plots and residual plots) and statistically (chi-square ( $\chi^2$ ) test). A single-sided t-test was performed to evaluate whether the optimised parameters were significantly different from zero at a chosen significance level of 5%. This is particularly relevant for the degradation rate constants (k) of the SFO, HS and DFOP models. The t-test is required to be significant for modelling purposes. In case of persistence endpoints, the non-significance of parameters was not seen as cut-off criterion but the t-test was used as supporting information for the decision making process.

## II. RESULTS AND DISCUSSION

Regarding persistence endpoints the kinetic evaluation of all data sets resulted in robust kinetic fits for glyphosate with DegT<sub>50</sub> values ranging from 1.0 to 60.2 days with a median DegT<sub>50</sub> of 5.8 days across all soils. In most cases (12 out of 15 soil types examined) the DegT<sub>50</sub> values for glyphosate degradation were less than 10 days. Only in Speyer 2.2, Arrow, and 18-Acres soils glyphosate degraded with DegT<sub>50</sub> values of 18.7, 37.8 and 60.2 days, respectively. For those studies that the pattern of decline of glyphosate is clearly established within the experimental period of the study, the calculated time for 90% degradation of

<sup>6</sup> SETAC (1995): Procedures for assessing the environmental fate and ecotoxicity of pesticides.



glyphosate ( $\text{DegT}_{90}$ ) ranged from 7.2 to 159.4 days. However, due to the relatively slow rate of degradation of glyphosate in Speyer 2.2, 18-Acres, and Arrow soils and the study duration of 120 days, degradation to 10% of the initial glyphosate concentration was not reached within the experimental period in these soils. This indicates that a reliable  $\text{DegT}_{90}$  estimate cannot be derived in these three soils, since extrapolation of the bi-phasic non-linear model beyond the duration of the study generally results in unrealistically long  $\text{DegT}_{90}$  values. All degradation patterns were biphasic with ten soils exhibiting DFOP (double first-order in parallel) and five soils exhibiting FOMC kinetics (first-order multi-compartment).

For the major metabolite AMPA, only the degradation studies conducted with the parent glyphosate were available for kinetic evaluation. Eight out of 15 soils could be kinetically evaluated. Mainly due to the continuous formation of AMPA and the short duration of the studies (120 days) a clear pattern of decline of AMPA was not established in a few studies and no accurate  $\text{DegT}$  value could be calculated for AMPA. In the study of [REDACTED] (1993), AMPA was not detected and, therefore no kinetic fitting could be conducted for the metabolite. Persistence  $\text{DegT}_{50}$  values of AMPA ranged from 99.0 to 134.8 days ( $10^{\circ}\text{C}$ ) and 126.6 ( $20^{\circ}\text{C}$ ). All pathway fits were conducted using the SFO kinetic model for AMPA.

Regarding modelling endpoints to be used in environmental fate models, fourteen soils could be kinetically evaluated for the parent compound glyphosate resulting in  $\text{DegT}_{50}$  values from 1.9 to 173.3 days (one soil was considered not suitable for the kinetic evaluation). Since all degradation patterns better fitted a biphasic model, whereas SFO kinetics are needed for environmental fate models, the  $\text{DegT}_{50}$  values are expressed as pseudo-SFO following FOCUS guidance (FOCUS, 2006, 2011a). Normalisation to  $20^{\circ}\text{C}$  and pF2 led to  $\text{DegT}_{50}$  values ranging from 2.1 to 92.7 days with a geometric mean of 12.8 days. For the major metabolite AMPA, seven soils could be evaluated resulting in  $\text{DegT}_{50}$  values from 42.1 to 133.7 days, while normalised  $\text{DegT}_{50}$  values ( $20^{\circ}\text{C}$  and pF2) ranged from 25.6 to 110.3 days with a geometric mean of 55.7 days.

The formation fraction of AMPA derived from persistence endpoints was determined to be between 0.18 and 0.57 (arithmetic mean = 0.34) and for the modelling endpoints it ranged from 0.18 to 0.61 (arithmetic mean = 0.34). For use in environmental fate models for groundwater exposure an arithmetic mean value of 0.34 was used for AMPA formation fraction.

The kinetic endpoints are summarised in Table 9.1-1 (glyphosate), Table 9.1-2 (AMPA) and Table 9.1-3 (formation fraction for AMPA).

Table 9.1-1: Persistence and modelling endpoints of glyphosate according to FOCUS degradation kinetics<sup>7)</sup>

Study	Soil	Temp. (°C)	Persistence endpoints			Modelling endpoints		
			Model	DegT <sub>50</sub> (days)	DegT <sub>90</sub> (days)	Model	Non-normalised DegT <sub>50</sub> (days)	Normalised DegT <sub>50</sub> (days) (20°C, pF2)
(2010a) (IIA7.1.1/01)	Gartenacker	20	DFOP	7.9	56.3	FOMC	17.8 <sup>1)</sup>	9.4 <sup>1)</sup>
(1995) (IIA7.1.1/02)	Arrow	20	FOMC	37.8	(> 1000 <sup>5)</sup> )	DFOP	93.7 <sup>2)</sup>	63.1 <sup>2)</sup>
(1996) (IIA7.1.1/03)	Soil B	25	FOMC	1.2	20.7	FOMC	6.2 <sup>1)</sup>	6.9 <sup>1)</sup>
(1993)	Les Evouettes	20	DFOP	8.8	159.4	DFOP	69.3 <sup>2)</sup>	92.2 <sup>2)</sup>
(1996a) (IIA7.1.1/04)	Visalia	25	DFOP	1.0	1.9 <sup>4)</sup>	FOMC	1.9 <sup>4)</sup>	2.1 <sup>1)</sup>
(1993)	Maasdijk	20	DFOP	4.6	62.0	FOMC	18.0 <sup>1)</sup>	15.2 <sup>1)</sup>
(2010b) (IIA 7.2.1/01)	Drusenheim	20	DFOP	2.1	15.4	FOMC	5.4 <sup>1)</sup>	2.9 <sup>1)</sup>
	Pappelacker	20	FOMC	3.9	43.4	FOMC	13.7 <sup>1)</sup>	5.9 <sup>1)</sup>
	18-Acres	20	FOMC	60.2	(61000 <sup>5)</sup> )	DFOP	173.3 <sup>2)</sup>	92.7 <sup>2)</sup>
(1993), (2002)	Speyer 2.2	20	DFOP	1.6	150.6	- <sup>3)</sup>	- <sup>3)</sup>	- <sup>3)</sup>
	Speyer 2.3	20	DFOP	5.8	22.0	FOMC	7.2 <sup>1)</sup>	5.5 <sup>1)</sup>
(1996) (IIA7.1.1/05)	Speyer 2.1	20	DFOP	8.3	51.3	FOMC	19.5 <sup>1)</sup>	18.1 <sup>1)</sup>
	Speyer 2.2	20	FOMC	18.7	(428.6 <sup>5)</sup> )	DFOP	72.2 <sup>2)</sup>	60.2 <sup>2)</sup>
	Speyer 2.3	20	DFOP	2.7	15.0	FOMC	3.8 <sup>1)</sup>	4.7 <sup>1), 4)</sup>
	Speyer 2.3	10	DFOP	8.1	50.8	FOMC	19.5 <sup>1)</sup>	
Number of values				15	12		14	13
Minimum				1.0	7.2		1.9	2.1
Maximum				60.2	159.4		173.3	92.7
Geometric mean				5.7	36.8		17.3	12.8

1) Back-calculated from FOMC DegT<sub>90</sub>/3.32

2) Calculated from slower k-rate of DFOP model

3) No acceptable fit for the derivation of modelling endpoints could be obtained

4) Arithmetic mean of normalised DegT<sub>50</sub> (20°C, pF2) of 10°C and 20°C soil

5) KinGUI does not extrapolate beyond 1000 days

6) Compared with the results from the other data sets, the DT<sub>90</sub> estimated with the FOMC model and extrapolated beyond the study duration seems to be unrealistically long (FOCUS 2006, 2011a). The value was therefore excluded from statistics.7) DegT<sub>50</sub> or DegT<sub>90</sub> = description for time taken for 50 percent or 90 percent of a substance to disappear from a compartment due to degradation processes alone

Values in brackets were not considered for calculation of mean values.

Study	Soil	Temp. (°C)	Persistence endpoints			Modelling endpoints (for environmental fate models)		
			Model	DegT <sub>50</sub> (days)	DegT <sub>90</sub> (days)	Model	Non-normalised DegT <sub>50</sub> (days)	Normalised DegT <sub>50</sub> (days) (20°C, pF2)
██████ (2010a) (IIA7.1.1/01)	Gartenacker	20	SFO	120.1	398.9	SFO	133.7	70.9
██████ (1995) (IIA7.1.1/02)	Arrow	20	_ <sup>1)</sup>	_ <sup>1)</sup>	_ <sup>1)</sup>	_ <sup>1)</sup>	_ <sup>1)</sup>	_ <sup>1)</sup>
██████ (1996) (IIA7.1.1/03)	Soil B	25	SFO	99.1	329.1	SFO	99.1	110.3
██████ (1993)	Les Evouettes	20	_ <sup>1)</sup>	_ <sup>1)</sup>	_ <sup>1)</sup>	_ <sup>1)</sup>	_ <sup>1)</sup>	_ <sup>1)</sup>
██████ (1996a) (IIA7.1.1/04)	Visalia	25	SFO	70.7	234.9	SFO	68.6	76.3
██████ (1993)	Maasdijk	20	_ <sup>2)</sup>	_ <sup>2)</sup>	_ <sup>2)</sup>	_ <sup>2)</sup>	_ <sup>2)</sup>	_ <sup>2)</sup>
██████ (2010b) (IIA 7.2.1/01)	Drusenheim	20	SFO	39.0	129.5	SFO	47.0	25.6
	Pappelacker	20	SFO	126.6	420.5	SFO	126.6	57.2
	18-Acres	20	_ <sup>1)</sup>	_ <sup>1)</sup>	_ <sup>1)</sup>	_ <sup>1)</sup>	_ <sup>1)</sup>	_ <sup>1)</sup>
██████ (1993), ██████ (2002)	Speyer 2.2	20	_ <sup>1)</sup>	_ <sup>1)</sup>	_ <sup>1)</sup>	_ <sup>1)</sup>	_ <sup>1)</sup>	_ <sup>1)</sup>
	Speyer 2.3	20	SFO	70.5	257.4	SFO	70.9	54.5
██████ (1996) (IIA7.1.1/05)	Speyer 2.1	20	_ <sup>1)</sup>	_ <sup>1)</sup>	_ <sup>1)</sup>	_ <sup>1)</sup>	_ <sup>1)</sup>	_ <sup>1)</sup>
	Speyer 2.2	20	_ <sup>1)</sup>	_ <sup>1)</sup>	_ <sup>1)</sup>	_ <sup>1)</sup>	_ <sup>1)</sup>	_ <sup>1)</sup>
	Speyer 2.3	20	SFO	47.9	139.1	SFO	42.1	35.1
	Speyer 2.3	10	SFO	134.8	447.9	_ <sup>3)</sup>	_ <sup>3)</sup>	_ <sup>3)</sup>
Number of values				8	8		7	7
Minimum				39	129.5		42.1	25.6
Maximum				134.8/ 126.6 <sup>4)</sup>	447.7/ 420.5 <sup>4)</sup>		133.7	110.3
Geometric mean				80.8	268.4		77.1	55.7

- 1) Due to the continued formation of AMPA from glyphosate in the study and short study duration, a clear pattern of decline of AMPA was not established; no acceptable fit for AMPA obtained
- 2) Metabolite AMPA was not detected in study
- 3) T-test for k-rate not significant; DegT<sub>50</sub> was excluded from obtained modelling endpoints
- 4) Maximum at 10°C and 20°C

Table 9.1-3: Formation fractions of AMPA in aerobic soil degradation studies

Study	Soil	Formation fraction persistence endpoints	Formation fraction modelling endpoints
		Glyphosate → AMPA	Glyphosate → AMPA
(2010a) (IIA7.1.1/01)	Gartenacker	0.18	0.18
(1995) (IIA7.1.1/02)	Arrow	0.40 <sup>5)</sup>	0.40 <sup>5)</sup>
(1996) (IIA7.1.1/03)	Soil B	0.26	0.26
(1993)	Les Evouettes	0.34 <sup>5)</sup>	0.34 <sup>5)</sup>
(1996a) (IIA7.1.1/04)	Visalia	0.28	0.28
(1993)	Maasdijk	- <sup>1)</sup>	-
(2010b) (IIA 7.2.1/01)	Drusenheim	0.26	0.26
	Pappelacker	0.18	0.18
	18-Acres	0.21 <sup>5)</sup>	0.22 <sup>5)</sup>
(1993), (2002)	Speyer 2.2	- <sup>2)</sup>	-
	Speyer 2.3	0.34	0.34
(1996) (IIA7.1.1/05)	Speyer 2.1	0.51 <sup>5)</sup>	0.52 <sup>5)</sup>
	Speyer 2.2	0.57 <sup>5)</sup>	0.61 <sup>5)</sup>
	Speyer 2.3 (20°C)	0.42	0.43 <sup>4) 6)</sup>
	Speyer 2.3 (10°C)	0.45	
Number of values		13	12
Minimum		0.18	0.18
Maximum		0.57	0.61
Arithmetic mean		0.34	0.34

1) Metabolite AMPA was not detected in study

2) Decline phase of AMPA not reached during study, no acceptable visual fit for formation phase

3) No pathway fit possible; parent fit was excluded due to non-significant t-test and great variations in confidence intervals

4) Arithmetic mean of 10°C and 20°C, not

5) Acceptable visual fit for formation phase of AMPA, however no statistically acceptable fit could be obtained in this pathway

6) Acceptable visual fit for formation phase of AMPA, however no statistically acceptable fit could be obtained in this pathway for the 10°C soil

### III. CONCLUSION

For use in environmental fate models, the geometric mean values of the normalised modelling endpoints (20 °C, pF2), *i.e.* **12.8 days** (n=13) and **55.7 days** (n=7), for glyphosate and AMPA, respectively, are recommended. The arithmetic mean formation fraction of AMPA is **0.34** (n=12).

For use in soil persistence (PEC) calculations (e.g. ModelMaker™, spreadsheet calculations), the maximum persistence DT<sub>50</sub> field values of glyphosate and AMPA are recommended (please refer to IIIA 9.2.1/01).

#### IIIA 9.1.2 Anaerobic degradation of the preparation in soil

Studies on anaerobic degradation in soil with the formulation were not performed, since it is possible to extrapolate from data obtained with the active substance. During the 2001 EU glyphosate review, laboratory studies on anaerobic route of degradation of glyphosate in soil (2000) showed that glyphosate degradation was negligible under anoxic anaerobic conditions as dictated by the old SETAC anaerobic soil test guideline.

Since the EU review, a new laboratory anaerobic degradation study with glyphosate has been conducted according to the requirements of the new OECD Guideline 307 for anaerobic transformation in soil

(Lowrie et al., 2003). In the new study the degradation of [ $^{14}\text{C}$ ] glyphosate was investigated in a flooded sandy loam soil following an aerobic aging period equivalent to one half-life. The results of the new anaerobic laboratory degradation study show that glyphosate also degrades under anaerobic conditions although at slower rate than under aerobic conditions. The anaerobic DegT<sub>50</sub>, calculated over a period of 120 days of anaerobic incubation was established as 142 and 205 days for the soil and total system (soil/water compartments), respectively. The metabolite distribution resulting from the degradation of glyphosate in soil is similar under both aerobic and anaerobic conditions. Levels of AMPA, the most significant degradation product, increased to 30% of applied dose after 84 days and subsequently declined to 28% of the dose after 120 days of anaerobic incubation. Due to the relatively fast rate of formation of AMPA in the study and the short duration of the study (120 days) a clear pattern of decline of AMPA was not established in the study and no accurate DegT<sub>50</sub> value can be calculated for AMPA (see section 5, Annex Tier II, point 7.1.2 for a detailed discussion of anaerobic soil degradation of glyphosate).

According to GAP information, for glyphosate use in arable cropping systems fully anaerobic conditions are expected to be rare throughout the surface soil zone where glyphosate occurs. Where anaerobic conditions occur in the surface soil layer, aerobic conditions are normally re-established quickly resulting in rapid degradation as shown previously. Therefore, true anaerobic conditions in the surface layers of soil are expected to be transient and the anaerobic studies were not considered relevant for the PEC calculations. For the same reason, no kinetic evaluation following current FOCUS guidance (FOCUS, 2006, 2011a) was conducted.

## III A 9.2 Field studies

No new field dissipation studies were conducted for the renewal dossier. However, the kinetics used to derive dissipation half-lives of the existing soil dissipation studies, which have already been reviewed during the 2001 EU evaluation of glyphosate, were re-calculated by the GTF in accordance with the latest guidance (FOCUS, 2006, 2011a).

### III A 9.2.1 Soil dissipation testing on a range of representative soils

The environmental fate of glyphosate in soil has been evaluated under typical field use conditions where glyphosate was applied to bare soil. The studies were carried out on sites in Northern America and Central Europe in areas representative for middle Europe (multiple field locations in Germany and Switzerland) and areas with climate and soil characteristics comparable with those in Southern Europe (USA/Tennessee, California, Georgia) and northern Europe (Canada). Kinetic endpoints were derived following the recommendations of FOCUS guidance (2006, 2011a). Results are summarised below. Studies that were not considered acceptable, e.g. because of missing soil characterisation, were reported in the overview but excluded prior to analysis. Therefore, 21 trials from seven studies were evaluated. The kinetic endpoints (persistence endpoints) were used for calculation of PEC in soil as recommended by FOCUS.

Annex point	Author(s)	Year	Study title
IIIA 9.2.1/01	██████████	2012	Kinetic modelling analysis of the degradation behaviour of glyphosate and its metabolite AMPA in field soil dissipation studies  Company: ██████████ ██████████  Report No: 303604-2 Date: April 27, 2012 GLP: No (kinetic evaluation: does not contain laboratory work) Not published
Guideline:			FOCUS (2006): Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration. Report of the Work Group on Degradation Kinetics of FOCUS, EC Document Reference SANCO/10058/2005 version 2.0, June 2006.  FOCUS (2011a): Generic Guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration, version 1.0.
Deviations:			None
Dates of experimental work:			Not relevant

### Executive summary

The field soil dissipation studies of glyphosate were evaluated following FOCUS guidance (FOCUS, 2006, 2011a) in order to derive persistence  $DT_{50}$  values as trigger endpoints and for  $PEC_s$  calculations using best-fit kinetics for glyphosate and its major soil metabolite AMPA. The evaluation was based on residue data from seven independent field soil dissipation studies, including 21 independent trials. The dissipation rates of glyphosate and AMPA were evaluated using KINGUI v. 1.1 (██████████, 2006; ██████████, 2005).

$DT_{50}$  values for glyphosate dissipation in the field ranged from 2.3 to 40.9 days with the exception of only one site in Iowa, USA, for which the  $DT_{50}$  was 143.3 days. The corresponding  $DT_{90}$  values ranged from 22.6 to 706.6 days, but were typically less than one year (15 out of 18 trials) with a geometric mean  $DT_{90}$  value of 121 days across all 18 locations. Persistence  $DT_{50}$  values of AMPA ranged from 48.5 to 514.9 days, but were typically less than one year (seven out of nine trials). Pathway fits were acceptable in four soils resulting in formation fractions between 0.25 and 0.55.

For use in soil persistence ( $PEC_s$ ) calculations, the maximum persistence endpoints, i.e. 143.3 days (n=18) and 514.9 days (n=9), for glyphosate and AMPA, respectively, are recommended. The formation fraction of AMPA, corresponding to the kinetic fit with the maximum  $DT_{50}$  of AMPA, is 0.51.

## I. MATERIALS AND METHODS

### A. MATERIALS

Not applicable, no materials were used as this study is a computer simulation.

KINGUI v1.1 in the framework of MatLab 7.0.4.365 (\_\_\_\_\_, 2006; \_\_\_\_\_, 2005) was used as fitting software. Microsoft Excel™ 2003 was used for statistical evaluation of the optimised parameters.

### B. STUDY DESIGN AND METHODS

The evaluation was based on soil residue data from seven field soil dissipation studies (21 trials) with different soil types and application rates where glyphosate, formulated as a salt, was applied as test substance.

The seven field soil dissipation studies (\_\_\_\_\_ 1993; \_\_\_\_\_ 1993; \_\_\_\_\_ 1992a – 1992d; \_\_\_\_\_ 1992) were conducted on 21 sites in North America and Central Europe. Different amounts of glyphosate-trimesium or the isopropylamine-salt of glyphosate were applied to bare soil. Glyphosate is a strong acid, therefore, in spray solutions and in soil, glyphosate acid and the corresponding counter ions are rapidly ionized resulting in the formation of the freely dissociated anion (glyphosate) and the corresponding cation (*e.g.*, isopropylamine and trimesium cations). Regardless of the glyphosate formulation used in the soil dissipation studies, the exact ionic form of glyphosate in the environment will be determined mainly by the pH and the presence of other naturally occurring counter ions in soil and spray solutions. Thus, soil samples from studies conducted with both salts and both formulations of glyphosate were analysed for glyphosate and its metabolite AMPA in accordance with the degradation scheme obtained from the lab studies.

According to FOCUS (2006, 2011a) true replicates should be used for the kinetic evaluation if available. Following this principle, the soil sampling strategy in the studies was evaluated and mean values were used in all cases. Since residue data from several soil layers were available, the measured residues (mg/kg) of the soil layers had to be converted considering the layer depth and bulk density (expressed in kg/ha,) and then summed up. The experimental data were then adjusted for the kinetic modelling as recommended by FOCUS (2006, 2011a).

Persistence endpoints for glyphosate and AMPA were derived following the guidance of FOCUS (2006, 2011a). Additionally, formation fractions for AMPA were determined.

The initial hypothesis for each dataset was that the glyphosate residue data were best described by single first-order (SFO) kinetics. As a first step, first-order kinetics were fitted to the glyphosate residue data. The fit of the SFO model was compared to the fit of the First-Order Multi-Compartment (FOMC) kinetic model to test this hypothesis. Where the hypothesis was rejected the bi-exponential or Double First-Order in Parallel (DFOP) bi-phasic model was compared to the FOMC model to assess which was the most appropriate bi-phasic model for describing the dissipation kinetics of glyphosate in soil. In each case the data were fitted un-weighted with the complete data set. The goodness of fit of the kinetic models was assessed both statistically and visually in accordance with the guidance provided by FOCUS (2006, 2011a). The Chi-square test ( $\chi^2$ -test) was employed as a statistical measure of the goodness of fit. For fits conducted with the SFO and DFOP models, parameter confidence was additionally assessed using the t-test function. For fits conducted with the FOMC model, however, the t-test is not appropriate as a measure of confidence (FOCUS, 2006, 2011a). Therefore 95% confidence intervals were assessed for every parameter estimated using the SFO, FOMC and DFOP models, and a fit was considered acceptable if the confidence intervals of all estimated parameters did not include zero.

As suggested by FOCUS guidance (2006, 2011a), the metabolite AMPA was fitted, applying the SFO model for the metabolite, in a “pathway fit” simulating the simultaneous formation of AMPA from glyphosate and its subsequent degradation in soil. If the pathway fit did not provide visual and statistically

acceptable results, the fitting procedure was repeated using the decline phase of AMPA from the point of maximum concentration observed. The kinetic evaluation of both AMPA and glyphosate was based on soil residue data from seven field soil dissipation studies (21 trials) in North America and Central Europe.

## II. RESULTS AND DISCUSSION

Regarding the parent compound glyphosate, robust kinetic fits could be derived for 18 soils of the 21 sites with sufficient data to describe the decline of glyphosate.  $DT_{50}$  values for glyphosate dissipation in field ranged from 2.3 to 40.9 days with the exception of only one site in Iowa, USA, for which the  $DT_{50}$  was 143.3 days. The degradation patterns were biphasic in 13 cases with ten soils exhibiting DFOP and three soils exhibiting FOMC kinetics. For the other four soils the SFO model provided the best fit. The corresponding  $DT_{90}$  values ranged from 22.6 to 706.6 days, but were typically less than one year (15 out of 18 trials) with a geometric mean  $DT_{90}$  value of 121 days across all 18 locations.

Due to pronounced and continuous non-linear transformation of glyphosate to AMPA in soil, only nine out of 21 soil dissipation locations contain sufficient data to adequately describe the pattern of decline of AMPA in these studies. Pathway fits were acceptable in four soils resulting in formation fractions between 0.25 and 0.55. For the other five soils, only the decline phase of AMPA was used for the kinetic fitting. Persistence  $DT_{50}$  values of AMPA ranged from 48.5 to 514.9 days, but were typically less than one year (seven out of nine trials). All pathway fits were conducted using the SFO kinetic model for AMPA. The SFO model also provided the best-fit fits except for one soil which exhibited DFOP kinetics.

The kinetic endpoints are summarised in Table 9.2-1.

This document is controlled by the Bayer Transparency website. Please note that its content is subject to copy-right and other IP rights. Any use for commercial purposes is prohibited.



Table 9.2-1: Persistence endpoints of glyphosate and AMPA derived from field studies

Study	Site	Glyphosate			AMPA			
		DT <sub>50</sub>	DT <sub>90</sub>	Model	Formation fraction	DT <sub>50</sub>	DT <sub>90</sub>	Model
█ (1993)	Arizona, USA	25.7	85.3	SFO	<sup>-1)</sup>	<sup>-1)</sup>	<sup>-1)</sup>	<sup>-1)</sup>
	California, USA	12.8	105.7	DFOP	<sup>-1)</sup>	<sup>-1)</sup>	<sup>-1)</sup>	<sup>-1)</sup>
	Georgia, USA	9.1	79.7	FOMC	<sup>-1)</sup>	<sup>-1)</sup>	<sup>-1)</sup>	<sup>-1)</sup>
	Iowa, USA	143.3	706.6	DFOP	<sup>-1)</sup>	<sup>-1)</sup>	<sup>-1)</sup>	<sup>-1)</sup>
	Minnesota, USA	12.6	113.8	DFOP	<sup>-2)</sup>	302.0	(> 1000 <sup>4)</sup> )	SFO
	New York, USA	34.1	634.3	FOMC	<sup>-1)</sup>	<sup>-1)</sup>	<sup>1)</sup>	<sup>-1)</sup>
	Ohio, USA	2.3	60.0	DFOP	<sup>-2)</sup>	63.5	692.5	DFOP
	Texas, USA	6.8	22.6	SFO	<sup>-1)</sup>	48.5	161.0	SFO
█ (1993)	Alberta, Canada	<sup>-3)</sup>	<sup>-3)</sup>	<sup>-3)</sup>	<sup>-1), 3)</sup>	<sup>-1)</sup>	<sup>-1)</sup>	<sup>-1)</sup>
	Manitoba, Canada	15.0	49.8	SFO	0.25	304.5	(> 1000 <sup>4)</sup> )	SFO
	Ontario, Canada	10.6	48.6	DFOP	0.55	248.1	824.2	SFO
█ (1992a)	Diegten, Switzerland	6.1	116.1	DFOP	<sup>-1)</sup>	<sup>-1)</sup>	<sup>-1)</sup>	<sup>-1)</sup>
█ (1992b)	Egerkingen, Switzerland	<sup>-3)</sup>	<sup>-3)</sup>	<sup>-3)</sup>	<sup>-1), 3)</sup>	<sup>-1)</sup>	<sup>-1)</sup>	<sup>-1)</sup>
█ (1992c)	Bad Krozingen, Germany	<sup>-3)</sup>	<sup>-3)</sup>	<sup>-3)</sup>	<sup>-1), 3)</sup>	<sup>-1)</sup>	<sup>-1)</sup>	<sup>-1)</sup>
█ (1992d)	Menslage, Germany	5.7	200.8	DFOP	<sup>-1)</sup>	<sup>-1)</sup>	<sup>-1)</sup>	<sup>-1)</sup>
█ (1992)	Buchen, Germany	40.9	187.3	DFOP	<sup>-1)</sup>	<sup>-1)</sup>	<sup>-1)</sup>	<sup>-1)</sup>
	Kleinzecher, Germany	38.3	386.6	DFOP	0.51	514.9	(> 1000 <sup>4)</sup> )	SFO
	Unzhurst, Germany	27.7	122.3	DFOP	<sup>-1)</sup>	<sup>-1)</sup>	<sup>-1)</sup>	<sup>-1)</sup>
	Rohrbach, Germany	60.1	66.9	SFO	<sup>-1)</sup>	374.9	(> 1000 <sup>4)</sup> )	SFO
	Herrngiersdorf, Germany	33.7	111.9	SFO	<sup>-2)</sup>	288.4	958.1	SFO
	Wang-Inzkofen, Germany	17.8	165.5	FOMC	0.55	283.6	942.3	SFO
Number of values		18	18		4	9	9	-
Minimum		2.3	22.6		0.25	48.5	161.0	
Maximum		143.3	706.6	-	0.55	514.9	>1000 <sup>4)</sup>	-
Geometric mean (degradation)		16.5	121.0	-	<sup>-5)</sup>	217.9	607.8	-
Arithmetic mean (FF)			<sup>-5)</sup>	-	0.42	<sup>-5)</sup>	<sup>-5)</sup>	-

1) No acceptable fit for metabolite

2) Fit for metabolite = decline fit

3) No acceptable fit for parent

4) KinGUI does not extrapolate beyond 1000 days

5) According to FOCUS (2006, 2011a) the geometric mean should be used for averaging degradation rates and half-lives while the arithmetic mean should be used for formation fractions.

Values in brackets were not considered for the calculation of mean values.

### III. CONCLUSION

For use in soil persistence (PEC<sub>s</sub>) calculations, the maximum persistence endpoints, *i.e.* **143.3 days** (n=18) and **514.9 days** (n=9), for glyphosate and AMPA, respectively, are recommended. The formation fraction of AMPA, corresponding to the kinetic fit with the maximum DT<sub>50</sub> of AMPA, is **0.51**.

For use in environmental fate models, the geometric mean values of the normalised modelling endpoints (20 °C, pF2) derived from **laboratory** studies of glyphosate and AMPA are recommended (please refer to IIIA 9.1.1/01).

### IIIA 9.2.2 Soil residue testing

During the 2001 EU review of glyphosate it was concluded that:

“Soil residues studies for glyphosate are not required because  $DT_{50}$  lab of glyphosate is less than one-third of the period between the application and harvest in most cases and absorption by the succeeding crop is not possible.”

This conclusion can be confirmed in the renewal dossier based upon the up-dated lab  $DegT_{50}$  data presented in Section IIIA 9.1.

### IIIA 9.2.3 Soil accumulation testing

During the 2001 EU review of glyphosate it was concluded that:

“soil accumulation studies are not required for glyphosate because the  $DT_{90}$  values for glyphosate in field dissipation studies are in most cases less than 1 year. The differing results for the degradation rates of the relevant metabolite AMPA cause further consideration of its accumulation potential for a confirmatory evaluation.”

This conclusion can be confirmed in the renewal dossier based upon the updated persistence endpoints derived from field dissipation studies in Section IIIA 9.2.  $DT_{90}$  values for glyphosate dissipation from 15 out of the 18 trials, with sufficient data to describe the decline of glyphosate and representing the various soil types and climatic conditions in Europe, were less than one year. The geometric mean  $DT_{90}$  value for glyphosate dissipation across all 18 locations was 121 days.

$DT_{90}$  values of AMPA from the glyphosate soil dissipation studies were generally higher than one year. However, due to the non-linear transformation of glyphosate to AMPA, there were not sufficient data to adequately describe the pattern of decline of AMPA in the majority of the soil dissipation studies. As a consequence, the potential for accumulation in soil was addressed by modelling. The long-term plateau  $PEC_s$  are presented in Annex Point IIIA 9.4.

### IIIA 9.2.4 Aquatic (sediment) field dissipation

This item is not an EU 91/414EEC data requirement.

### IIIA 9.2.5 Forestry field dissipation

This item is not an EU 91/414EEC data requirement.

## IIIA 9.3 Mobility of the plant protection product in soil

Studies on adsorption and desorption behaviour of the preparation were not performed, since it is possible to extrapolate from data obtained with the active substance (see section AII 7.4.1 and AII 7.4.2 for details).

Several studies were conducted to determine the adsorption and desorption behaviour of glyphosate and its principal soil metabolite AMPA in soil. Only studies in which  $K_f/K_{foc}$  and  $1/n$  values were calculated based on the Freundlich Isotherm were considered for modelling purposes and in the following summary. The  $K_f$  and  $K_{foc}$  values for glyphosate ranged from 9.4 to 897 (arithmetic mean: 259 mL/g) and 1600 to 60000 mL/g (arithmetic mean: 16810), respectively. The  $K_f$  and  $K_{foc}$  values for AMPA ranged from 10 to 509 (arithmetic mean: 112 mL/g) and 1119 to 45900 mL/g (arithmetic mean: 9749 mL/g), respectively. In general, the pH, % organic carbon, % clay, or cation-exchange capacities (CEC) had minimal effect upon glyphosate and AMPA adsorption to soils.

These results demonstrate that glyphosate and AMPA possess a very low potential for leaching in soil. Both compounds can be classified as 'non mobile' according to the classification indexes of Briggs (1973)<sup>7</sup>. Details are presented in AII 7.4.1 and AII 7.4.2 and are summarised in Table 9.3-1 (glyphosate) and Table 9.3-2 (AMPA). For environmental fate modelling, the arithmetic mean  $K_{foc}$  and 1/n value of glyphosate (16810 mL/g and 0.80, n=15) and AMPA (9749 mL/g and 0.80, n=16) were used.

**Table 9.3-1 Overview of the glyphosate adsorption desorption studies**

Reference		Soil	Soil type	OC [%]	pH [-]	K <sub>f</sub> [mL/g]	K <sub>foc</sub> / K <sub>oc</sub> [mL/g] <sup>o</sup>	Freundl. exp. 1/n
Studies from the 2001 evaluation	[redacted] 1986	Drummer	Silty clay loam	1.45	6.5 <sup>2)</sup>	324.0	2300	0.92
		Dupo	Silt loam	0.87	7.4 <sup>2)</sup>	33.0	8800	0.80
		Spinks	Loamy sand	1.10	5.2 <sup>2)</sup>	660.0	60000	1.16
	[redacted] 1992	Greenan sand	Sand	0.80	3.7 <sup>2)</sup>	-	32808 <sup>6)</sup>	-
		Auchincruive	Sand loam	1.60	7.1 <sup>2)</sup>	-	50060 <sup>6)</sup>	-
		Headley Hall	Sandy clay loam	1.40	7.8 <sup>2)</sup>	-	3598 <sup>6)</sup>	-
		Californian sandy soil	Loamy sand	0.60	8.32 <sup>2)</sup>	-	884 <sup>6)</sup>	-
		Les Evouettes II	Silt loam	1.40	6.1 <sup>2)</sup>	-	3404 <sup>6)</sup>	-
		Darnconner sediment	Loam	3.00	7.1 <sup>2)</sup>	-	17010 <sup>6)</sup>	-
Studies not reviewed in the 2001 evaluation or new studies	[redacted] 1996 (IIA7.1.4/03)	Lilly Field	Sand	0.9	5.5 <sup>2)</sup>	64.0	22000	0.75
		Visalia	Sandy loam	0.58	8.4 <sup>2)</sup>	9.4	1600	0.72
		Wisborough Green	Silty clay loam	2.26	5.7 <sup>2)</sup>	470.0	21000	0.93
		Champaign	Silty clay loam	2.15	6.2 <sup>2)</sup>	700.0	33000	0.94
		18 Acres	Sandy loam	1.80	4.2 <sup>2)</sup>	90.0	5000	0.76
	[redacted] 2001 (IIA7.4.1/01)	Speyer 2.1 <sup>1)</sup>	Sand	0.56	6.0 <sup>3)</sup>	57.2 <sup>4)</sup>	10000	0.60
		Cranfield 115	Clay loam	1.70	7.9 <sup>2)</sup>	216.0 <sup>4)</sup>	12500	0.66
		Cranfield 164	Silt loam	3.00	7.1 <sup>2)</sup>	897.0 <sup>4)</sup>	30000	0.73
		Cranfield 243	Sandy loam	1.10	5.4 <sup>2)</sup>	222.5 <sup>4)</sup>	20000	0.59
	[redacted] 1996 (IIA7.1.4/02)	Speyer 2.1 <sup>1)</sup>	sand	0.62	5.9 <sup>3)</sup>	29.5 <sup>5)</sup>	4762	0.84
		Speyer 2.2 <sup>1)</sup>	loamy sand	2.32	5.6 <sup>3)</sup>	71.7 <sup>5)</sup>	3091	0.84
		Speyer 2.3 <sup>1)</sup>	loamy sand	1.22	6.4 <sup>3)</sup>	37.7 <sup>5)</sup>	3092	0.84
Arithmetic Mean						259	16810	0.80
Median						90	12500	0.80
Min.						9.4	1600	0.59
Max.						897	60000	1.16

1) BBA Soil Texture Parameterisation

2) Buffer Solution = H<sub>2</sub>O

3) Buffer Solution = CaCl<sub>2</sub>

4) For this study, the units of the  $K_f$  and  $K_{foc}$  values were converted from [10<sup>2</sup> cm<sup>3</sup>/g] and [10<sup>3</sup> cm<sup>3</sup>/g] to [mL/g]

5) For this study, the  $K_{foc}$  values were not rounded

6)  $K_{oc}$  values determined for a single concentration. The values were not included in the calculation of the statistics and for modelling purposes (in italic)

<sup>7</sup> Briggs G.G. (1973): A simple relationship between soil adsorption of organic chemicals and their octanol/water partition co-efficients. Proceedings: 7th British Insecticide and Fungicide conference.

Table 9.3-2– Overview of the AMPA adsorption/desorption studies

Reference		Soil	Soil type	OC (%)	pH (-)	K <sub>f</sub> value (mL/g)	K <sub>foc</sub> / K <sub>oc</sub> (mL/g)	Freundl. exp. (1/n)
Study from the 2001 evaluation	[REDACTED] 1992	SLI Soil #1	Clay loam	2.09	7.7 <sup>1)</sup>	77.1	3640	0.79
		SLI Soil #2 <sup>3)</sup>	Sand	18.68 <sup>3)</sup>	4.7 <sup>1,3)</sup>	1570.0 <sup>3)</sup>	8310 <sup>3)</sup>	0.90 <sup>3)</sup>
		SLI Soil #4	Sand	1.33	7.4 <sup>1)</sup>	15.7	1160	0.75
		SLI Soil #5	Clay loam	0.93	7.6 <sup>1)</sup>	53.9	5650	0.79
		SLI Soil #9	Loamy sand	1.57	6.3 <sup>1)</sup>	110.0	6920 °	0.77
		SLI Soil #11	Sand	0.29	4.6 <sup>1)</sup>	73.0	24800	0.79
Studies not reviewed in the 2001 evaluation or new studies	[REDACTED] 1996 (IIA7.4.2/03)	Lilly Field	Sand	0.29 <sup>2)</sup>	5.7 <sup>1)</sup> °	133.0	45900	0.86
		Visalia	Sandy loam	0.58	8.4	10.0	1720	0.78
		Wisborough Green	Silty clay loam	2.26	7.7 <sup>1)</sup>	509.0	22500	0.91
		Champaign	Silty clay loam	2.15	6.2 <sup>1)</sup>	237.0	1000	0.86
		18 Acres	Sandy loam	1.80	7.4 <sup>1)</sup>	74.2	4130	0.84
	[REDACTED] 2003 (IIA7.4.2/01)	Schwalbach	Silt loam	1.59	6.1 <sup>1)</sup>	137.4	8642	0.98
		Hofheim	Silt loam	1.24	6.1 <sup>1)</sup>	87.9	7089	0.92
		Bergen-Enkheim	Silty clay	2.25	8.3 <sup>1)</sup>	33.9	1507	0.91
	[REDACTED] 2002 (IIA7.4.2/02)	Soil 2.1	Sand	0.96	5.5	46.7	1861	0.67
		Soil 2.2	Loamy sand	2.30	5.6 <sup>2)</sup>	189.7	8248	0.55
		Soil 3A	Sandy silty loam	2.60	7.1 <sup>2)</sup>	29.1	1119	0.67
Arithmetic mean						112	9749	0.80
Median						76	6285	0.79
Min.						10	1119	0.55
Max.						509	45900	0.98

1) buffer Solution = H<sub>2</sub>O2) buffer Solution = CaCl<sub>2</sub>

3) not included for calculation of statistics and for modelling purposes due to high OC content (in italic)

Remark. All K<sub>foc</sub> values were rounded

### IIIA 9.3.1 Column leaching

Although this type of study is not required, three soil column studies ([REDACTED] 1978; [REDACTED] 1992; [REDACTED], 1991) were evaluated in the 2001 evaluation and reported in the Glyphosate Monograph. In addition, an aged residue column leaching study ([REDACTED], 1978) was submitted which was evaluated as not acceptable. Since then, another aged residue column leaching study ([REDACTED], 1996) was provided by a Glyphosate Task Force (GTF) member. Overall the soil column studies show that glyphosate and its principal soil metabolite AMPA can be classified as immobile in soil. Please refer to IIA 7.4.3 and IIA 7.4.5.

### IIIA 9.3.2 Lysimeter studies

The 2001 EU evaluation concluded that a lysimeter study for glyphosate is not required and none was conducted. The provision in inclusion Directive 2001/99 EC does however state “Member States must pay particular attention to the protection of groundwater in vulnerable areas in particular with respect to non-crop-uses”, therefore three lysimeter studies conducted close to the BBA test guideline<sup>8</sup> which are available in the public literature (Stadlbauer et al., 2005; Grundmann et al., 2008 and Fomsgaard et al., 2003) are included in this section.

<sup>8</sup> Biological Research Centre for agriculture and forestry, federal republic of Germany (1990): Guideline for the Testing of Plant Protection Products in Registration Procedure, Part IV, 4-3: Lysimeter tests for the translocation of plant protection products into the subsoil.

The lysimeter studies from the open literature provide additional and supportive documentations on the leaching potential of glyphosate and AMPA. All three lysimeter studies are summarised in IIA 7.4.7 and IIA 7.13 and they document that the overall risk for the leaching of glyphosate and AMPA to groundwater is low.

### IIIA 9.3.3 Field leaching studies

The 2001 EU evaluation concluded that a field leaching study for glyphosate is not required, but based on field dissipation studies performed in the USA and Canada (see IIA 7.4.8) it can be concluded that glyphosate and AMPA have low potential to leach in agricultural soils.

### IIIA 9.3.4 Volatility – laboratory study

The volatility of glyphosate was evaluated during the 2001 EU evaluation prior to initial Annex I inclusion. Glyphosate has low vapour pressure ( $1.31 \times 10^{-5}$  Pa at 25°C, for details see IIA 2.3.1) and significant concentrations are not expected to be found in air through volatilisation following the use of the MON52276 according to the proposed GAP. The 2001 EU glyphosate evaluation concludes that:

“glyphosate can be classified as not volatile based on its Henry’s law constant and on volatilization experiments from soil and plants with no significant rates. Due to no significant UV-absorption, direct photolysis in air will not occur. Once in the atmosphere rapid photochemical oxidative degradation of glyphosate will occur.”

Supplementary data from two additional studies (1997; 1996) available from Glyphosate Task Force (GTF) member companies confirm this conclusion.

### IIIA 9.3.5 Volatility – field study

This type of study is not required due to the low vapour pressure of glyphosate ( $1.31 \times 10^{-5}$  Pa at 25°C, for details see IIA 2.3.1) and a significant concentration of glyphosate is not expected to be found in air through volatilisation following the use of the MON52276 according to the proposed GAP.

**IIIA 9.4 Predicted environmental concentrations in soil (PEC<sub>s</sub>)**

The following report describes the calculation of predicted environmental concentrations in soil (PEC<sub>s</sub>) of glyphosate and its major soil metabolite aminomethylphosphonic acid (AMPA). A worst-case application scenario which covers the uses of glyphosate to all crops in the EU was considered. Potential accumulation of the compounds was assessed as well.

Annex point	Author(s)	Year	Study title
IIIA 9.4/01 IIIA 9.5	[REDACTED]	2012a	<p>Predicted environmental concentrations of glyphosate and its metabolite AMPA in soil (PEC<sub>s</sub>) following application to various crops in the EU</p> <p>Company: [REDACTED]</p> <p>Report No: 303605-0</p> <p>Date: April 25, 2012</p> <p>GLP: No (modelling study: does not contain laboratory work)</p> <p>Not published</p>
Guideline:			<p>FOCUS (1997): Soil persistence models and EU Registration. The final report of the work of the Soil Modelling Work group of FOCUS. February 1997.</p> <p>FOCUS (2006): Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration. Report of the Work Group on Degradation Kinetics of FOCUS. EC Document Reference SANCO/10058/2005 version 2.0, June 2006.</p> <p>FOCUS (2011a): Generic Guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration, version 1.0.</p>
Deviations:			None
Dates of experimental work:			Not relevant

**Executive Summary**

Initial concentrations, maximum and minimum plateau concentrations, and actual and time weighted average concentrations of glyphosate and AMPA in soil were calculated for a single maximum application rate of 4320 g glyphosate acid/ha. It is important to mention that single application rate of 4320 g glyphosate acid/ha is not supported in the representative GAP, but rather represents the recommended maximum total annual application rate for all crops and therefore presents a conservative worst-case approach. ModelMaker™ (version 4.0) was used to calculate concentrations in soil as a function of time for glyphosate acid and its metabolite AMPA. Accumulation potential was investigated in soil layers of 0 - 5 cm (the standard depth assumed for products applied directly to the soil surface) and 0 - 20 cm (the standard depth assumed for products where incorporation is involved). The PEC<sub>s</sub> calculations for glyphosate acid and AMPA were based on their respective longest half-lives derived from field dissipation studies.

The initial PEC<sub>s</sub> values for glyphosate acid and AMPA at 5 cm depth were 5.76 and 1.48 mg/kg, respectively. Maximum plateau PEC<sub>s</sub> values of glyphosate acid and AMPA were calculated to be 8.07 and 5.35 mg/kg for 0 - 5 cm soil layer. For 0 - 20 cm soil layer, the corresponding values were predicted to be 2.02 and 1.34 mg/kg.

## I. MATERIALS AND METHODS

### A. MATERIALS

Not applicable, no materials were used as this study is a computer simulation.

ModelMaker™ (version 4.0; [REDACTED]) and Microsoft Excel™ 2003 were used for calculation of PEC<sub>s</sub>.

### B. STUDY DESIGN AND METHODS

Calculations were carried out according to recommendation of FOCUS (FOCUS, 1997<sup>9</sup>, 2006, 2011a).

#### Application scenario

The exposure assessment was based on a worst-case use pattern derived from the representative GAP information. Following a conservative approach, a single application at the maximum total yearly rate of 4320 g glyphosate acid/ha was used which is protective for all glyphosate uses included in the representative GAP. A worst-case crop interception of zero was assumed in all calculations.

The initial PEC<sub>s</sub> values (initial PEC<sub>s,5</sub>), i.e. maximum values after single application to the soil surface were calculated for the soil depth of 5 cm (FOCUS, 1997). The accumulation of glyphosate and AMPA was considered by calculating the concentration in soil for two depths. For the field crops, annual field mixing by ploughing was assumed and therefore, the accumulation was considered at 20 cm soil depth. In order to consider scenarios with regular ploughing (e.g. perennial crops), the accumulation was calculated for 5 cm depth. The long-term concentrations for both soil depths were calculated for a period of 30 years. The TWA values were derived based on a moving time-frame approach applied to the ModelMaker™ results. In all instances, the soil bulk density was 1.54 g/L.

#### Input parameters and calculation methods

Parameters for degradation of glyphosate and formation and degradation of AMPA were derived from field dissipation studies evaluated according to FOCUS degradation kinetics (2006, 2011a) (please refer to Annex Point IIIA 9.2.1).

Two compartment models were set up for parent and metabolite separately. For the calculation of glyphosate PEC<sub>s</sub>, a maximum DT<sub>50</sub> value of 143.3 days was used for glyphosate (DFOP kinetics) derived from field dissipation studies ([REDACTED] 1993; [REDACTED] 2012). To represent the biphasic degradation pattern two compartments were installed representing fast (compartment 1) and slow (compartment 2) degradation of glyphosate. The actual concentrations are calculated by summing up the concentrations of each compartment for each time step. The time step was set to one day. Time weighted-average concentrations were determined from the actual concentrations using a moving time-frame approach in Microsoft Excel.

AMPA PEC<sub>s</sub> values were calculated considering the simultaneous formation of the metabolite from the parent as well as its degradation. Since the degradation from glyphosate to AMPA follows DFOP kinetics while the degradation of AMPA follows SFO kinetics, the glyphosate parameterisation differs from the one chosen for calculation of glyphosate PEC<sub>s</sub>: For the calculation of AMPA PEC<sub>s</sub>, the maximum DT<sub>50</sub> value of 514.9 days and the corresponding formation fraction of 0.51 (SFO kinetics) derived from field

<sup>9</sup> FOCUS (1997): Soil persistence models and EU Registration. The final report of the work of the Soil Modelling Work group of FOCUS. February 1997.

dissipation studies (█ 1992, █ 2012) were chosen as a model input. The corresponding glyphosate half-life of 38.3 days (DFOP kinetics) was used in the calculation of  $PEC_s$  for AMPA *i.e.* the value determined for the same soil (█ 1992, █ 2012). A summary of the relevant substance related model input data is given in Table 9.4-1.

**Table 9.4-1: Model input data of glyphosate and its metabolite AMPA used for  $PEC_s$  simulations**

Compound	DT <sub>50</sub> soil, field (days)	Degradation parameters (-)	Model
Glyphosate <sup>1)</sup>	143.3	k1: 0.1305 <sup>3)</sup> k2: 0.0029 <sup>4)</sup> g: 0.2470 <sup>5)</sup>	DFOP
Glyphosate <sup>2)</sup>	38.3	k1: 0.0384 <sup>3)</sup> k2: 0.0037 <sup>4)</sup> g: 0.5453 <sup>5)</sup> formation fraction AMPA: 0.51	DFOP
AMPA	514.9	k: 0.0013 <sup>6)</sup>	SFO

1) Worst-case regarding parent compound

2) Worst-case regarding formation of AMPA

3) Degradation constant in the fast phase (DFOP model)

4) Degradation constant in the slow phase (DFOP model)

5) Glyphosate fraction assigned to the fast degrading compartment

6) AMPA degradation constant (SFO model)

## II. RESULTS AND DISCUSSION

The initial  $PEC_s$  values of glyphosate acid and AMPA after application to the soil surface calculated for a soil depth of 5 cm are shown in the table below (see Table 9.4-2).

**Table 9.4-2: Initial  $PEC_s$  of glyphosate acid and AMPA (at 5cm depth)**

Use pattern	Glyphosate acid (mg/kg)	AMPA (mg/kg)
Worst-case application scheme	2.76	1.48

The results of the accumulation investigation for glyphosate acid and AMPA for both the 0- 5 cm and 0 – 20 cm soil layer are shown in Table 9.4-3 and Figure 9.4-1 to Figure 9.4-4. The plateau maximum  $PEC_s$  values for glyphosate acid were 8.07 and 2.02 mg/kg at 5 and 20 cm depth, respectively. The corresponding plateau maximum  $PEC_s$  values for AMPA were 5.35 and 1.34 mg/kg.

**Table 9.4-3: Plateau  $PEC_s$  of glyphosate acid and AMPA for tillage and no-tillage systems (maximum in bold)**

PEC <sub>s</sub>	Glyphosate acid (mg/kg)	AMPA (mg/kg)
<b>0 - 5 cm</b>		
Plateau minimum PEC <sub>s</sub>	2.31	4.32
Plateau maximum PEC <sub>s</sub>	<b>8.07</b>	<b>5.35</b>
<b>0 - 20 cm</b>		
Plateau minimum PEC <sub>s</sub>	0.578	1.08
Plateau maximum PEC <sub>s</sub>	2.02	1.34
Plateau minimum PEC <sub>s</sub> <sup>1)</sup> + initial PEC <sub>s</sub> <sup>2)</sup>	6.34	2.56
1) calculated at 20 cm soil depth 2) calculated at 5 cm soil depth		



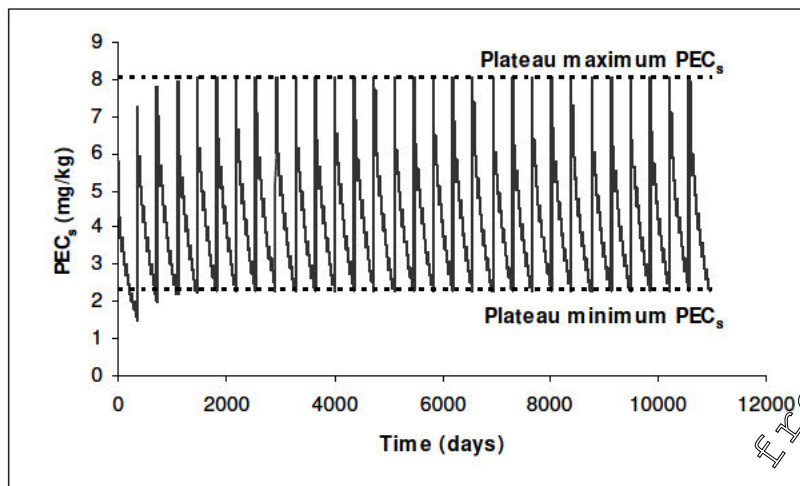


Figure 9.4-1: Glyphosate acid concentration in soil for 30 years at 5 cm soil mixing depth. The dotted lines represent plateau maximum and minimum PEC<sub>s</sub>.

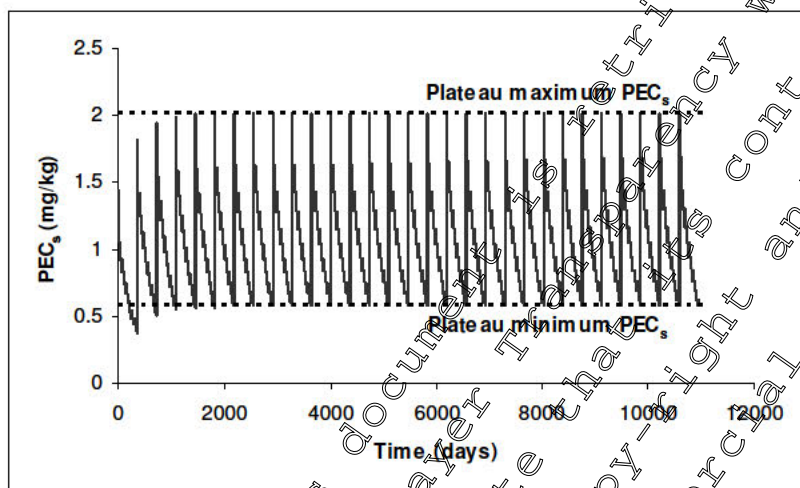


Figure 9.4-2: Glyphosate acid concentration in soil for 30 years at 20 cm soil mixing depth. The dotted lines represent plateau maximum and minimum PEC<sub>s</sub>.

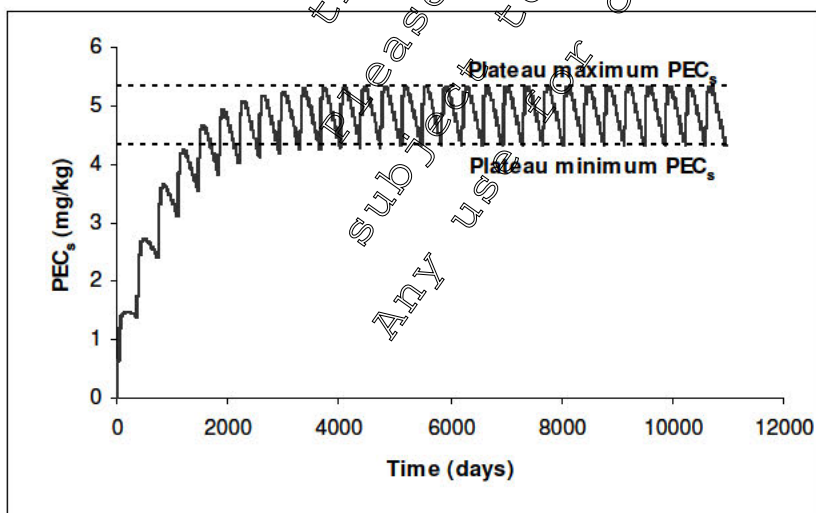


Figure 9.4-3: AMPA concentration in soil for 30 years at 5 cm soil mixing depth. The dotted lines represent plateau maximum and minimum PEC<sub>s</sub>.

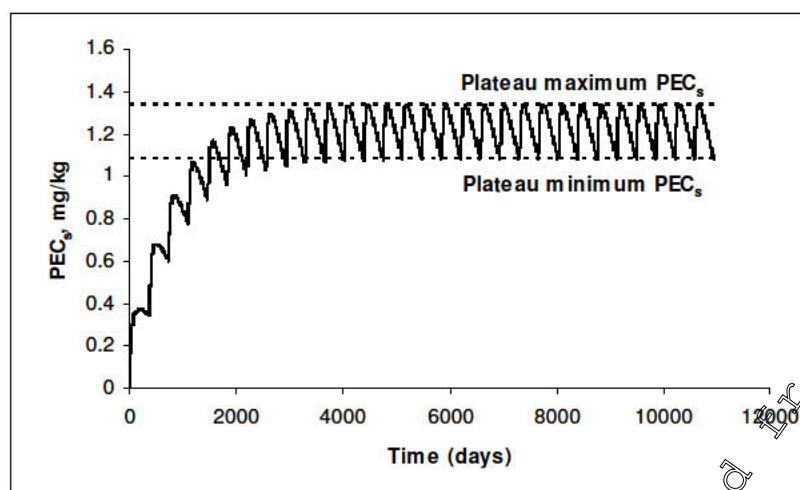


Figure 9.4-4: AMPA concentration in soil for 30 years at 20 cm soil mixing depth. The dotted lines represent plateau maximum and minimum  $PEC_s$ .

Maximum actual and time-weighted average (TWA)  $PEC_s$  values are shown in Table 9.4-4 and Table 9.4-5. Only the values for the maximum initial  $PEC_s$  (5.76 mg/kg for single year application and 5 cm soil depth) and the maximum plateau  $PEC_s$  (8.07 mg/kg for 30 years application and 5 cm soil depth) are reported representing a worst-case for all other cases (distribution over 20 cm soil depth).

Table 9.4-4: Maximum actual and time weighted average  $PEC_s$  of glyphosate acid and AMPA for single-year application (5 cm soil depth)

		Glyphosate acid		AMPA	
		Actual $PEC_s$	TWA $PEC_s$	Actual $PEC_s$	TWA $PEC_s$
Days after maximum		(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Initial	0	5.76		1.48	-
Short term	1	5.57	5.67	1.48	1.48
	2	5.41	5.58	1.48	1.48
	4	5.13	5.43	1.48	1.48
Long term	7	4.82	5.24	1.48	1.48
	14	4.39	4.92	1.48	1.48
	21	4.17	4.71	1.47	1.48
	28	4.04	4.56	1.47	1.47
	50	3.95	4.27	1.47	1.47
	100	3.25	3.88	1.44	1.46

**Table 9.4-5: Maximum plateau and time weighted average PEC<sub>s</sub> of glyphosate acid and AMPA for 30 years application (5 cm soil depth)**

		Glyphosate acid		AMPA	
		Actual PEC <sub>s</sub>	TWA PEC <sub>s</sub>	Actual PEC <sub>s</sub>	TWA PEC <sub>s</sub>
Days after maximum		(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Initial	0	8.07	-	5.35	-
Short term	1	7.87	7.97	5.35	5.35
	2	7.70	7.88	5.35	5.35
	4	7.41	7.72	5.34	5.35
Long term	7	7.08	7.52	5.34	5.35
	14	6.61	7.18	5.33	5.34
	21	6.34	6.94	5.32	5.34
	28	6.16	6.77	5.31	5.34
	50	5.75	6.41	5.25	5.33
	100	4.97	5.88	5.07	5.30

### III. CONCLUSION

Predicted environmental concentrations for glyphosate acid and its metabolite AMPA in soil (PEC<sub>s</sub>) were calculated for the use on various crops in Europe in accordance with FOCUS guidelines (FOCUS, 1997, 2006). Soil accumulation was investigated for both the 0 – 5 cm and 0 – 20 cm soil layer, based on a single application of MON 52276 formulation at a maximum rate of 4320 g glyphosate acid/ha.

The initial PEC<sub>s</sub> values for glyphosate acid and AMPA were 5.76 and 1.48 mg/kg, respectively. Maximum plateau PEC<sub>s</sub> values of glyphosate acid and AMPA were calculated to be 8.07 and 5.35 mg/kg, respectively, for the 5 cm soil depth. For distribution over the 20 cm soil depth, the respective values were predicted to be 2.02 and 1.34 mg/kg.

#### IIIA 9.4.1 Initial PEC<sub>s</sub> value

The initial PEC<sub>s</sub> value of glyphosate based on a worst-case single-year application of MON 52276 formulation at a maximum rate corresponding to 4320 g glyphosate acid/ha and assuming that 100% of the applied dose reaches the soil surface was 5.76 mg/kg (5 cm soil depth). This assessment should be considered as extremely conservative. The maximum plateau PEC<sub>s</sub> value of glyphosate acid considering application over 30 years was calculated to be 8.07 mg/kg for the 5 cm soil depth. For the 20 cm soil depth, the corresponding value was 2.02 mg/kg. For details, please refer to Annex point IIIA 9.4.

#### IIIA 9.4.2 Short-term PEC<sub>s</sub>

The short-term PEC<sub>s</sub> of glyphosate acid following the maximum PEC<sub>s</sub> value (8.07 g/kg = maximum plateau PEC<sub>s</sub>) are presented in Table 9.4-6. For details, please refer to Annex point IIIA 9.4.

**Table 9.4-6: Maximum actual and time weighted average PEC<sub>s</sub> of glyphosate acid (5 cm soil depth) – Short-term**

		Glyphosate acid	
		Actual PEC <sub>s</sub>	TWA PEC <sub>s</sub>
Days after maximum		(mg/kg)	(mg/kg)
Initial	0	8.07	-
Short term	1	7.87	7.97
	2	7.70	7.88
	4	7.41	7.72

**IIIA 9.4.3 Long-term PEC<sub>s</sub>**

The long-term PEC<sub>s</sub> of glyphosate acid following the maximum PEC<sub>s</sub> value (8.07 g/kg = maximum plateau PEC<sub>s</sub>) are presented in Table 9.4-7. For details, please refer to Annex point IIIA 9.4.

**Table 9.4-7: Maximum actual and time weighted average PEC<sub>s</sub> of glyphosate acid (5 cm soil depth) – Long-term**

		Glyphosate acid	
		Actual PEC <sub>s</sub>	TWA PEC <sub>s</sub>
Days after maximum		(mg/kg)	(mg/kg)
Initial	0	8.07	-
Long term	7	7.08	6.52
	14	6.61	7.18
	21	6.34	6.90
	28	6.16	6.77
	50	5.75	6.41
	100	4.97	5.88

**IIIA 9.5 Predicted environmental concentration in soil (PEC<sub>s</sub>) for relevant metabolites**

Please refer to Annex Point IIIA 9.4 and study IIIA 9.4.6 for explanation.

**IIIA 9.5.1 Initial PEC<sub>s</sub> value**

PEC<sub>s</sub> values for the metabolite AMPA were estimated based on the kinetic analysis of the glyphosate field dissipation studies, which indicated a maximum AMPA DT<sub>50</sub> of 514.9 days. The formation fraction of 0.51, corresponding to the maximum DT<sub>50</sub> was considered for the calculations as well (see Annex Point IIIA 9.2.1). The initial PEC<sub>s</sub> value of AMPA considering a single-year application was 1.48 mg/kg (5 cm soil depth). The maximum plateau PEC<sub>s</sub> value of AMPA considering application over 30 years was calculated to be 5.35 mg/kg for the 5 cm soil depth. For the 20 cm soil depth, the corresponding value was 1.34 mg/kg. For details, please refer to Annex point IIIA 9.4.

**IIIA 9.5.2 Short-term PEC<sub>s</sub> values**

The short-term PEC<sub>s</sub> of AMPA following the maximum PEC<sub>s</sub> value (5.35 g/kg = maximum plateau PEC<sub>s</sub>) are presented in Table 9.5-1. For details, please refer to Annex point IIIA 9.4.

**Table 9.5-1: Maximum actual and time weighted average PEC<sub>s</sub> of AMPA (5 cm soil depth) – Short-term**

		AMPA	
		Actual PEC <sub>s</sub>	TWA PEC <sub>s</sub>
Days after maximum		(mg/kg)	(mg/kg)
Initial	0	5.35	-
Short term	1	5.35	5.35
	2	5.35	5.35
	4	5.34	5.35

**IIIA 9.5.3 Long-term PEC<sub>s</sub> values**

The long-term PEC<sub>s</sub> of AMPA following the maximum PEC<sub>s</sub> value (5.35 g/kg = maximum plateau PEC<sub>s</sub>) are presented in Table 9.5-2. For details, please refer to Annex point IIIA 9.4.

**Table 9.5-2: Maximum actual and time weighted average PEC<sub>s</sub> of AMPA (5 cm soil depth) – Long-term**

		AMPA	
		Actual PEC <sub>s</sub>	TWA PEC <sub>s</sub>
Days after maximum		(mg/kg)	(mg/kg)
Initial	0	5.35	-
Long term	7	5.34	5.35
	14	5.33	5.34
	21	5.32	5.34
	28	5.31	5.34
	50	5.25	5.33
	100	5.07	5.30

This document is retrieved from  
the Bayer Transparency website.  
Please note that its content could be  
subject to copy-right and other IP-rights.  
Any use for commercial purposes is prohibited

### IIIA 9.6 Predicted environmental concentration in ground water (PEC<sub>gw</sub>)

The following report describes a FOCUS groundwater modelling study for the determination of predicted environmental concentrations in groundwater (PEC<sub>gw</sub>) of glyphosate acid and its major soil metabolite aminomethylphosphonic acid (AMPA). A worst-case application scenario which covers the uses of glyphosate to all crops in the EU was considered.

Annex point	Author(s)	Year	Study title
IIIA 9.6/01		2012b	<p>Predicted environmental concentrations of glyphosate and its metabolite AMPA in groundwater (PEC<sub>gw</sub>) using FOCUS PEARL 4.4.4 and FOCUS PELMO 4.4.3 following application to various crops in the EU</p> <p>Company: </p> <p>Report No: 3036052</p> <p>Date: April 25, 2012</p> <p>GLP: No (modelling study: does not contain laboratory work)</p> <p>Not published</p>
Guideline:			<p>FOCUS (2002): FOCUS groundwater scenarios in the EU review of active substances. Report of the FOCUS Groundwater Scenarios Workgroup, EC Document Reference Sanco/321/2000, version 2002.</p> <p>FOCUS (2009): Assessing potential for movement of active substances and their metabolites to ground water in the EU. Report of the FOCUS Ground Water Work Group, EC Document Reference Sanco/13144/2010 version 1, 604 pp.</p> <p>FOCUS (2011b): Generic guidance for Tier 1 FOCUS ground water assessments, version 2.0. FOCUS groundwater scenarios working group.</p>
Deviations:			None
Dates of experimental work:			Not relevant

#### Executive Summary

Predicted environmental concentrations in groundwater, as represented by the 80<sup>th</sup> percentile leachate concentration at a soil depth of 1 m, were calculated for glyphosate acid and its major soil metabolite AMPA for a range of uses in various crops in the EU. The exposure assessment was based on a representative use pattern derived from the representative GAP. Depending on the crop, two- or three-consecutive applications (respective intervals as defined in the joint representative GAP) at rates ranging from 720 to 2880 g glyphosate acid/ha were evaluated. In order to cover a wide range of uses, the representative FOCUS crop-scenarios were chosen so as to ensure that all FOCUS groundwater scenarios are considered for representative uses chosen for modelling. The assessment was performed using the leaching models FOCUS PEARL 4.4.4 and FOCUS PELMO 4.4.3.

The predicted environmental concentrations in groundwater (PEC<sub>gw</sub>) of glyphosate acid and its metabolite AMPA were calculated to be < 0.001 µg/L in all scenarios for both models. Therefore, it can be concluded

that the use of glyphosate is not likely to pose an unacceptable risk to groundwater if the active substance is used in compliance with the label recommendations.

## I. MATERIALS AND METHODS

### A. MATERIALS

Not applicable, no materials were used as this study is a computer simulation.

The groundwater leaching models FOCUS PEARL 4.4.4 and FOCUS PELMO 4.4.3 (FOCUS, 2002<sup>10</sup>, 2009<sup>11</sup>, 2011b<sup>12</sup>) were used for calculation of  $PEC_{gw}$ .

### B. STUDY DESIGN AND METHODS

#### Application scenarios

The exposure assessment was based on a representative use pattern derived from the representative GAP. The application scenarios selected for the leaching assessment are summarised in Table 9.6-1.

**Table 9.6-1 Application scenarios considered for simulations**

Crop	FOCUS <sub>gw</sub> crop	Application rate (g glyphosate acid/ha)	No. of appl.	Maximum yearly application rate (g glyphosate acid/ha)	Min. interval between applications (d)	Application period
Various crops (autumn application)	Winter cereals	2160	2	4320	21	Pre-planting /pre-emergence
Various crops (spring + autumn application)	Spring cereals	2160	2	4320	21	Pre-planting /pre-emergence + post-harvest
Various crops (spring application)	Potatoes	2160	2	4320	21	Pre-planting /pre-emergence
Orchards, citrus, vines, tree nuts	Apples	2880 + 720 + 720	1 + 1 + 1	4320	28	Post-emergence of weeds

For winter cereals and potato crops, the applications dates (representing pre-planting applications as defined in the representative GAP) were chosen using the planting dates defined for the respective crop (FOCUS, 2002, 2011b). The second application was set to the day of planting; and the first application to 21 days before planting according to the minimum application interval. For spring cereals, the first application was assumed to take place 14 days before seeding and the second application 14 days after harvest in order to account for a realistic worst case pre-emergence + pre- or post-harvest use in summer. The first application in apples was based on a realistic estimate of the first possible date of weed emergence and the following two applications were arranged with respect to the minimum interval of

<sup>10</sup> FOCUS (2002): FOCUS groundwater scenarios in the EU review of active substances. Report of the FOCUS Groundwater Scenarios Workgroup, EC Document Reference Sanco/321/2000, version 2002.

<sup>11</sup> FOCUS (2009): Assessing potential for movement of active substances and their metabolites to ground water in the EU. Report of the FOCUS Ground Water Work Group, EC Document Reference Sanco/13144/2010 version 1, 604 pp.

<sup>12</sup> FOCUS (2011b): Generic guidance for Tier 1 FOCUS ground water assessments, version 2.0. FOCUS groundwater scenarios working group.

28 days. A worst-case zero interception was assumed for all applications. The detailed application dates are summarised in Table 9.6-3.

**Table 9.6-2 Application dates used for modelling**

Crop	Scenario	1 <sup>st</sup> application	2 <sup>nd</sup> application	3 <sup>rd</sup> application
Winter cereals	Châteaudun	29-Sep	20-Oct	n/a
	Hamburg	21-Sep	12-Oct	n/a
	Jokioinen	20-Aug	10-Sep	n/a
	Kremsmünster	04-Oct	25-Oct	n/a
	Okehampton	16-Sep	07-Oct	n/a
	Piacenza	04-Nov	25-Nov	n/a
	Porto	25-Oct	15-Nov	n/a
	Sevilla	25-Oct	15-Nov	n/a
	Thiva	25-Oct	15-Nov	n/a
Spring cereals	Châteaudun	6-Feb	3-Aug	n/a
	Hamburg	24-Feb	6-Sep	n/a
	Jokioinen	23-Apr	8-Sep	n/a
	Kremsmünster	24-Feb	3-Sep	n/a
	Okehampton	11-Mar	3-Sep	n/a
	Porto	6-Feb	3-Aug	n/a
	Thiva	25-Jan	15-Feb	n/a
Potatoes	Châteaudun	25-Mar	15-Apr	n/a
	Hamburg	10-Apr	1-May	n/a
	Jokioinen	24-Apr	15-May	n/a
	Kremsmünster	10-Apr	1-May	n/a
	Okehampton	25-Mar	15-Apr	n/a
	Piacenza	11-Mar	1-Apr	n/a
	Porto	7-Feb	28-Feb	n/a
	Sevilla	25-Dec	10-Jan	n/a
	Thiva	25-Jan	15-Feb	n/a
Apples	Châteaudun	15-Feb	15-Mar	12-Apr
	Hamburg	01-Mar	29-Mar	26-Apr
	Jokioinen	15-Mar	12-Apr	10-May
	Kremsmünster	01-Mar	29-Mar	26-Apr
	Okehampton	01-Mar	29-Mar	26-Apr
	Piacenza	15-Feb	15-Mar	12-Apr
	Porto	15-Feb	15-Mar	12-Apr
	Sevilla	15-Feb	15-Mar	12-Apr
	Thiva	15-Feb	15-Mar	12-Apr

n/a = not analysed

#### Substance properties and input parameters

Parameters used for estimating the predicted environmental concentration of glyphosate acid and its metabolite AMPA in groundwater ( $PEC_{gw}$ ) are presented in Table 9.6-3. The normalised geometric mean laboratory half-lives of glyphosate and AMPA of 12.8 days (n=13) and 55.7 days (n=7) were used for modelling purposes. The arithmetic mean formation fraction of 0.34 (n=12) was used for formation of AMPA (for details on the laboratory degradation studies, see Annex point IIIA 9.1.1, Table 9.1-1 and Table 9.1-2). Regarding sorption, the arithmetic mean  $K_{foc}$  and  $1/n$  value of glyphosate (16810 mL/g and 0.80, n=15) and AMPA (9749 mL/g and 0.80, n=16) were selected for modelling purposes (for details, see Annex point IIIA 9.3, Table 9.3-1 and Table 9.3-2). Since FOCUS PEARL requires input of  $K_{fom}$ , the  $K_{fom}$  value was derived by dividing the  $K_{foc}$  by 1.724. In order to obtain a conservative simulation, plant uptake factors for both glyphosate and AMPA were set to zero. Apart from the input parameters explicitly discussed, all variables in the models were left at their default values.



**Table 9.6-3 Summary of input parameters for glyphosate acid and its metabolite AMPA for the leaching simulation models FOCUS PEARL 4.4.4 and FOCUS PELMO 4.4.3**

Parameter	Unit	Glyphosate acid	AMPA
Molecular Mass	g/mol	169	111
Water solubility (20°C)	mg/L	10500	10500 <sup>1)</sup>
Vapour pressure (25°C)	Pa	$1.31 \times 10^{-5}$	$1.31 \times 10^{-5}$ <sup>1)</sup>
DegT <sub>50</sub> soil <sup>2)</sup>	days	12.8	55.7
K <sub>foc</sub>	mL/g	16810	9749
K <sub>fom</sub>	mL/g	9750.6	5654.9
Freundlich exponent (1/n)	-	0.80	0.80
Formation fraction	-	-	0.34
Plant uptake factor	-	-	0 <sup>2)</sup>

1) parent data

2) worst-case assumption

## II. RESULTS AND DISCUSSION

In all simulations the PEC<sub>gw</sub> values of glyphosate acid and AMPA at 1 m soil depth were below the groundwater threshold value of 0.1 µg/L. The results of the calculations with FOCUS PEARL 4.4.4 and FOCUS PELMO 4.4.3 predicting the leaching of glyphosate acid and AMPA are presented in Table 9.6-4 and Table 9.6-5 respectively.

Table 9.6-4  $PEC_{gw}$  of glyphosate acid and AMPA at 1 m soil depth (simulations with PEARL 4.4.4)

Crop	Scenario	$PEC_{gw}$ (µg/L)	
		Glyphosate acid	AMPA
Winter cereals	Châteaudun	<0.001	<0.001
	Hamburg	<0.001	<0.001
	Jokioinen	<0.001	<0.001
	Kremsmünster	<0.001	<0.001
	Okehampton	<0.001	<0.001
	Piacenza	<0.001	<0.001
	Porto	<0.001	<0.001
	Sevilla	<0.001	<0.001
	Châteaudun	<0.001	<0.001
Spring cereals	Châteaudun	<0.001	<0.001
	Hamburg	<0.001	<0.001
	Jokioinen	<0.001	<0.001
	Kremsmünster	<0.001	<0.001
	Okehampton	<0.001	<0.001
	Porto	<0.001	<0.001
	Châteaudun	<0.001	<0.001
Potatoes	Châteaudun	<0.001	<0.001
	Hamburg	<0.001	<0.001
	Jokioinen	<0.001	<0.001
	Kremsmünster	<0.001	<0.001
	Okehampton	<0.001	<0.001
	Piacenza	<0.001	<0.001
	Porto	<0.001	<0.001
	Sevilla	<0.001	<0.001
	Châteaudun	<0.001	<0.001
	Châteaudun	<0.001	<0.001
Apples	Hamburg	<0.001	<0.001
	Jokioinen	<0.001	<0.001
	Kremsmünster	<0.001	<0.001
	Okehampton	<0.001	<0.001
	Piacenza	<0.001	<0.001
	Porto	<0.001	<0.001
	Sevilla	<0.001	<0.001
	Châteaudun	<0.001	<0.001
	Châteaudun	<0.001	<0.001

**Table 9.6-5** **PEC<sub>gw</sub> of glyphosate acid and AMPA at 1 m soil depth (simulations with PELMO 4.4.3)**

Crop	Scenario	PEC <sub>gw</sub> (µg/L)	
		Glyphosate acid	AMPA
Winter cereals	Châteaudun	<0.001	<0.001
	Hamburg	<0.001	<0.001
	Jokioinen	<0.001	<0.001
	Kremsmünster	<0.001	<0.001
	Okehampton	<0.001	<0.001
	Piacenza	<0.001	<0.001
	Porto	<0.001	<0.001
	Sevilla	<0.001	<0.001
	Châteaudun	<0.001	<0.001
Spring cereals	Châteaudun	<0.001	<0.001
	Hamburg	<0.001	<0.001
	Jokioinen	<0.001	<0.001
	Kremsmünster	<0.001	<0.001
	Okehampton	<0.001	<0.001
	Porto	<0.001	<0.001
	Châteaudun	<0.001	<0.001
Potatoes	Châteaudun	<0.001	<0.001
	Hamburg	<0.001	<0.001
	Jokioinen	<0.001	<0.001
	Kremsmünster	<0.001	<0.001
	Okehampton	<0.001	<0.001
	Piacenza	<0.001	<0.001
	Porto	<0.001	<0.001
	Sevilla	<0.001	<0.001
	Châteaudun	<0.001	<0.001
	Châteaudun	<0.001	<0.001
Apples	Hamburg	<0.001	<0.001
	Jokioinen	<0.001	<0.001
	Kremsmünster	<0.001	<0.001
	Okehampton	<0.001	<0.001
	Piacenza	<0.001	<0.001
	Porto	<0.001	<0.001
	Sevilla	<0.001	<0.001
	Châteaudun	<0.001	<0.001
	Châteaudun	<0.001	<0.001

### III. CONCLUSION

Predicted environmental concentrations for glyphosate acid and its metabolite AMPA in groundwater (PEC<sub>gw</sub>) were calculated for use on various crops in Europe according to guidance provided by FOCUS using two models, FOCUS PEARL 4.4.4 and FOCUS PELMO 4.4.3 (FOCUS, 2002, 2009, 2011b).

In all simulations the 80<sup>th</sup> percentile PEC<sub>gw</sub> values of glyphosate acid and AMPA at 1 m soil depth were below the groundwater threshold value of 0.1 µg/L. Therefore, it can be concluded that the use of glyphosate is not likely to pose an unacceptable risk to groundwater if the active substance is used in compliance with the label recommendations.

**IIIA 9.6.1 Active substance PEC<sub>gw</sub> value**

In all simulations the 80<sup>th</sup> percentile PEC<sub>gw</sub> values of glyphosate acid at 1 m soil depth were below the groundwater threshold value of 0.1 µg/L. For detail, please refer to Annex point IIIA 9.6.

**IIIA 9.6.2 Relevant metabolites, PEC<sub>gw</sub> values**

In all simulations, the 80<sup>th</sup> percentile PEC<sub>gw</sub> values of AMPA at 1 m soil depth were below the groundwater threshold value of 0.1 µg/L. For details, please refer to Annex Point IIIA 9.6.

**IIIA 9.6.3 Additional field testing**

Not required based on results of Annex Point IIIA 9.6.1.

**IIIA 9.6.4 Information on the impact on water treatment procedures**

The 2001 EU glyphosate evaluation concludes “Glyphosate and its metabolite AMPA may be classified as low mobile in soil. Therefore, it is not necessary to consider the impact on water treatment procedures.” However, the impact of glyphosate and its removal from surface water sources by treatment processes commonly used for production of drinking water have been extensively studied. Laboratory and pilot plant scale treatments using chlorinating disinfectants and ozonolysis have shown destruction of glyphosate in water during the standard water purification processes.

Annex point	Author(s)	Year	Study title
IIA 9.6.4/01	██████████	2012	Review of sustainable water treatment Company: Monsanto Europe S.A. (on behalf of the European Glyphosate Association) Report No: ██████████ 8408v2 Date: March 2012 GLP: Not applicable Not published
Guideline:	Not applicable		
Deviations:	Not applicable		
Contractor :	██ ██		

**Executive summary**

As the European water industry is moving towards ‘simple treatments’, a review of literature information on the performance of low chemical/energy processes - Bank Filtration (BF), Slow Sand Filtration (SSF) and Biological Activated Carbon (BAC) – for removal of glyphosate and AMPA was conducted. The limited information suggests that BF and SSF can remove glyphosate and AMPA, although the results are inconsistent between studies. No information is available for BAC, but significant removal is not expected through this treatment.

**I. MATERIALS AND METHODS**

This is a desk study, based on literature review.

## II. RESULTS AND DISCUSSION

The results are of the literature study are summarized in Table 9.6-6.

**Table 9.6-6 Overview on different treatments and results**

Compound	Redox conditions	Process	C <sub>0</sub> (µg/l)	Residence time (days)	Removal (%)	Reference
Glyphosate	Anaerobic	BF	0.07	30-300	>30	Post et al., 2000
Glyphosate	Anaerobic	BF	0.12	Unknown	17	Post et al., 2000
Glyphosate	Aerobic & anaerobic	BF and SSF	<0.05-0.09	Unknown	~50	Schlett et al, 2005
Glyphosate	Aerobic	SSF	<0.05-0.19	Unknown	>75	Schlett et al, 2005
Glyphosate	Aerobic	Soil column	10	25	>95	Lindner et al., 2000
Glyphosate	Aerobic	Batch river water	150000	72	40-72	Zamanyika and Nyandoro, 1993
Glyphosate	Aerobic	Batch soil samples	100 µg/g	50	95	Getenga and Kengara, 2004
Glyphosate	Initially aerobic	Batch river water	100	56	54-89	Wang et al., 1994
Glyphosate	Initially aerobic	BF	3.5, 11.6	Half life 7-10 days	80 <sup>1</sup>	Krause et al. (2009)
AMPA	Anaerobic	BF	0.46	30-300	46-87	Post et al., 2000
AMPA	Anaerobic	BF	0.54	450-2000	85-94	Stuyfzand et al., 2004
AMPA	Anaerobic	BF	1.8	Unknown	90	Post et al., 2000
AMPA	Aerobic & anaerobic	BF and SSF	0.23-1.1	Unknown	≤ 95	Schlett et al, 2005
AMPA	Aerobic	SSF	0.05-0.7	Unknown	>89	Schlett et al, 2005
AMPA	Aerobic	SSF	0.04-0.45	Unknown	≤ 94	Hopman et al, 1995

BF=Bank Filtration, SSF=Slow Sand Filter, C<sub>0</sub>=initial concentration

1) 80% removal under test conditions, but removal to <0.4 µg/l identified from modelling for high initial concentrations with half life shown - see Appendix A

This table shows that BF and SSF can remove glyphosate and AMPA. The general trend seems to be that the concentration of AMPA is higher than glyphosate but that AMPA is more readily degraded or removed. The degradation of glyphosate seems to benefit from aerobic conditions whereas AMPA is readily degraded both under aerobic and anaerobic conditions. Although no information was found for BAC, previous tests by WRC using powdered activated carbon (PAC) suggest that GAC alone is not effective for adsorption of either glyphosate or AMPA. The mechanism of biological removal of organic contaminants by BAC could rely on adsorption of the organics before biodegradation and BAC may therefore be less effective for glyphosate and AMPA. Krause et al. (2009) studied the removal of glyphosate from surface water using a variety of methods; adsorption experiments, degradation experiments, leaching experiments, enclosure experiments, and lysimeter experiments. Overall, the results from the tests carried out confirm that bank filtration should be effective for removal of glyphosate through the range of mechanism investigated.

## III. CONCLUSION

Glyphosate and AMPA can be removed by sustainable water treatments like BF and SSF. Although no information is available for BAC, this treatment is not expected to effectively remove glyphosate and AMPA from raw water.

Annex point	Author(s)	Year	Study title
IIA 9.6.4/02	██████████ ██████████	2010	Removal of glyphosate and AMPA by water treatment Company: Monsanto Europe S.A.(on behalf of the European Glyphosate Association) Report No: ████████8164v2 Date: October 2010 GLP: Not applicable Not published
Guideline:			Not applicable
Deviations:			Not applicable
Contractor :			██ ██

### Executive summary

The first part of this study reports the performance of commonly used water treatment processes for the removal of glyphosate and AMPA from raw water during drinking water production. The results show that two of the most common oxidants used in water treatment, ozone and chlorine, can provide a high degree of removal (>95%) for glyphosate and AMPA under typical conditions used in water treatment. The majority of water treatment works use one (mainly chlorine) or both of these oxidants. The most common water treatment process installed for removal of pesticides worldwide is adsorption using granular activated carbon (GAC). However, this does not provide an effective barrier to glyphosate or AMPA. Other processes commonly used in water treatment (bankside or dune infiltration, coagulation/clarification/ filtration and slow sand filtration) would each contribute some removal, but alone would not provide a secure barrier in relation to meeting a  $0.1 \mu\text{g l}^{-1}$  standard.

The second part of this study assessed the removal of glyphosate and AMPA by a number of treatment processes in laboratory trials using oxidation and activated charcoal, as well as combinations of ozone, high dose ultraviolet (UV) and hydrogen peroxide in advanced oxidation pilot plant tests. Ozone ( $\text{O}_3$ ) and ozone plus hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) are highly efficient in removing glyphosate and AMPA and better than 99% removal was seen for all conditions tested. Chlorine ( $\text{Cl}_2$ ) was similarly efficient at higher temperature but removal decreased with decreasing temperature to about 70% at  $5^\circ\text{C}$  for glyphosate (but remained >99% for AMPA). The removal of glyphosate by chlorine dioxide ( $\text{ClO}_2$ ) was not as efficient and more variable, 17-93% removed, whilst complete removal was achieved for AMPA under these conditions. PAC was the least efficient treatment for glyphosate & AMPA removal, with removals in the range 0-30%.

Advanced oxidation pilot plant tests with combinations of UV, ozone and hydrogen peroxide confirmed the result of the batch tests with ozone and ozone/peroxide. However, advanced oxidation using UV alone, or UV with peroxide, was less effective for glyphosate removal than ozonation based treatment, particularly with respect to AMPA formation and removal.

## I. MATERIALS AND METHODS

The first part of the study was based on a literature review.

Laboratory Batch tests were carried out to investigate the removal of glyphosate and AMPA by oxidation using ozone,  $\text{O}_3$  in combination with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ),  $\text{Cl}_2$  and  $\text{ClO}_2$ , and by adsorption using PAC.

The stock solutions of glyphosate and AMPA were prepared by dissolving high purity solids in deionised water. For the AMPA tests using PAC and for all glyphosate tests, a 10 litre sample of Swindon tap water was spiked with  $3 \mu\text{g l}^{-1}$  of either glyphosate or AMPA. Samples of the spiked water were taken for analysis to establish the initial concentration of pesticides, and the remainder of the spiked water was used in the tests. This concentration was agreed as the maximum concentration likely to be found in raw waters.

Ozonation alone: A one litre sub-sample of spiked water was ozonated using a pilot-scale  $\text{O}_3$  generator and a bubble diffuser stone. Following ozonation for 10 s, the  $\text{O}_3$  residual was measured immediately, and at 5 minute intervals, during a 15 minute contact time. At the end of the contact period, the residual ozone was quenched with sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ).

Ozonation with hydrogen peroxide: A further set of tests were carried out with simultaneous use of  $\text{O}_3$  and  $\text{H}_2\text{O}_2$ , at 0.5 and  $1.0 \text{ mg l}^{-1}$ . The ozonation conditions were identical to the test with  $\text{O}_3$  alone with the temperature kept constant at  $15 \pm 0.6^\circ\text{C}$ . The  $\text{O}_3$  residual was measured immediately after ozonation, and then at 5 minute intervals, during a 15 minute contact time. At the end of the contact period, the residual  $\text{O}_3$  was quenched with sodium thiosulphate.

Chlorine: One-litre samples of the spiked water were dosed with sodium hypochlorite ( $\text{NaClO}$ ) at  $1.5 \text{ mg Cl}_2 \text{ l}^{-1}$ . The dosed water was left for 30 minutes at the desired temperature. At the end of the contact period, the residual  $\text{Cl}_2$  was measured and then quenched with sodium thiosulphate.

Chlorine dioxide: The tests with  $\text{Cl}_2$  was repeated but with  $\text{ClO}_2$  as the oxidant. The  $\text{ClO}_2$  was added as crushed tablets, supplied by Accepta. The initial target concentration of  $\text{ClO}_2$  was  $1 \text{ mg l}^{-1}$ .

Powdered Activated Charcoal (PAC): Tests were carried out to investigate the performance of 3 different types of coal based PAC. One litre samples of the spiked water were dosed with the three different PAC at 5, 15, and  $25 \text{ mg l}^{-1}$ . The dosed water was left stirring for 1 hour, to keep the PAC in suspension. The samples were then filtered through GF/C grade filter paper to remove the carbon, prior to analysis.

UV and hydrogen peroxide: After a literature review, an advanced oxidation process (AOP) pilot plant test was performed. The AOP pilot rig, consists of in-line hydrogen peroxide dosing, ozone dosing and a UV reactor, which can be used individually or in combination. The retention time in the unit is around 30-60 s, most of which is in the UV reactor. Two tests were performed, each with the same matrix of operating conditions. For the first test, the feed tap water was spiked with glyphosate to the same target concentration as previous tests  $3 \mu\text{g/l}$ . For the second test, the feed water was spiked with AMPA to a target concentration of  $3 \mu\text{g/l}$ . The matrix of operating conditions was:

UV, dose  $740 \text{ mJ/cm}^2$

UV,  $1240 \text{ mJ cm}^{-2}$

UV,  $740 \text{ mJ cm}^{-2}$ , +  $\text{H}_2\text{O}_2$ ,  $5 \text{ mg l}^{-1}$

UV,  $1240 \text{ mJ cm}^{-2}$ , +  $\text{H}_2\text{O}_2$ ,  $5 \text{ mg l}^{-1}$

$\text{O}_3$ ,  $2 \text{ mg l}^{-1}$  +  $\text{H}_2\text{O}_2$ ,  $2 \text{ mg l}^{-1}$

$\text{O}_3$ ,  $2 \text{ mg l}^{-1}$

$\text{O}_3$ ,  $2 \text{ mg l}^{-1}$ , with sample left standing for 9 minutes to provide ozone contact time

In the oxidation tests with glyphosate spiking, the treated water samples were also analysed for AMPA, to investigate whether any of the glyphosate was degraded only to AMPA by oxidation.

All samples were analysed for glyphosate and AMPA using the following method. Water samples are treated with fmoc (9-fluorenylmethyl chloroformate) derivatising reagent prior to concentration by solid phase extraction. The extracts are then analysed by high performance liquid chromatography (HPLC) using primary mass spectroscopic (MS) detection in negative ion electrospray with selective ion monitoring. The reported limit of detection (LOD) for the method is  $0.006 \mu\text{g l}^{-1}$  for glyphosate and  $0.016 \mu\text{g l}^{-1}$  for AMPA.

## II. RESULTS AND DISCUSSION

The results are of the literature study are summarized in Table 9.6-7.

Chlorine, which is one of the most common disinfectants (oxidants) used in water treatment in Europe, can provide a high degree of removal (>95%) for glyphosate and AMPA under typical conditions used in water treatment.. Ozonation, another oxidant commonly used for pesticide removal, can also provide more than 95% removal of glyphosate and AMPA. Bankside or dune infiltration, coagulation/ clarification/ filtration and slow sand filtration, commonly used in water treatment, would each contribute some removal, but alone would not provide a secure barrier in relation to meeting a 0.1 µg l<sup>-1</sup> standard. Depending on the treatment processes used, waterworks which include chlorine could deal with between 1 and 4 µg l<sup>-1</sup> (glyphosate + AMPA) in the raw water to maintain less than 0.1 µg l<sup>-1</sup> in the treated water, but if the works also includes ozonation total concentrations of above 30 µg l<sup>-1</sup> could be treated. The most common water treatment process installed for removal of pesticides worldwide is adsorption using granular activated carbon (GAC). However, this does not provide an effective barrier to glyphosate or AMPA.

**Table 9.6-7 Removal of glyphosate and AMPA by treatment processes**

Treatment Process	Glyphosate removal (%)	AMPA removal (%)
<b>Bank and dune filtration</b>	20 to 50	25 to 95
<b>Aluminium coagulant and clarification</b>	15 to 40	20 to 25
	Not a reliable barrier for Glyphosate and AMPA	
<b>Iron coagulant and clarification</b>	40 to 70	20 to 85
	Not a reliable barrier for Glyphosate and AMPA	
<b>Slow sand filtration</b>	Insufficient information but likely to be less effective than bank or dune filtration and therefore of little practical benefit	
<b>Chlorination</b>	74 to > 99	40 to >95
	Likely to provide the main barrier to Glyphosate and AMPA at most water treatment works	
<b>Chlorine dioxide</b>	Insufficient information but not expected to be effective	
<b>Ozonation</b>	60 to >99	25 to 95
	Provides an additional barrier at works where already installed for other pesticides and micropollutants	
<b>UV irradiation</b>	No information found. Highly unlikely to be effective alone at doses used in water treatment. May be effective at very high doses not currently used for water treatment.	
<b>UV/hydrogen peroxide</b>	Little direct information available, but indications that a combination of UV with hydrogen peroxide would be effective	
<b>Advanced oxidation</b>	No information found, but would be expected to be effective through free radical mechanisms. Little used for water treatment at the present time.	
<b>Activated carbon adsorption</b>	10 to 90	20 to 70
	Higher removals relate to virgin GAC and are unlikely to be achieved under practical conditions. Not a reliable barrier for Glyphosate and AMPA.	
<b>Membrane filtration</b>	>90 (NF/RO) >50 (UF)* *depending on membrane type	>95 (NF/RO) No information found for UF
	Membrane processes not widely used in water treatment, and unlikely to be installed solely as a barrier to pesticides and other organic micropollutants.	
<b>Air stripping</b>	No information found, not expected to be effective based on chemical characteristics.	

The results of the laboratory batch tests are summarized in Table 9.6-8.



Ozone was highly effective in removing both glyphosate and AMPA and virtually complete removal was achieved under all conditions tested. The combination of  $O_3/H_2O_2$  was as effective as  $O_3$  alone in removing glyphosate and complete removal was achieved under all conditions tested. The  $Cl_2$  results indicate that changes in pH had little influence on the removal of glyphosate by chlorine; but that the temperature had a larger influence on the glyphosate removal with 71% being removed at 5°C compared to 96% at 20°C. The removal of glyphosate by  $ClO_2$  was less effective than that for other oxidants, ranging from 17% to 93%. The highest removal was seen for the low pH samples (pH ~6) with high temperature (~22°C) and high  $ClO_2$  concentrations. However, complete removal of AMPA was seen for all conditions tested, suggesting AMPA is readily removed by  $ClO_2$ . Although the results are somewhat scattered, it is clear the investigated PACs would not provide adequate removal of glyphosate and AMPA.

**Table 9.6-8 Removal of glyphosate and AMPA during laboratory batch tests**

Treatment Process	Glyphosate		AMPA	
	Conditions	Removal (%)	Conditions	Removal (%)
<b>Ozonation</b>	T° : 7, 11, 15 °C Residual $O_3$ : 0.41, 0.76 mg/L Conc : 2.6, 2.7 µg/L	>99	T° : 5, 10, 13 °C Residual $O_3$ : 0.5 mg/L Conc : 3.65 µg/L	>99
<b>Ozonation + hydrogen peroxide</b>	$H_2O_2$ : 0.5, 1.0 mg/L Residual $O_3$ : 0.09, 0.18, 0.24, 0.46 mg/L Conc : 2.6, 2.7 µg/L	98 - >99	$H_2O_2$ : 0.5, 1.0 mg/L Residual $O_3$ : 0.16, 0.04 mg/L Conc : 3.65 µg/L	85 - 97
<b>Chlorine</b>	pH : 6, 7.5, 8.5 T° : 5, 10, 20°C Residual $Cl_2$ : 1.4 mg/L Conc : 2.17, 3.17 µg/L	71 - >99 (removal decrease with T°)	pH : 6, 7, 8.5 T° : 6, 10, 20°C Residual $Cl_2$ : 1.4 mg/L Conc : 3.65 µg/L	>99
<b>Chlorine dioxide</b>	pH : 6-8.6 T° : 4-23°C Residual $ClO_2$ : 0.4-1.35 mg/L Conc : 2.17, 2.47 µg/L	17-93% (removal decrease with T°)	pH : 6.2 - 8.4 T° : 6, 10, 20°C Residual $Cl_2$ : 1 - 1.4 mg/L Conc : 3.65 µg/L	>99
<b>Powdered Activated Charcoal</b>	PAC conc : 5, 15, 25 mg/L Conc : 3.13 µg/L	0-22	PAC conc : 5, 15, 25 mg/L Conc : 3.13 µg/L	0-31

The results of the Advanced Oxidation Processes (AOP) pilot plant tests are summarized in Table 9.6-9. UV alone did not remove significant amounts of glyphosate or AMPA even at relatively high doses (1240  $mJ\ cm^{-2}$ ). UV in conjunction with  $H_2O_2$  showed good removal of glyphosate (approximately 90%) but significant amounts of AMPA was also generated and AMPA was poorly removed by this treatment (<10%).

An applied dose of 2  $mg\ l^{-1}$  ozone removed greater than 95% of the glyphosate, this removal being essentially achieved within 1 minute contact time after the eductor. This indicates a very high rate of reaction with molecular ozone. This is consistent with the previous laboratory tests with ozone, but the earlier laboratory tests showed better removal of AMPA (literature search) by ozone alone. Near complete removal of glyphosate was also seen for the combination of ozone and  $H_2O_2$ , >95% was removed after 1 minute. Again, the removal of AMPA was not as good as in previous tests, but this is probably an effect of the short contact time (1 minute).

**Table 9.6-9 Removal of glyphosate and AMPA during AOP pilot plant tests**

Treatment Process	Glyphosate		AMPA	
	Conditions	Removal (%)	Conditions	Removal (%)
UV (740 mJ/cm <sup>2</sup> )	1 min contact time Conc: 1.72 µg/L	25	1 min contact time Conc: 2.31 µg/L	6
UV (1240 mJ/cm <sup>2</sup> )	1 min contact time Conc: 1.72 µg/L	36	1 min contact time Conc: 2.31 µg/L	32
UV (740 mJ/cm <sup>2</sup> ) H <sub>2</sub> O <sub>2</sub> 5 mg/L	1 min contact time Conc: 1.72 µg/L Residual H <sub>2</sub> O <sub>2</sub> : 5.5 mg/L	88	1 min contact time Conc: 2.31 µg/L Residual H <sub>2</sub> O <sub>2</sub> : 4.98 mg/L	8
UV (1240 mJ/cm <sup>2</sup> ) H <sub>2</sub> O <sub>2</sub> 5 mg/L	1 min contact time Conc: 1.72 µg/L Residual H <sub>2</sub> O <sub>2</sub> : 5.16 mg/L	91	1 min contact time Conc: 2.31 µg/L Residual H <sub>2</sub> O <sub>2</sub> : 4.65 mg/L	6
O <sub>3</sub> 2 mg/L H <sub>2</sub> O <sub>2</sub> 2 mg/L	1 min contact time Conc: 1.72 µg/L	96->99 (duplicates)	1 min contact time Conc: 2.31 µg/L	35
O <sub>3</sub> 2 mg/L	1 min contact time Conc: 1.72 µg/L Residual O <sub>3</sub> : 0.83 mg/L	96	1 min contact time Conc: 2.31 µg/L Residual O <sub>3</sub> : 0.96 mg/L	63
O <sub>3</sub> 2 mg/L	10 min contact time Conc: 1.72 µg/L Residual O <sub>3</sub> : 0.36 mg/L	97	10 min contact time Conc: 2.31 µg/L Residual O <sub>3</sub> : 0.52 mg/L	>99

### III. CONCLUSION

The majority of water treatment works worldwide use chlorine for disinfection, and therefore have an effective barrier for glyphosate and AMPA. Exceptions to this would be works in mainland Europe which use chlorine dioxide for disinfection and protection of the water in distribution, instead of chlorine. In this situation, the removal of glyphosate would be more variable, but complete removal of AMPA (>99%) could be expected.

The most common water treatment process installed for removal of pesticides worldwide is adsorption using granular activated carbon. This system does not provide an effective barrier to glyphosate and AMPA. However, at many treatment works ozone is also installed for removal of pesticides or other organic micropollutants, and would be highly effective for glyphosate and AMPA removal under the dose and contact time conditions typically used. As expected, UV disinfection processes are not very effective in removing glyphosate and AMPA, but in combination with hydrogen peroxide could provide an efficient barrier for glyphosate (but not AMPA).

Other processes commonly used in water treatment (bankside or dune infiltration, coagulation/clarification/ filtration and slow sand filtration) would each contribute some removal, but each process in isolation is unlikely to provide a secure barrier in relation to meeting a 0.1 µg l<sup>-1</sup> standard.

### IIIA 9.7 Predicted environmental concentration in surface water (PEC<sub>sw</sub>)

The predicted environmental concentrations of glyphosate acid and metabolites AMPA (soil-and aquatic degradate) and hydroxymethylphosphonic acid (HMPA; degradate in water/sediment systems only) in surface water (PEC<sub>sw</sub>) and sediment (PEC<sub>sed</sub>) have been calculated using the FOCUS surface water scenario tools. For glyphosate acid, calculations were carried out using the FOCUS Step 1 to Step 3 modules, while for AMPA the calculations were conducted using the FOCUS Steps 1 to 2 modules only. For HMPA; the maximum PEC<sub>sw</sub> and PEC<sub>sed</sub> were calculated based on the Step 1 and 2 results of parent glyphosate acid, corrected for the molar mass difference and its maximum fraction formed in the only glyphosate water/sediment study where it was observed. The FOCUS "Steps" are briefly described below<sup>13</sup> (FOCUS 2001<sup>13</sup>, FOCUS 2011c<sup>14</sup>).

- **FOCUS Step 1** considers inputs to a water body of spray drift, run-off, erosion and/or drainage. These inputs are evaluated as a single loading to the water body; 'worst-case' water and sediment concentrations are calculated.
- **FOCUS Step 2** considers inputs to a water body of spray drift, run-off, erosion and/or drainage. These inputs are evaluated as a series of individual loadings (drift events) followed by a loading representing a run-off, erosion and/or drainage event that occurs 4 days after the application. Degradation of the active substance in the field is considered between these events.
- **FOCUS Step 3** incorporates more sophisticated modelling estimations of exposure, considering runoff and drainage events determined by local climate, field slopes, and soil and water body characteristics.

The key input parameters for the FOCUS modelling (glyphosate and AMPA degradation DT<sub>50</sub>-values for both the water- and sediment compartment and the maximum occurrences), have been derived from all available glyphosate and AMPA water/sediment studies in accordance with the methods recommended in the FOCUS kinetics guidance document (FOCUS 2006, 2011a). The updated kinetic evaluation of water/sediment studies is summarised below. The results from the FOCUS surface water modelling are provided in Annex Point IIIA 9.1.1.

**Evaluation of glyphosate and AMPA water/sediment studies** - The results of the aerobic laboratory water-sediment studies have consistently demonstrated that glyphosate is microbially degraded in total water-sediment systems over time. In addition to microbial degradation a major contributor to the aquatic dissipation of glyphosate is adsorption to the sediment. One major metabolite of glyphosate, aminomethylphosphonic acid (AMPA), was detected in the studies with maximum amounts of 15.7% (water phase), 15.9% (sediment) and 27.1% (total system). Another metabolite in water, hydroxymethylphosphonic acid (HMPA), was found in only one of the water/sediment studies evaluated during the 2001 EU evaluation (██████████ 1993), with a maximum amount of 10% of the glyphosate applied.

The water/sediment studies that were independently conducted with AMPA, when applied as test item, showed a very similar behaviour in water-sediments systems as glyphosate. AMPA quickly dissipated from the water phase by both adsorption to the sediment and by degradation by the sediment micro-flora. Studies demonstrated that from 8 to 40% of the applied AMPA is mineralized to carbon dioxide. Degradation of AMPA revealed metabolites with amounts <10% in water and up to 23% in sediment (Metabolite M3.3 = 1-oxo AMPA, ██████████, 2002). No risk assessment was conducted for 1-oxo AMPA since this metabolite was only seen in an AMPA water/sediment study and was never detected in any of the four available glyphosate water/sediment studies. Taking into account that 1-oxo-AMPA was only found at 23% of the applied AMPA in a water-sediment system, this metabolite does not qualify as a major aquatic metabolite of parent glyphosate anyway. Indeed, when assuming the worst case, that 27.1%

<sup>13</sup> FOCUS (2001): FOCUS Surface Water Scenarios in the EU Evaluation Process under 91/414/EEC. Report of the FOCUS Working Group on Surface Water Scenarios, EC Document Reference SANCO/4802/2001 rev. 2, 245 pp.

<sup>14</sup> FOCUS (2011c): Generic guidance for FOCUS surface water Scenarios, version 1.0.

<sup>15</sup> OECD (2002) OECD Guideline for the Testing of Chemicals: Aerobic and Anaerobic Transformation in Aquatic Sediment Systems. 24th April 2002

Residue data of twelve water-sediment systems from six studies were kinetically evaluated. All datasets were initially evaluated by simple first-order (SFO) and if necessary by bi-phasic models. Persistence endpoints were then evaluated using best-fit kinetics. A set of different rules of acceptance criteria were followed for determining modelling endpoints to be used in PEC<sub>sw</sub> simulations. An assessment of the goodness-of-fit of optimised degradation curves was used to evaluate the reliability of all parameter estimates in accordance with FOCUS kinetics guidance.

At Level P-I, single first-order and biphasic kinetic models were used to describe the behaviour of glyphosate and AMPA in the water phase, the sediment phase and the total system. No Level P-II was calculated. All endpoints were derived from studies where glyphosate and AMPA were applied as test items in separate studies. No pathway fit was evaluated to obtain endpoints for the metabolite AMPA from the glyphosate studies. As no level P-II values were obtained in the present evaluation, the geometric means of the total system modelling endpoints (DegT<sub>50</sub>) are recommended for FOCUS surface water modelling for both substances.

Kinetic analysis of HMPA was not carried out in this evaluation because of an insufficient number of samples after peak concentration.

## I. MATERIALS AND METHODS

### A. MATERIALS

Not applicable; no materials were used as this study is a computer simulation.

ModelMaker™ (version 4.0; [REDACTED]) was used as fitting software. The Microsoft Excel™ 2003 *Degradation Kinetics Spreadsheet* (v2, June 2007), as provided by FOCUS Work Group, was used for statistical evaluation of the optimised parameters.

### B. STUDY DESIGN AND METHODS

The degradation of glyphosate and its major metabolite in water and sediment, AMPA, was initially investigated in eight laboratory water-sediment systems under aerobic conditions in the dark between 1993 and 2004 ([REDACTED] 1999; [REDACTED], 1993; [REDACTED] 1996; [REDACTED] 1993; [REDACTED] 2002; [REDACTED] 2003; [REDACTED] 1999; [REDACTED] 2004). Each study tested two independent aquatic sediment systems with different characteristics. As test item, [<sup>14</sup>C]-labelled glyphosate ([REDACTED] 1993; [REDACTED] 1996; [REDACTED] 1993), [<sup>14</sup>C]-labelled glyphosate-trimesium ([REDACTED] 1999) with [<sup>14</sup>C]-labelled in the glyphosate anion portion of the molecule), [<sup>14</sup>C]-labelled AMPA ([REDACTED] 2002; [REDACTED], 1999; [REDACTED], 2003; [REDACTED], 2004) were used.

The studies of [REDACTED] (1993) and [REDACTED] (2004) revealed several deviations from OECD Guidelines for Testing of Chemicals No. 308 (OECD, 2002<sup>16</sup>) such as analytical artefacts and insufficient reporting of important parameters and thus these studies were excluded from kinetic evaluation.

Replicate samples for residue data were available for all studies on AMPA degradation. However, for the study by [REDACTED] (2002), mean values of duplicate samples were kinetically evaluated. The study by [REDACTED] (1999) on degradation of AMPA provided replicate samples for each sampling time and each of the sediment systems, which again were analysed with two different TLC systems. These values (derived from the different TLC-systems) were considered to be analytical replicates and were therefore averaged prior to kinetic evaluation to obtain true replicates per sampling time. All other study reports provided true replicates to be used in kinetic analyses without further pre-processing.

<sup>16</sup> OECD (2002): OECD Guidelines for Testing of Chemicals. Test No. 308: Aerobic and Anaerobic Transformation in Aquatic Sediment Systems.

Preparation of water-sediment residue data as input data for the kinetic optimisation, as well as the mathematical optimisation process of the respective models itself and the subsequent derivation of endpoints were conducted according to FOCUS (2006, 2011a).

All datasets were initially evaluated by comparing single first-order (SFO) and first-order multi-compartment (FOMC) kinetic models. Persistence endpoints were then evaluated using best-fit kinetics. A set of different rules of acceptance criteria were followed for determining modelling endpoints to be used in PEC<sub>sw</sub> simulations. An assessment of the goodness-of-fit of optimised degradation curves was used to evaluate the reliability of all parameter estimates following FOCUS guidance (2006, 2011a).

For water-sediment studies, two levels of kinetic assessments are proposed by FOCUS:

- Level I is for one-compartment approaches to estimate the kinetic endpoints such as degradation in the whole system, dissipation from the water column compartment alone, and dissipation from the sediment compartment alone.
- Level II is for two-compartment approaches that take degradation and partitioning into account to estimate degradation in the water column and sediment compartments.

For parent substances these levels are denoted P-I and P-II.

At Level P-I, single first-order (SFO) and biphasic kinetic models were used to describe the degradation behaviour of glyphosate and AMPA in the water phase, the sediment phase and the total system. Sediment data were modelled from the maximum ( $M_{\max}$ ) onwards. Level P-II was not calculated. All endpoints were derived from studies where glyphosate and AMPA were applied as test items in separate studies. No pathway fit was evaluated to obtain endpoints for the metabolite AMPA from the glyphosate studies.

## II. RESULTS AND DISCUSSION

The optimisation of the kinetic analysis was conducted following decision schemes as defined in the FOCUS kinetics guidance document (FOCUS, 2006, 2011a). As a first step for all datasets, the fit of a SFO kinetic model was tested for the applied substance. For modelling endpoints, in cases where SFO was not appropriate, the decision whether to test only the HS and DFOP models (>10% AR) or additionally FOMC (<10% AR) as bi-phasic models depended on the amount of residue in the respective compartment (water, sediment, total system) at the end of the experimental phase. For persistence (best-fit) endpoints the SFO model was compared to the FOMC model. In cases, where SFO was not appropriate as the best-fit model, DFOP and HS were tested as further bi-phasic models.

Persistence endpoints for glyphosate at Level P-I were almost exclusively derived from robust fits of bi-phasic models. Only sediment DT<sub>50/90</sub> values were partly derived from a SFO model. Persistence endpoints for glyphosate ranged from 2.5 to 210.7 days (total system), 1.0 to 12.0 days (water phase), and 34.1 to 146.3 days (sediment phase) (Table 9.7-1).

Modelling endpoints for glyphosate at Level P-I ranged from 13.8 to 329.9 days (total system), 6.8 to 21.8 days (water phase), and 34.1 to 303.3 days (sediment phase). DT<sub>50</sub> values for the water phase of all water-sediments systems were exclusively back-calculated from DT<sub>90</sub> by DT<sub>90</sub>/3.32 (assuming first order kinetics), when derived from bi-phasic models. This indicated that less of 10% of the initially measured glyphosate concentration were available in the water-phase at the end of the experimental period.

Persistence endpoints for AMPA at Level P-I were exclusively derived from robust fits of bi-phasic models, with DegT<sub>50</sub> values for the total system ranging from 2.5 to 77.4 days, and with DT<sub>50</sub> values for the water phase ranging from 1.0 to 6.6 days. For dissipation of AMPA from the sediment phase, only a single DT<sub>50</sub> of 184.3 days could be obtained.

Modelling endpoints for AMPA ranged from 61.8 to 102.9 days (total system) and 1.6 to 15.5 days (water phase). No reliable kinetic fit could be achieved for the degradation behaviour of AMPA in the sediment

phase as the peak concentration of AMPA in sediment was observed too late to allow the decline phase to be fitted. Consequently, no modelling endpoints for AMPA could be derived for the sediment phase.

All kinetic endpoints for glyphosate and AMPA, are provided in Table 9.7-1 and Table 9.7-2, respectively.

**Table 9.7-1 Persistence and modelling endpoints of glyphosate in water-sediment systems**

Study	System	Persistence endpoints at Level P-I			Modelling endpoints at Level P-I	
		Model	DT <sub>50</sub> <sup>4)</sup> (days)	DT <sub>90</sub> <sup>4)</sup> (days)	Model	SFO DT <sub>50</sub> <sup>4)</sup> (days)
Glyphosate (total system)						
██████████ (1999)	Cache	FOMC	8.47	45.89	FOMC	13.82 <sup>1)</sup>
	Putah	DFOP	210.66	976.54	DFOP	329.85 <sup>2)</sup>
██████████ (1993)	Loamy Sediment	DFOP	116.56	1328.20	DFOP	354.19 <sup>2)</sup>
	Sandy Sediment	HS	16.03	346.81	HS	16.78
██████████ (1996)	Creek	HS	16.10	65.83	SFO	16.78
	Pond	FOMC	65.86	2053.35	SFO	72.75
		Minimum	8.47	45.89		13.82
		Maximum	210.66	2053.35		329.85
		Geometric mean	39.03	375.31		61.19
Glyphosate (water phase)						
██████████ (1999)	Cache	HS	4.98	26.84	SFO	6.94
	Putah	FOMC	8.25	72.40	FOMC	21.81 <sup>1)</sup>
██████████ e (1993)	Loamy Sediment	FOMC	1.06	24.11	FOMC	7.26 <sup>1)</sup>
	Sandy Sediment	DFOP	2.03	22.63	DFOP	6.82 <sup>1)</sup>
██████████ (1996)	Creek	DFOP	11.95	48.10	SFO	13.15
	Pond	HS	1.00	26.89	HS	8.10 <sup>1)</sup>
		Minimum	1.00	22.63		6.82
		Maximum	11.95	72.40		21.81
		Geometric mean	3.19	33.33		9.63
Glyphosate (sediment phase)						
██████████ (1999)	Cache	SFO	34.05	113.10	SFO	34.05
	Putah	<sup>3)</sup>	<sup>3)</sup>	<sup>3)</sup>	<sup>3)</sup>	<sup>3)</sup>
██████████ (1993)	Loamy Sediment	<sup>3)</sup>	<sup>3)</sup>	<sup>3)</sup>	<sup>3)</sup>	<sup>3)</sup>
	Sandy Sediment	HS	146.26	850.52	HS	303.31 <sup>2)</sup>
██████████ (1996)	Creek	SFO	47.88	159.06	SFO	47.88
	Pond	<sup>3)</sup>	<sup>3)</sup>	<sup>3)</sup>	<sup>3)</sup>	<sup>3)</sup>
		Minimum	34.05	113.10		34.05
		Maximum	146.26	850.52		303.31
		Geometric mean	62.01	248.26		79.08

1) Back-calculated from DT<sub>90</sub> of bi-phasic model (DT<sub>90</sub>/3.32)

2) Calculated from slower k-rate

3) no reliable fit achieved

4) DT<sub>50</sub> = DegT<sub>50</sub> for total system but DT<sub>50</sub> for water and sediment phase

Table 9.7-2 Persistence and modelling endpoints of AMPA in water-sediment systems

Study	System	Persistence endpoints at Level P-I			Modelling endpoints at Level P-I	
		Model	DT <sub>50</sub> <sup>4)</sup> (days)	DT <sub>90</sub> <sup>4)</sup> (days)	Model	SFO DT <sub>50</sub> <sup>4)</sup> (days)
AMPA (total system)						
[redacted] (2002)	Rückhaltebecken	FOMC	13.80	1513.00	DFOP	102.87 <sup>2)</sup>
	Schäphysen	DFOP	2.48	354.99	- <sup>3)</sup>	- <sup>3)</sup>
[redacted] (2003)	Bickenbach	HS	10.54	191.25	HS	77.83 <sup>2)</sup>
	Unter-Widdersheim	HS	77.36	307.19	HS	98.98 <sup>2)</sup>
[redacted] (1999)	Bickenbach	HS	44.53	205.21	HS	61.81 <sup>1)</sup>
	Unter-Widdersheim	HS	18.02	640.66	- <sup>3)</sup>	- <sup>3)</sup>
		Minimum	2.48	191.25	61.8	
		Maximum	77.36	1513.00	102.9	
		Geometric mean	16.79	400.85	83.7	
AMPA (water phase)						
[redacted] (2002)	Rückhaltebecken	FOMC	2.20	22.50	FOMC	6.78 <sup>1)</sup>
	Schäphysen	FOMC	1.00	7.80	SFO	1.58
[redacted] (2003)	Bickenbach	DFOP	2.54	47.57	DFOP	14.33 <sup>1)</sup>
	Unter-Widdersheim	DFOP	1.81	19.29	DFOP	5.81 <sup>1)</sup>
[redacted] (1999)	Bickenbach	DFOP	6.59	51.40	DFOP	15.50 <sup>1)</sup>
	Unter-Widdersheim	HS	2.02	17.15	HS	5.17 <sup>1)</sup>
		Minimum	1.00	7.80	1.58	
		Maximum	6.59	47.57	15.50	
		Geometric mean	2.26	22.85	6.44	
AMPA (sediment phase)						
[redacted] (2002)	Rückhaltebecken	DFOP	184.33	678.38	- <sup>3)</sup>	- <sup>3)</sup>
	Schäphysen	- <sup>3)</sup>	- <sup>3)</sup>	- <sup>3)</sup>	- <sup>3)</sup>	- <sup>3)</sup>
[redacted] (2003)	Bickenbach	- <sup>3)</sup>	- <sup>3)</sup>	- <sup>3)</sup>	- <sup>3)</sup>	- <sup>3)</sup>
	Unter-Widdersheim	- <sup>3)</sup>	- <sup>3)</sup>	- <sup>3)</sup>	- <sup>3)</sup>	- <sup>3)</sup>
[redacted]let (1999)	Bickenbach	- <sup>3)</sup>	- <sup>3)</sup>	- <sup>3)</sup>	- <sup>3)</sup>	- <sup>3)</sup>
	Unter-Widdersheim	- <sup>3)</sup>	- <sup>3)</sup>	- <sup>3)</sup>	- <sup>3)</sup>	- <sup>3)</sup>
		Geometric mean	184.33	678.38	-	

1) Back-calculated from DT<sub>90</sub> of bi-phasic model (DT<sub>90</sub>/3.32)

2) Calculated from slower k-rate

3) No reliable fit achieved

4) DT<sub>50</sub> = DegT<sub>50</sub> for total system but DT<sub>50</sub> for water and sediment phase

### III. CONCLUSION

For FOCUS surface water modelling the geometric mean DegT<sub>50, total system</sub> of **61.2 days** for glyphosate and of **83.7 days** for AMPA are considered to be acceptable as half-lives for the water phase in combination with a conservative default DegT<sub>50</sub> of **1000 days** for sediment.

In one of the glyphosate water/sediment studies evaluated during the 2001 EU evaluation (██████████ 1993), an additional metabolite, hydroxymethylphosphonic acid (HMPA), was also detected in the water compartments at several time-points late during incubation (maximum amount of about 10% of the applied dose). However, kinetic analysis of HMPA was not carried out in this evaluation because of an insufficient number of samples after peak concentration.



The overall maximum PEC<sub>sw</sub> value of glyphosate acid at Steps 1, 2 and 3 was 101.2, 39.0 and 17.7 µg/L, respectively. The overall maximum PEC<sub>sw</sub> value of AMPA at Step 1 and 2 was 41.0 and 16.9 µg/L. The overall maximum PEC<sub>sw</sub> value of HMPA at Step 1 and 2 was 6.71 and 2.63 µg/L.

## I. MATERIALS AND METHODS

### A. MATERIALS

Not applicable, no materials were used as this study is a computer simulation.

FOCUS STEPS 1-2 (version 2.1), FOCUS SWASH (version 3.1), including FOCUS MACRO (version 4.4.2), FOCUS PRZM (version 1.1.1) and FOCUS TOXSWA (version 3.3.1), and Microsoft Excel™ 2003 were used for calculation of  $PEC_{sw}$  and  $PEC_{sed}$ .

### B. STUDY DESIGN AND METHODS

Calculations were carried out according to FOCUS (2001 and 2011c) at Steps 1 to 3. For glyphosate acid, calculations were carried out at Step 1 to Step 3, while for AMPA the calculations were conducted at Steps 1 to 2 level only. For HMPA; maximum  $PEC_{sw}$  and  $PEC_{sed}$  were calculated based on Step 1 and 2 results of glyphosate acid, considering the molar mass difference and assuming 10% maximum occurrence for HMPA.

#### Application scenarios

At Steps 1 to 2 level, the chosen multiple application scenarios were simulated using the highest dose rate of the scenario for all applications, *i.e.* 2x2160 and 1x4320 g glyphosate acid/ha. At Step 2, all regions ('North Europe' and 'South Europe') and application periods ('October-February', 'March-May' and 'June-September') were taken into account for modelling. No interception was considered for calculations with Step 1 and 2 representing therefore worst-case maximum soil loads (see Table 9.7-3).

**Table 9.7-3 Steps 1 and 2: Application settings used for modelling**

Crop scenario	Region	Application period	Interception
2x2160 g glyphosate acid./ha	North / South Europe	All periods	No crop interception
1x4320 g glyphosate acid/ha <sup>1)</sup>	North / South Europe	All periods	No crop interception

1) Since the model STEPS 1-2 can only handle one application rate within a multiple application scenario, the highest single dose rates were used for modelling as a worst-case approach.

The application scenarios considered for simulations at Step 3 are presented in Table 9.7-4. Multiple applications were considered in modelling reflecting the representative GAP. The simulations were also performed for single applications in accordance with FOCUS (2001 and 2011c) to account for the fact that single applications might result in higher  $PEC_{sw}$  values if the drift entry is the main entry route. A twofold application taking place before crop emergence in winter cereals was chosen as a representative use of glyphosate in autumn. Glyphosate use on spring cereals was selected to reflect one pre-planting / pre-emergence application in spring followed by an application in autumn. To fill the gap for some surface water scenarios not covered by spring cereals crop, additional simulations were performed with potatoes to simulate spring uses of glyphosate. FOCUS crop "pome/stone fruit, early applns" was chosen to account for up to three applications in orchards, citrus, vines, and tree nuts.

**Table 9.7-4 Application scenarios considered in simulations at STEP3**

Crop	FOCUS crop	Application rate (g glyphosate acid/ha)	No. of appl.	Min. interval between applications (d)	Application period
Various crops (autumn application)	Winter cereals	2160 2160	2 1 <sup>2)</sup>	21 -	Pre-planting / pre-emergence
Various crops (spring + autumn application)	Spring cereals	2160 2160 2160	2 1 <sup>1)</sup> 1 <sup>2)</sup>	21 <sup>3)</sup> - -	Pre-planting / pre-emergence + post-harvest
Various crops (spring application)	Potatoes	2160 2160	2 1 <sup>1)</sup>	21 -	Pre-planting / pre-emergence
Orchards, citrus, vines, tree nuts	Pome/ stone fruit	2880 / 720 / 720 2880	1+/1+/1 1 <sup>1)</sup>	28 -	Post-emergence of weeds

1) Single application in spring (according to FOCUS 2001, FOCUS 2011c, a single application should be evaluated additionally)

2) Single application in autumn (according to FOCUS 2001, FOCUS 2011c, a single application should be evaluated additionally)

3) For the determination of the application window, an application interval of 160 days was assumed in order to reflect pre-emergence application in spring and the following application in autumn

Step 3 simulations for glyphosate acid were carried out using FOCUS SWASH 3.1 with the Chemical Application Method (CAM) 1 (soil linear) including a standard application depth of 4 cm. The 'ground spray' application method was chosen for winter and spring cereals and potatoes. For pome/stone fruit, 'granular' application method was chosen to exclude simulation with unrealistically high spray drift rates which are assigned for pome/stone fruit by FOCUS (2001, 2011c) but are unrealistic for the application around the base of trunks as intended for glyphosate. Since 'granular' application method implies drift rate of 0, the realistic drift rates had to be manually set. Therefore, a special drift assessment was performed (FOCUS, 2001, 2011c) when running the TOXSWA program. The spray drift rates were amended manually in the respective \*.twa files of the model. The drift rates used were taken from the FOCUS spray drift calculator for 'application hand, crop <50cm'.

Appropriate application windows for winter and spring cereals as well as for potatoes were chosen based on GAP information for glyphosate and on emergence/harvest dates specified in FOCUS (FOCUS, 2001, 2011c). For winter cereals, up to two pre-planting / pre-emergence application in autumn were considered. Similarly, up to two pre-planting / pre-emergence applications in spring were considered for potatoes. In the case of spring cereals, the first application before emergence in spring and the second application after harvest were taken into account. The beginning of the application window was assigned to each individual scenario for pome/stone fruit by expert judgement. The length of application window was determined according to FOCUS (2001, 2011c) considering the number of applications and the minimum application interval. The actual date of application within the application windows was determined by the Pesticide Application Timer (PAT) incorporated in FOCUS SWASH 3.1.

#### Substance properties and input parameters

A summary of the relevant physical properties, maximum occurrences, and degradation parameters used as inputs to the FOCUS modelling are given in Table 9.7-5.

Degradation of glyphosate in soil was described by the normalised geometric mean laboratory half-life of 12.8 days (n=13, for details on the studies and the kinetic evaluation, please refer to Annex point IIIA 9.1.1, Table 9.1-1). Degradation behaviour of glyphosate in water and sediment was modelled using the geometric mean of the total system modelling endpoints of 61.2 days at Step 1 and Step 2. In compliance with recommendations by the FOCUS work group on degradation kinetics (FOCUS, 2006, 2011a), DT<sub>50, sed</sub> was set to the worst case default value of 1000 days and the DT<sub>50, water</sub> of 61.2 days was used to determine degradation in the water phase at Step 3 (for details on the degradation behaviour of glyphosate

in water/sediment systems, please refer to Annex point IIIA 9.7/01). Regarding sorption, the arithmetic mean  $K_{\text{foc}}$  and  $1/n$  value of glyphosate (16810 ml/g and 0.80,  $n=15$ ) were selected for modelling purposes (for details, see Annex point IIIA 9.3, Table 9.3-1).

Degradation of AMPA in soil was described by the normalised geometric mean laboratory half-life of 55.7 days ( $n=7$ , for details on the studies and the kinetic evaluation, please refer to Annex point IIIA 9.1.1, Table 9.1-2). The geometric mean of the total system modelling endpoints of 83.7 days was used to determine degradation in water ( $DT_{50, \text{water}}$ ), in sediment ( $DT_{50, \text{sediment}}$ ), and in total system ( $DT_{50, \text{total system}}$ ) at Step 1-2 level (for details on the degradation behaviour of AMPA in water/sediment systems, please refer to Annex point IIIA 9.7/01). The maximum occurrences of AMPA of 50.1% in soil (McLaughlin & Schanné, 1996) and of 27.26% in water/sediment systems (maximum value of one replicate in Cache sandy loam, Bowler & Johnson, 1999) were used for modelling.

HMPA was observed in the water phase of one water/sediment study with the parent glyphosate (Möllerfeld & Römbke, 1993) with a maximum occurrence of 10% of applied glyphosate, which was used as input for the calculations. As a worst-case approach, PEC in sediment were calculated using the same maximum occurrence from the water phase, although HMPA was not observed in the sediment phase of any water/sediment study.

Apart from the input parameters explicitly discussed, all variables in the models were left at their default values.

**Table 9.7-5 Input data of glyphosate acid and its metabolites AMPA and HMPA used in FOCUS modelling**

Parameter	Unit	Glyphosate acid	AMPA	HMPA
Molecular Mass	g/mol	169	111	112
Water solubility	mg/L	10500 (20°C)	10500 (20°C) <sup>1)</sup>	- <sup>2)</sup>
DegT <sub>50</sub> soil	Days	10.8	55.7	- <sup>2)</sup>
DegT <sub>50</sub> water	Days	61.2	83.7	- <sup>2)</sup>
DegT <sub>50</sub> sediment	Days	61.2 / 1000	83.7	- <sup>2)</sup>
DegT <sub>50</sub> total system	Days	61.2	83.7	- <sup>2)</sup>
$K_{\text{foc}}$	ml/g	16810	- <sup>4)</sup>	- <sup>2)</sup>
Max. occurrence soil	(%)	100 <sup>5)</sup>	50.1	- <sup>2)</sup>
Max occurrence w/sed	(%)	100 <sup>5)</sup>	27.26	10 <sup>5)</sup>
Freundlich exponent (1/n)	-	0.80	- <sup>4)</sup>	- <sup>2)</sup>
Plant uptake factor		0	- <sup>4)</sup>	- <sup>2)</sup>

1) Parent data

2) Not relevant (calculations based on  $PEC_{\text{sw}}$  and  $PEC_{\text{sed}}$  of glyphosate acid)

3) Value used in Steps 1-2 / Step 3 calculations

4) Not relevant (Steps 1-2 calculations only)

5) HMPA observed in one study only (Möllerfeld & Römbke, 1993) with a maximum occurrence of 10% in water

## II. RESULTS AND DISCUSSION

### Global maximum $PEC_{\text{sw}}$ and $PEC_{\text{sed}}$ at Step 1 and 2

At Step 1, the overall maximum  $PEC_{\text{sw}}$  were 101, 41.0 and 6.7  $\mu\text{g/L}$  for glyphosate acid, AMPA and HMPA, respectively. At Step 2, the maximum concentrations resulted from the worst-case single application scenario at the maximum total allowed yearly application rate. The overall maximum  $PEC_{\text{sw}}$  were 39.7, 16.9 and 2.6  $\mu\text{g/L}$  for glyphosate acid, AMPA and HMPA, respectively.

Global maximum  $PEC_{\text{sw}}$  and  $PEC_{\text{sed}}$  of glyphosate acid and its metabolites AMPA and HMPA at Step 1 and 2 level are shown in Table 9.7-6.

**Table 9.7-6 Steps 1-2: Maximum PEC<sub>sw</sub> and PEC<sub>sed</sub> of glyphosate acid and its metabolites AMPA and HMPA following pre- and post-emergence application to various crops**

FOCUS STEP	Scenario	Glyphosate acid		AMPA		HMPA	
		PEC <sub>sw</sub> (µg/L)	PEC <sub>sed</sub> (µg/kg)	PEC <sub>sw</sub> (µg/L)	PEC <sub>sed</sub> (µg/kg)	PEC <sub>sw</sub> (µg/L)	PEC <sub>sed</sub> (µg/kg)
Step 1	1x4320 g/ha <sup>3)</sup>	101	10500	41.0	3320	6.71	696
Step 2 (North Europe, Oct – Feb)	2x2160 g/ha <sup>4)</sup>	18.4	2960	14.9	1430	1.22	196
	1x4320 g/ha <sup>5)</sup>	39.7	4430	16.9	1620	2.63	293
Step 2 (North Europe, March – May) <sup>1)</sup>	2x2160 g/ha <sup>4)</sup>	18.4	1310	6.31	593	1.22	86.8
	1x4320 g/ha <sup>5)</sup>	39.7	1930	7.21	674	2.63	128
Step 2 (South Europe, Oct. – Feb.) <sup>2)</sup>	2x2160 g/ha <sup>4)</sup>	18.4	2410	12.0	1150	1.22	160
	1x4320 g/ha <sup>5)</sup>	39.7	3590	13.7	1300	2.63	238
Step 2 (South Europe, Jun. – Sep.)	2x2160 g/ha <sup>4)</sup>	18.4	1860	9.16	891	1.22	123
	1x4320 g/ha <sup>5)</sup>	39.7	2760	10.4	988	2.63	183

1) Same results for North Europe, Jun.-Sep period

2) Same results for South Europe, Mar.-May period

3) Not crop specific

4) Cereals (winter and spring)

5) Orchard use considering spray drift associated with Appln, hand (crop &lt; 50cm)

**Maximum actual and time-weighted average PEC<sub>sw</sub> and PEC<sub>sed</sub> at Step 1 and 2**

Actual and time-weighted average concentrations of glyphosate acid and AMPA in surface water and sediment at Step 1 and Step 2 for the worst-case application scenario 1x 4320 g glyphosate acid/ha are presented in Table 9.7-7 and Table 9.7-8.

**Table 9.7-7 Step 1: Maximum actual and time-weighted average concentrations in surface water and sediment of glyphosate acid and AMPA (application rate of 1x4320 g glyphosate acid/ha)**

Scenario	Compound	Time (d)	Actual PEC <sub>sw</sub> (µg/L)	TWA PEC <sub>sw</sub> (µg/L)	Actual PEC <sub>sed</sub> (µg/kg)	TWA PEC <sub>sed</sub> (µg/kg)
Step 1	Glyphosate acid	0	101	-	10300	-
		1	62.5	81.9	10500	10400
		2	61.8	72.0	10400	10400
		4	60.4	66.5	10200	10400
		7	58.4	63.5	9810	10200
		14	53.9	59.8	9070	9810
		21	49.8	57.2	8380	9450
		28	46.0	54.8	7740	9100
		42	39.3	50.7	6600	8450
		50	35.9	48.6	6030	8110
		100	20.4	38.0	3420	6360
Step 1	AMPA	0	41.0	-	3300	-
		1	34.1	37.5	3320	3310
		2	33.8	35.7	3300	3310
		4	33.3	34.6	3240	3290
		7	32.4	33.9	3160	3250
		14	30.6	32.7	2980	3160
		21	28.9	31.7	2820	3070
		28	27.3	30.8	2660	2990
		42	24.3	29.1	2370	2830
		50	22.7	28.2	2210	2740
		100	15.0	23.4	1460	2280

**Table 9.7-8 Step 2: Maximum actual and time-weighted average concentrations in surface water and sediment of glyphosate acid and AMPA (application rate of 1x4320 g glyphosate acid/ha)**

Scenario	Compound	Time (d)	Actual PEC <sub>sw</sub> (µg/L)	TWA PEC <sub>sw</sub> (µg/L)	Actual PEC <sub>sed</sub> (µg/kg)	TWA PEC <sub>sed</sub> (µg/kg)
Step 2	Glyphosate acid	0	39.7	-	4430	-
		1	14.2	27.0	4390	4410
		2	6.14	18.6	4340	4380
		4	27.5	14.4	4240	4340
		7	25.5	19.4	4100	4260
		14	23.6	22	3780	4100
		21	21.8	22.2	3500	3950
		28	20.1	21.9	3230	3800
		42	17.2	20.8	2760	3530
		50	15.7	20.1	2520	3390
		100	8.89	16.0	1430	2650
Step 2	AMPA	0	16.9	-	1690	-
		1	16.5	16.7	1610	1610
		2	16.3	16.5	1590	1600
		4	16.1	16.4	1570	1590
		7	15.7	16.1	1530	1570
		14	14.8	15.7	1440	1530
		21	14.0	15.2	1360	1490
		28	13.2	14.8	1280	1440
		42	11.2	14.0	1140	1370
		50	11.0	13.6	1070	1330
		100	7.25	11.3	707	1100

**Global maximum PEC<sub>sw</sub> and PEC<sub>sed</sub> at Step 3**

Calculations at Step 3 were only carried out for the active substance glyphosate acid with the purpose to confirm that values calculated using lower Tiers (Steps 1-2) are appropriate for use in the aquatic risk assessment.

Maximum PEC<sub>sw</sub> and PEC<sub>sed</sub> of glyphosate acid at the Step 3 level are shown in Table 9.7-9 to Table 9.7-16. The main input pathway into surface waters was identified as spray drift. As a result, a majority of PEC<sub>sw</sub> values simulated for single application exceeded the respective values for two- or threefold application. Overall maximum PEC<sub>sw</sub> values resulting from applications to winter and spring cereals, potatoes and pome/stone fruit were predicted to be 13.5 (D2 ditch), 13.4 (D1 ditch), 11.1 (D6 ditch) and 17.7 µg/L (D3 ditch), respectively. Overall maximum PEC<sub>sed</sub> values resulting from applications to winter and spring cereals, potatoes and pome/stone fruit were predicted to be 1703 (R3 stream), 86.4 (D1 ditch), 1690 (R2 stream) and 23.8 µg/kg (R4 stream), respectively.

**Table 9.7-9 Step 3: Global maximum PEC<sub>sw</sub> of glyphosate acid following pre-planting / pre-emergence application to winter cereals**

Scenario	Water body	PEC <sub>sw,max</sub> (µg glyphosate acid/L)	
		1x2160 glyphosate acid/ha winter cereals (autumn)	2x2160 glyphosate acid/ha winter cereals (autumn)
D1	ditch	13.4	13.2
D1	stream	11.7	10.1
D2	ditch	13.5	12.2
D2	stream	12.0	10.7
D3	ditch	13.2	11.6
D4	pond	0.445	0.528
D4	stream	11.5	9.91
D5	pond	0.445	0.54
D5	stream	12.4	10.7
D6	ditch	13.4	11.9
R1	pond	0.445	0.53
R1	stream	8.72	7.57
R3	stream	12.1	10.7
R4	stream	8.23	7.57

**Table 9.7-10 Step 3: Global maximum PEC<sub>sw</sub> of glyphosate acid following pre-planting / pre-emergence and post-harvest application to spring cereals**

Scenario	Water body	PEC <sub>sw,max</sub> (µg glyphosate acid/L)		
		1x2160 glyphosate acid/ha spring cereals (spring)	1x2160 glyphosate acid/ha spring cereals (autumn)	2x2160 glyphosate acid/ha winter cereals (spring+autumn)
D1	ditch	13.4	13.4	11.8
D1	stream	11.0	11.0	10.1
D3	ditch	13.2	13.3	11.7
D4	pond	0.445	0.445	0.386
D4	stream	10.3	11.5	9.56
D5	pond	0.445	0.445	0.385
D5	stream	8.47	12.4	10.7
R4	stream	8.68	8.76	7.57

**Table 9.7-11 Step 3: Global maximum PEC<sub>sw</sub> of glyphosate acid following pre-planting / pre-emergence application to potatoes**

Scenario	Water body	PEC <sub>sw,max</sub> (µg glyphosate acid/L)	
		1x2160 glyphosate acid/ha potatoes (spring)	2x2160 glyphosate acid/ha potatoes (spring)
D3	ditch	11.0	9.51
D4	pond	0.431	0.477
D4	stream	9.17	7.88
D6	stream	11.0	9.38
D6	ditch	11.1	9.60
R1	pond	0.431	0.472
R1	stream	7.57	6.53
R2	stream	9.98	8.60
R3	stream	10.7	9.23

**Table 9.7-12 Step 3: Global maximum PEC<sub>sw</sub> of glyphosate acid following post weed emergence application to pome/stone fruit**

Scenario	Water body	PEC <sub>sw,max</sub> (µg glyphosate acid/L)	
		1x2880 glyphosate acid/ha pome/stone fruit (spring)	1x2880 + 2x720 glyphosate acid/ha pome/stone fruit (spring)
D3	ditch	17.7	12.9
D4	pond	0.595	0.417
D4	stream	13.1	9.47
D5	pond	0.594	0.417
D5	stream	11.3	8.18
R1	pond	0.595	0.417
R1	stream	11.7	8.36
R2	stream	14.4	10.4
R3	stream	16.5	11.9
R4	stream	11.6	8.37

**Table 9.7-13 Step 3: Global maximum PEC<sub>sed</sub> of glyphosate acid following pre-planting / pre-emergence application to winter cereals**

Scenario	Water body	PEC <sub>sed,max</sub> (µg glyphosate acid/kg)	
		1x2160 glyphosate acid/ha winter cereals (autumn)	2x2160 glyphosate acid/ha winter cereals (autumn)
D1	ditch	81.2	138
D1	stream	7.82	12.6
D2	ditch	60.8	98.0
D2	stream	58.9	85.7
D3	ditch	7.05	16.1
D4	pond	7.21	11.8
D4	stream	2.55	4.18
D5	pond	7.60	12.4
D5	stream	3.62	5.93
D6	ditch	48.9	80.8
R1	pond	8.79	14.5
R1	stream	28.0	50.1
R3	stream	809	1703
R4	stream	488	239

**Table 9.7-14 Step 3: Global maximum PEC<sub>sed</sub> of glyphosate acid following pre-planting / pre-emergence and post-harvest application to spring cereals**

Scenario	Water body	PEC <sub>sed,max</sub> (µg glyphosate acid/kg)		
		1x2160 glyphosate acid/ha spring cereals (spring)	1x2160 glyphosate acid/ha spring cereals (autumn)	2x2160 glyphosate acid/ha winter cereals (spring+autumn)
D1	ditch	29.7	81.1	86.4
D1	stream	0.963	7.84	7.27
D3	ditch	7.63	10.9	22.5
D4	pond	7.05	7.19	10.8
D4	stream	0.428	2.47	1.14
D5	pond	6.78	6.86	10.2
D5	stream	0.105	3.61	3.19
R4	stream	57.8	31.7	178



**Table 9.7-15 Step 3: Global maximum PEC<sub>sed</sub> of glyphosate acid following pre-planting / pre-emergence application to potatoes**

Scenario	Water body	PEC <sub>sed,max</sub> (µg glyphosate acid/kg)	
		1x2160 glyphosate acid/ha potatoes (spring)	2x2160 glyphosate acid/ha potatoes (spring)
D3	ditch	7.7	12.6
D4	pond	6.32	10.5
D4	stream	0.479	0.704
D6	stream	8.15	5.19
D6	ditch	36.4	38.9
R1	pond	8.05	16.5
R1	stream	34.3	123
R2	stream	35.0	1690
R3	stream	25.3	63.4

**Table 9.7-16 Step 3: Global maximum PEC<sub>sed</sub> of glyphosate acid following post weed emergence application to pome/stone fruit**

Scenario	Water body	PEC <sub>sed,max</sub> (µg glyphosate acid/kg)	
		1x2880 glyphosate acid/ha pome/stone fruit (spring)	2x720 glyphosate acid/ha pome/stone fruit (spring)
D3	ditch	12.2	10.8
D4	pond	9.19	9.45
D4	stream	0.39	0.555
D5	pond	8.98	9.29
D5	stream	0.441	0.268
R1	pond	9.32	9.43
R1	stream	2.18	3.47
R2	stream	2.74	4.29
R3	stream	4.46	3.79
R4	stream	18.6	23.8

### III. CONCLUSION

Predicted environmental concentrations in surface water and sediment were calculated for glyphosate acid and its metabolites AMPA and HMPA according to FOCUS.

The overall maximum PEC<sub>sw</sub> value of glyphosate acid at Step 1, 2 and 3 was 101, 39.7 and 17.7 µg/L, respectively. The overall maximum PEC<sub>sw</sub> value of AMPA at Step 1 and 2 was 41.0 and 16.9 µg/L. The overall maximum PEC<sub>sw</sub> value of HMPA at Step 1 and 2 was 6.71 and 2.63 µg/L.

Simulations using the more realistic Step 3 FOCUS surface water scenarios confirm that Step 1-2 calculations represent a conservative exposure estimate that is appropriate to be used for the aquatic risk assessment of glyphosate.

#### IIIA 9.7.2 Initial PEC<sub>sw</sub> value for slow moving water bodies

The initial values for all water bodies are presented in Annex Point IIIA 9.7.1/01.

**IIIA 9.7.3 Short-term PEC<sub>sw</sub> values for static water bodies**

The short-term PEC<sub>sw</sub> and PEC<sub>sed</sub> of glyphosate acid following the maximum PEC<sub>sw</sub> and PEC<sub>sed</sub> value at Steps 1 and 2 are presented in Table 9.7-17. For details, please refer to Annex point IIIA 9.7.1. Short-term concentrations for FOCUS Step 3 modelling are available in the modelling report summarized at Annex Point IIIA 9.7.1/01.

**Table 9.7-17 Step 1 and 2: Maximum actual and time-weighted average concentrations in surface water and sediment of glyphosate acid – Short-term**

Scenario	Compound	Time (d)	Actual PEC <sub>sw</sub> (µg/L)	TWA PEC <sub>sw</sub> (µg/L)	Actual PEC <sub>sed</sub> (µg/kg)	TWA PEC <sub>sed</sub> (µg/kg)
Step 1	Glyphosate acid	0	101	-	103000	-
		1	62.5	81.9	10500	10400
		2	61.8	72.0	10400	10400
		4	60.4	66.5	10200	10400
Step 2	Glyphosate acid	0	39.7	-	4430	-
		1	14.2	27.0	4390	4410
		2	6.14	18.6	4340	4380
		4	27.5	34.4	4240	4340

**IIIA 9.7.4 Short-term PEC<sub>sw</sub> values for slow moving water bodies**

This point is covered by the information given at Annex Point IIIA 9.7.3. Short-term concentrations for FOCUS Step 3 modelling for all water bodies are available in the modelling report summarized at Annex Point IIIA 9.7.1/01.

**IIIA 9.7.5 Long-term PEC<sub>sw</sub> values for static water bodies**

The long-term PEC<sub>sw</sub> and PEC<sub>sed</sub> of glyphosate acid following the maximum PEC<sub>sw</sub> and PEC<sub>sed</sub> value at Steps 1 and 2 are presented in Table 9.7-18. For details, please refer to Annex point IIIA 9.7.1. Long-term concentrations for FOCUS Step 3 modelling are available in the modelling report summarized at Annex Point IIIA 9.7.1/01.

**Table 9.7-18 Step 1 and 2: Maximum actual and time-weighted average concentrations in surface water and sediment of glyphosate acid – Long-term**

Scenario	Compound	Time (d)	Actual PEC <sub>sw</sub> (µg/L)	TWA PEC <sub>sw</sub> (µg/L)	Actual PEC <sub>sed</sub> (µg/kg)	TWA PEC <sub>sed</sub> (µg/kg)
Step 1	Glyphosate acid	0	101	-	10300	-
		7	58.4	63.5	9810	10200
		14	53.9	59.8	9070	9810
		21	49.8	57.2	8380	9450
		28	46.0	54.8	7740	9100
		42	39.3	50.7	6600	8450
		50	35.9	48.6	6030	8110
		100	20.4	38.0	3420	6360
Step 2	Glyphosate acid	0	39.7	-	4430	-
		7	25.5	19.4	4100	4260
		14	23.6	22	3780	4100
		21	21.8	22.2	3500	3950
		28	20.1	21.9	3230	3800
		42	17.2	20.8	2760	3530
		50	15.7	20.1	2520	3390
		100	8.89	16.0	1430	2650

**IIIA 9.7.6 Long-term PEC<sub>sw</sub> values for slow moving water bodies**

This point is covered by the information given at Annex Point IIIA 9.7.5. Long-term concentrations for FOCUS Step 3 modelling for all water bodies are available in the modelling report summarized at Annex Point IIIA 9.7.1/01.

**IIIA 9.8 Predicted environmental concentration in surface water (PEC<sub>sw</sub>) for the relevant metabolites**

Predicted environmental concentrations in surface water and sediment were calculated for AMPA and HMPA (the metabolites of glyphosate), according to FOCUS (2001 and 2011c).

**IIIA 9.8.1 Initial PEC<sub>sw</sub> value for static water bodies**

The overall maximum PEC<sub>sw</sub> value of AMPA at Step 1 and 2 was 41.0 and 16.9 µg/L. The overall maximum PEC<sub>sw</sub> value of HMPA at Step 1 and 2 was 6.7 and 2.6 µg/L. For details, please refer to Annex Point IIIA 9.7.1.

**IIIA 9.8.2 Initial PEC<sub>sw</sub> value for slow moving water bodies**

This point is covered by the information given at Annex Point IIIA 9.8.1.

**IIIA 9.8.3 Short-term PEC<sub>sw</sub> values for static water bodies**

The short-term PEC<sub>sw</sub> and PEC<sub>sed</sub> of AMPA following the maximum PEC<sub>sw</sub> and PEC<sub>sed</sub> value at Steps 1 and 2 are presented in Table 9.8-1. For HMPA, only maximum values were calculated as a worst-case approach using the maximum PEC of glyphosate acid at Step 1 and 2 and considering the molar mass difference and the maximum HMPA occurrence of 10% of applied glyphosate. For details, please refer to Annex point IIIA 9.7.1.

**Table 9.8-1 Step 1 and 2: Maximum actual and time-weighted average concentrations in surface water and sediment of AMPA – Short-term**

Scenario	Compound	Time (d)	Actual PEC <sub>sw</sub> (µg/L)	TWA PEC <sub>sw</sub> (µg/L)	Actual PEC <sub>sed</sub> (µg/kg)	TWA PEC <sub>sed</sub> (µg/kg)
Step 1	AMPA	0	41.0	-	3300	-
		1	34.1	37.5	3320	3310
		2	33.8	35.7	3300	3310
		4	33.3	34.6	3240	3290
Step 2	AMPA	0	16.9	-	1620	-
		1	16.5	16.7	1610	1610
		2	16.3	16.5	1590	1600
		4	16.1	16.4	1570	1590

**IIIA 9.8.4 Short-term PEC<sub>sw</sub> values for slow moving water bodies**

This point is covered by the information given in Annex Point IIIA 9.8.3.

**IIIA 9.8.5 Long-term PEC<sub>sw</sub> values for static water bodies**

The long-term PEC<sub>sw</sub> and PEC<sub>sed</sub> of AMPA following the maximum PEC<sub>sw</sub> and PEC<sub>sed</sub> value at Steps 1 and 2 are presented in Table 9.8-2. For HMPA, only maximum values were calculated as a worst-case approach using the maximum PEC of glyphosate acid at Step 1 and 2 and considering the molar mass

difference and the maximum HMPA occurrence of 10%. For details, please refer to Annex point IIIA 9.7.1.

**Table 9.8-2 Step 1 and 2: Maximum actual and time-weighted average concentrations in surface water and sediment of AMPA – Long-term**

Scenario	Compound	Time (d)	Actual PEC <sub>sw</sub> (µg/L)	TWA PEC <sub>sw</sub> (µg/L)	Actual PEC <sub>sed</sub> (µg/kg)	TWA PEC <sub>sed</sub> (µg/kg)
Step 1	AMPA	0	41.0	-	3300	-
		7	32.4	33.9	3160	3250
		14	30.6	32.7	2980	3160
		21	28.9	31.7	2820	3070
		28	27.3	30.8	2660	2990
		42	24.3	29.1	2370	2830
		50	22.7	28.2	2210	2740
		100	15.0	23.4	1460	2280
Step 2	AMPA	0	16.9	-	1620	-
		7	15.7	16.0	1530	1570
		14	14.8	15.7	1440	1530
		21	14.0	15.2	1360	1490
		28	13.2	14.8	1280	1440
		42	11.7	14.0	1140	1370
		50	11.0	13.6	1070	1330
		100	7.25	11.3	707	1100

### IIIA 9.8.6 Long-term PEC<sub>sw</sub> values for slow moving water bodies

This point is covered by the information given in Annex Point IIIA 9.8.5.

### IIIA 9.8.7 Additional field testing

Additional field testing was not required.

## IIIA 9.9 Fate and behaviour in the air

Glyphosate has very low vapour pressure ( $1.31 \times 10^{-5}$  Pa at 25°C, for details see IIA 2.3.1) and significant concentrations are not expected to be found in air following the use of the compound according to the proposed GAP.

In the 2001 EU evaluation it was concluded that glyphosate can be classified as not volatile substance based on its Henry's law constant and on volatilization experiments from soil and plants with no significant rates. Due to no significant UV-absorption, direct photolysis in air will not occur. Once in the atmosphere rapid photochemical oxidative degradation of glyphosate will occur."

As the expected distribution to the atmosphere by glyphosate is likely to be extremely low in field use based on very low vapour pressure, no estimates of environmental concentrations expected in air were provided. This is not considered a significant route of exposure in practice or likely to lead to significant environmental contamination.

### IIIA 9.9.1 Spray droplet size spectrum – laboratory studies

This item is not an EU 91/414/EEC requirement.

### IIIA 9.9.2 Drift – field evaluation

This item is not an EU 91/414/EEC requirement.

## IIIA 9.10 Other/special studies

### IIIA 9.10.1 Other/special studies – laboratory studies

No additional studies were conducted for the parent and metabolites.

### IIIA 9.10.2 Other/special studies – field studies

No additional studies were conducted for the parent and metabolites.

This document is retrieved from  
the Bayer Transparency website.  
Please note that its content could be  
subject to copy-right and other IP-rights.  
Any use for commercial purposes is prohibited.