Fate of bromide, nicosulfuron and prosulfocarb in a system of watercourses

Field experiment near Brakel

W.H.J. Beltman and G.H. Aalderink

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Abstract

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To test the TOXSWA model, we conducted a field experiment in a watercourse system with flowing water. Tracer bromide, weakly sorbing nicosulfuron, and strongly sorbing prosulfocarb were sprayed onto a 50 m stretch. At 47 m from application, stretch concentrations decreased by 20% due to longitudinal dispersion. At 302 m, the stretch decrease was > 60% (based on bromide) due to mixing with clean water. After 29 hours, higher concentrations of prosulfocarb (2.8% of total applied prosulfocarb) were found in the sediment than those of nicosulfuron. The Freundlich sorption parameters were determined for prosulfocarb in a 24h laboratory batch test with sediment from the field location, resulting in a Freundlich sorption coefficient, $K_{f,om}$ of 945 L kg^{-1} and a Freundlich exponent, N of 0.98. Our findings show the rapid process of pesticide transport in flowing water, demonstrating that pesticide transport dominates pesticide fate processes.

Om het TOXSWA-model te testen, is een veldexperiment uitgevoerd in een waterloop met stromend water. De tracer bromide, het zwak sorberende nicosulfuron en het sterk sorberende prosulfocarb werden toegediend over een lengte van 50 meter in de waterloop. Op 47 meter afstand van het toedieningstraject namen de concentraties met 20% af door longitudinale dispersie. Op een afstand van 302 meter was de afname meer dan 60% (gebaseerd op bromide), als gevolg van vermenging met schoon water. In het sediment werden hogere concentraties prosulfocarb aangetroffen dan nicosulfuron, waarbij 2,8% van de totaal toegepaste hoeveelheid prosulfocarb zich na 29 uur in het sediment bevond. Een 24-uurs laboratoriumtest met sediment afkomstig van de veldlocatie gaf een Freundlich-sorptiecoëfficiënt ($K_{f,om}$) van 945 L kg^{-1} en een Freundlich-exponent (N) van 0,98. De resultaten tonen aan dat het transport van bestrijdingsmiddelen in stromend water een snel proces kan zijn, wat bepalend is voor het gedrag en de verspreiding van bestrijdingsmiddelen.

Keywords: pesticide, surface water, water flow, field test, sorption

Photo cover: Paulien Adriaanse

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Preface

In 2008, we conducted a field test to study pesticide fate in a system of watercourses. We studied the dilution and fate of three compounds in a system of watercourses situated in the Bommelerwaard polder in the centre of the Netherlands. We quantified the effect of mixing water from a treated ditch with pesticide-free water from lateral ditches. After the study, reporting was not finalized for several reasons. This report now fulfils the task.

I would like to thank the many people who helped to execute and report the study. Waterboard Rivierenland helped us find a suitable location for the study and provided information about water management in the Bommelerwaard polder. The landowner gave access to the ditches and provided practical information about the location's maintenance. Anton Dommerholt† (Wageningen University) helped us with a method to measure discharge and dimensioning of the electromagnetic measurement for five weirs. Our (former) colleagues Han te Beest prepared and maintained the ditch water level measurements, Jan Elbers built the infrastructure to provide power to the discharge measurement equipment and automated sampling equipment, and Hans Zweers helped with the chemical analysis of the water samples on the day of application. Our colleagues from Wageningen Plant Research prepared a spray boom and executed spraying of the three compounds. Jos Boesten and Paulien Adriaanse co-developed the field test design, and Paulien commented on this report. In the final phase Bastian Polst provided editorial suggestions. Finally, Steven Crum reviewed this report and helped me find a direction to finish the report.

The field study was financed by the Ministry of LVVN via the policy support program (BO in 2007-2009). Reporting was financed by the Ministry of LVVN via WOT-04-008-024 Modelinstrumentarium toelating Gewasbeschermingsmiddelen.

Wim Beltman

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Summary

The mechanistic model TOXSWA is used in environmental risk assessment of aquatic ecosystems to describe the behaviour and predict environmental concentrations of pesticides in edge-of-field waterbodies. Exposure concentrations are predicted for regulatory scenarios based on pesticide process parameters obtained in standardized laboratory experiments. Tests of the model performance based on field data have previously been carried out for watercourses with stagnant water, but not with flowing water.

To fill this gap, we set up a field experiment in a Dutch polder to study the fate of pesticides in watercourses with flowing water. The Brakel watercourse system was selected as we were able to manage the water flow and determine detailed watercourse characteristics, e.g. water depth, vegetation, suspended solids, and sediment. The water in the watercourse system contained 1.2 mg L^{-1} suspended solids, of which organic matter content was not determined. In the treated ditch *Algae* flab was settled at the bottom (coverage 80 - 90%). *Elodea nuttallii* was the predominant macrophyte species, however present in less than 5% in the ditches. The ditches had a clay sediment with an organic matter content of 14.3% in the top 4 cm.

The active pesticide ingredients nicosulfuron and prosulfocarb were selected due to their contrasting adsorption to sediment organic matter; nicosulfuron adsorbs weakly, prosulfocarb adsorbs strongly. Additionally, we selected the tracer bromide to track discharge and flow of water. All three compounds were applied to a 50 m stretch of the watercourse. Their concentration in the water and the upper layers of the sediment (1-4 cm) were measured at several sampling points (horizontal and vertical) and distances (up to 302 m) from the application stretch, permitting a discharge, cross-section and time sensitive tracking of their fate/flow. Additional lab studies on the pesticides' sorption and transformation were conducted with water and sediment from the field site.

After applying the bromide, the distribution in the cross section was fairly homogeneous. Bromide was applied separately and not with a formulation, so it was expected to diffuse and mix easily in the water layer. Nicosulfuron and prosulfocarb were applied in a formulation which initially floated on the water surface, therefore diffusion and mixing in the water layer may have been slower.

During the field study, water discharge varied between 15 – 23 L s^{-1} (active pumping for 4x3h) and 7 – 13 L s^{-1} (rest of the experiment).

The dilution of substance concentration was driven by dispersion due to differences in flow velocity in the watercourse and due to mixing with clean water from other watercourses.

We evaluated the effect of dilution due to longitudinal dispersion at 47 m from the application stretch. After 5h, the peak concentration of bromide (6 633 μg L^{-1}) was 80% of the nominal concentration; for nicosulfuron the values were (99.8 μg L^{-1}) and 80% at 5 h, and for prosulfocarb (596 ng L^{-1}) and 50% at 5.5h. For bromide and nicosulfuron, longitudinal dispersion resulted in a 20% decrease in concentration. Prosulfocarb has a high sorption coefficient; hence sorption to the sediment may explain the stronger reduction in peak concentration compared to nicosulfuron. The substances were sprayed over a length of 50 m. Longitudinal dispersion leads to a decrease of concentration at the front and back of the initial 50 m long concentration distribution in the form of a "block" shape. The peak concentrations of bromide and nicosulfuron were 20% lower than nominal, and the width of the Gaussian distributions (bell shaped) of nicosulfuron and prosulfocarb were slightly broader than that of bromide. This may be due to a slower mixing of the nicosulfuron and prosulfocarb formulations in the application stretch, fortifying the effect of longitudinal dispersion.

At 302 m from the application stretch, we evaluated the effect of dilution due to mixing with clean water and due to longitudinal dispersion. The peak concentration of bromide was 1 873 μg L^{-1}, measured 18h after application; 13h after the peak at the first sampling point at 47 m. The decrease of peak concentration between the two sampling points of a factor 3.5 can be attributed to dilution from entries of uncontaminated

water from lateral watercourses (factor calculated from the water volumes is 2.6) and the remainder by longitudinal dispersion. At 18h after application, the peak concentration of nicosulfuron was 22.5 µg L^{-1}. The decrease in peak concentration between the two sampling points is a factor 4.4, higher than that of 3.5 for bromide. In this short period, no dissipation of nicosulfuron was expected; sorption to sediment is not relevant as the sorption coefficient of nicosulfuron is small. However, at 47 m, the peak concentration of nicosulfuron was already lower than nominal and the concentrations Gaussian distributed, and the wave already broader than for bromide. Hence, the decrease of the peak between 47 m and 302 m is also larger than for bromide. The peak concentration of prosulfocarb at 302 m was 141 ng L^{-1} measured 17h after application. We calculated a factor 4.2 decrease in peak concentration between the two sampling points, similar to that of nicosulfuron and higher than that of bromide.

At 9.5h (bromide) and 9h (pesticides) after application, 47 m from the application stretch most of the total mass measured at the sampling point (total 100%) had passed; bromide 92%, nicosulfuron 90% and prosulfocarb 86%. After 25h ≥98% of the total mass of all three compounds had passed. Within 22h, at 302 m from the application stretch more than 50% of the total mass measured at the sampling point had passed; bromide 59%, nicosulfuron 65%, and prosulfocarb 72%. At 42h after application, ≥93% of this total mass of all three compounds had passed.

Higher concentrations of prosulfocarb than of nicosulfuron were found in the sediment, with an approx. 2.8% of total applied prosulfocarb absorbed in the sediment after 29 hours. After passing of the prosulfocarb peak in the water column, prosulfocarb diffused from the sediment back to the water layer, highlighting the role of flowing water on the fate dynamics.

The transformation rates of nicosulfuron and of prosulfocarb were determined in a lab study by adding the compounds to ditch water from the field location and determining the concentrations for one week (relevant period for the field test). After 8 days, the decrease of concentration was less than 10% for both compounds. The Freundlich sorption parameters were determined for prosulfocarb in a 24h batch test with sediment from the field location; with a sorption coefficient of $K_{f,om}$ = 945 L kg^{-1} and its Freundlich exponent N = 0.98. The lab-determined sorption coefficient is expected to contribute well to test the TOXSWA model to calculate sediment contents.

The results show that pesticide transport in flowing water can be rapid and demonstrate that pesticide transport dominates pesticide fate processes. The results can be used for testing the TOXSWA pesticide fate model.

Samenvatting

TOXSWA is een mechanistisch model dat het gedrag van bestrijdingsmiddelen simuleert in een sloot naast een perceel waar een bestrijdingsmiddel is toegepast. Het model wordt gebruikt om blootstellingsconcentraties te berekenen voor aquatische organismen in de risicobeoordeling van gewasbeschermingsmiddelen. Blootstellingsconcentraties worden berekend voor scenario's op basis van eigenschappen van bestrijdingsmiddelen die verkregen zijn in gestandaardiseerde laboratoriumtesten. TOXSWA is getoetst met velddata voor waterlopen met stilstaand water, maar niet voor waterlopen met stromend water.

Om deze leemte op te vullen is een veldexperiment opgezet om het gedrag van bestrijdingsmiddelen in waterlopen met stromend water te bestuderen. Een stelsel van waterlopen nabij Brakel is geselecteerd, omdat dit stelsel de mogelijkheid bood de waterstroming te controleren en de karakteristieken van de waterlopen te bepalen, zoals waterdiepte, vegetatie, zwevendestofgehalte en sediment. Het water bevatte 1,2 mg L^{-1} zwevende stof, waarvan het gehalte aan organische stof niet was bepaald. In de sloot waaraan de bestrijdingsmiddelen werden toegediend lag algenflab op de bodem (dekking 80 tot 90%). *Elodea nuttallii* was de overheersende waterplantensoort, die in beperkte mate aanwezig was in de sloten (<5%). Het sediment in de sloten bestond uit klei met 14,3% organische stof in de bovenste 4 cm.

De actieve stoffen nicosulfuron en prosulfocarb zijn gekozen vanwege hun contrasterende adsorptie eigenschappen; nicosulfuron adsorbeert zwak en prosulfocarb adsorbeert sterk aan organisch materiaal. Daarnaast werd bromide als tracer toegediend om de afvoer en stroming van water te volgen. Alle drie de stoffen werden toegediend over een lengte van 50 meter in de waterloop. De concentraties van deze stoffen werden in het water en de bovenste lagen van het sediment (1-4 cm) gemeten op verschillende bemonsteringspunten (horizontaal en verticaal) en afstanden (tot 302 m) vanaf het toedieningsstraject. Aanvullend werden laboratoriumtesten voor bepaling van de sorptie en de omzetting van deze bestrijdingsmiddelen uitgevoerd met water en sediment uit de waterloop waaraan de stoffen waren toegediend.

Na het toedienen van bromide was de verdeling in de doorsnede van de waterloop redelijk homogeen. Nicosulfuron en prosulfocarb werden aangebracht in een geformuleerd product waarvan werd waargenomen dat deze aanvankelijk op het wateroppervlak dreef. Er kan dus sprake zijn geweest van een langzamere diffusie vanuit deze drijflaag en van een langzamere menging in de waterlaag. Bromide werd afzonderlijk toegediend en niet in een geformuleerd product. Er werd dus verwacht dat de stof zich gemakkelijk in de waterlaag zou verspreiden en mengen.

Tijdens het veldonderzoek varieerde de waterafvoer tussen 15-23 L s^{-1} (tijdens actief pompen gedurende 4x3 uur) en 7-13 L s^{-1} gedurende de rest van het experiment.

Verdunning van stofconcentraties werd bepaald door dispersie als gevolg van verschillen in stroomsnelheid in de waterloop en door vermenging met schoon water uit andere waterlopen.

Het effect van verdunning als gevolg van longitudinale dispersie werd op 47 m van het toedieningstraject geëvalueerd. De piekconcentratie van bromide (6633 µg L^{-1}) werd 5 uur na de toepassing gemeten en bedroeg 80% van de nominale concentratie. Voor nicosulfuron was de piekconcentratie (99,8 µg L^{-1}) eveneens 80% van de nominale concentratie en voor prosulfocarb was de piekconcentratie (596 ng L^{-1}) de helft van de nominale concentratie. De piekconcentratie van prosulfocarb kwam een half uur eerder (5 uur na de toediening) dan de piekconcentratie van nicosulfuron (5½ uur na de toediening). Voor bromide en nicosulfuron verminderde longitudinale dispersie de concentratie met 20%. Prosulfocarb heeft een hoge sorptiecoëfficiënt. In vergelijking met nicosulfuron kan sorptie van prosulfocarb aan het sediment de sterkere verlaging van de piekconcentratie verklaren. De stoffen werden over een lengte van 50 m gespoten. Longitudinale spreiding leidt tot een afname van de concentratie voor en achter de aanvankelijke 50 m lange blokvormvormige concentratieverdeling. De piekconcentraties van bromide en nicosulfuron waren al 20% lager dan nominaal, en de breedte van de Gaussische concentratieverdelingen van nicosulfuron en van prosulfocarb zijn iets breder dan de verdeling van bromide. Dit kan te wijten zijn aan een langzamere menging in het toedieningstraject van de nicosulfuron- en prosulfocarb-formuleringen, waardoor het effect van longitudinale dispersie werd versterkt.

Het effect van verdunning als gevolg van vermenging met schoon water en als gevolg van longitudinale verspreiding werd op 302 m van het toepassingstraject geëvalueerd. De piekconcentratie van bromide bedroeg 1873 µg L^{-1}, gemeten 18 uur na de toepassing en 13 uur nadat de piek was gepasseerd op het eerste bemonsteringspunt op 47 m. De afname van de piekconcentratie tussen de twee bemonsteringspunten met een factor 3,5 kan worden toegeschreven aan verdunning door het binnenstromen van niet-verontreinigd water uit laterale waterlopen (de factor berekend op basis van de watervolumes is 2,6) en de rest door longitudinale dispersie.

De piekconcentratie van nicosulfuron was 22,5 µg L^{-1}, gemeten 18 uur na de toediening. De afname van de piekconcentratie tussen de twee monsternamepunten bedroeg een factor 4,4, en was hoger dan de voor bromide berekende factor van 3,5. In de korte verblijftijd werd geen omzetting van nicosulfuron verwacht en was sorptie aan sediment niet relevant omdat de sorptiecoëfficiënt van nicosulfuron klein is. Op 47 m was de piekconcentratie van nicosulfuron echter al lager dan nominaal en waren de concentraties normaal verdeeld, en was de golf al breder dan voor bromide. De afname van de piek tussen 47 m en 302 m is ook groter dan voor bromide. De piekconcentratie van prosulfocarb op 302 m was 141 ng L^{-1}, gemeten 17 uur na de toediening. De afname van de piekconcentratie tussen de twee bemonsteringspunten bedraagt een factor 4,2, dus vergelijkbaar met deze factor voor nicosulfuron en ook hoger dan de berekende factor voor bromide van 3,5.

Op 47 m van het toedieningstraject was 9,5 uur (bromide) en 9 uur (bestrijdingsmiddelen) na de toediening het grootste deel van de totale massa gemeten op het monsterpunt (dus totaal is 100%) gepasseerd; bromide 92%, nicosulfuron 90% en prosulfocarb 86%. Na 25 uur was ≥98% van deze totale massa van alle drie de stoffen gepasseerd. Op 302 m van het toedieningstraject was 22 uur na toediening van de totale massa gemeten op het bemonsteringspunt meer dan 50% gepasseerd; bromide 59%, nicosulfuron 65% en prosulfocarb 72%. Binnen 42 uur na de toediening was ≥93% van de totale massa van alle drie de stoffen het bemonsteringspunt op 302 m gepasseerd.

In het sediment werden hogere concentraties prosulfocarb dan nicosulfuron aangetroffen. Na 29 uur was circa 2,8% van de totaal toegediende prosulfocarb in het sediment aanwezig. Na het passeren van de prosulfocarb-piek in de waterlaag, diffundeerde prosulfocarb vanuit het sediment terug naar de waterlaag. Dit benadrukt de rol van waterstroming op het gedrag van bestrijdingsmiddelen in oppervlaktewater.

Tijdens de duur van het veldexperiment van drie dagen kan de omzetting van nicosulfuron en van prosulfocarb als verwaarloosbaar worden beschouwd. De omzettingssnelheden van nicosulfuron en van prosulfocarb zijn bepaald door de stoffen in het lab toe te dienen aan slootwater van de veldlocatie en de concentraties gedurende één week (relevante periode voor de veldproef) te bepalen. Voor beide stoffen is de concentratiedaling na acht dagen minder dan 10%.

De Freundlich-sorptieparameters werden voor prosulfocarb bepaald in een 24-uurs batchtest met sediment afkomstig van de veldlocatie. De Freundlich-sorptiecoëfficiënt $K_{f,om}$ = 945 L kg^{-1} en de Freundlich-exponent N = 0,98. Deze in het laboratorium bepaalde sorptieparameters zullen naar verwachting goed bijdragen om gehalten in het sediment te berekenen bij een modeltoets met TOXSWA.

Het veldexperiment laat zien dat het transport van bestrijdingsmiddelen in stromend water een snel proces kan zijn en dat transport het gedrag van bestrijdingsmiddelen domineert. De resultaten kunnen worden gebruikt voor het testen van het simulatiemodel voor gedrag van bestrijdingsmiddelen in oppervlaktewater, TOXSWA.

1 Introduction

The mechanistic model TOXSWA (Adriaanse, 1996; Ter Horst et al., 2016) is widely used to predict pesticide exposure in regulatory risk assessment of edge-of-field aquatic ecosystems (Ctgb, 2020; FOCUS, 2001; European Food Safety Authority, 2020; Tiktak et al., 2012; Van der Linden et al., 2015; Wipfler et al., 2014; Adriaanse et al., 2017) and of drinking water derived thereof (Van Leerdam et al., 2010). The TOXSWA model is also part of a modular model system to simulate pesticide fate at the catchment scale (Buddendorf et al., 2023, Focks et al., 2012).

In regulatory scenarios, standardized laboratory experiments are used to obtain process parameters for modelling pesticide exposure concentrations in surface water. The performance of the TOXSWA model has been tested with field data for watercourses with stagnant water (Adriaanse et al., 2013; Adriaanse et al., 2022). Yet, regulatory exposure scenarios for watercourses and field tests validating the model's performance with flowing water are notably absent. To address this gap we conducted a field experiment to examine the fate of two pesticides in watercourses with flowing water.

The aim of the field study was to quantify the effect of flow and mixing of water and sorption to sediment of a treated edge of field ditch on pesticide concentrations in and downstream from the treated area. The resulting data are important for future testing (and the potential adaptation) of the TOXSWA model.

In April 2008, we conducted a field experiment in a system of watercourses near Brakel, situated in the Bommelerwaard polder in the centre of the Netherlands. We used the tracer bromide along with plant protection products containing the active ingredients nicosulfuron and prosulfocarb. These were chosen due to their difference of sorption to organic matter, allowing us to distinguish the impact of sorption on pesticide fate. Nicosulfuron adsorbs weakly to organic matter ($K_{\mathrm{f,om}}$ = 52 L kg^{-1}; Lewis et al., 2016) whilst prosulfocarb adsorbs strongly to organic matter ($K_{\mathrm{f,om}}$ = 1693 L kg^{-1}; Lewis et al., 2016). The field study was accompanied by laboratory tests on the sorption of prosulfocarb and transformation of both active ingredients.

We first give a description of the system of watercourses near Brakel in Chapter 2, followed by the procedures used in the field study in Chapter 3, and the procedures for the laboratory tests in Chapter 4. The results of the field study are described in Chapter 5, and those of the laboratory studies in Chapter 6. Finally, the general discussion and conclusions of the study are given in Chapter 7.

2 System of watercourses in the Bommelerwaard polder

2.1 Description of hydrological situation and meteorological conditions

A system of watercourses located near Brakel in the Bommelerwaard polder in the centre of the Netherlands was selected for the field test. The study area is situated between the Waal river and a 12-km long branch of the Meuse river ("Afgedamde Maas") as depicted in Figure 1 (see also background information in Annex 1). The selected area is situated in the middle of a water-managed area of approx. 1500 ha (Toelichting peilbesluit, 2018). Water is actively pumped out of the watercourse network twice a day into the Afgedamde Maas (near Poederooijensehoek) by the station Dijkgraaf Van Dam at Brakel. The seepage rate driven by the Waal river's water level varies, ranging from 5 mm day^{-1} during high water levels to -0.5 mm day^{-1} during periods with downward seepage, i.e. infiltration. A reduction of a few cm in the water depth is visible in the watercourses after pumping.

On the day of application of pesticides marking the start of the field test (3 April 2008), the prevailing wind conditions were characterized by a north-western direction and a velocity of 4.2 m s^{-1} (daily values, measured at 10 meters above surface) (KNMI, station Herwijnen). On 3 April, 1.0 mm rain fell on/around the 7th hour of the day, hence before application. On 4 April, rainfall was 1.8 mm and on 5 April, 5.2 mm.

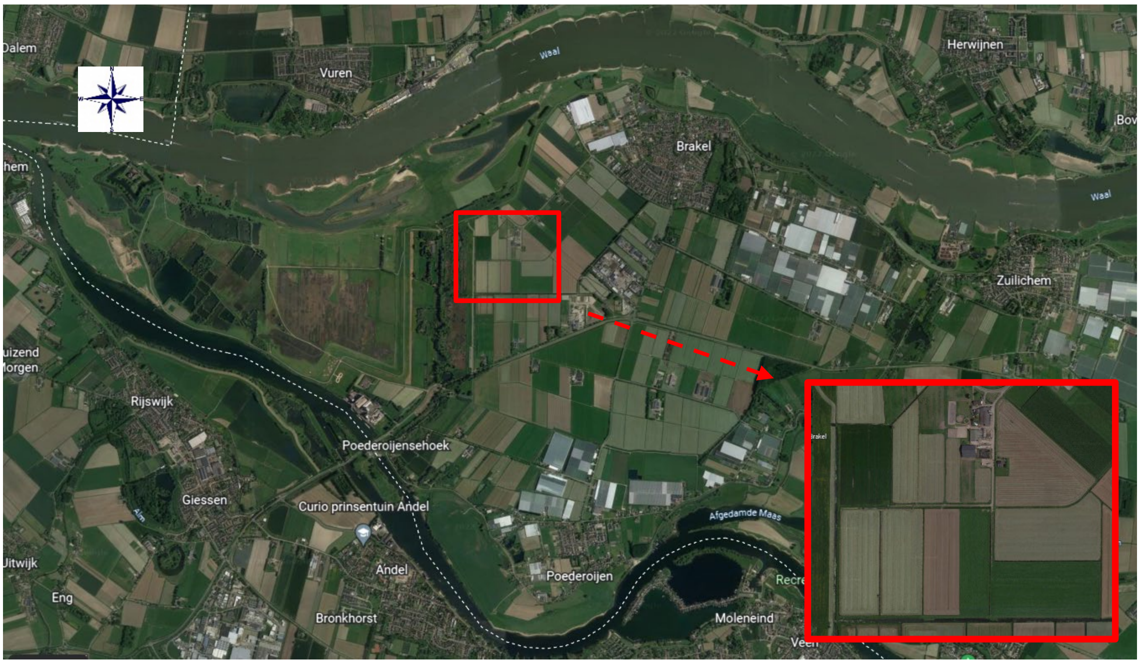

Figure 1 *Western part of the Bommelerwaard polder; selected area indicated in red squares. Maps data: Google Airbus, 2023.*

A detailed overview of the system of watercourses is shown in Figure 2, in which the different types of watercourses are highlighted. The dark blue watercourses (so-called A-watercourses) are 3 – 6 m wide and their water level is managed by the waterboard. The light blue watercourses are 1-3 m wide, and the median blue watercourses are the smallest with a width <1 m; these latter watercourses are maintained by farmers. All watercourses permanently carry water. The dimensions of the watercourses were measured on 14 March 2008 (see Annex 2). The upper section of the watercourse's sidewall is characterized by a sloping design, while the lower part, where the water level experiences fluctuations, has vertical walls (Figure 5). During our field test, only the lower part is relevant; the water level did not reach the upper part.

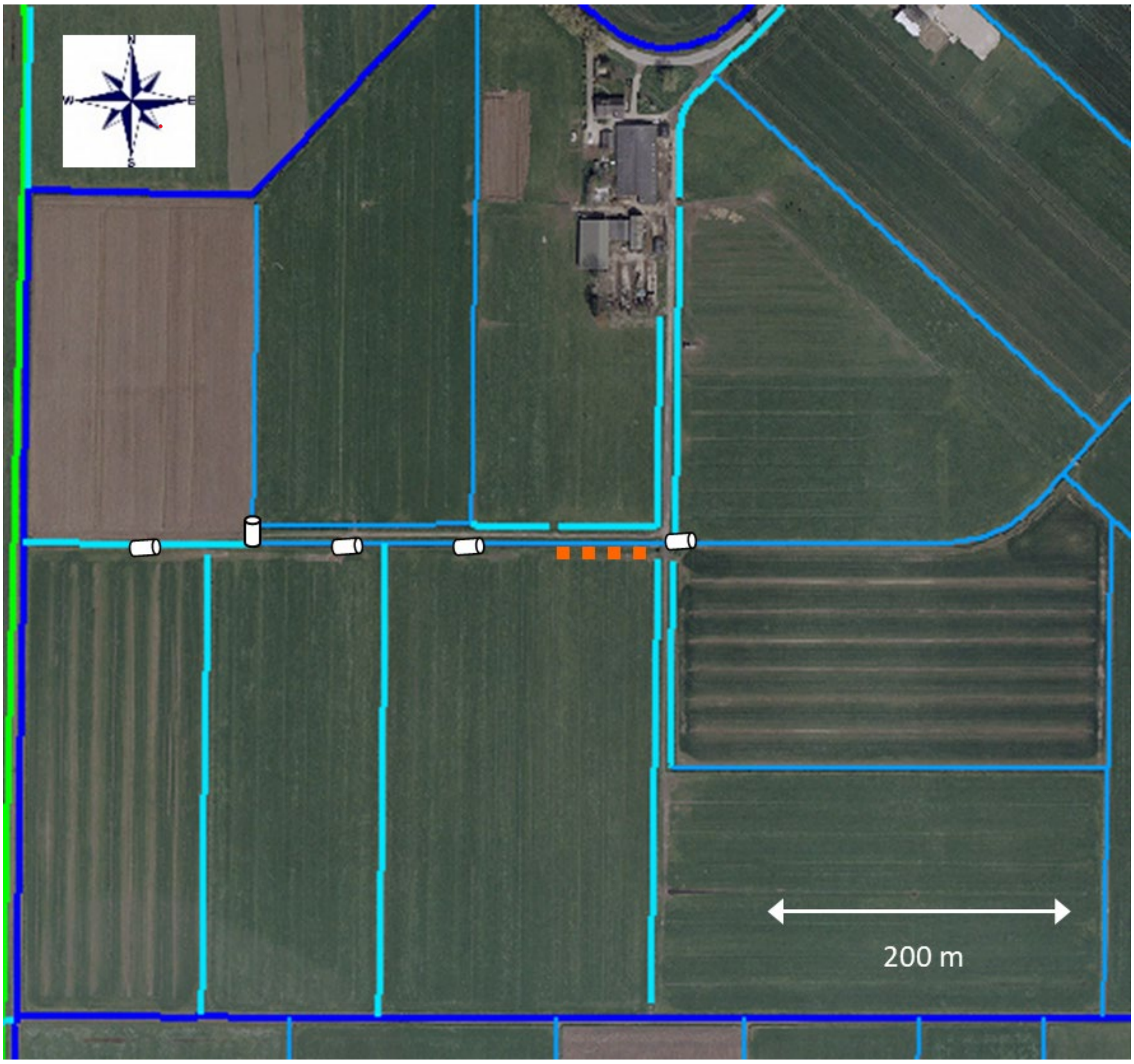

Figure 2 *Overview of system of watercourses with positions of culvert pipes ▭ . Watercourses 3-6 m wide (dark blue), 1-3 m (light blue) and < 1 m (median blue). The sprayed stretch is located between the two most right hand culverts, indicated by orange dashed line. The figure only indicates culverts relevant for the studied system of watercourses. Maps data: Google Airbus, 2023.*

2.2 Setup of hydrological equipment

A schematic overview of the system of watercourses is given in Figure 3. It spans from the inlet at weir A to immediate downstream of weir E. Water flows into the system from the east at weir A, from the south at weir B, from the north at weir C, and from north of weir E. Via weirs D and E, the water flows south and moves towards the pumping station where it is pumped out of the polder. By measuring the discharge at the five weirs, we calculated the discharge in each part/section of the watercourse A-E: directly measured at A and D; calculated based on measured discharges at B, C, and E.

Weirs were positioned to ensure the unidirectional flow of the water (Figure 3; grey and yellow). Pumps 1 and 2 (Figure 3; yellow with blue circle) were installed at two of these weirs to pump water into the watercourse system, east of weir A (pump 1) and south of weir B (pump 2). Additionally, two natural dams are present in the system (grey locations). A third pump (Figure 3; blue circle with cross) was placed north of weir C. By measuring discharges at the pink weirs, all relevant discharges for the studied watercourse A-E could be computed. (Annex 3).

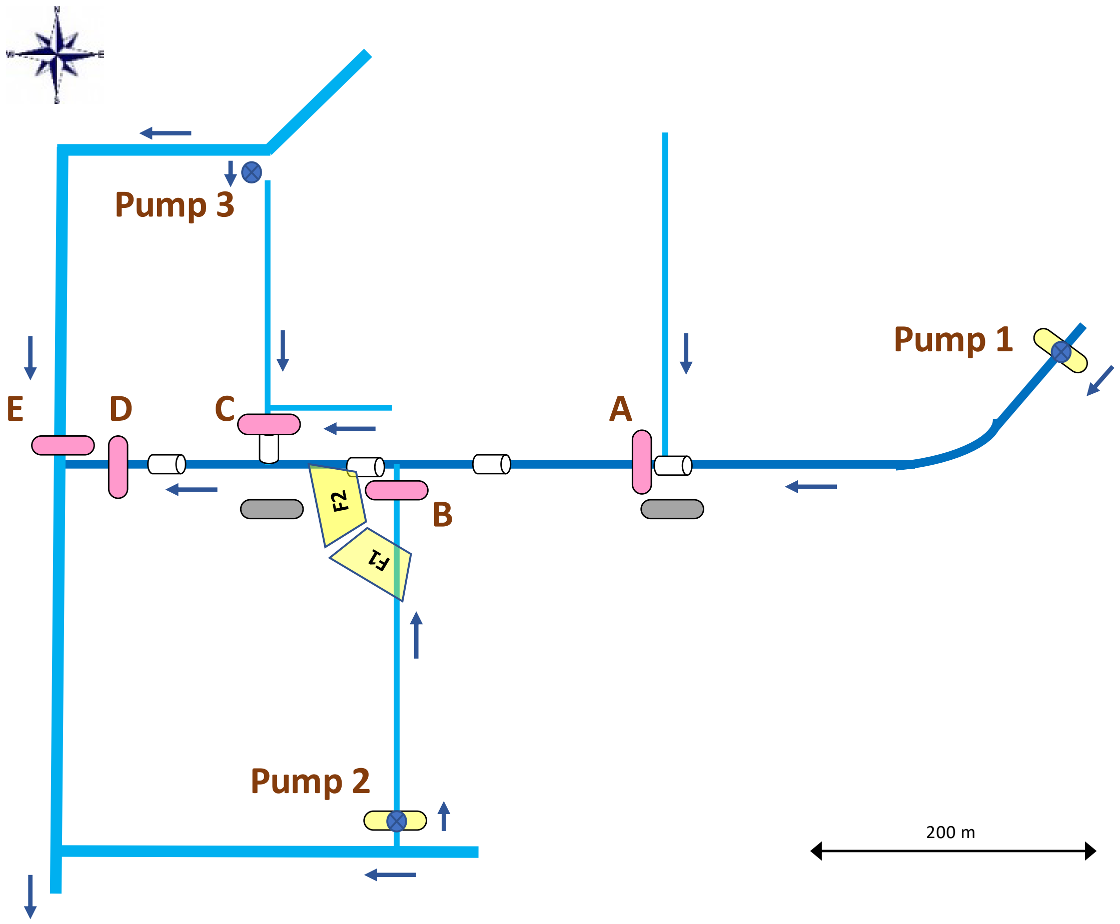

Figure 3 *Overview of system of watercourses with blue arrows indicating direction of flow, positions of weirs where discharge was measured (pink), weirs where watercourses were closed (grey), and positions of Pump 1 and Pump 2 at weirs and Pump 3 at dam (blue circle with cross) where water is pumped into the system. The field study is the horizontal watercourse from weir A to E. F1 and F2 indicate the position and direction of the photos shown in Figure 4.*

Pumping water out of the polder affected the water flow in the watercourses, as observed in the period preceding our experiment. Flow velocity increased during pumping; after pumping stopped the flow direction was shortly reversed. During pumping, the water level is higher in the vicinity of the pump at the outlet of the polder than at a distance from the pump. Once pumping stops, the water levels in the area equilibrated and at weir D water flows back into the system of watercourses. To prevent water flowing in two directions during the experiment, water was pumped continuously into the system of watercourses at three places, Pump 1, Pump 2 and Pump 3 with a rate of approximately 1.5 L s^{-1}. Pumps 1 and 2 pumped water across their weir into the system of watercourses (see the direction of the arrows in Figure 3). At Pump 3 there is no physical connection between the A-watercourse and the system of watercourses, but it pumped water from the A-watercourse into the smaller watercourse north of weir C (Figure 3). The three pumps always pumped water into field study watercourse A-D and induced flow in the direction of the arrows in Figure 3.

The width of the ditch stretch where the application took place (25 - 75 m from weir A; Annex 2) was 2.60 m wide at water level (average of values at 40 and 60 m from weir A) and 4.50 m between the top of banks (Figure 5). During application of the three substances (11.00 – 12.00) the water depth was 0.37 m on average.

Figure 4 *View from position F1 (left) and position F2 (right) as indicated in Figure 3.*

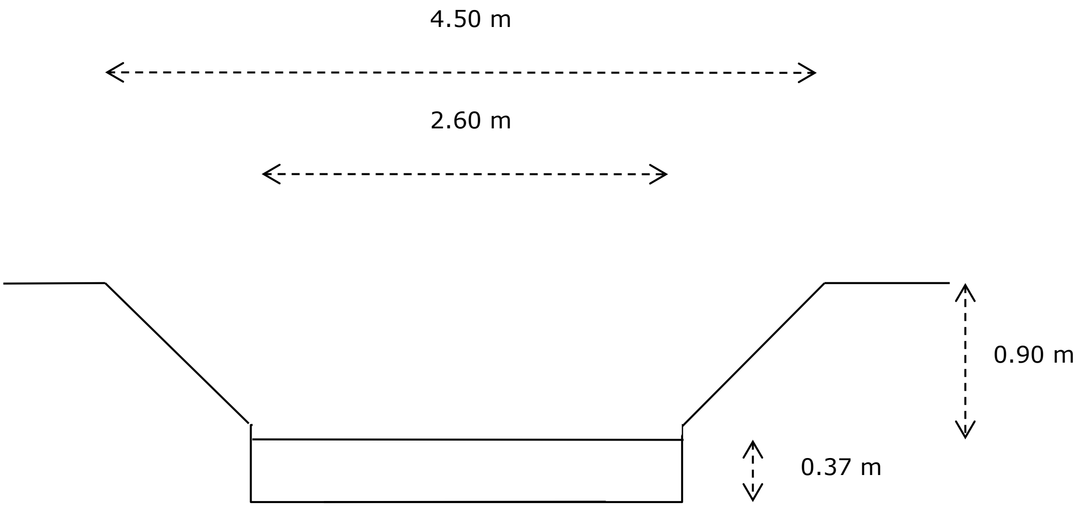

Figure 5 *Profile of ditch of the application stretch at the time of application (3 April 2008).*

3 Field study: material and methods

3.1 Monitoring and sampling locations

An overview of monitoring and sampling locations in the system of watercourses is given in Figure 6. The discharge was measured at weirs A – E. The water depth, temperature and pH were measured and suspended solids, water (spot) and sediment sampled at locations MP1-MP3. Discharge proportional water was sampled at locations P1 and P2.

The tracer bromide used in this study is present in surface water. This background concentration was calculated as the average of six spot samples taken in the application stretch at 10:30 on 3 April 2008 (samples NPB001-NPB006, Table 37 in Annex 10) and of the first six samples taken at P1 on 3 April 2008 (samples NPB081-NPB086; Annex 11), resulting in a background concentration of bromide of 90.5 µg L^{-1}.

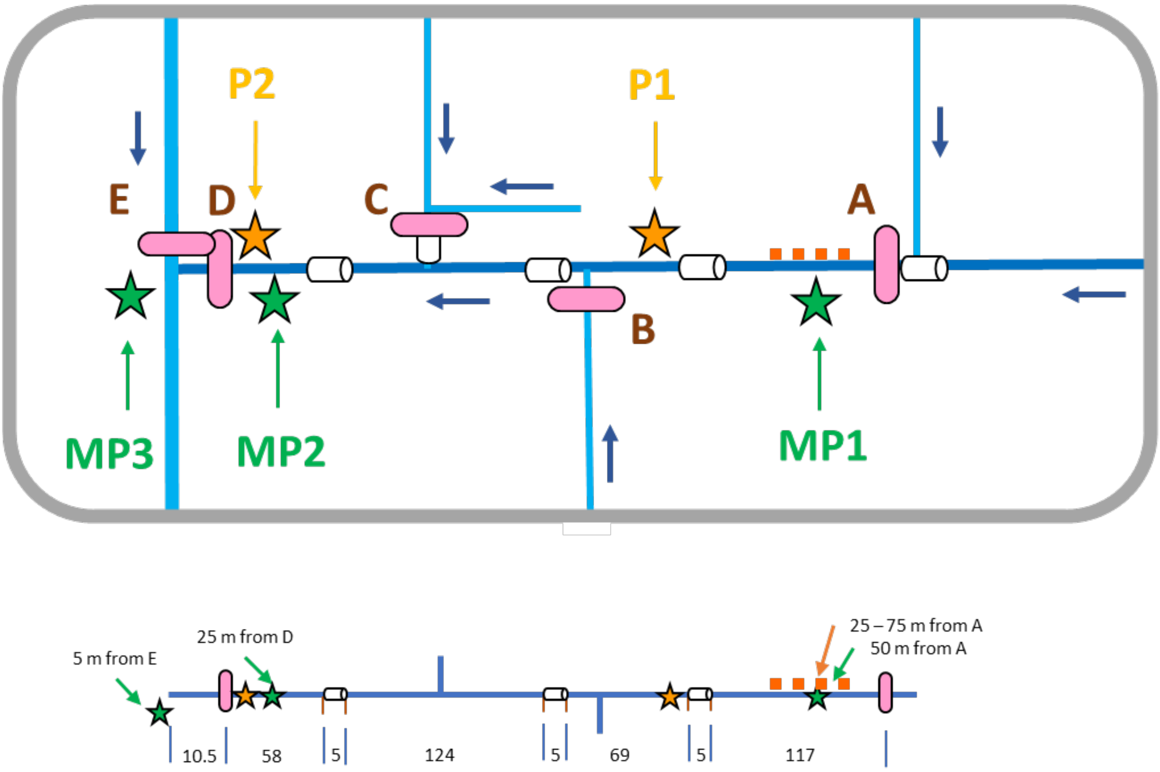

Figure 6 *Monitoring and sampling locations in the system of watercourses. Weirs A-E: discharge measurement; MP 1-3: diver for measuring water depth, spot water samples and sediment samples; P1, P2: discharge proportional water sampling at 47 m (in outflow of culvert) and at 302 m (in inflow of culvert). The 50-m stretch where the substances were applied is indicated by the orange dashed line near MP1. Distances between the different objects in the studied watercourse are given in meters.*

3.2 Time schedule of the experiment

On 2 April 2008 (one day before application) flap flowing on the water surface of the stretch where the applications were planned was removed using a rake to pull the flap to and onto the side of the watercourse.

The Waterboard Rivierenland operates a pumping station to maintain the desired water levels in the Bommelerwaard polder. On 3 April to facilitate the experiment, Waterboard Rivierenland switched on the pump of the pumping station for longer (3.5 hours) than normal to lower the water level in the receiving polder somewhat more than usual. Thereafter, during the application of the compounds, the three pumps 1, 2 and 3 of the experiment generated a flow in the studied watercourse A-E, obtaining a period of low flow in one direction.

On 3 April 2008, we started the experiment by spraying solutions of bromide at 11:30 and a mixture of the plant protection product of nicosulfuron and prosulfocarb at 12:00 on the application stretch of the watercourse.

We continually measured the hydrology and concentrations in discharge water between 3-6 April, taking samples at several times during this period from cross sections of the water layer and from the sediment at three positions in the watercourse.

3.3 Application of bromide, nicosulfuron and prosulfocarb

3.3.1 Preparation of the spray solution with compounds

As the formulated pesticides Milagro (nicosulfuron; Syngenta) and Boxer (prosulfocarb; Syngenta) were not miscible with potassium bromide (Alfa Caesar), they were sprayed separately to the bromide.

Bromide
For a total volume of 2 L, 775.48 g of potassium bromide (Alfa Caesar, purity KBr 99%) was dissolved in 1710 g of tap water (density 1.243 kg L^{-1}). The potassium bromide salt contained 67% bromide (w/w), and considering the 99% purity, resulted in a net amount of bromide of 514.4 g in the dose solution. The stock solution was transferred to the spray tank and topped up with 10.5 L ditch water to a total volume of 12.5 L resulting in a bromide concentration of 41.2 g L^{-1} and a density of 1.04 kg L^{-1}.

Mixed dose solution of formulated products Boxer and Milagro
A 1 L glass bottle was prepared containing 181.3 g Milagro (4% nicosulfuron, w/w, Syngenta). An amount of 0.933 g of the formulated product Boxer (78.4% prosulfocarb, w/w, Syngenta) was dissolved in 100.37 g of tap water. From this solution, 10.05 g was added to the 1 L glass bottle containing Milagro. An amount of 368 g tap water was added to this stock solution. The stock solution contained net amounts of 7.252 g nicosulfuron and 0.0732 g prosulfocarb. This was then transferred to the spray tank and filled with ditch water to a total volume of 13.00 L, resulting in nicosulfuron and prosulfocarb concentrations of 557.8 mg L^{-1} and 5.63 mg L^{-1} respectively. After transferring the stock solution to the spray tank, a white residue remained at the top of the flask. Hence, it is likely that some of the formulated product remained in the flask and was not added to the spray tank. This white deposit may also have occurred in the spray tank, however this was not checked, nor was an attempt made to dissolve the white residue in the flask for analysis.

3.3.2 Spraying of the compounds onto the ditch

The spray equipment consisted of a 7 m long aluminium pipe (carrier) with an attached spray boom (approximately 1.5 m below). The spray boom had four nozzles, two Lechler IS 80-04 low drift side cap nozzles at both ends, and two Lechler ID 120-04 low drift nozzles in the middle, both with a top angle of 80°. The distance between the nozzles was 0.5 m. The spray tank's pressure could be adjusted by a pressure reducing valve fitted with a manometer. Initiating or halting the spraying process was achieved by opening and closing the spray valve. An air tube extended nearly to the bottom of the tank to induce turbulence in the spray fluid during application, preventing settling of the active ingredients. The spray tank had a capacity of 15 L and was pressurized through a compressed air cylinder.

On 3 April 2008, first the spray solution containing potassium bromide (end time 11:30) followed by the spray solution containing the active ingredients nicosulfuron and prosulfocarb (end time 12:00) were sprayed onto the ditch's water surface. Before spraying, both solutions were mixed vigorously and the spray equipment was pre-rinsed with about 1 L of the spray solution. The spray tank was weighed and sampled accordingly before and after spraying. We calculated the volume and concentration of spray solution dosed to the ditch from the mass sprayed and the density of the spray solution of 1.04 kg L^{-1} (potassium bromide) and 1 kg L^{-1} (formulated products). A Mettler PM34 balance was used for weighing components in the field.

The ditch west of weir A was dosed over a length of 50 meter. At a water depth of 0.37 m and a width of 2.60 m at the water surface (see Section 2.2), the ditch then contained approximately 48.3 m^3 water. A width of 0.25 m of the water layer on both sides of the ditch was not sprayed to avoid contamination of the side walls and to quantify the dose to water well.

During spray application, two people held the spray boom at an elevation of approximately 30 cm above the water surface, a third held the spray tank, a fourth held the air cylinder and a fifth acted as a time observer and counted the seconds elapsing during spraying out loud to indicate walking speed (Figure 7). The spray fluid was sprayed onto the ditch water surface at a pressure of 5 bar in the spray tank and at a walking speed of approximately 0.5 m s^{-1} for a duration of 50 seconds.

From the bromide spray solution, 9.95 kg (density 1.04 kg L^{-1}, hence 9.57 L sprayed) was applied to the ditch containing 394 g of bromide. Based on the ditch volume of 48.3 m^3 and concentration of the spray solution of 41.2 g L^{-1}, the resulting nominal ditch water concentration of bromide was 8 163mg L^{-1}. The dose solution of bromide was not sampled; hence the concentration could not be verified.

From the dose solution of pesticides, 9.42 L (9.42 kg) was applied to the ditch. Duplicate samples were taken from the solution in the spray tank before and after application to validate the dosing of the two active ingredients. The measured concentrations for nicosulfuron were 666 mg L^{-1} and 642 mg L^{-1} before, and 628 mg L^{-1} and 605 mg L^{-1} after spraying; the measured concentrations were higher than calculated based on the weighed product (558 mg L^{-1}). A dose of 5.97 g nicosulfuron was calculated based on the average concentration of nicosulfuron (634 mg L^{-1}) and the sprayed volume (9.42 L). For prosulfocarb, the measured concentrations were 5.80 mg L^{-1} and 5.61 mg L^{-1} before, and 5.26 mg L^{-1} and 5.23 mg L^{-1} after spray application. The measured concentrations were thus slightly lower than calculated based on the weighed product (5.63 mg L^{-1}). Based on the average concentration of prosulfocarb (5.47 mg L^{-1}) and the sprayed volume (9.42 L), a dose of 0.0516 g prosulfocarb was calculated for the applied spray. Based on these doses and the ditch volume (48.3 m^3) the resulting nominal ditch water concentration of was 124 µg L^{-1} for nicosulfuron and 1.07 µg L^{-1} for prosulfocarb. A summary of the dosed mass and nominal concentrations is given in Table 1.

A whitish, floating layer of product was observed, drifting to the north side of the ditch after completing the spray application. Therefore, we took two water samples from the surface of the water layer to catch the visibly floating layer (after application at 13:40). The concentrations of nicosulfuron were 220.5 µg L^{-1} and 757.2 µg L^{-1}, and prosulfocarb 9.51 µg L^{-1} and 9.75 µg L^{-1}. Thus, the concentrations of both active ingredients in the floating layer were significantly higher than the nominal concentrations of 124 µg L^{-1} nicosulfuron and 1.07 µg L^{-1} prosulfocarb respectively.

Figure 7 *Spraying the application stretch of the ditch.*

Table 1 *Dose of compounds for 50 m ditch length.*

Compound	Mass applied over 50 m (g)	Nominal concentration in 50-m ditch (µg L^{-1})
bromide	394	8 163
nicosulfuron	5.97	124
prosulfocarb	0.0516	1.07

A background concentration of bromide of 90.5 µg L^{-1} was determined (Section 3.1) in ditch water from the Brakel location; approximately 1% of the nominal bromide concentration.

3.4 Sampling of water

3.4.1 Discharge proportional sampling

Discharge proportional samples were taken with an ISCO 4700 refrigerated sampler (Figure 8) and the ISCO 3700 portable sampler. The ISCO 4700 sampler was placed at the end of the studied ditch between weir D and the upstream culvert (P2, Figure 6). The ISCO 3700 sampler was placed in the second part of the ditch immediately downstream the first culvert at weir A (P1, Figure 6). Both samplers took water samples in the respective culverts. The samplers were linked to an electromagnetic flow meter that generates pulses corresponding to a specific volume as it passes through: the sampler at P1 by the flow meter at weir A, and the sampler at P2 by the flow meter at weir D. the discharge was therefore not measured at sampling point P1, but from weir A. The discharge at P1 was calculated by estimating lateral fluxes between weir A and sampling location P1.

The ISCO samplers were programmed to collect water samples after a predefined water volume had passed the electromagnetic flow meter based on the anticipated discharge and desired frequency. Both ISCO samplers had a capacity of 24 samples each with a volume of 300 mL, the ISCO 4700 sampler stored samples at 4°C. To avoid sorption of prosulfocarb, water samples were taken via stainless steel pipes to polyethylene and Teflon tubing; tubes were pre-rinsed before taking each sample.

Figure 8 *Discharge proportional sampling device ISCO 4700.*

An overview of the dimensions and calculated water volumes for the two stretches upstream of the two sampling is presented in Table 2.The slope of the ditch below the water surface was vertical; hence the cross-section is the width at the water surface multiplied by the water depth (14 March 2008).

Table 2 *Dimensions and water volume of the ditch stretches. Slopes below the water surface were vertical.*

Compound	Length (m)	Width at water surface (m)	Water depth (m)	Volume (m^3)
Stretch from weir A to second culvert (P1 sampling point)	117	2.74	0.35	112
Stretch from second culvert to weir D (P2 sampling point)	240	3.00	0.35	252

The frequency and total number of samples taken for the two discharge proportional sampling locations P1 and P2 is shown in Table 3. At P1, one sample represents 2 m^3 passing the sampling point in the culvert. Each sample consisted of four subsamples, each taken from a distinct 0.5 m^3. Similarly, at P2, one sample represents 10 m^3 water passing the sampling point, consisting of four subsamples each taken from a distinct 2.5 m^3. The total sampled volume per sample was 240 mL; four subsamples of 60 mL.

Table 3 *Sampling frequency at discharge proportional sampling locations P1 and P2.*

Sampling location	Frequency (expressed as m^3 water passed)	Total number of samples
P1	2	150
P2	10	109

3.4.2 Transversal spot sampling

The transversal distributions of prosulfocarb, nicosulfuron and bromide in the water compartment were investigated during the flow period by means of a purpose-built transversal sampler, allowing six locations over the transversal ditch profile to be sampled simultaneously. The apparatus consisted of six stainless steel tubes (internal diameter 2 mm), fixed in a framework (Figure 9). The figure shows more than six sampling tubes but not all were used in this study. Each of the stainless steel tubes was individually connected to 250 cm^3 flasks by a short piece of polyethylene tubing. The lower end (0.5 cm) of each individual tube was bent in a horizontal direction. Sampling tubes at two depths were situated at both ends and in the middle of the framework. For sampling, the framework with the tubes was carefully lowered below the water surface. After the tubes had been flushed with ditch water, water samples were collected simultaneously by lowering the pressure in the flasks with a vacuum pump.

Using the first sample apparatus (total width of 1.7 m) six samples (2 vertical x 3 horizontal; i.e. at both ends and the middle of framework) were taken at 5 cm and 20 cm depths at locations MP1 and MP2 with a horizontal difference between sample tubes of 85 cm. At location MP3, six samples at similar points were taken with the second sample apparatus (total width 3 m) at 15 and 25 cm depth with a horizontal difference of 150 cm between the sample tubes. The sample locations are indicated in Figure 6.

In the application stretch around MP1, the apparatus was used at 5, 25 and 45 m. At MP2 and MP3, samples were taken at one location only. The distribution of the samples over the cross-sectional area of the ditch is indicated in Figure 10. The sample times for the three locations are given in Table 4.

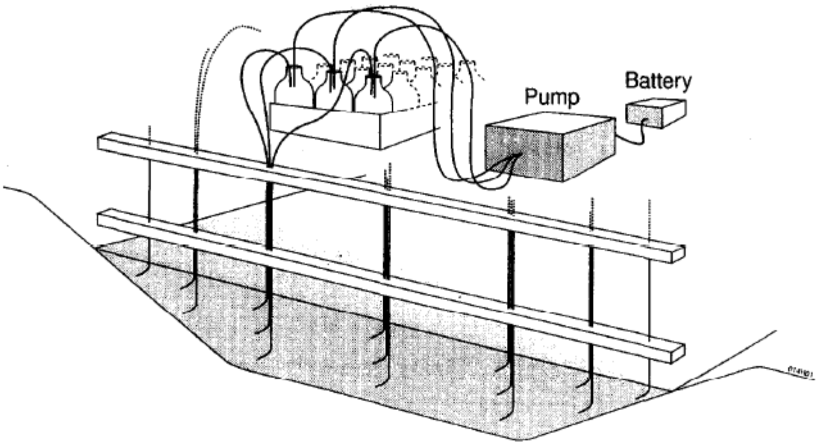

Figure 9 *Spot sampling device. Note, only mid-three series and two depths of sampling positions used.*

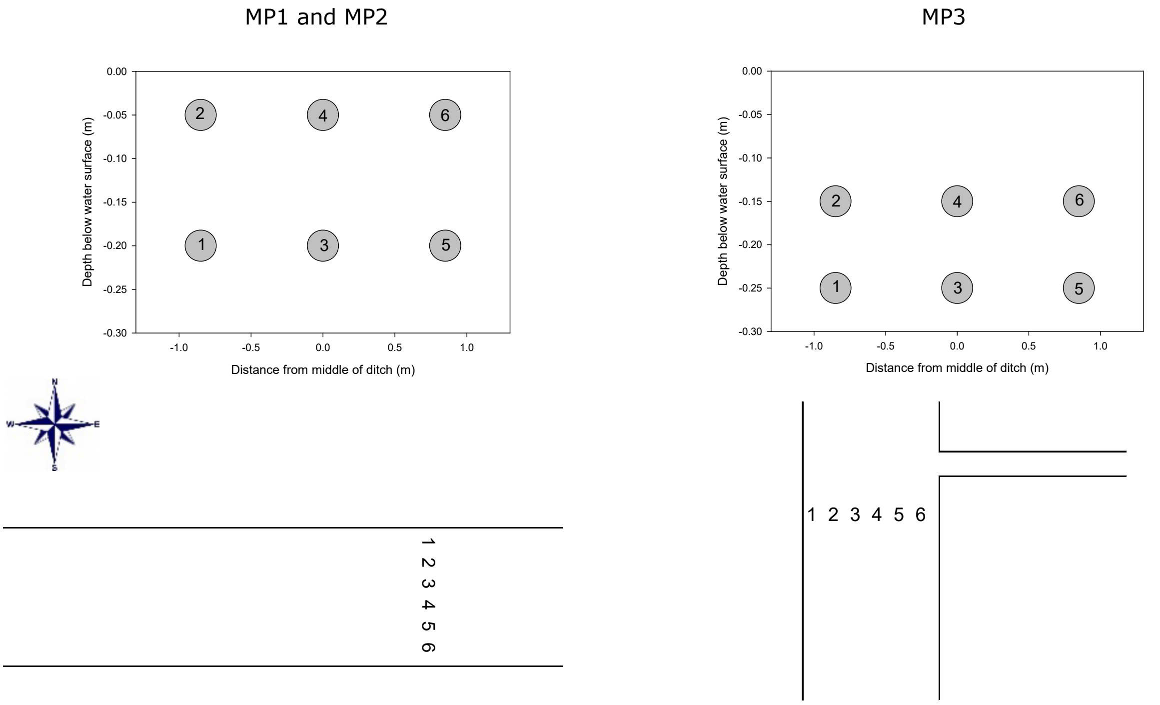

Figure 10 *Position of the sampling points in the cross section of the ditch (upper part) and sequence of sampling points at the sampling locations MP1, MP2 and MP3 from above at the ditch; sampling point 1 North for MP1/MP2 and West for MP3 (lower part).*

Table 4 *Spot sampling; number of hours after application at locations MP1 – MP3.*

Time of sampling (nr or hours after application)	MP1	MP2 and MP3
-48	+	+
1	+	-
3	+	-
11	+	-
12	-	+
20	-	+
22	+	-
25	-	+
28	-	+

3.5 Sampling of sediment

Sediment cores were taken to investigate the concentration of nicosulfuron and prosulfocarb in the sediment layer. The cores were collected by means of Perspex tubes with an internal diameter of 4.0 cm and a length of 30 cm. A tube was inserted carefully into the sediment by hand to a depth of approximately 0.1 m, and then turned once along its vertical axis. Its top opening was then closed with a rubber stopper below the water surface, and the tube with sediment was pulled up carefully. The lower end of the tube was then also closed below the water surface with a rubber stopper. The water layer on top of the sediment was carefully decanted from the tube immediately after the samples had been taken. Sediment samples were taken four times at location MP1, once before application, three times after application (t = 3h, 12h and 23h after application) and three times at location MP2 (t = 12h, 25h and 29h after application).

The tubes with the sediment were stored vertically in a freezer (-20°C) until extraction and analysis.

3.6 Characterisation of the watercourses

3.6.1 Water depth

Water depth was determined by placing a perforated standpipe in the bottom of the ditch with a diver that registered the water level in the tube. Water level was recorded every 15 minutes from 1 - 6 April 2008 and measurements corrected to NAP (Normal Amsterdam level). Divers were installed at locations MP1 (50 m downstream from weir A), close to MP2 (5 m upstream from weir D) and at MP3 (5 m downstream from weir E) (Figure 6).

3.6.2 Discharge

The area in which the system of watercourses is situated is flat, thus there is hardly any gravity flow. Using a measuring weir to measure discharge by overflow was therefore not an appropriate option. Instead, we fitted electromagnetic flow meters (ABB MagMaster Electromagnetic Flowmeter) in the pipe of steel plate weirs (Figure 11). Dommerholt (2007, Annex 4) tested an 8-inch flowmeter in the hydraulics Lab to calibrate flow rates to the water level difference at both sides of the weir. These results were used to determine the required dimensions of the flow meters to fit to the expected discharges in the system of watercourses. Inner diameters selected for the flow meters were: weir A and B: 10 cm, weir C: 15 cm, weir D and E: 20 cm. The flow meters were positioned horizontally in the ditches with the top of the flow meter located 10 cm below the waterboard controlled winter level. The top of the steel plate weirs was positioned 10 cm above the controlled summer level; note that the summer level is higher than the winter level. The electromagnetic flow meters were logged every 15 minutes and signals were transferred by a MobiSense datalogger to a DNS server, providing access to the data.

Figure 11 *Weir E including electromagnetic flow meter placed into the ditch.*

3.6.3 Temperature and pH in water

Water temperature and pH were measured at MP1 and MP2 on 3 and 4 April 2008 using a WTW pH323 meter at 10 cm below the water surface. The temperatures of water at MP2 in were 7.8 and 11.7˚C; a large difference of 2.2˚C (Table 5). This may have been due to time depending different contributions from seepage water and water flowing in from upstream (with higher temperature) contributing to the total volume. The pH values ranged from 8.0 to 8.3. Measurements taken during the night (3 April 24:00) did not differ from those taken during the day.

Table 5 *Temperature and pH of water at MP1 and MP2 in the watercourses during the experiment.*

Date and time	Location	Temperature (˚C)	pH (-)
3 April 24:00	MP1	9.3	8.1
4 April 9:40	MP1	10.0	8.0
4 April 9:30	MP2	7.8	8.3
4 April 16:35	MP2	11.7	8.0

3.6.4 Suspended solids

Surface water was sampled at two locations on 14 March 2008 to determine the amount of suspended solids. The first sample of approximately 10 L was sampled west of weir D, and the second sample of approximately 4 L was taken near MP3. Water was sampled at those two locations because the water colour visually differed, with the water at MP3 being much more turbid, possibly due to higher flow velocity.

The total suspended solids content of the surface water was determined by filtering the water sample through a pre-weighed filter (0.45 µm). The residue retained on the filter was dried in an oven at 105°C and weighed. The increase in filter weight represents the total suspended solids.

The sample taken near weir D contained 1.2 mg L^{-1} suspended solids and that taken near MP3 contained 8.6 mg L^{-1} suspended solids. Organic matter content (loss on ignition, ash free dry weight) was determined, but results are inaccurate because of the low net mass of suspended solids sampled (0.003 g from 0.0143 g and 0.0011 g from 0.0393 g; 20% and 28% respectively). The loss on ignition method for determining organic matter involves heated destruction of organic matter in the suspended solids in an oven at 550°C.

3.6.5 Sediment properties

Sediment for sediment characterization and sorption study
On 2 April 2008, sediment was sampled from the ditch upstream of the application stretch (8, 12 and 16 m; 10 cores each) at the test location in Brakel. This was used for sediment characterisation and for the sorption study with prosulfocarb (Section 4.3). Sediment cores were taken using Perspex tubes with an internal diameter of 4.0 cm. A tube was inserted by hand into the sediment to a depth of approximately 7 cm and then turned along its vertical axis. The top of the tube was closed using a rubber stopper and the tube with sediment gently pulled up. The lower end of the tube was kept below the water surface and closed with a second rubber stopper. Immediately after the tube with sediment sample was retrieved from the water column, the water layer in the tube was carefully decanted.

The sediment tubes were transported upright to the laboratory and frozen at a temperature of approximately – 20˚C. In the laboratory, the frozen sediment cores were separated from the tubes. The remaining water above the sediment layer was carefully removed and the top 1 cm of the frozen core was separated from the rest. The upper 1 cm sediment of all the cores was collected and stored in the refrigerator at 10˚C. The rest of the sediment (approx. 6 cm) was sieved through a 2 mm sieve. Water was removed from the settled sediment.

The nitrogen content of the sieved sediment was determined using a dry combustion method (Dumas method) and the total organic carbon content was determined with a Leco carbon analyser. The upper sediment layer (duple determination) had a nitrogen content of 0.58% and 0.58%, and a total organic carbon content of 5.44% and 5.48%. The organic matter content was determined via loss on ignition, resulting in an organic carbon content of 13.5% (s.d.=0.1%, n=3). The amount of Fe was determined by destruction with aqua regia (HNO_3-HCL) and analysis by ICP-AES. The sediment contained 48.7 g Fe kg^{-1} d.w. and 49.1 g Fe kg^{-1} d.w..

The particle size distribution of the sieved sediment was determined using the pipette method, resulting in mass fractions: 38.8% <2 μm; 72.6% <16 μm; 77.8% <50 μm; 7.08% >50 μm. The total for the mineral part was 84.9% with the remaining 15.1% being organic matter. The texture of the sediment was calculated for the mineral parts only, resulting in: 45.7% <2 μm (clay); 39.8% 2-16 μm; 6.1% 16-50 μm (2-50 μm, silt 45.9%); 8.3% >50 μm (sand). Following the USDA classification, the sediment is a silty clay.

Sediment cores for pesticide concentration and sediment properties per layer

Sediment cores to determine pesticide concentrations and the sediment properties bulk density, porosity and organic matter content as a function of depth were similarly sampled. In the laboratory, the frozen cores were cut into three layers: 0-1 cm, 1-2 and 2-4 cm. After extraction of the samples for chemical analysis, bulk density and volume fraction of liquid were determined per sampled sediment layer using dry weight and water volume. The dry mass of each layer was determined by drying the layer in a centrifuge tube at a temperature of 105°C for 24 hours after removing the solvent used for extracting the pesticides (Section 3.8.2). The sediment was then transferred to ceramic crucibles and the loss on ignition was determined in an oven at 550°C.

The average values of bulk density, volume fraction of liquid and organic matter content, for every sediment layer are shown in Table 6; the measurement results are given in Annex 5. The volume of each layer was corrected for the lower density of frozen water in its liquid phase, using the method described in Section 4.3 of Adriaanse et al. (2015).

The volume fraction of liquid of the top layers of the sediment is high and likely overestimated. When the volume fraction of water and sediment (dry weight) of the original data (Annex 5) is summed, the volume of the 0-1 cm layer (volume 12.57 cm^3) is exceeded, indicating the separated frozen sediment layers had a larger volume than the volume core up to 1 cm, an impossibility. This overestimation of the volume fraction of water in the upper layer may be due to cone formation resulting from physical changes of the core during the freezing process. The unrealistic volume of the 1 cm layer was corrected assuming that instead of exactly 1.0 cm 1.1 cm was cut off (Annex 5). The water content of layers 0-1 and 1-2 cm was high, leading to calculated volumetric fraction of liquid > 1; in these cases the value was set to 1 (8 times for 0-1 cm, and 11 times for 1-2 cm), as values greater than one are unrealistic.

The average bulk density of the 1-2 cm layer is 0.33 kg L^{-1}; higher than the average for the 2-4 cm layer of 0.30 kg L^{-1}. However the small number of ten samples of layer 2-4 cm showed a high variation of 34%, indicating a variable bulk density for this layer; even more variable than for other layers.

Table 6 *Bulk density and volume fraction of liquid of three layers (n = 24 (0-1 cm), 20 (1-2 cm) and 8 (2-4 cm)) and loss on ignition (n = 24 (0-1 cm), 18 (1-2 cm) and 10 (2-4 cm)) of the top 4 cm of sediment. Locations MP1 (3 April 14:40/21:45, 4 April 10:50) and MP2 (4 April 00:30/13:00/17:00). Note the different number of samples for all three layers due to priorities for chemical analysis of top layers above lower layers.*

Layer (cm)	Bulk density (kg L^{-1})		Volume fraction of liquid (L L^{-1})		Organic matter content (%)	
	Average	s.d.	Average	s.d.	Average	s.d.
0 – 1	0.198	0.036	0.98	0.05	14.6	1.1
1 – 2	0.329	0.065	0.93	0.04	14.1	0.8
2 – 4	0.301	0.102	0.81	0.05	14.2	1.8

To check for background concentrations, the sediment was sampled at MP1 on 3 April. No nicosulfuron was detected in the top 2 cm. However, prosulfocarb concentrations were found in all three layers down to 3 cm depth. The depth average of total concentration of both cores taken was 0.09 µg L^{-1}, with the highest total concentrations found for layer 2-3 cm, 0.12 and 0.13 µg L^{-1}. This concentration corresponds to 2.7 µg per m^2 bottom of the ditch, present in the top 3 cm of the sediment. The analysis of prosulfocarb on LC-MSMS was checked using qualifier and quantifier, and therefore false positive results are unlikely. As a control, sediment from one of the WENR experimental ditches was analysed, where sediment prosulfocarb concentrations were < LOD. It is unlikely that prosulfocarb was applied in the adjacent fields in Brakel as prosulfocarb is not applied in grass, but it may have been used in crops in the area as it is registered for fibre crops. Upstream from the application stretch willow was grown and prior to planting, prosulfocarb may have been applied. However, we are unsure whether willow is a classified as a fibre crop; in addition to hemp and flax, the Ctgb's DTG-list entry for fibre crops includes "other fibre crops" (Evaluation manual Ctgb).

3.6.6 Distribution of plants

Algae flab was settled at the bottom of the ditches with a coverage 80 to 90% in the treated ditch stretch. The most abundant macrophyte was *Elodea nuttallii* (coverage < 5%). With a negligible presence of other macrophytes. All data on macrophyte presence in the watercourses are given Annex 6.

3.7 Analysis of bromide in water

The bromide was analysed on an isocratic HPLC setup with UV-detector. Samples of 200 µL were injected into liquid chromatographic column (Agilent Hypersil ODS, 5 µm extraction column, 25 x 4.6 mm) at 25°C. The mobile phase was 0.72 g L^{-1} Na_2HPO_4, 0.85 g L^{-1} KH_2PO_4, and 0.001 M tetrabutylammonium dihydrogen phosphate, with a flow rate of 1.0 mL min^{-1}. Bromide was detected at wavelength 210 nm. The retention time was approximately 11 min.

A subsample of approximately 1.5 mL was transferred via a Millex-HV 0.45 µm PVDF Durapore filter in an HPLC-vial. Standard stock and other solutions of potassium bromide were prepared in MilliQ water. Concentrations were calculated from the calibration curve of standard solutions, where a minimum of three concentration levels were used. Concentrations of samples were always lower than the highest standard.

3.8 Extraction and analysis of nicosulfuron and prosulfocarb

3.8.1 Water

Prior to analysis, sampled water stored in the bottles was homogenized and then 4 mL was transferred with a capilettor to a 10 mL tube containing 1 mL of acetonitrile. If necessary an amount of the sampled water was concentrated on an OASIS C-18 columns and again eluted with acetonitrile. The samples were analysed by LC-MS/MS. Prosulfocarb and nicosulfuron were analysed in one workflow using gradient elution (Annex 7).

A subsample of approximately 4.0 mL was transferred into a 10 mL tube to which 1.0 mL acetonitrile was added. The subsample was filtered through a Millex-HV 0.45 µm PVDF Durapore filter. Stock solutions of nicosulfuron and prosulfocarb were prepared in acetonitrile and stored in the freezer. Standards were prepared in 20v/80v acetonitrile/MilliQwater. Concentrations were calculated from the calibration curve of standard solutions, where minimally three concentration levels were used. Concentrations of samples were always lower than the highest standard.

No matrix effects were found with Brakel surface water in the LC-MSMS analyses when measuring nicosulfuron and prosulfocarb.

3.8.2 Sediment

The sediment samples with cores (Section 3.6.5; S*ediment cores for pesticide concentration and sediment properties per layer*) were divided in layers in order to study the stratification of nicosulfuron and prosulfocarb. Three layers (0-1 cm, 1-2 cm, 2-4 cm) were cut from the frozen sediment cores sampled at 2 (before application) and 3 April 2008. The layer 2-4 cm was not sampled because it was expected that concentrations below 2 cm would be negligible at that time due to diffusion back into the water layer. Two layers were cut (0-1 cm, 1-2 cm) from the cores sampled on 4 and 5 April. After thawing, the layers were transferred to 100 mL centrifuge tubes and weighed. The sediment was extracted with 60 mL acetonitrile, by shaking the suspension intensively for 1h on a shaking device (200 rpm). After phase separation, a subsample of the acetonitrile layer was removed and analysed directly by LC-MSMS. When further concentration was necessary, a volume of the extract was evaporated to a fixed volume.

The extraction efficiency of prosulfocarb from sediment was determined. Brakel sediment used in the sorption study (Section 6.2) was spiked with a small amount of dose solution (100 µL) at three concentration levels in triplicate (3, 13 and 107 µg kg^{-1} dry weight sediment). During a contact time of 1h the sediment was manually swerved several times. After 1h, the sediment was extracted with acetonitrile (ca. 30 mL g^{-1} dry sediment) on a shaking device for 1h (200 rpm) at room temperature. The extract was centrifuged for 10 min. at 3000 rpm. If necessary acetonitrile was concentrated by evaporation. The recovery for prosulfocarb application levels 3, 13 and 107 µg kg^{-1} dry weight sediment amounted to 85% (s.d.=2%, n=3), 97% (s.d.=6%, n=3) and 94% (s.d.=1%, n=3), respectively.

The extraction efficiency of nicosulfuron from sediment was not tested as nicosulfuron adsorbs weakly to organic matter and sediment concentrations are calculated from porewater concentrations.

4 Laboratory experiments on transformation and sorption: materials and methods

4.1 Introduction

To simulate the field study in models, the sensitive compound parameters is determined with material from the studied field location. The main sensitive compound parameters for simulation of fate in surface water are the transformation rates in water and sorption coefficients (Westein et al., 1998). Hence these compound parameters were determined for nicosulfuron and for prosulfocarb. As the residence time of these compounds in water in the system of watercourses is in the order of a few days, we analysed the degradation of the two compounds in surface water from the Brakel ditches for eight days.

Nicosulfuron has a low sorption coefficient (K_{foc} 21 L kg^{-1} in PPDB; Lewis et al., 2016), so adsorption to sediment organic matter is expected to be negligible. Therefore, we did not conduct a sorption study, but only studied its transformation in water.

Prosulfocarb has a higher sorption coefficient (K_{foc} 1693 L kg^{-1} in PPDB; Lewis et al., 2016), so adsorption to sediment organic matter and fate of prosulfocarb in sediment is expected to be relevant for the fate in the system of watercourses. Therefore, we conducted a sorption lab study with prosulfocarb with sediment from the treated watercourse stretch. Note that sorption coefficients determined for sediment are also used for adsorption to suspended solids.

In principle, the transformation of prosulfocarb in sediment cannot be determined from a water-sediment study as sorption dominates the fate in the study and thus the less important process of degradation rate cannot be ideally fitted (ter Horst and Koelmans, 2016). Thus, a degradation study should only use sediment. However, with a residence time of prosulfocarb in the system of watercourses of only a few days, with little time for penetration into the sediment, the transformation in the expected low prosulfocarb mass in the sediment was considered to have a negligible effect on the overall fate of prosulfocarb. Moreover, the overall system half-life from a water-sediment study is 214 days (PPDB; Lewis et al., 2016), representing the degradation in the mass sorbed to the sediment in test tubes. This supports our assumption of negligible relevance of the degradation in sediment for the overall fate of prosulfocarb in the test period. Therefore, we opted for performing transformation water studies for nicosulfuron and prosulfocarb in water, and a sorption study for prosulfocarb only.

4.2 Transformation of nicosulfuron and of prosulfocarb in water

4.2.1 Experimental design

For the experiment, surface water was sampled from the watercourse of the test location in Brakel at approximately 10 m west of weir A on 6 March 2008. Eleven Schott bottles (2 L) were filled with 2 L of surface water. The bottles were transported to Wageningen on the same day and stored at 5°C until use. During the experiment the bottles were placed in a water bath for temperature regulation. Artificial daylight was provided by HPI-T 400 W high pressure metal halide lamps. A daily light period (200 µE m^{-1} s^{-1}) of 14h and a temperature of 10°C ± 2°C was maintained; the temperature is comparable with that at the test location. Three bottles containing blank surface water were included for background analyses. Evaporation of the water was quantified in the third blank bottle during the degradation experiment.

The degradation experiment of prosulfocarb and nicosulfuron lasted eight days. The degradation of both compounds was determined at two concentration levels in duplicate, one concentration approximating the field concentration after dosing and one concentration level five times lower (1.11 µg L^{-1} and 0.22 µg L^{-1} for prosulfocarb and 100 µg L^{-1} and 20 µg L^{-1} for nicosulfuron). Samples were taken at day 0 (t=0, t=6h), 2, 3, 4 and 8 after application. During the test, the pH, dissolved oxygen, and temperature in the blank test bottles were monitored.

4.2.2 Preparation of dose solution

An amount of 5.97 g of potassium bromide (Alpha Ceasar, purity KBr 99%) was dissolved in 500.35 g tap water. The potassium bromide salt contains 67% bromide (w/w), resulting in a concentration of bromide of 8 g L^{-1} (stock C). Stock C was diluted four times with tap water, resulting in a bromide concentration of 2 g L^{-1} (stock D).

An amount of 1.41 g of the formulated product Boxer (78.4% prosulfocarb, w/w, Syngenta) was dissolved in 100.6 g of tap water. Of this solution, 1.01 mL was diluted in 100.2 mL tap water resulting in a prosulfocarb concentration of 111 mg L^{-1} (stock E).

An amount of 2.51 g of the formulated product Milagro (4% nicosulfuron, w/w, Syngenta) was added to a 1 L Schott flask, before adding 10 g of prosulfocarb solution stock E (111 mg L^{-1}). The flask was filled with tap water to a total volume of 1000 mL, resulting in a concentration of nicosulfuron of 100 mg L^{-1} and prosulfocarb of 1.11 mg L^{-1} (Stock A). Dose solution stock A was diluted five times by adding 40 mL tap water to 10 mL stock A to prepare stock B.

4.2.3 Dosing

From dose solutions Stock A and B, a volume of 2.0 mL was transferred in triplicate with a capilettor to 2 L of surface water sampled from Brakel ditches on 6 March 2008, thereby preparing theoretical concentrations of 1.11 µg L^{-1} and 0.22 µg L^{-1} for prosulfocarb and of 100 µg L^{-1} and 20 µg L^{-1} for nicosulfuron. To the solutions, 2 mL of stock C (8 g L^{-1} bromide) and stock D (1.6 g L^{-1} bromide) were applied to the highest and the lowest concentration level of pesticides, respectively. This resulted in theoretical bromide concentrations of 8 and 1.6 mg L^{-1}. After application of the test compounds, the bottles with test water were shaken manually.

4.2.4 Sampling and analysis

Before sampling, the test water in the flasks was shaken again, before transferring 4 mL of test water to a 10 mL tube containing 1 mL of acetonitrile with a capilettor. Samples of day 1 and day 8 were analysed after mixing, eight days after starting the degradation experiment. Remaining samples were analysed at a later time.

4.3 Sorption of prosulfocarb to sediment

4.3.1 Collection of sediment

As described in Section 3.5.5., the frozen sediment cores were taken out of the tubes, overlying water was carefully removed, and the top 1 cm of the frozen sediment core was separated from the rest by sawing. After thawing, the sediment mass (1-cm top layers) of all the cores was collected and stored in a refrigerator at 10 °C. The sediment was sieved through a 2 mm sieve, left to settle before carefully decanting overlying water. The remaining sediment was used for the sorption study and contained ca. 6% water and an organic matter content of ca. 13% (loss on ignition).

4.3.2 Preparation of prosulfocarb solutions

To avoid the use of organic solvents in the sorption system, as this may influence the sorption of the test compound, we prepared a saturated dose solution of prosulfocarb in water using a generator column. An amount of prosulfocarb (ca. 5 mg) was dissolved in acetone (4 mL) and added to glass beats (Ø 0.2 mm). Through evaporating the acetone, the glass beads were coated with prosulfocarb and added to an HPLC-column (ca. 10 g). The column was eluted with demineralised water (0.01M $CaCl_2$) and collected in a glass vessel. A prosulfocarb concentration of approximately 12 mg L^{-1} was prepared comparable with the solubility of 13.2 mg L^{-1} in PPDB (Lewis et al., 2016). The saturated sample was diluted with demineralised water (0.01M $CaCl_2$) to various concentrations of prosulfocarb. The measured prosulfocarb concentrations in the dose solutions corresponds to the concentration calculated by dilution factors of the saturated solution (94-103% of the expected concentration).

4.3.3 Experimental design

The adsorption was determined using the WENR standard operation procedure based on OECD 106, The procedure is summarized below and amended with details specific for this study. The aim of the batch experiment is to measure sorption of prosulfocarb to Brakel sediment in a system where there is perfect mixing with water. The principle of the measurement procedure is to add an aqueous substance solution to the sediment and to measure the decrease in the concentration caused by sorption.

The experiment was conducted in triplicate at six concentration levels in the dark at 10°C. A blank sediment was rotated with a solution without prosulfocarb to check for background of prosulfocarb, in duplicate. The adsorption of prosulfocarb to glass was determined by taking two solutions of prosulfocarb without adding sediment, 126 µg L^{-1} and 896 µg L^{-1}, both in duplicate.

The sorption test was carried out in 10 mL glass tubes with screw caps with a Teflon inlay. The dry weight/water ratio was approximately 1:4.3. This ratio was chosen to use a minimum of water, reaching a suspension close to the water content of the original Brakel sediment and to produce a suspension miscible in the glass vessel on the sorption wheel.

Known volumes (ca. 5 mL) of solutions of prosulfocarb at six concentration levels (3, 30, 100, 300, 1000, 3000 µg L^{-1}) in triplicate were added to sediment samples with a wet weight of 6 g (65% water). Triplicate samples were taken from each dose solution of prosulfocarb.

The suspensions were mixed continuously on a rotation wheel (6 rpm) in an incubator at a temperature of 10˚C for 24h. After 24h, the soil suspensions were separated by centrifugation at 3000 rpm for 30 min at 10˚C. A part (ca. 3.2 mL) of the aqueous solution was added to a 4 mL vial containing 0.8 mL acetonitrile, another aqueous sample was taken as spare. The mass of prosulfocarb adsorbed to the sediment was calculated as the difference between the amount of prosulfocarb initially present in solution and the amount remaining in solution after 24h.

In blank Brakel sediment (duplicate) a background concentration of prosulfocarb was found of 1.4 µg kg^{-1} dry weight. The concentrations in the sorption study were not corrected for background concentrations of prosulfocarb, as the results of the 3 µg L^{-1} level were not used, and for the other (higher) levels this background concentration is not significant compared to the concentration levels applied in the sorption studies (Section 6.2).

To check adsorption of prosulfocarb to the glass tube (including Teflon inlay), a prosulfocarb solution was dosed without sediment at two concentration levels. Glass tubes were filled with water at one of the two concentration levels (126 µg L^{-1} and 896 µg L^{-1}) in fourfold. At each concentration level, tube caps had a Teflon inlayer. The eight tubes were agitated for 24h. For prosulfocarb application of 126 µg L^{-1} and 896 µg L^{-1}, we recorded recoveries of 95% (s.d.=1.2%, n=4) and 99% (s.d.=2%, n=4) respectively. Thus, we concluded that adsorption to glass tubes including the Teflon inlays could be neglected.

The mass balance of prosulfocarb in the sorption study was checked using the highest application level (3000 µg L^{-1}). After 24h of rotation and taking ca. 3.2 mL from the solution (see above) the sediment with the remaining water was extracted with acetonitrile (30 mL g^{-1} dry sediment) on a shaking device for 1h (200 rpm) at room temperature. The extract was centrifuged for 10 min. at 3000 rpm and analysed directly. The mass balance amounted to 92.3% (s.d.=0.8%, n=3), corresponding with the extraction efficiency test

(Section 3.8.2) for the highest application level (107 µg kg^{-1}) of 94%. During the test, prosulfocarb was considered stable; > 90% of the test compound is recovered, OECD 106.

For estimating the Freundlich isotherm (K_f), the prosulfocarb concentration in water (µg L^{-1}) and prosulfocarb adsorbed to the sediment (µg kg^{-1}) were fitted by linear regression after logarithmic transformation (reference concentration =1 mg L^{-1}) using the LINEST function in MS Excel.

The Freundlich isotherm (K_f and N parameters) were estimated for prosulfocarb by linear regression on the concentration in water (µg L^{-1}) versus content sorbed in sediment (µg kg^{-1}) after logarithmic transformation for a reference concentration =1000 µg L^{-1} using the LINEST function in MS Excel.

5 Field study: results and discussion

5.1 Water depth and discharge

Throughout the test, water depth and discharge were measured continuously to determine the dynamics of the water balance of the system of watercourses. The results are described in this Section. Annex 8 gives an overview of detailed data on water depth and discharge.

Water depths

The water depths in the watercourse at locations MP1 (50 m downstream from weir A; Figure 6), and close to MP2 (5 m upstream from weir D) from 3 April 10:00 to 6 April 00:00 are shown in Figure 12. The water depth was also measured at MP3, near weir E. The water depth profile at MP3 is similar to the water depth profile at MP2, but is generally approximately 3 cm lower (Annex 9).

The effect of the twice daily pumping water out of the polder district is clearly visible in the pattern of the water depth in the watercourse (Annex 9; water levels from 1–7 April). The water depth decreases as water is pumped out of the polder, increasing again due to entry of water via upward seepage through the ditch bottom and walls and because water was pumped into the watercourses by Pumps 1 – 3 (Figure 3).

The periods when water was pumped out of the polder and the water level dropped (Figure 12) were:
3 April 11:30 – 15:00 h,
4 April 7:30 – 10:00 h,
4 April 17:00 – 20:00h,
5 April 2:00 – 4:00h,
5 April 12:00 – 14:00h,
5 April 18:00 – 20:00h.

The difference in water depth before and after pumping at location MP2 was 7 cm on 3 April, whereas the difference at MP1 was 1 cm. The effect of pumping water out was small at MP1, as outflow was slowed by the presence of several weirs and partially compensated by inflow from Pump 1.

To facilitate the experiment on 3 April, Waterboard Rivierenland pumped water out of the polder for a longer (3.5h) than usual (Section 3.6.2), lowering the water level somewhat more. This generated a flow during the application of the compounds; thereafter a longer period of low, but still one-directional flow occurred.

Discharges

The discharge measured through weirs A, B, C, and D are shown in Figure 13, and the cumulative of the discharges in Figure 14. The discharge through weir E was measured, but was not considered relevant for the interpretation of the experiment, and is therefore not shown in the figures.

In periods when water was pumped out of the polder (indicated by dropping water levels), discharge in the watercourses increased. Hence, during the field experiment there were four short periods of 2 – 3.5h in which the discharge was 15 - 23 L s^{-1} at weir D, compared to the 'normal' discharge of approximately 7 – 13 L s^{-1}; a temporary factor 2 increase in discharge.

The water balance for the period 3 April 10h - 5 April 24h is presented in Annex 9. The total discharged volume was 2420 m^3 at weir D, and 590 m^3 at weir A. Thus at weir D, the water was diluted by a factor 2420/590 = 4.1; this dilution factor is expected for compounds entering the watercourse directly downstream from weir A.

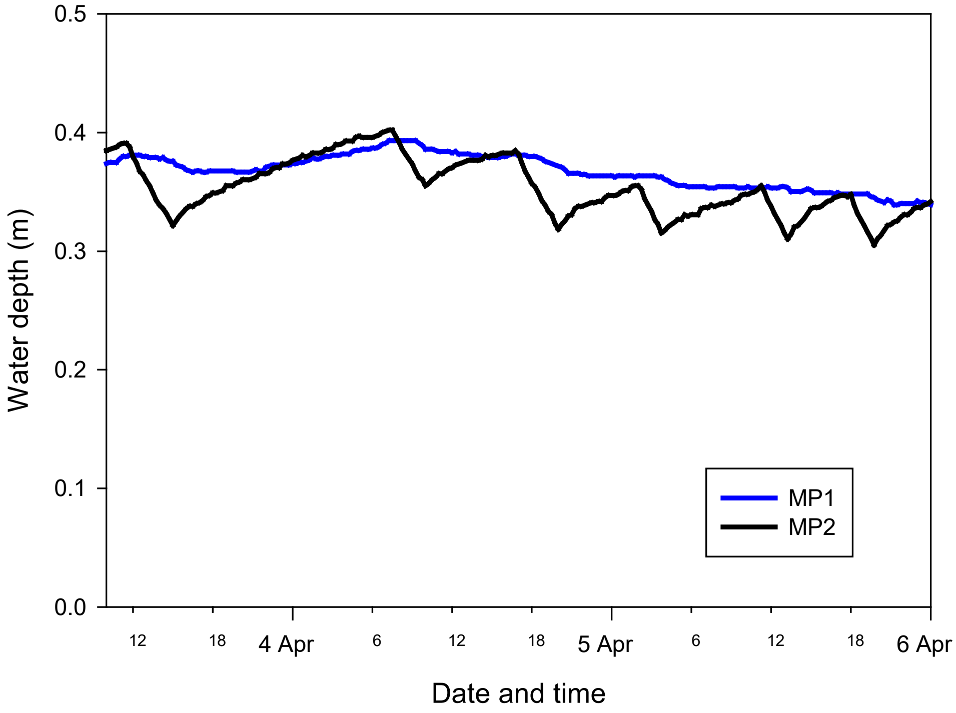

Figure 12 *Water depth at MP1 (downstream from weir A) and at MP2 (upstream from weir D) between 3 April 10h and 6 April 0h.*

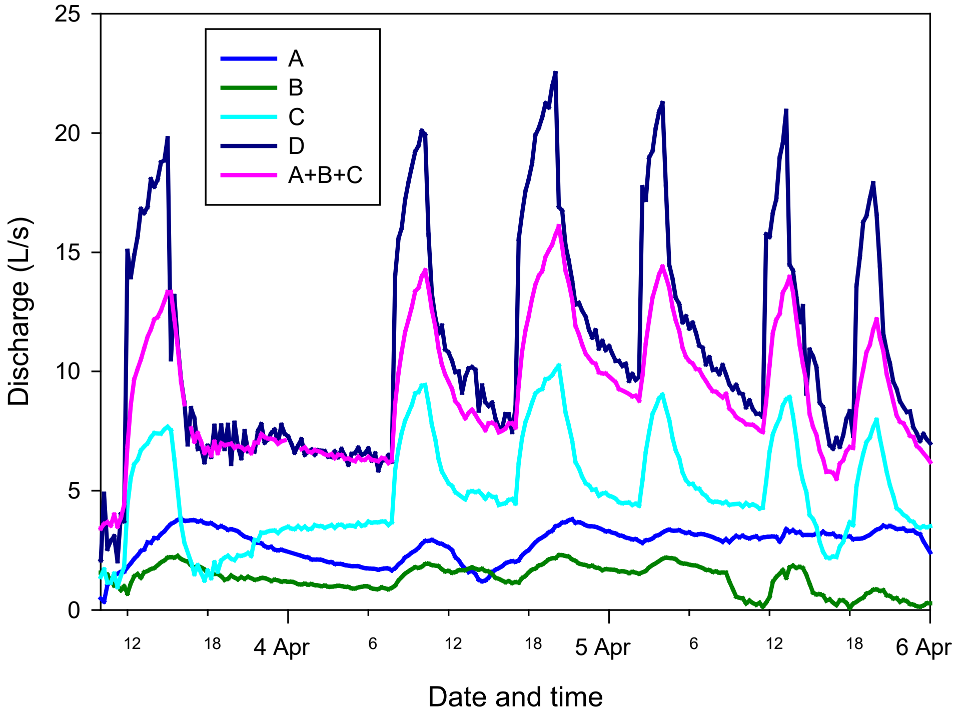

Figure 13 *Discharges at weir A – D between 3 April 10h and 6 April 0h. The cumulative discharge of weirs A – C is also given.*

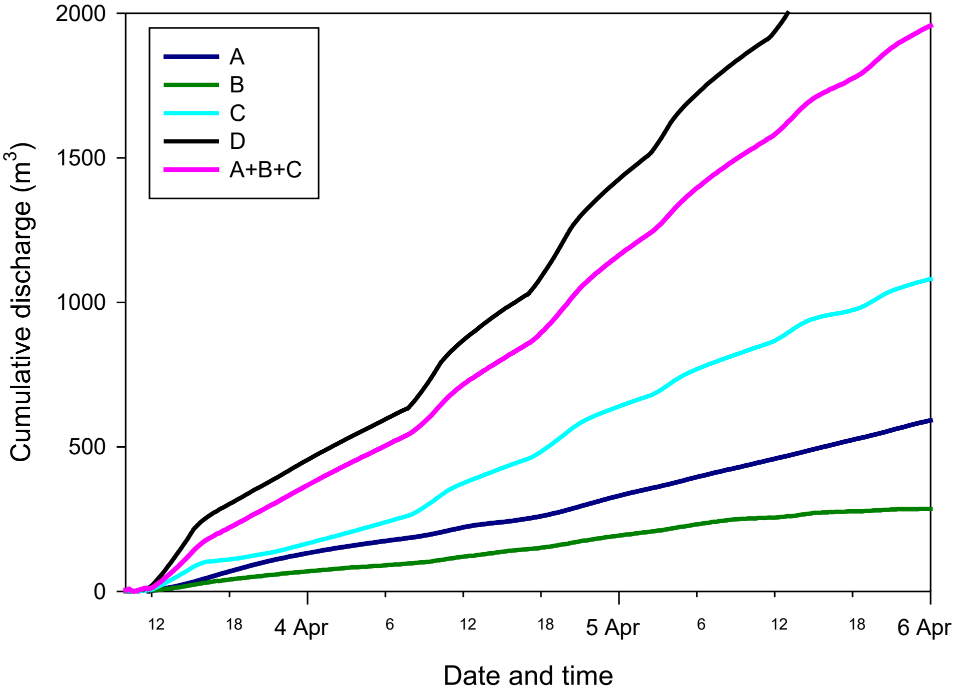

Figure 14 *Cumulative discharge at weirs A, B, C and D, as well as the cumulative discharge of weirs A+B+C between 3 April 10h and 6 April 0h.*

5.2 Concentration in water flow

Bromide, nicosulfuron and prosulfocarb were measured in discharge proportional samples at two locations (P1 and P2; Figure 6) to determine their transport. The results are described in this Section.

5.2.1 Nominal concentrations at time of application

The nominal concentrations were calculated from the volume of solutions sprayed on the 50 m application stretch and the measured concentration in the spray solutions in Section 3.3.2 (see Table 1). These are: bromide 8 163 µg L^{-1}, nicosulfuron 124 µg L^{-1} and prosulfocarb 1.07 µg L^{-1}.

5.2.2 Bromide

The concentration of bromide in water passing P1 and P2 is shown in Figure 15. At P1 the peak concentration was 6 633 µg L^{-1} measured on 3 April at 16:35, 5h after the application (Annex 10). This is 20% lower than the nominal concentration of 8 163 mg L^{-1}.

The distance between P1 and the middle of the application stretch was 67 m (117 m – 50 m). Based on the travel time of 5h, the flow velocity over 67 m is roughly 13 m h^{-1}. Transport from the application stretch was mainly determined by water flowing in at weir A. On 3 April from 11:30 to 16:35, discharge at weir A was between 1.8 L s^{-1} to 3.8 L s^{-1} (Figure 13), but relatively constant compared to discharge at weir C.

At P2, the peak concentration on 4 April at 5:45 was 1 873 µg L^{-1}, measured approximately 18h after the application, 13h after the peak passed at P1. Thus, the continuous entries of uncontaminated water from 3 April 16:35 and 4 April 5:45 between P1 and P2 via weir B (0.9 – 2.0 L s^{-1}) and via weir C (1.2 – 3.7 L s^{-1}) (Figures 3 and 13) caused a substantial (factor 3.5) decrease in peak concentration. The dilution, calculated by dividing the cumulative discharge in the 13h at weir D (equivalent to A+B+C; Figure 13); 595.1 - 263.3 = 331.8 m^3 by the cumulative discharge at weir A; 178.8 - 49.6 = 129.2 m^3, is 2.6. The decrease of peak concentration between P1 and P2 (factor 3.5) was thus higher than the calculated dilution factor 2.6; this can be attributed to dilution and longitudinal dispersion. Note that the dilution factor here is lower than that calculated for the full period (Section 5.1).

Pumping water out of the polder on 4 April from 7:30 - 10:00h interfered with the period that the bromide, nicosulfuron, and prosulfocarb passed P2. In this period the discharge at D was 2-3 times higher than in the preceding 14h (Figure 13). The timings of the samples were allocated by dividing the total time of the sampling interval by the number of samples taken. However, sampling at P2 was steered by the discharge measured at weir D (Section 3.4.1). Thus, in the period for P2 (4 April 00:00 – 9:33; see P2 in Annex 10) the samples taken from 7:30 – 9:33 (between 9:33 and 10:06 no samples taken) had shorter time intervals because of the higher discharge than in the first part of the period. Therefore the sample with the highest concentration, at 5:45, passed P1 at a later time. Assuming (worst case) that the discharge in the pumping period is three times that of the previous period (hence 3x shorter sampling intervals in this period) the passing of the peak would have occurred at approximately 7:00 instead of 5:45; approximately one hour later. This delay is not further considered in the analysis of the results.

In the final measurements, on 6 April (P1 6:48 and P2 14:55) concentrations had decreased to 95 µg L^{-1} at P1 and 135 µg L^{-1} at P2, still above the background concentration of approximately 90 µg L^{-1} (Section 3.3.2). Hence, there was still a tail of the applied bromide passing at P2.

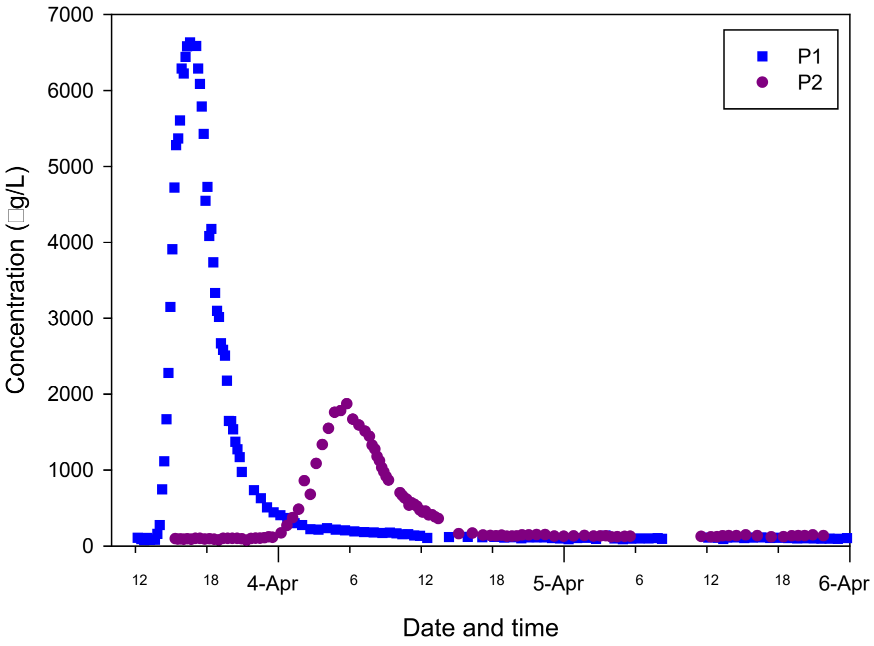

Figure 15 *Concentration of bromide in discharge water at sampling points P1 and P2 between 4 April 12h and 6 April 0h.*

5.2.3 Nicosulfuron

Figure 16 shows the concentration of nicosulfuron in discharge water passing P1 and P2. At P1 the peak concentration was 99.8 µg L^{-1} measured at 17:25, 5.5h after the application, 20% lower than the nominal concentration of 124 µg L^{-1}.

At P2 the peak concentration was 22.5 µg L^{-1} measured on 4 April at 6:15, approximately 18h after the application. The continuous entries of uncontaminated water between P1 and P2 via weir B and via weir C (Figure 3) had thus caused a substantial (factor 5.5) decrease in peak concentration (Section 5.2.2, discussion).

The nicosulfuron peak passed P1 one hour later than that of bromide. At P2 the delay was 15 min. The decrease in concentration of the peaks at P1 and P2, (factor 4.4),was higher than that calculated for bromide (factor 3.5). In this short time, no dissipation of nicosulfuron was expected, and sorption to sediment is not relevant as its sorption coefficient is small. Bromide was applied 30 min. earlier than nicosulfuron. Between 12:00 and 16:15, the discharge across weir C was higher (2.8 – 7.7 L s^{-1}) due to water being pumped out of the polder (Figure 13). This may have increased dispersion of the first part of the passing bromide “block”. Furthermore, we observed a white layer on the water directly after application, drifting to the north side of the ditch, expressing incomplete mixing of the pesticides in the water layer directly after application. This was confirmed by samples taken from the water surface (Section 3.3.2). This process may have increased the longitudinal dispersion of the nicosulfuron.

At P1 the concentration was below the Limit of Detection (LOD) on 5 April from 2:41, and at P2 on 5 April from 11:39, marking that the nicosulfuron applied to the upstream stretch passed P1 and P2, except for a small tail of concentrations below LOD.

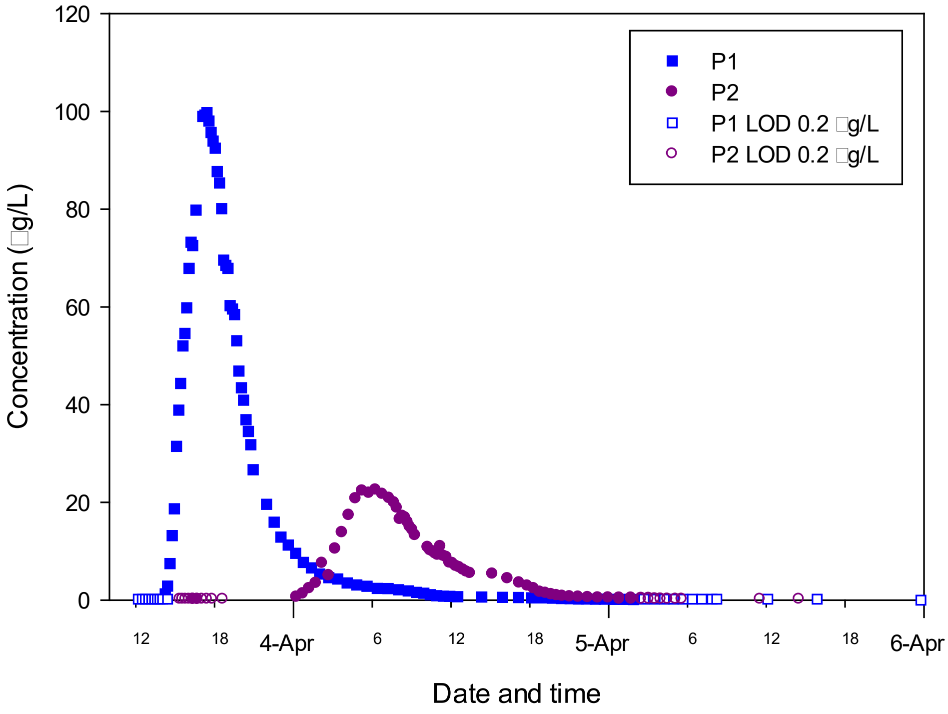

Figure 16 *Concentration of nicosulfuron in discharge water at sampling points P1 and P2 between 4 April 12h and 6 April 0h. Concentrations below LOD are shown as open symbols.*

5.2.4 Prosulfocarb

The concentration of prosulfocarb in discharge water passing P1 and P2 is shown in Figure 17. The peak concentration of 596 ng L^{-1} at P1 was measured at 17:06, 5h after application; 44% of the nominal concentration (1070 ng L^{-1}). Prosulfocarb has a high sorption coefficient; hence sorption to the sediment may explain this smaller decrease. Prosulfocarb was applied together with nicosulfuron, which adsorbs weakly and only showed a decrease in concentration of 20%.

At P2, a peak concentration prosulfocarb of 141 ng L^{-1} was measured on 4 April at 5:14, approximately 17h after application, around 1h earlier than that of nicosulfuron, although they were applied in the same solution. The concentration decreases from the peak at P1 to P2 by factor 4.2, similar to nicosulfuron and higher than the factor 3.5 calculated for bromide.

The LOD for direct measurements on LC-MSMS is 20 ng L^{-1}. Where concentrations of prosulfocarb were expected to drop below this LOD, samples were pooled and extracted together to the set volume of extraction solution for measuring lower concentrations (values below LOD limit shown in Figure 17). LOD of these pulled samples varied around 1 ng L^{-1}. The choice of which samples to pool due to decreasing LOD was made on the basis of expected concentration decrease. The unexpected decrease in concentration at P1 on 4 April between 5:30h - 12:30h was not measured. At P1 the concentration in the latest sample analysed was 1.34 ng L^{-1} (6 April 5:39) while at P2 the concentration was 1.28 ng L^{-1} (6 April 13:36), showing that most of the prosulfocarb applied to the upstream stretch had passed P1 and P2.

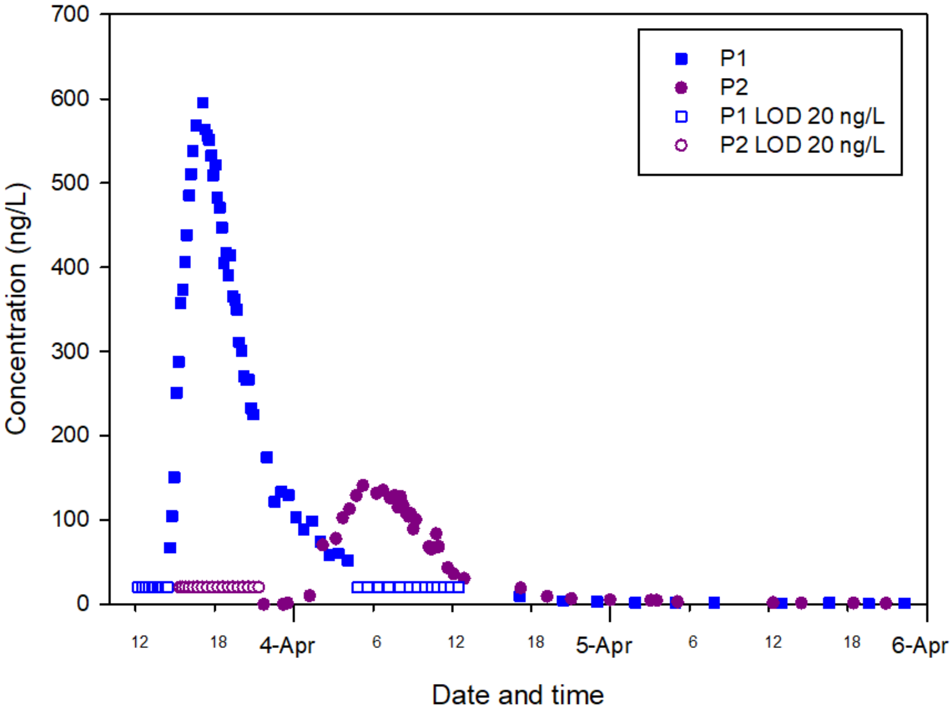

Figure 17 *Concentration of prosulfocarb in discharge water at sampling points P1 and P2 between 4 April 12h and 6 April 0h. Concentrations below LOD are shown with open symbols. Concentrations below shown LOD were determined by pooling of samples.*

5.3 Concentration in water at three locations

So-called spot samples were taken at three locations along the studied ditch: MP1 (at 5, 25 and 45 m distance in the 50-m stretch that received the application), MP2 (between weir C and D) and MP3 (downstream of weir E; Figure 6). At each location, six spot samples were taken to study the concentration distribution across the cross-sectional area of the watercourse during its flow through the watercourse. The six spot samples were taken at 5 and 20 cm deep in the cross section for MP1 and MP2, and at 15 and 25 cm deep for MP3 (a larger waterbody) as shown in Figure 10 (Section 3.4.2).

There were four sampling times at MP1 (i.e. applied stretch) and seven at MP2 and MP3. The time of sampling indicated is in hours *after* application of nicosulfuron and prosulfocarb, whereas bromide was applied 30 min, earlier. Thus, an indicated time of 1h for bromide corresponds to 1.5h after its own application.

The measurements at these three locations show the passage of the application 'block' of the three substances bromide, nicosulfuron and prosulfocarb. Pumps 2 and 3 caused dilution between MP1 and MP2 and thus lower peak concentrations, as well as the incoming additional water flow between MP2 and MP3 at weir E.

At the first sampling times for MP1, there are clear distribution effects for the three compounds. These are presented in Section 5.3.1. Results of measurements for MP1, MP2 and MP3 per compound and all sampling times are then presented and discussed in Sections 5.3.2– 5.3.4. Results of all measurements are given in Annex 11.

5.3.1 Concentration distribution in cross section in application stretch shortly after application

Figure 18 shows the distribution of concentrations of bromide, nicosulfuron and prosulfocarb (data in Tables 7, 10 & 13 respectively) in the cross-section of the water layer at three distances in the stretch where the compounds were applied. Note that the size of the circles is differently scaled for the three compounds thus the sizes of the circles between compounds cannot be compared, but only for a compound.

For bromide the distribution in the cross section is fairly homogeneous. Bromide was applied separately and not with a formulation; it dissolves easily in water (563 g L^{-1} at 20°C) and is expected to disperse and diffuse easily in the water layer.

After spraying the nicosulfuron-prosulfocarb mixture, a whitish floating layer of formulated product(s) was observed to drift to the north and north-east of the watercourse, close to weir A. Two water samples taken shortly after application (at 13:40) from the visibly floating layer of formulated products had concentrations of nicosulfuron (220.5 and 757.2 µg $L^{-1)}$ and prosulfocarb (9.51 and 9.75 µg $L^{-1)}$. These were significantly higher than the nominal concentrations of 124 µg L^{-1} and 1.07 µg L^{-1} respectively (Table 1) thus a slower diffusion and mixing in the water layer may have occurred. The formulation may have been pushed to the north side of the ditch, and then diffused downwards, resulting in higher concentrations in samples on the north side of the water layer. This is shown at the 25 m cross sections for both pesticides, and at 45 m for nicosulfuron (northern side corresponds to left in Figure 18).

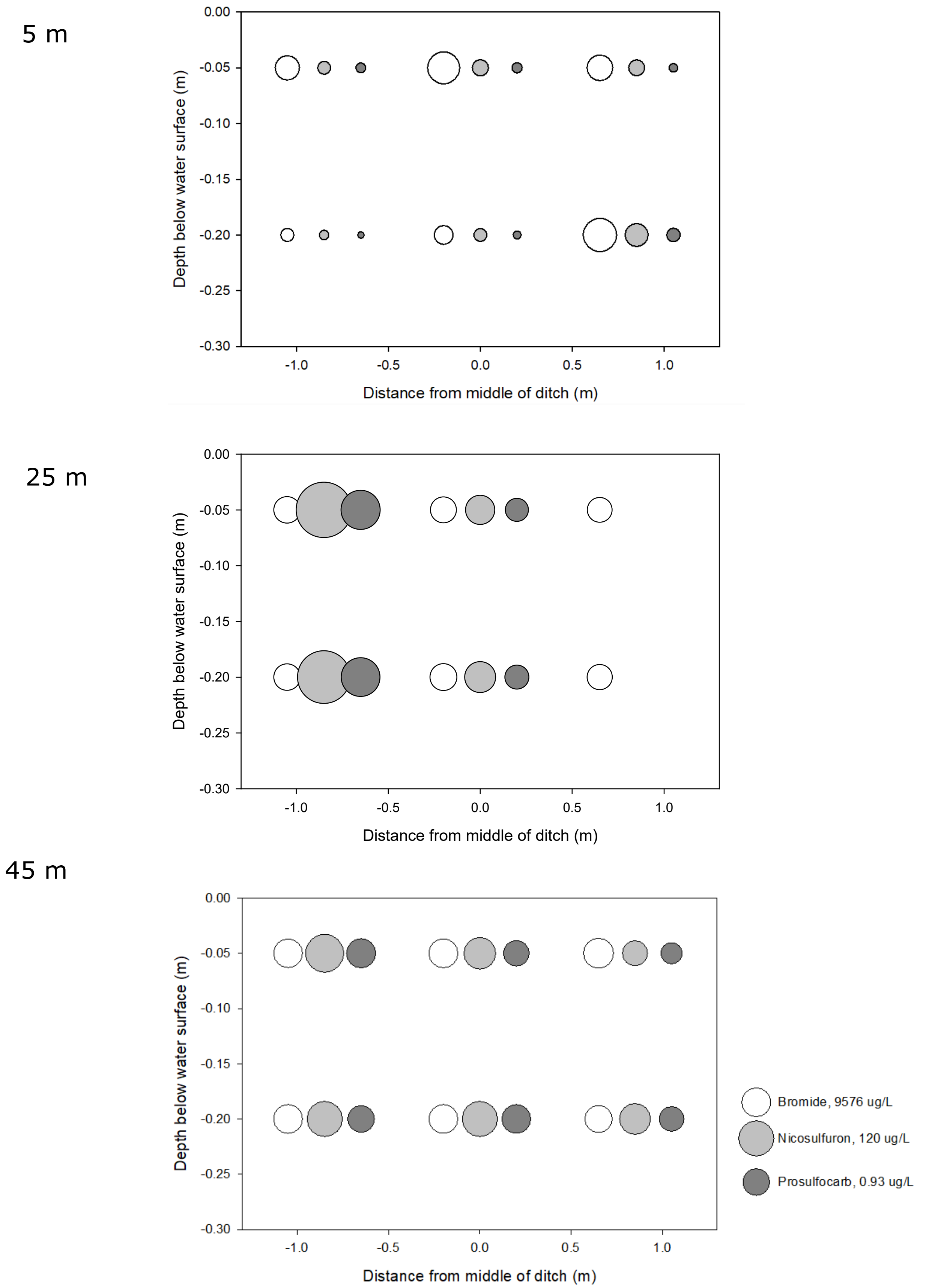

Figure 18 *Concentrations of bromide, nicosulfuron and prosulfocarb at 5, 25 and 45 m in 50 m application stretch at six positions in the cross section of the ditch at 1.5h (bromide) and 1h (nicosulfuron and prosulfocarb) after application. The area of the circles is relative to the concentration of the compound. Samples 5 and 6 (south side) for nicosulfuron and prosulfocarb at 25 m were lost.*

5.3.2 Bromide

Bromide concentrations in the cross section of the ditch taken at four times within 24h after application are shown in Table 7.

The first sampling time, 1.5h, is a check (comparing the nominal concentration) whether the bromide sprayed onto the 0-50 m water surface stretch was reasonably well mixed over the depth of the water layer. Transversal concentrations at 25 m corresponded well with the nominal concentration of 8163 µg L^{-1} (Section 3.3.2) and also at 45 m, where they were somewhat higher than the expected nominal concentration. No correlation with depth could be observed; positions 2, 4 and 6 at 5 cm depth do not appear to have higher concentrations than positions 1, 3 and 5 at 20 cm depth. At 5 m, close to the upper boundary of application, upstream water already diluted the applied bromide. Transversal concentrations at 5 m vary between 421 and 1048 µg L^{-1}; so, the extent of mixing with inflowing water differs in the cross section, but no apparent correlation with position (spot location) is shown.

The dissolved bromide in the 50 m stretch was expected to move downstream with the water flow and to further dilute at its upstream and downstream ends due to longitudinal dispersion. After 4h (15:35h) at 5 m, the concentrations dropped to almost the background concentration of 90.5 µg L^{-1}, due to upstream water entry. At 25 m and 4h (15:55h) after application, the concentrations had decreased by factor 20 due to dilution with upstream water, whereas at 45 m and 4h (16:05) after application, this was a factor 4-5. After 22h at 45 m, the concentrations had decreased down to the background concentration, showing that all bromide mass had flowed out of the 0-50 m stretch.

After 3h at 5 and 25 m, the concentrations at positions 3 and 4 in the centre of the cross-section were slightly lower than the concentrations in the outer sample points, 1, 2, 5 and 6 (Figure 18*).* Reasons for uncomplete mixing may be wind influences or that flow velocity at the side of the ditch is slightly slower due to friction with the side walls of the watercourse. However, at 45 m, this is less apparent.

Table 7 *Bromide concentration (µg L^{-1}) in spot water samples at 5, 25 and 45 m in the 50 m stretch where bromide was applied (around MP1), 1h, 4h, 10h and 23h after application of nicosulfuron and prosulfocarb (12:00). Time of sampling shown between brackets (- = not determined).*

Position	1h 3-April	3h, 4h 3 April	10h 3 April	23h 4 April
5 m	(13:10)	(15:35)		
1	420.9	119.7	-	-
2	772.1	119.1	-	-
3	595.2	101.8	-	-
4	1010.3	91.4	-	-
5	1047.5	148.8	-	-
6	810.9	126.2	-	-
25 m	(13:15)	(15:55)		
1	8352.1	439.0	-	-
2	8381.7	450.9	-	-
3	8468.4	389.6	-	-
4	8155.4	482.0	-	-
5	7965.0	489.8	-	-
6	7808.2	506.9	-	-
45 m	(13:20)	(16:05)	(21:30)	(10:45)
1	9185.5	2582.5	138.47	91.47
2	9137.2	2405.9	140.21	95.08
3	9181.7	2157.7	152.84	91.93
4	9285.9	2113.5	140.00	93.98
5	8648.9	2344.8	149.02	*
6	9575.8	2121.3	151.26	*

*sample lost

Bromide concentrations at MP2 are shown in Table 8. After 12h, the concentrations start to increase, with a maximum 1000 – 1100 µg L^{-1} at 21h, and decrease to values still above the background concentrations of 90.5 µg L^{-1} (Section 3.1) after 28h. Concentrations in the cross section are similar, so mixing over the cross-section has apparently taken place after flowing over approximately 200 m, including through three culverts up to MP2.

Table 8 *Bromide concentration in spot water samples at MP2 at seven times after application of nicosulfuron and prosulfocarb.*

Position	**3h** **3-April** **15:10**	**7h** **3 April** **19:05**	**12h** **4 April** **00:25**	**21h** **4 April** **8:45**	**22h** **4 April** **10:25**	**25h** **4 April** **12:45**	**28h** **4 April** **17:25**
1	97.4	90.7	326.12	1107.24	615.10	397.58	*
2	98.1	88.9	339.04	1113.17	612.62	395.33	240.23
3	98.8	90.9	402.09	982.70	552.85	392.36	182.04
4	96.4	82.4	387.11	1013.06	548.12	396.14	177.38
5	94.4	88.3	299.17	1045.81	590.87	400.47	153.85
6	96.7	87.1	302.75	1072.11	582.99	401.07	174.46

Bromide concentrations at MP3 are shown in Table 9. After 13h, the concentrations start to increase to a maximum at 21h, and decrease, but still above the background concentration, after 28h.

After 21h, 22h and 25h, the concentrations in position 1 and 2 (western side of ditch; both depths) are higher than in the other four positions (Table 9) showing that the water is not fully mixed in the cross section of the ditch. At these measurements, the discharge is high because water was being pumped out of the polder. These observations indicate that the water entering via weir D in the cross section is poorly mixed. After 28h, the concentrations are similar in the whole cross section, indicating good mixing. Notably, this pattern was not observed at locations MP1 and MP2. MP3 is directly downstream from the point where water with increased bromide concentration enters the watercourse with clean water from weir E, so a mixing zone. For the sample times 13h and 28h, the discharge is low (Figure 13), and the water is well mixed.

The highest concentrations in MP2, 1113 µg L^{-1}, and MP3, 978 µg L^{-1}, were found at 8:45 (20h, MP2) and 9:11 (21h, MP3). The peak concentration measured in the discharge proportional sample at P2 (between MP2 and MP3) was 1873 µg L^{-1} on 4 April 5:45, thus higher and 3h earlier. The distances between MP2 – P2 – MP3 are 25 m and approximately 13 m (Figure 6). On 4 April at 5:45, the discharge measured at P2 was 23.56 m^3 h^{-1} and water depth was 0.396 m; with width of watercourse 3 m (Table 2) resulting in a cross section of 1.19 m^2; a flow velocity of 23.65 m^3 h^{-1} /1.19 m^2 = 19.8 m h^{-1}. The peak had thus passed MP2 and MP3 within 2h after 5:45, prior to the highest concentrations measured at MP2 and MP3.

Table 9 *Bromide concentration in spot water samples at MP3, at seven times after application.*

Position	**3h** **3-April** **15:20**	**7h** **3 April** **19:25**	**13h** **4 April** **00:35**	**21h** **4 April** **9:11**	**22h** **4 April** **10:20**	**25h** **4 April** **13:10**	**29h** **4 April** **17:10**
1	99.1	83.2	146.7	939.5	581.5	279.6	232.5
2	97.9	85.9	136.5	977.9	588.2	271.4	230.5
3	94.7	85.9	131.9	499.4	224.3	191.9	226.3
4	87.0	87.2	126.8	621.9	197.3	191.8	222.2
5	91.5	85.6	131.6	258.2	188.8	186.4	233.9
6	98.4	*	125.9	260.2	185.6	*	224.3

*sample lost

5.3.3 Nicosulfuron

Table 10 shows nicosulfuron concentrations in the cross section of the ditch at four times within 24 hours after application. The first sampling time, 1h, is a check on the concentration expected from the application to the 0-50 m stretch when the nicosulfuron sprayed on the water surface has mixed well into the depth of the water layer.

Transversal concentrations at 25 m and 45 m were mostly lower than the expected concentration of 124 µg L^{-1} (Section 3.3.2). However at 25 m at positions 1 and 2 (north side of ditch), the concentrations were higher than expected which may have been due to the observed drifting of formulated product (Section 3.3.2). Due to floating on the water layer, not all nicosulfuron may have diffused into the water layer. However, concentrations at uneven positions (25 cm below surface) were not systematically lower than at even positions (10 cm below surface), indicating good mixing in the water layer.

At 5 m, close to the upper boundary of applications, upstream water already diluted the applied nicosulfuron. Transversal concentrations were a factor 3 – 4 lower than the expected concentration of 124 µg L^{-1}. At 4h after application at all three distances, transversal concentrations were similar, except at 5 m where concentrations on positions 5 and 6 (south side of ditch) were higher. This may have been due to slower flow velocities on the south side delaying the dilution with upstream clean water.

The concentrations at 45 m after 10 and at 23h decreased to approximately 1% and were lower than concentrations measured 1h after application, expressing the tail of the applied nicosulfuron mass.

Table 10 *Nicosulfuron concentration (µg L^{-1}) in spot water samples at 5, 25 and 45 m in the 50 m stretch where nicosulfuron was applied, 1, 3, 10 and 23h after application.*

Position	**1h**	**4h**	**10h**	**23h**
	3-April	**3 April**	**3 April**	**4 April**
5 m	(13:10)	(15:35)		
1	30.4	4.9	-	-
2	40.8	6.7	-	-
3	41.3	4.8	-	-
4	51.6	4.4	-	-
5	72.9	11.3	-	-
6	50.5	7.9	-	-
25 m	(13:15)	(15:55)		
1	165.6	25.7	-	-
2	173.8	27.6	-	-
3	97.3	23.6	-	-
4	92.2	23.6	-	-
5	*	24.8	-	-
6	*	25.1	-	-
45 m	(13:20)	(16:05)	(21:30)	(10:45)
1	112.0	72.9	1.6	0.4
2	120.4	76.9	1.5	0.3
3	112.3	65.2	1.8	0.3
4	100.9	64.3	1.5	0.3
5	99.0	65.9	1.9	0.3
6	79.9	60.8	2.0	0.3

*sample lost

Nicosulfuron concentrations at MP2 are presented in Table 11. From 12h, the concentrations start to increase, with a maximum at 21h, and then decrease to low concentrations present after 29h. Concentrations in the cross section are similar.

Table 11 *Nicosulfuron concentration in spot water samples at MP2, at seven times after application.*

Position	**3h** **3-April 15:10**	**7h** **3 April 19:05**	**12h** **4 April 00:25**	**21h** **4 April 8:45**	**22h** **4 April 10:25**	**25h** **4 April 12:45**	**29h** **4 April 17:25**
1	<	<	1.8	23.2	11.7	7.1	2.9
2	<	<	1.9	23.1	12.0	7.1	2.8
3	0.3	<	2.4	20.5	11.0	7.2	1.0
4	0.1	<	2.3	20.7	11.0	7.4	1.0
5	<	<	1.6	22.0	11.1	7.1	0.7
6	<	<	0.2	21.1	12.0	7.3	0.8

<: < LOD = 0.020 μg L^{-1}

Nicosulfuron concentrations at MP3 are shown in Table 12. After 13h, the concentrations start to increase to a maximum at 20h, and decrease but still present after 29h.

At 21h, 22h and 25h, the concentrations in positions 1 and 2 are higher (west at both depths) than in the other four positions. This indicates that water was not fully mixed in the cross section of the ditch. After 13h and 29h, the concentrations are similar in the whole cross section, indicating good mixing. The same effect was observed for bromide at MP3, and related to incomplete mixing of water from the watercourse discharging via weir D into the watercourse of weir E in the period that discharge was higher due to pumping water out of the polder.

Table 12 *Nicosulfuron concentration in spot water samples at MP3, at seven times after application.*

Position	**3h** **3-April 15:20**	**7h** **3 April 19:25**	**13h** **4 April 00:35**	**21h** **4 April 9:11**	**22h** **4 April 10:20**	**25h** **4 April 13:10**	**29h** **4 April 17:10**
1	<	<	0.1	18.2	10.5	3.2	2.8
2	<	<	0.1	18.7	10.6	3.0	2.8
3	<	<	0.1	8.1	1.9	1.2	2.5
4	<	<	0.1	10.7	1.2	1.1	2.6
5	<	<	<	2.1	1.0	1.1	2.8
6	<	<	<	2.2	0.9	0.9	2.8

<: < LOD = 0.020 μg L^{-1}

5.3.4 Prosulfocarb

Table 13 presents prosulfocarb concentrations in the cross section of the ditch at four times within 24h after application. The first sampling time, 1h, is a check on the concentration expected from the application to the stretch 0-50 m when the prosulfocarb sprayed on the water surface has mixed well into the depth of the water layer. Transversal concentrations at 25 m and 45 m were lower than the expected concentration of 1.07 μg L^{-1} (Section 3.3.2). However at 25 m, concentrations at positions 1 and 2 (north side of ditch) were higher than the expected concentration of 1.07 μg L^{-1}. These higher concentrations may be due to the observed drifting of formulated product described in Section 3.3.2. Due to this floating, not all prosulfocarb may have diffused into the water layer. However, concentrations at even and uneven positions (10 and 25 cm below surface) are only somewhat lower at 25 cm, indicating good mixing in the water layer. At 5 m, close to the upper boundary of applications and where upstream water has diluted the applied prosulfocarb, transversal concentrations are a factor 3 – 4 lower than the expected concentration of 1.07 μg L^{-1}.

Table 13 *Prosulfocarb concentration (µg L^{-1}) in spot water samples at 5, 25 and 45 m in the 50 m stretch where prosulfocarb was applied, 1h, 4h, 10h and 23h after application (LOD = 0.020 µg L^{-1}).*

Position	1h	4h	10h	23h
	3-April	3 April	3 April	4 April
5 m	(13:10)	(15:35)		
1	0.22	0.09	-	-
2	0.32	0.08	-	-
3	0.26	0.09	-	-
4	0.33	0.07	-	-
5	0.43	0.13	-	-
6	0.27	0.12	-	-
25 m	(13:15)	(15:55)		
1	1.22	0.26	-	-
2	1.23	0.26	-	-
3	0.76	0.26	-	-
4	0.73	0.25	-	-
5	-	0.26	-	-
6	-	0.23	-	-
45 m	(13:20)	(16:05)	(21:30)	(10:45)
1	0.86	0.46	< LOD	< LOD
2	0.93	0.49	< LOD	< LOD
3	0.92	0.47	< LOD	< LOD
4	0.82	0.44	< LOD	< LOD
5	0.79	0.46	< LOD	< LOD
6	0.68	0.45	< LOD	< LOD

The prosulfocarb concentrations at MP2 are shown in Table 14. After 7h, two observations above LOQ the north side of the ditch were noted. Thereafter at 21h, 22h, observations below LOQ were noted (so prosulfocarb detected), and at 25h and 29h in the whole cross section of the ditch.

Table 14 *Prosulfocarb concentration (µg L^{-1}) in spot water samples at MP2, at seven times after application (LOD = 0.020 µg L^{-1}, LOQ = 0.060 µg L^{-1}).*

Position	3h	7h	12h	21h	22h	25h	29h
	3-April 15:10	3 April 19:05	4 April 00:25	4 April 8:45	4 April 10:25	4 April 12:45	4 April 17:25
1	< LOD	0.077	< LOD	< LOD	< LOD	< LOQ	< LOD
2	< LOD	0.060	< LOD	< LOD	< LOQ	< LOQ	< LOD
3	< LOD	< LOD	< LOD	< LOQ	< LOD	< LOQ	< LOD
4	< LOD	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOD
5	< LOD	< LOD	< LOD	0.093	< LOQ	< LOQ	< LOD
6	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOQ	< LOD

Prosulfocarb concentrations at MP3 are shown in Table 15. From 13h on, prosulfocarb is detected (<LOQ), but no longer at 29h. Typically after 21h, 22h and 25h the concentrations were more often detected in position 1 or/and 2 than in the other four positions. This indicates that water was not fully mixed in the cross section of the ditch. Notably, this pattern was not observed at locations MP1 and MP2 therefore this may be the impact of incomplete mixing as described for bromide and for nicosulfuron.

Table 15 *Prosulfocarb concentration (µg L^{-1}) in spot water samples at MP3, at seven times after application (LOD = 0.020 µg L^{-1}, LOQ = 0.060 µg L^{-1}).*

Position	3h 3-April 15:20	7h 3 April 19:25	13h 4 April 00:35	21h 4 April 9:11	22h 4 April 10:20	25h 4 April 13:10	29h 4 April 17:10
1	< LOD	< LOD	0.001*	0.030*	< LOQ	< LOQ	< LOD
2	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOQ	< LOD
3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
4	< LOD	< LOD	< LOD	< LOQ	< LOQ	< LOD	< LOD
5	< LOD	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOD
6	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

* Water samples extracted with SPE (Solid Phase Extraction), to decrease LOQ from 60 ng L^{-1} to 1 ng L^{-1}

The measurements show that the steep front and end concentration gradients of the 50-m long applied concentration ‘blocks’ (one for bromide, and one for nicosulfuron-prosulfocarb) become blurred, i.e. the gradients become less steep during its flow through the watercourse.

5.4 Concentration in sediment

Sediment was sampled by taking cores (Section 3.5). From the upper part of these cores, two or three layers were separated and analysed for nicosulfuron and prosulfocarb. Nicosulfuron adsorbs weakly to organic matter, and for the time scale of the experiment, its degradation in sediment was expected to be negligible. This implies that by analysing nicosulfuron diffusion between water and sediment, its diffusion downwards into the sediment can be evaluated. As nicosulfuron is considered to behave like a tracer, the sediment was not analysed for bromide. Sediment concentrations of prosulfocarb have been determined. Prosulfocarb adsorbs strongly to organic matter, which enabled us to evaluate the effect of sorption in sediment on transport in the water layer and transport into the sediment.

5.4.1 Nicosulfuron

We determined nicosulfuron concentration in pore water and its total content in sediment. Contents in dry sediment were small as expected, as it weakly sorbs to organic matter, therefore the content in dry sediment is not presented. The total concentration in sediment was calculated from the nicosulfuron extracted from the wet sediment plus sampled porewater and its concentration. The total concentration was calculated from the volume of porewater in the volume of 1.1 cm, 1 cm and 2 cm layers, respectively (Section 3.6.5). Table 16 presents the concentrations for all samples; the underlying data of the chemical analysis are given in Annex 12.

At MP1 in samples taken on the day before the application (2 April 2008), all nicosulfuron concentrations were below LOD. Four hours after application, porewater concentrations in the upper 1 cm of the sediment in the application stretch were between 12.6 and 27.0 µg L^{-1}. These values match those concentration measured in spot samples from the water layer taken at the same location and time, i.e. between 23.6 and 27.6 µg L^{-1} (Table 10). This was expected as the upper millimetres of the sediment are expected to have concentrations similar to that of the water layer. However, averaging over 1 cm would decrease the concentration. In the period preceding the sediment sampling, the concentrations in the water were higher; see e.g. the concentrations measured downstream at 45 m in the applications stretch, 60.8 - 76.9 µg L^{-1} in Table 10. Therefore, it is plausible that concentrations in the upper part of the upper millimetres of the sampled 1 cm layer were also higher.

Table 16 *Nicosulfuron concentration in pore water and total concentration (calculated from concentration in pore water) per sediment layer (n = 4; blank n = 2) at measuring point MP1 at times indicated in the table (application 3 April at 12:00).*

Code	**Layer depth**	**Concentration in pore water** (µg L^{-1})	**Total concentration in layer** (µg L^{-1})
MP1 3-4-2008 15:40 (4h)			
P11	0-1 cm	19.7	26.5
P12	1-2 cm	2.1	4.2
P13	2-4 cm	0.6	1.3
P14	0-1 cm	27.0	32.9
P15	1-2 cm	5.1	5.3
P16	2-4 cm	0.8	0.6
P17	0-1 cm	22.1	23.3
P18	1-2 cm	4.7	4.9
P19	2-4 cm	0.7	0.8
P110	0-1 cm	12.6	17.2
P111	1-2 cm	2.2	3.2
P112	2-4 cm	0.1	0.1
MP1 3-4-2008 21:45 (10h)			
P113	0-1 cm	1.7	2.9
P114	1-2 cm	0.7	0.8
P115	2-4 cm	0.2	0.3
P116	0-1 cm	4.5	6.4
P117	1-2 cm	0.5	1.1
P118	2-4 cm	0.2	0.2
P119	0-1 cm	2.3	2.6
P120	1-2 cm	0.2	0.3
P121	2-4 cm	0.0	0.0
P122	0-1 cm	2.8	7.3
P123	1-2 cm	1.1	1.6
P124	2-4 cm	0.2	0.2
MP1 4-4-2008 10:50 (23h)			
P26	0-1 cm	1.8	1.1
P27	0-1 cm	1.0	2.7
P28	0-1 cm	0.9	0.9
P29	0-1 cm	3.2	2.0

Averages of the total concentration of four samples for each of the three sediment layers for MP1 are given in Table 17. The total concentrations in layers 0-1 cm and 1-2 cm as a function of time are shown for the separate measurements in Figure 19. The highest contents were noted at the first measurement time 4h after application for all three layers. These contents decreased in the following measurement times. The highest content was found in the top layer of 1 cm and decreased with depth at both times when the deeper layers were analysed. In the first measurement time, nicosulfuron is already present in the 2-4 cm layer. This may be because when pushing the sampling tube into the sediment, material from the top layers, containing nicosulfuron, was pushed downwards into the 2-4 cm layer. Furthermore, in the period between sampling and freezing (undocumented – but possibly 24h), nicosulfuron may have diffused downwards.

After application of nicosulfuron and diffusion into the sediment, the total concentrations in all three layers increased. During the day, the total concentrations decreased due to diffusion back into the water layer. One day later, nicosulfuron was only present in the 0-1 cm layer.

We used the highest mass found per m^2 at first measurement time to estimate how much nicosulfuron was present in the sediment of the application stretch. The mass per m^2 was (25.0*0.01 m + 4.4*0.01 m + 0.7*0.02m) x 1 m^2 0.31 mg. The sediment area is the width of the ditch 2.74 m * 50 m. Hence the total mass in sediment is 42 mg; 0.79% of the mass applied (5.26 g).

Table 17 *Nicosulfuron total concentration, per sediment layer at MP1 per measurement time (n = 4, average and standard deviation).*

Layer depth	4h 3-4-2008 15:40 (μg L^{-1})		10h 3-4-2008 21:45 (μg L^{-1})		23h 4-4-2008 10:50 (μg L^{-1})	
	average	**s.d.**	**average**	**s.d.**	**average**	**s.d.**
0-1 cm	25.0	6.5	4.8	2.4	1.7	0.8
1-2 cm	4.4	0.9	0.9	0.5	n.a.	n.a.
2-4 cm	0.7	0.5	0.2	0.1	n.a.	n.a.

n.a.: not analysed

At MP2, the highest concentration in pore water (between 4.9 and 13.4 μg L^{-1}) were found at the last sampling time, 29h after application (4 April 2008 17:00), (Table 18). These are higher than the concentrations in spot water samples at MP2 at this time, 0.7 – 2.9 μg L^{-1} (Table 11). However, concentrations in water were higher in the preceding period (Table 11) where nicosulfuron had entered the sediment.

Table 18 *Nicosulfuron concentration in pore water and total concentration per sediment layer (n = 4; blank n = 2) at measuring point MP2 at times indicated in the table (application 3 April at 12:00).*

Code	Layer depth	Concentration in pore water (μg L^{-1})	Total concentration in layer (μg L^{-1})
MP2 4-4-2008 0:30 (13h)			
P30	0-1 cm	1.3	1.4
P31	1-2 cm	0.1	0.2
P32	0-1 cm	0.7	0.7
P33	1-2 cm	0.1	0.2
P34	0-1 cm	1.1	0.7
P35	1-2 cm	0.2	0.2
P36	0-1 cm	1.2	1.0
P37	1-2 cm	0.1	0.2
MP2 4-4-2008 13:00 (25h)			
P38	0-1 cm	8.0	2.1
P39	1-2 cm	0.4	0.6
P40	0-1 cm	4.8	1.5
P41	1-2 cm	0.5	0.7
P42	0-1 cm	4.7	1.3

Code	**Layer depth**	**Concentration in pore water**	**Total concentration in layer**
		(μg L^{-1})	**(μg L^{-1})**
P43	1-2 cm	0.3	0.3
P44	0-1 cm	3.1	0.9
P45	1-2 cm	0.4	0.7
MP2 4-4-2008 17:00 (29h)			
P46	0-1 cm	13.4	2.8
P21	1-2 cm	<LOD	<LOD
P47	0-1 cm	12.8	2.3
P22	1-2 cm	<LOD	<LOD
P48	0-1 cm	7.3	1.9
P23	1-2 cm	<LOD	<LOD
P49	0-1 cm	4.9	2.9
P24	1-2 cm	<LOD	<LOD

Averages of the total concentration of four samples for each of the three layers for MP2 are given in Table 19. The total concentrations in both sediment layers were still low 13h after application, but started to increase thereafter, most prominently for the 0-1 cm layer. No further measurements were taken. Substances diffuse slowly into sediment and diffusion back to the water layer after water is depleted from the compound is also a slow process, so concentrations in sediment lag behind. Concentrations in spot water samples at that day were all below LOQ (Table 11).

MP2 is close to the discharge proportional sampling point P2. The content in sediment at MP2 shows a delayed response to the concentration in water; 4h after application the content in sediment is low because the concentration in front of nicosulfuron has only just arrived (Figure 16). However, 25h after application, most of the nicosulfuron had passed MP2, while at 29h the concentration in water had decreased and the content in sediment had further increased. This can be expected when concentrations in water are higher than those in sediment porewater.

Table 19 *Nicosulfuron total concentration per sediment layer at MP2 per measurement time (n = 4, average and standard deviation).*

Layer depth	**13h**		**25h**		**29h**	
	4-4-2008 00:30		**4-4-2008 13:00**		**4-4-2008 17:00**	
	(μg L^{-1})		**(μg L^{-1})**		**(μg L^{-1})**	
	average	**s.d.**	**average**	**s.d.**	**average**	**s.d.**
0-1 cm	1.0	0.3	1.4	0.5	2.5	0.5
1-2 cm	0.2	0.0	0.6	0.2	<LOD	<LOD

The total concentrations of nicosulfuron at MP1 and MP2 in the 0-1 cm and 1-2 cm layers are given as a function of time in Figure 19. The figure shows that at MP1 (in the application stretch) the sediment content decreases, and increases at MP2, starting 13h after application. The sediment content at MP2 after the last sampling is expected to decrease because the concentration in water has also decreased.

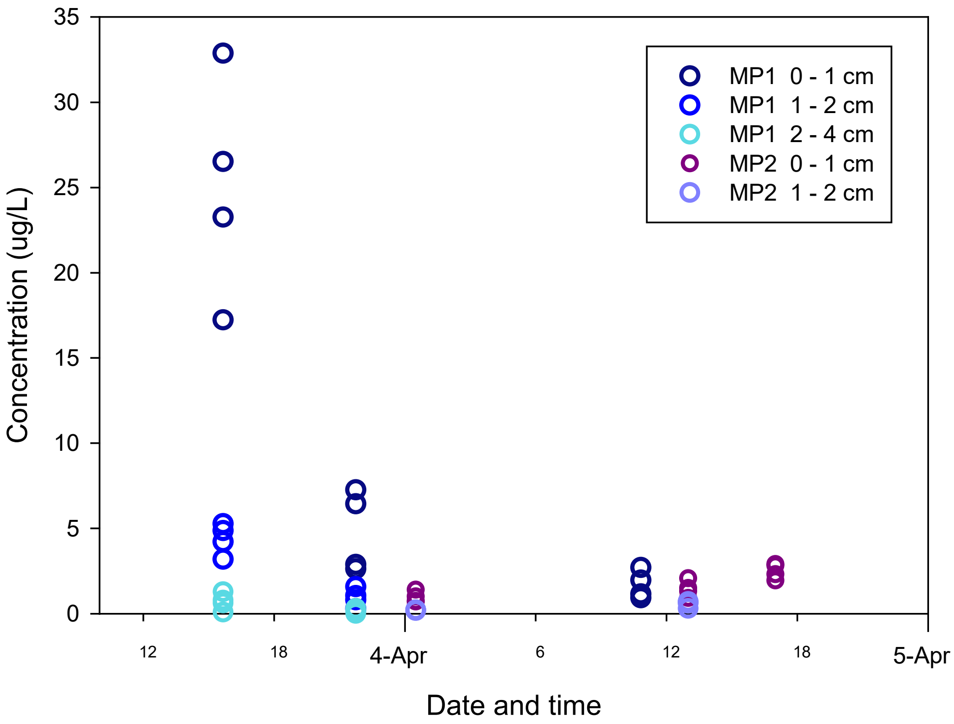

Figure 19 *Total concentrations of nicosulfuron in sediment layers indicated in the graph at sampling points MP1 and MP2 as a function of time (4 measurements per sampling time).*

5.4.2 Prosulfocarb

We determined the prosulfocarb concentration in pore water and in dry sediment. Results for prosulfocarb in sediment samples for sampling points MP1 and MP2 are given in Table 20. The underlying data of the chemical analysis are given in Annex 12.

The total mass of prosulfocarb per layer was calculated as the sum of mass determined in porewater and the mass determined in dry sediment in the volume of each of the layers (Section 3.6.5). The content in dry sediment was corrected for the prosulfocarb in the porewater of the wet sample. For this calculation we assumed that the distribution equilibrium between liquid and solid phase would not be affected by the small volume of pore water taken from the bulk sample.

At MP1 in samples taken one day before the application, prosulfocarb was measured in all the three layers analysed, down to 3 cm depth in the sediment (Section 3.6.5). The depth average of total concentration of both cores taken was 0.09 µg L^{-1}, with highest total concentrations are found for the layer 2-3 cm: 0.12 and 0.13 µg L^{-1}. Concentrations in pore water in the upper 1 cm of the sediment measured 4h after the application ranged from 0.08 - 0.17 µg L^{-1}. This is somewhat lower than the concentrations measured in water from the spot samples at MP1 (0.23 – 0.26 µg L^{-1}, 4h - 25 m in application stretch; Table 13). The total concentration measured in the top 1 cm layer ranged between 0.34 - 0.77 µg L^{-1}. Prosulfocarb entering the sediment via the pore water adsorbs to the sediment and therefore reduces the concentration in pore water.

Table 20 *Prosulfocarb concentration in pore water, solid phase, and total concentration per sediment layer at MP1 (n = 4, blank n = 2).*

Code	depth	Concentration in pore water (µg L^{-1})	Content sorbed per dry sediment (µg kg^{-1})	Content sorbed per organic matter (µg kg^{-1})	Total concentration (µg L^{-1})
2-4-2008 MP1 blank					
P09	0-1 cm	<LOD	0.3	2.0	0.06
P010	1-2 cm	<LOD	0.3	2.3	0.08
P011	2-3 cm	<LOD	0.5	3.4	0.12
P012	0-1 cm	<LOD	0.4	2.9	0.08
P013	1-2 cm	<LOD	0.3	2.1	0.08
P014	2-3 cm	<LOD	0.4	3.1	0.13
3-4-2008 MP1 15:40 (4h)					
P11	0-1 cm	0.15	3.0	21.9	0.77
P12	1-2 cm	<LOD	0.6	4.7	0.20
P13	2-4 cm	<LOD	0.6	4.3	0.32
P14	0-1 cm	0.13	2.3	17.9	0.57
P15	1-2 cm	<LOD	0.7	4.9	0.19
P16	2-4 cm	<LOD	0.3	2.9	0.26
P17	0-1 cm	0.17	1.6	12.3	0.55
P18	1-2 cm	<LOD	0.3	2.8	0.14
P19	2-4 cm	<LOD	0.2	2.0	0.21
P110	0-1 cm	0.08	1.4	10.7	0.34
P111	1-2 cm	<LOD	0.5	3.8	0.22
P112	2-4 cm	<LOD	0.6	4.4	0.38
3-4-2008 MP1 21:45 (10h)					
P113	0-1 cm	0.03	1.0	7.4	0.21
P114	1-2 cm	<LOD	0.6	4.2	0.15
P115	2-4 cm	<LOD	0.7	4.2	0.33
P116	0-1 cm	0.09	1.3	8.7	0.33
P117	1-2 cm	<LOD	0.5	3.3	0.12
P118	2-4 cm	<LOD	0.7	4.3	0.31
P119	0-1 cm	0.05	0.7	4.6	0.14
P120	1-2 cm	<LOD	0.4	2.6	0.08
P121	2-4 cm	<LOD	0.8	5.0	0.38
P122	0-1 cm	0.08	1.8	12.6	0.44
P123	1-2 cm	<LOD	0.6	4.4	0.15
P124	2-4 cm	<LOD	0.6	3.9	0.23
MP1 4-4-2008 10:50 (23h)					
P26	0-1 cm	<LOD	1.0	5.9	0.17
P27	0-1 cm	<LOD	0.9	5.9	0.16
P28	0-1 cm	<LOD	2.3	13.8	0.41
P29	0-1 cm	<LOD	0.9	5.4	0.18

Averages of the total prosulfocarb concentration of four samples for each of the three layers for MP1 are shown in Table 21. The total concentrations in the 0-1 cm and 1-2 cm layers as a function of time is shown for the separate measurements in Figure 20. The highest contents were found at 4h after application for the top two layers. These contents decreased at the following measurements. For both periods, the values in the 2-4 cm layer are similar to the concentration found before application 0.14 µg L^{-1}. The highest content was found in the 0-1 cm layer. Prosulfocarb concentrations only increased in the top 1-2 cm layer before returning to the background concentration.

We used the highest mass found per m^2 at the first measurement to estimate how much prosulfocarb was in the sediment of the application stretch. The mass per m^2 is calculated: (0.56*0.01 m + 0.19*0.01 m + 0.15*0.02 m) x 1 m^2 as 10.5 µg. The sediment area is the width of the ditch 2.74 m*50 m. Hence the total mass in sediment was 1.44 mg; is 2.8% of the mass applied (0.0516 g). With a background concentration of 0.10 µg L^{-1} in the 0-4 cm layer, the mass present before prosulfocarb was applied was 0.4 mg, i.e. 0.8% of the calculated mass.

Table 21 *Total concentration of Prosulfocarb (porewater and dry sediment combined) per sediment layer at MP1 per measurement time (n = 4, average and standard deviation).*

Layer depth	4h 3-4-2008 15:40 (µg L^{-1})		10h 3-4-2008 21:45 (µg L^{-1})		23h 4-4-2008 10:50 (µg L^{-1})	
	average	s.d.	average	s.d.	average	s.d.
0-1 cm	0.56	0.17	0.28	0.13	0.23	0.12
1-2 cm	0.19	0.03	0.13	0.03	n.a.	n.a.
2-4 cm	0.15	0.04	0.16	0.03	n.a.	n.a.

n.a.: not analysed

At MP2, concentrations measured were higher than the background concentrations of 0.10 µg L^{-1} at MP1. MP2 was not sampled before the application. Prosulfocarb concentrations in pore water in the 0-1 cm sediment layer are low for all three sampling times, ≤ 0.02 µg L^{-1} (13h, 25h and 29h after application; Table 22). This matches the concentrations in spot samples from the water layer of < 0.02 µg L^{-1} (LOD) at 13h and 28h and between 0.02 (LOD) and 0.06 µg L^{-1} (LOQ) at 25h (Table 14). The concentrations in pore water are lower than the concentrations in discharge water (0.13 – 0.14 µg L^{-1}) measured at P2 around 6:00, the peak passed (4:44-7:39, 18h after application; Annex 10 and Figure 17). However, the 13h and 25h sampling times of porewater are before and after the peak concentration; at 13h the concentration in discharge water was 0.0013 µg L^{-1} (3 April 2008 23:31) and at 25h 0.031 µg L^{-1} (4 April 2008 12:54). These correspond with the concentrations in pore water at those times.

Table 22 *Prosulfocarb concentration in pore water, solid phase and total concentration per sediment layer at MP2 (n = 4, blank n = 2).*

Code	depth	Concentration in pore water ($\mu g\ L^{-1}$)	Content sorbed per dry sediment ($\mu g\ kg^{-1}$)	Content sorbed per organic matter ($\mu g\ kg^{-1}$)	Total concentration ($\mu g\ L^{-1}$)
MP2 4-4-2008 0:30 (13h)					
P30	0-1 cm	<LOD	1.3	8.5	0.23
P31	1-2 cm	<LOD	0.6	3.7	0.18
P32	0-1 cm	0.01	1.6	10.8	0.24
P33	1-2 cm	<LOD	0.5	3.2	0.15
P34	0-1 cm	0.01	0.6	5.0	0.17
P35	1-2 cm	<LOD	0.6	4.0	0.16
P36	0-1 cm	0.002	1.4	9.4	0.18
P37	1-2 cm	<LOD	0.6	4.2	0.18
MP2 4-4-2008 13:00 (25h)					
P38	0-1 cm	0.01	1.9	12.6	0.28
P39	1-2 cm	<LOD	0.5	3.8	0.15
P40	0-1 cm	<LOD	1.7	11.4	0.27
P41	1-2 cm	<LOD	0.6	4.4	0.19
P42	0-1 cm	0.0001	1.2	8.6	0.23
P43	1-2 cm	<LOD	0.5	3.4	0.15
P44	0-1 cm	0.01	1.2	8.2	0.22
P45	1-2 cm	<LOD	0.5	3.5	0.19
MP2 4-4-2008 17:00 (29h)					
P46	0-1 cm	0.02	1.8	12.8	0.34
P21	1-2 cm	<LOD	0.5	3.2	0.13
P47	0-1 cm	<LOD	1.1	7.4	0.18
P22	1-2 cm	<LOD	0.7	4.6	0.20
P48	0-1 cm	<LOD	1.6	10.4	0.30
P23	1-2 cm	<LOD	0.4	2.9	0.12
P49	0-1 cm	<LOD	1.6	10.8	0.24
P24	1-2 cm	<LOD	0.5	3.6	0.15

The averages of the total concentration of four samples for two layers for MP2 are given in Table 23. All three sampling times were either before (13h) or after (25h and 29h) the prosulfocarb peak passed (centre of prosulfocarb wave measured in discharge water at 06:00 (18h); Figure 17). Moreover, the concentrations in the water layer are close to or below LOD when the sediment was sampled. The concentrations in both sediment layers at all three sampling times are similar for the 0-1 cm layer (range 0.20 -0.27 $\mu g\ L^{-1)}$, as well as for the 1-2 cm layer (range 0.15 – 0.17 $\mu g\ L^{-1}$). Thus, a short period of increased concentration of prosulfocarb in the water layer led to transport into the sediment, to under 1 cm depth. The prosulfocarb diffuses and adsorbs to organic matter in the sediment. Diffusion from the sediment layer to the clean water layer and desorption from the organic matter decreases the concentration in sediment. However, no measurements were taken before the application, deeper than 2 cm, and for a longer period after the application.

Table 23 *Prosulfocarb total concentration per sediment layer at MP2 per measurement time (n = 4, average and standard deviation).*

Layer depth	13h		25h		29h	
	4-4-2008 00:30		4-4-2008 13:00		4-4-2008 17:00	
	(µg L^{-1})		(µg L^{-1})		(µg L^{-1})	
	average	s.d.	average	s.d.	average	s.d.
0-1 cm	0.20	0.04	0.25	0.03	0.27	0.07
1-2 cm	0.17	0.01	0.17	0.03	0.15	0.04

The total concentrations at MP1 and MP2 in the 0-1 cm, 1-2 cm and 2-4 cm layers (only MP1) are given as a function of time in Figure 20. The figure shows that the sediment content decreases slowly at MP1 (in the application stretch). At MP2, the total concentration in the 1-2 cm layer is similar at the three time points, but the variation increases.

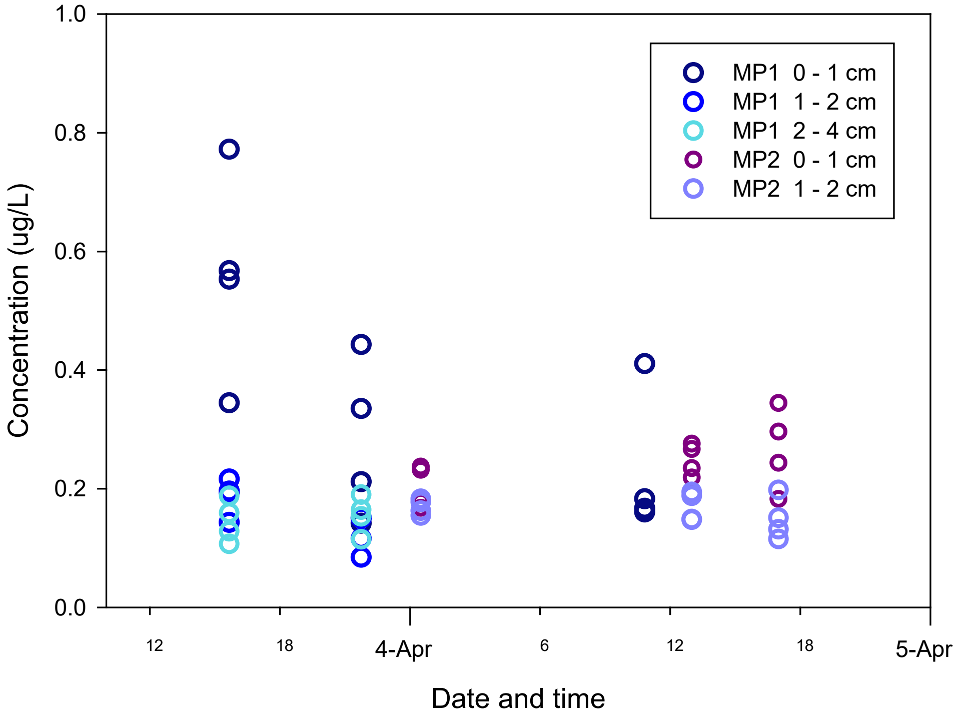

Figure 20 *Total concentrations of prosulfocarb in layers indicated at sampling points MP1 and MP2 as a function of time (4 measurements per sampling time; except 2 April 2008 12:00 2 measurements and 2–3 cm instead of 2–4 cm).*

At MP1, a background of prosulfocarb was detected in the top 2 cm before the application on 3 April. After the application and diffusion into the sediment, the total concentrations in all three sampled layers increased. During the day the total concentrations in the 0-1 cm and 1-2 cm layers decreased due to diffusion back to the water layer. One day later, increased prosulfocarb was still present in the sediment in the 0-1 cm layer.

For samples at MP1 with porewater concentrations above 0.02 µg L^{-1} (selected from Table 20; for lower concentrations uncertainty is considered too high) we calculated the distribution of prosulfocarb between organic matter and porewater (Table 24). We only found concentrations in porewater > LOD the 0-1 cm layer, with distribution coefficients ranging between 74.7 to 213 L kg^{-1}, and consistent. These values are lower than $K_{f,om}$ = 1693 L kg^{-1}, from Lewis et al. (2016). Reasons for the lower values may be due to the short contact time; equilibrium not yet reached and the prosulfocarb had not diffused down to 1 cm.

Table 24 *Distribution of prosulfocarb calculated for content sorbed per organic matter divided by concentration in pore water.*

Code	**depth**	**Concentration in pore water** **(µg L^{-1})**	**Content sorbed per organic matter** **(µg kg^{-1})**	**Distribution between organic matter and pore water** **(L kg^{-1})**
3-4-2008 MP1 15:40 (4h)				
P11	0-1 cm	0.15	21.9	150
P14	0-1 cm	0.13	17.9	142
P17	0-1 cm	0.17	12.3	74.7
P110	0-1 cm	0.08	10.7	138
3-4-2008 MP1 21:45 (10h)				
P113	0-1 cm	0.03	7.4	213
P116	0-1 cm	0.09	8.7	93.7
P119	0-1 cm	0.05	4.6	101
P122	0-1 cm	0.08	12.6	160

5.5 Mass balance in water of bromide, nicosulfuron and prosulfocarb

The mass balance was determined for the application stretch up to P1 and P2, accounting for the mass applied, mass inflow (for bromide), and mass outflow at P1 and at P2. The mass that initially diffused and sorbed into sediment is considered as it diffused back into the water layer, as well as for the mass sorbed to biota not moving with water.

Bromide mass inflow was calculated by multiplying the total discharge in the period (645.4 m^3 at P1 and 2435 m^3 at P2) with the background concentration of 90.5 µg L^{-1} (Section 3.1). The mass of the three substances passing at P1 and at P2 was calculated from the measured discharges and from the concentration in the discharge proportional sampled water volumes (Annex 10). Samples were not taken in short periods in which the sample bottles in the automatic sampler were replaced. The mass passing in this period was calculated by taking discharge multiplied by the average of the concentrations of the last sample of the previous period, and the first sample of the next period.

The mass balance of bromide, nicosulfuron and prosulfocarb for the two stretches for the whole period that discharge proportional samples were taken, are shown in Table 25. The total mass of bromide outflow at P1 was less than applied, and at P2 more than the mass applied. At P1 for nicosulfuron this was equivalent to the mass applied, with more at P2; for prosulfocarb this was less at both points. The mass passing at P2 is larger than at P1 for bromide and nicosulfuron; for prosulfocarb the values were equivalent. For periods with concentrations below LOD, mass may have passed; e.g. for prosulfocarb attributing LOD 20 ng L^{-1} for samples below LOD at P1 would result in 6.7% extra mass, so not substantial.

Discharge proportional sampling at P1 was directed by the flow meter at weir A, therefore the true discharge at P1 was higher as between weir A and P1, there was inflow of seepage water. Therefore, the mass of the three substances calculated to have passed at P1 is underestimated. We suggest that in future, the volume of seepage water between weir A and D (difference discharge D and A+B+C) is estimated in order to quantify the underestimation.

Table 25 *Mass balance for bromide, nicosulfuron and prosulfocarb for applied mass and mass flowing out at P1 and at P2. Between brackets corresponding percentages of applied mass are given.*

Compound	**Dose based on measured concentration in tank and sprayed volume (g)**	**Mass passed at P1 (g)**	**Mass passed at P2 (g)**
Bromide	394	421	712
Bromide inflow	-	58	220
Bromide outflow - inflow	-	363 (92%)	492 (125%)
Nicosulfuron	5.97	5.89 (99%)	6.77 (113%)
Prosulfocarb	0.0516	0.0397 (77%)	0.0379 (73%)

More detailed mass balances for P1 and P2 are given, per measurement period, in Tables 26 and 27.

At P1, within 5h after application 48% of bromide mass had passed, higher than the values for nicosulfuron (31%) and prosulfocarb (33%) (Table 26). This was reversed in the period 5h - 9h, with bromide lower (43%) than the pesticides (56% and 50% respectively). This was because bromide was applied at 11:30 and the pesticides 30 min later at 12:00. This effect is still visible in the period 9.5h - 24.5h. More than 98% of the mass of all three compounds had passed P1 at 24.5h after application.

At P2, between 12h and 22h after application, more than 4% of mass of all three compounds had passed; bromide (64%), nicosulfuron (65%), both somewhat lower than for prosulfocarb (72%) (Table 27). In the period 22h - 25.5h, the percentages of bromide (14%) and nicosulfuron (20%) were still lower than prosulfocarb (21%); this reversed in the period 26.5h – 42h with bromide (13%), nicosulfuron (14%), and prosulfocarb (5%). Within 42h after application, ≥93% of the mass of all three compounds had passed P2.

Table 26 *Discharge and mass passed P1 per sampling period for bromide, nicosulfuron and prosulfocarb.*

Period after application (h)	Start time	End time	Number of samples	Discharge (m³)	Bromide mass (g)	Bromide mass corrected* (g)	Bromide mass corrected (%)	Nicosulfuron mass (g)	Nicosulfuron mass (%)	Prosulfocarb mass (g)	Prosulfocarb mass (%)
0 – 4.5	3 April 12:01	3 April 16:33	24	47.8	133.5	129.2	36	1.230	21	0.00903	23
4.5 - 5	3 April 16:33	3 April 17:01		6.7	44.3	43.7	12	0.599	10	0.00390	10
5 - 9	3 April 17:01	3 April 21:00	24	48.2	161.7	157.4	43	3.276	56	0.01972	50
9 – 9.5	3 April 21:00	3 April 21:38		6.4	5.5	4.9	1	0.148	3	0.00128	3
9.5 – 24.5	3 April 21:38	4 April 12:36	24	115.4	31.4	21.0	6	0.592	10	0.00526	13
24.5 – 25.5	4 April 12:36	4 April 13:25		5.4	0.6	0.1	0	0.004	0	0.00005	0
25.5 - 45	4 April 13:25	5 April 08:52	24	193.9	20.9	3.3	1	0.040	1	0.00036	1
45 – 47.5	5 April 08:52	5 April 11:39		29.3	3.0	0.4	0	0.000	0	0.00004	0
47.5 - 75	5 April 11:39	6 April 14:55	24	192.2	20.0	2.6	1	0.001	0	0.00006	0
	total										
0 - 75	3 April 12:01	6 April 14:55		645.4	421.0	362.6	100	5.889	100	0.0397	100

*correction for background concentration bromide of 90.5 µg L^{-1}

Table 27 *Discharge and mass passed P2 per sampling period for bromide, nicosulfuron and prosulfocarb.*

Period after application (h)	Start time	End time	Number of samples	Discharge (m³)	Bromide mass (g)	Bromide mass corrected* (g)	Bromide mass corrected (%)	Nicosulfuron mass (g)	Nicosulfuron mass (%)	Prosulfocarb mass (g)	Prosulfocarb mass (%)
3 – 11:75	3 April 15:15	3 April 23:46	24	233.8	22.5	1.4	0	0.003	0	0.00002	0
11.75 - 12	3 April 23:46	3 April 24:00		6.0	0.9	0.3	0	0.000	0	0.00003	0
12 - 21.5	3 April 24:00	4 April 09:33	24	279.6	315.9	290.6	59	3.957	58	0.02371	63
21.5 - 22	4 April 09:33	4 April 10:06		38.8	30.4	26.9	5	0.466	7	0.00327	9
22 - 25.5	4 April 10:06	4 April 13:28	15	142.1	73.1	60.3	12	1.177	17	0.00729	19
25.5 – 26.5	4 April 13:28	4 April 14:34		36.8	12.8	9.5	2	0.199	3	0.00089	2
26.5 - 42	4 April 14:34	5 April 06:07	24	766.6	134.8	65.4	13	0.946	14	0.00207	5
42 - 48	5 April 06:07	5 April 11:39		171.0	22.6	7.2	1	0.024	0	0.00039	1
48 - 75	5 April 11:39	6 April 14:55	24	760.3	99.0	30.2	6	0.000	0	0.00026	1
	total										
0 - 75	3 April 12:01	6 April 14:55		2434.9	712.1	491.8	100	6.772	100	0.0379	100

*correction for background concentration bromide of 90.5 µg L^{-1}

6 Laboratory studies: results

6.1 Transformation rates of nicosulfuron and prosulfocarb in Brakel ditch water

We conducted laboratory studies with water taken from the watercourse at Brakel to obtain the transformation rates to be used for the TOXSWA field test. Lab studies were done with low and high concentrations. At six different time points after the start of the experiment, three individual samples were analysed in duplicate for nicosulfuron and prosulfocarb concentration.

The conditions in the blank test bottles were stable during the test period: dissolved oxygen concentration 9.2 - 11.3 mg L^{-1}, pH 8.2 - 8.3 and temperature 10.5 - 10.8°C. The irradiance at the water surface was measured once and was approximately 210 μE m^{-2} s^{-1}. The decrease in water level due to evaporation at day 8 was negligible. The concentrations in the dosage solution were not measured.

The results of the measurements of the transformation study with nicosulfuron are presented in Table 28. Results of the individual samples are given in Annex 13. Nicosulfuron average concentrations in the test bottles after dosing were 25.60 μg L^{-1} and 129.15 μg L^{-1}, corresponding to 126% and 129% of the aimed concentrations of 20 μg L^{-1} and 100 μg L^{-1} respectively (Annex 13). Note that a higher concentration was also found in the dose solution of the field experiment. Both findings may have been caused by inaccurate product information of the formulated product or inaccurate standards. At 0.25, 2, 3, and 4 days after application, concentrations were either similar or somewhat lower than the concentration after dosing, at both levels and in the three replicates. At 8 days, 98.8±3.8% and 93.3±3.5% of the initial concentrations were measured for low and high concentration levels, respectively.

Table 28 *Concentration of nicosulfuron in Brakel ditch water in transformation lab study as a function of time after dosing. Initial concentrations 20 (code "low") and 100 μg L^{-1} (code "high") (3 series each with duplicate samples).*

Sample code	Concentration, average of duplicate samples (μg L^{-1})						% of initial at day 8
Days from t = 0 d	0	0.25	2	3	4	8	
CAS1 low	25.47	25.73	25.62	24.75	26.02	24.79	97.3
CAS2 low	26.33	24.11	24.59	23.87	24.68	24.87	103.2
CAS3 low	25.11	24.35	24.96	24.22	24.46*	24.11	96.0
CAS4 low	25.93	-	-	-	-	-	-
average	25.60	24.73	25.06	24.28	25.35	24.59	98.83
s.d..	0.53	0.71	0.43	0.36	0.67	0.34	3.13
CAS5 high	130.76	130.22	134.10*	126.04	124.14	121.13	92.6
CAS6 high	131.72	129.04	130.15	121.81	125.51	118.80	90.2
CAS7 high	127.03	126.64	129.02	124.93	122.53	123.38	97.1
CAS8 high	127.09	-	-	-	-	-	-
average	129.15	128.63	129.59	124.26	124.06	121.10	93.30
s.d.	2.45	1.49	0.56	1.79	1.22	1.87	2.86

*one of duplicate samples lost

Results of the transformation study measurements with prosulfocarb are shown in Table 29, with results of the individual samples given in Annex 13. Prosulfocarb concentrations in the test bottles after dosing were

0.206 μg L^{-1} and 0.998 μg L^{-1},corresponding to 94% and 90% of the aimed concentrations[1] of 0.22 μg L^{-1} and 1.11 μg L^{-1} respectively. At 0.25, 2, 3, and 4 days after application, concentrations decreased slightly at both levels and in the three replicates. At 8 days, 91.1±4.5% and 93.4±2.8% of the initial concentrations were measured for low and high concentration levels, respectively.

Table 29 *Concentration of prosulfocarb in Brakel ditch water in transformation lab study over time. Initial concentration 0.22 (code low) and 1.11 μg L^{-1} (code high) (n=3).*

Sample code	**Concentration, average of duplicate samples (μg L^{-1})**						**% of initial at day 8**
Days from t = 0 d	0	0.25	2	3	4	8	
CAS1 low	0.214	0.200	0.181	nd	0.189	0.185	86.5
CAS2 low	0.206	0.194	0.180	nd	0.189	0.197	95.4
CAS3 low	0.205	0.212	0.179	nd	0.181	0.187	91.4
CAS4 low	0.179	-	-	-	-	-	-
average	0.206	0.202	0.180	-	0.186	0.190	91.1
s.d.	0.007	0.007	0.001	-	0.004	0.005	3.6
CAS5 high	1.005	0.930	0.872*	0.930	0.905	0.933	92.8
CAS6 high	0.999	0.976	0.988	0.937	0.929	0.909	91.0
CAS7 high	1.000	1.000	0.953	0.901	0.925	0.964	96.5
CAS8 high	0.976	-	-	-	-	-	-
average	0.998	0.969	0.971	0.923	0.920	0.935	93.4
s.d.	0.015	0.029	0.018	0.016	0.010	0.023	2.3

nd: could not be analysed properly, data not reliable

*one of duplicate samples lost

The concentrations of nicosulfuron and prosulfocarb (average of duplicate samples) in a period of 8 days after application are presented in Figures 21 and 22. The short period of the test in combination with the small decrease in concentrations does not permit a fit to a kinetic model for the transformation rate. For nicosulfuron, the decrease was less than 7% in 8 days; for prosulfocarb this was less than 9%.

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[1] The theoretical concentration in the test water is based on the weighted mass of formulated product and percentage a.i. in the product, dosed in 2 L Brakel ditch water (Sections 4.2.2 and 4.2.3).

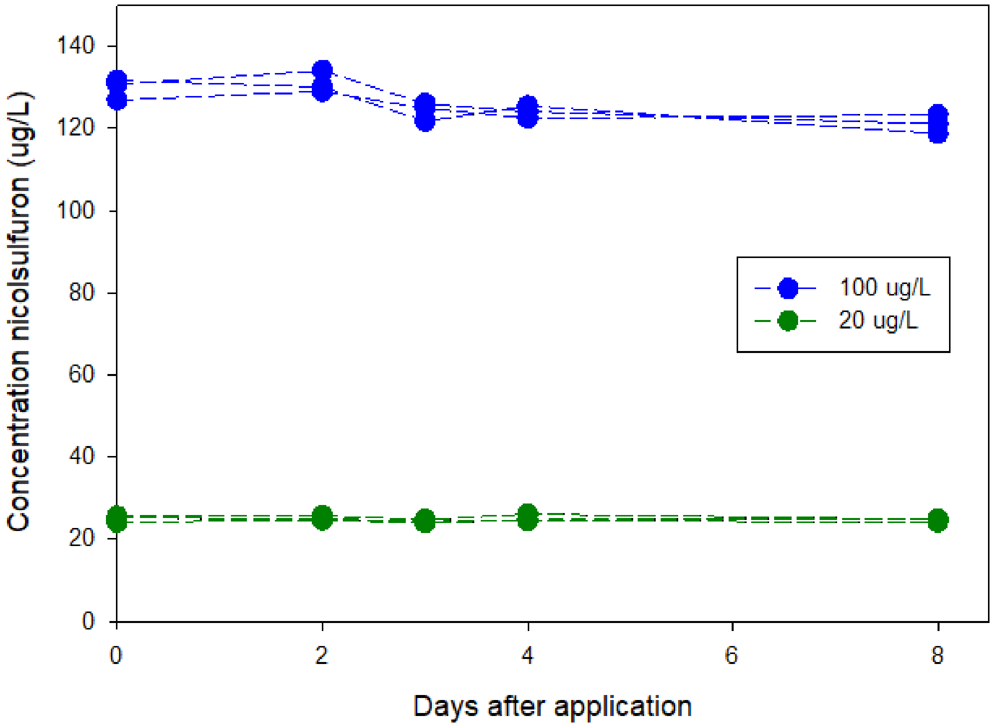

Figure 21 *Concentration of nicosulfuron in Brakel ditch water incubated at approximately 10°C and artificial daylight for 14h daily, at two concentration levels (20 and 100 µg L^{-1}).*

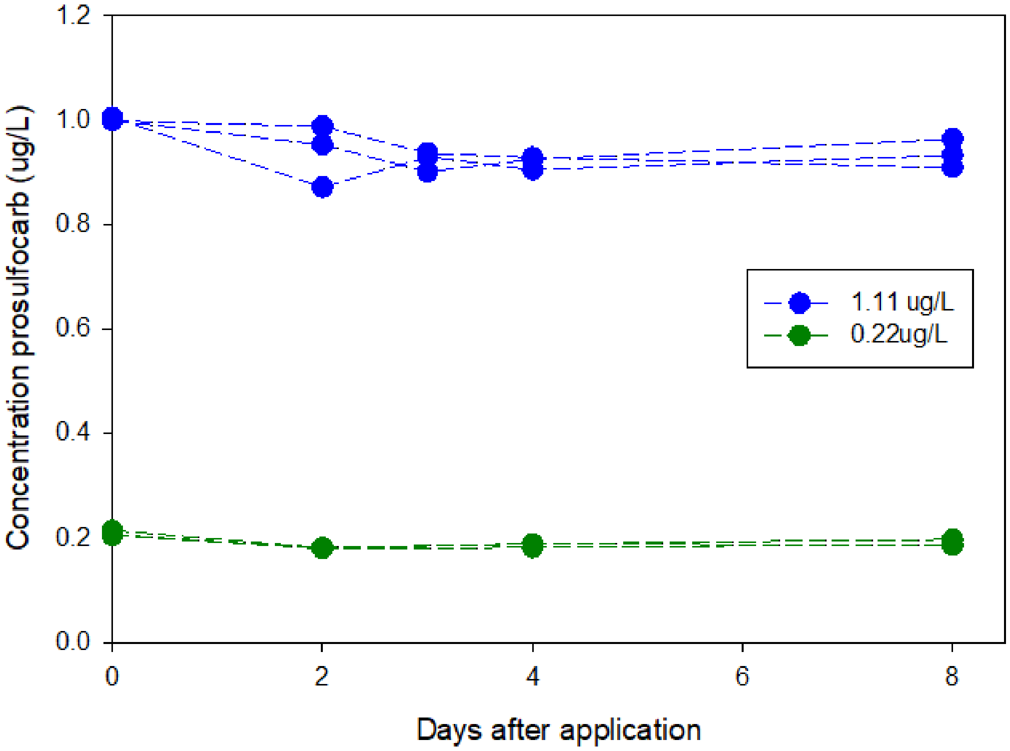

Figure 22 *Concentration of prosulfocarb in Brakel ditch water incubated at 10°C and artificial daylight for 14h daily, at two concentration levels (0.22 and 1.11 µg L^{-1}).*

6.2 Sorption of prosulfocarb to Brakel ditch sediment

We conducted a batch prosulfocarb sorption study with ditch sediment from the field site to obtain a sorption coefficient for use in the model test, applying six concentration levels in triplicate. The results were used to determine the sorption parameters from the sorption isotherm.

The sediment used for the sorption study had an organic matter content (loss on ignition) of 13.5% (s.d.=0.07, n=3) corresponding to an organic carbon content (Dumas) of 5.44% and 5.48% (duplicate) and a nitrogen content of twice 0.58% (duplicate). The sediment contained 48.9 g kg^{-1} Fe. The particle size distribution was determined with the pipette method: < 2 μm (clay): 38.8%; < 16 μm: 72.6%; < 50 μm: 77.8%; > 50 μm: 7.08%.

To estimate the Freundlich isotherm, the prosulfocarb concentration in water (mg L^{-1}) and prosulfocarb adsorbed to the sediment (mg kg^{-1}) were fitted by linear regression after logarithmic transformation (reference concentration =1 mg L^{-1}) using the LINEST function in Microsoft Excel. The data used for the linear regression are shown in Table 30 (also Annex 14). Note that due to 65% of added sediment in water, the initial concentration is diluted by approximately a factor 2. Equilibrium concentrations at the lowest concentration level (3 μg kg^{-1}) were < LOD and therefore not used to determine the sorption isotherm. In the lowest level used for the determination of the sorption isotherm, 5 mL of 15 μg L^{-1} prosulfocarb was added to 2 g dry sediment; 0.0375 μg g^{-1}. The background concentration determined for the material collected for the sorption study was 0.0014 μg g^{-1} d.w.; this is negligible compared to the mass added in the sorption test.

Table 30 *Prosulfocarb concentration in water and content in sediment layer at 24 hour equilibrium time in the batch sorption test.*

Concentration level and code	Initial concentration (μg L^{-1})	Concentration in water (μg L^{-1})	Content in sediment (μg kg^{-1})
30			
CAS E1	7.071	0.193	28.88
CAS E2		0.201	29.52
CAS E3		0.200	30.43
100			
CAS D1	23.65	0.663	99.90
CAS D2		0.624	96.37
CAS D3		0.672	100.1
300			
CAS C1	74.35	2.182	317.8
CAS C2		2.083	298.4
CAS C3		2.171	301.8
1000			
CAS B1	229.9	7.016	996.6
CAS B2		6.921	984.2
CAS B3		6.927	951.5
3000			
CAS A1	754.8	21.84	2985
CAS A2		22.58	3210
CAS A3		23.46	3150

A Freundlich sorption coefficient, K_f, of 127.6 L kg^{-1} dry sediment material with a Freundlich exponent of 0.98 (Annex 14) were calculated. Based on the organic matter content of the used sediment of 0.135 g g^{-1}, the $K_{f,\mathrm{om}}$ of prosulfocarb was calculated at 945 L kg^{-1}. In Figures 23 and 24, the concentrations prosulfocarb in water are plotted against prosulfocarb adsorbed to sediment in logarithmic and linear scales, respectively. The fitted Freundlich sorption isotherm describes the measurements well.

Based on the organic carbon content of the sediment of 0.0546 g g^{-1}, the $K_{f,\mathrm{oc}}$ of prosulfocarb was calculated at 2237 L kg^{-1}. The sorption coefficient derived for pesticide risk assessment is $K_{f,\mathrm{oc}}$ = 1693 L kg^{-1} with Freundlich exponent N 0.96 (Lewis et al., 2016). Thus, the sorption coefficient found in this study matches that of the sorption coefficient applied in risk assessment. Commonly, a factor of 1.72 is used for the estimation from carbon content to organic matter content. Both values were determined in our study, with a factor of 2.5 between organic carbon content end organic matter content for the Brakel sediment.

The value of the sorption coefficient for organic matter (945 L kg^{-1}) can be compared with the distribution calculated from prosulfocarb sorbed to organic matter and porewater concentrations in Table 24. Most distributions were lower than 945 L kg^{-1}, due to their not having reached equilibrium nor having penetrated down to 1 cm in sediment.

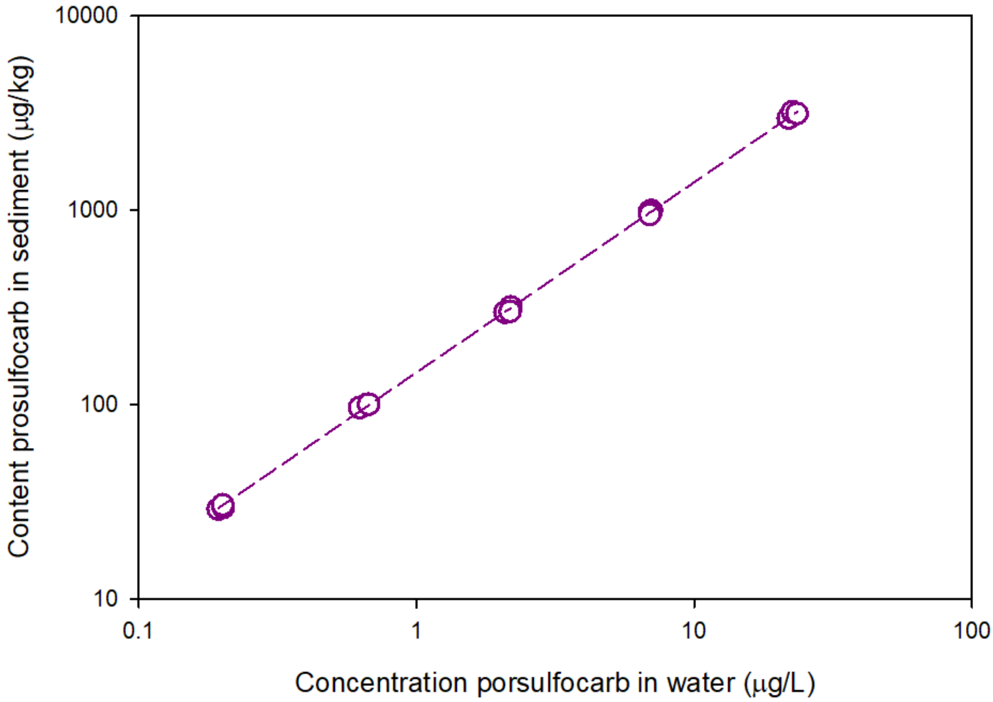

Figure 23 *Measurements of the sorption test of prosulfocarb with Brakel sediment (logarithmic scales) and resulting sorption isotherm;* $K_{f,om}$ *= 945 L kg*$^{-1}$ *and Freundlich exponent N = 0.98 (reference concentration = 1 mg L*$^{-1}$*).*

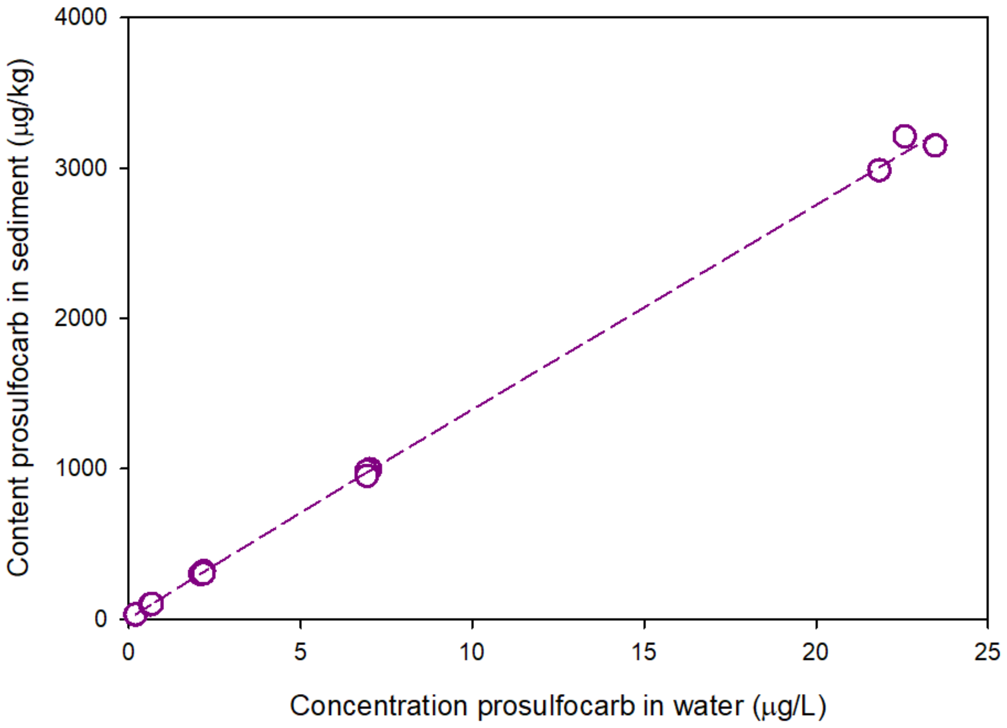

Figure 24 *Measurements of the sorption test of prosulfocarb with Brakel sediment (linear scales) and resulting sorption isotherm;* $K_{f,om}$ *= 945 L* kg^{-1} *and Freundlich exponent N = 0.98 (reference concentration = 1 mg* L^{-1}*).*

7 Discussion and conclusions

The overall aim of the field study was to quantify the effect of flow, dilution and sorption to sediment in and downstream of a treated ditch after the introduction of pesticides. Ultimately, we provide data for future testing and improving the TOXSWA model. In this chapter, we discuss our findings in relation to the study aims.

The Brakel system of watercourses was selected for the field test as it was necessary to determine water depth and water flow in every watercourse that could affect the fate of the introduced substances. Several adaptations were made to make this feasible, for example we added weirs to the watercourses to either close connections between watercourses (to simplify the system) or to measure watercourse discharges. As we observed that water flowed in two directions on the same day, water was pumped into the system of watercourses at three locations to maintain a unidirectional flow. Due to high upward seepage in the polder in which the system of watercourses is located, water is pumped out of the polder twice a day, leading to lowered water depth and increased flow velocity during pumping. The variation in water depth and in discharge was measured and recorded in sufficient detail. From our results, we were able to calculate mass balance of the substances and understand observed substance concentrations.

In the periods when the polder was drained, the discharge in the watercourses increased. The field experiment included six pumping periods of 2 – 3.5 hours in which discharge increased. At 302 m of the application stretch, the impact of 7cm was largest on the day of application, 3 April. The difference in water depth (1 cm) in the application stretch was small. The impact in the application stretch was small as water had to pass several weirs, and our measure to maintain unidirectional flow by pumping water compensated water outflow. At 302 m the discharge increased to 15 - 23 L s^{-1} whilst in the remaining time it was 7 – 13 L s^{-1}; a factor 2 variation in discharge over time at 302 m of the application stretch.

Prior to its introduction, the tracer bromide background concentration was low compared to the concentrations following application. No nicosulfuron was found. Surprisingly, background concentrations of prosulfocarb were found in sediment, hinting at an earlier contamination unrelated to but highlighting the relevance of this study. The background concentrations of both bromide and prosulfocarb were so low they could be neglected.

Spraying the dosing solution was well executed, however not all the sprayed pesticide formulations dissolved immediately. As a consequence, a white layer with higher concentration formed on the water surface, drifted a bit, before dissolving. Thus we did not meet the expected initial nominal concentrations, but were able to account for this by sufficient sampling. In this way, our transversal water sampling in the watercourses was sufficient to determine cross-sectional differences in concentrations, including those caused by the white surface layer. The discharge proportional sampling of water was sufficient to determine the “waves” of the substances passing the two measurement points. However, a longer sampling period for the measurement point at 302 m of 24h would have enabled better characterization of the tail of passing prosulfocarb. Sediment sampling was sufficient, but sampling a layer > 4 cm deep would have helped us better understand penetration into the sediment, as we had not expected that to reach these depths in such a short period of increased concentrations.

The treated stretch was dominated by flab and with a few macrophytes, thus the potential influence on sorption to macrophytes was not further considered.

Bromide, nicosulfuron and prosulfocarb were applied in the treated ditch to determine their dilution and sorption to sediment in flowing water conditions. The dilution was determined on the basis of concentrations measured at two locations downstream of the treated ditch. At the first discharge proportional sampling point at 47 m, dilution was assumed to be driven by longitudinal mixing of water or dispersion as there was no additional inflow from lateral watercourses. At the second discharge proportional sampling point, at 302 m, dilution was determined by additional water from lateral watercourses and from longitudinal mixing. Bromide and nicosulfuron were expected to behave similarly as bromide does not adsorb and nicosulfuron only adsorbs weakly to sediment organic matter. As prosulfocarb adsorbs strongly to sediment organic matter we expected its transport to be more strongly affected.

In the three-day field experiment, transformation of nicosulfuron and of prosulfocarb was negligible. In an eight day lab study with ditch water from the field location, the decrease of concentrations was less than 10%.

Dilution due to dispersion for the two pesticides and the tracer
At 47 m from the application stretch, we evaluated the effect of dilution due to longitudinal dispersion.

The peak concentration of bromide (6633 µg L^{-1}) was 80% of the nominal concentration measured 5h after application. For nicosulfuron, this was (99.8 µg L^{-1}) also 80% of the nominal concentration, and for prosulfocarb (596 ng L^{-1}) 50% of the nominal concentration. The peak concentration of prosulfocarb was 30 min earlier than that of nicosulfuron; 5h and 5.5h after application, respectively. For bromide and nicosulfuron, longitudinal dispersion reduced the concentration by 20%. Prosulfocarb has a high sorption coefficient thus sorption to the sediment may explain its stronger lowering in peak concentration. The substances were sprayed over a length of 50 m. Longitudinal dispersion leads to a decrease of concentration in the front and the back of the initial concentration distribution in the shape of a "block". Figures 15, 16 and 17 show that over a length of 50 m, the block form distribution no longer existed but moved as a Gaussian distributed wave through the watercourse. This may explain why the peak concentrations of bromide and nicosulfuron were already 20% lower than nominal. Furthermore, we note that the width of the Gaussian distributions of nicosulfuron and prosulfocarb were slightly broader than that of bromide. This may have been due to a slower mixing of the nicosulfuron and prosulfocarb formulations in the application stretch, strengthening the effect of longitudinal dispersion.

At 9.5h (bromide) and 9h (pesticides) after application, 47 m from the application stretch most of the total mass measured at the sampling point had passed: bromide 92%, nicosulfuron 90% and prosulfocarb 86%. After 25h, ≥98% of the total mass of all three compounds had passed. Scaled on dosed mass, after 2.5 days 82% of bromide, 99% of nicosulfuron, and 79% of prosulfocarb had passed.

Dilution due to mixing and dispersion for the two pesticides and the tracer
At 302 m from the application stretch, we evaluated the effect of dilution due to mixing with clean water and to longitudinal dispersion.

The peak concentration of bromide at 302 m was 1873 µg L^{-1}, measured 18h after application and 13h after the peak passed the first sampling point at 47 m. Part of the factor 3.5 decrease of peak concentration between the two sampling points could be attributed to dilution from entries of uncontaminated water from lateral watercourses (factor 2.6) with the remainder from longitudinal dispersion. At 2.5 days after the application, the concentration measured was 135 µg L^{-1}, still above the background concentration of 90.5 µg L^{-1}. Thus, a tail of the applied bromide was still passing.

The peak concentration of nicosulfuron at 302 m was 22.5 µg L^{-1} measured 18h after application. The factor 4.4 decrease in peak concentration between the two sampling points was higher than that of bromide (factor 3.5). In that short period, no dissipation of nicosulfuron was expected, and sorption to sediment was not expected to be relevant as nicosulfuron's sorption coefficient is small. However, at 47 m, its peak concentration was already lower than nominal and the concentrations were Gaussian distributed, with the wave already broader than for bromide. Hence, the decrease of the peak between 47 m and 302 m was larger than for bromide. At 24h after application, the concentration had dropped below LOD.

The peak concentration of prosulfocarb at 305 m was 141 ng L^{-1} at 17h after application. The factor 4.2 decrease in peak concentration between the two sampling points, similar to that of nicosulfuron and higher than that of bromide. In the sample analysed 65h after application, prosulfocarb was still detected, 0.0013 µg L^{-1}.

At 302 m from the application stretch, within 22h of total mass measured at the sampling point, more than 50% had passed for all three compounds: bromide 59%; nicosulfuron 65%: and prosulfocarb 72%. Within 42h after application, ≥93% of the total mass for all three compounds had passed the sampling point.

Nicosulfuron and prosulfocarb in sediment: strong sorption of prosulfocarb to sediment along the watercourse

After applying nicosulfuron in the application stretch, total concentrations in sediment layers 0-1 cm and 1-2 cm resulting from diffusion increased to 25 μg L^{-1} and 4.4 μg L^{-1} respectively. During the day, the total concentrations in both sediment layers decreased due to diffusion back to the water layer. One day later, 1.7 μg L^{-1} nicosulfuron was still found in the 0-1 cm layer.

At 330 m from the application stretch, the total concentrations of nicosulfuron in both sediment layers were still low 12h after application, but increased at 29h after application to 2.5 μg L^{-1} for the 0-1 cm layer. This was due to its concentrations in water being higher than in porewater, inducing diffusion into the sediment.

After applying prosulfocarb in the application stretch, its total concentration in the 0-1 cm sediment layer was 0.56 μg L^{-1}, in the 1-2 cm sediment layer 0.19 μg L^{-1}, and in the 2-4 cm sediment layer 0.15 μg L^{-1}. One day later, the total concentration in the 0-1 cm layer was 0.23 μg L^{-1}. Due to application and diffusion into the sediment, the total concentrations in both layers increased. After the peak of prosulfocarb dissolved in the water layer had passed, the total concentrations in both sediment layers decreased due to diffusion back to the water layer. Furthermore, upward seepage through the sediment to the water layer also caused prosulfocarb return to the water layer. These processes highlight the impact of flowing water for the fate of pesticides compared to stagnant water.

At 330 m from the application stretch, all prosulfocarb concentrations were higher than background concentrations (0.09 μg L^{-1}). Total concentrations at all three sampling times were at the same level, with total concentrations of 0.20 – 0.27 μg L^{-1} in layer 0-1 cm being somewhat higher than 0.15 – 0.17 μg L^{-1} in layer 1-2 cm. The increase in sediment concentrations observed for nicosulfuron did not occur for prosulfocarb; this difference may be due to their difference in sorption to organic matter,

We used the highest mass found per m^2 at the first measurement time to estimate how much total prosulfocarb adsorbed to the sediment in the application stretch: 1.4 mg. This is 2.8% of the mass applied to the water layer of the stretch (51.6 mg). With a background concentration of 0.10 μg L^{-1} in the 0-4 cm layer, the mass present prior to applying prosulfocarb was calculated at 0.4 mg, approximately 0.8% of the mass applied.

The mass of prosulfocarb in sediment does not explain why the peak concentration at 47 m from the application stretch was 50% of nominal concentration, compared to nicosulfuron's 80% of nominal concentration. Between the sediment and the water sampling point, more prosulfocarb would have been sorbed to the sediment, but not so much that this would cause an additional decrease of peak concentration of 30%. Therefore, we deduce that other processes must be responsible, for example due to sorption to flab found at the bottom of the ditch.

Sorption coefficient of prosulfocarb determined in lab study explains sorption of prosulfocarb in the field

The Freundlich sorption parameters were determined for prosulfocarb in a 24h batch test with sediment from the field location. The Freundlich sorption coefficient $K_{f,om}$ = 945 L kg^{-1} and its Freundlich exponent N = 0.98. These values match well with those values applied in the risk assessment for plant protection products, $K_{f,om}$ = 982 L kg^{-1} ($K_{f,om} = K_{f,oc}/1.742$) and Freundlich exponent N = 0.96 (Lewis et al., 2016).

For sediment samples with porewater concentration > LOD taken from sediment in the application stretch (layer 0-1 cm only), we compared the distribution between organic matter and porewater with the sorption coefficient. Most of the distributions were lower than 945 L kg^{-1}, most likely due to not having reached equilibrium in the short contact time and not having reached 1 cm depth. Thus, the lab-determined sorption coefficient is expected to contribute to a model test with TOXSWA to calculate sediment contents.

Dilution is dominant process regarding behaviour of pesticides in flowing water

Our study highlights three points that must be considered for the integration into TOXSWA and any other fate modelling: 1) The fast discharge/passing of pesticide peaks along the ditch, 2) the adsorption to the sediment during and dissipation to the water layer after passing of the peak of the pesticides in the water layer, and 3) that transformation processes can mostly be neglected due to the shorter residence times in flowing water.

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Justification

WOT-technical report: 274
BAPS-project number: WOT-04-008-024

The report has been reviewed and approved by Steven Crum (WENR). This study was supervised by Erwin van Boekel (Wot N&M, theme Agri-environment)] and Hans Schollaart (Agriculture, Fisheries, Food Security and Nature). The research methods and research approach were supervised by members of ERA (Team Environmental Risk Assessment, WENR).

Approved by External contact person

position: Senior policy officer Ministry of Agriculture, Fisheries, Food Security and Nature

name: Hans Schollaart

date: 3 January 2025

Approved by Internal contact person

name: Erwin van Boekel

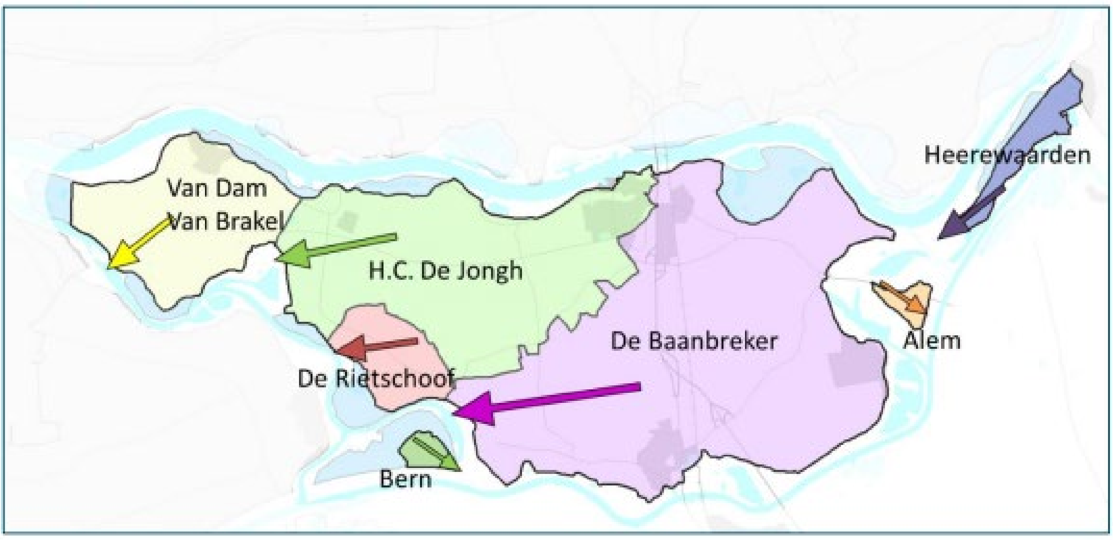
date: 30 August 2024

Annex 1 General information Bommelerwaard polder

The Van Dam - Van Brakel polder (ca. 1500 hectares) is situated in the North-Western part of the Bommelerwaard and discharges water via the pumping station Dijkgraaf Van Dam van Brakel to the Afgedamde Maas. Entry of water is via a free inlet from the Afgedamde Maas via pumping station Van Dam – Van Brakel. This seldom occurs. The polder is dominantly fed by rainwater and seepage water.

The map below shows the discharge areas and direction of discharge in the Bommelerwaard polder[2].

Afbeelding 2.7 Afvoergebieden en afvoerrichtingen Bommelerwaard



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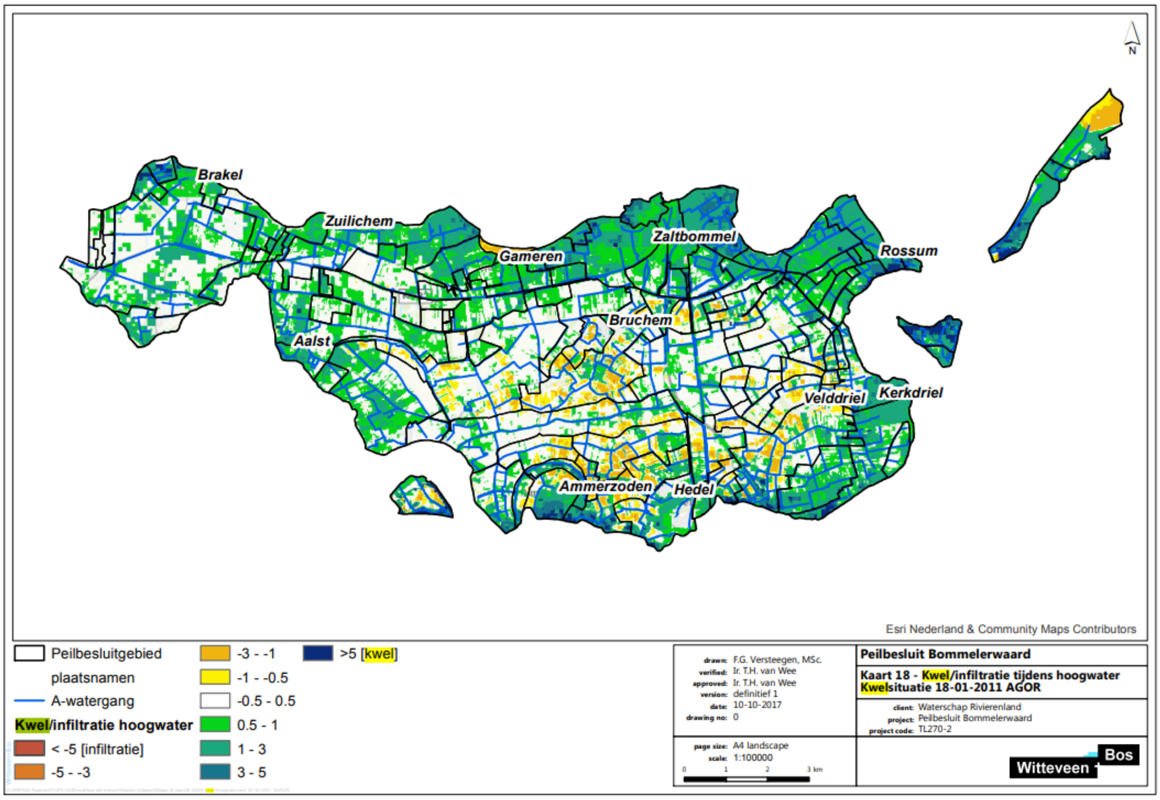
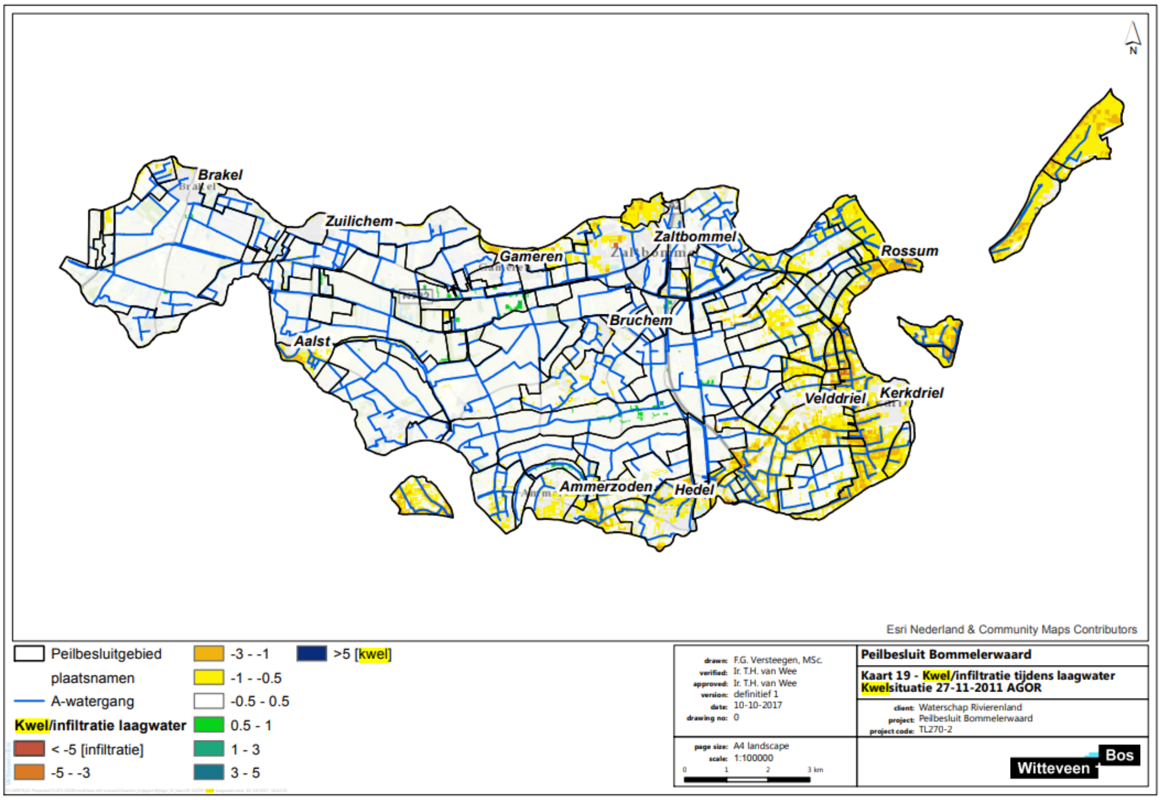
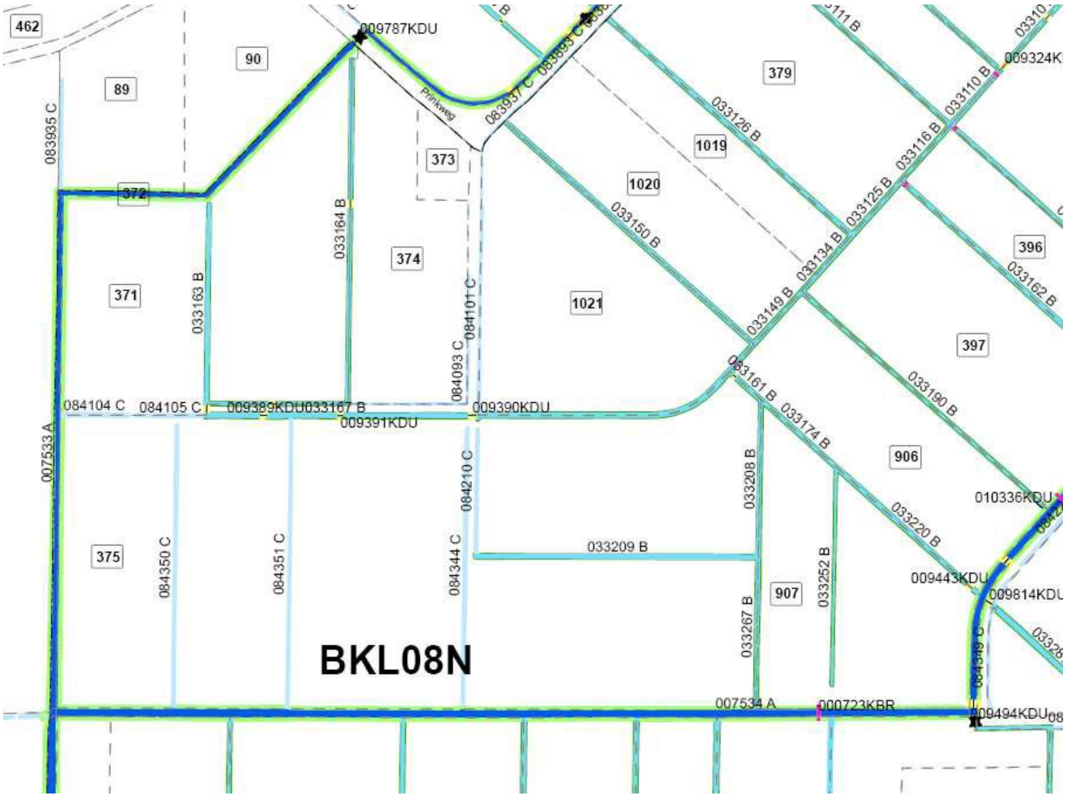
[2] From: exb-2018-28619.pdf (officiele-overheidspublicaties.nl)
Document Toelichting op het peilbesluit Vastgesteld door het algemeen bestuur van waterschap Rivierenland op 26 April 2018
Status Definitief 04 Datum 26 April 2018 Referentie TL270-2/18-006.512
Bijlage VI met kaart 18 en 19
exb-2018-28626.pdf (officiele-overheidspublicaties.nl)

The maps below show seepage at high water (top map) and low water in the river (bottom map).





The map below shows the watercourses with their reference number.



Annex 2 Dimensions of watercourses in system of watercourses in Brakel field study

Table 31 Dimensions of watercourses measured at several positions (north to south) in stretch from weir A to weir D (measured 17 October 2007).

Positon	Width (m)	Water depth (m) at distance from side:					Distance water surface to field level (m)		Time of measurement
		0.5 m	1 m	1 m	0.5 m	Average	N	S	
A+20 m	2.9	0.28	0.3	0.31	0.26	0.29	-	0.8	10:40
A+40 m	2.7	0.32	0.34	0.37	0.32	0.34	-	0.9	10:50
A+60 m	2.5	0.31	0.33	0.35	0.31	0.33	-	0.9	10:55
A+80 m	2.7	0.25	0.31	0.36	0.36	0.32	-	0.9	10:57
A+100 m	2.9	0.31	0.31	0.31	0.29	0.31	-	0.9	10:59
Average	**2.74**					**0.32**			
dam1+12 m	2.7	0.19	0.24	0.27	0.27	0.24	-	0.9	11:05
dam1+32 m	3	0.21	0.24	0.26	0.2	0.23	-	0.8	11:08
B-watercourse -dam2 halfway	3.2	0.19	0.24	0.27	0.27	0.24	-	0.9	11:12
dam2+20 m	3.1	0.3	0.32	0.31	0.3	0.31	-	1	11:17
dam2+40 m	3.1	0.27	0.35	0.35	0.34	0.33	-	0.9	11:19
dam2+60 m	2.9	0.27	0.3	0.36	0.3	0.31	1.05	0.9	11:21
dam2+80 m	3.8	0.29	0.37	0.36	0.28	0.33	0.9	0.8	11:23
dam2+100 m	2.8	0.24	0.29	0.34	0.3	0.29	0.9	0.8	11:31
D-40 m	3.2	0.27	0.28	0.33	0.27	0.29	0.9	0.9	11:37
D-20 m	2.2	0.32	0.32	0.32	0.32	0.32	0.9	0.92	11:42
Average	**3.00**					**0.29**			
In watercourse in front of B	2.3	0.46	0.47		0.37	0.43	-	-	11:14
E - bridge	4	0.3	0.3	0.31	0.3	0.30	-	-	11:50

Table 32 Distances between elements in stretch from weir A to weir D (measured 14 March 2008).

Watercourse elements from .. to ..	Length (m)
weir A – dam1	117
dam1	5
dam1 – watercourse B	44
width watercourse B	2.5
watercourse weir B – dam2	11.5
dam2	5
dam2 – dam3	124
dam3	5
dam3 – weir D	58
total	**372**

Annex 3 Flow meters

Five flow meters were installed in weirs in the system of watercourses on 22 October 2007. The weir locations A - E are indicated in Figure 25. The diameter of the flow meters and water depth and width of the water surface at their location in the system of watercourses is given in Table 33. The determination of the diameter of the flow meter is reported in Annex 4.

Table 33 *Overview of flow meters positioned in weir A - E with their diameter and water depth and width at the water surface at the position of the weir (measured 17 October 2007).*

Positon flow meter	Diameter flow meter (cm)	Water depth (cm)	Width at the water surface (cm)
A	10	40	260
B	10	40	260
C	15	55	300
D	20	50	300
E	20	50	300

Figure 25 *Position of five flow meters in the field study indicated by capital letters A to E. The watercourse between A and E is fed by direct runoff via trenches (purple arrows) and via drainage (pink-greyish area with white arrows).*

Annex 4 Setup of discharge measurement (in Dutch)

Leerstoelgroep Hydrologie en kwantitatief waterbeheer

Advies

Afvoermeetopstelling t.b.v. pesticiden-onderzoek in de Bommelerwaard

A. Dommerholt

Juli 2007

Opdrachtgever: Alterra, ERA

Inhoud

1. Inleiding

2. Bespreking meetopstelling

3. Meetresultaten

4. Opmerkingen/aanbevelingen

Bijlage I

1. Inleiding

Op verzoek van Alterra, ERA (Paulien Adriaanse en Wim Beltman) is advies uitgebracht over het meten van afvoeren in een stelsel van waterlopen in de Bommelerwaard ten behoeve van veldproeven. Het gebied is volkomen vlak en daardoor is er nauwelijks verval beschikbaar. Het oorspronkelijke plan om meetstuwtjes te plaatsen is daarom voorlopig verlaten, omdat voor een goede meting zoveel verval moet worden gecreëerd dat ontoelaatbaar veel opstuwing wordt veroorzaakt.

Bij twee eerder uitgebrachte adviezen voor het meten van afvoeren waar zo min mogelijk opstuwing mocht worden veroorzaakt, is gekozen voor een elektromagnetische flowmeter, geplaatst in een schot in de waterloop (project Vlietpolder bij Hoogmade voor Hoogheemraadschap Rijnland en project De Noordplas voor Waterschap Wilck en Wiericke).

De complete opstelling zoals die is gebruikt bij De Noordplas, kon worden geleend. Bijlage I is het verslagje dat is gemaakt van het meetadvies voor De Noordplas, met een beschrijving van de meetopstelling en een berekening van de te verwachten waterhoogteverschillen bij een aantal debieten.

Besloten is deze opstelling enigszins aan te passen en te testen in een van de stroomgoten van het hydraulica laboratorium van de leerstoelgroep Hydrologie en Kwantitatief Waterbeheer.

2. Bespreking meetopstelling

De meetopstelling in De Noordplas was symmetrisch uitgevoerd in verband met stroming in twee richtingen. Het betrof een 8-inch flowmeter. Bij het huidige onderzoekje is de uitstroompijp ingekort tot 0,50 m, hetgeen overeenkomt met 2,5 x de diameter. De instroompijp is ongewijzigd gebleven, dus 1,12 m.

Omdat de verwachting is dat bij de grootste te verwachten debieten (ca. 50 à 60 l/s) het waterhoogteverschil te groot zal worden, zal worden getracht dit te reduceren door het aanbrengen van standaard te koop zijnde taps verlopende in- en uitstroomgedeelten (zie foto's). Dit in plaats van de bij De Noordplas toegepaste dummy. Indien dit niet voldoende reductie oplevert kunnen nog zodanig vormgegeven in- en uitstroomgedeelten gemaakt laten worden die een minimaal energieverlies veroorzaken. Dit zal de opstelling echter aanmerkelijk duurder maken.

3. Meetresultaten

Tijdens het onderzoekje zijn de volgende varianten doorgemeten:

I : basisvariant zoals toegepast in De Noordplas (uitstroomgedeelte ingekort)
II : als I, met aan de instroomzijde een afronding met een straal van 0,06 m.
III : als I, met aan de instroomzijde een trechtervormig verloop van 0,200 naar 0,280 m.
IV : als III, met aan de uitstroomzijde eenzelfde trechtervormig verloop als aan de instroomzijde teneinde de uitstroomverliezen te reduceren.

In tabel I en figuur 1 zijn de meetresultaten weergegeven.

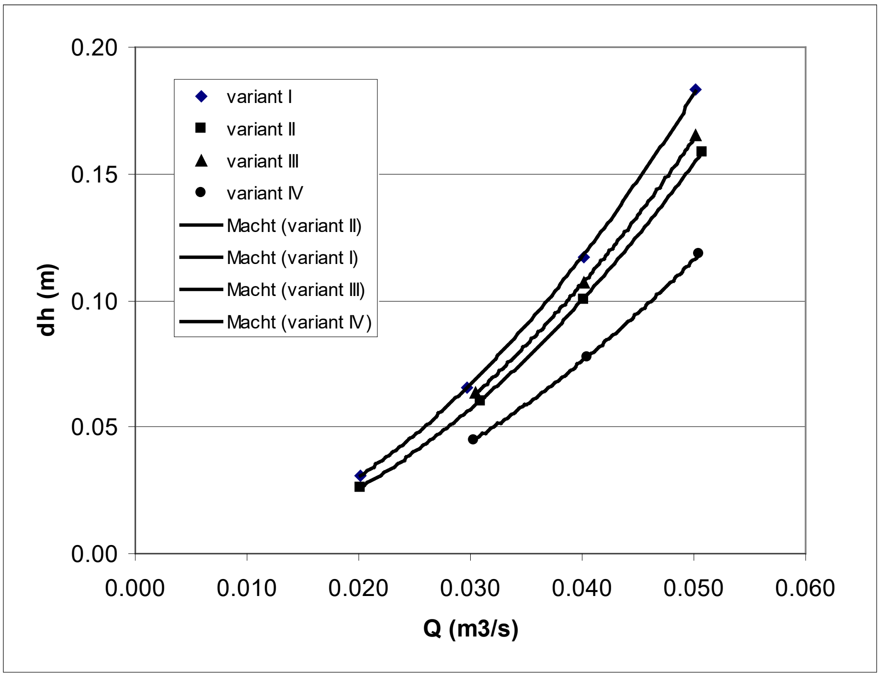
Tabel I

variant	Q m^3/s	dh m	ξ -
I	0.02011	0.0307	1.47
I	0.0297	0.0657	1.44
I	0.0401	0.1171	1.41
I	0.0502	0.1832	1.41
II	0.02012	0.0263	1.26
II	0.0309	0.0604	1.23
II	0.0401	0.1004	1.21
II	0.0507	0.1588	1.20
III	0.0305	0.0634	1.32
III	0.0402	0.1070	1.28
III	0.0502	0.1654	1.27
IV	0.0303	0.0449	0.95
IV	0.0404	0.0775	0.92
IV	0.0505	0.1182	0.90

dh = verschil in waterhoogte boven- en benedenstrooms van de totale opstelling

ξ = coëfficiënt waarmee de snelheidshoogte $v^2/2g$ moet worden vermenigvuldigd om dh te berekenen

v = gemiddelde stroomsnelheid in de meter en pijpstukken.



Figuur 1 waterhoogteverschil bij verschillende debieten voor de vier varianten.

In bijlage I is te zien dat de te verwachten waterhoogteverschillen over de opstelling (variant I) ongeveer 2 x $v^2/2g$ zullen bedragen, waarbij vooral de waarde van ξ_{intree} moeilijk is in te schatten. De wanddikte van de in- en uitstroompijp bedraagt 11 mm en is enigszins afgerond. Dit heeft een aanzienlijke invloed op de instroomverliezen en dus de waarde van ξ_{intree}.
Uit tabel I blijkt dat de totale verliezen aanzienlijk minder bedragen dan in bijlage I was geschat, namelijk ca. 1,45 x $v^2/2g$. Waarschijnlijk is de waarde van ξ_{intree} door de geringe afronding van de dikwandige pijp aanzienlijk lager dan geschat.
Een afronding met een grotere straal aan de instroomzijde (variant II) reduceert het verlies nogmaals met ca. 0,2 tot ca. 1,25 x $v^2/2g$.
Een standaard verkrijgbaar en dus veel eenvoudiger aan te brengen trechtervormige instroming geeft een iets minder goed resultaat, maar dat is slechts marginaal.
Tenslotte blijkt een trechtervormige uitstroom zoals verwacht de uitstroomverliezen aanmerkelijk te reduceren. Het totale verlies komt dan uit op ca. 0,95 x $v^2/2g$. Dit is een resultaat dat volstaat voor de opstelling in het veld.

Wanneer bij flowmeters met een andere diameter de afmetingen van de in- en uitstroomgedeelten met een evenredige factor worden aangepast mogen we ervan uitgaan dat de verliesfactor van 0,95 x $v^2/2g$ min of meer hetzelfde zal blijven. In onderstaande tabel II is voor enkele debieten voor de diameters D = 150 mm en D = 100 mm berekend wat de benodigde waterhoogteverschillen dh zullen zijn.

Tabel II

D m	A m^2	Q m^3/s	v m/s	$dh=0{,}95v^2/2g$ m
0.200	0.0314	0.065	2.070	0.207
0.200	0.0314	0.050	1.592	0.123
0.200	0.0314	0.045	1.433	0.099
0.200	0.0314	0.040	1.274	0.079
0.200	0.0314	0.030	0.955	0.044
0.200	0.0314	0.020	0.637	0.020
0.200	0.0314	0.010	0.318	0.005
0.150	0.0177	0.030	1.699	0.140
0.150	0.0177	0.025	1.415	0.097
0.150	0.0177	0.020	1.132	0.062
0.150	0.0177	0.010	0.566	0.016
0.150	0.0177	0.005	0.283	0.004
0.100	0.0079	0.015	1.911	0.177
0.100	0.0079	0.010	1.274	0.079
0.100	0.0079	0.005	0.637	0.020

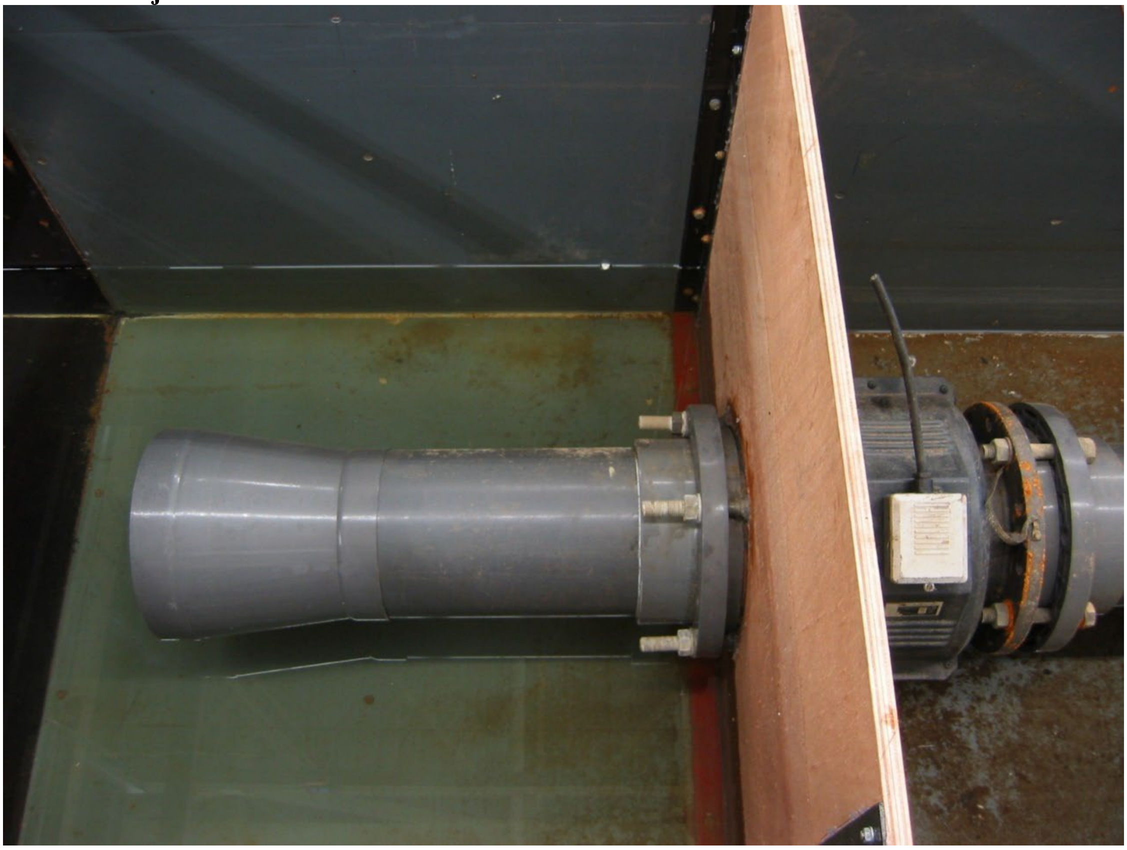
4. Opmerkingen/aanbevelingen

- Aan de instroomzijde ontstaan gemakkelijk wervels, vooral bij hogere debieten. Hierdoor is het mogelijk dat door de “slurf” lucht in de pijp wordt gezogen. Het was niet mogelijk te constateren of dit invloed heeft op de waarde die door de flowmeter wordt aangegeven omdat deze niet was aangesloten. Aanbevolen wordt daarom om in het veld te constateren of die wervels daar ook optreden en dan een eenvoudige voorziening aan te brengen om die te voorkomen. Dit kan bijvoorbeeld een op het water drijvend plaatje zijn dat met behulp van een paar paaltjes in het talud en touw of draad op zijn plaats wordt gehouden boven de instroomzijde van de opstelling. De afmetingen van het plaatje proefondervindelijk vast te stellen. Vermoedelijk is ca. 0,8 x 0,8 m voldoende.

Aan de uitstroomzijde kan door de hoge uitstroomsnelheid mogelijk bodemerosie optreden. Bijvoorbeeld is de gemiddelde stroomsnelheid aan de uitstroomzijde van het trechtervormige stuk bij 50 l/s ongeveer 0,8 m/s. Aangezien hier bij het waterschap veel meer ervaring mee is, wordt geadviseerd om in overleg met het waterschap te bepalen of het nodig is om enige vorm van bodembescherming aan te brengen.

Instroomzijde

Uitstroomzijde



BIJLAGE I Advies – Inrichting afvoermeetopstelling project De Noordplas

Inhoud

1. Inleiding

2. Bespreking meetopstelling

3. Nauwkeurigheid

4. Literatuur

1. Inleiding

In April 2002 verzocht het waterschap Wilck en Wiericke de Sectie Waterhuishouding van Wageningen Universiteit om een advies voor het meten van de aan- en afvoer in één van de watergangen in de polder De Noordplas nabij Zoetermeer. Het betrof een tijdelijke meting in het kader van een gezamenlijk onderzoeksproject samen met het Hoogheemraadschap Rijnland en TNO. Gedacht werd hierbij aan een meetopstelling zoals eerder gerealiseerd in De Vlietpolder bij Hoogmade, die al enige tijd naar tevredenheid functioneert. Het betreft een onder water in een damwand geplaatste elektromagnetische debietmeter waarmee het mogelijk is het debiet in twee richtingen te meten.

De meetopstelling moet aan de volgende voorwaarden voldoen:
- de meting dient automatisch en continu plaats te vinden;
- er dient in twee richtingen te worden gemeten;
- bij een afvoer van 25 l/s mag het verval over de meetopstelling niet meer dan 0,10 m bedragen, de maximale afvoer wordt op meer dan het dubbele hiervan geschat;
- bij een afvoer van 1 l/s mag de onnauwkeurigheid niet meer dan 5% bedragen;
- voeding van de opstelling dient door middel van accu’s te geschieden.

2. Bespreking meetopstelling

Een elektromagnetische debietmeter wordt door de fabriek met een ijkingscertifikaat geleverd. De ijking wordt alleen gegarandeerd als wordt voldaan aan de eis van een aanstroming door een rechte buis met een diameter van 5 tot 10 x de diameter (D) van de meter en een rechte uitstroming van 2 tot 3 x D. In het geval van stroming in twee richtingen wordt de opstelling symmetrisch.
De minimale diameter van de meter wordt bepaald door de eis dat het verval bij 25 l/s niet meer dan 0,10 m mag bedragen. Dit verval wordt veroorzaakt door de energieverliezen die optreden tussen de bovenstroomse en de benedenstroomse waterhoogte bij stroming door de meter inclusief in- en uitstroombuis. De grootte van de energieverliezen kan aan de hand van literatuurgegevens vrij goed worden ingeschat, maar het blijven schattingen en dus geen exacte berekeningen.

Een eerste globale berekening leerde dat de minimaal benodigde (leverbare) diameter 200 mm moest bedragen. Uitgegaan is van de gegevens van de MagMaster Electromagnetic Flowmeter van de firma ABB, geleverd door de firma Brinck HMT te Amersfoort, die ook de flowmeter voor de meetopstelling in de Vlietpolder had geleverd.

Met het waterschap was afgesproken dat het in- en uitstroomgedeelte door de sectie Waterhuishouding zouden worden geleverd. Hiertoe werd opdracht gegeven aan de werkplaats van het departement. Daarbij bleek het vinden van de juiste diameter buis en de benodigde flenzen voor bevestiging aan de flowmeter een probleem. Uiteindelijk is gekozen voor uitvoering in PVC. De verkrijgbare diameter van de buis week slechts enkele mm's af van de diameter van de flowmeter (zie ook berekening).

Bij afvoeren veel groter dan 25 l/s zal het verval over de meter snel toenemen (verval neemt ongeveer kwadratisch toe met de afvoer) en dus de max. toegestane 0,10 m ruim overschrijden. Als oplossing daarvoor werd het idee geopperd om naast de meetopstelling een afsluitbare "dummy" te installeren, die hetzelfde energieverlies heeft als de opstelling met de meter, zodat deze bij openen dezelfde afvoer zal hebben als de meter zelf. De afvoer is dan dus verdubbeld bij hetzelfde verval. De voorziening om deze dummy af te sluiten mag echter geen extra energieverlies veroorzaken. Voorgesteld werd om dit met een opblaasbare rubber bal te doen.
De dummy is vervaardigd van dezelfde pijp als het in- en uitstroomgedeelte. Met de aanwezige apparatuur was het niet mogelijk de diameter van de dummy gelijk te maken aan de diameter van de debietmeter. Ook de ruwheid van de debietmeter is moeilijk na te bootsen. Zoals uit onderstaande berekening zal blijken, zijn de wrijvingsverliezen in de debietmeter/dummy, slechts een fractie van de in- en uittredeverliezen. Het debiet door de dummy zal daarom slechts in geringe mate afwijken van het debiet door de meter zelf. Omdat bovendien bij het merendeel van de te verwachten debieten, de dummy gesloten zal zijn, lijkt dit een aanvaardbare oplossing.

Zowel de debietmeter als de dummy worden met behulp van flenzen aan een stalen rijplaat gemonteerd, die verticaal en min of meer loodrecht op de stroomrichting in de waterloop wordt geplaatst en wel zodanig dat geen onder- en achterloopsheid op kan treden. De meter en de dummy dienen enerzijds zo diep mogelijk onder de waterspiegel te worden geplaatst vanwege bereikbaarheid door onbevoegden en het voorkomen van verstopping door drijvend vuil en anderzijds op voldoende afstand tot de bodem om vervuiling door bodemmateriaal te voorkomen, en om een ongestoorde toestroming van water mogelijk te maken. Afstand tot de bodem min. ca. 0,30 m.

Berekening

Gegevens:

- diameter debietmeter: $D_m = 0,207$ m
- diameter pijp/dummy: $D_p = 0,203$ m
- lengte debietmeter/dummy: $L_m = 0,345$ m
- lengte in- en uitstroompijpen: $L_p = 1,12$ m

Alle energieverliezen worden uitgedrukt in een coëfficiënt ξ x de snelheidshoogte $v^2/2g$, waarbij v = de gemiddelde stroomsnelheid in de opstelling. Aangezien het verschil in diameter tussen de pijpstukken en de meter zelf klein is, is voor de berekening van de stroomsnelheid de diameter van de pijpstukken gebruikt (0,203 m).

Voor de verschillende coëfficiënten zijn de volgende schattingen gemaakt:
intreeverlies: $\xi_{intree} = 0{,}75$
uittredeverlies: $\xi_{uittree} = 1{,}0$
weerstandscoëfficiënt pijpstukken: $\lambda_p = 0{,}02$
weerstandscoëfficiënt debietmeter: $\lambda_m = 0{,}03$

Door het verschil in diameter tussen de debietmeter en de in- en uitstroompijp treden op de overgang tussen beide ook nog kleine verliezen op. Voor verwijding en vernauwing geldt: $\xi_{overgang} = 0{,}02$.

Het wrijvingsverlies kan ook worden uitgedrukt in een coëfficiënt $\xi_{wrijving} = \lambda.(L/D)$

Het totale energieverlies ΔH wordt nu:

<u>Debietmeter</u>

$$\Delta H = \{\xi_{intree} + \lambda_p .(L_p/D_p) + \xi_{overgang} + \lambda_m .(L_m/D_m) + \xi_{overgang} + \lambda_p .(L_p/D_p) + \xi_{uittree}\} . v^2/2g$$
$$\{0{,}75 + 0{,}02(1{,}12/0{,}203) + 0{,}02 + 0{,}03(0{,}345/0{,}207) + 0{,}02 + 0{,}02(1{,}12/0{,}203) + 1{,}0\} . v^2/2g$$
$$\{0{,}75 + 0{,}11 + 0{,}02 + 0{,}05 + 0{,}02 + 0{,}11 + 1{,}0\} . v^2/2g = \mathbf{2{,}06} . v^2/2g$$

Bij een maximale toegestane ΔH = 0,10 m betekent dit:

$v^2/2g = 0{,}10/2{,}06 = 0{,}0485$ m en $v = (0{,}0485 . 19{,}62)^{1/2} = 0{,}976$ m/s.
De dwarsdoorsnede van de pijp $A_p = 0{,}0324$ m^2

Het debiet bij een waterhoogteverschil van 0,10 m bedraagt dus: $Q = v . A_p = \mathbf{0{,}0316}$ m^3/s.

<u>Dummy</u>

Op identieke wijze kan voor de dummy inclusief in- een uitstroompijp ΔH worden berekend.

$$\Delta H = \{\xi_{intree} + \lambda_p .(L_p/D_p) + \lambda_p .(L_p/D_p) + \lambda_p .(L_p/D_p) + \xi_{uittree}\} . v^2/2g$$
$$\{0{,}75 + 0{,}02(1{,}12/0{,}203) + 0{,}02(0{,}345/0{,}203) + 0{,}02(1{,}12/0{,}203) + 1{,}0\} . v^2/2g$$
$$\{0{,}75 + 0{,}11 + 0{,}03 + 0{,}11 + 1{,}0\} . v^2/2g = \mathbf{2{,}00} . v^2/2g$$

Dit komt bij een waterhoogteverschil van 0,10 m overeen met een debiet van $Q = \mathbf{0{,}0321}$ m^3/s.

Dit debiet bedraagt ca. 1,6% meer dan het debiet door de meter zelf.

Resumé

Tot een debiet van ca. 30 l/s zal het waterhoogteverschil niet meer dan 0,10 m bedragen.

Bij geopende dummy zal het waterhoogteverschil niet groter worden dan 0,10 m tot een debiet van ca. 60 l/s. Daarmee voldoet deze opstelling aan de gestelde eisen voor wat betreft het maximaal toegestane verval over de meetopstelling.

3. Nauwkeurigheid

In onderstaand overzicht wordt aangegeven wat volgens de fabrieksopgave de nauwkeurigheid is van de debietmeter bij verschillende debieten.

Debiet (l/s)	Max. onnauwkeurigheid (%)
15,7	0,2
6,28	0,5
3,14	1
1,57	2
0,63	5
0,31	10

Deze debietmeter voldoet dus aan de eis dat een debiet van 1,0 l/s moet kunnen worden gemeten met een nauwkeurigheid beter dan 5%.

4. Literatuur

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ABB Instrumentation Ltd, England. Magmaster Electromagnetic Flowmeter, Specification Data File and Magmaster Sizing Table.

Primayer Aqua Technology Solutions, England. Primelog Data Logger Systems.

Annex 5 Organic matter content, bulk density and porosity of sediment of Brakel field ditch

Sediment cores were sampled at three locations and at several times during the experiment (Section 3.5). We determined sediment properties from the sediment cores taken at locations MP1 and MP2 sampled on 3 and 4 April 2008. From the top of the cores the layers 0-1 cm, 1-2 cm and 2-4 cm were analysed.

The organic matter content in sediment based on measurement of loss of ignition is given in Table 34 Organic matter content of sediment sampled at locations MP1 and MP2 (based on loss on ignition). Average and standard deviation given at bottom of table. The average organic matter content of all samples is given in the bottom part of the table.

The bulk density and volume fraction of water in sediment from three locations is given in Table 35 Bulk density and volume fraction of liquid of top 4 cm of sediment at locations MP1 and MP2. Average and standard deviation given at bottom of table. The average of bulk density and volume fraction of liquid of all samples is given in the bottom part of the table.

For sediment sampled by core, layers of 1 and 2 cm were cut off. However in many samples the volume of water in sediment (see Table 36) exceeded the volume of the slice of 1 cm in the sediment column (12.57 cm^3), e.g. for P1 and P116; apparently more than 1 cm was cut off in these cases. It is suggested that when cutting, the thickness of the slice was larger than intended. So, for the thickness of layer 1, 1.1 cm was used for the calculations. In a small test, 35 g dry sediment added to 100 mL water increased the volume to 114 mL, and bulk density of 35 g/114 mL = 0.307 kg L^{-1}. This was compared to the thickness weighted average of the layers 1-2 and 2-4 cm (excluding layer 0-1 cm as this layer contributes less to the bulk sampled sediment). The average was 0.311 kg L^{-1}. Thus, increasing the layer thickness by 0.1 cm seems justified. When applying the thicknesses of 1 and 2 cm the thickness weighted average is 0.333 kg L^{-1}, much larger than the 0.307 kg/L found in the small test.

The volume of the layer was corrected for the density of water being lower when cut, using the method described by Adriaanse et al. (2015) in Annex 5.

Table 34 *Organic matter content of sediment sampled at locations MP1 and MP2 (based on loss on ignition). Average and standard deviation given at bottom of table.*

Code	Depth sediment	Bowl empty	Bowl + dry sediment 105˚C	Bowl + dry sediment 550˚C	Nett dry sediment 105˚C	Loss on ignition	Loss on ignition
	(cm)	(g)	(g)	(g)	(g)	(g)	(%)
P09	0-1 cm	19.560	22.6491	22.2266	3.089	0.4225	13.7
P010	1-2 cm	19.821	22.7626	22.3312	2.941	0.4314	14.7
P011	2-4 cm	18.151	21.3302	20.8548	3.179	0.4754	15.0
P012	0-1 cm	20.018	22.6615	22.2879	2.644	0.3736	14.1
P013	1-2 cm	20.595	24.1108	23.6199	3.516	0.4909	14.0
P014	2-4 cm	17.572	21.5822	20.9969	4.010	0.5853	14.6
MP1 3-4-2008 15h40		**(4h)**					
P11	0-1 cm	18.233	21.2779	20.867	3.045	0.4109	13.5
P12	1-2 cm	18.556	22.736	22.1662	4.180	0.5698	13.6
P13	2-4 cm	17.446	23.9493	23.055	6.503	0.8943	13.8
P14	0-1 cm	19.602					
P15	1-2 cm	18.767	22.6146	22.0853	3.848	0.5293	13.8
P16	2-4 cm	18.454	27.8679	26.7693	9.414	1.0986	11.7
P17	0-1 cm	19.456	23.094	22.6367	3.638	0.4573	12.6
P18	1-2 cm	19.211	25.2338	24.5319	6.023	0.7019	11.7
P19	2-4 cm	19.472	31.6583	30.3549	12.186	1.3034	10.7
P110	0-1 cm	20.600	23.0564	22.7248	2.457	0.3316	13.5
P111	1-2 cm	20.250	26.1339	25.3888	5.884	0.7451	12.7
P112	2-4 cm	24.169	32.0344	30.9649	7.865	1.0695	13.6
MP1 3-4-2008 21h45		**(10h)**					
P113	0-1 cm	20.579	23.085	22.7424	2.506	0.3426	13.7
P114	1-2 cm	26.553	30.0188	29.5379	3.466	0.4809	13.9
P115	2-4 cm	24.977	31.0752	30.1026	6.098	0.9726	15.9
P116	0-1 cm	24.444	27.0181	26.6355	2.574	0.3826	14.9
P117	1-2 cm	22.168	25.6608	25.1735	3.493	0.4873	13.9
P118	2-4 cm	25.893	31.6344	30.7411	5.741	0.8933	15.6
P119	0-1 cm	30.493	32.4496	32.1603	1.957	0.2893	14.8
P120	1-2 cm	23.226	26.1441	25.7022	2.918	0.4419	15.1
P121	2-4 cm	19.602	25.8822	24.9384	6.280	0.9438	15.0
P122	0-1 cm	23.495	26.3318	25.9266	2.837	0.4052	14.3
P123	1-2 cm	23.420	26.6320	26.1575	3.212	0.4745	14.8
P124	2-4 cm	22.915	27.3813	26.6563	4.467	0.725	16.2
MP1 4-4-2008 10h50		**(23h)**					
P26	0-1 cm	19.418	21.754	21.3571	2.336	0.3969	17.0
P27	0-1 cm	18.766	21.2161	20.8295	2.450	0.3866	15.8
P28	0-1 cm						
P29	0-1 cm	18.454	21.1585	20.6875	2.704	0.471	17.4
MP2 4-4-2008 0h30		**(13h)**					
P30	0-1 cm	20.600	23.1627	22.7765	2.563	0.3862	15.1
P31	1-2 cm	20.421	24.915	24.2519	4.494	0.6631	14.8
P32	0-1 cm	18.652	20.9859	20.6453	2.334	0.3406	14.6
P33	1-2 cm	18.2322	22.9988	22.3262	4.767	0.6726	14.1
P34	0-1 cm	18.150	21.7224	21.2632	3.572	0.4592	12.9
P35	1-2 cm	17.4459	21.4368	20.8651	3.991	0.5717	14.3
P36	0-1 cm	17.970	19.7299	19.4655	1.760	0.2644	15.0
P37	1-2 cm	19.2104	23.4012	22.786	4.191	0.6152	14.7
MP2 4-4-2008 13h00		**(25h)**					
P38	0-1 cm	19.9957	21.9413	21.6494	1.946	0.2919	15.0
P39	1-2 cm	19.472	23.3419	22.7817	3.870	0.5602	14.5
P40	0-1 cm	17.5704	19.7618	19.4366	2.191	0.3252	14.8
P41	1-2 cm	20.2496	24.5397	23.9198	4.290	0.6199	14.4
P42	0-1 cm	19.6014	22.2353	21.8582	2.634	0.3771	14.3
P43	1-2 cm	19.8208	24.002	23.3976	4.181	0.6044	14.5
P44	0-1 cm	19.4541	22.072	21.7021	2.618	0.3699	14.1
P45	1-2 cm	20.0172	25.1625	24.4022	5.145	0.7603	14.8
MP2 4-4-2008		**(29h)**					
P46	0-1 cm	24.0129	26.5374	26.1741	2.525	0.3633	14.4
P47	0-1 cm	25.2984	27.5775	27.2405	2.279	0.337	14.8
P48	0-1 cm	22.6502	25.2167	24.8296	2.567	0.3871	15.1
P49	0-1 cm	18.5563	20.7555	20.4338	2.199	0.3217	14.6
					Loss on ignition (%)		
					0-1 cm	1-2 cm	2-4 cm
				average	14.6	14.1	14.2
				sd	1.1	0.8	1.8
				n	24	18	10

Table 35 *Bulk density and volume fraction of liquid of top 4 cm of sediment at locations MP1 and MP2. Average and standard deviation given at bottom of table.*

Code	Depth sediment	Total dry sediment 105C	Water in sediment	Volume sediment column	Correction volume for freezing	Bulk density	Bulk density	Bulk density	Volume fraction of liquid	Volume fraction of liquid	Volume fraction of liquid
	(cm)	(g)	(g)	(cm^3)	(cm^3)	0-1 cm	1-2 cm	2-4 cm	0-1 cm	1-2 cm	2-4 cm
						(kg/L)	(kg/L)	(kg/L)	(L/L)	(L/L)	(L/L)
MP1 3-4-2008 15h40 (4h)											
P11	0-1 cm	2.96	13.27	12.57	12.62	0.23			1.00		
P12	1-2 cm	4.21	11.66	12.57	11.51		0.37			1.00	
P13	2-4 cm	6.7	18.58	25.14	23.45			0.29			0.79
			0								
P14	0-1 cm	2.74	12.3	12.57	12.71	0.22			0.97		
P15	1-2 cm	4.01	12.37	12.57	11.45		0.35			1.00	
P16	2-4 cm	9.35	20.04	25.14	23.32			0.40			0.86
P17	0-1 cm	3.75	11.09	12.57	12.82	0.29			0.87		
P18	1-2 cm	6.1	10.89	12.57	11.58		0.53			0.94	
P19	2-4 cm	12.48	18.93	25.14	23.42			0.53			0.81
P110	0-1 cm	2.62	12.5	12.57	12.69	0.21			0.98		
P111	1-2 cm	6.2	14.69	12.57	11.24		0.55			1.00	
P112	2-4 cm	7.95	20.11	25.14	23.31			0.34			0.86
MP1 3-4-2008 21h45 (10h)											
P113	0-1 cm	2.5	11.7	12.57	12.76	0.20			0.92		
P114	1-2 cm	3.54	12.08	12.57	11.47		0.31			1.00	
P115	2-4 cm	6.19	20.81	25.14	23.25			0.27			0.90
P116	0-1 cm	2.61	13.47	12.57	12.60	0.21			1.00		
P117	1-2 cm	3.52	11.4	12.57	11.53		0.31			0.99	
P118	2-4 cm	5.79	20.5	25.14	23.28			0.25			0.88
P119	0-1 cm	2.04	12.71	12.57	12.67	0.16			1.00		
P120	1-2 cm	2.96	12.65	12.57	11.42		0.26			1.00	
P121	2-4 cm	6.31	21.39	25.14	23.20			0.27			0.92
P122	0-1 cm	2.9	11.28	12.57	12.80	0.23			0.88		
P123	1-2 cm	3.23	12.07	12.57	11.47		0.28			1.00	
P124	2-4 cm	4.5	18.64	25.14	23.44			0.19			0.80
MP1 4-4-2008 10h50 (23h)											
P26	0-1 cm	2.3	11.87	12.57	12.75	0.18			0.93		
P27	0-1 cm	2.4	12.32	12.57	12.71	0.19			0.97		
P28	0-1 cm	2.47	13.23	12.57	12.63	0.20			1.00		
P29	0-1 cm	2.7	13.82	12.57	12.57	0.21			1.00		
MP2 4-4-2008 0h30 (13h)											
P30	0-1 cm	2.5	12.95	12.57	12.65	0.20			1.00		
P31	1-2 cm	4.43	11.91	12.57	11.49		0.39			1.00	
P32	0-1 cm	2	13.28	12.57	12.62	0.16			1.00		
P33	1-2 cm	4.71	13.06	12.57	11.38		0.41			1.00	
P34	0-1 cm	3.51	11.89	12.57	12.75	0.28			0.93		
P35	1-2 cm	3.92	11.79	12.57	11.50		0.34			1.00	
P36	0-1 cm	1.73	12.01	12.57	12.74	0.14			0.94		
P37	1-2 cm	4.12	13.11	12.57	11.38		0.36			1.00	
MP2 4-4-2008 13h00 (25h)											
P38	0-1 cm	1.93	11.97	12.57	12.74	0.15			0.94		
P39	1-2 cm	3.78	11.35	12.57	11.54		0.33			0.98	
P40	0-1 cm	2.16	12.11	12.57	12.73	0.17			0.95		
P41	1-2 cm	4.2	12.16	12.57	11.47		0.37			1.00	
P42	0-1 cm	2.61	12.99	12.57	12.65	0.21			1.00		
P43	1-2 cm	4.13	11.82	12.57	11.50		0.36			1.00	
P44	0-1 cm	2.53	11.3	12.57	12.80	0.20			0.88		
P45	1-2 cm	5.08	11.31	12.57	11.54		0.44			0.98	
MP2 4-4-2008 (29h)											
P46	0-1 cm	2.48	11.77	12.57	12.76	0.19			0.92		
P21	1-2 cm	3.95	10.13	12.57	11.65		0.34			0.87	
P47	0-1 cm	2.31	11.28	12.57	12.80	0.18			0.88		
P22	1-2 cm	4.16	11.91	12.57	11.49		0.36			1.00	
P48	0-1 cm	2.6	11.41	12.57	12.79	0.20			0.89		
P23	1-2 cm	3.75	10.1	12.57	11.65		0.32			0.87	
P49	0-1 cm	2.13	14.97	12.57	12.47	0.17			1.00		
P24	1-2 cm	3.97	10.83	12.57	11.59		0.34			0.93	
						Bulk density (kg/L)			Volume fraction of liquid (L/L)		
					avg	0.198	0.366	0.317	0.95	0.98	0.85
					sd	0.036	0.072	0.107	0.05	0.04	0.05
					n	24	20	8	24	20	8
					layer	0-1 cm	1-2 cm	> 2 cm	0-1 cm	1-2 cm	> 2 cm

Annex 6 Macrophytes in Brakel watercourse

Table 36 *Observations of density of macrophytes and algae mats in watercourse Brakel (2 April 2008).*

Distance from (m)	Density (%)	Observations
Weir A		
10		No view due to floating layer
15	80-90	Algae mat at bottom
20	80-90	Algae mat at bottom
25	85-95	Algae mat at bottom
30	85-95	Algae mat at bottom
35	80-90	Algae mat at bottom
40	80-90	Algae mat at bottom, some parts floating flab
45	80-90	Algae mat at bottom, some parts floating flab
50	80-90	Algae mat at bottom, some parts floating flab
55	80-90	Algae mat at bottom, some parts floating flab
60	80-90	Algae mat at bottom, some parts floating flab
65	80-90	Algae mat at bottom, some parts floating flab
70	80-90	Algae mat at bottom, some parts floating flab
75	80-90	Algae mat at bottom, some parts floating flab
80	80-90	Algae mat at bottom, some parts floating flab
85	80-90	Algae mat at bottom
90	80-90	Algae mat at bottom, some parts floating flab
95	80-90	Algae mat at bottom, some parts floating flab
100	70-80	Algae mat at bottom, some parts floating flab
105	70-80	Algae mat at bottom
110	70-80	Algae mat at bottom
115		Final 5 m no view on bottom
Culvert 1		
15	none	Floating layer, no view on bottom
20	none	No algae at bottom
75	none	Till end flab alongside some plants
Culvert 2		
5		Floating layer, no view on bottom
10		Floating layer, no view on bottom
15		Floating layer, no view on bottom
20		Floating layer, no view on bottom
25		No view on bottom, 25 - 55 m some floating flab
30		No view on bottom
35		No view on bottom
40		No view on bottom
45		No view on bottom
50		No view on bottom
55		No view on bottom
60		Development of plomp leaves
65		No view on bottom
70		Some places with flab along the side
75		No view on bottom
80		No view on bottom
85		No view on bottom

Distance from (m)	Density (%)	Observations
90		No view on bottom
95	<5%	Elodea
100	<5%	Elodea
105		Some leaves along the side
110	<5%	Elodea
115	<5%	Elodea
120	<5%	
120-125	<5%	Elodea
Till culvert 3		
0-5		Floating layer, no view on bottom
10		Floating layer, no view on bottom
15		Floating layer, no view on bottom
20	<5%	Elodea
25	<5%	Elodea
30		Plant along side
35	<5%	
40	<5%	Some leaves along the side
45	<5%	
50		Some stems at the bottom
55	<5%	Elodea
55-60	5-10%	Plant bottom

Annex 7 LC-MS/MS analysis of nicosulfuron and prosulfocarb

An Agilent 6410 LC/MS triple quadrupole equipped with a standard ESI source was used for LC-MS/MS analyses. The instrument operated in positive ion mode with a capillary voltage of 4000V. Nitrogen was used as the drying gas (10 L min^{-1}, 350°C) and as nebulising gas (40 psi).

For prosulfocarb, fragmentor energy was set to 99 V. Mass spectra were collected by monitoring the ion m/z 252 in the first quadrupole. For the MS/MS analysis, the product ions 128 and 91 were monitored in MRM mode. Nitrogen was used as collision gas with a collision voltage of 8 V.

For nicosulfuron, fragmentor energy was set to 80 V. Mass spectra were collected by monitoring the ion m/z 411 in the first quadrupole. For the MS/MS analysis, the product ions 213 and 182 were monitored in MRM mode. Nitrogen was used as collision gas with a collision voltage of 20 V.

Chromatographic conditions LC-MS/MS:

Column : Agilent Analytical Zorbax Eclips XDB-C18, 4.6 mm x 150 mm
Column temperature : 40 °C
Mobile phase : (A)Acetonitrile (0.1% formic acid)/(B)HPLC- water (0.1% formic acid)
Gradient elution : 0 min - 40% solution A
1.5 min - 40% solution A
2.5 min - 80% solution B
8.5 min - 80% solution B
9 min - 40% solution B
Degasser : Agilent 1200, type G1379B
Autosampler : Agilent 1200, type G1329A
Injection volume : 25 mL
Pump : Agilent 1200, type G1312A
Flow-rate : 1 mL min^{-1}.

Annex 8 List of ASCII files with data

Some basic data collected in the study are reported in text files. The data and files are:

1. Water depth as a function of time at measurement points MP1, MP2 and MP3 (Brakel_h.dat)
2. Discharge as a function of time at weirs A, B, C, D and E (Brakel_Q.dat)
3. Water balance of the system of watercourses as a function of time (Brakel_watbal.dat)

Annex 9 Water levels at MP2 and MP3

The water depth measured at MP2 and MP3 in the system of watercourses from 1 to 7 April 2008 is given in Figure 26.

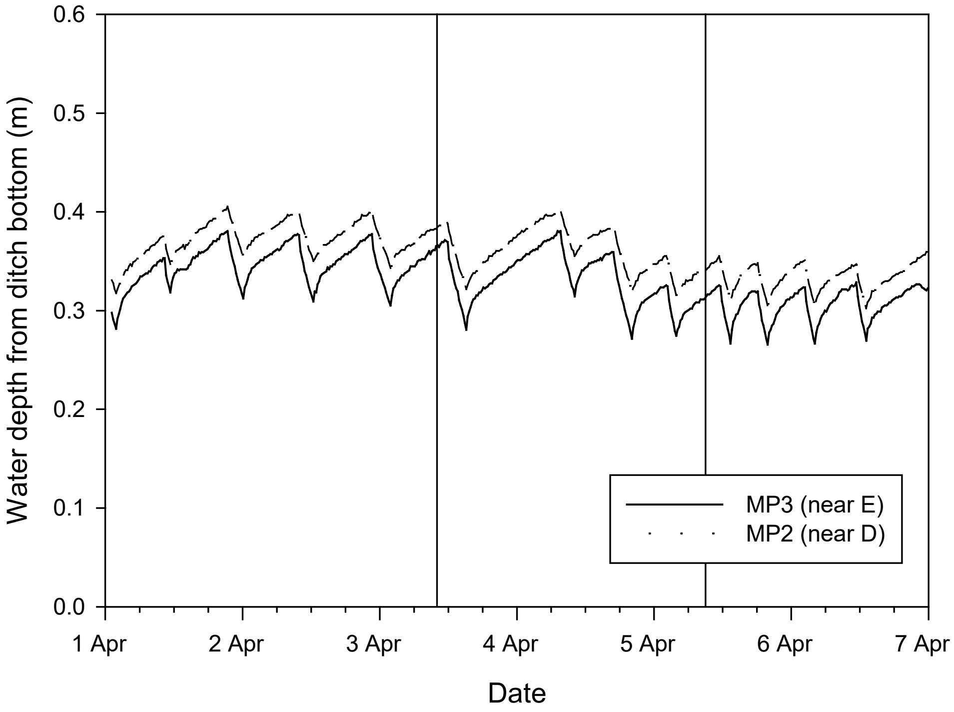
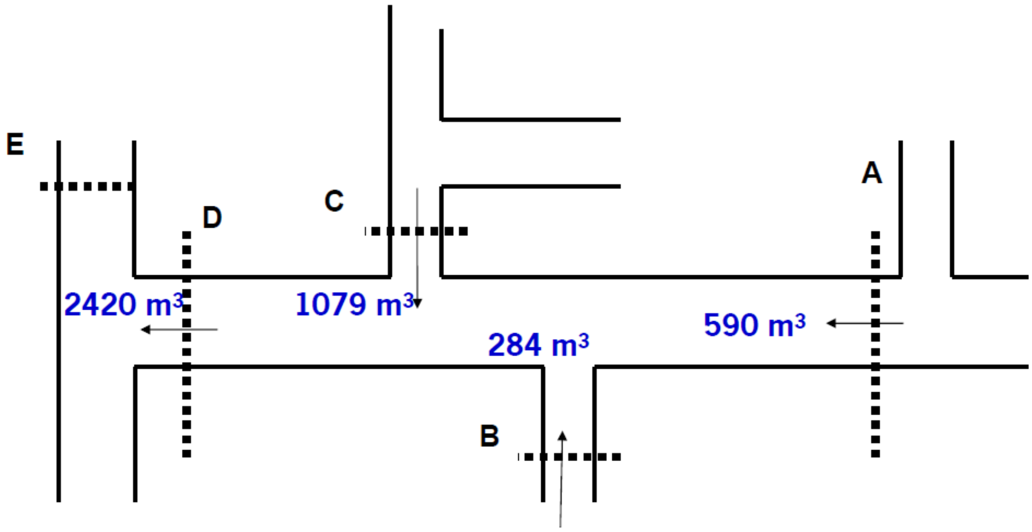


Figure 26 *Water depth at MP2 (upstream from weir D) and at MP3 (downstream from weir E) from 1 April to 7 April 2008.*

Water balance 3 April 10:00 to 5 April 24:00



Water balance: -D + A + B + C – 25 (volume change) = - 492 m^3.

The difference in volume on 3 April and 5 April is 25 m^3, based on measured water depths. The additional 492 m^3 can be attributed to seepage water entering the watercourse during this period. In this period, total rainfall was 7 mm (see Section 2.1), a minor impact on the entry of water.

Annex 10 Concentrations and mass in discharge proportional samples

The concentrations measured in discharge proportional samples are given in this annex for sampling points P1 and P2. The mass in the volume of water sampled is calculated as described in Section 5.5.

P1

		bromide	prosulfocarb	nicosulfuron		Discharge volume	bromide	prosulfocarb	nicosulfuron
datum		(µg/L)	(ug/L)	(µg/L)		(m3)	mg	mg	mg
3/04/08 12:11	NPB081	110.6	< LOD	0.0		1.99	220.1	0.0000	0.00
3/04/08 12:29	NPB082	92.1	< LOD	0.0		1.99	183.3	0.0000	0.00
3/04/08 12:44	NPB083	79.9	< LOD	0.0		1.99	159.1	0.0000	0.00
3/04/08 12:59	NPB084	106.9	< LOD	0.0		1.99	212.7	0.0000	0.00
3/04/08 13:13	NPB085	82.3	< LOD	0.0		1.99	163.8	0.0000	0.00
3/04/08 13:26	NPB086	87.4	< LOD	0.0		1.99	173.9	0.0000	0.00
3/04/08 13:38	NPB087	84.0	< LOD	0.0		1.99	167.1	0.0000	0.00
3/04/08 13:50	NPB088	161.7	< LOD	0.0		1.99	321.8	0.0000	0.00
3/04/08 14:02	NPB089	277.8	< LOD	0.0		1.99	552.9	0.0000	0.00
3/04/08 14:14	NPB090	745.3	< LOD	1.3		1.99	1483.1	0.0000	2.54
3/04/08 14:25	NPB091	1114.3	< LOD	2.9		1.99	2217.5	0.0000	5.72
3/04/08 14:36	NPB092	1668.6	0.067	7.5		1.99	3320.6	0.1330	14.87
3/04/08 14:46	NPB093	2280.8	0.105	13.2		1.99	4538.8	0.2081	26.27
3/04/08 14:56	NPB094	3150.3	0.151	18.7		1.99	6269.1	0.3007	37.15
3/04/08 15:06	NPB095	3909.0	0.251	31.4		1.99	7778.8	0.4999	62.56
3/04/08 15:16	NPB096	4722.9	0.288	38.9		1.99	9398.5	0.5725	77.37
3/04/08 15:25	NPB097	5280.1	0.358	44.3		1.99	10507.4	0.7118	88.18
3/04/08 15:35	NPB098	5369.0	0.373	52.0		1.99	10684.4	0.7425	103.46
3/04/08 15:44	NPB099	5605.3	0.406	54.6		1.99	11154.5	0.8088	108.63
3/04/08 15:53	NPB100	6289.8	0.438	59.8		1.99	12516.7	0.8724	119.07
3/04/08 16:03	NPB101	6224.8	0.486	67.9		1.99	12387.4	0.9665	135.14
3/04/08 16:12	NPB102	6441.5	0.511	73.3		1.99	12818.6	1.0162	145.78
3/04/08 16:20	NPB103	6582.9	0.538	72.6		1.99	13100.0	1.0716	144.40
3/04/08 16:35	NPB104	6633.1	0.568	79.8		1.99	13199.9	1.1304	158.83
	interpolated	6609.1	0.582	89.4		6.7	44281.3	3.8983	598.97
3/04/08 17:06	NPB133	6585.2	0.596	99.0		2.01	13236.3	1.1972	198.96
3/04/08 17:16	NPB134	6290.6	0.564	99.3		2.01	12644.1	1.1337	199.51
3/04/08 17:25	NPB135	6085.5	0.557	99.8		2.01	12231.8	1.1190	200.55
3/04/08 17:34	NPB136	5789.4	0.551	98.0		2.01	11636.6	1.1079	197.05
3/04/08 17:44	NPB137	5427.7	0.533	95.7		2.01	10909.8	1.0705	192.33
3/04/08 17:53	NPB138	4548.4	0.509	93.9		2.01	9142.3	1.0237	188.83
3/04/08 18:03	NPB139	4730.3	0.522	92.5		2.01	9507.9	1.0485	185.86
3/04/08 18:12	NPB140	4083.1	0.483	87.7		2.01	8207.1	0.9713	176.29
3/04/08 18:22	NPB141	4178.4	0.471	85.4		2.01	8398.6	0.9471	171.56
3/04/08 18:32	NPB142	3737.2	0.447	80.1		2.01	7511.8	0.8992	161.04
3/04/08 18:41	NPB143	3335.7	0.405	69.6		2.01	6704.8	0.8139	139.85
3/04/08 18:51	NPB144	3098.2	0.417	68.5		2.01	6227.4	0.8389	137.66
3/04/08 19:01	NPB145	3014.3	0.391	67.9		2.01	6058.8	0.7850	136.48
3/04/08 19:11	NPB146	2668.6	0.414	60.3		2.01	5364.0	0.8320	121.16
3/04/08 19:21	NPB147	2584.8	0.366	59.6		2.01	5195.5	0.7354	119.79
3/04/08 19:31	NPB148	2508.3	0.362	58.4		2.01	5041.8	0.7276	117.47
3/04/08 19:41	NPB149	2178.2	0.350	53.1		2.01	4378.1	0.7027	106.68
3/04/08 19:51	NPB150	1648.4	0.311	46.8		2.01	3313.2	0.6250	94.17
3/04/08 20:02	NPB151	1647.5	0.301	43.4		2.01	3311.4	0.6049	87.31
3/04/08 20:12	NPB152	1537.0	0.271	40.9		2.01	3089.3	0.5445	82.22
3/04/08 20:23	NPB153	1373.6	0.266	36.9		2.01	2761.0	0.5354	74.18
3/04/08 20:34	NPB154	1273.6	0.267	34.5		2.01	2560.0	0.5365	69.34
3/04/08 20:45	NPB155	1171.0	0.233	31.8		2.01	2353.7	0.4677	63.87
3/04/08 20:56	NPB156	976.9	0.225	26.7		2.01	1963.6	0.4523	53.58
	interpolated	856.4	0.200	23.1		6.4	5481.0	1.2774	148.02
3/04/08 21:57	NPB181	735.9	0.174	19.6		4.81	3539.6	0.8376	94.27
3/04/08 22:32	NPB182	628.3	0.121	15.9		4.81	3022.2	0.5843	76.61
3/04/08 23:03	NPB183	508.5	0.133	12.9		4.81	2445.9	0.6412	61.94
3/04/08 23:36	NPB184	443.0	0.130	11.3		4.81	2131.1	0.6229	54.15
4/04/08 0:10	NPB185	405.6	0.104	9.6		4.81	1950.8	0.4985	45.96
4/04/08 0:45	NPB186	370.7	0.089	7.7		4.81	1783.1	0.4266	37.01
4/04/08 1:22	NPB187	302.2	0.099	6.6		4.81	1453.6	0.4747	31.61
4/04/08 2:00	NPB188	277.8	0.074	5.3		4.81	1336.1	0.3563	25.68
4/04/08 2:41	NPB189	222.9	0.058	4.6		4.81	1071.9	0.2794	22.11
4/04/08 3:22	NPB190	215.6	0.060	4.3		4.81	1037.2	0.2903	20.80
4/04/08 4:05	NPB191	235.8	0.052	3.5		4.81	1134.1	0.2491	16.79
4/04/08 4:49	NPB192	215.4	< LOD	3.1		4.81	1036.3	0.0000	14.98
4/04/08 5:36	NPB193	207.1	< LOD	2.8		4.81	996.2	0.0000	13.61
4/04/08 6:23	NPB194	193.2	< LOD	2.4		4.81	929.4	0.0000	11.49
4/04/08 7:12	NPB195	185.1	< LOD	2.3		4.81	890.5	0.0000	11.26
4/04/08 8:00	NPB196	179.2	< LOD	2.1		4.81	861.8	0.0000	10.10
4/04/08 8:44	NPB197	172.7	< LOD	1.9		4.81	830.7	0.0000	8.97
4/04/08 9:22	NPB198	177.3	< LOD	1.6		4.81	852.9	0.0000	7.54
4/04/08 9:55	NPB199	167.8	< LOD	1.4		4.81	806.9	0.0000	6.84
4/04/08 10:25	NPB200	154.8	< LOD	1.1		4.81	744.8	0.0000	5.37
4/04/08 10:54	NPB201	156.4	< LOD	0.9		4.81	752.0	0.0000	4.25
4/04/08 11:24	NPB202	138.7	< LOD	0.8		4.81	667.3	0.0000	3.90
4/04/08 11:54	NPB203	135.8	< LOD	0.8		4.81	653.4	0.0000	3.64
4/04/08 12:30	NPB204	106.8	< LOD	0.7		4.81	513.6	0.0000	3.32

P1 (continued)

		bromide	prosulfocarb	nicosulfuron		Discharge volume	bromide	prosulfocarb	nicosulfuron
Date and time		(µg/L)	(ug/L)	(µg/L)		(m3)	mg	mg	mg
	interpolated	113.4	0.010	0.7		5.4	612.1	0.0549	3.52
4/04/08 14:20	NPB298	119.9	0.010	0.6		8.08	969.1	0.0822	4.95
4/04/08 15:54	NPB299	122.3	< LOD	0.6		8.08	988.4	0.0000	4.51
4/04/08 17:08	NPB300	116.1	< LOD	0.5		8.08	937.9	0.0000	4.34
4/04/08 18:09	NPB301	121.3	< LOD	0.5		8.08	980.3	0.0000	3.80
4/04/08 18:59	NPB302	110.7	0.0	0.5		8.08	894.3	0.0317	3.79
4/04/08 19:44	NPB303	114.7	< LOD	0.4		8.08	927.0	0.0000	3.23
4/04/08 20:25	NPB304	100.9	0.005	0.3		8.08	815.0	0.0412	2.61
4/04/08 21:04	NPB305	113.2	< LOD	0.3		8.08	914.7	0.0000	2.27
4/04/08 21:42	NPB306	114.3	0.003	0.2		8.08	923.4	0.0254	1.80
4/04/08 22:20	NPB307	114.2	< LOD	0.2		8.08	922.4	0.0000	1.89
4/04/08 23:00	NPB308	106.2	< LOD	0.2		8.08	858.3	0.0000	1.47
4/04/08 23:40	NPB309	100.2	< LOD	0.2		8.08	809.5	0.0000	1.44
5/04/08 0:23	NPB310	89.8	0.0022	0.2		8.08	725.5	0.0175	1.29
5/04/08 1:06	NPB311	104.7	0.0022	0.1		8.08	846.2	0.0175	1.13
5/04/08 1:53	NPB312	110.4	0.0022	0.1		8.08	891.7	0.0175	1.02
5/04/08 2:41	NPB313	96.1	0.0022	< LOD		8.08	776.3	0.0175	0.00
5/04/08 3:29	NPB314	139.3	0.0019	< LOD		8.08	1125.2	0.0151	0.00
5/04/08 4:14	NPB315	99.6	0.0019	< LOD		8.08	805.1	0.0151	0.00
5/04/08 4:57	NPB316	90.6	0.0019	< LOD		8.08	732.2	0.0151	0.00
5/04/08 5:39	NPB317	97.1	0.0019	< LOD		8.08	784.6	0.0151	0.00
5/04/08 6:22	NPB318	99.5	0.0017	< LOD		8.08	804.2	0.0134	0.00
5/04/08 7:06	NPB319	100.1	0.0017	< LOD		8.08	808.9	0.0134	0.00
5/04/08 7:52	NPB320	105.0	0.0017	< LOD		8.08	848.3	0.0134	0.00
5/04/08 8:14	NPB321	96.4	0.0017	< LOD		8.08	778.9	0.0134	0.00
	interpolated	103.9	0.0014	-		29.3	3045.5	0.0425	0.00
5/04/08 12:07	NPB370	111.5	0.0012	< LOD		8.01	893.1	0.0099	1.00
5/04/08 12:57	NPB371	109.9	0.0012	NA		8.01	880.6	0.0000	0.00
5/04/08 13:42	NPB373	111.1	0.0012	NA		8.01	890.3	0.0000	0.00
5/04/08 14:24	NPB374	114.4	0.0012	NA		8.01	916.4	0.0000	0.00
5/04/08 15:08	NPB375	106.3	0.0016	< LOD		8.01	851.5	0.0129	0.00
5/04/08 15:52	NPB376	111.4	0.0016	NA		8.01	892.3	0.0000	0.00
5/04/08 16:35	NPB377	114.5	0.0016	NA		8.01	917.2	0.0000	0.00
5/04/08 17:19	NPB378	107.7	0.0016	NA		8.01	863.0	0.0000	0.00
5/04/08 18:03	NPB379	109.3	0.0010	NA		8.01	875.4	0.0083	0.00
5/04/08 18:50	NPB380	106.0	0.0010	NA		8.01	848.7	0.0000	0.00
5/04/08 19:35	NPB381	100.7	0.0010	NA		8.01	806.4	0.0000	0.00
5/04/08 20:17	NPB382	102.6	0.0010	NA		8.01	822.1	0.0000	0.00
5/04/08 20:58	NPB383	100.6	0.0011	NA		8.01	806.0	0.0087	0.00
5/04/08 21:37	NPB384	98.5	0.0011	NA		8.01	789.3	0.0000	0.00
5/04/08 22:18	NPB385	97.2	0.0011	NA		8.01	778.4	0.0000	0.00
5/04/08 23:00	NPB386	95.4	0.0011	< LOD		8.01	763.9	0.0000	0.00
5/04/08 23:46	NPB387	105.96	0.0011	NA		8.01	848.7	0.0087	0.00
6/04/08 0:46	NPB388	100.68	0.0011	NA		8.01	806.4	0.0000	0.00
6/04/08 2:14	NPB389	102.63	0.0011	NA		8.01	822.1	0.0000	0.00
6/04/08 3:52	NPB390	100.63	0.0011	NA		8.01	806.0	0.0000	0.00
6/04/08 5:17	NPB391	98.54	0.0013	NA		8.01	789.3	0.0107	0.00
6/04/08 6:56	NPB392	97.18	0.0013	NA		8.01	778.4	0.0000	0.00
6/04/08 10:39	NPB393	95.37	0.0013	NA		8.01	763.9	0.0000	0.00
6/04/08 13:22	NPB394	94.70	0.0013	NA		8.01	758.6	0.0000	0.00
	Sum					645.4	420976	39.7	5889.0

values < LOD set to zero
interpolated for period of replace sample bottles: discharge in this period from discharge measurements and average of previous and of next sample

P2

Date and time		bromide (µg/L)	prosulfocarb (ug/L)	nicosulfuron (µg/L)		Discharge volume (m3)	bromide mg	prosulfocarb mg	nicosulfuron mg
3/04/08 15:21	NPB109	96.4	< LOD	< LOD		9.74	939	0.0000	0.00
3/04/08 15:33	NPB110	88.9	< LOD	< LOD		9.74	866	0.0000	0.00
3/04/08 15:47	NPB111	92.1	< LOD	< LOD		9.74	897	0.0000	0.00
3/04/08 16:03	NPB112	88.3	< LOD	< LOD		9.74	860	0.0000	0.00
3/04/08 16:21	NPB113	94.2	< LOD	0.2		9.74	918	0.0000	1.80
3/04/08 16:41	NPB114	87.8	< LOD	0.1		9.74	855	0.0000	1.43
3/04/08 17:02	NPB115	100.1	< LOD	< LOD		9.74	975	0.0000	0.00
3/04/08 17:25	NPB116	98.8	< LOD	< LOD		9.74	963	0.0000	0.00
3/04/08 17:49	NPB117	90.6	< LOD	< LOD		9.74	882	0.0000	0.00
3/04/08 18:13	NPB118	94.8	< LOD	< LOD		9.74	924	0.0000	0.00
3/04/08 18:37	NPB119	87.3	< LOD	< LOD		9.74	850	0.0000	0.00
3/04/08 19:00	NPB120	80.2	< LOD	< LOD		9.74	781	0.0000	0.00
3/04/08 19:22	NPB121	100.6	< LOD	< LOD		9.74	980	0.0000	0.00
3/04/08 19:45	NPB122	99.0	< LOD	< LOD		9.74	964	0.0000	0.00
3/04/08 20:08	NPB123	100.7	< LOD	< LOD		9.74	981	0.0000	0.00
3/04/08 20:32	NPB124	100.6	< LOD	< LOD		9.74	980	0.0000	0.00
3/04/08 20:56	NPB125	94.7	0.0003	< LOD		9.74	922	0.0031	0.00
3/04/08 21:20	NPB126	75.6	< LOD	< LOD		9.74	736	0.0000	0.00
3/04/08 21:43	NPB127	98.6	< LOD	< LOD		9.74	960	0.0000	0.00
3/04/08 22:05	NPB128	100.9	< LOD	< LOD		9.74	983	0.0000	0.00
3/04/08 22:27	NPB129	102.3	0.0009	< LOD		9.74	996	0.0083	0.00
3/04/08 22:50	NPB130	107.4	< LOD	< LOD		9.74	1046	0.0000	0.00
3/04/08 23:12	NPB131	118.6	< LOD	< LOD		9.74	1155	0.0000	0.00
3/04/08 23:31	NPB132	114.0	0.0013	< LOD		9.74	1111	0.0127	0.00
	interpolate	142.1	0.0056	0.6		6	853	0.0339	0.00
4/04/08 0:14	NPB157	170.1	0.0100	0.6		11.65	1982	0.1164	7.35
4/04/08 0:43	NPB158	269.8	< LOD	1.3		11.65	3144	0.0000	14.85
4/04/08 1:12	NPB159	373.1	< LOD	2.3		11.65	4346	0.0000	27.36
4/04/08 1:42	NPB160	482.5	< LOD	3.4		11.65	5622	0.0000	39.93
4/04/08 2:11	NPB161	859.4	0.0703	7.5		11.65	10012	0.8185	87.68
4/04/08 2:41	NPB162	679.0	0.07	5.0		11.65	7910	0.0000	58.31
4/04/08 3:11	NPB163	1085.4	0.0780	10.5		11.65	12645	0.9087	122.10
4/04/08 3:42	NPB164	1333.7	0.1025	13.8		11.65	15538	1.1937	161.32
4/04/08 4:13	NPB165	1547.9	0.1131	17.3		11.65	18033	1.3174	201.95
4/04/08 4:44	NPB166	1759.2	0.1290	20.7		11.65	20495	1.5028	241.63
4/04/08 5:14	NPB167	1781.3	0.1409	22.3		11.65	20752	1.6419	260.07
4/04/08 5:45	NPB168	1872.5	0.14	21.9		11.65	21814	0.0000	254.75
4/04/08 6:15	NPB169	1667.9	0.1315	22.5		11.65	19432	1.5320	262.40
4/04/08 6:46	NPB170	1590.5	0.1350	21.7		11.65	18530	1.5723	252.38
4/04/08 7:17	NPB171	1510.8	0.1259	20.8		11.65	17600	1.4667	242.77
4/04/08 7:39	NPB172	1443.0	0.1290	19.9		11.65	16811	1.5024	232.27
4/04/08 7:53	NPB173	1327.3	0.1152	18.8		11.65	15463	1.3415	219.56
4/04/08 8:06	NPB174	1275.0	0.1275	16.5		11.65	14854	1.4849	192.24
4/04/08 8:18	NPB175	1179.5	0.1175	17.1		11.65	13741	1.3684	199.67
4/04/08 8:30	NPB176	1122.0	0.1082	16.8		11.65	13072	1.2609	195.86
4/04/08 8:41	NPB177	1031.7	0.1043	15.9		11.65	12020	1.2151	185.68
4/04/08 8:52	NPB178	975.3	0.1077	15.0		11.65	11362	1.2543	174.76
4/04/08 9:03	NPB179	915.3	0.0895	14.4		11.65	10663	1.0426	167.19
4/04/08 9:15	NPB180	865.4	0.1003	13.3		11.65	10082	1.1685	154.46
	interpolate	783.0	0.1	12.0		38.8	30381	3.2714	465.68
4/04/08 10:13	NPB205	700.6	0.0683	10.7		9.47	6635	0.6471	101.76
4/04/08 10:25	NPB206	664.0	0.0654	10.1		9.47	6288	0.6191	95.97
4/04/08 10:36	NPB207	633.7	0.0673	9.9		9.47	6002	0.6376	93.94
4/04/08 10:47	NPB208	612.9	0.0836	9.5		9.47	5804	0.7914	90.28
4/04/08 10:59	NPB209	535.6	0.0683	9.2		9.47	5072	0.6471	87.05
4/04/08 11:11	NPB210	568.4	0.0430	11.0		9.47	5383	0.4072	103.75
4/04/08 11:25	NPB211	547.6	0.0624	9.0		9.47	5186	0.5911	85.32
4/04/08 11:39	NPB212	523.4	0.0601	8.7		9.47	4956	0.5693	82.60
4/04/08 11:53	NPB213	473.7	0.0300	7.6		9.47	4486	0.2841	71.89
4/04/08 12:07	NPB214	445.3	0.0358	7.5		9.47	4217	0.3391	70.65
4/04/08 12:22	NPB215	456.6	0.0300	6.9		9.47	4324	0.2841	65.51
4/04/08 12:38	NPB216	407.7	0.0300	6.7		9.47	3861	0.2841	63.18
4/04/08 12:54	NPB217	410.3	0.0306	6.2		9.47	3886	0.2896	58.46
4/04/08 13:10	NPB218	383.2	0.0654	5.8		9.47	3629	0.6191	54.74

P2

		bromide	prosulfocarb	nicosulfuron		Discharge volume	bromide	prosulfocarb	nicosulfuron
Date and time		(µg/L)	(ug/L)	(µg/L)		(m3)	mg	mg	mg
4/04/08 13:26	NPB219	360.37	0.0291	5.5		9.47	3413	0.2756	51.86
	interpolate	349.0	0.0	5.4		36.8	12842	0.8909	198.83
4/04/08 15:09	NPB322	337.6	0.0193	5.3		31.94	10782	0.6170	170.23
4/04/08 16:18	NPB323	298.2	0.0193	4.4		31.94	9525	0.0000	140.45
4/04/08 17:12	NPB324	271.0	0.0193	3.5		31.94	8655	0.0000	113.38
4/04/08 17:49	NPB325	251.3	0.0193	2.9		31.94	8028	0.0000	92.51
4/04/08 18:18	NPB326	228.76	0.0125	2.4		31.94	7307	0.3993	75.39
4/04/08 18:46	NPB327	206.2	0.0094	1.7		31.94	6585	0.3007	52.77
4/04/08 19:12	NPB328	180.9	0.0094	1.4		31.94	5777	0.0000	45.17
4/04/08 19:38	NPB329	166.9	0.0094	1.1		31.94	5330	0.0000	36.33
4/04/08 20:02	NPB330	159.3	0.0066	0.9		31.94	5087	0.2111	29.21
4/04/08 20:29	NPB331	161.8	0.0066	0.8		31.94	5167	0.0000	25.94
4/04/08 21:03	NPB332	168.0	0.0066	0.7		31.94	5365	0.0000	21.98
4/04/08 21:42	NPB333	143.0	0.0066	0.6		31.94	4569	0.0000	20.05
4/04/08 22:25	NPB334	137.2	0.0052	0.5		31.94	4383	0.1655	16.37
4/04/08 23:11	NPB335	133.4	0.0052	0.5		31.94	4261	0.0000	14.92
4/04/08 23:59	NPB336	141.6	0.0052	0.5		31.94	4521	0.0000	14.62
5/04/08 0:49	NPB337	128.1	0.0052	0.4		31.94	4090	0.0000	13.23
5/04/08 1:43	NPB338	130.02	0.0044	0.4		31.94	4153	0.1405	12.14
5/04/08 2:29	NPB339	132.0	0.0045	0.3		31.94	4215	0.1433	10.91
5/04/08 3:03	NPB340	144.7	0.0045	0.3		31.94	4621	0.0000	10.50
5/04/08 3:31	NPB341	145.4	0.0045	0.3		31.94	4644	0.0000	8.25
5/04/08 3:58	NPB342	149.6	0.0029	0.2		31.94	4777	0.0927	6.74
5/04/08 4:29	NPB343	149.5	0.0029	0.2		31.94	4774	0.0000	5.85
5/04/08 5:06	NPB344	128.7	0.0029	0.2		31.94	4112	0.0000	4.96
5/04/08 5:34	NPB345	127.6	0.0029	0.1		31.94	4075	0.0000	4.47
	interpolate	132.4	0.0023	0.1		171	22633	0.3879	23.91
5/04/08 11:31	NPB346	137.1	0.0016	< LOD		31.68	4345	0.0518	0.00
5/04/08 12:20	NPB347	130.4	0.0016	NA		31.68	4130	0.0000	0.00
5/04/08 12:51	NPB348	131.8	0.0016	NA		31.68	4175	0.0000	0.00
5/04/08 13:19	NPB349	133.9	0.0016	NA		31.68	4243	0.0000	0.00
5/04/08 13:50	NPB350	119.9	0.0015	< LOD		31.68	3798	0.0472	0.00
5/04/08 14:29	NPB351	122.2	0.0015	NA		31.68	3872	0.0000	0.00
5/04/08 15:16	NPB352	124.5	0.0015	NA		31.68	3945	0.0000	0.00
5/04/08 16:14	NPB353	127.5	0.0015	NA		31.68	4039	0.0000	0.00
5/04/08 17:24	NPB354	126.4	0.0015	NA		31.68	4004	0.0488	0.00
5/04/08 18:26	NPB355	124.8	0.0015	NA		31.68	3954	0.0000	0.00
5/04/08 19:08	NPB356	119.3	0.0015	NA		31.68	3778	0.0000	0.00
5/04/08 19:40	NPB357	122.0	0.0015	NA		31.68	3864	0.0000	0.00
5/04/08 20:13	NPB358	132.4	0.0011	NA		31.68	4195	0.0342	0.00
5/04/08 20:54	NPB359	134.6	0.0011	NA		31.68	4266	0.0000	0.00
5/04/08 21:47	NPB360	135.2	0.0011	NA		31.68	4282	0.0000	0.00
5/04/08 22:51	NPB361	145.2	0.0011	NA		31.68	4599	0.0000	0.00
6/04/08 0:03	NPB362	135.0	0.0013	< LOD		31.68	4276	0.0402	0.00
6/04/08 1:22	NPB363	119.25	0.0013	NA		31.68	3778	0.0000	0.00
6/04/08 2:34	NPB364	121.98	0.0013	NA		31.68	3864	0.0000	0.00
6/04/08 3:22	NPB365	132.42	0.0013	NA		31.68	4195	0.0000	0.00
6/04/08 3:59	NPB366	134.65	0.0013	NA		31.68	4266	0.0406	0.00
6/04/08 4:36	NPB367	135.16	NA	NA		31.68	4282	0.0000	0.00
6/04/08 5:25	NPB368	145.17	NA	NA		31.68	4599	0.0000	0.00
6/04/08 6:00	NPB369	134.96	NA	NA		31.68	4276	0.0000	0.00
						2434.9	712124	37.9	6772

values < LOD set to zero
values NA interpolated and marked yellow
values prosulfocarb < LOQ set to 0.5*LOQ = 0.03, marked in blue

interpolated for period of replace sample bottles: discharge in this period from discharge measurements and average of previous and of next sample

Annex 11 Concentration of bromide, nicosulfuron and of prosulfocarb in cross section of water layer at MP1, MP2 and MP3

Table 37 *Concentration of bromide, nicosulfuron and of prosulfocarb in spot samples at measurement points MP1, MP2 and MP3.*

MP1	plaats	datum	tijdstip			
				bromide	prosulfocarb	nicosulfuron
				(µg/L)	(ug/L)	(µg/L)
NPB001	noord diep 6	03/04/2008	10:30	97.88	< LOD	< LOD
NPB002	noord 5		10:30	90.8	< LOD	< LOD
NPB003	midden 4		10:30	90.4	< LOD	< LOD
NPB004	diep midden 3		10:30	90.7	< LOD	< LOD
NPB005	zuid 2		10:30	89.8	< LOD	< LOD
NPB006	zuid diep 1		10:30	67.3	< LOD	< LOD
NPB007	5m 1	03/04/2008	13:10	9185.5	0.86	112.0
NPB008	2		13:10	9137.2	0.93	120.4
NPB009	3		13:10	9181.7	0.92	112.3
NPB010	4		13:10	9285.9	0.82	100.9
NPB011	5		13:10	8648.9	0.79	99.0
NPB012	6		13:10	9575.8	0.68	79.9
NPB013	25m 1	03/04/2008	13:15	8352.1	1.22	165.6
NPB014	2		13:15	8381.7	1.23	173.8
NPB015	3		13:15	8468.4	0.76	97.3
NPB016	4		13:15	8155.4	0.73	92.2
NPB017	5		13:15	7965.0	-	-
NPB018	6		13:15	7808.2	-	-
NPB019	45m 1	03/04/2008	13:20	420.9	0.22	30.4
NPB020	2		13:20	772.1	0.32	40.8
NPB021	3		13:20	595.2	0.26	41.3
NPB022	4		13:20	1010.3	0.33	51.6
NPB023	5		13:20	1047.5	0.43	72.9
NPB024	6		13:20	810.9	0.27	50.5
NPB025	stuw drijflaag I	03/04/2008	13:40	102.2	9.51	220.5
NPB026	stuw drijflaag II		13:40	88.7	9.75	757.2
NPB039	5m 1	03/04/2008	15:35	2582.5	0.46	72.9
NPB040	2		15:35	2405.9	0.49	76.9
NPB041	3		15:35	2157.7	0.47	65.2
NPB042	4		15:35	2113.5	0.44	64.3
NPB043	5		15:35	2344.8	0.46	65.9
NPB044	6		15:35	2121.3	0.45	60.8
NPB045	25m 1	03/04/2008	15:55	439.0	0.26	25.7
NPB046	2		15:55	450.9	0.26	27.6
NPB047	3		15:55	389.6	0.26	23.6
NPB048	4		15:55	482.0	0.25	23.6
NPB049	5		15:55	489.8	0.26	24.8
NPB050	6		15:55	506.9	0.23	25.1
NPB051	45m 1	03/04/2008	16:05	119.7	0.09	4.9
NPB052	2		16:05	119.1	0.08	6.7
NPB053	3		16:05	101.8	0.09	4.8
NPB054	4		16:05	91.4	0.07	4.4
NPB055	5		16:05	148.8	0.13	11.3
NPB056	6		16:05	126.2	0.12	7.9
NPB071	5m 1	03/04/2008	21:30	138.47	< LOD	1.6
NPB072	2		21:30	140.21	< LOD	1.5
NPB073	3		21:30	152.84	< LOD	1.8
NPB074	4		21:30	140.00	< LOD	1.5
NPB075	5		21:30	149.02	< LOD	1.9
NPB076	6		21:30	151.26	< LOD	2.0
NPB261	zuid 1	04/04/2008	10:45	*91.47*	< LOD	0.4
NPB262	2		10:45	*95.08*	< LOD	0.3
NPB263	3		10:45	*91.93*	< LOD	0.3
NPB264	4		10:45	*93.98*	< LOD	0.3
NPB265	5		10:45	-	< LOD	0.3
NPB266	6		10:45	-	< LOD	0.3

MP2	plaats	datum	tijdstip			
				bromide	prosulfocarb	nicosulfuron
				(µg/L)	(ug/L)	(µg/L)
NPB027	1	03/04/2008	15:10	97.4	< LOD	< LOD
NPB028	2		15:10	98.1	< LOD	< LOD
NPB029	3		15:10	98.8	< LOD	0.3
NPB030	4		15:10	96.4	< LOD	0.1
NPB031	5		15:10	94.4	< LOD	< LOD
NPB032	6		15:10	96.7	< LOD	< LOD
NPB057	1	03/04/2008	19:05	90.7	0.077	< LOD
NPB058	2		19:05	88.9	0.060	< LOD
NPB059	3		19:05	90.9	< LOD	< LOD
NPB060	4		19:05	82.4	< LOD	< LOD
NPB061	5		19:05	88.3	< LOD	< LOD
NPB062	6		19:05	87.1	< LOD	< LOD
NPB077	1	04/04/2008	00:25	326.12	< LOD	1.8
NPB078	2		00:25	339.04	< LOD	1.9
NPB079	3		00:25	402.09	< LOD	2.4
NPB080	4		00:25	387.11	< LOD	2.3
NPB229	5		00:25	299.17	< LOD	1.6
NPB230	6		00:25	302.75	< LOD	0.2
NPB237	1	04/04/2008	08:45	1107.24	< LOD	23.2
NPB238	2		08:45	1113.17	< LOD	23.1
NPB239	3		08:45	982.70	< LOQ	20.5
NPB240	4		08:45	1013.06	< LOD	20.7
NPB241	5		08:45	1045.81	0.093	22.0
NPB242	6		08:45	1072.11	< LOD	21.1
NPB255	zuid 1	04/04/2008	10:25	615.10	< LOD	11.7
NPB256	2		10:25	612.62	< LOQ	12.0
NPB257	3		10:25	552.85	< LOD	11.0
NPB258	4		10:25	548.12	< LOD	11.0
NPB259	5		10:25	590.87	< LOQ	11.1
NPB260	6		10:25	582.99	< LOQ	12.0
NPB269	1	04/04/2008	12:45	397.58	< LOQ	7.1
NPB270	2		12:45	395.33	< LOQ	7.1
NPB271	3		12:45	392.36	< LOQ	7.2
NPB272	4		12:45	396.14	< LOQ	7.4
NPB273	5		12:45	400.47	< LOQ	7.1
NPB274	6		12:45	401.07	< LOQ	7.3
NPB281	1	04/04/2008	17:25	-	< LOD	2.9
NPB282	2		17:25	240.23	< LOD	2.8
NPB283	3		17:25	182.04	< LOD	1.0
NPB284	4		17:25	177.38	< LOD	1.0
NPB285	5		17:25	153.85	< LOD	0.7
NPB286	6		17:25	174.46	< LOD	0.8

MP3	plaats	datum	tijdstip			
				bromide	prosulfocarb	nicosulfuron
				(µg/L)	(ug/L)	(µg/L)
NPB033	1	03/04/2008	15:20	99.1	< LOD	< LOD
NPB034	2		15:20	97.9	< LOD	< LOD
NPB035	3		15:20	94.7	< LOD	< LOD
NPB036	4		15:20	87.0	< LOD	< LOD
NPB037	5		15:20	91.5	< LOD	< LOD
NPB038	6		15:20	98.4	< LOD	< LOD
NPB063	1	03/04/2008	19:25	83.2	< LOD	< LOD
NPB064	2		19:25	85.9	< LOD	< LOD
NPB065	3		19:25	85.9	< LOD	< LOD
NPB066	4		19:25	87.2	< LOD	< LOD
NPB067	5		19:25	85.6	< LOD	< LOD
NPB068	6		19:25	-	< LOD	< LOD
NPB231	1	04/04/2008	00:35	146.7	0.001	0.1
NPB232	2		00:35	136.5	< LOD	0.1
NPB233	3		00:35	131.9	< LOD	0.1
NPB234	4		00:35	126.8	< LOD	0.1
NPB235	5		00:35	131.6	< LOD	< LOD
NPB236	6		00:35	125.9	< LOD	< LOD
NPB243	1	04/04/2008	09:11	939.5	0.030	18.2
NPB244	2		09:11	977.9	< LOD	18.7
NPB245	3		09:11	499.4	< LOD	8.1
NPB246	4		09:11	621.9	< LOQ	10.7
NPB247	5		09:11	258.2	< LOD	2.1
NPB248	6		09:11	260.2	< LOD	2.2
NPB249	Oost 1	04/04/2008	10:20	581.5	< LOQ	10.5
NPB250	2		10:20	588.2	< LOQ	10.6
NPB251	3		10:20	224.3	< LOD	1.9
NPB252	4		10:20	197.3	< LOD	1.2
NPB253	5		10:20	188.8	< LOQ	1.0
NPB254	6		10:20	185.6	< LOD	0.9
NPB275	1	04/04/2008	13:10	279.6	< LOD	3.2
NPB276	2		13:10	271.4	< LOD	3.0
NPB277	3		13:10	191.9	< LOD	1.2
NPB278	4		13:10	191.8	< LOD	1.1
NPB279	5		13:10	186.4	< LOD	1.1
NPB280	6		13:10	-	< LOD	0.9
NPB287	1	04/04/2008	17:10	232.5	< LOD	2.8
NPB288	2		17:10	230.5	< LOD	2.8
NPB289	3		17:10	226.3	< LOD	2.5
NPB290	4		17:10	222.2	< LOD	2.6
NPB291	5		17:10	233.9	< LOD	2.8
NPB292	6		17:10	224.3	< LOD	2.8

Annex 12 Nicosulfuron and prosulfocarb content in sediment layers

Data used for determining nicosulfuron and for prosulfocarb the concentration in pore water and the content in sediment. Bromide was not determined in sediment.

Table 38 *Nicosulfuron and prosulfocarb content in sediment layers.*

																							PROSULFOCARB							NICOSULFURON					
Code	Layer depth	Centrifuge tube empty	Tube + wet sediment	Tube + wet sediment after sampling nicosulfuron poriewater	amount poriewater sampled	total Wet sediment	total wet sediment after sampling water (nicosulfuron)	Tube + wet sediment + acetonitril	Tube + dry sediment 105C	total dry sediment 105C	Loss on ignition sediment	Water in sediment	Acetonitril in system extracted	Volume acetonitril in system extraction	Density extract	10 mLl tube empty	10 mL tube + acetonitril extract	10 mL tube + acetonitril extract after evaporation	Amount extract before evaporation	Amount after evaporation	End volume extract calculated	End volume extract visueel	Concentration prosulfocarb LC-MS in porie water	Concentration prosulfocarb LC-MS extract	Net amount prosulfocarb gemeten in extract	Net amount prosulfocarb gemeten in water	Prosulfocarb sorbed per dry sediment	Prosulfocarb sorbed per organic matter	Prosulfocarb mass in layer	Dilution Nicosulfuron in extract	Concentration nicosulfuron LC-MS in sediment extract	Dilution nicosulfuron in water	LC-MS nicosulfuron in water	Concentration in pore water	Nicosulfuron mass in layer
		(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(%)	(g)	(g)	(mL)	(g/mL)	(g)	(g)	(ng/L)	(g)	(g)	(mL)	(mL)		(ng/L)	(ng)	(ng)	(ng/g)	(ng/g)	(ng/mL)	(x)	(ng/L)	(x)	(ng/L)	(ug/L)	(ug/L)
2-4-2009 P1 blank																																			
P09	0-1 cm	122.17				16.61	20.21	166.25	125.31	3.14	13.7	17.07	23.87	30.52	0.860	19.38	27.90	23.14	8.52	3.76	4.37	4.20	<LOD	42.98	0.9	-	0.3	2.0	0.06	-	2.30	-	<LOD	<LOD	<LOD
P010	1-2 cm	124.41				13.21	14.71	170.23	127.58	3.17	14.7	11.54	31.11	39.78	0.831	19.34	27.63	22.63	8.29	3.29	3.96	3.80	<LOD	54.07	1.1	-	0.3	2.3	0.08	-	0.00	-	<LOD	<LOD	<LOD
P011	2-3 cm	125.32				8.15	13.32	168.61	128.64	3.32	15.0	10.00	29.97	38.32	0.827	19.39	27.70	22.33	8.31	2.94	3.55	3.60	<LOD	98.52	1.7	-	0.5	3.4	0.14	-	14.21	-	<LOD	<LOD	<LOD
P012	0-1 cm	123.21				13.93	21.91	174.82	125.97	2.76	14.1	19.15	29.70	37.98	0.855	19.59	28.83	23.75	9.24	4.16	4.87	4.40	<LOD	49.02	1.1	-	0.4	2.9	0.08	-	0.00	-	<LOD	<LOD	<LOD
P013	1-2 cm	123.33				13.21	18.31	169.81	126.92	3.59	14.0	14.72	28.17	36.02	0.845	19.06	27.66	22.67	8.60	3.61	4.27	4.00	<LOD	52.24	1.0	-	0.3	2.1	0.08	-	0.00	-	<LOD	<LOD	<LOD
P014	2-3 cm	124.49				8.15	18.11	169.43	128.61	4.12	14.6	13.99	26.83	34.31	0.845	19.14	**lost**[1]	23.18	**8.45**	4.04	4.78	4.20	<LOD	90.93	1.8	-	0.4	3.1	0.15	-	25.41	-	<LOD	<LOD	<LOD
3-4-2009 P1 15h40																																			
P11	0-1 cm	122.15	138.38	136.69	1.69	16.23	14.54	189.1	125.11	2.96	13.5	11.58	52.41	67.02	0.814	19.58	27.66	23.69	8.08	4.11	5.05	5.00	145.77	257.74	10.4	1.7	3.0	21.9	0.77	10	841.62	20	985	19.7	26.5
P12	1-2 cm	121.42	137.29	135.84	1.45	15.87	14.42	186.78	125.63	4.21	13.6	10.21	50.94	65.14	0.812	19.19	27.04	22.68	7.85	3.49	4.30	4.30	<LOD	79.26	2.7	-	0.6	4.7	0.20	5	297.49	-	2119	2.1	4.2
P13	2-4 cm	126.58	151.86	150.28	1.58	25.28	23.70	197.72	133.28	6.70	13.8	17	47.44	60.66	0.830	19.45	28.01	23.51	8.56	4.06	4.89	4.80	<LOD	108.36	4.0	-	0.6	4.3	0.16	5	172.16	-	605	0.6	1.3
P14	0-1 cm	124.74	139.09	137.46	1.63	14.35	12.72	182.96	**lost**	2.74	**12.8**	10.67	45.5	58.18	0.816	-	19.33	22.2	**6.53**	-	-	3.85	126.34	225.14	7.6	1.3	2.3	17.9	0.57	10	1238.1	20	1352	27.0	32.9
P15	1-2 cm	125.40	141.78	140.14	1.64	16.38	14.74	183.14	129.41	4.01	13.8	10.73	43	54.99	0.818	19.10	27.20	23.1	8.10	4.02	4.92	4.90	<LOD	80.48	2.7	-	0.7	4.9	0.19	5	356.0	-	5125	5.1	5.3
P16	2-4 cm	125.82	155.21	153.75	1.46	29.39	27.93	198.52	135.17	9.35	11.7	18.58	44.77	57.25	0.835	-	27.88	24.1	**8.52**	-	-	5.50	<LOD	77.20	3.2	-	0.3	2.9	0.13	5	70.0	-	834	0.8	0.6
P17	0-1 cm	124.79	139.63	138.02	1.61	14.84	13.23	183.65	128.54	3.75	12.6	9.48	45.63	58.35	0.812	19.43	27.66	24.0	8.23	4.57	5.62	5.70	165.20	188.87	7.4	1.6	1.6	12.3	0.55	10	749.0	20	1107	22.1	23.3
P18	1-2 cm	120.88	137.87	136.57	1.3	16.99	15.69	182.76	126.98	6.10	11.7	9.59	46.19	59.07	0.812	19.44	27.78	23.2	8.34	3.77	4.64	4.70	<LOD	61.69	2.0	-	0.3	2.8	0.14	5	350.2	-	4702	4.7	4.9
P19	2-4 cm	122.50	153.91	152.7	1.21	31.41	30.20	198.77	134.98	12.48	10.7	17.72	46.07	58.91	0.832	18.96	27.52	22.9	8.56	3.96	4.76	4.70	<LOD	75.38	2.7	-	0.2	2.0	0.11	5	108.4	-	696	0.7	0.8
P110	0-1 cm	123.91	139.03	137.47	1.56	15.12	13.56	184.18	126.53	2.62	13.5	10.94	46.71	59.73	0.816	19.36	27.65	22.8	8.29	3.47	4.25	4.40	77.77	148.37	4.6	0.9	1.4	10.7	0.34	10	714.4	10	1259	12.6	17.2
P111	1-2 cm	124.61	145.5	143.92	1.58	20.89	19.31	180.03	130.81	6.20	12.7	13.11	36.11	46.18	0.830	19.32	27.78	23.2	8.46	3.90	4.70	4.60	<LOD	108.63	3.0	-	0.5	3.8	0.22	5	272.9	-	2207	2.2	3.2
P112	2-4 cm	123.33	151.39	150.28	1.11	28.06	26.95	195.12	131.28	7.95	13.6	19	44.84	57.34	0.836	19.36	27.74	24.4	8.38	5.05	6.04	6.05	<LOD	101.03	4.7	-	0.6	4.4	0.19	5	8.3	-	99	0.1	0.1
3-4-2009 P1 21h45																																			
P113	0-1 cm	123.36	137.56	136.07	1.49	14.20	12.71	179.65	125.86	2.50	13.7	10.21	43.58	55.73	0.816	19.36	27.68	23.3	8.32	3.90	4.78	4.90	34.62	88.68	2.9	0.4	1.0	7.4	0.21	5	234.9	10	170	1.7	2.9
P114	1-2 cm	122.04	137.66	136.12	1.54	15.62	14.08	183.61	125.58	3.54	13.9	10.54	47.49	60.73	0.814	19.08	27.34	22.9	8.26	3.86	4.74	4.85	<LOD	59.54	2.1	-	0.6	4.2	0.15	5	52.8	-	716	0.7	0.8
P115	2-4 cm	124.66	151.66	150.37	1.29	27.00	25.71	196.00	130.85	6.19	15.9	19.52	45.63	58.35	0.837	19.17	27.96	24.2	8.79	5.05	6.04	5.90	<LOD	93.03	4.1	-	0.7	4.2	0.16	5	33.4	-	163	0.2	0.3
P116	0-1 cm	122.92	139	137.45	1.55	16.08	14.53	181.77	125.53	2.61	14.9	11.92	44.32	56.68	0.820	19.30	28.14	23.7	8.84	4.37	5.33	5.40	92.88	127.65	4.5	1.1	1.3	8.7	0.33	5	476.8	10	452	4.5	6.4
P117	1-2 cm	123.95	138.87	137.74	1.13	14.92	13.79	181.39	127.47	3.52	13.9	10.27	43.65	55.82	0.816	19.24	27.53	23.4	8.29	4.12	5.05	5.00	<LOD	48.46	1.6	-	0.5	3.3	0.12	5	77.9	-	520	0.5	1.1
P118	2-4 cm	123.22	149.51	148.78	0.73	26.29	25.56	195.31	129.01	5.79	15.6	19.77	46.53	59.50	0.836	19.58	27.12	23.8	7.54	4.22	5.05	4.90	<LOD	88.57	3.9	-	0.7	4.3	0.15	5	23.7	-	173	0.2	0.2
P119	0-1 cm	125.35	140.1	138.97	1.13	14.75	13.62	179.29	127.39	2.04	14.8	11.58	40.32	51.56	0.822	19.28	27.54	23.4	8.26	4.10	4.99	5.10	45.39	58.40	1.9	0.5	0.7	4.6	0.14	5	210.2	10	226	2.3	2.6
P120	1-2 cm	123.48	139.09	137.7	1.39	15.61	14.22	183.74	126.44	2.96	15.1	11.26	46.04	58.87	0.817	19.46	27.70	23.3	8.24	3.81	4.66	4.70	<LOD	34.92	1.2	-	0.4	2.6	0.08	5	20.7	-	154	0.2	0.3
P121	2-4 cm	123.44	151.14	149.75	1.39	27.70	26.31	194.58	129.75	6.31	15.0	20	44.83	57.33	0.838	19.31	27.67	24.3	8.36	5.01	5.98	5.90	<LOD	102.49	4.8	-	0.8	5.0	0.19	5	0.0	-	35	0.0	0.0
P122	0-1 cm	125.35	139.53	138.4	1.13	14.18	13.05	178.83	128.25	2.90	14.3	10.15	40.43	51.70	0.818	19.59	26.87	23.5	7.28	3.86	4.72	4.75	78.85	179.44	6.0	0.8	1.8	12.6	0.44	5	588.7	10	282	2.8	7.3
P123	1-2 cm	122.94	138.24	137.08	1.16	15.30	14.14	179.86	126.17	3.23	14.8	10.91	42.78	54.71	0.818	19.02	26.86	22.5	7.84	3.52	4.30	4.30	<LOD	69.74	2.1	-	0.6	4.4	0.15	5	125.5	-	1149	1.1	1.6
P124	2-4 cm	124.36	147.5	145.95	1.55	23.14	21.59	193.14	128.86	4.50	16.2	17.09	47.19	60.35	0.830	19.59	27.89	24.4	8.30	4.78	5.76	5.70	<LOD	63.93	2.9	-	0.6	3.9	0.11	5	16.1	-	190	0.2	0.2
P1 4-4-2009 10h50																																			
P26	0-1 cm	123.43	137.6	136.10	1.50	14.17	12.67	177.91	125.73	2.30	17.0	10.37	41.81	53.46	0.817	19.37	28.40	23.2	9.03	3.79	4.64	4.50	<LOD	87	2.3	-	1.0	5.9	0.17	-	505	-	1811	1.8	1.1
P27	0-1 cm	126.60	141.32	139.96	1.36	14.72	13.36	186.88	129.00	2.40	15.8	10.96	46.92	60.00	0.816	19.50	28.16	22.9	8.66	3.37	4.13	4.10	<LOD	79	2.2	-	0.9	5.9	0.16	evaporated	1309	-	1050	1.0	2.7
P28	0-1 cm	122.17	133.83	132.26	1.57	11.66	10.09	188.44	**lost**	**2.47**	**16.7**	11.66	56.18	71.84	0.812	19.66	29.03	22.7	9.37	3.04	3.74	3.80	<LOD	203	5.7	-	2.3	13.8	0.41	evaporated	414	-	872	0.9	0.9
P29	0-1 cm	123.39	139.91	138.35	1.56	16.52	14.96	180.19	126.09	2.70	17.4	12.26	41.84	53.50	0.823	19.30	28.52	22.9	9.22	3.56	4.33	4.20	<LOD	100	2.5	-	0.9	5.4	0.18	-	895	-	3216	3.2	2.0
P2 4-4-2009 0h30																																			
P30	0-1 cm	123.43	138.88	137.4	1.48	15.45	13.97	185.68	125.93	2.50	15.1	11.47	48.28	61.74	0.816	19.28	28.85	22.7	9.57	3.40	4.17	4.10	<LOD	123	3.2	-	1.3	8.5	0.23	evaporated	683	-	1250	1.3	1.4
P31	1-2 cm	125.39	141.73	141.17	0.56	16.34	15.78	186.47	129.82	4.43	14.8	11.35	45.3	57.93	0.818	19.59	28.81	23.2	9.22	3.57	4.37	4.40	<LOD	90	2.5	-	0.6	3.7	0.18	evaporated	99	-	74	0.1	0.2
P32	0-1 cm	124.49	138.49	136.96	1.53	14.00	12.47	185.44	125.21	2.00	14.6	11.75	48.48	61.99	0.817	19.29	29.32	23.0	10.03	3.71	4.54	4.40	8.74	121	3.3	0.1	1.6	10.8	0.24	evaporated	326	-	732	0.7	0.7
P33	1-2 cm	124.38	142.15	140.7	1.45	17.77	16.32	179.04	129.09	4.71	14.1	11.61	38.34	49.03	0.824	19.11	28.30	22.6	9.19	3.46	4.20	4.15	<LOD	93	2.1	-	0.5	3.2	0.15	evaporated	110	-	96	0.1	0.2
P34	0-1 cm	122.16	137.56	136.14	1.42	15.40	13.98	183.70	125.67	3.51	12.9	10.47	47.56	60.82	0.814	19.34	29.60	23.4	10.26	4.04	4.96	5.10	5.81	78	2.3	0.1	0.6	5.0	0.17	evaporated	296	-	1122	1.1	0.7
P35	1-2 cm	123.32	139.03	138.12	0.91	15.71	14.80	186.21	127.24	3.92	14.3	10.88	48.09	61.50	0.815	19.25	29.15	22.9	9.90	3.69	4.53	4.50	<LOD	83	2.3	-	0.6	4.0	0.16	evaporated	75	-	157	0.2	0.2
P36	0-1 cm	123.31	137.05	135.52	1.53	13.74	12.21	186.81	125.04	1.73	15.0	10.48	51.29	65.59	0.812	19.20	29.12	21.8	9.92	2.55	3.14	3.10	1.67	125	2.5	0.0	1.4	9.4	0.18	evaporated	625	-	1197	1.2	1.0
P37	1-2 cm	124.79	142.02	140.95	1.07	17.23	16.16	182.36	128.91	4.12	14.7	12.04	41.41	52.95	0.822	19.12	28.14	23.5	9.02	4.36	5.30	5.40	<LOD	78	2.5	-	0.6	4.2	0.18	evaporated	80	-	119	0.1	0.2
P2 4-4-2009 13h00																																			
P38	0-1 cm	122.89	136.79	135.21	1.58	13.90	12.32	183.90	124.82	1.93	15.0	10.39	48.69	62.26	0.813	19.30	27.66	21.5	8.36	2.17	2.67	2.75	12.71	191	3.8	0.1	1.9	12.6	0.28	-	820	10	805	8.0	2.1
P39	1-2 cm	125.32	140.45	139.72	0.73	15.13	14.40	186.20	129.10	3.78	14.5	10.62	46.48	59.44	0.815	19.46	28.36	21.8	8.90	2.37	2.91	2.80	<LOD	113	2.1	-	0.5	3.8	0.15	evaporated	403	-	374	0.4	0.6
P40	0-1 cm	125.32	139.59	138.08	1.51	14.27	12.76	185.09	127.48	2.16	14.8	10.6	47.01	60.12	0.815	19.44	29.48	22.3	10.04	2.90	3.56	3.50	<LOD	180	3.7	-	1.7	11.5	0.27	-	672	-	4772	4.8	1.5
P41	1-2 cm	125.31	141.67	140.57	1.1	16.36	15.26	184.71	129.51	4.20	14.4	11.06	44.14	56.45	0.818	19.29	27.97	22.1	8.68	2.84	3.47	3.35	<LOD	124	2.7	-	0.6	4.4	0.19	evaporated	389	-	490	0.5	0.7
P42	0-1 cm	124.59	140.19	138.55	1.64	15.60	13.96	187.74	127.20	2.61	14.3	11.35	49.19	62.90	0.815	19.17	27.84	21.8	8.67	2.63	3.23	3.20	0.81	142	3.2	0.0	1.2	8.6	0.23	-	465	-	4691	4.7	1.3
P43	1-2 cm	123.19	139.14	138.7	0.44	15.95	15.51	186.76	127.32	4.13	14.5	11.38	48.06	61.46	0.816	19.05	27.94	22.1	8.89	3.03	3.71	3.70	<LOD	82	2.0	-	0.5	3.4	0.15	evaporated	149	-	292	0.3	0.3
P44	0-1 cm	123.67	137.5	136.66	0.84	13.83	12.99	184.83	126.20	2.53	14.1	10.46	48.17	61.60	0.814	18.96	28.38	22.1	9.42	3.10	3.81	3.70	7.88	129	3.0	0.1	1.2	8.2	0.22	-	433	-	3115	3.1	0.9
P45	1-2 cm	125.73	142.12	141.16	0.96	16.39	15.43	185.44	130.81	5.08	14.8	10.35	44.28	56.62	0.816	19.43	28.52	22.4	9.09	2.96	3.63	3.50	<LOD	122	2.6	-	0.5	3.5	0.19	evaporated	386	-	431	0.4	0.7
	P2 4-4-2009																																		
P46	0-1 cm	121.36	135.61	134.32	1.29	14.25	12.96	186.48	123.84	2.48	14.4	10.48	52.16	66.70	0.812	19.34	28.91	22.5	9.57	3.14	3.87	3.90	15.19	183	4.7	0.2	1.8	12.8	0.34	-	851	20	669	13.4	2.8
P21	1-2 cm	126.46	140.54			14.08		188.08	130.41	3.95	14.4	10.13	47.54	60.79	0.813	19.83	28.93	23.1	9.10	3.22	3.96	3.90	<LOD	73	1.8	-	0.5	3.2	0.13	evaporated	417	-	nd	<LOD	<LOD
P47	0-1 cm	123.94	137.53	136.98	0.55	13.59	13.04	184.49	126.25	2.31	14.8	10.73	47.51	60.75	0.815	19.17	28.70	22.2	9.53	3.06	3.76	3.70	<LOD	111	2.5	-	1.1	7.4	0.18	-	1099	20	638	12.8	2.3
P22	1-2 cm	123.22	139.29			16.07		186.85	127.38	4.16	14.4	11.91	47.56	60.82	0.818	19.44	27.93	22.5	8.49	3.06	3.74	4.00	<LOD	98	2.7	-	0.7	4.6	0.20	evaporated	683	-	nd	<LOD	<LOD
P48	0-1 cm	122.52	136.53	135.49	1.04	14.01	12.97	184.28	125.12	2.60	15.1	10.37	48.79	62.39	0.813	19.40	28.83	22.1	9.43	2.65	3.26	3.40	<LOD	189	4.1	-	1.6	10.4	0.30	-	898	10	733	7.3	1.9
P23	1-2 cm	123.11	136.96			13.85		185.56	126.86	3.75	14.4	10.10	48.60	62.15	0.812	19.10	27.77	22.4	8.67	3.31	4.07	4.10	<LOD	57	1.6	-	0.4	2.9	0.12	evaporated	260	-	nd	<LOD	<LOD
P49	0-1 cm	123.24	140.34	137.89	2.45	17.10	14.65	188.93	125.37	2.13	14.6	12.52	51.04	65.27	0.817	19.33	27.83	23.2	8.50	3.86	4.72	4.55	<LOD	96	3.4	-	1.6	10.8	0.24	-	824	-	4928	4.9	2.9
P24	1-2 cm	123.10	137.9			14.80		185.93	127.07	3.97	14.4	10.83	48.03	61.42	0.815	19.05	29.09	22.3	10.04	3.22	3.95	3.90	<LOD	91	2.1	-	0.5	3.6	0.15	evaporated	536	-	nd	<LOD	<LOD

P09 - P014 weighted wet in aluminium foil giving “total wet sediment”. Column “Total wet sediment after sampling water (nicosulfuron) is wet sediment including rinse water at when transferring to centrifuge tube

P014: due to lost tube, 10mL used to calculate amount extract before evaporation

P14: loss on ignition sediment: average of P15-P112; amount extracted before evaporation, used 8 mL for the calculation

P16: amount extracted before evaporation, used 10.2 mL for the calculation

P28: total dry sediment 105°C: average of P26-P29; loss on ignition sediment: average of P26-P29

Yellow: extract evaporated not given: therefore value of visual used

Annex 13 Data transformation of prosulfocarb and of nicosulfuron in water lab study experiment

Data of the transformation experiment.

Table 39 *Nicosulfuron and prosulfocarb transformation in water in lab experiment. Sampling times and measured pH, O_2 and temperature. The measurements were done in CAS4 low and CAS8 high.*

Date	Time	Day number	pH (-)	O_2 (mg L^{-1})	Temperature (˚C)
10-Apr-2008 (start)	10h50	<1h	8.3/8.2	10.0/10.1	
10-Apr-2008	16h50	6h			
11-Apr-2008	12h05	2	8.2/8.2	9.9/9.9	
12-Apr-2008	12h15	3			10.6
14-Apr-2008	13h20	4	8.3/8.3	9.9/9.2	10.8/10.5
18-Apr-2008		8	8.2/8.2	11.3/10.9	

Table 40 *Nicosulfuron and prosulfocarb concentrations in water in lab transformation experiment. Duplicate measurements and averages are given.*

code	sample code	Nicosulfuron	corrected for dilution	avg	Prosulfocarb	corrected for dilution	avg
		ng/L LC-MS	µg/L	µg/L	ng/L LC-MS	µg/L	µg/L
t= 0h							
CAS1 low	CAS 1	19732	24.7	25.5	165.1	0.206	0.214
	CAS 1A	21021	26.3		177.6	0.222	
CAS2 low	CAS 2	19805	24.8	26.3	168.5	0.211	0.206
	CAS 2A	22328	27.9		161.5	0.202	
CAS3 low	CAS 3	19642	24.6	25.1	165.1	0.206	0.205
	CAS 3A	20542	25.7		162.9	0.204	
CAS4 low	CAS 4	19839	24.8	25.4	156.2	0.195	0.197
	CAS 4A	20778	26.0		159.1	0.199	
CAS5 high	CAS 5	99414	124.3	130.8	811.4	1.014	1.005
	CAS 5A	109800	137.2		796.9	0.996	
CAS6 high	CAS 6	99529	124.4	131.7	828.9	1.036	1.010
	CAS 6A	111221	139.0		787.9	0.985	
CAS7 high	CAS 7	102134	127.7	127.0	815.2	1.019	0.999
	CAS 7A	101111	126.4		782.9	0.979	
CAS8 high	CAS 8	101675	127.1	127.1	784.9	0.981	0.976
	CAS 8A	101664	127.1		776.6	0.971	
t= 6h							
CAS9 blank	CAS 11 A		-		-	-	
	CAS 11 B		-		-	-	
CAS10 blank	CAS 12 A		-		-	-	
	CAS 12 B		-		-	-	
CAS1 low	CAS 13 A	20664	25.8	25.7	156.7	0.196	0.200
	CAS 13 B	20511	25.6		163.0	0.204	
CAS2 low	CAS 14 A	19601	24.5	24.1	153.1	0.191	0.194
	CAS 14 B	18969	23.7		156.9	0.196	
CAS3 low	CAS 15 A	19339	24.2	24.4	162.8	0.204	0.212
	CAS 15 B	19625	24.5		175.9	0.220	
CAS5 high	CAS 16 A	100113	125.1	130.2	726.7	0.908	0.930
	CAS 16 B	108245	135.3		761.8	0.952	
CAS6 high	CAS 17 A	101329	126.7	129.0	788.4	0.985	0.976
	CAS 17 B	105129	131.4		773.1	0.966	
CAS7 high	CAS 18 A	100705	125.9	126.6	791.9	0.990	1.000
	CAS 18 B	101921	127.4		807.7	1.010	
t= 2 dgn							
CAS9 blank	CAS 19 A		-		-	-	
	CAS 19 B		-		-	-	
CAS10 blank	CAS 20 A		-		-	-	
	CAS 20 B		-			-	
CAS1 low	CAS 21 A	13421	16.8	21.2	97.5	0.122	0.151
	CAS 21 B	20500	25.6	25.6	144.6	0.181	0.181
CAS2 low	CAS 22 A	19660	24.6	24.6	148.0	0.185	0.180
	CAS 22 B	19688	24.6		139.9	0.175	
CAS3 low	CAS 23 A	19326	24.2	25.0	142.5	0.178	0.179
	CAS 23 B	20605	25.8		144.4	0.181	
CAS5 high	CAS 24 A	85825	134.1	134.1	697.5	0.872	0.872
	CAS 24 B	lost	lost		lost	lost	
CAS6 high	CAS 25 A	103438	129.3	130.2	788.6	0.986	0.988
	CAS 25 B	104804	131.0		792.7	0.991	
CAS7 high	CAS 26 A	108402	135.5	129.0			0.953
	CAS 26 B	98024	122.5		762.6	0.953	
t= 3 dgn							
CAS9 blank	CAS 27 A		-		-	-	
	CAS 27 B		-		-	-	
CAS10 blank	CAS 28 A		-		-	-	
	CAS 28 B		-		-	-	
CAS1 low	CAS 29 A	20276	25.3	24.7	Prosulfocarb was not measurable in the low concentrations, approxim. A factor 2 lower. Not clear why. Nicosulfuron in same samples good measurable.		
	CAS 29 B	19324	24.2				
CAS2 low	CAS 30 A	19164	24.0	23.9			
	CAS 30 B	19033	23.8				
CAS3 low	CAS 31 A	19897	24.9	24.2			
	CAS 31 B	18850	23.6				
CAS5 high	CAS 32 A	97556	121.9	126.0	700.0	0.875	0.930
	CAS 32 B	104108	130.1		787.8	0.985	
CAS6 high	CAS 33 A	99537	124.4	121.8	752.3	0.940	0.937
	CAS 33 B	95362	119.2		747.1	0.934	
CAS7 high	CAS 34 A	98535	123.2	124.9	693.5	0.867	0.901
	CAS 34 B	101358	126.7		748.8	0.936	
t= 4 dgn							
CAS9 blank	CAS 35 A		-		-	-	
	CAS 35 B		-		-	-	
CAS10 blank	CAS 36 A		-		-	-	
	CAS 36 B		-		-	-	
CAS1 low	CAS 37 A	21127	26.4	26.0	147.9	0.185	0.189
	CAS 37 B	20510	25.6		154.0	0.192	
CAS2 low	CAS 38 A	19035	23.8	24.7	149.6	0.187	0.189
	CAS 38 B	20461	25.6		152.6	0.191	
CAS3 low	CAS 39 A	18878	23.6	24.5	101.9	0.127	0.181
	CAS 39 B	20258	25.3		145.1	0.181	
CAS5 high	CAS 40 A	97938	122.4	124.1	715.0	0.894	0.905
	CAS 40 B	100691	125.9		733.6	0.917	
CAS6 high	CAS 41 A	98738	123.4	125.5	748.5	0.936	0.929
	CAS 41 B	102076	127.6		737.9	0.922	
CAS7 high	CAS 42 A	98909	123.6	122.5	735.0	0.919	0.925
	CAS 42 B	97145	121.4		745.7	0.932	
t=8 dgn							
CAS9 blank	CAS 43A	-	-		-	-	
	CAS 43B	-	-		-	-	
CAS10 blank	CAS 44A	-	-		-	-	
	CAS 44B	-	-		-	-	
CAS1 low	CAS 45A	19785	24.7	24.8	154.5	0.193	0.185
	CAS 45B	19872	24.8		141.9	0.177	
CAS2 low	CAS 46A	19729	24.7	24.9	159.6	0.199	0.197
	CAS 46B	20056	25.1		155.3	0.194	
CAS3 low	CAS 47A	19361	24.2	24.1	155.6	0.195	0.187
	CAS 47B	19220	24.0		144.2	0.180	
CAS5 high	CAS 48A	95517	119.4	121.1	720.5	0.901	0.933
	CAS 48B	98285	122.9		772.3	0.965	
CAS6 high	CAS 49A	92300	115.4	118.8	716.9	0.896	0.909
	CAS 49B	97777	122.2		738.1	0.923	
CAS7 high	CAS 50A	99114	123.9	123.4	775.4	0.969	0.964
	CAS 50B	98294	122.9		767.6	0.960	
Values in red: much evaporated from 10 mL tube (vol < 4 mL), possibly degradation of prosulfocarb because acetonitril no longer present.							
Value not used for calculations.							
nicosulfuron low (µg/L)	dag						

Annex 14 Data prosulfocarb sorption to sediment experiment

Data of the sorption experiment.

Table 41 *Results of the prosulfocarb adsorption study; concentration in water and content in sediment after 24 hours of equilibration. Note that concentration (C) in series 3 µg kg^{-1} are below LOD of 0.020 µg L^{-1}.*

codes SWV E2504 -->	**Mvs**	**Mds**	**Vd**	**Cd**		**Vd x Cd**	**C (Input GenStat)**	**m**	**Xs (Input GenStat)**	**Gom**
Code sample + dose	Net wet sediment in system	Dry sediment in sediment	Net water (CaCl2 0.01M) dosed as dose solution		Concentration prosulfocarb in dose solution	Net prosulfocarb dosed in system	Concentration prosulfocarb in water after 24h sorption	Net prosulfocarb in water after 24h sorption	Net prosulfocarb adsorbed per dry sediment	Organic matter
	(g)	(g)	(g)		(µg/L)	(ng)	(µg/L)	(ng)	(µg/kg)	(g/g)
CAS H1 **0** µg.kg-1	6.11	2.13	5.15		-	-	<LOD	-	-	-
CAS H2	5.97	2.07	5.12		-	-	<LOD	-	-	-
CAS F1 **3** µg.kg-1	6.08	2.13	5.10	avg	1.26	6.41	0.006	0.05	2.983	0.135
CAS F2	6.09	2.13	5.15	sd	0.02	6.47	0.005	0.04	3.018	0.135
CAS F3	5.99	2.09	5.12	n	3	6.43	0.008	0.07	3.045	0.135
CAS E1 **30** µg.kg-1	6.14	2.14	5.11	avg	12.44	63.56	0.193	1.76	28.88	0.135
CAS E2	5.98	2.10	5.13	sd	0.08	63.81	0.201	1.81	29.52	0.135
CAS E3	5.88	2.07	5.21	n	3	64.81	0.200	1.81	30.43	0.135
CAS D1 **100** µg.kg-1	5.98	2.10	5.18	avg	41.66	215.8	0.663	6.01	99.90	0.135
CAS D2	6.13	2.15	5.11	sd	0.92	212.9	0.624	5.67	96.37	0.135
CAS D3	5.89	2.07	5.12	n	3	213.3	0.672	6.01	100.14	0.135
CAS C1 **300** µg.kg-1	5.83	2.04	5.16	avg	129.45	667.9	2.182	19.5	317.8	0.135
CAS C2	6.22	2.17	5.15	sd	3.30	666.6	2.083	19.2	298.4	0.135
CAS C3	6.16	2.16	5.19	n	3	671.8	2.171	20.0	301.8	0.135
CAS B1 **1000** µg.kg-1	5.86	2.05	5.17	avg	407.34	2105.9	7.016	63.0	996.6	0.135
CAS B2	5.91	2.06	5.13	sd	15.48	2089.6	6.921	62.1	984.2	0.135
CAS B3	6.08	2.13	5.13	n	3	2089.6	6.927	62.9	951.5	0.135
CAS A1 **3000** µg.kg-1	5.98	2.19	5.11	avg	1317.51	6732.5	21.84	194.4	2985.4	0.135
CAS A2	5.97	2.07	5.2	sd	110.74	6851.1	22.58	205.4	3210.4	0.135
CAS A3	5.83	2.10	5.18	n	3	6824.7	23.46	209.0	3150.3	0.135
Controle										
CAS BL1 EXCL.			7.86				<LOD	<LOD		
CAS BL2			10.12				<LOD	<LOD		
CAS G1 EXCL. HER 5/12			9.03		0.87	7.85	0.87	7.82		
CAS G2 HER			9.21	sd	0.0007	8.01	0.85	7.65		
CAS G1 EXCL. 1/12			9.03		0.98	8.85	0.83	7.53		
CAS G2			9.21	sd	0.02	9.03	0.84	7.78		

Table 42 *Mass balance of prosulfocarb in highest application level.*

codes SWV E2504 -->		**Mds**			**Xg**			
sample code	Dosering prosulfocarb	Dry sediment	Net prosulfocarb adsorbed to sediment	Net prosulfocarb in water	Adsorbed prosulfocarb per dry sediment	Total net prosulfocarb in system	Net prosulfocarb dosed in system	recovery
	(µg/kg)	(g)	(ng)	(ng)	(ng/g)	(ng)	(ng)	(%)
CAS A1	3074	2.19	5876.5	194.4	2683.3	6158.2 [1]	6732.5	91.5
CASA2	3310	2.07	6129.7	205.4	2961.2	6335.1	6851.1	92.5
CASA3	3250	2.10	6140.6	209.0	2924.1	6349.7	6824.7	93.0
	3211						**avg**	**92.3**
H1 BLANK		2.13		<LOD	1.3	2.8	**sd**	**0.8**
H2		2.07		<LOD	1.5	3.2	-	

[1] 87.4 ng prosulfocarb was added due to loss of previous sampling

Table 43 *Extraction efficiency of prosulfocarb in Brakel sediment at three application levels (corrected for prosulfocarb in blank sediment).*

Recovery experiment sediment brakel														
Dosering prosulfocarb	code sample	code doseer-oplossing 100 µl	netto nat sediment	netto droog	water in sediment	netto acetontril	volume deel extract acetonitril	eindvolume deel extract na indamp	concentratie prosulfocarb LC-MS	netto prosulfocarb in totaal extract	correctie blank	recovery		
(µg/kg)			(g)	(g)	(g)	(ml)	(ml)	(ml)	(ng/L)	(ng)	(ng)	(%)		
	laag													
2.6	P1	E	2.57	0.92	1.65	30.91	9.77	4.64	182.7	2.82	2.02	84	avg	85
	P2	E	2.47	0.89	1.58	29.28	9.91	4.61	199.2	2.86	2.06	85	sd	2
	P3	E	2.63	0.94	1.69	31.39	9.65	4.01	212.8	2.93	2.12	88		
	middel													
13.0	P4	C	2.46	0.86	1.60	30.18	9.98	3.51	984.8	11.00	10.19	91	avg	97
	P5	C	2.78	1.00	1.78	29.96	9.57	3.95	873.9	11.46	10.66	95	sd	6
	P6	C	2.33	0.83	1.50	30.43	9.69	3.21	1170.2	12.36	11.55	103		
	hoog													
106.7	P7	A	2.99	1.06	1.93	28.98			1735.4	53.64	52.83	93	avg	94
	P8	A	2.46	0.85	1.61	31.51			1622.2	53.73	52.92	94	sd	1
	P9	A	2.11	0.74	1.37	29.82			1753.2	54.69	53.88	95		
	Blank sediment													
	P10 bl		2.64	0.95	1.69	30.56	9.99	4.13	62.1	0.83				
	P11 bl		2.47	0.88	1.59	29.21	9.97	3.92	58.6	0.71				
	P12 bl		2.08	0.74	1.34	30.55	9.67	3.99	57.4	0.76				
	P13 bl		2.90	1.03	1.87	29.94	9.95	3.89	74.6	0.93				
									avg blank	**0.81**				
	Blank chemicalien													
	bl chem1								13.16					
	bl chem2								12.66					
	Matrix effect													
	bl acetonitril								75.9					
	Bl acetonitril + 100 µl doseer D	D							1067.3					
	bl extract p10								65.5					
	bl extract p10 + 100 µl doseer D	D							1072.9					

Table 44 *Adsorption test of prosulfocarb to glass tubes used in adsorption study.*

Inzet 5-12-08	**Na 24h adsorptierad**				
code sample + dosering	doseeroplossing toegevoegd	concentratie prosulfocarb LC-MS	netto prosulfocarb in buis	netto prosulfocarb toegevoegd berekend uit doseer oplossing	recovery
	(ml)	(µg/L)	(µg)	(µg)	(%)
C1	9.07	117.4	1.07	1.14	93
C2	8.90	119.9	1.07	1.12	95
C1+ teflon inlage	8.68	120.7	1.05	1.09	96
C2+	9.11	120.7	1.10	1.14	96
				avg	**95**
		(ng/L)	(ng)	**sd**	**1.2**
G1	8.79	869.08	7.64	7.87	97
G2	9.01	889.64	8.02	8.07	99
G1+ teflon inlage	9.57	903.17	8.64	8.57	101
G2+	9.12	884.89	8.07	8.17	99
				avg	**99**
				sd	**2**

Table 45 *Organic matter (loss on ignition) and carbon content (Dumas method) of sediment used for the prosulfocarb sorption study.*

Organic matter (loss on ignition)					
Container empty	Container + dry sediment (105C)	Container + sediment (550C)	Net dry sediment	Net loss on ignition	Loss on ignition
(g)	(g)	(g)	(g)	(g)	(%)
11.6211	14.9157	14.4725	3.2946	0.4432	13.5
11.8855	15.2051	14.7544	3.3196	0.4507	13.6
11.4743	14.663	14.2337	3.1887	0.4293	13.5
The sediment in 10 ml tubes used in the sorption study was collected after drying (105C) and homoginized				**avg**	**13.5**
A triplicate sample was determined				**sd**	**0.07**
Carbon content (Dumas methode)					
	Nitrogen	Carbon			
	(%)	(%)			
	0.581	5.44			
	0.578	5.48			
avg	**0.5795**	**5.46**			
sd	**0.002**	**0.028**			

The Freundlich equation used for fitting the data is:

$$X = K_F c_{ref} \left(\frac{c}{c_{ref}} \right)^N$$

with:

K_F = Freundlich adsorption coefficient (L kg^{-1})
X = amount adsorbed substance (mg kg^{-1})
c = concentration in water in equilibrium (mg L^{-1})

c_{ref} = reference value of concentration c (mg L^{-1})
N = Freundlich exponent (-)

The parameters K_F and N is calculated from the measurement after logarithmic transformation of X and of c, followed by linear regression. The reference concentration is 1 mg L^{-1}.

K_F is based upon dry sediment material and not on organic matter or organic carbon.

Table 46 *Calculation of Freundlich sorption parameters with LINEST function in Excel. By using concentration in solution (c) in mg L^{-1} and content in sediment (X) in mg kg^{-1}. The implicit assumption is that the reference concentration in the Freundlich sorption equation is 1 mg L^{-1}. The fitted K_F is 127.58 and fitted N is 0.980.*

c **(mg L^{-1})**	***X*** **(mg kg^{-1})**	**log *c***	**log *X***
0.000193	0.028880	-3.71427	-1.5394
0.000201	0.029523	-3.69621	-1.52984
0.000200	0.030434	-3.69811	-1.51663
0.000663	0.099899	-3.1784	-1.00044
0.000624	0.096375	-3.2046	-1.01604
0.000672	0.100139	-3.1725	-0.9994
0.002182	0.319069	-2.66124	-0.49612
0.002083	0.299521	-2.68126	-0.52357
0.002171	0.302949	-2.66331	-0.51863
0.007016	0.996555	-2.15392	-0.0015
0.006921	0.984222	-2.15984	-0.00691
0.006927	0.951524	-2.15944	-0.02158
0.021838	2.985444	-1.66079	0.475009
0.022576	3.210442	-1.64636	0.506565
0.023461	3.150316	-1.62965	0.498354

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