Organic Trace Substances Relevant for Drinking Water – Assessing their Elimination through Bank Filtration

Project acronym: TRACE

by

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In the initial phase of the project ‘Organic Trace Substances Relevant for Drinking Water – Assessing their Elimination through Bank Filtration (TRACE)’ the total herbicide glyphosate was classified as highly relevant for further investigations [Chorus & Wessel 2007]. Glyphosate is one of the most widely used and distributed herbicides in the world. Even though it has been on the market since 1974 its use increased with the expiry of the patent at the beginning of the 1990s, in the context of “soil conserving” agriculture (no ploughing) and with the introduction of glyphosate resistant, genetically manipulated cultures like corn, soy beans and cotton wool in 1997. To estimate the occurrence of glyphosate and its main metabolite AMPA in the surroundings of Berlin samples from 22 surface water sites were analysed within this study. In 5 samples the glyphosate concentration was above the European threshold for herbicides of 0.1 µg/L in drinking water. Up to 70 % of Berlin’s drinking water is produced via bank filtration and aquifer recharge characterized by comparatively low flow velocities (< 1 m/d), long contact times (3-6 months) and mainly anoxic redox conditions. To evaluate the potential of bank filtration to protect the drinking water from glyphosate contaminations an experimental study was conducted in the second phase of the TRACE project. Three enclosures at the UBA’s center for aquatic simulations were dosed with three different concentration levels (average concentration: 0.7, 3.5 and 11.6 µg/L) over a time period of 14 days. The effluent was sampled daily for 34 days. Glyphosate and AMPA were analysed applying the HPLC method according to the German Standard DIN 38407-22/2001. In parallel the applicability of the ELISA kit of the company Abraxis was tested without adequate results. The one-dimensional substance transport model VisualCXTFit was applied to obtain substance specific parameters of glyphosate and hydrodynamic parameters of the filter substrate from observed and measured breakthrough curves. The obtained results show that the breakthrough of glyphosate was retarded remarkably (retardation coefficient (R): 18.3 to 25) despite of the initially postulated low adsorption potential of the sandy filter substrate. Also a significant reduction, probably due to degradation was observed (1st order decay-rate (λ): 0.069 to 0.092 d⁻¹). In addition to the semi-technical scale enclosure experiments laboratory and lysimeter tests were carried out to investigate the processes responsible for glyphosate removal during subsurface passage. The laboratory experiments yielded a Kf-value of $1.8998 \cdot \frac{m}{g} \cdot \frac{L}{n} \cdot \frac{1}{kg \cdot d}$ and a Freundlich exponent of 0.4805, from which a retardation coefficient of 53.4 was calculated for a glyphosate concentration of 20 µg/L. Furthermore, delayed degradation under sub-oxic conditions could be observed. The lysimeter experiments ensured no glyphosate breakthrough in the effluent of a 2 m thick column of fine to medium sandy material within 7 months. The data obtained in this project prove that there is a potential of bank filtration to eliminate the herbicide glyphosate: Taking into account that
glyphosate concentrations in surface water are highly variable a good protection of the drinking water source by bank filtration especially in respect to peak concentration is ensured. However, adsorption and degradation parameters obtained in the laboratory and semi-technical experiments vary significantly due to the difficulty to imitate natural conditions in the laboratory. Therefore the experimental study of the project TRACE emphasises the need to conduct semi-technical experiments in a near-natural environment to evaluate the risk of contamination.
In der Anfangsphase des Projektes “Organische, trinkwasserrelevante Spurenstoffe – Abschätzung ihrer Eliminierung während der Uferfiltration (TRACE)” wurde das Totalherbizid Glyphosat als besonders relevant klassifiziert und für weitere Untersuchungen ausgewählt [Chorus & Wessel 2007]. Glyphosat ist eins der weltweit am häufigsten benutzten und am weitesten verbreiteten Herbizide. Seit 1974 verkauft, stieg sein Anteil am Weltmarkt sprunghaft mit dem Auslaufen der Patente Anfang der 1990er, im Zusammenhang mit der bodenschohnenden Anbauweise und ab 1997 mit dem Anbau von glyphosatresistenten, genetisch manipulierten Kulturen wie Mais, Baumwolle und Sojabohnen. Um das Auftreten von Glyphosat und seinem Hauptabbauprodukt AMPA im Berliner Raum abzuschätzen, wurden in dieser Studie Oberflächenwasserproben an 22 Standorten in Berlin analysiert. In 5 Proben wurden Glyphosatkonzentrationen oberhalb des in Europa gültigen Grenzwertes für Herbizide im Trinkwasser (0,1 µg/L) gefunden. Bis zu 70 % des Berliner Trinkwassers wird durch Uferfiltration oder Grundwasseranreicherung gewonnen. Im Vergleich zu anderen Standorten, zeichnet sich Berlin durch geringe Fließgeschwindigkeiten (< 1 m/d), hohen Aufenthaltszeiten (3-6 Monate) und vorwiegend anoxische Redoxbedingungen aus. Um das Potenzial der Uferfiltration hinsichtlich des Schutzes vor Trinkwasserkontaminationen mit Glyphosat zu beurteilen, ist in der zweiten Phase des Projektes TRACE eine experimentelle Studie durchgeführt worden. Auf dem Versuchsfeld für aquatische Simulationen des UBA in Berlin wurden in den Zulaufen dreier Enclosure (Filtrationsversuchsanlagen im halbtechnischen Maßstab) für 14 Tage jeweils verschiedene Glyphosatkonzentrationen dosiert (mittlere Konzentrationen: 0,7; 3,5 and 11,6 µg/L). Die Abläufe wurden täglich über einen Zeitraum von 34 Tagen beprobti. Glyphosat und AMPA wurden mittels HPLC nach DIN 38407-22/2001 analysiert. Die parallel getestete Bestimmungsmethode mit ELISA Sets der Firma Abraxis erbrachte nur unzureichend genaue Ergebnisse. Das ein-dimensionale Stofftransportmodell VisualCXTFit wurde eingesetzt, um die stoffspezifischen Parameter des Glyphosats und die hydrodynamischen Parameter des Filtermaterials, ausgehend von den beobachteten Durchbruchskurven, zu bestimmen. Die Resultate zeigen, dass der Durchbruch des Glyphosats sich erheblich verzögerte (Retardation (R) = 18,3 bis 25), trotz des ursprünglich als gering angenommenen Adsorptionspotenzials des sandigen Filtermaterials. Ebenso war eine signifikante Reduktion zu beobachten, die vermutlich auf biologischen Abbau zurückzuführen ist (Abbaurate erster Ordnung (λ): 0,069 bis 0,092 d⁻¹). Zusätzlich zu den halbtechnischen Experimenten wurden Labor- und Lysimeterversuche unternommen, um die Prozesse der Glyphosatentfernung während der Untergrundpassage näher zu untersuchen. Die Laborexperimente ergaben einen Kₚ-Wert von 1.8998 $\text{mg}^{-\frac{1}{2}} \cdot L^\frac{1}{2} \cdot kg^{-1}$ und einen Freundlich Exponenten von
Résumé

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Responsable du projet : Dr. Gesche Gruetzmacher

Dans la phase initiale du projet TRACE « Composés traces organiques persistants dans les eaux de surface – Identification des risques liés à l’approvisionnement en eau potable par recharge artificielle », l’herbicide total glyphosate a été sélectionné pour la suite du projet [Chorus & Wessel 2007]. Le glyphosate est un des herbicides les plus utilisés et les plus répandus au monde. Vendu depuis 1974, son utilisation au niveau mondial a augmenté très rapidement avec l’expiration de son brevet au début des années 1990, puis à partir de 1997 avec la culture d’organismes manipulés génétiquement qui résistent au glyphosate comme le maïs, le coton et le soja. Pour évaluer la présence du glyphosate et de son métabolite principal, l’AMPA dans la région de Berlin, des échantillons d’eau de surface ont été prélevés dans le cadre de cette étude sur 22 sites berlinois. Des concentrations de glyphosate dépassant la valeur limite européenne de 0,1 µg/l ont été trouvées dans cinq échantillons. Jusqu’à 70% de l’eau potable de Berlin est puisée par filtration sur berges ou par recharge de l’aquifère. Par rapport à d’autres sites, Berlin se distingue par de faibles vitesses d’écoulement (<1m/d), des temps de séjour élevés et des conditions redox en grande partie anoxiques. Afin d’évaluer le potentiel de la filtration sur berge pour atténuer les concentrations en glyphosate, une étude expérimentale a été effectuée dans la deuxième phase du projet TRACE. Différentes concentrations de glyphosate (concentrations moyennes : 0,7 ; 3,5 et 11,6 µg/l) ont été dosées pendant 14 jours dans l’alimentation de trois dispositifs expérimentaux (enclosure) sur le site de l’UBA à Berlin. Les concentrations ont été mesurées quotidiennement pendant une période de 34 jours. Le glyphosate et l’AMPA ont été analysés par HPLC selon le standard allemand DIN 38407-22/2001. La méthode de détermination utilisant ELISA (compagnie Abraxis) qui a été testée en parallèle n’a pas apporté de résultats assez précis. Le modèle de transport de matière unidimensionnel VisualCXTFit a été appliqué pour déterminer les paramètres spécifiques liés du glyphosate et les paramètres hydrodynamiques. Les résultats montrent que la progression du glyphosate est fortement retardée (retardation (R) = 18,3 à 25) malgré le potentiel d’adsorption initialement présumé faible du matériel filtrant sablonneux. Une réduction importante, probablement due à une dégradation biologique, a aussi été observée (vitesse de dégradation du premier ordre (λ): 0,069 à 0,092 d⁻¹). En plus des expériences à l’échelle semi-technique, des expériences en laboratoire et en lysimètre ont été effectuées afin d’examiner de plus près les mécanismes d’élimination du glyphosate pendant le passage dans le sous-sol. Les expériences en laboratoire ont donné une valeur K_F de 1,8998 mg⁻¹.l⁻¹.n⁻¹.kg⁻¹ et un exposant de Freundlich de 0,4805, à partir desquels ont été calculé un facteur de retardation de 53,4 pour une concentration de glyphosate de 20 µg/l. En plus, on a pu observer une dégradation sous des conditions sub-oxiques. Les expériences en lysimètre ont montré qu’il n’y avait pas de glyphosate dans l’effluent d’une colonne de 2m d’épaisseur de sable fin et moyen
pendant un intervalle de 7 mois. Les résultats accumulés dans le cadre de ce projet montrent que la filtration sur berges a le potentiel d’atténuer les concentrations en glyphosate des eaux de surface. En considérant le fait que les concentrations de glyphosate dans les eaux de surface varient fortement, une bonne protection des sources d’eau potable par filtration sur berges peut être garantie en ce qui concerne les maximums de concentration. Les paramètres d’adsorption et de dégradation obtenus lors des expériences en laboratoire et en enclosure varient de manière significative à cause des difficultés à retrouver des conditions naturelles en laboratoire. L’étude expérimentale du projet TRACE met donc en évidence la nécessité d’effectuer des expériences à l’échelle semi-technique dans un environnement proche de la nature afin d’évaluer les risques de contamination.
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\[ m_{\text{tot}} = (c \cdot n + \beta \cdot (1 - n) \cdot \rho_b) \cdot V \]  
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\[ R \cdot \frac{\delta c}{\delta t} = D \cdot \frac{\delta^2 c}{\delta x^2} - v_p \cdot \frac{\delta c}{\delta x} - \mu \cdot c + \gamma(x) \]  
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\[ \rho_{\text{sat}} = n \cdot \rho_w + (1 - n) \cdot \rho_s \]  
\text{equation 3} .......................................................... 26

\[ n = \frac{\rho_{\text{sat}} - \rho_i}{\rho_w - \rho_s} \]  
\text{equation 4} .......................... 26

\[ c_{\text{ads}} = K_F \cdot c_{\text{dis}}^{\frac{1}{n}} \]  
\text{equation 5} ......................................................... 28

\[ \log c_{\text{ads}} = \log K_F + \frac{1}{n} \cdot \log c_{\text{dis}} \]  
\text{equation 6} ......................................................... 29

\[ c_a = c_t \cdot e^{-\lambda t} \]  
\text{equation 7} ..................................................... 33

\[ DT_{50} = \frac{\ln 0,5}{-\lambda} \]  
\text{equation 8} .................................................. 33

\[ R = \frac{v_{\text{tracer}}}{v_{\text{glyphosate}}} \]  
\text{equation 9} .................................................. 39

\[ R = 1 + \frac{\rho_b}{n_e} \cdot K_D = 1 + \frac{\rho_b}{n_e} \cdot K_F \cdot c_{\text{dis}}^{\frac{1}{n} - 1} \]  
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Chapter 1
Introduction

In the initial phase the project ‘Organic Trace Substances Relevant for Drinking Water – Assessing their Elimination Through Bank Filtration (TRACE)’ aimed at giving an up-to-date overview of the potential risk resulting from the occurrence of chelating agents, perfluorinated compounds (PFCs) and selected pesticides in surface waters and at showing if there is a potential for these substances to persist during bank filtration and artificial recharge. During this phase a literature study was conducted and all regarded substances were classified according to the criteria:

- Usage/ production,
- Occurrence in surface water (if possible also in groundwater and bank filtrate),
- Degradation potential, biological degradability, production of relevant metabolites and toxicity.

For the herbicide glyphosate as well as its metabolite AMPA high production rates and frequent occurrence in surface and groundwater world wide were determined. On the basis of their chemical properties and concentrations an increased risk for drinking water supply can not be ruled out. This would mean additional expenses for purification techniques, like ozonisation or chlorination, which could bring along new risks by other metabolites in drinking water.

Bank filtration, as one method for managed aquifer recharge (MAR), could be an effective, sustainable and less expensive alternative. Due to the fact that the knowledge on the fate of Glyphosate and AMPA during underground passage is limited, these substances were classified as highly relevant for further investigations.

The intention of the 2nd phase is to study more closely those characteristics of glyphosate and AMPA which are responsible for the transport and the persistence of the substance during bank filtration. Adsorption and degradation of glyphosate were to be examined during semi-technical scale experiments at the UBA’s center for aquatic simulations (CAS) at Berlin-Marienfelde (Germany), which serves as a site for experiments on technical scale.

Similar to the KWB project NASRI (Natural and Artificial Systems for Recharge and Infiltration), in which the behavior of algal toxins during bank filtration was investigated successfully, three almost identical enclosures (semi technical scale filter columns) were used to assess the elimination of glyphosate under continuous dosing. Glyphosate concentrations of 1 µg/L and 5 µg/L were applied to reflect the range measured in the River Havel with a maximum value of 4.6 µg/L [Tobian 2006]. To allow predictions on the effect of higher concentrations, a third concentration of 20 µg/L was applied.

This experiment was intended to investigate the potential for retention and elimination offered by a bank filtration system with respect to the threshold value for pesticides and herbicides in drinking water of 0.1 µg/L in Europe. Laboratory experiments and lysemeter...
tests were carried out in parallel as a support to the enclosure experiment. This was intended to create a more exact picture of the behaviour of glyphosate in the environment and to confer a broader validity on the investigation. The physically-based analytical model VisualCXTFit [Nützmann et al. 2005] was used to evaluate the measurement results; this model allows specific substance parameters such as degradation rates and retardation to be derived from the observations made in the course of the experiment.
Chapter 2
State of the art

2.1 Glyphosate

Glyphosate is one of the most commonly applied [De Jonge et al. 2001] and widely distributed [Vereecken 2005] herbicides in the world. It is used in agriculture, forestry and water management, as well as in urban environments [Giesy et al. 2000]. With this universality of use and glyphosate’s ubiquitarity in mind, the substance has to be considered highly relevant to environmental issues; it is therefore appropriate that intensive research be carried out into its effects in the natural environment above and beyond its specific areas of use.

2.1.1 Structure and properties

Glyphosate is a phosphoric acid ester with the structural name N-(Phosphonomethyl) Glycine and the sum formula C₃H₈NO₅P. Figure 1 shows the three characteristic functional groups, glyphosate consists of (phosphonate-, amino- and carboxyl- group).

![Structural formula of glyphosate](image)

Fig. 1: Structural formula of glyphosate

Glyphosate is a polar compound which dissociates in water. All three functional groups can, in dependence on the pH value, occur as proton donors. The charge of glyphosate can range from singly positive (pH < 2) to triple negative (pH > 10.6) [Sheals et al. 2002], as shown in figure 2.
The following table 1 gives important substance parameters from which the behaviour of Glyphosate in the natural environment can be assessed. Glyphosate is highly soluble in water. It hardly volatilises at all and is – according to the published data – removed from the watery phase mainly through adsorption in the course of contact with solid surfaces.

Tab. 1: Substance properties of glyphosate

<table>
<thead>
<tr>
<th>Substance property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight (g/mol)</td>
<td>169.07</td>
</tr>
<tr>
<td>Water solubility (g/L at 25 °C)</td>
<td>10 to 15.7 (^\text{A})</td>
</tr>
<tr>
<td>Vapour pressure (Pa at. 25°C)</td>
<td>(1.3 \times 10^{-5}) to (2.6 \times 10^{-5}) (^\text{A,F})</td>
</tr>
<tr>
<td>Henry constant (Pa·m(^3)·mol(^{-1}))</td>
<td>(1.4 \times 10^{-5}) to (2.1 \times 10^{-7}) (^\text{A,B})</td>
</tr>
<tr>
<td>Octanol-water distribution coefficient (log (K_{ow}))</td>
<td>(-4.59) to (-1.70) (^\text{A})</td>
</tr>
<tr>
<td>Freundlich coefficient ((K_r)) / Freundlich exponent (1/n)</td>
<td>0.6/0.92 (^\text{D}) – 303/1.14 (^\text{I})</td>
</tr>
<tr>
<td>Adsorption coefficient ((K_D)) in mL/g</td>
<td>3-1188 (average: 64), reversible (^\text{G})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substance property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photolysis (pH-dependent)</td>
<td>DT&lt;sub&gt;50&lt;/sub&gt;: 33 d (pH 5), 69 d (pH 7), 77 d (pH 9) C</td>
</tr>
<tr>
<td>Hydrolysis (pH-dependent) at 25 °C</td>
<td>Stable between pH 5 and pH 9 F</td>
</tr>
<tr>
<td>Bio-degradation/ transformation (aerobic)</td>
<td>5.8 to 80.1% in 28 to 150 d F, DT&lt;sub&gt;50&lt;/sub&gt;: 2 H to 14 d H</td>
</tr>
<tr>
<td>Bio-degradation/ transformation (anaerobic)</td>
<td>1 to 51.4% in 28 to 120 d F, DT&lt;sub&gt;50&lt;/sub&gt;: 14 to 22 d H</td>
</tr>
<tr>
<td>Degradation of Glyphosate / AMPA (field study)</td>
<td>DT&lt;sub&gt;50&lt;/sub&gt;: 2 to 198 d / 76 to 240 d G</td>
</tr>
</tbody>
</table>


2.1.2 History, occurrence and application

In 1972, Dr. John Franz and his colleagues, who were engaged in the search for a chemical with a powerful herbicidal effect, low persistence, and without effects on “non-target” organisms, observed the herb toxic characteristics of glyphosate. Tertiary amino methyl phosphonic acids – of which two compounds demonstrated at least low levels of herb toxicity – were derived from primary and secondary amino acids. Contrary to the trend whereby the toxicity of chemical substances is reduced through degradation, these compounds were deliberately subjected to degradation. In the case of the metabolite glyphosate, the desired level of toxicity and thereby the usability of the substance as herbicide could be established [Nord & Sikora 2006, Carlisle & Trevors 1988].

Since 1974, glyphosate has been on the market as an herbicide. In the meantime it has been spread and established in use worldwide. It is contained in many frequently traded product formulae as the main ingredient in combination with functional additives, such as surfactants, penetration agents and adhesives, whose function is to optimise the intensity of the active agent [Giesy et al. 2000]. Glyphosate is used in agriculture above all in the context of so called “soil conserving” agricultural practices which dispense with ploughing, it is used for field preparation for sowing and combat against weeds during the growth of plant cultures [Mensink & Janssen 1994]. In forestry work, glyphosate is used in tree nurseries to keep down competitor plants and in forest plantations to keep the undergrowth under control [Roy et al. 1989]. In water management it finds its use as a means to counteract the growth of floating algae [Giesy et al. 2000]. Glyphosate is also used to get rid of unwanted plant growth on railway track embankments, footpaths and cemeteries etc. [Henkelmann 2005]. With the expiry of the patent at the beginning of the 1990s and the subsequent fall in price of the herbicide, as well as the introduction of glyphosate resistant, genetically manipulated plant cultures like cotton wool, corn and soy beans in 1997, the quantities of glyphosate sold around the world and its share of
the worldwide herbicide market increased [Cox 1998, Giesy et al. 2000 and Kolpin et al. 2006]. This is clearly reflected by the example of genetically manipulated soy beans, which share increased from 2% in 1996 to 80% in 2003 in relation to agricultural area used for soy beans in the USA [Reddy et al. 2004]. In Germany the cultivation of genetically manipulated crops is still restricted though the situation is changing.

In addition to the industrial production of glyphosate for use as an herbicide, which is responsible for most of the immission of the substance into the environment, glyphosate can also arise as a degradation product of chemical compounds. The metabolic degradation of organic sequestrates, or amino-polyphosphonates, which are contained in washing and cleaning agents, boiler feed water, industrial and commercial cleaning agents, and is used in the paper and textile industries, leads supposedly to the formation of glyphosate, which is contained in these compounds as a structural element. The ozonisation of EDTMP (Ethylene diamine tetra methyl phosphonate), a complex sequestrate which is used as a corrosion inhibitor, water softener or bleach stabiliser in washing agents, has been shown in experiments to give rise to glyphosate. Water purification and treatment, in which metabolic degradation and ozonisation represent a further, though quantitatively insignificant, source for glyphosate [Post et al. 1999].

2.1.3 Herbicidal effect and ecotoxicology

Glyphosate owes its place as the frontrunner in the league of herbicidal substances due to its reputation as a successful means of combating weeds [Franz et al. 1997]. Glyphosate is a total herbicide i.e. it does not distinguish between different types of plants. The substance works systemically. It only makes its way into the organism via the green parts of the plant (leaves, stems and flower parts) and can, depending on the amount used, distribute itself via the sap flow to all parts of the plant [Giesy et al. 2000].

Glyphosate works by inhibiting the synthesis of an enzyme which occurs in all plants and is responsible for the production of vital amino acids (e.g. phenyl alanine, tyrosine and tryptophan). Without it the plant withers and dies. About a third of the dry mass of plants consists of those amino acids formed as a result of this enzyme system [Alibhai & Stalling 2001].

This is how glyphosate interferes with a plant’s vital metabolic processes: Erythrose-4-phosphate is a primal substance for the formation of the above mentioned essential amino acids. In the course of several intermediate stages it is transformed by reaction into shikimate-3-phosphate. The 5-hydroxy group of shikimate-3-phosphate bonds with phosphoenolpyruvate (PEP) to form 5-Enolpyruvylshikimate-3-phosphate (EPSP). This reaction is known as EPSP synthesis.

“At this point glyphosate enters into the metabolic process: glyphosate is a very strong inhibitor of EPSP synthesis. Due to the similarity of its structure it competes with PEP. As a consequence, neither EPSP nor aromatic amino acids are formed. The shikimate path does not occur amongst animals – which means that there is no danger for them” [Pöhner 2004]

Although there is most probably no direct risk to animals from glyphosate, it needs to be regarded that the amino acids produced in plants are also essential for animals. The amine acids cannot be directly synthesised by the animals themselves and must
therefore either be ingested directly by herbivorous animals or indirectly when those animals themselves become part of the food chain. Wild plants are therefore an important source of nutrition for all animals. Not only that, but they offer protection from predators, and can be used to cover eggs or as nesting material or a nesting place [Moch & Brauner 2006, Carlisle & Trevors 1988].

The use of herbicides may lead to a reduction in the diversity of flora, which would probably result in a reduction in diversity of fauna and might have a significant effect on the whole ecosystem [Moch & Brauner 2006].

Plant cultures which have been genetically manipulated to be glyphosate resistant are not affected by its toxic effects on plants. Such plants have received the gene for CP-4EPSP synthesis from the soil bacterium Agrobacterium tumefaciens, which, due to structural differences from plant-based EPSP synthesis, is not inhibited by glyphosate. Such a plant is capable of producing aromatic amino acids even in the presence of glyphosate, and is not damaged by it [Cordes 2008].

Wild plants and weeds can acquire natural resistance to the herbicide through the considerable pressure of natural selection and can protect themselves from the effects of agents used to combat them if they manage to adapt successfully to the changes in the environment brought about by the use of the herbicide. It is likely that the development of resistance becomes easier particularly in cases where only one herbicide is used, because the wild plant and weed organism only has to adapt to one poison. The spread of wild plants and weed after the acquisition of resistance is then accelerated due to the fact that the number of natural competitors is reduced by virtue of their inability to adapt [Moch & Brauner 2006].

“Weeds which are resistant to glyphosate are occurring in greater and greater numbers. We can also observe an overall change in the spectrum of weeds to be found. In addition, genetically manipulated herbicide resistant plants may themselves occur as weeds.” [Moch & Brauner 2006].

Glyphosate is not genotoxic, there is no evidence of any carcinogenic effect, and there are no relevant effects on the neuronal system. In table 2 and table 3 it can be observed that the toxic effect of glyphosate comes along with large doses and concentrations, which normally do not occur in ecosystems.
Tab. 2: Acute toxicity of Glyphosate [Bruno & Schaper 2002]

<table>
<thead>
<tr>
<th>Species</th>
<th>Glyphosate concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fish</td>
<td>EC$_{50}$ &gt; 1000 mg/L</td>
</tr>
<tr>
<td>Invertebrates</td>
<td>EC$_{50}$ &gt; 930 mg/L</td>
</tr>
<tr>
<td>Birds</td>
<td>LD$_{50}$ &gt; 2000 mg/kg</td>
</tr>
<tr>
<td>Mammals</td>
<td>LD$_{50}$ &gt; 2000 mg/kg</td>
</tr>
</tbody>
</table>

Tab. 3: Chronic toxicity of Glyphosate [Bruno & Schaper 2002]

<table>
<thead>
<tr>
<th>Species</th>
<th>Glyphosate concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Invertebrates</td>
<td>NOEC 455 mg/L</td>
</tr>
<tr>
<td>Algae</td>
<td>EC$_{50}$ &gt; 72.9 mg/L</td>
</tr>
<tr>
<td>Aquatic plants</td>
<td>EC$_{50}$ &gt; 53.6 mg/L</td>
</tr>
</tbody>
</table>

The primary degradation product AMPA seems to be equally or less toxic than glyphosate. Toxicological problems in consequence of the usage of glyphosate result mainly from the surfactants in the formulations (e.g. polyethoxylated tallowamine) which shall facilitate the penetration of glyphosate into the plant [Howe et al. 2004].

2.1.4 Fate in the environment

The following is intended to demonstrate how the substance characteristics of glyphosate impact the transport and metabolization of the substance in environmental compartments.

2.1.4.1 Soil

Soils have probably the greatest significance for the immobilisation and elimination of glyphosate in the environment. The fate of glyphosate in soil is determined above all by the sorption and degradation processes to be found there [Nomura & Hilton 1977]. The influences of these processes which will be described in the following should not be taken in isolation; they will mostly occur simultaneously in the soil-water system, albeit to varying degrees, and with mutually influencing effects [Wauchope et al. 2002].

The herbicidal activity of glyphosate is strongly reduced when it comes into contact with soil. This effect can be ascribed to the strong adsorption of glyphosate to the solid matrix [Hance 1976].
From the structure of the molecule it can be seen that various reaction partners come into consideration for the adsorptive behaviour of glyphosphate, depending on the environmental conditions. In the slightly acidic environment of most soils, glyphosphate occurs with a surplus of negative electrical charge. Since anionic sorption capacity of soils depends above all on the content of metal oxides, especially aluminium- and ferro oxides [Scheffer & Schachtschabel 2002], can be assumed, that their concentration could be of defining importance for immobilisation of glyphosate through adsorption [Sheals et al. 2002].

Due to similarities in the structure, no small measure of importance is ascribed to the phosphate content of the soil when it comes to the adsorptive behaviour of glyphosphate. Phosphate seems to be a significant competitor ion. It is postulated that glyphosate, amongst other substances, bonds with solids using the same mechanism as phosphate [Hance 1976]. The significance of phosphate is derived from its natural incidence in soil, above all as a product of the mineralization of organic material. Being an essential plant nutrient, it is also added to soil as a fertiliser. Phosphate and glyphosphate therefore continually occur together and compete for adsorption space in the soil structure [Mensink & Janssen 1994]. It has to be distinguished between common sites, which are able to sorb both sorbtives and specific sites correspondent to either glyphosate or phosphate [Borggard & Gimsing 2008].

Also of relevance to adsorption but less important is the influence of organic soil components [Glass 1987, Dion et al. 2001 & Piccolo et al. 1994]. It is supposed that glyphosate can bond with organic material by means of complex formation with metal ions of humic acids [Mensink & Janssen 1994].

On the other hand, humus can appear in the role of deliverers of competing anions, which occupy bonding space and reduce the adsorption capacity of soil for glyphosate [Wauchope et al. 2002 and Gerritse et al. 1996]. These observations make it clear just how complex the bonding mechanisms between glyphosate and soil really are.

With increasing pH value the adsorption decreases, because of the rise of the sorbtive’s negative electrical charge and the loss of the sorbent’s positive electrical charge. If the pH value is elevated by chalking, the adsorption capacity of soil will increase because of the formation of aluminium- and ferro oxides. [Borggard 2004]

Sorption of glyphosate is mainly due to ligand exchange or specific sorption by the formation of mononuclear, monodentate surface complexes. Glyphosate binds through the phosphonate group [Sheals et al. 2002]. It is sorbed by variable-charge AL-OH, Fe-OH and cationic surface sites and form strong Al-O-P and Fe-O-P bonds and Cation-O-P bonds as well. The complexation through hydrogen bonding between the phosphonic moiety with the soil surface is generally accepted, too [Vereecken 2005].

Investigations have shown that glyphosate creates metal complexes with free cations from soil solution and therefore does not adsorb to the solid surface of soil material [Subramaniam & Hoggard 1988]. With this process, nutrients are abstracted from soil and washed away and the potential for glyphosate migration increases, too [Wauchope et al. 2002].
Degradation of glyphosate in soil is mainly due to microbiological processes. However, recent research demonstrated also abiotic degradation by the manganese oxide Birnesite [Barrett & McBride, 2005].

There are two pathways for microbiological degradation. One leads to the metabolites aminomethylphosphonic acid (AMPA) and glyoxilate by cleavage of the C-N bond, AMPA is further degraded to inorganic phosphate and methylamine, which last is mineralized to \( \text{CO}_2 \) und \( \text{NH}_4^+ \). Glyphosate mineralization seems to be cometabolic, because there seems to be no usage of glyphosate as an energy source [Giesy et al. 2000]. Degradation is correlated with the general microbial activity and a lag phase has not been observed, which means enzymes used for degradation have to be present in soil in general [Franz et al. 1997]. Contrary to that, it has been shown in recent studies, that some organisms use glyphosate as carbon and nitrogen source [Borggaard & Gimsing 2008].

The other pathway results in sarcosine and inorganic phosphate by splitting the C-P bond of the glyphosate molecule, where microorganisms use glyphosate as an alternative phosphorus source [Shinabarger & Braimer 1986, Mensink & Janssen 1994].

A wide variability of soil microorganisms, including bacteria, actinomycetes, fungi and unknown microorganisms can degrade glyphosate, but bacteria seem to play the leading role [Forlani et al. 1999].

Whether AMPA or sarcosine is the main metabolite is uncertain. In fact, AMPA is more resistant to further degradation than sarcosine because of its strong sorption via the phosphonate group to soil matrix. That means AMPA is detectable during a longer period of time.

Chemical hydrolysis, thermal decomposition, and photolysis have only very little influence on the degradation of glyphosate [Nomura & Hilton 1977, Sprankle et al. 1975]; it seems that the very stable C-P bonds are responsible for this [Pessagno et al. 2005]. However, photolysis could gain more influence in aquatic ecosystems [Brønstad and Friestad 1985].

Research into the kinetics of degradation showed that it initially occurs very quickly, slowing down over time. In this case it can be supposed that at first the accessible glyphosate in the solution is degraded and that the adsorbed proportion is degraded more slowly. This assumption is supported by the results of investigations which associate a high level of adsorption with a slower rate of degradation [Hance 1976 and Nomura & Hilton 1977]. The reported half-life of glyphosate ranges from a few days to several weeks (see table 1). This may be due to the different adsorption strengths of the soil material and the microbiological activity of the soil fauna, or, alternatively, to those factors of the location which influence these processes, such as the quantity of organic material present, the pH value, moisture, temperature etc. [Giesy et al. 2000].

AMPA, one of the principal metabolites demonstrates a higher half-life value than glyphosate and a higher persistence, which has to be considered, discussing glyphosate and its fate in the environment. Water quality observations in the German rivers Neckar and Rhein from 1996 to 1998 have shown average concentrations of glyphosate below 0.1 µg/L, but AMPA concentrations 5 - 10 times higher than the threshold value of herbicides [Gellert 2007].
The biological degradation of substances which have been bound by adsorption is still open to questions, as the solute form is generally necessary for microorganisms to be available as nutrients (including co-metabolites). Glyphosate’s high adsorption tendency to soil means, however, that a major proportion of the substance binds out of the solution to the solid matrix, which prevents washing out and microbial decomposition. Literature reveals an initial explanation for the degradation of adsorbed glyphosate: if glyphosate attaches to the solid surface by means of the same mechanism as phosphate – favouring a relatively strong bond between the phosphatic acid remnants and the solid surface – the phosphatic acid remnants are shielded from attack by microorganisms and the resultant degradation, whereas the carboxyl group remains relatively free and, therefore, accessible to the decomposition efforts of the microorganisms [Sheals et al. 2002]. Investigation carried out at the molecular level support the theory that adsorbed glyphosate is, indeed, microbiologically biodegradable, provided the degradation is stimulated by the presence of nitrogen and glucose [Schnürer et al. 2006].

2.1.4.2 Surface water

Glyphosate is directly introduced into surface waters, in order, for instance, to control the spread of algal blooms [Giesy et al. 2000]. Underwater plants are not affected by this [Barrett 1978]. It also seems that, notwithstanding its high level of solubility in water, waterways play no significant role in the spread of glyphosate, as it quickly binds to sediment when introduced into lake or river water [Schuette 1998] or degrades through photolysis [Brenstad & Friestad 1985].

Increased concentrations in surface waters in Germany up to 4.6 µg/L [Tobian 2006], presented in figure 38 in the appendix, and above 0.1 µg/L [Henkelmann 2005], however, speak against the theory that surface waters are not to be seen as relevant in the spread of glyphosate. In general, concentrations of glyphosate in surface waters range from sub-µg/L to mg/L [Borggard & Gimsing 2008]. In France, an overstepping of the drinking water threshold for pesticides was observed several times in the river Elorn, which is also use as a drinking water source in Brittany. In 1999 the permitted maximum was highly exceeded with 17.2 µg/L [Moch & Brauner 2006]. In the literature study of the initial phase of the TRACE project, maximum surface water concentrations of 162 µg/L in Canada [Mensink & Janssen 1994], 1700 µg/L in the USA [Mensink & Janssen 1994] and 170 µg/L at the end of the 90s in Germany [Grunewald et al. 2001] were found to have been observed.

The entry of glyphosate into surface waters mainly occurs through runoff from agricultural land; increased concentrations can also be correlated with frequent precipitation events [Henkelmann 2005]. Drainage systems in the vadose zone and drainage channels transport glyphosate into runoff ditches, thus preventing glyphosate from penetrating into deeper strata and there being immobilised by metal oxides or degraded by microorganisms [Vereecken 2005]. Glyphosate can be transported dissolved in solution or particle bound in suspension. The transport is influenced by factors similar to water erosion, like rainfall intensity, soil composition, slope characteristics and vegetation [Hart et al. 2004].
The direct drainage of treated gardens, footpaths, roads, cemeteries and railway tracks via the sewerage system into runoff ditches also represents a further important path [Henkelmann 2005].

In addition to the literature study, samples were taken from surface waters in Berlin and its surrounding areas to check for the status quo of the herbicide's concentrations. The surface water samples were delivered partly from the Berliner Wasser Betriebe (BWB) and partly they were taken by the laboratory staff of the TRACE project.

The glyphosate- and AMPA- concentrations found, are presented in figure 3 and 4 and in the table 13 in the Appendix.
Fig. 3: Map of the sites of surface water sampling in Berlin and its surroundings
Fig. 4: Glyphosate (violet bars) and AMPA (white bars) in surface waters in and around Berlin (2008): a (26.2.), b (6.3.), c (2.6.), d (6.6.), e (9.6.) and f (10.6.).
Additionally determined Isoproturon (measurements carried out by the BWB laboratory) did not exceed the detection limit of the analytical method (0.05 µg/L).

It can be seen that in general the concentrations of glyphosate are below the threshold value for drinking water, with exception of five sampling sites in the Rivers Havel and Spree and in the Channel Teltowkanal. The concentrations of AMPA exceed the permitted level for herbicides more often, especially where high glyphosate concentrations were observed. The origin of the high glyphosate concentrations and its corresponding AMPA concentrations could possibly be traced back to the use of the herbicide in urban environments, as the sampling sites are located within urban areas.

2.1.4.3 Groundwater

In view of bank filtration the behaviour of glyphosate in environmental conditions similar to those in groundwater is very important.

Due to the fact that glyphosate usually enters into contact with groundwater after the former passage through soil or surface water, the ability of the superposed compartments to immobilise and degrade the substance plays an important role in the further spreading of glyphosate.

Reports on the occurrence of glyphosate in groundwater are very rare [Vereecken 2005, Borrgard & Gimsing 2008]. It once was found exceeding the threshold value for herbicides in drinking water with 0.54 µg/L [Smolka S. 2003/ ‘Glyphosat kontaminiert Grundwasser’/ unpublished]. The use of glyphosate has been restricted in Denmark since 2003, after concentrations above the tolerated threshold value were found in areas with short distances between the soil surface and the groundwater table [Nixon et al. 2000].

Complex and comprehensive studies [Kjaer et al. 2005, Torstensson et al. 2005] have shown that leaching from glyphosate to deeper soil layers is possible. In non-structured soils a low adsorption capacity and high hydraulic conductivity linked to coarse material and preferential flow linked to macro pores result in leaching of glyphosate. In this case a long-term use of Glyphosate could endanger shallow groundwater. In structured soils preferential flow, which is assumed to be restricted to the upper 1 to 2 m, is required for leaching.

In structured and non-structured soils glyphosate can be leached dissolved and particle-bound and heavy rainfall, especially shortly after application of the herbicide seems to be decisive for leaching [Borrgard & Gimsing 2008].

2.1.4.4 Air

As glyphosate hardly volatilises at all from the liquid phase – in contrast to the high degree of water solubility, the low vapour pressure and the Henry constant – the soil air only plays a role in sorption inasmuch as it affects the hydraulic properties of the soil. Due to the low vapour pressure (2.59 · 10⁻⁵ Pa at 25°C), the direct path of glyphosate into the air is negligible [Franz et al. 1997]. In the air, due to its high level of water solubility (10 – 15.7 g/L at 25°C), glyphosate can, in the company of aerosols, transform into a drifting spray [Schuette 1998]. Glyphosate is often applied as a spray; particularly in large areas there are used planes or helicopters for this purpose. Depending on wind
speed and direction, glyphosate can spread to a distance of up to 200 m, although decreasing with the range down to 5 % of its original concentration [Riley et al. 1991].

2.1.4.5 Fauna

Glyphosate’s octanol - water coefficient is very low, meaning that it does not tend towards bioaccumulation in the same way as other poisonous substances in the environment. For this reason the risk of accumulation in animal bodies and consequent risk to the upper links of the food chain can safely be neglected.
3.1 Computational methods (VisualCXTFit)

Within the interdisciplinary NASRI research project the CXTFIT code [Toride et al. 1995] was selected and embedded in a pre- and post processing routine programmed under Visual Basic for Applications. With the help of a graphical interface and using EXCEL worksheets and graphs, experimental data sets can easily be transferred and results – observed and fitted breakthrough curves – are depicted simultaneously [Nützmann et al. 2005].

The CXTFit code provides a one-dimensional substance transportation model for stationary flow conditions in homogeneous soil. The following mass balance equation applies on the basis that the complete pore volume is saturated with water:

\[ m_{\text{tot}} = (c \cdot n + \beta \cdot (1 - n) \cdot \rho_b) \cdot V \]  

**equation 1**

- \( m_{\text{tot}} \) = total mass [g]
- \( c \) = concentration [g/cm\(^3\)]
- \( n \) = porosity/ pore volume per total volume [-]
- \( \beta \) = charge [g/g]
- \( \rho_b \) = bulk density [g/cm\(^3\)]
- \( V \) = volume [cm\(^3\)]

On this basis the program calculates with analytical solution methods into which the substance flows can enter on the basis of convection and hydrodynamic dispersal, as well sorptive, degradative, and production processes.

\[ R \cdot \frac{\delta c}{\delta t} = D \cdot \frac{\delta^2 c}{\delta x^2} - v_p \cdot \frac{\delta c}{\delta x} - \mu \cdot c + \gamma(x) \]  

**equation 2**

- \( t \) = time [d]
- \( R \) = retardation coefficient [-]
- \( x \) = distance [cm]
\[ v_p = \text{pore velocity [cm/d]} \]

\[ D = \text{hydrodynamic dispersion coefficient [cm}^2/\text{d]} \]

\[ \mu = \text{first-order decay coefficient for degradation [1/d]} \]

\[ \gamma = \text{zero-order production term [g/cm}^3/\text{d]} \]

Laboratory and field data from adsorption, degradation and leaching experiments can be used to estimate substance-specific (retardation coefficient \( R \)), first-order decay coefficient for degradation \( \mu \)) and hydrodynamic (pore-water velocity \( v_p \) and hydrodynamic dispersion coefficient \( D \)) parameters. The solution to this inverse problem is achieved of using the least square error method. By this method a parameter-dependent model curve is fitted as closely as possible to the point cloud of measured concentrations, whereby the sum of the square deviations between the model curve and the observed points is minimised [Toride et al. 1995]. The parameters of this model curve give rise to an estimation of the real parameters of the naturally-occurring paradigm.

Through the input of observed and measured substance parameters and the hydrodynamic properties of the soil, a direct solution approach can also be used to predict the progression of substance concentration both in time and space.

It has to be mentioned, that the substance specific parameter first-order decay coefficient for degradation \( \mu \), which is presented by the model due to indirect solution is composed as the product of the rate of degradation \( \lambda \) and the retardation coefficient \( R \).

The model requires some specific data for simulation of natural conditions as observed in the filter columns at laboratory and semi-technical scale. A deterministic equilibrium CDE model type, which requires an equilibrium reaction, is considered to be appropriate assuming the presence of chemically and physically determined sorption equilibrium, based on low filtration velocity, constant concentrations and homogeneous flow conditions in the filter column. Since sorption of glyphosate is dependent upon concentration; the experimental set-up, should guarantee to a great extent that the concentration of the solute glyphosate in the reaction zone (dispersal front of the glyphosate) can be regarded as constant.

Partial differential equations as basis of the model require initial and boundary conditions for an unambiguous solution to be found. To solve the initial value problem the initial concentration of glyphosate or the tracer in the column, is set at zero; the boundary value problem solution assumes that the glyphosate is added as a constant concentration dosage in a specific time and the tracer is applied as an impulse in the laboratory and as a constant concentration in the enclosure. No production of glyphosate or tracer is expected. In the appendix in the table 14 all basic settings for the modelling for the glyphosate breakthrough curve in this project are depicted.

This model is adopted to gain the above mentioned substance-specific parameters of glyphosate and hydrodynamic parameters of the filter substance from observed and measured data of their break through curves, obtained by laboratory and semi technical scale experiments. The parameters determined in that way can be used to compare the
laboratory and semi technical scale conditions and prove the transferability of laboratory results at field scale. The substance specific parameters of glyphosate gained from modelling with VisualCXTFit can be used to simulate elimination and retardation processes under natural conditions to forecast development of glyphosate’s concentration in the field’s reality.

3.2 Analytical methods

3.2.1 HPLC

For the quantitative determination of glyphosate, gas chromatographic (GC) as well as liquid chromatographic (LC) methods are described in the literature. In the project Trace both of them were tested in parallel for their applicability under the present conditions.

The GC method was not pursued any further in the course of the project because it was not possible to increase its sensitivity to a sufficient level in a short time, while at the same time the liquid chromatography began to give satisfying results.

The applied method was the DIN 38407-22/2001: Determination of Glyphosate and Amino methyl phosphonic acid (AMPA) by high performance liquid chromatography (HPLC), post-column derivatization and fluorescence detection (F 22). The combination of LC and mass spectrometry (LC/MS) was not available in the project.

3.2.1.1 Extraction, preparation and enrichment of water and soil samples

Prior to analysis by HPLC a process comprising an enrichment step and a clean up step using ion exchange columns is necessary. Alternatively the DIN-method describes enrichment on other materials (cross linked polystyrene). This method uses smaller sample volumes leading to higher detection limits if no very sensitive detector is available. As the applied derivatization and detection system produced some noise increasing the detection limits (see below) and reducing the sensitivity, polymer resins were not used.

The water samples of the laboratory-, the lysemeter- and of the enclosure-experiments (typically 100-500 mL) were filtrated through glass fibre filters and adjusted with hydrochloric acid to pH 2 ± 0.1. The samples were given onto a column filled with a cation exchange resin which had been loaded with Fe³⁺ ions. After percolation of the sample the column was washed with 20 mL water and 40 mL 0.02 M HCl. The analyte-iron complex was eluted with 10 mL 6 M HCl, 4 mL 32% HCl were added to the eluate. This solution was given onto an anion exchange column. By elution of the column with 6 M HCl the iron was retained on top of the column. The colourless eluate was subsequently evaporated in a rotary evaporator. It was dried completely under a stream of nitrogen and the residue was dissolved in 1 mL elution buffer for the HPLC.

The soil samples of the laboratory degradation experiment were extracted with the following method: A 10-g amount of soil was extracted for 30 min with 25 mL of 1 M NaOH. Afterwards the mixture was centrifuged for 15 min at 3000 rpm. The supernatant was taken off with a pipette and the extraction was repeated once again. 4.2 mL concentrated HCl was poured into the mix of both supernatants and all was diluted with
deionised water to a volume of 200 mL. The samples were further treated like the water samples as described above [Börjesson & Torstensson 2000].

In figure 5 the steps of liquid sample preparation before HPLC analysis are shown in detail.

Fig. 5: Scheme of liquid sample preparation
3.2.1.2 HPLC analysis

The DIN method had to be adapted to laboratory capacities. The main differences are mentioned below.

While the DIN method uses a cation exchange column for the separation of glyphosate and AMPA by HPLC, an anion exchange column was used in the project. The conditions of separation and derivatization are identical for both types of columns only the sequence of elution of the analytes is inversed. The properties of the anion exchange column altered during use leading to gradually decreasing retention times for glyphosate. The anion exchange column was applicable only with glyphosate. It was of minor usefulness with real samples containing AMPA, because this compound was mostly interfered by matrix components.

The concentration of AMPA was determined separately with an analytical cation exchange column. This column was an item of loan of the former Federal Biological Research Centre for Agriculture and Forestry (BBA), now Julius-Kuehn-Institute.

For financial reason a detection system was composed of already existing components. The only disadvantage was that the pulsations of the reagent pumps detected by the fluorescence detector lead to an increased background noise.

As eluent a solution of 1 g KH₂PO₄ and 4 g H₃PO₄ in 1 L water was used. The separation was carried out on the anion exchange column Supelcosil LC-SAX column, 25 cm x 4 mm, 5 µm with pre-column (20 mm) and the cation exchange column for glyphosate of the company Pickering. The flow rate was 0.4 mL/min at 50°C.

In the literature it is sometimes mentioned that glyphosate might adsorb to the surface of glass. In the project no evidence for this was found.

3.2.1.3 Derivatization and detection

Because the molecules of glyphosate and AMPA exhibit no functional groups that absorb radiation in the UV or visible range, a derivatization as preparation for fluorescence detection is necessary. In principle a derivatization is possible before and after the separation of the sample components. In this project the two step post column derivatization was applied which is described in the above mentioned DIN method and in the report about a ring test of this method.

After passage of the analytical column in a first step glyphosate was oxidized to glycine. The oxidation solution consisted of 10 g NaCl, 1 g KH₂PO₄ and 1 g NaOH in a 1 L aqueous solution, which was filtrated immediately prior to use through a membrane filter 0.45 µm and complemented with a 50 µL/L NaOCl solution. A 10 m PEEK-capillary (inner diameter 0.25 mm, volume 500 µL) was used as oxidation reactor. The reagent flow rate was 0.4 mL/min. In a second step the glycine was brought into reaction via its amino group with o-phthaldialdehyde and mercaptoethanol to a fluorescing compound. The derivatization solution can consist of 54 g K₂B₂O₇ *4 H₂O in 1 L water or 25 g H₃BO₃ and 11 g NaOH in 1 L aqueous solution. The first variant was later preferred because of the good solubility of the potassium compound. Prior to use 100 mg o-phthaldialdehyde in MeOH and 400 µL mercaptoethanol were added. A 2 m capillary of the same type as
the oxidation reactor was used as derivatization reactor and the reagent flow rate was 0.3 mL/min. AMPA could be derivated without the oxidation step.

The oxidation was performed at ambient temperature, the derivatization at 50°C.

The pH of the reagent solutions being approx. 9.5 is at the limit of the stability of the PEEK material. Therefore PTFE capillaries which had a greater diameter and an accordingly reduced length in order to keep the inner volume constant had been used at first. As later tests revealed, PEEK was stable under these conditions and used as well.

The compounds were detected with a fluorescence detector, excitation at 330 nm, emission at 450 nm. In the Appendix in figure 39 and 40 two detection diagrams are presented as examples.

3.2.1.4 Validation

As a DIN method had been used (with minor modifications according to the facilities of the laboratory) no complete validation had been performed. As proof of the proper performance of the method the recovery of glyphosate in spiked pond water samples was determined, as shown in table 4. These samples were individually prepared together with real samples; therefore the results represent an average over the time of the project.

<table>
<thead>
<tr>
<th>Spiked glyphosate concentration [µg/L]</th>
<th>Recovery [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (n = 4)</td>
<td>83.4</td>
</tr>
<tr>
<td>0.5 (n = 4)</td>
<td>101.4</td>
</tr>
<tr>
<td>0.1 (n = 4)</td>
<td>118.3</td>
</tr>
<tr>
<td>0.05 (n = 5)</td>
<td>99.2</td>
</tr>
<tr>
<td>0.02 (n = 4)</td>
<td>115.8</td>
</tr>
</tbody>
</table>

n: number of samples

The accuracy of the detection method can be described by the standard deviation as percentage of the average value. On the basis of a manifold detection of the samples these values range between 2 and 20 %.
3.2.1.5 Limits of detection and quantification

The limits of detection and quantification were estimated by examination of the signal/noise (S/N) ratio. Usually an S/N ratio of 3 is assumed as limit of detection and an S/N ratio of 10 as limit of quantification. As mentioned above due to the increased noise of the fluorescence detector caused by the pulsations of one of the reagent pumps, the limit values are a little higher than those that were found in the ring test for the validation of the DIN method.

The limit of detection for glyphosate was estimated to be 0.02 µg/L, the limit of quantification to be 0.07 µg/L if an assumed sample volume of 300 mL had been enriched. The respective values for AMPA, 0.005 µg/L and 0.02 µg/L respectively, are lower, as is was determined separately. The noise mentioned above was mainly caused by the pump for the oxidation solution which is used only with glyphosate.

3.2.2 ELISA

ELISA is the acronym for competitive Enzyme Linked Immuno-Sorbent Assay. Initially it was planned to use this method for glyphosate analysis in the project TRACE. Based on an antibody reaction this test determines quantitatively the concentration of the respective analyte. The applied test was purchased from the company Abraxis. The microtiter plate should enable the fast threefold analysis of 25 samples plus the standards for the calibration curve.

According to Abraxis the lower limit of detection is 0.1 µg/L, the upper limit of the test is 5.0 µg/L. Samples containing higher concentration have to be diluted prior to measurement.

The following compounds should, according to the producer, exhibit no significant influence on the result of the ELISA kit in the given concentration range:

- 10000 mg/L (ppm): nitrate, phosphate, sulphate, sodium fluoride, calcium, magnesium, copper, zinc, iron, sodiumthiosulfate.
- 100 mg/L (ppm): manganese
- 10 mg/L (ppm): humic acid
- 1.0 M sodium chloride (NaCl = 58.44 g/mol; tracer concentrate = 25% NaCl-solution)

The average recovery of glyphosate from groundwater should be 104% according to Abraxis, cross reaction with the main degradation product AMPA was not observed.

As other ELISA kits for the determination of the algae toxin microcystin had been used previously at the FEA the general method and the use of such kits was known.

Arguments for the application of the ELISA as alternative to the determination by HPLC are:

- the method is specific for glyphosate
- there is no cross reaction with AMPA
- the costs are lower compared to GC/MS or HPLC
- sample preparation is fast
which stands in opposition to the disadvantages:

- no detection of AMPA is provided
- the analytical limit is too high.

The preconditions for the application of the ELISA kits were given by the TRACE project. Unfortunately pre-tests, with which precision, recovery and reproducibility were checked, led to the conclusion that the disadvantages outweighed the advantages.

The derivatization step is a cause of high imprecision, because the subjective decision when to stop the colour reaction allows only little deviation. The permitted range of the dependence of absorption and concentration can easily be exceeded.

The interpretation of the test is not yet fully developed. The concentration range of 1.0-5.0 µg/L is not covered by standards. The instruction for the interpretation is erroneous. Only one half of 8 performed tests could be interpreted.

The lower limit of detection of the ELISA (0.05 µg/mL) is too high since concentration beyond that value are expected. Besides the lower detection limit as given by Abraxis has considerably increased (0.2-0.3 µg/L and higher), because strong matrix effects influenced the results especially at low concentrations. Very high glyphosate concentrations had been measured in different test waters though no herbicide had been added.

A considerable overestimation of the glyphosate concentration is observed over the entire working range of the ELISA. The commercial product “Roundup” is only poorly detectable which may be caused by components of the formulation.

The examination of the applicability of the ELISA kit required high inputs of time and costs without giving adequate results. The inevitable change of the analysis method demanded a laborious adoption of the laboratory capacities of the Federal Environment Agency. After a time-consuming test of the alternative determination methods by GC/MS or HPLC the latter showed a better performance. All further work was done with HPLC.

As these additional efforts were very costly in terms of time, commercial analytical laboratories were enquired about facilities and costs of glyphosate analysis in case that the project should fall behind. This alternative was no longer followed when the joint efforts of the personal of the UBA laboratory were finally successful.
Chapter 4
Laboratory experiments

As supplementation for the enclosure experiments on a semi technical scale originally planned, laboratory experiments were conducted. The aim was to generalize the research, gain broad knowledge about the behaviour of glyphosate and to facilitate the interpretation of the enclosure results with a different point of view and an investigation of the occurring and interacting processes, which can be investigated separately from each other in the laboratory. With adsorption-, degradation- and leaching- experiments transferable parameters like degradation rate and retardation coefficient can be obtained under controlled conditions.

4.1 Material

Since the same materials are used for adsorption-, degradation- and leaching-experiments in the laboratory, they should be detailed presented in this place, in order to avoid repetition. The descriptions of all laboratory experiments correspond to the following explanations.

4.1.1 Filter substrate

The sediment of an open infiltration pond in the center for aquatic simulations at UBA in Berlin-Marienfelde was used as filter substrate for the laboratory experiments. It seems to be advantageous to use filter substrate directly from the enclosures, because the laboratory experiments could extend the knowledge about the processes in the enclosure wider, if the conditions in the enclosure are best reflected. In order to do not disturb the enclosure experiments, the filter substrate from the pond, which is surrounding the enclosures shall be sufficient. It is originally the same material as in the enclosures. The similarity could only be affected by a variation in the content of organic material, because of the enclosures were used for several experiments with microorganisms and nutrients.

The pond is an artificial concrete basin, which is filled with sandy, coarse to medium grain size material. The pond is fed by surface water from a storage lake. The lake was originally filled with groundwater, treated for iron and manganese removal in 1997. Since then it has mainly been circulated – only evaporation losses are replenished by treated groundwater. A layer of fine organic material establish on the filter surface and the upper region of the sediment in consequence of microbiological activity. Those conditions bring about colmation and reduction of volumetric water flux. A more detailed description of the hydraulic and hydro-chemical properties of the filter substrate is given in figure 16 and table 9 in chapter 5.

The sampling of the sediment was carried out with an installation, which enabled a sample representing the stratification and the grain composition of the sediment down to 30 cm. Before sampling the layer of overlying algae was removed in order to imitate the enclosure’s conditions best possible.
The filter substrate was extracted and homogenized shortly before each laboratory experiment and was stored in closed containers maximal 1 day in the refrigerator. The first step of each experiment was to evaluate the water content (mass difference before and after drying at 105 °C), the content of organic carbon (mass difference before and after combusting at 505°C of the dried sample) and the porosity.

The porosity can be calculated with consideration of the material’s densities, as given in equation 3 and 4.

\[
\rho_{\text{sat}} = n \cdot \rho_w + (1-n) \cdot \rho_s
\]  \hspace{1cm} \text{equation 3}

\[
\rho_{\text{sat}} = \text{density of the water saturated sediment sample [g/cm}^3]\]
\[
\rho_S = \text{density of solid sand [g/cm}^3]\hspace{0.5cm} = 2.67 \text{ g/cm}^3
\]
\[
\rho_W = \text{density of water [g/cm}^3]\hspace{0.5cm} = 1 \text{ g/cm}^3
\]
\[
n = \text{porosity}
\]

Concerning the porosity it follows:

\[
n = \frac{\rho_{\text{sat}} - \rho_s}{\rho_w - \rho_s}
\]  \hspace{1cm} \text{equation 4}

4.1.2 Solvent

Additionally to the original pore water of the sediment sample deionised water is used as solvent in order to calibrate filter substrate-solution ratios as demanded in the different experiments and to avoid reactions with background residues, which could interact with the ingredients of the sample and affect the results in an uncontrolled manner.

4.1.3 Background electrolyte

Calcium chloride (CaCl₂) is used as background electrolyte. With that a basic concentration of well known ions can be provided in the deionised water, which is used in the laboratory experiments. During an adequate incubation time (approx. 12 hours) equilibrium of electrolytes between solid and liquid phase can be observed, which avoid unwanted interruptions of sorption. Additionally calcium chloride improves the centrifugation process of the filter substrate-solution-mixture [OECD 106].

The influence of calcium chloride at the adsorption behaviour of glyphosate was proved in earlier studies. The effect seems to be negligibly low [Gimsing & Borggaard 2001].
4.1.4 Glyphosate

The glyphosate of the producer Sigma-Aldrich has got a purity degree of 98.7% and is available in solid form. To apply it in the experiments it’s dissolved in a 0.01 M CaCl$_2$-solution, in order to be sure of an equal distribution.

4.2 Adsorption experiment

4.2.1 Experimental method

Because adsorption is soil specific and can vary widely (see table 1), batch experiments on adsorption were carried out with filter material from the filtration pond.

The batch experiment was conducted according to the guideline of chemical experiments of the Organisation for Economic Co-operation and Development [OECD 106, 2000]. The guideline is applied to the investigations in a slightly modified form in order to make allowances for the conditions and capacities of the laboratory. The intention was, by observing the basic structure and, at the same time, giving references to the modifications, to ensure that the results are reproducible and classifiable according to the OECD standard.

The adsorption potential of the filter material is expected to be low, because of the lack of sorptive properties. A high filter substrate-solution mass ratio of 1:2 was assumed. This choice can ensure that the values of residual concentrations of glyphosate in solution will, in comparison to the input concentrations, be sufficiently reduced to allow the adsorbed proportions to be calculated.

The glyphosate concentrations were so selected as to make it highly probable that the experiment will succeed - all uncertainty about the adsorptive behaviour of the filter substrate to be investigated notwithstanding. To ensure evaluable results in the output of the batch experiment provided by the analytical method a wide range of concentrations (0.1 mg/L, 1 mg/L, 10 mg/L and 100 mg/L) were chosen.

The duration of the batch experiment depends upon the equilibration time necessary to balance the glyphosate ions in the filter substrate and in the solution. Some studies have shown that the distribution of herbicides in general and also glyphosate in particular can achieve a balance within a few hours [Gimsing & Borggaard 2001, Wauchope et al. 2002 and Piccolo et al. 1994]. According to experience with batch experiments at UBA a duration of 4 hours was chosen for the experiment, also under the additional aspect of avoiding degradation.

After the material for adsorption experiment was extracted from the pond sediment the water content of the extracted filter substrate was determined. This was necessary for the determination of the actual filter substrate-solution ratio, in order to adjust the intended filter substrate-solution ratio by adding missing water quantities and to regulate the CaCl$_2$-concentration.

Taking into account the water content an analytical scale was used to weigh in 13 lots of 20g (dry weight) of filter substrate, each of which was decanted into a centrifuge flask. CaCl$_2$ solution was added until the mass ratio of filter substrate to water of 1:2 was
achieved. The mixture was shaken and left for 12 hours to allow a state of background ion equilibrium to ensue.

The dilution series, as a method of producing the desired levels of concentration, is supposed to make this working step less error prone. The chosen concentrations were adjusted in three parallels to double-check and to ensure the correctness of the measurement values. Blank and background tests were conducted to quantify the adsorption of the glyphosate to the centrifuge flask and to exclude the possibility of prior soil contamination with glyphosate, respectively.

The centrifuge flasks were shaken overhead. The rotation speed was set at 20 revolutions per minute. This was high enough to keep the filter substrate-solution mixture of the batch experiment in constant movement and to break up structures formed through sedimentation and any accompanying stratification-dependent reaction gradients, and low enough to ensure that hardly any changes occur in the structure of the filter substrate matrix and that no new reactive surfaces were created through the friction between the grains of sand themselves and with the walls of the centrifuge flask.

After centrifugation the supernatant was carefully extracted, filled into glass bottles and frozen. The reaction partners are exposed to a temperature of 20°C throughout the whole experiment.

4.2.2 Method for the interpretation of the experiment

For the purposes of the interpretation of the results the glyphosate concentrations measured in the solution after the batch experiment are contrasted to the concentrations subsequently calculated for the adsorbed glyphosate. The Freundlich adsorption isothermal model is used to describe the distribution relations in the investigated filter substrate. This enables a good description of the glyphosate adsorption to be made [Vereecken 2005].

The Freundlich adsorption isotherm represents the temperature and concentration-dependent distribution behaviour of the glyphosate between solid matrix and fluid phase [OECD 106], as to be seen in the following equation.

\[ c_{\text{ads}} = K_F \cdot c_{\text{dis}}^{\frac{1}{n}} \]  \hspace{1cm} \text{equation 5}

\[
\begin{align*}
  c_{\text{ads}} &= \text{charge or adsorbed glyphosate mass per filter substrate mass mg/kg} \\
  c_{\text{dis}} &= \text{dissolved glyphosate concentration [mg/L]} \\
  K_F &= \text{Freundlich distribution coefficient [mg}^{1-1/n} \cdot \text{L}^{1/n} \cdot \text{kg}^{-1}] \\
  \frac{1}{n} &= \text{Freundlich Exponential [-]}
\end{align*}
\]

Equation 5 can be linearised by taking the logarithm, as shown in equation 6. The adsorption coefficients can be read, if the corresponding graphs are sufficiently linear, as
the slope of the logarithmised Freundlich isotherms \( \frac{1}{n} \), respectively as the intersection with the ordinate (logKF).

\[
\log c_{ads} = \log K_F + \frac{1}{n} \cdot \log c_{dis}
\]  

**equation 6**

**4.2.3 Results**

In figure 6 the linearization of the Freundlich isotherm by logarithmization of the values for the adsorbed and dissolved glyphosate concentrations is shown. The concentrations are presented in the appendix in table 16. It characterizes the distribution of glyphosate between solid and liquid phase according to the adjustment of the equilibrium in the batch experiment.

*Fig. 6: Linearisation of the Freundlich isotherm (corresponding Freundlich equation: \( y = 1.8998x^{0.4805} \))*

Exponential regression results in the Freundlich distribution coefficient of 1.8998 \( mg^{-\frac{1}{n}} \cdot L^n \cdot kg^{-1} \) or 0.00145 \( L^n \cdot kg^{-\frac{1}{n}} \) and the Freundlich exponential of 0.4805.
The distribution of the glyphosate is represented as it occurs in the batch experiment between the liquid and solid phases in table 5.

**Tab. 5: Distribution of the glyphosate after adsorption experiment**

<table>
<thead>
<tr>
<th>Input concentration [mg/L]</th>
<th>Residual concentration in solution after experiment [mg/L]</th>
<th>Reduction [%]</th>
<th>Adsorption [mg/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min.</td>
<td>max.</td>
<td>average</td>
</tr>
<tr>
<td>0.1</td>
<td>0.013</td>
<td>0.014</td>
<td>0.0135</td>
</tr>
<tr>
<td>1</td>
<td>0.24</td>
<td>0.29</td>
<td>0.265</td>
</tr>
<tr>
<td>10</td>
<td>6.8</td>
<td>7.2</td>
<td>7</td>
</tr>
<tr>
<td>100</td>
<td>93</td>
<td>94</td>
<td>93.5</td>
</tr>
</tbody>
</table>

Taking in account only the low input concentrations which output concentrations are distributed in a more linear manner, it is possible to calculate an adsorption coefficient (K_D-value). The results are represented in table 6.

**Tab. 6: Distribution coefficients of glyphosate in the filter substrate**

<table>
<thead>
<tr>
<th>Range of concentrations [mg/L]</th>
<th>K_f-value [mg^{1-n} * L^{n} *kg^{-1}]</th>
<th>1/n [-]</th>
<th>R²</th>
<th>K_D-value [L/kg]</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1, 1, 10 and 100</td>
<td>1.8998</td>
<td>0.4805</td>
<td>0.96</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.1, 1 and 10</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.8635</td>
<td>0.89</td>
</tr>
<tr>
<td>0.1 and 1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.4445</td>
<td>0.95</td>
</tr>
</tbody>
</table>

**4.2.4 Interpretation and discussion**

The adsorption experiment exhibited that the partition behaviour of glyphosate is well described by a Freundlich isotherm. This assumption is supported by a high correlation coefficient for the linear regression of the logarithms of the measured values (see figure 6).

As expected the material proved to have poor adsorptivity. Published values for the Freundlich partition coefficient of glyphosate are in average higher (see table 1). But those soils with high values for K_f (e.g. 33-76 [Glass 1987], 13.8-152.9 [Piccolo et al
1994] or 37-303 [Autio et al. 2004] had higher contents of adsorption enhancing components than the examined filter substrate in the experiments of the project TRACE.

For the low environmentally relevant concentrations of glyphosate (threshold value of 0.1 mg/L and examined concentrations in the enclosure experiments of 1 - 20 µg/L) the adsorption capacity of the filter substrate seems to be sufficient to retard glyphosate to a significant amount, thus leading to higher contact times for enhanced degradation. But with increasing concentrations the strong curvature of the Freundlich isotherm which is described by the Freundlich exponent becomes noticeable and the ratio of the adsorbed and dissolved fraction decreases considerably. Thus the partition of glyphosate in the liquid and the solid phase of the filter substrate is clearly depending on the total input concentration. The decrease of adsorption at higher concentrations could be explained by a saturation of the available binding sites. This seems to be reasonable if the general factors which influence adsorption are looked at. The filter substrate has a low content of organic material and of iron oxides as well (see table 9).

Of special interest for the adsorption could be the content of iron oxides. If the binding behaviour of glyphosate is similar to or even corresponds to that of phosphate, these anion acceptors might be the binding sites determining adsorption to the filter substrate. Under the given environmental condition the iron exists as Fe(OH)$_3$ and FeOOH, respectively [Scheffer & Schachtschabel 2002]. These compounds are therefore predestined for replacing a hydroxyl group (ligand exchange) by glyphosate. The total iron concentration (0.03-0.06%) is in the lower range of frequently found iron concentrations. As already low iron concentrations (1-3 %) allow the adsorption of phosphate, the quite low iron content could be sufficient for binding the small amounts of glyphosate which are found in surface waters.

The inhibition of adsorption, caused by saturation of scarce binding sites with increasing concentrations, could be enhanced by the charge of glyphosate ions: Glyphosate belongs to the group of polar organic herbicides which by dissociation forms either cations or anions depending on the pH. Its adsorption behaviour depends strongly on soil pH-value [Wauchope et al. 2002]. When looking at the dissociation diagram of glyphosate (figure 2) it can be assumed that at pH 7 to 8 the molecule is charged mainly twofold negatively resulting in a negative charge excess after binding to a solid phase surface. Increasing supply of glyphosate presumably leads to increasing mutual repulsion due to the same kind of charge. The adsorption of solute ions to free binding sites could be inhibited by ions already bound and by the excess of negative charge. Borggard & Gimsing (2008) had found that due to the spatial structure of glyphosate only 50% of the available binding sites can be utilised for adsorption.

4.3 Degradation experiment

4.3.1 Experimental method

The degradation experiment was intended to enable an assessment of the biological degradation behaviour of glyphosate in the filter substrate under groundwater conditions. This could help to increase the general knowledge about the persistence of glyphosate
as a supplement to the enclosure experiments. The stability of a substance especially in respect of biological degradation trends is an important factor when it comes to the evaluation of the environmental relevance of a substance.

A saturated defined sediment sample was taken and mixed with 10 mg glyphosate per kg filter substrate (dry mass). This concentration was chosen for analytical reasons as they are described in the adsorption experiment. The experimental vessels were stored in the lysemeter cellar of the Marienfelde center for aquatic simulations in a frost-free state and protected from light at a temperature of around 8°C, and left for a period of up to 73 days to allow biological degradation processes to establish. The airtight stoppers of the vessels protect the sample from the atmosphere. During the experiment the vessels are left undisturbed. This experimental arrangement was intended to simulate naturally deposited filter substrate under partly reduced conditions, as it would be expected in the groundwater. Thus it becomes possible to observe the microbial degradation of normal glyphosate concentrations under unfavourable conditions.

Once the filter substrate was extracted and the water content and the dry weight were determined, 455 g of it was filled into each of the 12 degradation experiment vessels. Each vessel was filled up to the brim with deionised water and the quantity of glyphosate dissolved in deionised water which is necessary to achieve the glyphosate concentration, as described above. The vessel was then sealed in order to prevent any other oxygen from entering, other than that contained in the pore and the added deionised water. Taking the specifically adjusted water content into account the input concentration of solute glyphosate was around 25 mg/L. After the contents of the vessel were thoroughly mixed and filter substrate was sedimented two duplicates were opened after 4 hours. The redox potential, oxygen content, pH value and the temperature in the supernatant were determined. During sedimentation a partial demixing of the filter substrate, medium to coarse–grain material and organic, fine-grain material could be observed in the short distance from bottom to top of the flask. The redox potential was also determined in the voluminous surface layer of organic fine-grain material. Then the fluid, still cloudy, supernatant was extracted, centrifuged and stored in the freezer as a clear water sample at a temperature of -20°C. The finer components which sedimented during the centrifugation of the water sample were mixed back homogenous into the filter substrate and a proportion of around 50 g was frozen in sample flasks as a soil sample for later analysis.

At intervals (7, 14, 21, 28 und 73 days) two degradation experiment vessels were opened at a time. The sampling procedure described above was repeated - without the centrifugation, because particles which were suspended by mixing have sedimented in the meantime. In this manner it was attempted over a longer period of time to track the extent and progression of microbial degradation. The step of mixing in CaCl₂ as in the adsorption experiment as a background electrolyte was dispensed with, because the length of the experiment is probably sufficient to allow an electrolytic balance to arise between soil and water phases.

4.3.2 Method for the interpretation of the experiment

The microbial degradation rate was established by observing the changes in the residual concentration observed when the vessels are opened at particular intervals. It is
probable that the degradation kinetic follows a reaction of the first order according to equation 7.

\[ c_a = c_i \cdot e^{-\lambda t} \]  \hspace{1cm} \text{equation 7}

\[
\begin{align*}
 c_0 & = \text{input concentration [mg/L]} \\
 c_t & = \text{concentration at time } t \text{ [mg/L]} \\
 \lambda & = \text{rate of degradation [1/d]} \\
 t & = \text{time [d]}
\end{align*}
\]

The half life value \( DT_{50} \) is the time at which only 50\% of the output concentration can be found in the system under observation. This results in:

\[ DT_{50} = \frac{\ln 0.5}{-\lambda} \]  \hspace{1cm} \text{equation 8}

The sorption should be taken into account in the observations, because it partly shields glyphosate from microbial degradation, and partly exposes it through desorption. Through extraction of the glyphosate from the filter substrate samples after opening the degradation experiment vessel [Börjesson & Torstenson 2000] and the adjustment of the analytical results by the solute quantity of glyphosate on the basis of the water content, the sorption progression during the experimental phase can be established.

4.3.3 Results

The analysis of the solvent samples in the degradation experiment gives rise to the process in respect of the residual glyphosate concentrations in solution, as shown in figure 7. In the appendix in table 17 the corresponding values are presented.
The input concentration of glyphosate in solution was planned with 25 mg/L. In the first opened degradation experiment vessels only 15 mg/L could be observed.

Table 7 shows the time, in which 50% of the glyphosate was degraded, as observed and the time, in which 90% of glyphosate should be degraded, as calculated.

<table>
<thead>
<tr>
<th></th>
<th>DT$_{50}$</th>
<th>30.5 days</th>
<th>4 to 5 weeks</th>
</tr>
</thead>
<tbody>
<tr>
<td>DT$_{90}$ (calculated)</td>
<td>101.5 days</td>
<td>14 to 15 weeks</td>
<td></td>
</tr>
</tbody>
</table>

The measured values of the parameters with which the redox ratios in the degradation experiment vessels could be determined are given in figure 8. The development of the redox potential during the degradation experiment shows that partially reduced ratios in
the fine material of the filter substrate were obtained. The pH value remained constant. The oxygen in the supernatant was almost completely consumed.

![Graph: Development of the redox potential and oxygen content during the degradation experiment](image)

**Fig. 8: Development of the redox potential and oxygen content during the degradation experiment**

The results of the filter substrate extraction are shown as a balance observation in figure 9. The content of total recovered glyphosate is presented in comparison with the content of glyphosate in the solution and at the filter substrate. The value of adsorbed glyphosate for day zero is the difference between the solution's concentration and the theoretic input concentration.
4.3.4 Interpretation and discussion

The prompt decrease of glyphosate concentration in the solvent from the input concentration of 25 mg/L to 15 mg/L can be explained by adsorption. This reduction of the share of dissolved glyphosate results in a loading of around 4 mg glyphosate per kg filter substrate.

The opening of the first degradation experiment vessels 4 hours after mixing of the experiment’s ingredients was conducted after sedimentation of the majority of the dissolved particles, in order to sample a quite clear supernatant for analysis. The time of sedimentation is estimated to be too short for degradation, but was thought to be long enough for quantifiable adsorption. 40% adsorbed glyphosate seems to be quite high with reference to the results of the adsorption experiment in that range of concentration (see table 5), but the deviation could be attributed to the different conditions of the considered experiments. Perhaps adsorption is less limited in the degradation experiment due to a higher mass ratio of filter substrate and solution (2.5:1), which means more binding sites.

The flexion of the degradation curve seems to be less intensive as it would be expected from microbiological degradation, first-order decay. An explanation could be the overlay with other processes, like chemical or physical decomposition, which are
characterised by quasi zero-order decay under the premise of no limitations. On the basis of storage conditions, photolysis and thermal decomposition could be excluded. Hydrolysis should be negligible, because it is unimportant for degradation of glyphosate in soil and stable in solution (see table 1).

The weak flexion could be explained with the proliferation from glyphosate out of the supernatant into the sediment by diffusion. The low rate of degradation could also be caused by filling the left volume of the vessel with deionised water, which is characterized by an absence of nutrients and could have affected the metabolism of the microbiology. The ratio of pond water and deionised water is 1:1.2, which should not have completely interrupted the degradation activity. That can be proved by the measurements of the redox potential and oxygen content which decrease noticeably during the experiment.

The supernatant was inevitable, for dosing of glyphosate, taking liquid samples, doing measurements and mixing the filter substrate and the solution sufficiently in order to impede the implementation of reactive hot spots. But it was tried to kept small enough, that dissolved glyphosate could enter into the sediment by diffusion.

The replicates did show significant deviations. This probably due to a different development of microorganism’s populations in the different vessels in spite of the provision of equal starting conditions. The values for the degradation curve were chosen under consideration of plausibility. Outliers were discharged.

The evaluation of the degradation curve due to residual concentrations in the solution results in a rate of degradation of 0.0227 d⁻¹. That means a half-life of 30.5 days.

The evaluation of the glyphosate in the filter substrate’s extract should show the amount of glyphosate adsorbed, in order to make a balance of glyphosate’s input and output. Analysis results of the first (0 days) and the last (73 days) samplings had to be excluded due to contrariness after balance control.

Strong sorption in the beginning, less delayed sorption [Gimsing et al. 2004 and Gerritse et al. 1996] during the experiment and a lack between input and recovered mass of glyphosate due to degradation was expected, but the results in figure 9 show that adsorption continued remarkably and in the end of the experiment all glyphosate which was not dissolved seemed to be bonded.

This observation cannot be explained sufficiently. Probably the dissolved glyphosate in the supernatant, which makes the half of the water volume was very slowly transported by diffusion to the adsorption sites of the filter substrate. Maybe an increase of adsorption sites due to the change of conditions in the experiment occurred during time.

Concluding, slow filtration velocities as occurring in groundwater could support continuous adsorption of glyphosate under the premise that the microbiological degradation of glyphosate is strongly limited, as it seems to be in the experiment. It was not completely prevented because small amounts of AMPA, which is the main metabolite and with that an important indicator for microbiological degradation, could be observed. However the microbiological participation in the evaluated degradation rate, which seems to be rather a rate of reduction of glyphosate from solution, has to be reappraised.
In order to distinguish the reduction processes and to determine the limitative factors for microbiological degradation, the method of observing the development of radioactive marked carbon dioxide should be consulted for further experiments.

4.4 Leaching experiment

4.4.1 Experimental method

The leaching experiment can be used to estimate the retardation as an indication for the mobility of glyphosate in the filter substrate. The experiment was carried out according to OECD 312 (2007) with slight adaptations to the given laboratory conditions.

The principle of the experiment is based on the leachate investigation of an artificially irrigated soil or sediment column, to which the substance to be investigated is added, either continuously or as an impulse. The test is applicable because of the low volatilization of glyphosate from water and soil into the surrounding air (see table 1).

The OECD guideline 312 recommends a column length of 30 cm. In the present study the column length was 20.5 cm and the diameter amounted to 9.5 cm (figure 10). This setting had been used in other leaching experiments (brominated fire retardants, atrazine).

The filter substrate was placed into the column under saturated conditions and in layers in order to prevent the dehomogenisation of the grain fractions and the penetration of air into the pore space. The glass cylinder was filled up to a height of 17.5 cm. The remaining clear height of 3 cm was left for homogeneous precipitation.

Instead of the recommended 24 hours incubation time with undisturbed 0.01 M CaCl₂-solution, 16 hours were considered sufficient, because for the loss of time an additional rinsing with 0.01 M CaCl₂-solution was carried out four hours before and four hours after the incubation period respectively. This procedure was intended to guarantee the even distribution of the 0.01 M CaCl₂-solution in the filter substrate. In a preliminary test the volumetric flux provided by the pump was determined at which the solute supernatant in the column remains at a constant level of 1mm above the surface of the filter substrate, so that the column in the experiment remained water-saturated throughout the experiment. This volumetric flux was established at 0.26 mL/s (cm³/s). The continuity of the flux was controlled during the experiment.

Sodium chloride (NaCl) was used as a tracer and detected by measuring the electrical conductivity.

After the last rinsing phase had been completed and the supernatant had reached a level of 1 mm above the filter substrate the tracer (1 g NaCl in 15 mL 0.01 M CaCl₂-solution) was distributed evenly over the surface of the filter substrate column. As soon as the NaCl-solution has seeped in, sprinkling with the glyphosate-spiked 0.01 M CaCl₂-solution and sampling commenced.

Sample extraction of 100ml leachate took place at an interval of 26 sec, which means that the entire leachate was taken. After the discharge of 3 L of filtrate the solvent sampling ended and the samples were frozen for later analysis at a temperature of -20°C. The amount of 3 L corresponds to the exchange of a roughly six fold pore volume.
This amount was assumed to be sufficient for glyphosate breakthrough due to the low level of adsorption given in the literature of between 3 and 6 for soils with higher adsorption capacities [De Jonge & De Jonge 1999]. The tracer breakthrough was continuously measured at the samples. The temperature was 20°C throughout the experiment.

20 µg/L was selected as the input concentration for glyphosate. In contrast to the tracer, glyphosate was added continuously. Concentration and dosing method corresponded to the method applied at the enclosures (see chapter 5). The aim was to achieve the comparability of experimental conditions at the laboratory and the semi-technical scale.

Fig. 10: Leaching experiment installation

4.4.2 Methods for the interpretation of the experiment

The tracer experiment yields information on the pore velocity \(v_p\). It is determined as the meridian of the tracer breakthrough curve. By calculating the filtration velocity \(v_f\) from flux \(Q\) (0.26 cm³/s) and surface area (70.88 cm²), the effective porosity \(n_e\) as a further hydrodynamic property of the filter substrate can be determined as the ratio of \(v_f\) and \(v_p\). The effective porosity \(n_e\) describes the flow active partition of the porosity \(n\).

Retardation of glyphosate is calculated according to equation 9.

\[
R = \frac{v_{\text{tracer}}}{v_{\text{glyphosate}}}
\]  

\textit{equation 9}
\[ R = \text{retardation ["]} \]

\[ v_{\text{glyphosate}} = \text{average velocity (}= v_p \text{) of glyphosate [m/s]} \]

\[ v_{\text{tracer}} = \text{average velocity (}= v_p \text{) of the tracer [m/s]} \]

### 4.4.3 Results

The hydrodynamic parameters of the filter substrate in the laboratory column were determined on the basis of the laboratory column’s dimensions and the tracer breakthrough curve, as shown in figure 11. The pore velocity was thus measured at 0.00878 cm/s (759 cm/d). The filtration velocity amounted to 0.00367 cm/s (317 cm/d). Thus the effective porosity is determined with a value of 41.8%. The hydrodynamic dispersion coefficient was calculated to be 86 cm²/d by VisualCXTFit.

![Tracer breakthrough curve of the laboratory leaching experiment](image)

**Fig. 11: Tracer breakthrough curve of the laboratory leaching experiment**

Figure 12 shows the distribution of glyphosate concentrations at the column outlet. The values are given in the appendix in table 18.
With exception of four samples taken 0.96 h, 2.55 h, 2.68 h and 2.77 h after the beginning of the experiment, no concentration values for glyphosate were determined in the effluent. It was therefore not possible to determine the retardation of the glyphosate. However, the retardation of glyphosate could be estimated using the results of the adsorption experiment (Freundlich distribution coefficient and Freundlich exponent), as it can be seen in equation 10.

\[ R = 1 + \frac{\rho_b}{n_e} \cdot K_D = 1 + \frac{\rho_b}{n_e} \cdot K_F \cdot c_{dis} \frac{1}{n} - 1 \]  

equation 10

- \( R \) = retardation [-]
- \( \rho_b \) = bulk density [kg/L] = 1.51 kg/L.
- \( n_e \) = effective porosity [-] = 41.8 %
- \( K_D \) = adsorption coefficient [(L/kg)]
- \( c_{dis} \) = concentration of the dissolved glyphosate [kg/L]
- \( K_F \) = Freundlich coefficient [(L/kg)^1/n] = 0.00145 \( L^n \cdot kg^{-\frac{1}{n}} \)
- \( \frac{1}{n} \) = Freundlich exponential [-] = 0.4805
The prerequisites for applying equation 10 are:

- the concentration remains constant throughout the leaching experiment (This condition is realised by adding glyphosate continuously with a constant input concentration \( c_0 \) throughout the experiment. At the adsorption equilibrium the concentration of the dissolved glyphosate \( (c_{\text{dis}}) \) is represented by the constant input concentration \( c_0 \), which can be used as \( c_{\text{dis}} \) to determine the retardation),
- at the start of the experiment the glyphosate concentration in the column has to be zero,
- the substance retention can be described using a Freundlich isotherm
- and the Freundlich exponent is not greater than 1.

These conditions were deemed to be fulfilled in the experiment.

Table 8 show theoretical \( K_D \) and retardation values for glyphosate in the filter substrate basing on the adsorption experiments. \( K_D \) value and retardation coefficient for 20 µg/L are results of an extrapolation.

<table>
<thead>
<tr>
<th>Input concentration [µg/L]</th>
<th>( K_D )-value [L/kg]</th>
<th>Retardation [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>14,5</td>
<td>53,4</td>
</tr>
<tr>
<td>100</td>
<td>6,3</td>
<td>23,7</td>
</tr>
<tr>
<td>1000</td>
<td>1,9</td>
<td>7,9</td>
</tr>
<tr>
<td>10000</td>
<td>0,6</td>
<td>3,1</td>
</tr>
<tr>
<td>1000000</td>
<td>0,2</td>
<td>1,6</td>
</tr>
</tbody>
</table>

4.4.4 Interpretation and discussion

In the leaching experiment no glyphosate breakthrough curve was observed, so that it was impossible to calculate the retardation of glyphosate in the filter column under laboratory conditions. The detected concentration values of glyphosate in the outlet of the column were scarce and accidentally distributed, so that they had to be considered as outliers.

An estimation of the retardation on the basis of literature values did not succeed. Although the values did depend on studies with apparently more sorptive materials the retardation potential of the filter substrate was underestimated in the range of the
considered concentrations. That leads to an underestimation of the breakthrough time and an abort of the experiment before arrival of glyphosate in the outlet.

The results of the adsorption experiment on which the estimation of the retardation in table 8 is based, were not available when the leaching experiment was conducted. According to table 8 the breakthrough of glyphosate in the filter column would have been occurred approximately after 24 hours. How close to reality those calculated retardation coefficients are, has to be proved with the enclosure experiments.
Chapter 5
Enclosure Experiments

5.1 Method and Materials

In order to simulate the behaviour of glyphosate in a bank filtration setting, semi-technical scale experiments with saturated filters, so called enclosures, were conducted.

The enclosures allow experiments on a smaller scale then technical scale slow sand filters and therefore under conditions easier to change and to control. The enclosure experiments with relatively short contact times are useful especially for those substances that are usually readily removed from the solution by filter substrate contact (e.g. algal toxins, viruses and bacteria). Glyphosate is also known as readily binding at adsorption sites, therefore the enclosures seem to be appropriate for the planned experiments.

By comparing the glyphosate concentration in the inlet and the outlet of the enclosure and by analyzing the development of glyphosate’s concentration in the outlet retardation and elimination potential of the subsurface passage can be assessed.

The experiments were carried out in three enclosures, metal-walled upstanding cylinders with a cross section area of 1 m² and a height of 1.85 m. They are placed in an open infiltration pond of the UBA’s center for aquatic simulations to be exposed to natural climate conditions. The experimental set-up is illustrated in figure 13 and 14.
Fig. 13: Cross-section and schematic map (upper left) of the filtration pond #1 in the artificial aquifer at the UBA’s center for aquatic simulations, including the position of the three enclosure columns inside the infiltration pond, without tubing, pumps and sampling ports. [Grützmacher et al. 2006]

Fig. 14: Picture of the three enclosures during sampling by I. Flieger (UBA)
The enclosures were filled from bottom to top with 0.25 m of gravel and 1 m of sand. The water reservoir above the sediment surface was about 0.6 m deep (figure 15).

![Schematic cross section of enclosure III with sampling ports](image)

**Fig. 15: Schematic cross section of enclosure III with sampling ports [Grützmacher et al. 2006]**

The flow rate was set and controlled at 50 cm/d by adjustable pumps connected to enclosure outlet (bottom of the enclosures. The water body above the filter substrate was kept constant by siphoning the water out of the open infiltration pond into the enclosure without additional pumping. A 7,000 m³ storage lake feeds the infiltration pond and hence the enclosures.

According to previous investigations during the NASRI project the virgin filter substrate is a medium to coarse sand with small amounts of fine sand (see figure 16). Silt and clay are not present. The drainage stratum consists of fine gravel with large shares of medium grained gravel.
Fig. 16: Grain-size distribution curve of the virgin filter substrate (left) and the drainage stratum (right) [Grützmacher et al. 2006]

Tab. 9: Characterisation of the enclosure filling material (Massmann et al. 2004)

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Clogging layer</th>
<th>Filter substrate</th>
<th>Drainage stratum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil type</td>
<td>n.a.</td>
<td>mS, gS, fG</td>
<td>fG, mg</td>
</tr>
<tr>
<td>Thickness [m]</td>
<td>0,05**</td>
<td>1</td>
<td>0,25</td>
</tr>
<tr>
<td>(C_u^<em>/C_o^</em>)</td>
<td>n.a.</td>
<td>3,2 / 0,7</td>
<td>2,0 / 1,0</td>
</tr>
<tr>
<td>Fe(ox) [mg/kg]</td>
<td>605</td>
<td>275</td>
<td>n.a.</td>
</tr>
<tr>
<td>Mn(ox) [mg/kg]</td>
<td>68,8</td>
<td>11</td>
<td>n.a.</td>
</tr>
<tr>
<td>(C_{org}/C_{anorg}) [%]</td>
<td>0,343/1,4</td>
<td>0,022/0,12</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

* Parameters for classification of non-structured sediments (uniformity coefficient, coefficient of gradation, ** the clogging layer is situated in the upper layer of the filter substrate
The evaluation of the content of organic carbon from the sampling of the upper layer of the filter substrate (30 cm) during the current project provided more up-to-date values of around 0.6%, which is probably due to organic activity during three additional years of running the enclosures.

The geochemistry of the filter substrate resembles fairly well that of sand taken from the bank filtration site at the shore of Lake Wannsee, with exception of the total iron content (13 % less in the filter substrate) and the cation exchange capacity (CEC_{eff}: 82 % less in the filter substrate) [Massmann et al. 2004].

The surface water used for the experiments originates from the surrounding aquifer and is treated for iron (2.6 mg/L -> 0.007 mg/L) and manganese (313.35 µg/L -> 3.566 µg/L) in the water works of the center for aquatic simulations before being fed into the storage lake. Its high electrical conductivity (about 919 µS/cm) is due to relatively high concentrations of salts (HCO_{3}⁻: 145 mg/L, SO_{4}^{2}⁻: 234 mg/L, Cl⁻: 104 mg/L, Ca^{2+}: 118 mg/L and Na⁺: 55 mg/L) evaluated in samples taken in September 2007. Nitrate was usually not present in detectable amounts. During the experiment the pH value was around 7.85, the content of oxygen was 11.47 mg/L and the water temperature averaged 14 °C.

The experiments were carried out with a continuous application of glyphosate (1µg/L on enclosure I, 5µg/L on enclosure II and 20µg/L on enclosure III). Application started on 20th October and ended on 6th November. In preparation of the experiments the flow rate was adjusted to the desired value, corresponding to the envisaged filtration velocity of 50 cm/d. Care was taken to achieve constant flow rates during the experiment by adjusting the pump when flow rate decreased due to clogging. The changes in hydraulic conductivity could be observed by monitoring the suction pressure.

In order to evaluate the pore velocities, tracer tests were conducted from the 4th to the 9th October and during the enclosure experiment. The tracer applied was sodium chloride (1 % NaCl-solution) so that the breakthrough could be observed by measuring the electrical conductivity. Care was taken to increase the electrical conductivity by more than 50 µS/cm to obtain a signal different from the oscillations of the background electrical conductivity.

A stock solution of glyphosate and NaCl was prepared and stored in a closed storage reservoir made of stainless steel from which the dosing pumps conveyed the solution to the dosing installations and subsequently to the water reservoir of the enclosures with a constant flow rate. The different glyphosate concentrations in the enclosures were adjusted by adequate flow rates of the associated pumps. The water reservoir of the enclosures was mixed with a circulation pump to disperse the glyphosate equally. The stock solution was refilled five times during the experiment.

Samples (300 mL) were taken from the inlet and the outlet daily or twice a day from the 23rd October to 16th November 2007 except on Sundays and some Saturdays. Later the rate of sampling was reduced and on 26th November sampling was terminated. Samples from the ports at different depths (figure 21) were taken once on 6th November to check depth-dependent development of concentration. Samples from the dosing reservoir were taken daily except for weekends, but additionally before and after input of a new glyphosate and tracer stock solution. The electrical conductivity as well as other
physico-chemical parameters (pH value, redox potential, temperature and oxygen content) were measured continuously at the inlet and the outlet of the enclosures.

The interpretation of the enclosure experiments was conducted analogue to the laboratory leaching experiment.

5.2 Results

Figure 17 shows the results of the tracer tests in the beginning of October (enclosure II and III) and during the enclosure experiment (enclosure I). Because of a malfunction of the electrical conductivity probe in the former tracer test in the enclosure I, the results from the control measurement of tracer concentrations, which was conducted during the enclosure experiments was used for the evaluation of the experiment.

![Tracer breakthrough curve](image)

**Fig. 17: Tracer breakthrough curve in the outlet of the enclosure I (23.10.-26.11.07), II and III (4.-9.10.07)**

With the model VisualCXTFit the tracer breakthrough curves could be modeled, which yields to the hydrodynamic properties of the enclosure filling material as shown in table 10. The tracer breakthrough curve of enclosure I consists of few data points in comparison with enclosure II and III due to measurement by hand, which could influence especially the accuracy of the hydrodynamic dispersion coefficient of the enclosure filling.
Tab. 10: Hydrodynamic properties of the enclosures I, II and III

<table>
<thead>
<tr>
<th>Properties</th>
<th>Enclosure I</th>
<th>Enclosure II</th>
<th>Enclosure I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore velocity ( (v_p) )</td>
<td>126 cm/d</td>
<td>132 cm/d</td>
<td>133 cm/d</td>
</tr>
<tr>
<td>Hydrodynamic dispersion coefficient ( (D) )</td>
<td>343 cm²/d</td>
<td>185 cm²/d</td>
<td>231 cm²/d</td>
</tr>
<tr>
<td>Effective porosity ( (n_e) )</td>
<td>0.397</td>
<td>0.379</td>
<td>0.376</td>
</tr>
</tbody>
</table>

The glyphosate concentrations in samples taken directly from the storage reservoir showed that the stability of the stock solution was unexpectedly insufficient (see figure 18).

Fig. 18: Development of the stock solution concentration

Figure 19 and 20 show the glyphosate concentrations in the water reservoir and the outlet during the enclosure experiments.
Fig. 19: Glyphosate concentration in the water reservoir

Fig. 20: Glyphosate concentration in the outlet
The corresponding values are given in the appendix in table 19 and 20. The vertical concentration development is illustrated exemplarily for enclosure III in figure 21. The values on the left refer to the depth beneath the surface of the filter substrate.

![Glyphosate concentration graph](image)

**Fig. 21: Vertical Development of glyphosate concentration in enclosure III on 05.11.2007 (16 days after dosing commenced)**

Because the degradation of glyphosate was expected to occur the samples were also analysed for AMPA. Figure 22 to 24 show the analysed AMPA concentrations in comparison to the glyphosate concentrations in the outlet of the enclosures. The corresponding values are presented in the appendix in table 20.
Fig. 22: Glyphosate- and AMPA- concentrations in the outlet of enclosure I

Fig. 23: Glyphosate- and AMPA- concentrations in the outlet of enclosure II
Fig. 24: Glyphosate and AMPA concentrations in the outlet of enclosure III

The glyphosate concentrations in the outlets of the enclosures II and III were modelled with VisualCXTFit as it was done with the tracer breakthrough curves. On the basis of the already obtained hydrodynamic properties of the filter substrate an estimation of the retardation and degradation capacity of the filter substrate concerning glyphosate was possible.

The glyphosate concentrations in the outlet of enclosure I did not differ much from the quantification limit and showed only an irregular weak increase after day 17, as shown in figure 22. First attempts of modeling provided implausible results, so further interpretation was not carried out.

In figure 25 the results of the modelling of the glyphosate concentrations' development in enclosure II and III are presented and compared to the observed breakthrough curves.
In table 11 the parameters are shown which characterise the elimination and retardation potential of the filter substrate.

**Tab. 11: Characteristic parameters of glyphosate and filter substrate due to modelling**

<table>
<thead>
<tr>
<th></th>
<th>Pore velocity [cm/d]</th>
<th>Hydro-dynamic dispersion coefficient [cm²/d]</th>
<th>Retardation</th>
<th>Rate of degradation [1/d]</th>
<th>Reduction of maximum concentration [%]</th>
<th>Reduction of amount [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>enclosure II</td>
<td>132</td>
<td>185</td>
<td>25,0</td>
<td>0,069</td>
<td>80,71</td>
<td>80,00</td>
</tr>
<tr>
<td>enclosure III</td>
<td>133</td>
<td>231</td>
<td>18,3</td>
<td>0,092</td>
<td>78,88</td>
<td>78,68</td>
</tr>
</tbody>
</table>

It was attempted to predict the necessary length of the filter substrate in order to ensure a reduction of the glyphosate concentration starting from 3.5 µg/L (enclosure II).
and 11.6 µg/L (enclosure III) to below the European threshold for drinking water of 0.1 µg/L. The results are presented in figure 26 and 27.

**Fig. 26:** Modelling of the sufficient filtration length in enclosure II

**Fig. 27:** Modelling of the sufficient filtration length in enclosure III
5.3 Interpretation and discussion

Hydrodynamic framework in the laboratory column and the enclosures

The results of the modelling of the tracer breakthrough curves, which are presented in figure 11 and table 10 show that the model is suitable for simulating the flow conditions in the laboratory column and the enclosure. Because of data loggers in the enclosures II and III there are sufficient values for tracer concentration and the model curve approximates very closely to the observed curves with a high coefficient of determination ($R^2 = 0.998$). Although the data on the tracers’ concentration in the outlet of enclosure I consists of comparatively fewer values, the approximation of the model curve can be seen as sufficient as well ($R^2 = 0.986$).

The obtained pore velocity of the enclosure I was within the range of those obtained from the enclosures II and III. That means the effective porosities of all enclosures differs only slightly (0.376 to 0.397). The effective porosity of the filter substrate in the laboratory experiments (0.418) lies within the same range.

Against the good conformity of the effective porosities stands a high deviation between the hydrodynamic dispersion coefficients in laboratory and enclosure, taking the same filtration velocity in account.

The hydrodynamic dispersion coefficients of the enclosure I to III doesn’t differ that much and can be explained with a different number of sampling ports and the varying development of the colmation layers, due to earlier experiments as well as the filling process of the enclosures, which probably was difficult to replicate accurately. The dimension of the hydrodynamic dispersion coefficient in the laboratory column is extraordinary (see 4.4 Leaching experiment).

It can be expected, that the higher value in the enclosures corresponds to the stratification of gravel, sand and organic material and a greater filter length, while the filter substrate in the short laboratory column doesn’t contain gravel and is homogeneously mixed.

Glyphosate inlet concentrations

The target of providing a continuous and constant concentration of 500 µg/L in the storage reservoir could not be achieved. Along with strong fluctuations (measured values ranged from 200 to 510 µg/L) only an average concentration of glyphosate around 360 µg/L, which means 20 % of the average concentration. These fluctuations are probably the reason for the fluctuations of the concentrations measured in the water reservoir of the enclosures. A first indication is the equally shaped concentration development in enclosure III, when compared to the concentration in the storage reservoir. In enclosure II und I those coherences are less obvious, probably due to lower concentrations. However, the ratios of standard deviation and average are also around 20 %. That means the reduction of observed inlet concentrations compared to planed inlet concentrations is caused in the storage reservoir by reasons which could not be explained sufficiently, yet.

Adsorption of glyphosate on the walls of the storage reservoir should be negligible, because it is not expected that glyphosate adsorb to stainless steel. Formation of
complexes with solved or particularly distributed ingredients would be cracked by sample preparation. It therefore seems that glyphosate is exposed to a degradation process. That could be proved by the step in the concentration curve between those values from samples taken directly before and after recharge and mixing of the stock solution. After adding new stock solution with a concentration of 500 µg/L the mixed concentration increases definitely. But the degradation path is uncertain. Photolysis und thermal decomposition can be excluded under storage conditions. In solution glyphosate should be stable (see table 1). Obviously small amounts of microorganisms due to addition of treated groundwater from the waterworks should not be responsible for remarkable microbiological degradation. However, high contents of AMPA up to 180 µg/L could be analysed. This observations offer new questions to research.

Fate of glyphosate in the enclosures and comparison to the results of the laboratory experiments

The retardation coefficients obtained from the enclosure experiments exceeded those expected from the literature study – though not as far as those, which were obtained from the laboratory experiments. In the outlet of enclosure III, which was spiked with the highest concentration of glyphosate the complete breakthrough curve could be observed (see figure 24). In the outlet of enclosure II only the increase, possibly even the climax of the glyphosate breakthrough curve could be detected. The shape of the decreasing part of the curve remains uncertain.

The glyphosate concentration in the outlet of enclosure I fluctuated around the quantification limit of the analytic method. The detected concentrations might support a weak increase.

With that the enclosure experiments affirm the results of the laboratory experiments in so far as the adsorption behaviour is linked to concentration and the retardation decreases with increasing concentrations. However the retardation factors evaluated in the laboratory experiments differed remarkably from those observed in the enclosure experiments.

The modelling of the glyphosate breakthrough curves observed in enclosure III and II provided a retardation coefficient of 18.3 and 25, respectively (table 11). These retardation coefficients range far below those calculated on the basis of the laboratory experiments which amounted to around 54 for 20 µg/L (table 8) and more for lower concentrations.

For this deviation a systematic reason could be responsible. In the batch experiments conditions for adsorption are idealistic. Due to an optimal mixing definite equilibrium relations are possible in batch experiments. The probability of contacts is higher, which leads to greater amount of bindings. In addition, the amount of binding sites in the enclosures is reduced by permanent contact of the filter substrate grains at their touch points [Fehse 2004].

The modelling of the degradation rates in the enclosure II and III results in 0.069 d⁻¹ and 0.092 d⁻¹, respectively. Their half-lives of 10 d and 7.5 d, respectively match good the values mentioned in the literature (see table 1).
In comparison with the rate of degradation in the laboratory experiment (0.023 d\(^{-1}\)) the values obtained from the enclosures are higher. The difference is probably based on different conditions of the experiments: In the enclosures an environment is established with high content of oxygen, while in the degradation experiment in the laboratory partly sub-oxygenic conditions could be observed. The degradation of glyphosate is suspected to be faster under aerobic conditions (see table 1). Secondly, the substance transport in the enclosure experiment is dominated by convection and dispersion, while in the degradation experiment mainly diffusion is responsible for the distribution of the glyphosate.

Table 12 gives an overview of half-lives of selected trace organics present in groundwater (as a result of managed aquifer recharge – bank filtration or aquifer storage and recovery) as published elsewhere. They show very high variations between only a few hours for the cyanobacterial toxin microcystin up to decades for some persistent pharmaceuticals as carbamazepine. Compared to the persistent pharmaceuticals, the half-lives obtained for glyphosate in the enclosure experiments are two orders of magnitude lower. Keeping in mind that there may be limited removal under anoxic conditions (see degradation experiments) glyphosate would be classified as “well removable” or “redox-depentantly removable” according to the classification of Wiese et al. (2009).

Table 12: Overview of half-lives of selected trace organics present in groundwater as a result of managed aquifer recharge.

<table>
<thead>
<tr>
<th>Substance</th>
<th>degradation rate (h(^{-1}))</th>
<th>degradation rate (d(^{-1}))</th>
<th>half life (h)</th>
<th>half life (d)</th>
<th>Environment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microcystins</td>
<td>0.17</td>
<td>4.1</td>
<td>0.17</td>
<td>oxic, Sand, enclosure, UBA</td>
<td>Grützmacher et al. (2006)</td>
<td></td>
</tr>
<tr>
<td>Microcystins</td>
<td>0.04</td>
<td>17.3</td>
<td>0.72</td>
<td>oxic, Sand, enclosure, UBA</td>
<td>Grützmacher et al. (2006)</td>
<td></td>
</tr>
<tr>
<td>Microcystins</td>
<td>0.05</td>
<td>13.9</td>
<td>0.58</td>
<td>oxic, Sand, enclosure, UBA</td>
<td>Grützmacher et al. (2006)</td>
<td></td>
</tr>
<tr>
<td>Microcystins</td>
<td>&gt; 7300</td>
<td>anoxic, dune infiltration, NL</td>
<td></td>
<td></td>
<td>Stuyfzand et al. (2008)</td>
<td></td>
</tr>
<tr>
<td>MTBE</td>
<td>&gt; 9999</td>
<td>anoxic, dune infiltration, NL</td>
<td></td>
<td></td>
<td>Stuyfzand et al. (2008)</td>
<td></td>
</tr>
<tr>
<td>Bentazone</td>
<td>&gt; 2200</td>
<td>anoxic, dune infiltration, NL</td>
<td></td>
<td></td>
<td>Stuyfzand et al. (2008)</td>
<td></td>
</tr>
<tr>
<td>Phenols</td>
<td>2-5</td>
<td>aerobic, sand, in-situ, Serbia</td>
<td></td>
<td></td>
<td>Dimkic et al. (2008)</td>
<td></td>
</tr>
<tr>
<td>Glyphosate</td>
<td>0.07</td>
<td>9.9</td>
<td></td>
<td>oxic, Sand, enclosure II, UBA</td>
<td>TRACE project (2008)</td>
<td></td>
</tr>
<tr>
<td>Glyphosate</td>
<td>0.09</td>
<td>7.7</td>
<td></td>
<td>oxic, Sand, enclosure III, UBA</td>
<td>TRACE project (2008)</td>
<td></td>
</tr>
</tbody>
</table>

The reduction of glyphosate in the enclosures is mainly due to degradation by microbiological activity. Other degradation processes should be negligible. Those degradation processes in the storage reservoir probably due to conditions in free water. In soils only microbiological processes are reasonable for degradation of glyphosate [Borggaard & Gimsing 2008]. The only abiological degradation path which is mentioned requires manganese oxide Birnesite [Barrett & McBride 2005], but there was very little manganese oxide in the virgin filter substrate and that should not have changed because the experiment water is treated by reducing manganese.

Although the organic material which was expected to be concentrated in the colmation layer and very important for retardation and degradation of glyphosate, the analysis of the vertical distribution of glyphosate (figure 21) shows that the reduction of the concentration is distributed evenly along the depth.
In this research the analysis of one of the main metabolites (AMPA) can only be an indication for degradation of glyphosate. The data base does not allow including AMPA into the balance calculation of input and output of glyphosate. The concentration breakthrough curves of AMPA are not that definite in their development and the model VisualCXTFit is not able to determine degradation rate and production rate at once on the basis of a breakthrough curve.

Conclusion

The enclosure experiments showed that although there is a significant reduction of glyphosate, the outlet concentrations of glyphosate still exceed the threshold value for herbicides in European drinking water.

It is possible to use the model VisualCXTFit for an estimate of a sufficient filter length, which theoretically would be sufficient to reduce the glyphosate outlet concentration under the permitted maximum of 0.1 µg/L. In figure 26 a glyphosate concentration of around 3.5 µg/L (enclosure II), which seems to be in the range of maximum concentrations in Berlin and its surrounding areas (see figure 3 and 4), could be decreased below the threshold with a filter length of 2.75 m. The extreme case of 11.6 µg/L (enclosure III) seems to be resolved with a filter length of 3.75 m (see figure 27). To consider aspects of uncertainty about the development of retardation and degradation by increasing the length of the enclosure a simulation of the filter length necessary for a reduction of the input concentration down to 0.01 µg/L was conducted. These values would provide a safer estimation of the needed filter length for sufficient reduction of glyphosate. The calculated lengths would extend to 4.25 m for enclosure II and to 5.5 m for enclosure III.

Those predictions have to be checked in further experiments, with which the theoretical results have to be proved in practice.
Chapter 6
Lysemeter experiments

6.1 Method and Materials

In order to observe the unsaturated migration behaviour of glyphosate on a technical scale in mature layered soil under the influence of local climatic events lysemeter experiments were carried out on the grounds of the Federal Environment Agency. Using these experiments as an intermediate stage between laboratory and field investigations means that the displacement of glyphosate can be observed under conditions close to those obtaining in nature without elaborate control measures and technical interventions.

For the experiments the commonly used herbicidal formula from the Scotts Celaflor Company ROUNDUP® LB Plus Unkrautfrei, whose active ingredient is glyphosate, was used to simulate the agricultural application in soil preserving cultivation techniques. The product contains 360 g/L glyphosate in the form of isopropyl salt. Potassium bromide was used as a tracer to determine the pore velocity of the leachate, the concentrations of which were monitored via a bromide electrode. A comparison of the breakthrough velocities of glyphosate and the tracer could be used to make statements about the adsorptive degradative behaviour.

The following system sketch (figure 28) shows the gravity lysemeter and its components.

![Diagram of lysemeter](image)

1 = equilibrium vessel
2 = water reservoir
3 = valve
4 = leachate vessel
5 = lysemeter scale
6 = scale for the weighing of leachate volume
7 = water column corresponding to the unsaturated flow (63 cm, pF 1.8)
8 = soil monolith

Fig. 28: Principle sketch of a lysemeter (2m in height, 1m² surface area)
The soil material of both lysemeter is a sandy brown soil, which was extracted in 1979 in the sewage fields of Gatow in Berlin from layered sediment of the boulder marl upland area around Nauen [Ahlsdorf 1991]. The soil was extracted in 2 cm layers, packed into bags and introduced into the lysemeter and compacted in a way consonant with its natural bedding conditions. By this means conditions similar to those obtaining in the original location could be recreated.

In the topsoil of approximately 50 cm the content of C$_{org}$ is high (4%). The fine-to-medium grained sand fraction is responsible for the hydraulic characteristics of the soil. The content of clay is comparatively low (less than 5%). The field capacity is 12 % of the pore volume and the pH value is around 5.7. At the time of spiking the lysemeter were covered with grasses and herbaceous, perennial, deeper rooted plants. The past 28 years have seen experiments carried out with these lysemeters with the primary aim of determining the regeneration of groundwater, with the additional aim of carrying out investigations into the migratory behaviour of bisphenol-A, atrazine, dichlorpropene, aldicarp and phthalates.

In the TRACE experiment samples were extracted from the lysemeters for 7 ½ months from 14.06.2007 to 03.01.2008. Climatic factors throughout the course of the year are given in the appendix in figure 43. During the experiment a total of 444 mm precipitation was recorded (approx. 80 % of total annual precipitation). The figure given by Haude for total evaporation of 361 mm yields a positive water balance and a theoretically estimated leachate amount of 83 mm.

On 14th June a bromide tracer was applied in two lysemeter. 50 g potassium bromide (KBr) were dissolved in 5 L deionised water and was spread evenly across the surface of each lysemeter, using a watering can. After infiltration of the dissolved tracer each lysemeter was irrigated with 5 L pure deionised water to wash the potassium into the lysemeter to avoid unwanted interactions with glyphosate. The day after the herbicide was sprayed evenly with a vaporizer onto the lysemeter’s surface. Glyphosate was applied on lysemeter Nr. 18 with the recommended dose of 10 L/ha (e.g. 3.6 kg glyphosate/ha). Therefore 1 mL ROUNDUP® LB Plus Unkrautfrei (e. g. 3.6 g glyphosate) was diluted within deionised water in order to apply 300 mL fluid on the 1 m$^2$ surface area of the lysemeter. On lysemeter Nr. 17 a 10 times higher dose of 10 mL (e.g. 36 g glyphosate) was applied. This high application rate was chosen to simulate an overlapping of tractor tracks, cleaning of the herbicide tanks on the fields or an overdosing due to false adjustment of dosing mechanism or careless application by users and to evaluate the effects. This exceeding of the recommended maximum amount is associated with a very low level of risk as far as the experiment is concerned, as the lysemeter are completely separated from the natural soil-groundwater system.

In Europe a maximal dose of 4.32 kg glyphosate/ha (e.g. 12 L /ha) is permitted. According to [Viehweger G. & Danneberg H. 2007] 17.3 kg glyphosate/ ha are allowed in the United States of America. So the glyphosate load of 36 kg/ha at lysemeter Nr 17 is approx. double the rate which is permitted in the U.S.A. For a better comparison of the two lysemeter the herbicide-water solution was sprayed on both lysemeter in the same manner, as it is shown in figure 29.
During spiking, there was little wind, meaning that the drift was minimal but not negligible. Heavy rain only set in around 14 hours after the spiking was carried out. According to the producers’ instructions there should be no exposure to rain in the first 4 hours so that the glyphosate cannot be washed off the plants and the full effect can be attained, as shown in figure 30.

Sampling was initiated four days after the start of the experiment using glass flasks. The sampling routine complied with the natural hydro-meteorological conditions, but at least three times per week. The samples were selected according to the bromide concentration in the effluent. Shorter sampling intervals after the breakthrough of the bromide tracer should enable a good reproduction of glyphosate and its main metabolite AMPA in the outlet of the lysemeter. The conductivity was measured immediately. The
sampling bottles (300-400 mL) were stored in deep freezers for the later analysis of tracer, glyphosate and AMPA concentrations.

6.2 Results

Figure 31 shows the results of flow rate measurement in comparison with heavy rain events.

Fig. 31: Diurnal cycle of lysimeter discharge and precipitation

Figure 32 shows the comparison of the tracer breakthrough curves in the observed lysimeter.

Fig. 32: Tracer (potassium bromide) concentration progression
The following diagrams (figure 33 and 34) illustrate the measurements of glyphosate- and AMPA- concentrations in the lysimeter discharge samples.

**Fig. 33: Glyphosate- and AMPA- values in the discharge from lysimeter 17**

**Fig. 34: Glyphosate- and AMPA- values in the discharge from lysimeter 18**
The corresponding values for figure 33 and 34 are presented in the appendix in table 21.

6.3 Interpretation and discussion

The results of the bromide and flow rate measurements yield hydraulic differences between the two lysimeter used in the experiment. Lysimeter 18 shows a higher total discharge-320 L - than that of 245 L in lysimeter 17.

Although the two lysimeter were filled using the same type of soil and layer system, lysimeter 18 seems to possess a higher proportion of flow-through promoting coarse pores, resulting in a higher level of hydraulic permeability. The water retention of lysimeter 17 is assumed to be higher.

Figure 31, depicting the time-dependent flow rate, shows that lysimeter 17 is less susceptible to fluctuations in discharge due to heavy rain events.

The comparison of the potassium bromide flow-through curves in the two lysimeter shows an earlier increase in lysimeter 18 and an earlier attainment of maximum concentration. It is probable that the tracer in lysimeter 17 remains longer within the system.

These observations allow to conclude that the coarse pores in lysimeter 18 have a strong influence on the flow rate due to the fact that they create preferential flow paths, whereas in lysimeter 17 the introduced substances are transported both in medium-coarse and coarse pores (matrix flow), which would explain the longer retention time in the system.

The Glyphosate- and AMPA- concentration progressions, which are shown in figure 33 and 34 make it clear that both the glyphosate and the AMPA concentrations are below the quantification limits, 0.07 µg/L and 0.02 µg/L respectively, of the selected analytical method, besides few outliers, meaning that no breakthrough of the herbicidal agent or its metabolite is recorded under the conditions described.

The approximate observation of the water balance in the experimental period and the tracer breakthrough both show that the hydro-meteorological experimental conditions would be sufficient to allow a breakthrough of glyphosate and AMPA.

But the AMPA concentrations in the TRACE lysimeter experiment did not at any time exceed the quantification limit of 0.02 µg/L. The mean glyphosate concentrations are above those for AMPA but rarely reach their quantification limit, too. Presenting replicated measurements, may lead to a reassessment of the recorded maximum glyphosate measurements. The apparent statistical outliers which show glyphosate quantities above the quantification limit cannot be correlated, at least not without ambiguity, with the heavy rain events observed during the experimental period.

The preferential flow paths opened up by coarse pore flow, wall effect or root paths do not seem to have any influence on the breakthrough of the contaminants at the recommended dosage level of the herbicide, as is shown by the test arrangement in the case of lysimeter 18.

The lysimeter experiments show that, in the case of noncultivated soil with a thickness of 2 m in the given weather conditions, under the extreme conditions of a tenfold
concentrated herbicide application and an undisturbed matrix flow, there is no risk of groundwater contamination with Glyphosate or AMPA within seven months.

In comparison with investigations using lysimeter of up to 1.5 m of thickness with maximum concentrations of “Round up” of 10 L/ha and a mean annual precipitation of 1000 mm, were able to measure no glyphosate at all and only 0.07 µg/L AMPA in the discharge. The AMPA concentration maxima arose in conjunction with a heavy rain event. [Stadlbauer et al. 2005]

In addition no conclusions can be drawn from the Trace lysimeter experiments, whether or when glyphosate or AMPA break through. For such statement to be made the progression of glyphosate and AMPA concentration over the whole height of the lysimeter would be necessary, which could not be measured under the conditions in which the experiment took place. Because there is no contaminant breakthrough it is impossible to estimate under which conditions glyphosate was bonded or degraded. It would merit further investigation to see whether, under the influence of preferential flow paths, the increased concentration might pose a risk to groundwater.

The absence of glyphosate or AMPA in the discharge after an experimental period of 7.5 months, the high retention time of water in the soil, the high level of glyphosate retardation in the enclosure experiments, as well as the high content of organic substance in the upper soil and the associated microbiological activity lead to the belief that the danger of groundwater contamination after a soil passage of 2 m is remote.
Chapter 7
Summary and Conclusion

General aspects

In the initial phase of the project ‘Organic Trace Substances Relevant for Drinking Water – Assessing their Elimination through Bank Filtration (TRACE)’ the total herbicide glyphosate was classified as highly relevant for further investigations. Glyphosate is one of the most widely used and distributed herbicides in the world. It is applied in agriculture, forestry, water management and in urban areas. Its herbicidal effect was observed already in 1972 and it has been on the market since 1974. Its use increased with the expiry of the patent at the beginning of the 1990s, in the context of “soil conserving” agriculture (no ploughing) and with the introduction of glyphosate resistant, genetically manipulated plant cultures like corn, soy beans and cotton wool in 1997.

According to the initial literature review within the TRACE project maximum glyphosate concentrations of up to 1,700 µg/L had been found in surface water worldwide. To estimate the occurrence of glyphosate and its main metabolite AMPA in the surroundings of Berlin samples of 22 surface water sites were analysed within this study. In 5 samples the glyphosate concentration was above the European threshold for herbicides in drinking water of 0.1 µg/L. The highest observed value was approx. 0.5 µg/L in the channel Teltowkanal (Böckmannbrücke) in the south-west of Berlin. At this sampling point the highest observed AMPA concentration of 3.4 µg/L was measured, too. In the river Havel in Potsdam, south-west of Berlin, a glyphosate concentration of 4.6 µg/L had been observed by a sampling routine carried out by the local environmental agency (LUA) in 2005.

The second phase of the TRACE project focused on the potential of bank filtration to protect drinking water from glyphosate contamination. Three enclosures (filter columns with 1 m² surface area and 1.25 m filter depth) at the UBA’s center for aquatic simulations in Berlin, Marienfelde were used to evaluate glyphosate elimination and retardation on a semi-technical scale. Preliminary tests showed that all enclosures had comparable hydraulic conditions. A system to adjust the flow rate to a constant filtration velocity of 0.5 m/d and to constantly dose a glyphosate stock solution in the water reservoir of the enclosures was established. Three different concentration levels were dosed over a time period of 14 days. The effluent was sampled daily for 34 days.

To analyse glyphosate and AMPA gas chromatographic (GC) as well as liquid chromatographic (LC) methods were tested in parallel for their applicability under the conditions in the project TRACE. The HPLC method according to the German Standard DIN 38407-22/2001 gave satisfying results while it was not possible to increase the sensitivity of the GC method within the given time schedule. In addition the method of Enzyme Linked ImmunoSorbent Assay (ELISA) was tested to analyse glyphosate on the basis of an antibody reaction. The results were, however, not satisfying, so the HPLC method was used for analyzing the samples from the conducted experiments.
Enclosure experiments

Even though the stock solution (planned concentration level of about 500 µg/L) was refilled 3 times a week, the stability was unexpectedly insufficient. High contents of AMPA of up to 180 µg/L were analyzed and lead to the conclusion that even though photolysis and thermal decomposition can be excluded under the storage conditions degradation processes took place. This and additional elimination processes in the water reservoir of the enclosure columns caused an average dosing concentration of 70 % of the initially planned concentrations. Thus the average dosing glyphosate concentrations for the 14 days of dosing were 0.7 µg/L (enclosure I), 3.5 µg/L (enclosure II) and 11.6 µg/L (enclosure III). Due to the low adsorption potential of the sandy filter material (medium to coarse sand with small amounts of fine sand, no silt and clay present) the glyphosate breakthrough had been expected earlier than observed. The maximum glyphosate concentration in the effluent of enclosure III was reduced to 2.7 µg/L, detected 20 days after the beginning of the experiment, which means less than 25 % of the initially dosed glyphosate concentration (11.6 µg/L). In enclosure II the maximum glyphosate concentration in the outlet was observed on the 30th day after the beginning of the experiment with 0.7 µg/L (20 % of the dosed concentration). The glyphosate concentrations in the outlet of enclosure I was in the range of the quantification limit and only an irregular weak increase was recorded over the 34 days of sampling, with a maximum value of approx. 0.15 µg/L (21 % of the amended glyphosate concentration) 34 days after the beginning of the experiment.

Although the organic material which was thought to be very important for retardation and degradation of glyphosate was expected to be concentrated in the colmation layer the analysis of the vertical distribution of glyphosate (figure 21) showed that the reduction of the concentration was distributed evenly throughout the depth of the enclosure.

The AMPA concentrations reached a maximum value of 1.4 µg/L (enclosure III), 0.4 µg/L (enclosure II) and 0.09 µg/L (enclosure I) during the experiments. Only in enclosure III a distinctive decrease of the AMPA concentration after the maximum on the 20th day was recorded.

Additional laboratory and lysemeter experiments

Additionally to the semi-technical scale enclosure experiments laboratory and lysemeter tests were conducted to complement and broaden the knowledge on the behaviour of glyphosate during the subsurface passage. For comparability reasons sediment out of the surrounding slow sand filter was used. This material had the same origin and had been exposed to comparable conditions as the filter material within the enclosures itself.

The adsorption isotherm was determined for glyphosate concentrations of 0.1, 1, 10 and 100 mg/L. The reaction time in the batch experiment was 4 h and the temperature during the adsorption experiment remained at constantly 20°C. As described in the literature the Freundlich adsorption isotherm represents the temperature- and concentration-dependent behaviour of the glyphosate between the solid matrix and the fluid phase. A Freundlich distribution coefficient of $1.8998 \text{ mg}^{-1/2} \cdot \text{L}^{1/2} \cdot \text{kg}^{-1}$ or
and the Freundlich exponential of 0.4805 were determined ($R^2=0.964$). Thus the partition of glyphosate in the mobile and the solid phase of the sediment clearly depends on the total concentration. The decrease of adsorption at higher concentrations can be explained by a saturation of the available binding sites. Hence for the lowest input concentration an adsorption of 86 to 87% and for the highest input concentration an adsorption of only 6 to 7% were observed. As supposed the sandy filter material proved to have a minor adsorption capacity compared to other materials. Published values for the Freundlich partition coefficient of glyphosate are in average higher (see table 1). But those soils with high values for $K_F$ (e.g. 33-76 [Glass 1987], 13.8-152.9 [Piccolo et al 1994] or 37-303 [Autio et al. 2004] had higher contents of adsorption enhancing components (e.g. iron and aluminium oxides, organic material) than the examined filter substrate in the experiments of the project TRACE. Nevertheless, for environmentally relevant glyphosate concentrations (EU threshold for drinking water of 0.1 µg/L and examined concentrations in the enclosure experiments of 1 – 20 µg/L) the adsorption capacity of the filter substrate is assessed to be considerable.

To determine the degradation rate under environmental conditions close to groundwater a degradation experiment was conducted. The experimental vessels were stored at a temperature of around 8°C. They were protected from light and atmosphere exchange to establish partly reduced conditions. Two duplicates were analyzed after 4 hours and after 7, 14, 21, 28 and 73 days. The prompt decrease of glyphosate concentration in the solvent from the input concentration of 25 mg/L to 15 mg/L (after 4 h) could be explicated by adsorption. With reference to the adsorption experiment 40% adsorbed glyphosate seems to be quite high which might be explained with higher binding sites due to a relatively higher ratio of filter substrate and solvent. According to the obtained first order kinetic degradation curve a degradation rate of 0.0227 d$^{-1}$ was calculated. 50% of the glyphosate was degraded within 30.5 days and an extrapolation of the curves yielded that 90% of glyphosate would be degraded within 101.5 days. However, according to the results of a filter substrate extraction after the degradation experiment another interpretation of the glyphosate reduction in the solution is proposed. Thus, adsorption continued remarkably during the experiment and due to a balance calculation glyphosate degradation under the experiment’s conditions has to be questioned.

To estimate the retardation of glyphosate in the filter substrate a leaching experiment was conducted under laboratory conditions. The same glyphosate concentration as initially planned in enclosure III (20 µg/L) was continuously dosed over a time period of 3 h. Within this time six fold pore volume were exchanged and the hydrodynamic parameters of the filter substrate were determined on the basis of the tracer breakthrough. In the effluent of the glass column no increase in glyphosate concentration could be detected. Because the results of the adsorption test were not available before the leaching test the following calculation could not be used to plan it. Estimating the retardation coefficient for the leaching experiment, according to the Freundlich coefficients observed in the adsorption experiment a value of 53.4 was calculated. This means that for a concentration of 20 µg/L the breakthrough of glyphosate had to occur approx. after 1 d. Hence the duration of the leaching test (3h) was not sufficient.
Modelling results

The one-dimensional substance transport model VisualCXTFit was applied to obtain substance specific parameters of glyphosate and hydrodynamic parameters of the filter substrate from observed data of the laboratory and semi-technical scale experiments. The substance specific parameters of glyphosate obtained from modelling with VisualCXTFit could serve to simulate elimination and retardation processes under natural conditions to forecast the development of glyphosate concentrations in reality. The effective porosity values ($n_e$) of the three enclosures (0.376, 0.379 and 0.397) and of the filter substrate in the laboratory experiment (0.418) did not differ much. Against a good conformity of the effective porosities stood a high deviation between the hydrodynamic dispersion coefficients in the laboratory ($86 \text{ cm}^2/\text{d}$, $\nu_P = 759 \text{ cm/d}$) and in the enclosures (enclosure I: $343 \text{ cm}^2/\text{d}$, enclosure II: $185 \text{ cm}^2/\text{d}$ and enclosure III: $231 \text{ cm}^2/\text{d}$, $\nu_P = 126, 132$ and $133 \text{ cm/d}$, respectively). It was supposed, that the higher values in the enclosures were due to the stratification of gravel, sand and organic material and a greater filter length, while the filter substrate in the short laboratory column did not contain gravel and was homogeneously mixed.

Modelling of the glyphosate breakthrough curves observed in the enclosures II and III provided a retardation coefficient of 25 and 18.3, respectively. Enclosure I could not be considered due to uncertain results caused by glyphosate concentration near the quantification limit. Thus, the enclosure experiments affirm the results of the laboratory experiments in so far as the adsorption behaviour of glyphosate is linked to concentration. The retardation decreased with increasing concentrations. However, the retardation factors observed in the enclosure experiments range far below those calculated on the basis of the laboratory experiments (53.4 and higher). This could be explained by the idealistic conditions during the laboratory adsorption test (e.g. homogeneous mixing of sand and water). In addition the amount of binding sites in the enclosures is reduced by permanent contact of the filter substrate grains at their touch points [Fehse 2004].

The modelling results in a degradation rate of $0.069 \text{ d}^{-1}$ (enclosure II) and $0.092 \text{ d}^{-1}$ (enclosure III). The half-lives of $10 \text{ d}$ and $7.5 \text{ d}$, respectively match well the values mentioned in the literature with $2 ... 14 \text{ d}$ for aerobic conditions (see table 1).

The difference between the glyphosate degradation in the enclosures and in the laboratory experiment ($0.023 \text{ d}^{-1}$) is not really clear. Ascribed to different environmental conditions, like oxygen content and distribution kinetics it is uncertain, which influence unfavourable conditions for metabolism and remarkable continuous adsorption have on the deceleration of degradation in the laboratory experiment. Those processes should be investigated more detailed in further investigations, because they could be important for the retardation and degradation of glyphosate under partly oxygen reduced and stagnant conditions.

The results show that although there is a significant reduction of the concentrations and the amount of glyphosate after the passage of the enclosures, the threshold for drinking water is exceeded after the short passage of 1.25 m. Using the obtained model parameters the theoretically required filtration length that is necessary to reduce the concentrations below the permitted limit of $0.1 \mu\text{g/L}$ was calculated. For the conditions in enclosure II 2.75 m and in enclosure III 3.75 m filter length would be sufficient.
In this research the analysis of AMPA, one of the main metabolites of glyphosate, could only be an indication for the degradation of glyphosate. The data did not allow including AMPA into the glyphosate balance. No modelling of AMPA concentrations was possible because firstly the concentration breakthrough curves for AMPA were not that definite in their development and secondly the model VisualCXTFit was not able to determine degradation rate and production rate at once on the basis of a breakthrough curve. Further studies should be conducted about the behaviour of AMPA, because it can deliver more information about the fate of glyphosate.

Adsorption and degradation parameter obtained in the different experiments emphasise the need to conduct semi-technical experiments to evaluate risks in a near-natural environment. Laboratory experiments can only complement the knowledge about the fate of glyphosate.

Lysemeter observations
To evaluate the risk of groundwater pollution over soil passage the commercial formula ROUNDUP® LB Plus Unkrautfrei, whose active ingredient is glyphosate, was applied on two lysemeter at the UBA’s center for aquatic simulations. At one lysemeter the recommended dose of 10 L/ha (e.g. 3.6 kg glyphosate/ha) and at the other a 10 times higher dose of 10 mL (e.g. 36 g glyphosate) was applied on 14.06.2007. In Europe a maximal dose of 4.32 kg glyphosate/ha (e.g. 12 L/ha) is permitted, but in the US 17.3 kg glyphosate/ha are allowed. Therefore the glyphosate load of 36 kg/ha at the second lysemeter is approx. double the rate which is permitted in the US. This high application rate was chosen to evaluate the effects of overlapping tractor tracks, cleaning of the herbicide tanks on the fields or an overdosing due to false adjustment of dosing mechanism. No breakthrough of glyphosate or its metabolite AMPA was recorded under the conditions described. Only few measurements could be observed above the quantification limit (outliers: glyphosate on the 1st and 63th d and AMPA on the 176th d). The lysemeter study shows that the retardation potential of an uncultivated sandy soil with a high content of organic carbon and a thickness of 2 m is sufficient to protect groundwater from a glyphosate or AMPA contamination within seven months.

Vulnerability of bank filtration sites to glyphosate breakthrough
The data obtained in this project proves that there is a potential of bank filtration to eliminate the herbicide glyphosate. For the observed environmental concentrations in Berlin a high retardation and additional degradation has been recorded for sandy filter substrate as a “worst-case” with low adsorptive capacity. Taking into account that glyphosate concentrations in surface water are highly variable and do not exceed the threshold of glyphosate in drinking water continuous mixing with uncontaminated bank filtrate and ambient groundwater will additionally provide a good protection of the drinking water source. The experiments showed also that the elimination potential is limited if regarding higher concentrations of glyphosate. At those concentrations a decrease of the filter substrate’s retardation capacity is expected and therefore an insufficient elimination due to a lack of time for degradation by microorganisms.

Final conclusion
The experiments carried out during this research project cover the behaviour of glyphosate in a broad spectrum of different subsurface environments. The results can help to assess the risk of drinking water contamination by glyphosate for sites that use bank filtration as treatment technique and to deduce precautions in order to secure drinking water supply.

Due to the knowledge about retardation and degradation of glyphosate from the enclosure experiments an analysis of different scenarios for the bank filtration sites in Berlin can be conducted. On the other hand it has to be kept in mind that there are hydrochemical and hydrological differences between the enclosures and the bank filtration sites.

For this comparison the three field sites of the NASRI project [Pekdeger et al 2006] were selected. In table 12 characteristic parameters are presented which reflect the differences between the semi-technical scale enclosure and the fieldsites. It has to be noted that the Berlin situation is characterized by comparatively fine sediments, low flow velocities and mainly anoxic to anaerobic conditions.

<table>
<thead>
<tr>
<th>Site</th>
<th>Enclosure III</th>
<th>Infiltration pond Tegel</th>
<th>Bank Filtration Site Lake Tegeler See</th>
<th>Bank Filtration Site Lake Wannsee</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil type</td>
<td>Medium to coarse sized sand</td>
<td>Medium to coarse sized sand</td>
<td>Medium sized sand</td>
<td>Fine to medium sized sand</td>
</tr>
<tr>
<td>Filtration length [m]</td>
<td>1.25</td>
<td>220</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>Pore velocity [m/d]</td>
<td>1.33</td>
<td>4.4</td>
<td>0.98 (average)</td>
<td>0.63 (average)</td>
</tr>
<tr>
<td>Dispersion length [m]</td>
<td>0.0175</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Dispersion coefficient [m²/d]</td>
<td>0.0233</td>
<td>&lt;4.4</td>
<td>&lt;0.98</td>
<td>&lt;0.63</td>
</tr>
<tr>
<td>Content of iron oxides [g/kg]</td>
<td>0.3-0.6</td>
<td>1-2</td>
<td>1-2</td>
<td>0.2 - 1</td>
</tr>
<tr>
<td>Content of organic carbon [%]</td>
<td>0.6</td>
<td>0.02 – 0.16</td>
<td>0.02 – 0.08</td>
<td>0.1 - 2</td>
</tr>
<tr>
<td>Redox zone</td>
<td>Aerobic</td>
<td>Aerobic - anaerobic</td>
<td>Aerobic - anaerobic</td>
<td>Aerobic - anaerobic</td>
</tr>
</tbody>
</table>

The simulation of glyphosate elimination in the field sites with the concentrations applied in the enclosure experiments showed, that the risk of glyphosate contaminations in the bank filtrate is very low (figure 35-37):
Fig. 35: Virtual glyphosate elimination by bank filtration (Lake Wannsee)

Fig. 36: Virtual glyphosate elimination by bank filtration (Lake Tegeler See)
The glyphosate concentrations would fall below the European threshold for drinking water (0.1 µg/L) in the bank filtration sites of Lake Wannsee and Tegel and of the infiltration ponds in Tegel after 4 m, 6 m and 14 m, respectively. That means that only 8%, 6% and 6.4% of the total filtration length would be needed for the sufficient elimination of glyphosate.

It has to be considered that the parameters for retardation and degradation used in the simulation refer to the filter substrate in the enclosures. On the one hand the content of iron in the bank filtration sites, responsible for adsorption, is higher than in the enclosures which should promote retardation and consequently degradation. On the other hand the redox potential changes from aerobic (first 5-10 meters) to anaerobic (deeper regions of the aquifer), while the enclosures are completely aerobic. Anaerobic conditions are said to be unfavourable for degradation of glyphosate and results in a slow down of its metabolization by microorganisms (see table 1).

However, this deviation between the filter substrates of the bank filtration sites and the enclosures seems to be negligible taking into account the strong influence of the filtration length. The awareness that at most 8% of the available maximum filtration length would be needed for sufficient aerobic degradation, it can be suspected that even under anaerobic conditions with two to seven times slower degradation processes (see table 1) and considering dilution processes by mixing with uncontaminated waters in the underground a sufficient reduction of glyphosate can be expected. The distance between entrance of the surface water into the underground and its entrance into the wells seems to be long enough to reduce glyphosate in the bank filtrate as it is demanded by the
European drinking water threshold for herbicides. Therefore the risk for breakthrough of 
glyphosate to Berlin’s drinking water is rated as low.

Nevertheless the need for further experimental researches is given, because the 
results from the present study, have shown, that there are some uncertainties about the 
behaviour of glyphosate. Field studies concerning the filtration lengths for sufficient 
reduction of glyphosate and AMPA, retardation behaviour of glyphosate and AMPA and 
elimination potential of filter substrates under the influence of competitors for binding 
sites or different environmental conditions could provide further interesting results, as 
well as experiments under anoxic and anaerobic conditions.

Glyphosate’s ubiquitous occurrence in the environment, a steady increase of applied 
quantities of the herbicide, as well as not yet completely understood mechanisms of 
environmental behaviour and the indirect impact of glyphosate on ecosystems demands 
an observation of changes in the potential of bank filtration sites for the elimination of 
glyphosate in the future. This will be necessary to guarantee a long-term use of the bank 
filtration as treatment technique for surface water.
Chapter 8
Appendix

Fig. 38: Glyphosate concentrations in the River Havel (2004-2006)
Tab. 13: Concentrations of herbicides and their metabolites in surface waters in and around Berlin (sampling by UBA and BWB)

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Water</th>
<th>Name of the sampling</th>
<th>Date</th>
<th>Glyphosate [µg/L]</th>
<th>AMPA [µg/L]</th>
<th>Sampling institute</th>
<th>Description of the sampling site</th>
</tr>
</thead>
<tbody>
<tr>
<td>1c</td>
<td>Spree</td>
<td>DST 105 2.6.08</td>
<td>0.027</td>
<td>0.115</td>
<td>UBA</td>
<td>Lake Dämeritzsee, center (entry Berlin)</td>
<td></td>
</tr>
<tr>
<td>2a</td>
<td></td>
<td>26/111 26.2.08</td>
<td>0.022</td>
<td>0.097</td>
<td>BWB</td>
<td>River Müggelspree, Rahnsdorf - fairy boat station</td>
<td></td>
</tr>
<tr>
<td>2c</td>
<td></td>
<td>DST 110 2.6.08</td>
<td>0.034</td>
<td>0.131</td>
<td>UBA</td>
<td>Lake Großer Müggelsee, center</td>
<td></td>
</tr>
<tr>
<td>3c</td>
<td>Spree</td>
<td>DST 115 2.6.08</td>
<td>0</td>
<td>0.085</td>
<td>UBA</td>
<td>Tunnel Spreetunnel</td>
<td></td>
</tr>
<tr>
<td>4c</td>
<td></td>
<td>DST 120 2.6.08</td>
<td>0.027</td>
<td>0.165</td>
<td>UBA</td>
<td>After inflow of river Erpe at Krusenick</td>
<td></td>
</tr>
<tr>
<td>5a</td>
<td></td>
<td>26/121 26.2.08</td>
<td>0.037</td>
<td>0.26</td>
<td>BWB</td>
<td>Bridge Dammbrücke, inflow Dahme</td>
<td></td>
</tr>
<tr>
<td>6c</td>
<td>Dahme</td>
<td>DST 125 2.6.08</td>
<td>0.17</td>
<td>0.886</td>
<td>UBA</td>
<td>Lake Seddinsee, Seddinwall (connection to River Spree)</td>
<td></td>
</tr>
<tr>
<td>7c</td>
<td></td>
<td>DST 215 2.6.08</td>
<td>0</td>
<td>0.078</td>
<td>UBA</td>
<td>Bridge Schmöckwitz Brücke (entry Berlin)</td>
<td></td>
</tr>
<tr>
<td>8c</td>
<td>Dahme</td>
<td>DST 220 2.6.08</td>
<td>0.015</td>
<td>0.103</td>
<td>UBA</td>
<td>Lake Langer See – Grünau – fairy boat station</td>
<td></td>
</tr>
<tr>
<td>9a</td>
<td></td>
<td>26/225 26.2.08</td>
<td>0.026</td>
<td>0.226</td>
<td>BWB</td>
<td>Lake Langer See - Bammelecke</td>
<td></td>
</tr>
<tr>
<td>10c</td>
<td></td>
<td>DST 225 2.6.08</td>
<td>0.014</td>
<td>0.077</td>
<td>UBA</td>
<td>Bridge Lange Brücke</td>
<td></td>
</tr>
<tr>
<td>11c</td>
<td></td>
<td>DST 230 2.6.08</td>
<td>0</td>
<td>0.066</td>
<td>UBA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nr.</td>
<td>Water</td>
<td>Name of the sampling</td>
<td>Date</td>
<td>Glyphosate [µg/L]</td>
<td>AMPA [µg/L]</td>
<td>Sampling institute</td>
<td>Description of the sampling site</td>
</tr>
<tr>
<td>-----</td>
<td>--------------</td>
<td>-----------------------</td>
<td>-------</td>
<td>------------------</td>
<td>-------------</td>
<td>--------------------</td>
<td>-----------------------------------------------------------------------</td>
</tr>
<tr>
<td>12d</td>
<td>Mühlenbeck</td>
<td>6.6.08</td>
<td>0</td>
<td>0,012</td>
<td></td>
<td>UBA</td>
<td>Mühlenbeck, motorway</td>
</tr>
<tr>
<td>13d</td>
<td>MB Brücke</td>
<td>6.6.08</td>
<td>0</td>
<td>0,024</td>
<td></td>
<td>UBA</td>
<td>Mühlenbeck, center</td>
</tr>
<tr>
<td>14d</td>
<td>Tegeler Fließ</td>
<td>Schildow</td>
<td>6.6.08</td>
<td>0,055</td>
<td>0,343</td>
<td>UBA</td>
<td>Schildow</td>
</tr>
<tr>
<td>15d</td>
<td>Lübars</td>
<td>6.6.08</td>
<td>0,049</td>
<td>0,326</td>
<td></td>
<td>UBA</td>
<td>Alt - Lübars (entry Berlin)</td>
</tr>
<tr>
<td>16d</td>
<td>Tegel</td>
<td>6.6.08</td>
<td>0,045</td>
<td>0,303</td>
<td></td>
<td>UBA</td>
<td>Tegel, Titusweg</td>
</tr>
<tr>
<td>17e</td>
<td>10/Tegel</td>
<td>9.6.08*</td>
<td>0</td>
<td>0,292</td>
<td></td>
<td>BWB</td>
<td>Tegel, after surface water treatment</td>
</tr>
<tr>
<td>18b</td>
<td>6/305</td>
<td>6.3.08</td>
<td>0,02</td>
<td>0,082</td>
<td></td>
<td>BWB</td>
<td>River Oberhavel, Aalemanufer (entry Berlin)</td>
</tr>
<tr>
<td>18f</td>
<td>10/305</td>
<td>10.6.08</td>
<td>0,043</td>
<td>0,117</td>
<td></td>
<td>BWB</td>
<td></td>
</tr>
<tr>
<td>19b</td>
<td>6/325</td>
<td>6.3.08</td>
<td>0,022</td>
<td>0,22</td>
<td></td>
<td>BWB</td>
<td>Bridge Freybrücke</td>
</tr>
<tr>
<td>19f</td>
<td>10/325</td>
<td>10.6.08</td>
<td>0,06</td>
<td>0,469</td>
<td></td>
<td>BWB</td>
<td></td>
</tr>
<tr>
<td>20b</td>
<td>Havel</td>
<td>6/430</td>
<td>0,172</td>
<td>0,356</td>
<td></td>
<td>BWB</td>
<td>Channel Teltowkanal, Böckmannbrücke</td>
</tr>
<tr>
<td>20f</td>
<td>10/430</td>
<td>10.6.08</td>
<td>0,492</td>
<td>3,375</td>
<td></td>
<td>BWB</td>
<td></td>
</tr>
<tr>
<td>21b</td>
<td>6/355</td>
<td>6.3.08</td>
<td>0,085</td>
<td>0,645</td>
<td></td>
<td>BWB</td>
<td>Lake Stölpchensee, Kohlhasenbrücker Str.</td>
</tr>
<tr>
<td>21f</td>
<td>10/355</td>
<td>10.6.08</td>
<td>0,367</td>
<td>2,616</td>
<td></td>
<td>BWB</td>
<td></td>
</tr>
<tr>
<td>22b</td>
<td>6/345</td>
<td>6.3.08</td>
<td>0,06</td>
<td>0,168</td>
<td></td>
<td>BWB</td>
<td>Bridge Glienicker Brücke (exit Berlin)</td>
</tr>
<tr>
<td>22f</td>
<td>10/345</td>
<td>10.6.08</td>
<td>0,367</td>
<td>2,973</td>
<td></td>
<td>BWB</td>
<td></td>
</tr>
</tbody>
</table>

*daily mixed sample*
Tab. 14: Model setting to evaluate the hydrodynamic and substance-specific parameters on the basis of observed breakthrough curves

**Block A (Model description)**

<table>
<thead>
<tr>
<th>Settings</th>
<th>Enclosure II + III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model type</td>
<td>1: deterministic equilibrium CDE</td>
</tr>
<tr>
<td>Problem type</td>
<td>1: inverse problem</td>
</tr>
<tr>
<td>Input and Output</td>
<td>0: time and position are dimensional (adsorbed conc. is &lt;s&gt;)</td>
</tr>
<tr>
<td>Concentration mode</td>
<td>3: resident concentration (third type inlet)</td>
</tr>
<tr>
<td>Characteristic length [cm]</td>
<td>125</td>
</tr>
</tbody>
</table>

**Block B (Parameters for inverse problem)**

<table>
<thead>
<tr>
<th>Settings</th>
<th>Enclosure II + III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter constraints</td>
<td>1: use minimum and maximum constraints</td>
</tr>
<tr>
<td>Total mass estimation</td>
<td>0: no estimation for total mass</td>
</tr>
<tr>
<td>Max number of iterations</td>
<td>1000</td>
</tr>
</tbody>
</table>

**Block C (Transport parameters)**

<table>
<thead>
<tr>
<th>Settings</th>
<th>Enclosure II</th>
<th>Enclosure III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial parameters (min. - max. constraints)</td>
<td>v [cm/d] 132</td>
<td>133</td>
</tr>
<tr>
<td></td>
<td>D [cm²/d] 185</td>
<td>231</td>
</tr>
<tr>
<td></td>
<td>R [-] 1 (1-1000)</td>
<td>1 (1-1000)</td>
</tr>
<tr>
<td></td>
<td>μ [d⁻¹] = λ [d⁻¹] · R [-]</td>
<td>0 (0-1000)</td>
</tr>
</tbody>
</table>

**Block D (Boundary Value Problem)**

<table>
<thead>
<tr>
<th>Settings</th>
<th>Enclosure II</th>
<th>Enclosure III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input type</td>
<td>Pulse input of application time</td>
<td>Pulse input of application time</td>
</tr>
<tr>
<td>Pulse 1 [µg/L]</td>
<td>3.5</td>
<td>11.6</td>
</tr>
<tr>
<td>Tpulse2 [d]</td>
<td>14</td>
<td>14</td>
</tr>
</tbody>
</table>
**Block E (Initial Value Problem)**

<table>
<thead>
<tr>
<th>Settings</th>
<th>Enclosure II + III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial concentration</td>
<td>0: no initial concentration</td>
</tr>
</tbody>
</table>

**Block F (Production value problem)**

<table>
<thead>
<tr>
<th>Settings</th>
<th>Enclosure II + III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production type</td>
<td>0: no production</td>
</tr>
</tbody>
</table>

**Block G (Observe data for inverse problem)**

<table>
<thead>
<tr>
<th>Settings</th>
<th>Enclosure II + III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input data code</td>
<td>1: T1,C1, ...</td>
</tr>
<tr>
<td>Position of the breakthrough curve</td>
<td>125</td>
</tr>
</tbody>
</table>

**Tab. 15: Model setting to simulate breakthrough curves on the basis of hydrodynamic and substance-specific parameters**

**Block A (Model description)**

<table>
<thead>
<tr>
<th>Settings</th>
<th>Enclosure II + III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model type</td>
<td>1: deterministic equilibrium CDE</td>
</tr>
<tr>
<td>Problem type</td>
<td>0: direct problem</td>
</tr>
<tr>
<td>Input and Output</td>
<td>0: time and position are dimensional (adsorbed conc. is (&lt;s&gt;)</td>
</tr>
<tr>
<td>Concentration mode</td>
<td>1: flux average concentration</td>
</tr>
<tr>
<td>Characteristic length [cm]</td>
<td>125</td>
</tr>
</tbody>
</table>

**Block C (Transport parameters)**

<table>
<thead>
<tr>
<th>Settings</th>
<th>Enclosure II</th>
<th>Enclosure III</th>
</tr>
</thead>
</table>
| Initial parameters
| \(\nu\) [cm/d]            | 132          | 133           |
| \(D\) [cm²/d]             | 185          | 231           |
| \(R\) [-]                 | 25           | 18.3          |
| \(\mu\) [d⁻¹] = \(R\) [-] \(\cdot\) \(\lambda\) [d⁻¹] | 1.73 = 25 \(\cdot\) 0.069 | 1.68 = 18.3 \(\cdot\) 0.092 |
### Block D (Boundary Value Problem)

<table>
<thead>
<tr>
<th>Settings</th>
<th>Enclosure II</th>
<th>Enclosure III</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Input type</strong></td>
<td>Pulse input of application time</td>
<td>Pulse input of application time</td>
</tr>
<tr>
<td>Pulse 1 [µg/L]</td>
<td>3.5</td>
<td>11.6</td>
</tr>
<tr>
<td>Tpulse2 [d]</td>
<td>14</td>
<td>14</td>
</tr>
</tbody>
</table>

### Block E (Initial Value Problem)

<table>
<thead>
<tr>
<th>Settings</th>
<th>Enclosure II + III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial concentration</td>
<td>0: no initial concentration</td>
</tr>
</tbody>
</table>

### Block F (Production value problem)

<table>
<thead>
<tr>
<th>Settings</th>
<th>Enclosure II + III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production type</td>
<td>0: no production</td>
</tr>
</tbody>
</table>

### Block H (Position and time for direct problem)

<table>
<thead>
<tr>
<th>Settings</th>
<th>Enclosure II + III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Output print code</td>
<td>1: Concentration vs. time</td>
</tr>
</tbody>
</table>
Fig. 39: HPLC-diagram of glyphosate detection in a spiked filtration pond water sample
Fig. 40: HPLC-diagram of glyphosate and AMPA detection in a spiked standard sample (0.025 µg/L Glyphosate and AMPA, respectively)
Tab. 16: Results of the adsorption experiment

<table>
<thead>
<tr>
<th>Input glyphosate concentration in solution [mg/L]</th>
<th>Output glyphosate concentration in solution [mg/L]</th>
<th>Adsorbed glyphosate [%]</th>
<th>Adsorbed glyphosate [mg/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>100.00</td>
<td>93.2140</td>
<td>6.79</td>
<td>13.5720</td>
</tr>
<tr>
<td>100.00</td>
<td>94.0193</td>
<td>5.98</td>
<td>11.9614</td>
</tr>
<tr>
<td>10.00</td>
<td>6.7496</td>
<td>32.50</td>
<td>6.5007</td>
</tr>
<tr>
<td>10.00</td>
<td>7.2353</td>
<td>27.65</td>
<td>5.5294</td>
</tr>
<tr>
<td>1.00</td>
<td>0.2442</td>
<td>75.58</td>
<td>1.5116</td>
</tr>
<tr>
<td>1.00</td>
<td>0.2905</td>
<td>70.95</td>
<td>1.4190</td>
</tr>
<tr>
<td>0.10</td>
<td>0.0137</td>
<td>86.32</td>
<td>0.1726</td>
</tr>
<tr>
<td>0.10</td>
<td>0.0127</td>
<td>87.30</td>
<td>0.1746</td>
</tr>
</tbody>
</table>

Tab. 17: Results of the degradation experiment (mean of the replicates)

<table>
<thead>
<tr>
<th>Duration of the experiment [d]</th>
<th>Mean concentration of replicates [mg/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>15.00</td>
</tr>
<tr>
<td>7</td>
<td>11.35</td>
</tr>
<tr>
<td>14</td>
<td>9.95</td>
</tr>
<tr>
<td>21</td>
<td>7.14</td>
</tr>
<tr>
<td>28</td>
<td>6.96</td>
</tr>
<tr>
<td>73</td>
<td>3.33</td>
</tr>
</tbody>
</table>
Tab. 18: Results of the leaching experiment

<table>
<thead>
<tr>
<th>Duration of the experiment [hours]</th>
<th>Glyphosate concentration [µg/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.64</td>
<td>0.01</td>
</tr>
<tr>
<td>0.96</td>
<td>0.09</td>
</tr>
<tr>
<td>0.96</td>
<td>0.00</td>
</tr>
<tr>
<td>1.27</td>
<td>0.00</td>
</tr>
<tr>
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Tab. 19: Glyphosate concentration in the water reservoir of the enclosure I, II and III

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Tab. 20: Glyphosate- and AMPA- concentration in the outlet of the enclosure I, II and III

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Fig. 41: Modelling results of the glyphosate breakthrough in enclosure II

Fig. 42: Modelling results of the glyphosate breakthrough in enclosure III
Tab. 21: Glyphosate- and AMPA- concentrations in the lysemeter 17 (left) and 18 (right)

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Fig. 43: Weather situation in the year of the experiments (2007)
Chapter 9

Bibliography

9.1 Books

Ahlsdorf, B. 1991. Grundwasserkontamination durch Pflanzenschutzmittelanwendung im Baumschulgebiet Pinneberg. Published by Institut für Pflanzenernährung und Bodenkunde, Universität Kiel, Germany


9.2 Articles


A. L. 2008. Fate of glyphosate in soil and the possibility of leaching to ground and surface waters: a review. Published in Pest. Manag. Sci., No. 64, P. 441-456.


9.3 Other Sources


