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Surface water intended for the abstraction of drinking water after use of plant protection products on hard surfaces

Evaluation of plant protection products

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Abstract

Surface water intended for the abstraction of drinking water after use of plant protection products on hard surfaces
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The presence of active substances of Plant Protection Products (PPP) in surfaces water has been shown to occur above acceptable drinking water limits. Therefore, the Dutch registration authorities were urged by the judge to take this situation into account in making decisions on the authorisation of PPPs.

To protect the production of drinking water, an evaluation instrument has been developed to estimate the concentration of PPPs in surface water after application on hard surfaces. Up to now such a methodology was lacking in the evaluation system for the Dutch authorisation process of active substances based on the EU-Directive 91/414/EC.

The proposal described in this report contains a decision making scheme with a tiered approach. The basis is the assumption that a relation exists between the application of PPPs on hard surfaces and the established concentration in receiving surface waters to prevent residues of active substances in drinking water. The method may be used to evaluate whether drinking water prepared from surface water contains too high residue concentrations of these active substances.

To, finally, come to a good estimate of the Predicted Environmental Concentration (PEC) of an active substance in surface water several assumptions have to be made, for instance :
- the application method used takes place according to a predefined protocol;
- the dose applied on hard surfaces is correct;
- the total area in the Netherlands to which the substance is applied is based on data available in the Netherlands; and
- the catchment areas of the water courses to the intake points of the water works can be based on county data in the Netherlands.

These assumptions have been checked against the results of the case of glyphosate.

Now experience has to be gained with this new methodology in applying the system to new substances that could be used in the Netherlands on hard surfaces. Recommended potential improvements are to take into consideration in the evaluation the use of specific characteristics of the substance, like sorption and degradation. It is also recommended to develop an EU-wide equivalent of the method comparable with this Dutch proposal.

Key words: risk assessment, authorisation, plant protection products, hard surfaces, surface water, run-off, drinking water, glyphosate

Rapport in het kort

Oppervlaktewater bestemd voor drinkwater na toepassing van gewasbeschermingsmiddelen op verhardingen
Beoordelingsmethode voor gewasbeschermingsmiddelen

In oppervlaktewater is de aanwezigheid van actieve stoffen van gewasbeschermingsmiddelen in concentraties boven acceptabele drinkwaterniveaus vastgesteld. Daarom zijn de Nederlandse registratie-autoriteiten door de rechter gedwongen deze situatie nadrukkelijk in de toelatingsbeslissing te betrekken.

Om de drinkwatervoorziening te beschermen is een instrument ontwikkeld om de concentraties van gewasbeschermingsmiddelen in oppervlaktewater te schatten na de toepassing op verhardingen. Tot nu toe bestond een dergelijke methodiek nog niet in het Nederlandse beoordelingsinstrumentarium voor de toelating van gewasbeschermingsmiddelen op basis van de EU-Richtlijn 91/414/EC.

Het voorstel beschreven in dit rapport behelst een beslisboom met een getrapte benadering. De basis vormt de veronderstelling dat er een relatie bestaat tussen de toepassing van gewasbeschermingsmiddelen op verhardingen en de gevonden concentratie in ontvangende oppervlaktewateren. De methodiek kan worden gebruikt om te beoordelen of drinkwater bereid uit dit oppervlaktewater een te hoge concentratie residuen van deze middelen bevat. De ervaringen met een bestaande actieve stof, glyfosaat, zijn gebruikt om te anticiperen op evaluaties voor nieuwe stoffen.

Om uiteindelijk te komen tot een goede schatting van de waterconcentratie van een actieve stof zijn verscheidene veronderstellingen gedaan voor onder andere:
- de toepassingstechniek van het middel geschiedt volgens vastgesteld protocol;
- de dosering op verhardingen is correct;
- de totale oppervlakte in Nederland waarop de stof wordt toegepast wordt gebaseerd op gegevens in Nederland;
- het ontvangende stroomgebied voor een bepaald drinkwateronttrekkingspunt voor de drinkwatervoorziening wordt gebaseerd op gemeentelijke gegevens in Nederland.

Deze veronderstellingen zijn gecontroleerd aan de hand van de resultaten verkregen met de voorbeeldstof glyfosaat.

In de komende tijd moet ervaring worden opgebouwd met de nieuwe methodologie door het system toe te passen op nieuwe stoffen die in Nederland gebruikt kunnen worden op verhardingen. Een van de aanbevolen potentiële verbeteringen is om het gebruik van specifieke eigenschappen van een bepaalde stof, zoals adsorptie en afbraakgegevens, in de beoordeling te betrekken. Ook wordt aanbevolen een EU-methodiek te ontwikkelen, vergelijkbaar met dit Nederlandse voorstel.

Trefwoorden: risicobeoordeling, toelatingsprocedure, gewasbeschermingsmiddelen, verhardingen, oppervlaktewater, afstroming, drinkwater, glyfosaat

Preface

The National Institute for Public Health and the Environment has been requested by the Netherlands Ministry of Housing, Spatial Planning and the Environment to develop an assessment methodology for drinking water production from surface waters in the Netherlands to be used in the authorisation procedure of plant protection products (PPP). With the publication of the report 'Development of an assessment methodology to evaluate agricultural use of plant protection products for drinking water production from surface waters' (Adriaanse et al., 2008) only one part of the decision process for PPPs in their threat of drinking water production is covered. The second part, related to the protection of drinking water from the contamination by the application of PPPs on hard surfaces, part of the amenity use of PPP, will be dealt with in this report.

In addition the need for the development of an evaluation method within the authorisation process of plant protection products, for surface waters intended for the abstraction of drinking water, is stressed by the court case of glyphosate in the Netherlands.

In many ways this report should be considered as a supplement to Adriaanse et al. (2008) and therefore most of the general issues are not repeated here but may be found in the other report.

Contents

Summary

An evaluation instrument has been developed to estimate the concentration of plant protection products (PPPs) in surface water intended for the production of drinking water after application on hard surfaces. Up to now such a methodology was lacking in the evaluation system for the authorisation process of active substances as described in the EU-Directive 91/414/EC.

Based on actual measurements at the drinking water abstraction points performed by national authorities (Ministry of Transport, Public Works and Water Management) and the drinking water companies, the presence of active substances of PPPs in surfaces water has been shown to occur above acceptable limits. There are two routes defined that may cause pollution of surface waters by the application of plant protection products that may end up at the location at which water is abstracted for drinking water production. The first is caused by products applied to agricultural soils and has been further developed by Adriaanse et al. (2008), whilst the second is caused by the application of substances in amenity use and is subject of the current report. The most important of the latter is the use of PPPs by local authorities to hard surfaces. After rain events these substances may run-off to the sewer system and enter surface water. The problem was already known for many years. Therefore, the Dutch registration authorities were urged by the judge to take this situation into account in making decisions on the authorisation of PPPs.

A decision making scheme is proposed as a tiered approach and is based on the assumption that a relation exists between the application of PPPs on hard surfaces and the established concentration in receiving surface waters to prevent residues of active substances in drinking water. The aim was to develop a realistic worst case situation taking into account estimations of 90th percentile run-off values and 10th percentile flow data. Experiences with an existing substance, like glyphosate, are used to extrapolate to evaluations of new active substances. In the report the first and second tier of the tiered approach are described. The first tier consists of a calculation method estimating the amount of substance used and the transport behaviour of the substance to the drinking water abstraction point. The second tier makes use of the real measurement data of the substances after having granted a conditional registration. The condition is that post-registration measurements are carried out.

To determine the Predicted Environmental Concentration (PEC) of an active substance several assumptions are needed, e.g. the application method is according to a specified protocol, the dose used on hard surfaces, the total area in the Netherlands to which the substance is applied, the catchment areas of the water courses to the intake points of the water works, etc. Also the market share of the product is taken into account based on estimations of the plant protection product industry in the Netherlands. These assumptions have been checked against the results of the case of glyphosate.

It is proposed that currently some experience has to be built up with this new instrument in the application to new substances or to substances that have been shown a problem for the water works in the Netherlands. Regularly, national and local authorities carry out measurement programmes to establish the state-of-the-environment. These results will be used to check the results of the predictions based on the methodology developed. Potential improvements have been recommended in the area of substance specific run-off data and taking into account degradation and dissipation of the active substance. It is also recommended to develop an EU-wide equivalent of the method. Finally, as a recommendation, the methodology has to be incorporated into the computerised tools of the registration authority, Ctgb.

1. Introduction

The methodology for carrying out a risk assessment for the application of PPPs on hard surfaces is not yet developed in the European Union. Although the need for such an instrument is mentioned in the Uniform Principles, it has never been made operational. In this report, a tool is developed that may serve as a method to evaluate PPPs on the effects on the drinking water production if the water is abstracted from surface water sources. The methodology for hard surfaces is as much as possible based on the methodology for PPPs used in agriculture (Adriaanse et al., 2008). It is clear that the emission of PPPs applied in amenity use is completely different from the application of PPPs in agriculture. Certainly in the Netherlands, the application of PPPs on hard surfaces will lead in most cases to a discharge to surface water through a waste water treatment plant (WWTP). Therefore, the methods described in this report may be used if the application of a PPP is requested for authorisation in amenity use, in this case application on hard surfaces that are subject to run-off.

After application and possibly the run-off event, the substance will be withheld during some time in the WWTP and may be subject to degradation. Although the residence time in the WWTP is generally quite short, circa three days, favourable conditions for biological degradation, (for example due to turbulence and elevated oxygen concentrations), occur in the aeration tank and many active substances (a.i.) may (partly) be transformed. In case of a storm overflow the substance may be discharged directly into surface waters (see chapter 2).

The Dutch Ministry of Housing, Spatial Planning and the Environment has charged RIVM with the development of the methodology and installed a working group. The members of the working group are:

- A.J.A. van der Linden (RIVM)
- J.B.H.J. Linders (RIVM)
- Y.I. Stienstra (Ctgb).

Part of the development process has been the consultation of all stakeholders during a workshop, which took place on 26th May 2009. Stakeholders included the Waterdienst, Alterra, Kiwa, VEWIN, the regional water management, industry (Nefyto), the agricultural organisation (LTO) and several departments of RIVM. Comments and suggestions of these parties have been included in the report. The Ministry of Agriculture, Nature and Food Quality (LNV), the Ministry of Housing, Spatial Planning and the Environment (VROM), the Ministry of Social Affairs and Employment (SZW), and the Ministry of Health, Welfare and Sport (VWS) did not take part in the workshop, as they decided to have a separate political discussion on the report.

The current report, therefore, offers the methodology as proposed and discussed with stakeholders in the Netherlands but not yet the implementation of the methodology as an evaluation instrument in the authorisation process of PPPs (European Commission, 1991). Criteria for xenobiotics have been part of EU legislation ever since the Drinking water Directive (European Commission, 1975), but they were not effectuated. It is the intention of the Ministry of VROM to bring the methodology to the attention of the designated national authorities (DNA) in the European Union and to the Commission in Brussels. In addition, the legislation of the Water Framework Directive (European Commission, 2001) has been taken into account as well.

2. Approach

Considering the differences in discharges - the emissions - of PPPs applied in agriculture and of PPPs applied in amenity use, especially those on hard surfaces, a thorough analysis of the discharges is necessary. Application of PPPs on hard surfaces is mainly taking place by the local authorities or private companies for the treatment of the hard surfaces under their responsibility to clean the surface from unwanted weeds, the so-called amenity use. In the Netherlands, the uncontrolled run-off emission from hard surfaces directly into surface waters is still occurring to considerable amounts. Recent figures (Waterdienst, personal communication) indicate that about 27% is directly discharged to surface water, 19% is discharged to soil and the remaining part to the waste water treatment plants. Therefore, most of the run-off water is transported to the waste water treatment plants. In cases of high rainfall events that cause overflows of the sewage systems such a discharge may happen.

Currently, a few methods have been proposed in the Netherlands and in the UK. These will be evaluated by the working group and a new methodology will be proposed based on the methodology developed for agricultural products. It is the intention to keep both methods as close together as possible. Earlier proposals are described in chapter 3, together with a final presentation of the proposal of the exposure assessment for the application of substances on hard surfaces with respect to their ability to influence the drinking water abstraction from surface water in the Netherlands.

In addition, the contribution of the application of active substances in amenity use will be abstracted from the total use of the substance in the Netherlands, in this way accounting for a total application in amenity use by local authorities. The proposed calculation methodology is described in chapter 4.

In the Netherlands glyphosate is extensively used for weed control on hard surfaces with a market share of over 90 percent for this specific application. Therefore, monitoring data on glyphosate in surface water are used to check this calculation methodology. It should be kept in mind, however, that the methodology developed in this document is not intended to describe the situation on glyphosate and also not to find the sources for the findings of the substance glyphosate in surface water.

Chapter 5 gives an overview of all the monitoring data on glyphosate in the Netherlands from 2000 onwards. Only for two stations, Amsterdam-Rijnkanaal and Heel, the period from 2002 onwards is used as no earlier data are available. Conclusions to be drawn from these monitoring programmes are dealt with also in chapter 5. Chapter 6 gives a comparison between the measured and calculated data based on the methodology proposed. In chapter 7 some conclusions and recommendation based on the proposals developed here are indicated.

3. Proposed decision making scheme

In Figure 3-1 the decision making scheme for plant protection products applied on hard surfaces is presented as proposed in this report. The scheme is intended to be used for new and existing plant protection products and for active substances for which monitoring programmes are already in use or for which (post) authorisation monitoring programmes are considered.

The scheme describes two tiers: the first tier is according to the calculation procedure described in chapter 4, whilst the second tier consists of the monitoring programmes. For existing active substances, like e.g. glyphosate the results of monitoring programmes are taken into account and calculations and measurements are compared to each other to finally decide on the authorisation of the product. This section is not different from the assessment methodology developed for plant protection products in agricultural applications as described in Adriaanse et al. (2008). According to the working group on hard surfaces there is no reason to deviate in any way from the proposal set forward in Adriaanse et al. (2008).

The drinking water standard (DWS) has currently been set to 0.1 µg/L and if needed may be defined more strictly depending on the policy in the Netherlands. In addition, the value of Y should be defined by policy agreement in the Netherlands as well. A value of 10 or 5 may be considered appropriate in agreement with the proposal in Adriaanse et al. (2008). The factor Y represents a 'safety' factor and is further discussed in Adriaanse et al. (2008).
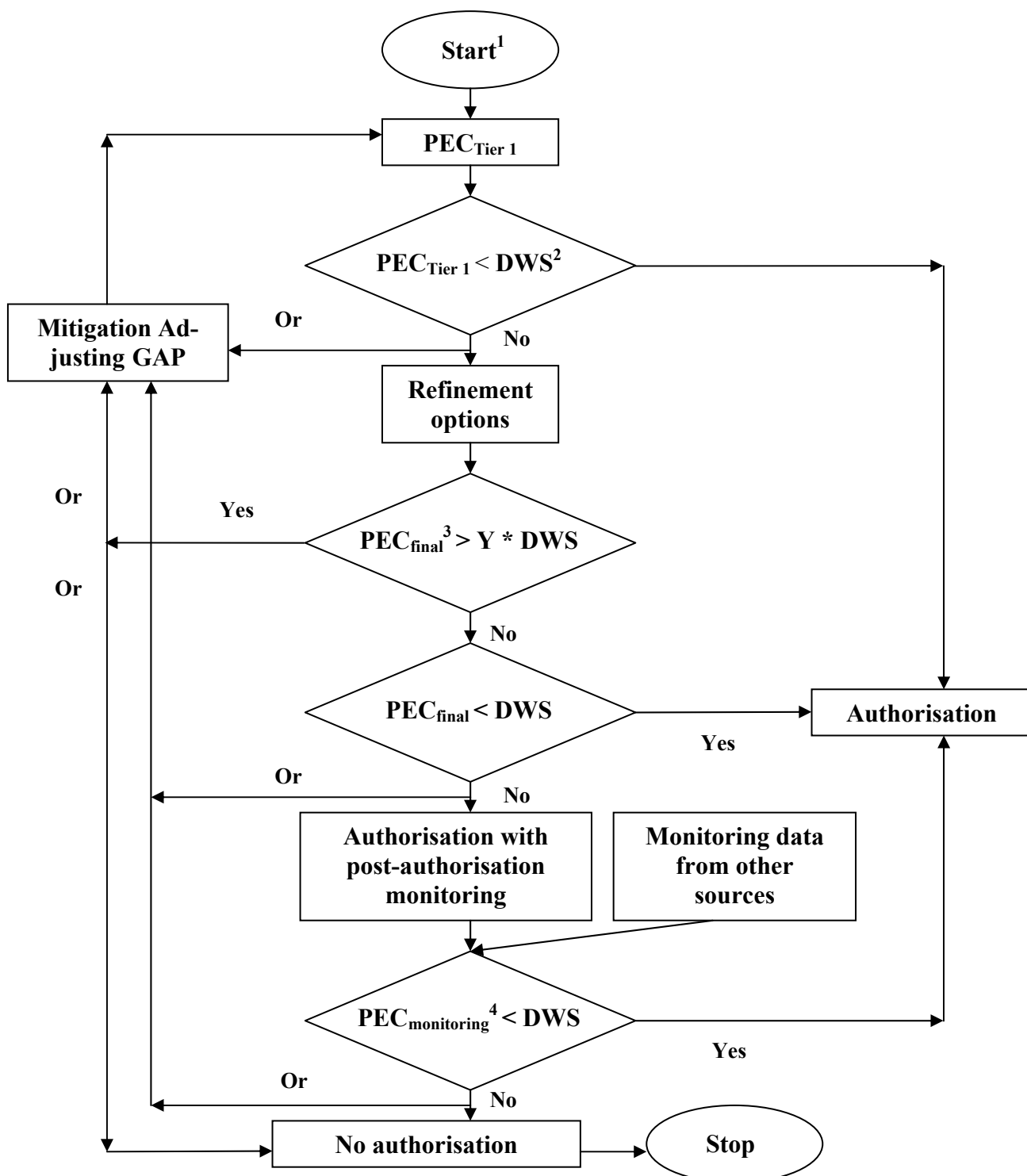
Legend: 1 = This is as well applicable to new compounds as to compounds already allowed on the market

2 = DWS is the drinking water standard which is at this moment when the report was issued 0.1 μg/L

3 = In case no refined assessment has been applied the PEC_{final} is $PEC_{Tier\,1}$

4 = Before making a decision it has to be analysed whether the compound is of Dutch origin or not

Figure 3.1 Proposed risk assessment scheme to evaluate the drinking water standard in the registration procedure of the Ctgb in the Netherlands. N.B. The factor Y represents a 'safety' factor and is further discussed in Adriaanse et al. (2008).

4. Proposed evaluation methodology

4.1 Introduction

One of the substances breeching the standard for drinking water abstraction in Dutch surface waters appears to be glyphosate. A possible source of these findings is run-off after application in amenity use, mainly applications to paved areas. Currently three methods are available claiming to be suited to evaluate the Predicted Environmental Concentrations (PECs) after the application of a substance in amenity use. These methods will be described shortly below.

USES

In the Dutch Uniform System for the Evaluation of Substances (USES, version 4.0) four scenarios are available to estimate the concentration in different types of surface waters and depending on the paved area of some example towns in the Netherlands. These scenarios are used by Ctgb to estimate the risks for aquatic organisms after application of paved areas with PPP. A detailed description of the scenarios is presented in Linders et al. (2002). The four scenarios are the following:
1. direct run-off to surface water;
2. discharge through rain water overflow of a separated sewer system;
3. discharge through pour over of a mixed sewage system
4. discharge through a WWTP connected to a mixed sewage system.

For each scenario some basic assumptions underlie the calculations required to conclude to a final concentration in the surface water body, a PEC.

Waterdienst

The *Waterdienst* (Center for Water Management) of the Netherlands proposed a method, during the discussion on the topic, but considered further publication not appropriate. The method was based on the estimation of the amount of living space and roads in the Netherlands and on the estimation of the treated area. Depending on the period to be considered averaging would result in a concentration over that period. (Waterdienst, personal communication. 2009)

UK

Also in the UK, for quite an extent based on the Dutch approach, a calculation system has been set up called HardSPEC, which consists of an Excel spreadsheet with three scenarios (Hollis et al., 2004). The UK scenarios are defined as follows:
1. Urban catchment within which the hard surface areas drain via gully pots. Surface drainage water is delivered into surface water stream. The urban catchment measures 10 ha, contains asphalt (1.5 ha), concrete (0.75 ha), buildings (4.5 ha) and non-hard surfaces (3.25 ha).
2. As 1, but now surface drainage water is delivered into a pond. This scenario is intended to be similar to the use of collecting ponds within Sustainable Urban Drainage Systems (SUDS).
3. Surface water stream receiving surface drainage from a major road in a rural setting where the hard surface areas drain via gully pots. The stream also receives water from an adjacent 1 ha agricultural field. The scenario has a 100 m long asphalt road, 7 m wide, plus 12 cm curb stones, plus 1 m wide grass verge, all draining into the stream. The agricultural field drains directly into the 100 m stream.

The working group discussed the applicability of these methods and scenarios for the purpose of protecting drinking water abstraction points within the framework of the current study.

Although the potential methods presented all have their advantages and disadvantages the working group decided that the main requirement of the method to be followed for the evaluation methods of applications on hard surfaces should be the close connection and relation to the method developed for agricultural applications. Especially the features of taking into account a distribution of the areas contributing to a specific concentration at a drinking water abstraction point and some other assumptions are favourable for a close connection of the two methods. This will be further elaborated below.

4.2 Proposal

The preference for development of new scenarios is of course based on the use of the scenarios for the decision tree for agricultural products and their effects on the concentrations at drinking water abstraction points. The question to be answered is how to calculate the concentration at abstraction points due to the application of substances in amenity use. For a preliminary test of the proposal the results of the monitoring programmes of glyphosate at the different abstraction points for drinking water are compared to the calculated values (see chapter 5).

A sequence of the events happening in the application of substances on hard surfaces is given in Figure 4.1.

Figure 4.1 Analysis sequence hard surfaces.

Use
The use of a substance, i.c. glyphosate, is determined by the use of the substance in agriculture, on hard surfaces and possible other applications. Currently there are no products, or active substances in products, that are used exclusively on hard surfaces. Therefore, it is proposed to combine the evaluation of substances on hard surfaces with the application in agriculture.

For the evaluation of an active substance in agriculture, of course with respect to the evaluation of the drinking water criterion, the methodology described in Adriaanse et al. (2008) is valid and for the application on hard surfaces the methodology from this report applies.

As the agricultural use of a substance is much better surveyed than the non-agricultural use, the non-agricultural use is determined from the total use and the agricultural use:

$$Use_{paved\_areas} = Use_{total} - Use_{agriculture} \qquad (1)$$

where:

Use_{paved_areas} = amount used on hard surfaces [kg y^{-1}]
Use_{total} = total amount used [kg y^{-1}]
$Use_{agriculture}$ = amount used in agriculture [kg y^{-1}].

The total amount used is taken from the sales data as recorded by the Ministry of LNV and the amount used in agriculture is estimated according to the method described by Adriaanse et al. (2008). If for a substance an accurate non-agricultural use is available, for instance because of an adequate survey, then a calculation is not necessary. For authorisation purposes, also a potential use may be taken.

From the use on hard surfaces the treated area ($A_{treated}$) with a specific substance may be calculated:

$$A_{treated} = \frac{Use_{paved\_areas}}{D}$$ (2)

with:

$A_{treated}$ = the total area [ha] in the Netherlands treated with the substance
D = the dose [kg ha^{-1}].

As the frequency of application may be above 1, the absolute total area receiving one or more applications may be smaller than calculated according to the formula.

The total area 'hard surfaces' is around 600.000 ha (Te Molder, personal communication, March 2009). Table 4.1 provides estimates for hard surface areas for the individual catchment areas, as far as located in the Netherlands. The estimates are based on Figure 4.2, CBS-data on the distinction of local administrations in the Netherlands in the year 2006 and registrations of hard surfaces for each municipality in the database of Emission Registration (Te Molder, personal communication, March 2009). About 60% of the total area on hard surfaces belongs to the catchment area of one or more abstraction points.

Table 4.1 Paved areas for the 9 abstraction points.

Name abstraction point	Paved area in ha
Scheelhoek	176015
Petrusplaat	128453
Brakel	116465
Heel	30700
De Punt	12691
Nieuwegein	34017
Amsterdam-Rijnkanaal	48879
Inlaat Andijk	147213
Twentekanaal	7614

For first tier calculations we assume that 50 % is a good approximation of the total area that will receive an application. There is no information on the distribution of the applications over the Netherlands, so we assume that the distribution is even, i.e. each hectare of paved area has the same chance of receiving one or more treatments per year.

It is highly unlikely that all the area to be treated with the substance is treated on one and the same day. As a worst case assumption for first tier calculations, $A_{treated}$ is taken to be treated in ten days (10% of the area per day). One neighbourhood may probably be treated in one day, but more neighbourhoods will be contributing to a single sewage treatment system.

Emission
Although in some cases drift to surface water may occur, drift emission to surface water is neglected in the assessment procedure for applications on hard surfaces. Drift emission is small compared to run-off emissions observed shortly after treatment. (Beltman et al., 2001, 2006; De Rooy and Beltman, 2003). The observed run-off emission values as found by Beltman are, however, too high to be representative for emissions occurring at larger scale. Withagen et al. (2003, 2004, 2005), Beltman et al. (2005, 2006),

Van Dijk et al. (2006), and Kempenaar and Kok (2005) reported run-off percentages between 0 and 5.7% (glyphosate and AMPA as percentage of the amount glyphosate) at the neighbourhood scale, after applying glyphosate according to the DOB procedure (for further explanation see chapter 6). The 90th percentile run-off value for glyphosate was 3.5%. It is proposed to use this 90th percentile for emission calculations for first tier assessments. In the (rather few) experiments at the neighbourhood scale, no obvious relation between the emission and the amount of precipitation could be established. It is assumed that most of the run-off of the substance takes place with the first few mm of rain regardless of the intensity of the rain event. In reality the emission may be dependent of the rain intensity and the time span between application and the rain event but this is in the current proposal not taken into account. It may be used in a higher tier development. In addition, the direct emission of potential metabolites is also not included in this proposal. If metabolites do have to be evaluated the normal procedure should be followed in estimating the maximum percentage a metabolite has been formed and correcting for molecular weight.

Most of the hard surfaces treated with herbicides are located in areas equipped with a sewer system. The run-off is collected by the sewer system and consecutively discharged to the sewage treatment system. With respect to the situation in the Netherlands on the municipal sewage treatment systems it has been determined (RIONED, 2005) that 75% of the sewage systems is of a mixed type, 18% of a separated type and 7% of an improved separated type. In a separated type system, rain water is collected separately and discharged to surface water without passing a treatment system. In an improved separated system, the first flush of a rain event is directed towards the treatment system, but the rest is discharged directly to surface water. Almost all sewage systems are equipped with an additional basin to collect water during high rainfall events in order to prevent overflow of the sewage system. However, in extreme events, still overflow may occur.

The purification efficiency of a sewage treatment plant for a specific substance will be influenced by both substance properties and properties and management of the treatment plant. For glyphosate, purification efficiencies between 5 and 40% have been reported. A (reasonable) worst-case estimation is therefore 0%. This would mean that, in the first tier, the type of sewage system is not important for calculating discharge (emission) of the substance to the surface water. Also, the residence time of the substance in the sewage system and the treatment plant is not important with respect to the amount discharged as the substance is assumed not to degrade.

Under the assumptions given above, the total emission to surface water may be calculated according to:

$$E_{tot} = A_{treated}\ D\ f_{run-off}\ f_{pd}\ \left(1 - f_{pur}\right) f_{use} \tag{3}$$

with:

E_{tot} = total emission [kg/d]
$f_{run-off}$ = fraction run-off [-], suggestion to use the 90th percentile (see text)
f_{pd} = fraction of area treated per day [d^{-1}], suggestion to use default 0.05
f_{pur} = purification efficiency of sewage treatment system [-], suggestion to use default 0.

The above equation can be used to calculate the emission for the whole of the area (the Netherlands), but also for sub-regions (defined catchment areas for the abstraction points). In the latter case, it is suggested to distribute the $A_{treated}$ according to the distribution of paved area. The factor f_{pd} is used to take account of the assumption that the application with the substance is not carried out in one day. A worst-case assumption of a twenty day application period is adopted in this proposal.

The catchment areas are the same as used in Adriaanse et al. (2008) (see Figure 4.2). A specific value is assumed for f_{use}, which is related to the intensity of the use of the substance. In Adriaanse et al. (2008), some topics are mentioned that are included in the $f_{use\_intensity}$, like the area treated with the substance, the estimated market share factor (0.4) and the drift deposition factor. In the approach here, for hard surfaces, the area is used in the same way as in Adriaanse et al. (2008), by taking the area treated per county divided by the total draining area of the counties in the specific catchment area of the abstraction point under consideration. For the market share, however, in this approach a value of 1 is proposed based on the current market share for glyphosate in the application on hard surfaces. The drift deposition factor is not relevant here. So:

$$f_{use} = \frac{Area_{treated}}{Area_{dw\_abstraction}} \cdot f_{market\_share} \qquad (4)$$

with:

f_{use}	= use factor, based on the fraction of the area of use
$Area_{treated}$	= area treated with the substance in ha
$Area_{dw\_abstraction}$	= total area draining to abstraction point
f_{market_share}	= market share of the substance, default 1.0.

For authorisation of new substances, in the first tier it is assumed further that the area potentially treated is 50% of the whole paved area in a catchment area.

$$Area_{treated} = 0.5 \cdot Area_{paved} \qquad (5)$$

The value of 0.5 is estimated from the amenity use of glyphosate, the whole paved area and label instructions for use on paved areas (valid until 2006).The value of 0.5 is then a somewhat conservative estimate.

Transport
As for the methodology for Agricultural products it is proposed to use a mean travelling time from discharge / emission point (i.e. point where run-off takes place) to the abstraction point of six days. This means that the substance on average will reach the abstraction point after six days. Although this value may differ per catchment area the same value for all catchments is used. In a higher tier assessment this may be refined.

Concentration at abstraction point
As stated earlier, there seems to be no relation between the amounts emitted via run-off and the intensity of rain events. It seems therefore reasonable to base concentration calculations on the flow rate of the surface water at the abstraction points. For first tier calculations usually a realistic worst case situation is taken. In this case the realistic worst case would be the 10th percentile of the flow rate at the abstraction point, i.e. a relatively low flow rate. Using a relative low flow rate will result is a relatively high realistic worst case concentration. Table 4.2 gives these flow rates for selected points in Meuse, Rhine and Drentsche Aa. The data for Meuse and Drentsche Aa can be used as approximations for the flow rate at the abstraction points. Flow rates are for the period April – September, the period in which most of the applications on paved surfaces will occur. Abstraction points in the Rhine catchment area actually are situated in Amsterdam-Rijnkanaal branch. The flow rate in the canal is regulated to some extent therefore not suitable for calculating concentrations. The concentration at the canal inlet most

probably will not differ much from the concentration at the abstraction points, so probably it would be better to use a flow rate for the inlet point.

Table 4.2 April – September flow rates (m³/s) in the period 2000 – 2006.

location	river	percentiles						
		min	5	10	50	90	95	max
Eijsden	Meuse	21.2	33.7	40.9	100.7	274.9	293.2	687.6
Keizersveer	Meuse	49.3	64.8	76.8	151.7	327.9	393.6	830.9
Lith	Meuse	50.0	65.3	77.3	153.5	327.5	398.5	825.5
Schipborg	Drentsche Aa	0.4	0.6	0.7	1.2	2.4	2.4	4.1
Lobith	Rhine	934.9	1255.3	1470.8	1977.5	2665.2	3081.8	4396.3
Weesp	AR-canal	22.95	23.37	23.75	28.66	40.89	43.37	47.94
Tiel	Waal	736.9	1001.7	1165.6	1454.4	1888.7	2169.6	3070.3

The predicted concentration at a given abstraction point is then calculated according to:

$$PEC_{x,Tier1} = \frac{E_{tot,x}}{flow\ rate_x} f_{diss} \tag{6}$$

with:

$PEC_{x,tier1}$	= predicted concentration at abstraction point x [µg/L]
$E_{tot,x}$	= total emission [kg] in catchment area x
$flow\ rate_x$	= flow rate [m³/d] of the surface water at abstraction point x, suggested to use the long-term average 10th percentile of the flow rate over the months April - September
f_{diss}	= factor accounting for dissipation / degradation [-].

In the factor f_{diss} the dissipation or degradation is included:

$$f_{diss} = e^{-k_{diss} \cdot t} \tag{7}$$

with:

$$k_{diss} = \ln(2) / DT50$$

k_{diss}	= the first order dissipation / degradation coefficient [d⁻¹]
t	= the average residence time [d] of the substance in the surface water
DT50	= the dissipation / degradation half-live of the substance in water in [d].

For glyphosate it is assumed that the k_{diss} is equal to the degradation rate in water of glyphosate as determined in the EU List of Endpoints (see Annex 3).

Finally, the PEC$_{final}$ is determined after the incorporation of risk mitigation measures considered if required and after making the appropriate adjustments in the parameter values.
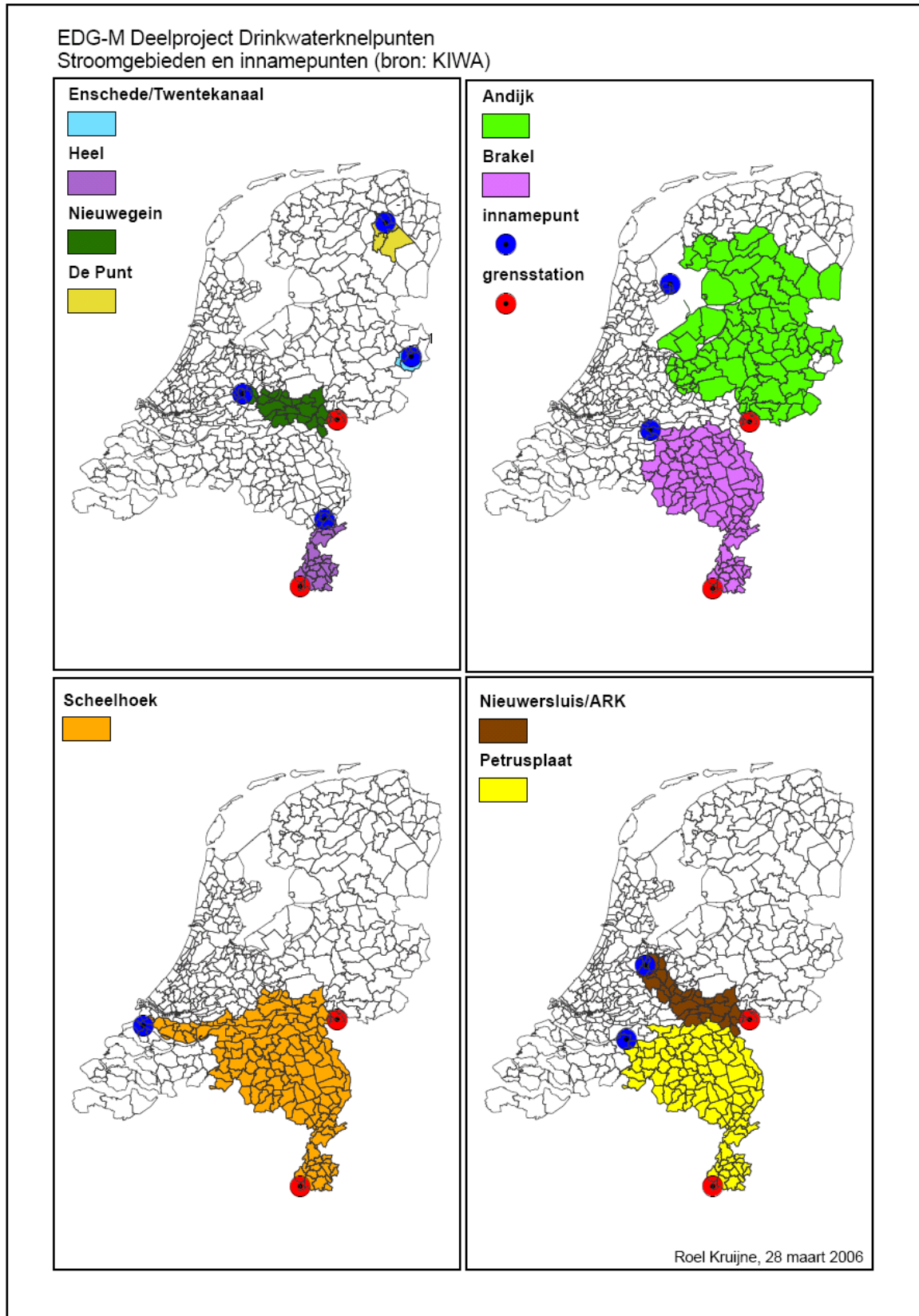
Figure 4.2 Intake areas and drinking water abstraction points (Adriaanse et al., 2008).

5. Measured concentrations of glyphosate

The intake points in the Netherlands for the production of drinking water are the same as in the report on PPPs (Adriaanse et al., 2008). For all information on the drinking water abstraction points, reference is made to this report. Table 5.1 summarizes the identification of the drinking water abstraction points.

Table 5.1 Identification of drinking water abstraction points in the Netherlands.

#	name	location	point of intake
1	Scheelhoek	Scheelhoek	Haringvliet
2	Petrusplaat	Biesbosch	Maas
3	Brakel	Andel	Andelse Maas
4	Heel	Heel	Lateraalkanaal
5	De Punt	De Punt	Drentsche Aa
6	Nieuwegein	Nieuwegein-Jutphaas	Lekkanaal
7	Amsterdam-Rijnkanaal	Nieuwersluis	Amsterdam-Rijnkanaal
8	Inlaat Andijk	Prinses Juliana	IJsselmeer
9	Twentekanaal *	Elsbeekweg	Twentekanaal

Legend: * Currently Twentekanaal is not in use anymore.

In this report the emphasis is put only on glyphosate as that substance is currently the most used substance in amenity use and particularly on hard surfaces.

The Figures 5.1 to 5.10 give the results of the measurements programmes on glyphosate of all the drinking water companies in the Netherlands as far as they make use of surface water as the source for the drinking water in April up to and including September of the years 2000 to 2006, except for Amsterdam-Rijnkanaal and Heel where monitoring has been carried out from 2002 to 2006. The periods October – March have been excluded from the presentation as in these periods glyphosate will usually not be applied on hard surfaces in the Netherlands, so the use of the substance on hard surfaces may have influenced the measurements shown in the figures.
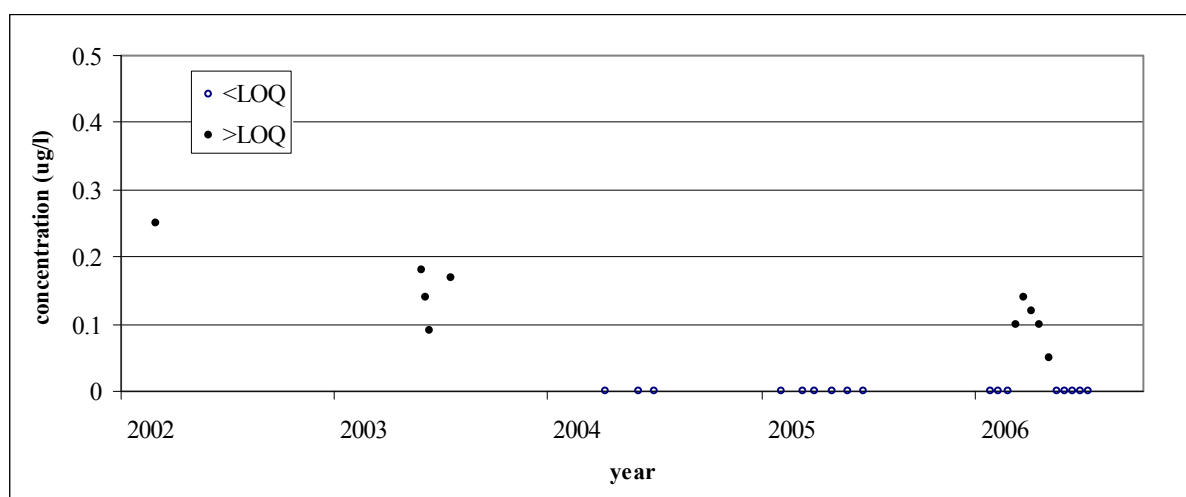
Figure 5.1 Measured glyphosate concentrations Amsterdam-Rijnkanaal in the period 2002 – 2006.
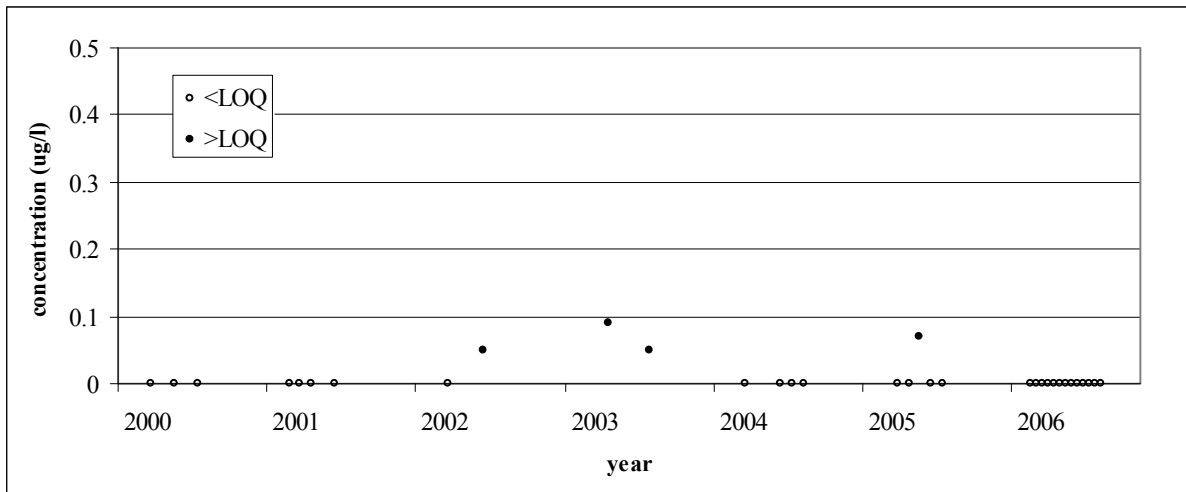
Figure 5.2 Measured glyphosate concentrations at Andijk in the period 2000 – 2006.

Figure 5.3 Measured glyphosate concentrations at Brakel in the period 2000 – 2006.

Figure 5.4 Measured glyphosate concentrations at De Punt in the period 2000 – 2006.

Figure 5.5 Measured glyphosate concentrations at Eijsden in the period 2000 – 2006.
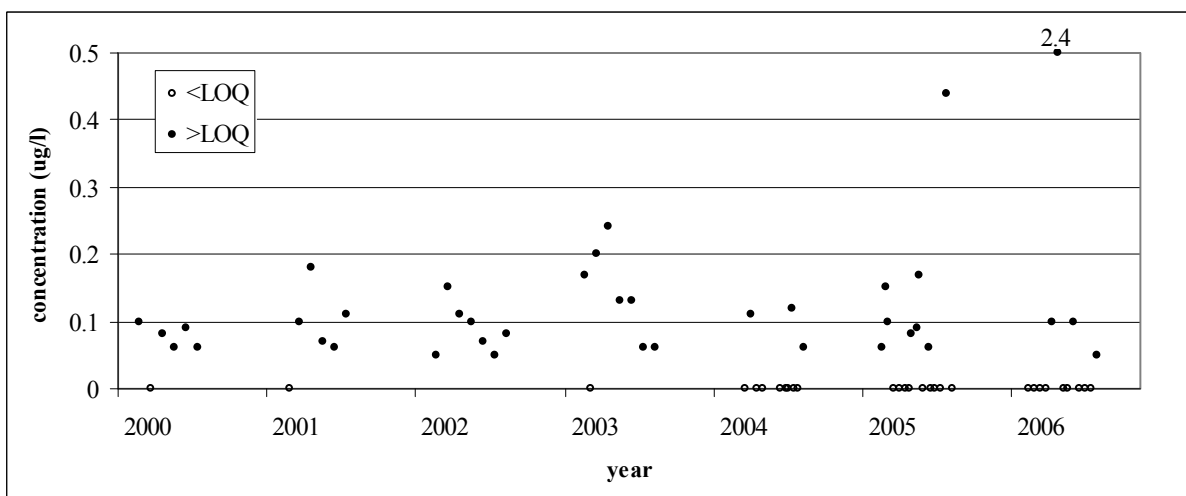
Figure 5.6 Measured glyphosate concentrations at Heel in the period 2002 – 2006.

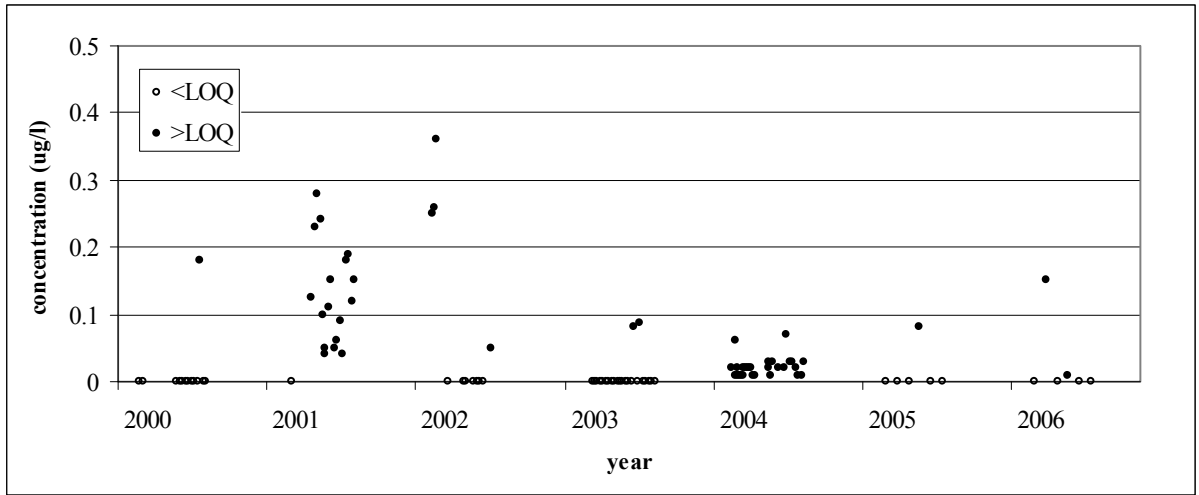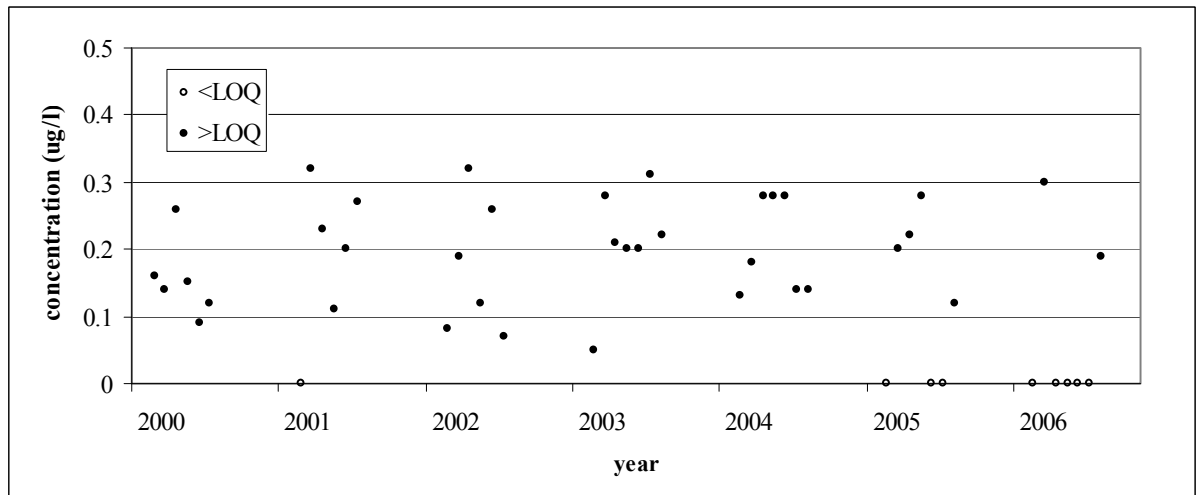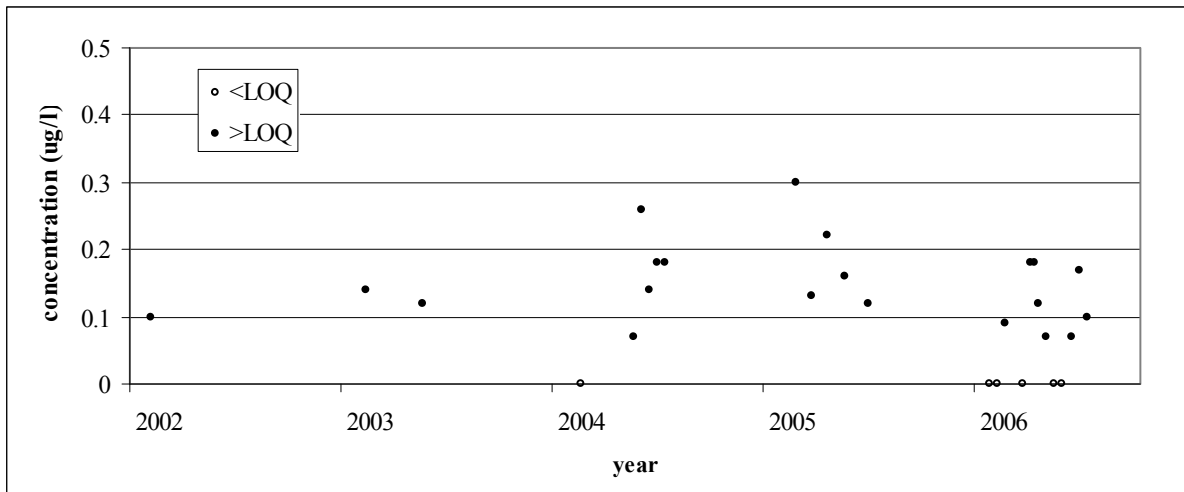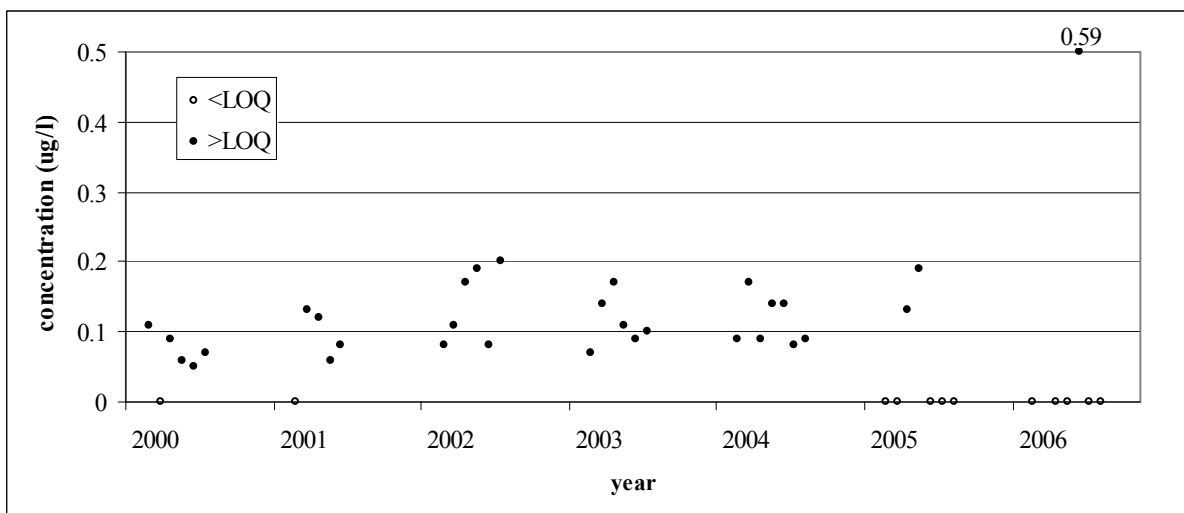**Figure 5.7 Measured glyphosate concentrations at Lobith in the period 2000 – 2006.**
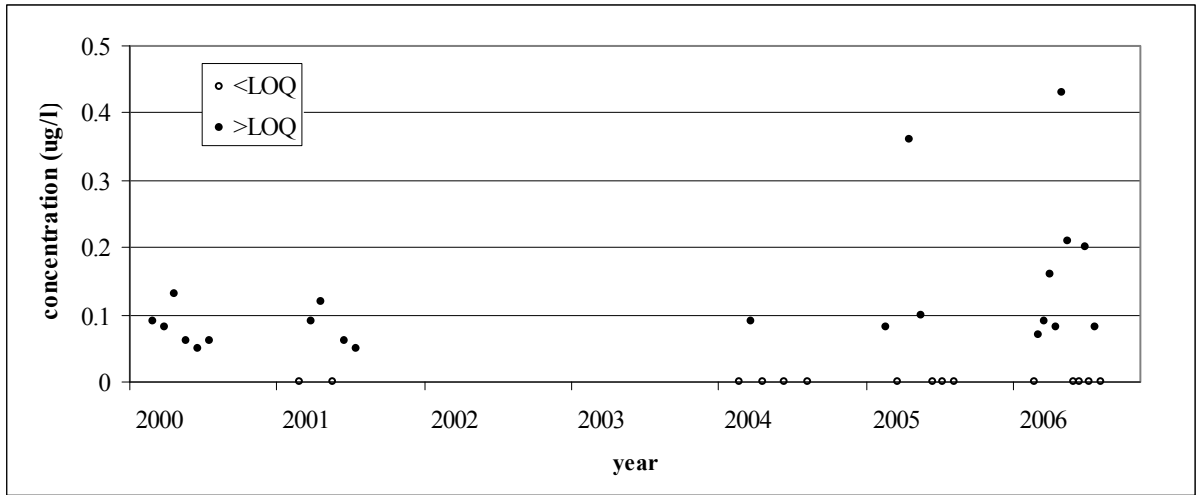
Figure 5.8 Measured glyphosate concentrations at Nieuwegein in the period 2000 – 2006.
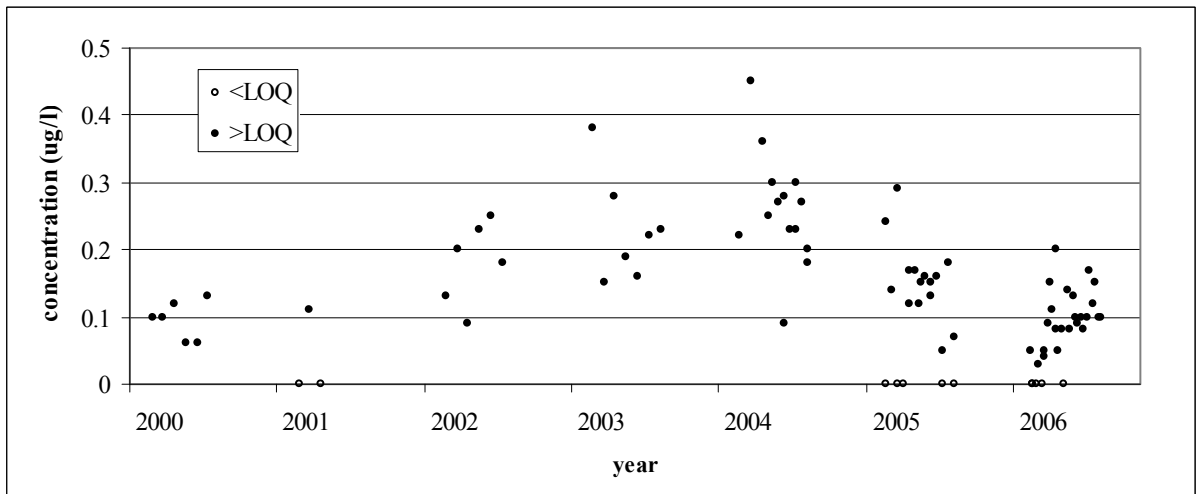

Figure 5.9 Measured glyphosate concentrations at Petrusplaat in the period 2000 – 2006.
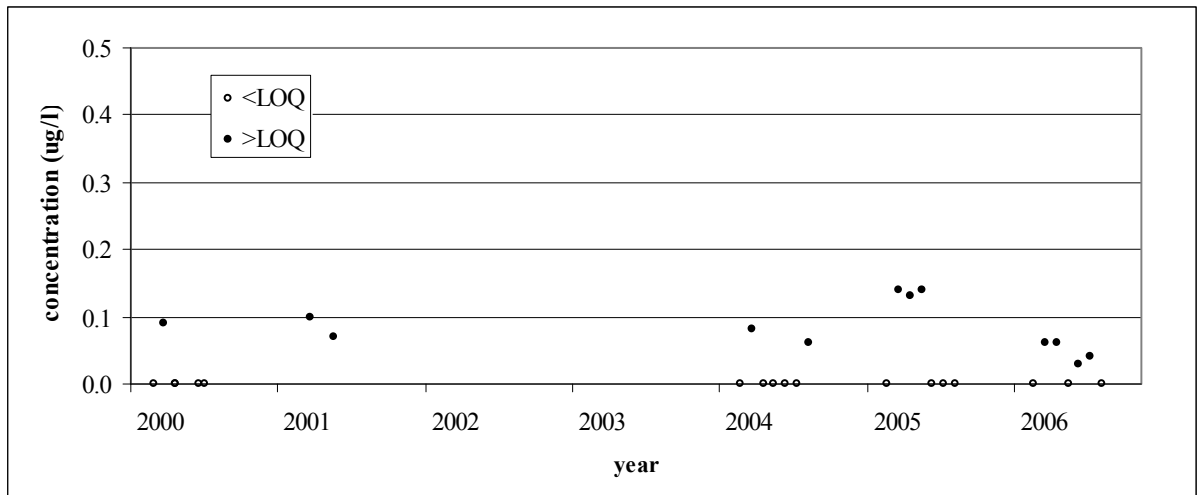
Figure 5.10 Measured glyphosate concentrations at Scheelhoek in the period 2000 – 2006.

The abstraction point Twentekanaal is not used anymore and therefore it is not included in the figures. Two measurement points have been added, Lobith and Eijsden, as they give the situation at the border with Germany and Belgium. These two points are not drinking water abstraction points but are included as reference points to explain possible introduction of the substance into surface water of the Netherlands by foreign activities, both agricultural and amenity use. Although each drinking water abstraction point has its own catchment area, another classification based on catchment area is possible. The following abstraction points Amsterdam-Rijnkanaal, Andijk, Nieuwegein belong to the catchment area of the river Rhine with Lobith as reference point. Most others, Brakel, Heel, Petrusplaat and Scheelhoek belong to the catchment area of the river Meuse. Finally, De Punt belongs to the catchment area of the river Drentsche Aa, which is a river completely situated in the Netherlands. The further analysis of the monitoring data at the abstraction points is carried out taking into account the wider catchment area of the rivers Rhine and Meuse and the, quite uniquely, isolated catchment of the river Drentsche Aa.

As can be seen easily from the Figures 5-1 to 5-10, higher concentrations than 0.1 μg/L occur at all drinking water abstraction points during the application season of glyphosate, except at Andijk. Probably there an additional dilution is taking place due to the large IJsselmeer.

River Rhine catchment
Looking at the measurement data at Lobith a slight increasing trend may be seen over the years 2000 – 2004, possibly indicating an increase in the amount of glyphosate used in Germany and remaining in the water of the river Rhine at the entrance in the Netherlands. Both other stations in the Rhine catchment, Nieuwegein and Amsterdam-Rijnkanaal do not show this trend, although at Nieuwegein in the year 2005 and 2006 a few high concentrations have been detected, around 0.4 μg/L. The highest concentration was found at Lobith with 0.59 μg/L. This value was not related to the highest value at Nieuwegein: 0.43 μg/L. The dates were 2nd of August 2006 and 21st of June, respectively. At Amsterdam-Rijnkanaal even a slight decreasing trend is visible. It is not suggested here that there are significant differences; also a statistical analysis has not been carried out. It is clearly visible from the graphs that

the number of measurements below the LOQ is increasing over the years, while during the same period LOQ tended to decrease.

River Meuse catchment
At Eijsden nor at the other monitoring stations in the Meuse catchment a positive or negative trend is visible, except maybe at Petrusplaat, where in the years 2000 – early 2004 an increase of the glyphosate concentrations and from mid 2004 – end of 2006 a decrease is observed. Compared to Eijsden the level of the concentration is at Petrusplaat generally a little bit higher with maxima over or close to 0.4 µg/L. It can be concluded here that at Petrusplaat a contribution from the Netherlands is visible. However, it can not be determined whether this is due to agriculture or to the application on hard surfaces. At Scheelhoek definitively the lowest values are determined which could indicate a further dissipation of the substance. At Brakel a few high measurements are found, close to 0.5 µg/L. The highest values at Eijsden lie around 0.3 µg/L, which could indicate that sometimes local discharges have taken place somewhere between Eijsden and Brakel. Also in the Meuse catchment area an increasing number of measurements below the LOQ occur in the years 2005 and 2006. Also in this case an exception has to be made for Petrusplaat as still many concentrations are determined around the concentration of 0.1 µg/L.

Drentsche Aa catchment
A number of high concentrations of glyphosate in the Drentsche Aa catchment has been found in the period 2001 and 2002, even up to 0.4 µg/L. In later years a drastic decrease has been observed without values above 0.1 µg/L except for one occasion: 0.15 µg/L in 2006. Therefore, a clear improvement has taken place in this catchment.

6. Comparison between measured and calculated concentrations

In the preceding chapter an overview has been given of the available measurements of glyphosate in Dutch surface water. In this chapter some preliminary calculations will be carried out to estimate the concentration of glyphosate in surface water. Also the results of the methodology proposed and applied to glyphosate will be presented here.

The physico-chemical data and the data on the application of glyphosate on hard surfaces, the amenity use, are taken from the application dossier as available at the Board for the Authorisation of Plant Protection Products and Biocides (Ctgb). It is always assumed that the product that contains in this case glyphosate is applied according to Good Application Practice and that all the prescribed precautions have been taken into account. In Annex 1 an overview is presented of all the registered products containing glyphosate. Annex 2 gives an overview of the physico and chemical data and Annex 3 the data on environmental fate and behaviour of glyphosate are given as a result of the evaluation process in the European Union.

Concerning the dose rate of glyphosate it is assumed that application and dose are carried out according to the guideline presented in the DOB-procedure. This has been specifically developed for application on hard surfaces. Therefore, the dose D of glyphosate is taken as 0.36 kg/ha with in exceptional cases may be increased to 0.72 kg/ha. The emission percentage is estimated at 3.5% based on an evaluation of PRI and others (see chapter 4, emission). This percentage showed to be the 90percentile for glyphosate. Beltman et al. (2006) report a range from 0 to 5.7% for glyphosate residues (=glyphosate + AMPA, personal communication Wim Beltman). In addition, it is assumed that 50% of the potential area of hard surfaces is treated with glyphosate and that all concentrations are caused by the application of glyphosate to hard surfaces.

Table 6-1 gives input values and the calculated concentration for estimated average conditions for the catchment area of De Punt, Amsterdam-Rijnkanaal and Petrusplaat. These three catchments have been chosen based on the following considerations: Twentekanaal is not used any longer as an drinking water abstraction point, Andijk is a more complicated situation as the buffer capacity of the Lake IJsselmeer is also relevant for the final estimation and Amsterdam-Rijnkanaal is the only branch in that catchment where flow data are available. Petrusplaat is chosen as it is considered the most relevant abstraction point in the Meuse catchment. The surface paved area is taken from the data of CBS and Emission Registration as mentioned in section 4.2. The resulting estimated concentration PEC is 0.56, 0.09 and 0.04 for the three catchments respectively. The measured concentrations according to chapter 5 are generally in the range of 0.1 – 0.5 μg/L. As can be seen the values estimated at De Punt are about in the range of normally measured concentrations. In both other points the average calculated situation is lower than the measurements. The measured concentrations should be representative of the realistic worst case conditions as they span all conditions over the reported period.

Table 6.2 gives input values and the calculated concentration for estimated (realistic) worst case conditions for the catchment area of De Punt, Amsterdam-Rijnkanaal and Petrusplaat. The resulting estimated concentration is about 5 μg/L for Amsterdam-Rijnkanaal and Petrusplaat whilst for De Punt much higher values are calculated, a factor of 10 above normally measured concentrations. Therefore the overall conclusion is that the situation amongst the catchment areas in the Netherlands is more complicated than a rather simple approach would allow. Nevertheless, by using the three estimations

for the catchments De Punt, Amsterdam-Rijnkanaal and Petrusplaat a feeling for the expected concentrations can be reached.

Table 6.1 Parameter values for the test runs for glyphosate concentration, average case.

Parameter	De Punt	Amsterdam-Rijnkanaal	Petrusplaat
Potentially treated area in catchment [ha]	12691	48879	128453
Flow rate (50-percentile) [-]	1.2	24	152
Fraction treated (50-percentile) [-]	0.05	0.05	0.05
Time used to treat area [d]	20	40	40
Dosage [kg/ha]	0.4	0.4	0.4
Fraction run-off (median) [-]	0.011	0.011	0.011
DegT50 (mean) [d]	23	23	23
Residence time [d]	6	6	6
Approximate PEC (50-percentile) [µg/L]	0.56	0.09	0.04

Table 6.2 Parameter values for the test runs for glyphosate concentration, 90-percentile case.

Parameter	De Punt	Amsterdam-Rijnkanaal	Petrusplaat
Potentially treated area in catchment [ha]	12691	48879	128453
Flow rate (10-percentile) [-]	0.7	29	152
Fraction treated (90-percentile) [-]	0.4	0.4	0.4
Time used to treat area [d]	20	20	20
Dosage [kg/ha]	0.4	0.4	0.4
Fraction run-off (90-percentile) [-]	0.035	0.035	0.035
DegT50 (mean) [d]	23	23	23
Residence time [d]	6	6	6
Approximate PEC(90-percentile) [µg/L]	49	5.6	4.5

In judging these results it should be kept in mind that the peak concentration calculated here may not be measured during monitoring campaigns because the chance to measure just the peak is very small. As the method is currently developed it calculates rather high concentrations which can account for this difference between calculated and measured values. In this way, the high concentrations calculated could serve as a signal that there may be a risk for the drinking water production process. If the method would be set up more stringent, more calculated concentrations would be higher than the measured concentrations indicating a failure of the method. That would not be a reasonable tier I evaluation system anymore. Therefore, the results of the example calculation for glyphosate are considered to give the right order of magnitude for substances at risk.

Keeping in mind that there is only one substance that can be used for calibration of the method, it is therefore proposed to use the 90-percentile result as the preliminary evaluation target. If in the future more substances become available a further analysis of the situation should take place. At the moment the 90-percentile target seems to be safe for a tier I assessment because the resulting concentrations are higher than the measurements in Dutch surface water.

7. Conclusions and recommendations

The remit of the workgroup was to develop methodology for the risk assessment of the use of plant protection products on paved areas, with respect to the drinking water function of the surface water. The workgroup recommends using the method as outlined in chapter 4 in first tier assessments. The method uses 1) the (potential) use of a product in a catchment area, 2) the 90th percentile run-off value as measured after applications (according to the DOB-protocol) at the neighbourhood scale, and 3) the 10th percentile daily flow rate at the abstraction point. Further assumptions for first tier assessments are: 1) no dissipation from or degradation in surface water and sewage system, and 2) treatment of the area in forty (working) days.

The proposed method was checked with monitoring data on glyphosate. Reported glyphosate concentrations are reported in the range <LOQ to approximately 0.5 µg/L. If median values for run-off and daily flow rate are used and the area is treated in twenty working days, except for De Punt, calculated concentration fall within the observed range.

Refinements of the methodology are possible, but will require additional information. A rather simple refinement of the procedure would be the use of substance specific values for percentage run-off at the neighbourhood scale and the fraction of the paved area treated with the substance. More advanced refinements could take degradation and dissipation of a substance in surface water and sewage treatment plant into account. This however would also require additional information on the distribution of the various types of sewer systems (mixed, separated and improved separated) as then differences in dissipation and transformation will occur.

Monitoring at abstraction points is suggested as the highest possible tier. According to the estimations in this report, only a rather high treated area or high dosage rates would result in exceeding the threshold value of 0.1 µg/L. If the DOB protocol is followed exceeding the standard of 0.1 µg/L is not expected. Therefore, it is recommended that the use of this DOB protocol is outlined in the label instructions.

With this report a methodology to evaluate the effects of plant protection products on the quality of the intake water of water works in the Netherlands has become available, which is supported by all stakeholders in the Netherlands. The method is transparent, straight-forward and meeting its goals. At the European level in the EU such an instrument is still lacking. Therefore, it is recommended that the Dutch proposal developed here will be forwarded to the EU (DG SANCO and EFSA) to develop an equivalent system for the European Union as well.

Still, the policy makers in the Netherlands have to make some final choices in the methodology as currently developed. The main choice is of course the factor of Y as mentioned in the decision making scheme in chapter 3. The choice here should be the same as suggested in Adriaanse et al. (2008). In addition, some of the parameters listed in Table 6.1 or 6.2 are considered relevant, like e.g. the number of treatment days, the fraction treated and the residence time. In the methodology, these values have been determined based on the current knowledge but may be determined differently. Other parameters used are the area treated, that may change in the future and the market share of the product, but these do not belong to the policy dependent parameters.

Finally, it is recommended to develop a computerised tool to be used by the Dutch Registration Authority (Ctgb) in the decision making process for plant protection products applied to hard surfaces. This methodology should therefore be incorporated into the tool box of Ctgb where it is still missing (Ctgb, 2006). In the current research proposals the development of this computer tool is not yet foreseen.

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List of abbreviations

Abbreviation	Meaning
AMPA	Aminomethylphosphonic acid
a.s.	Active Substance
CBS	Centraal Bureau voor de Statistiek (Statistics Netherlands)
Ctgb	College toelating Gewasbeschermingsmiddelen en Biociden (Board for the Authorisation of Plant Protection Products and Biocides)
DegT50	Degradation time for 50% of the substance, generally in days
DegT50/DissT50	Degradation/dissipation time for 50% of the substance, generally in days
DG SANCO	Directorate-General for Sanitation and Consumer products
DOB	Duurzaam Onkruid Beheer verhardingen (sustainable use of plan protection products on paved areas)
DWS	Drinking water standard
EFSA	European Food Safety Agency
EU/EEC/EEC	European Union
FOCUS	Forum for the coordination of pesticide fate models and their use
g	Gram
GAP	Good Application Practice
HTB	Handboek Toelating Bestrijdingsmiddelen (Handbook for the Authorisation of Plant Protection Products)
Kiwa	Quality Assurance Institute, formerly Keuringsinstituut voor Waterleidingartikelen
Kom	Soil liquid partition normalised to organic matter (dm^3/kg)
L	Litre
LBOW	Landelijk Beleidsoverleg Water (National Water Policy Committee)
LNV	Ministerie van Landbouw, Natuur en Voeding (Ministry of Agriculture, Nature and Food quality)
LOD	Level of Determination
LOQ	Level of Quantification
PEC	Predicted Environmental Concentration (mg/L)
PNEC	Predicted No Effect Concentration (mg/L)
PPP	Plant Protection Product
RCA	Relative Cropped Area
RIVM	Rijksinstituut voor Volksgezondheid en Milieu (National Institute for Public Health and the Environment)
Riza	(former) Institute for Inland Water Management and Waste Water Treatment (Netherlands)
SUDS	Sustainable Urban Drainage Systems (UK)
SWS	Surface Water Scenario working group
SZW	Ministerie van Sociale Zaken en Werkgelegenheid (Ministry of Social Affairs and Employment)
t	Time
TER	Toxicity Exposure Ratio
TOXSWA	Toxic substances in water (calculation model for PECs)
TWA	Time Weighted Average

UP	Uniform Principles (Annex VI of 91/414/EEC)
USES	Uniform System for the Evaluation Substances
VEWIN	Vereniging van Waterleidingbedrijven in Nederland (Association of Dutch Water Companies)
VROM	Ministerie van Volkshuisvesting, Ruimtelijke Ordening en Milieu (Ministry of Housing, Spatial Planning and the Environment)
VWS	Ministerie van Volksgezondheid, Welzijn en Sport (Ministry of Health, Welfare and Sport)
WD	Waterdienst (Water Service)
WFD (KRW)	Kader Richtlijn Water (Water Framework Directive)
WWTP	Waste Water Treatment Plant

Annex 1 Intended uses of glyphosate

Table A.1 Overview of intended uses Roundup Evolution on hard or paved surfaces.

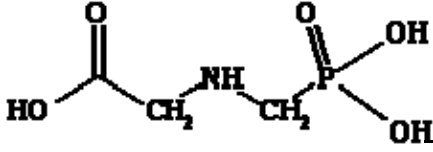| Uses	Dose (kg a.s./ha)	Number of applications	Interval be-tween appli-cations	Application time (growth stage and sea-son)
Professional use				
Application as herbicide				
Hardened or paved surfaces, spot treatment with special equipment	0.36-0.72 *	1		March-October

*) According to the label until late 2006 a dose of 0.72 – 2.16 was valid. Currently, the dose of 0.72 kg/ha is only possible in exceptional cases.

Annex 2 Physico-chemical properties

Profile physico and chemical properties taken from the List of End Points on which the decision on the listing on Annex I of guideline 91/414/EC was based.

Active substance glyphosate

Identity

Active substance (ISO Common Name)	glyphosate
Chemical name (IUPAC)	*N*-(phosphonomethyl)-glycine
Chemical name (CA)	glycin, *N*-(phosphonomethyl)-
CIPAC No	284
CAS No	1071-83-6
EEC No (EINECS or ELINCS)	213-997-4
FAO Specification (including year of publication)	FAO 284 (2001) > 950 g/kg glyphosate; max. 1.3 g/kg formaldehyde; max 1 mg/kg n-nitrosoglyphosate; max 0.2 g/kg insolubles
Minimum purity of the active substance as manufactured (g/kg)	950 g/kg
Identity of relevant impurities (of toxico-logical, environmental and/or other signifi-cance) in the active substance as manufac-tured (g/kg)	
Molecular formula	$C_3H_8NO_5P$
Molecular mass (g/mol)	169
Structural formula	
5-batch analysis	Accountability 99.5-100.0%. Complies with the FAO specifications.

Physical-chemical properties

Melting point (state purity)	Decomposition at about 200 °C; not possible to deter-mine a melting point (99.6%/97.4%)
Boiling point (state purity)	NA
Temperature of decomposition	Decomposition at about 200 °C (99.6%/97.4%)
Appearance (state purity)	White odourless solid (99.6%/97.4%)
Relative density (state purity)	1.70 g/cm^3 (99.6%) 1.69 g/cm^3 (97.4%)
Surface tension	72.7 mN/m (1g/L aqueous solution; 97.4%)

Vapour pressure (in Pa, state temperature)	< 1 x 10^{-5} Pa at 20 °C (99.6%)
Henry's law constant (in Pa m^3 mol^{-1})	< 2 x 10^{-7} Pa m^3 mol^{-1} (99.6%)
Solubility in water (in g/L or mg/L, state, temperature)	10 g/L in purified water at 20 °C (99.6%)
Solubility in organic solvents (in g/L or mg/L, state temperature)	Heptane: < 0.6 mg/L Octan-1-ol: < 0.6 mg/L Methanol: 10 mg/L Xylenes: <0.6 mg/L Ethyl acetate: <0.6 mg/L Acetonitrile: 0.8 mg/L Acetone: <0.6 mg/L 1,2-dichloroethane: <0.6 mg/L (20 °C; 97.4%)
Partition co-efficient (log P_{ow}) (state pH and temperature)	< -1.3 (pH 2.3; 20 °C; 99.6%)
Hydrolytic stability (DT_{50}) (state pH and temperature)	Stable to hydrolytic conditions at pH 5, 7 and 9 in darkness and 25 °C
Dissociation constant	<2; 2.25; 5.50; 10.34 (20 °C, 99.6%)
UV/VIS absorption (max.) (if absorption >290 nm state ε at wavelength)	< 200 nm (purified water) ε< 10 at wavelengths > 290 nm
Photostability (DT_{50}) (aqueous, sunlight, state pH)	pH 5: 45 days pH 7: stable (> 200 days) (natural sunlight, sterile conditions)
Quantum yield of direct photo-transformation in water at λ > 290 nm	Not applicable
Photochemical oxidative degradation in air	Half-life 1.6 hours
Flammability	Not highly flammable (97.4%)
Auto-flammability	Does not self-ignite below the upper limit of the test (400 °C) (97.4%)
Oxidative properties	No oxidising properties (97.4%)
Explosive properties	The chemical structure does not contain any bond groupings known to confer explosive properties.

Annex 3 Fate and behaviour

Fate and behaviour in the environment taken from the List of End Points on which the decision on listing on Annex I of guideline 91/414/EC was based.

Fate and behaviour in soil

Route of degradation

Aerobic	Glyphosate	Glyphosate trimesium
Mineralization after different periods of time (%)	3 soils, 3 different ^{14}C labels: 46.8 – 55.3 (28 d); 5.8 – 9.3 (112 d); 34.7 – 41.4 (84 d) 2 soils: 69.7 – 80.1 (150 d) 1 soil: 32.7 (112 d) 1 soil: 79.6 (100 d)	Glyphosate 2 soils: 37 (21 d), 75 (150 d) TMS: 2 soils: 46 (9 d), 74 (150 d)
Non-extractable residues after different periods of time (%)	3 soils, 3 different ^{14}C labels: 8.5 – 40.3 (28 d); 4.6 – 13.5 (112 d); 16.7 – 33.9 (84 d) 2 soils: 5.1 – 8.8 (150 d) 1 soil: 13.9 (112 d) 1 soil: 8.4 (100 d)	Glyphosate 2 soils: 32 (21 d), 20 (150 d) TMS: 2 soils: 26 (9 d), 10 (150 d)
Major metabolites above 10 % of applied, name and/or code, % of applied (range and maximum)	Aminomethylphosphonic acid (AMPA) 26-29% after 14 days	Aminomethylphosphonic acid (AMPA) 15.4% after 21 days (only in one study detected), no further degradation within 70 days

Supplemental studies	Glyphosate	Glyphosate trimesium
Anaerobic degradation	Mineralization after different periods of time (%): 3 soils, 3 different ^{14}C labels: 33.5 – 51.4 (28 d); 1.4 – 5.0 (112 d); 24.2 – 38.6 (84 d) 1 soil, < 1 (120 d) Non-extractable residues after different periods of time (%): 3 soils, 3 different ^{14}C-labels: 12.8 – 29.7 (28d); 0.4 – 12.0 (112 d); 15.1 – 31.6 (84d) 1 soil, 20 (120 d)	Mineralization after different periods of time (%): Glyphosate: 43 (63 d) TMS: 57 (63d) Non-extractable residues after different periods of time (%): Glyphosate: 24 (63 d) TMS: 16 (63d)

Soil photolysis	DT_{50}: 96 (90 d dark); 101 d (1236 d dark)	DT_{50} 200 hours (50 ° N) AMPA: max. 24%, DT_{50} 200 hours; No metabolites of TMS detected

Remarks	None	None

Rate of degradation

Laboratory studies	**Glyphosate**	**Glyphosate trimesium**
DT_{50}lab (20 °C, aerobic)	DT_{50lab} (20 °C, aerobic): 4 – 180 d (20 °C), mean 49 d, n=7 (first order kinetic) *AMPA: 136 d (20°C) n=1 (pseudo first order kinetic)*	Glyphosate: 3- 62 d , mean 29 d, n=8 (first order kinetic) TMS: 3-15 d, mean 7 d, n=8 (first order kinetic)
DT_{90}lab (20 °C, aerobic)	DT_{90lab} (20 °C, aerobic): 40 – 280 d (20 °C), mean 159 d, n=4 (first order kinetic)	Glyphosate: 81 - 207 d n= 4 (first order kinetic) TMS: 37-85 d (TMS anion), n= 4 (first order kinetic)
DT_{50}lab (10 °C, aerobic)	DT_{50lab} (10 °C, aerobic): not submitted (see field studies)	Glyphosate:67d TMS: 70 d (8 C)
DT_{50}lab (20°C, anaerobic)	DT_{50lab} (20 °C, anaerobic): comparable to aerobic (study one); (water phase) 3 d, (system) 1699 d (study two)	No significant degradation

Field studies (country or region)	**Glyphosate**	**Glyphosate trimesium**
DT_{50f} from soil dissipation studies	DT_{50f} (best fit): Germany 5;12 d; Switzerland7; 21d; USA: 1 d (Texas), 7 d (Ohio), 9 d (Georgia), 12 d (California), 17 d (Arizona), 31 d (Minnesota), 106 d (New York), 130 d (Iowa); Canada: 11 d (Manitoba), 16 d (Ontario), 63 d (Alberta) **AMPA DT_{50f}** (best fit): Germany 218 d (Menslage); Switzerland 135; 139 d	DT_{50f} (best fit): Germany: 9, 15, 17, 23, 34,34d; USA: 1.5, 1.8, 15 and 17 d **AMPA DT_{50f}** (first order kinetic) : Germany: 134, 242, 316, 362, 449, 875 d

Field studies (country or region)	Glyphosate	Glyphosate trimesium
	USA: 76 d (Ohio), 93 d (Texas), 103 d (Arizona), 145 d (New York), 170 d (Georgia), 174 d (Minnesota), 240 d (California); Canada: 128 d (Manitoba), 185 d (Ontario) *414 d Kleinzecher (Germany), 911 d Unzhurst (Germany), 251 d Rohrbach (Germany) 160 d Herrngiersdorf (Germany) 336 d Wang-Inzkofen (Germany)*	USA: 13, 23, 37, 147 d.
DT_{90f} from soil dissipation studies	not calculated; see DT_{50f}	DT_{90f}: Germany: 76, 89, 113, 124, 166, 326 d; USA: 24, 48, 61, 68 d **AMPA DT_{90f}:** Germany: 445, 804, 1050, 1203, 1491, 2907 d; USA: 42, 77, 124, 489d
	Glyphosate	**Glyphosate trimesium**
Soil accumulation and plateau concentration	Plateau concentration for AMPA: 5.62 mg/kg (mean DT_{50f}: 697 d (first order kinetic))	Plateau concentration for AMPA: 0.91 mg/kg (mean DT_{50f} (Germany): 396 d (first order kinetic))
Remarks e.g. effect of soil pH on degradation rate	None	None

Adsorption/desorption

K_f / K_{oc} K_d	Glyphosate				Glyphosate trimesium							
	soil type	1/n	K_{oc}	K_d	soil type	1/n	K_{oc}	K_d	1/n	K_{oc}	K_d	
	silty clay loam	1.16	60000	900	silt loam	0.98	25100	427	0.89	1179	20	
	silt loam	0.8	3800	34	loam	0.93	2860	66	0.89	530	12	
	loamy sand	0.92	22300	245	sandy loam	0.88	7880	39	0.84	1758	9	
	sand	*)	32830	263	clay	1.1	180000	2340	0.93	1659	22	
	sand loam	*)	50660	810								
	sandy clay loam	*)	3598	50								
	loamy sand	*)	884	5.3								
	silt loam	*)	3404	47								
	loam (sediment)	*)	17819	510								
	*)The advanced adsorption isotherm test wasn't conducted because in the screening test equilibrium was not reached after 72 hours											

pH dependence	No pH-dependence	No pH dependence

K_f / K_{oc} K_d	AMPA			
	soil type	1/n	K_{oc}	K_d
	clay loam	0.786	3640	76
	sand	0.904	8310	1554
	sand	0.752	1160	15
	clay loam	0.791	3330	30
	loamy sand	0.769	6920	111
	sand	0.788	24800	74

	pH dependence		No pH-dependence	

Mobility

	Glyphosate	Glyphosate trimesium
Column leaching	1. 0.12 – 1.45% as of applied in leachate (3 soils) 2. 0.03 – 6.56% as of applied in leachate (7 soils)	< 2 % as in leachate (BBA standard soils)
Aged residue leaching	1.56, 0.22 and 0.02% ^{14}C-activity in leachates 65.2, 59.0 and 2.1% evolved as CO_2 30.3, 40.4 and 97.5% ^{14}C in the upper 2 cm of columns	^{14}C distribution after 30 days: Glyphosate-^{14}C: 52% extractable (AMPA 26%), 12 % unextractable, 33% CO_2; TMS-^{14}C: 10 % extractable, 21% unextractable, 57% CO_2 0.1% Glyphosate and 0.5% TMS in leachate, total radioactivity in leachate not given.
Lysimeter/Field leaching studies	Not submitted	Not submitted
Remarks	None	None

Fate and behaviour in water

Abiotic degradation

	Glyphosate	Glyphosate trimesium
Hydrolytic degradation	pH__5____: stable (25 °C)	pH___5___: stable; 25 and 40 °C (glyphosate and TMS)
	pH__7____: stable (25 °C)	pH___7___: stable; 25 and 40 °C (glyphosate and TMS)
	pH__8____: stable (25 °C)	pH___9___: stable; 25 and 40 °C (glyphosate and TMS)
Photolytic degradation	DT_{50}: 33 d (pH 5), 69 d (pH 7), 77 d (pH 9)	Glyphosate: DT_{50}: 81 d (pH 7) 37°N TMS: stable

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Biological degradation

	Glyphosate	Glyphosate trimesium
Readily biodegradable	No.	No.
Water/sediment study		
DT_{50} water	1 and 4 days (Möllerfeld and Römbke)	Glyphosate: 14 and 24 d; TMS: 4 and 3 d
DT_{90} water	not calculated	Glyphosate: 46 and 80 d; TMS: 13 and11 d
DT_{50} whole system	27 and 146 days (Möllerfeld and Römbke), 31 and 124 days (Muttzall) *CTB: 23 days (15, 23 and 31 d) (recalculated; based on Möllerfeld and Römbke; Muttzall)*	Glyphosate: 21 and 202 (extrapol.) d; TMS: 5 and 7 d *CTB: 10.1 days, AMPA: 155 days (recalculated; based on Bowler; Cache)*
DT_{90} whole system	not calculated	Glyphosate: 69 d; TMS: 18 and 23 d
Mineralization	18 and 24% after 100 days (Möllerfeld and Römbke), 6 and 26% after 91 days (Muttzall)	Glyphosate: 48 and 6% after 100 days; TMS: 67 and 68% after 100 days
Non-extractable residues	14 and 22% after 100 days (Möllerfeld and Römbke), 31 and 35% after 91 days (Muttzall)	Glyphosate: 14 and 17% after 100 days; TMS: 7 and 8 % after 100 days
Distribution in water / sediment systems (active substance)	after 1 day: 47-64% in water, 31-44% in sediment; after 100 days 3% in water, 29-44% in sediment. In sediment: maximum 50-60% after 7 and 14 days, resp. and 30-50% after 100 days	*Glyphosate water: 1 and 5 %; sediment: 4 and 58%* *TMS water: < 1%; sediment: 2 and 5 %*
Distribution in water / sediment systems (major metabolites)	AMPA: if found, only in the water phase: maximum 16% after 14 days and 0.5 % after 100 days. Water/sediment studies with ^{14}C-**AMPA** (Knoch and Spirlet): 1 st system: water phase: 101% day 0; 4% day 100; sediment:	AMPA water: 4 and < 1%: AMPA sediment: 18 and 3%

	Glyphosate	**Glyphosate trimesium**
	max. 41% day 59; 20% day 100; 2 nd system water phase: 100% day 0; 1% day 59; sediment: max. 46% day 14; 32% day 100	
Accumulation in water and/or sediment	**No accumulation**	**No accumulation**

Degradation in the saturated zone

	Glyphosate	**Glyphosate trimesium**
	Not submitted	Not submitted

Remarks	None	None

Fate and behaviour in air
Volatility

	Glyphosate	**Glyphosate trimesium**
Vapour pressure	1.31×10^{-5} Pa (25 °C, acid)	$< 1 \times 10^{-11}$ Pa (20 °C)
Henry's law constant	2.1×10^{-7} Pa m^3 mol^{-1}	$< 2 \times 10^{-9}$ Pa m^3 mol^{-1}

Photolytic degradation

	Glyphosate	**Glyphosate trimesium**
Direct photolysis in air	No absorption for wavelengths > 290 nm. DT_{50} (water):33d (pH 5), 69 d (pH 7), 77 d (pH 9)	No absorption for wavelengths > 290 nm. DT_{50} (water): 81 d (pH 7) 37°N (stable for TMS)
	Glyphosate	**Glyphosate trimesium**
Photochemical oxidative degradation in air DT_{50}	DT_{50}: 1.6 d (Atkinson estimation)	DT_{50}: about 1.4 hours
Volatilisation	from plant surfaces: no significant volatilization from soil: no significant volatilization	from plant surfaces: negligible (glyphosate and TMS) from soil: negligible (glyphosate and TMS)
Remarks	None	None