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Sorption of pesticides to solid materials used in soilless stonewool cultures is relevant because it may reduce emissions to surface water. The sorption of pymetrozine and dimethomorph was studied in batch experiments with clean stonewool, drip-irrigation pipes, transport pipes and the plastic foil surrounding the stonewool. The sorption coefficient of stonewool was found to be 0.2 L/kg for pymetrozine and 1.0 L/kg for the two isomers of dimethomorph. Sorption of pymetrozine to the pipes and the foil was negligibly small. The sorption coefficients of the two isomers of dimethomorph were 0.07-0.12 L/kg for the transport pipes, 0.14-0.16 L/kg for the drip-irrigation pipes and 1.2-1.5 L/kg for the foil. Studies were performed in which an aqueous solution of the pesticides was circulated through stonewool mats containing an intact sweet-pepper plant (triplicate plant systems) sampled at the end of the growing cycle. Pymetrozine did not show any interaction with the solid phases in these circulation studies. Dimethomorph showed a concentration decrease that was 10% higher than expected from the batch studies with clean stonewool. An exploratory calculation showed that this 10% may be the result of partitioning into the roots and that this may correspond to 30% decrease in a stonewool growing system in the greenhouse. It is recommended to incorporate (i) sorption to stonewool and drip-irrigation pipes and (ii) partitioning into the roots into the GEM model and to assess the sensitivity of the emission concentrations to these processes for substances like dimethomorph.

Keywords: plant protection products, pesticides, soilless culture, stonewool

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Photo cover: Arrienne Matser (stonewool batch sorption system)

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Preface

We thank Nefyto and LTO Glaskracht for their financial support to conduct these sorption studies which enable to assess the significance of the sorption to substrate materials for the emission of plant protection products to Dutch surface water from soilless stonewool cultures in greenhouses. This project was established within the framework of the innovation programme 'Het Nieuwe Doen in Plantgezondheid Glastuinbouw' of LTO Glaskracht Nederland and partly financed by the Stichting Programmafonds Glastuinbouw (project nr P16006).

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Summary

It is a point of discussion whether sorption of plant protection products to substrate materials should be included in the GEM model which is currently used to assess the emission of PPPs to surface water from soilless cultures in Dutch greenhouses. Only very little data on this sorption are available in literature. Therefore the sorption of two pesticides (pymetrozine and dimethomorph) to substrate materials was studied in batch and circulation experiments. The batch experiments were carried out with clean stonewool and plastic materials used in the growing system. The circulation experiments were carried out using a piece of mat of about 30 cm long with in the centre an intact sweet-pepper plant (cut at approximately 50 cm height), taken from the greenhouse at the end of the sweet-pepper growing cycle. The argument for using the stonewool mats at the end of the growing cycle was that these will generate the highest sorption because of the increase in the organic-matter material in the mat during the growing cycle.

Batch adsorption experiments were conducted with stonewool from two manufacturers (Cultilene and Grotop) at a solid-liquid ratio of about 0.05 kg/L using an aqueous solution with a calcium nitrate concentration of 0.02 mol/L. The equilibration time was 1 h and the initial concentration of either pymetrozine or dimethomorph was about 0.07-0.08 mg/L. Two methods for measuring the sorption were used in parallel; the first is based on the decrease of the initial concentration and the second on an extraction with methanol at the end of the experiment. The extraction method was found to be the most reliable. Differences between the two types of stonewool and between the two isomers of dimethomorph were found to be insignificant. The resulting linear sorption coefficient of pymetrozine was estimated to be 0.2 L/kg and that of the isomers of dimethomorph was estimated to be 1.0 L/kg. In literature, stonewool sorption coefficients of two other pesticides were found and ranking of the four sorption coefficients based on the octanol-water coefficient of the pesticide showed a continuous increase of the sorption coefficient with increasing octanol-water coefficient.

Batch adsorption experiments were conducted with plastic materials that are used in the stonewool growing system: materials from drip-irrigation pipes, transport pipes and the foil surrounding the stonewool. Solid-liquid ratios ranged between 0.2 and 0.5 kg/L using an aqueous solution with a calcium nitrate concentration of 0.02 mol/L. The equilibration time was 1 h; the initial concentration of pymetrozine was about 0.1 mg/L and that of dimethomorph was 0.08-0.09 mg/L (the aqueous solution contained both substances). The same two methods for measuring the sorption were used as for the stonewool. For pymetrozine no sorption could be measured. For the isomers of dimethomorph, the extraction method was found to be more reliable for the drip-irrigation and the transport pipes and the concentration-decrease method was found to be more reliable for the stonewool foil. The sorption coefficients for the transport pipes were found to be 0.07 and 0.12 L/kg for the E- and the Z-isomer, respectively. The sorption coefficients for the drip-irrigation pipes were found to be 0.14 and 0.16 L/kg for the E- and the Z-isomer, respectively. The sorption coefficients for the stonewool foil were found to be 1.5 and 1.2 L/kg for the E- and the Z-isomer, respectively. In these batch experiments the sorption to both the inner and the outer side of the materials is measured whereas the pesticides are in contact with only the inner side of the materials in the growing system, so it is recommended to halve the above sorption coefficients when used in GEM for exposure modelling.

An exploratory calculation showed that the combination of the sorption coefficients of the stonewool and the drip irrigation pipes might lead to a concentration decrease close to 20% for dimethomorph. It is therefore recommended to include sorption to stonewool and the drip irrigation pipes in GEM and to assess the effect of these processes on the emission concentrations.

Circulation studies were conducted with pieces of mats (30 cm long) with a plant in the centre of each mat (in triplicate). The procedure was to circulate a solution containing the pesticides through the system for approximately 6 h and to measure the course of time of the pesticide concentration and compare it to the concentration to be expected if no sorption takes place. The circulation solution

contained both pymetrozine and dimethomorph. The concentration of pymetrozine was about 3 mg/L and that of dimethomorph was about 0.8 mg/L (assuming complete mixing of all the water and no sorption). Besides the studies with the triplicate plant systems, also a circulation study was carried out without any sorbing material (so a blank system) plus a circulation study with a piece of clean stonewool mat. In none of the experiments a concentration decrease of pymetrozine was observed so this showed no interaction with the solid phases in the system. The study with the blank system indicated a significant amount of sorption of dimethomorph to the plastic tubing material used in the circulation system (this material was different from the plastic materials studied in the batch experiments). Therefore at the end of the experiments with the plant systems and the clean stonewool mat the plastic tubes were flushed with acetone or methanol with the aim to correct for the masses of dimethomorph sorbed to the plastic tubes. This flushing resulted in recovery of 8-12% of the added mass of dimethomorph. Further interpretation of the experiments with the blank system and the clean stonewool mat indicated that probably an additional 10% of the added mass of dimethomorph was sorbed to the plastic tubes. After correcting for also this additional 10%, it was concluded that the circulation studies resulted in a dimethomorph concentration that was 10% lower than expected from the batch adsorption experiments with the clean stonewool. Exploratory calculations showed that these 10% may have been the result of partitioning of dimethomorph into the roots and that 10% decrease in this circulation system may correspond with about 30% decrease in the stonewool system in the greenhouse. It is therefore recommended to include this partitioning into the roots in the GEM model and to assess the sensitivity of the emission concentrations to this process.

1 Introduction

The Greenhouse Emission Model (GEM) is used in the Dutch pesticide registration procedure to assess emission of plant protection products (PPPs) from soilless growing systems (including stonewool substrate) to surface water. This model does not consider sorption of PPPs to the substrate and other materials in the substrate system because of lack of such sorption data.

Emission of PPPs from soilless growing systems into the surface water is an important aspect of the environmental risk assessment of these PPPs. Thus, it is desirable that the description of the behaviour of PPPs in the GEM model for these growing systems is as realistic as possible. An experiment from 2014 on the behaviour of three PPPs in a stonewool substrate system showed differences between the time of breakthrough of the substances in the drainage water (sequence from fast to slow was imidacloprid-fluopyram-dimethomorph). These differences were probably the result of differences in sorption to the substrate materials. The current version of the GEM model cannot describe such differences because it does not consider this sorption. Furthermore in June 2016 an experiment was conducted in a sweet-pepper/stonewool substrate system with imidacloprid and pymetrozine (results not yet available). In view of its properties, sorption of pymetrozine is expected to be larger than that of imidacloprid (Table 1). Thus, sorption measurements with dimethomorph and pymetrozine were considered relevant.

Table 1 *Physicochemical properties of dimethomorph, imidacloprid and pymetrozine (dimethomorph from EFSA, 2006, and imidacloprid and pymetrozine from PPDB database at http://sitem.herts.ac.uk/aeru/iupac).*

property	dimethomorph		imidacloprid	pymetrozine
	E-isomer	Z-isomer		
water solubility (mg/L)	47	11	610	270
saturated vapour pressure (µPa)	1	1	0.0004	4
log K_{ow}	2.6	2.7	0.6	-0.2
K_{oc} (L/kg)	300-600	300-500	200	1000

The project aimed to generate experimental data on the sorption of pymetrozine and dimethomorph to substrate materials with the expectation that these data will indicated the need to include the sorption of PPPs to substrate materials in the GEM model.

Sorption experiments were conducted with the following sorbing materials:
clean/fresh stonewool (as delivered by the manufacturer)
pieces of stonewool mats collected at the end of the sweet-pepper growing cycle (early November)
pipe materials that are used in the sweet-pepper growing system
the foil around the stonewool.
The argument for using both clean stonewool as the stonewool mats at the end of the growing cycle was that these will generate the extremes with respect to sorption (clean stonewool lowest sorption and mats at end of growing cycle highest sorption). The sorption to the clean stonewool, the pipe materials and the foil was measured in batch experiments, whereas the sorption to the stonewool mats was studied in a circulation study to keep the root material under realistic conditions.

Chapter 2 describes the studies with the clean stonewool, the pipe materials and the stonewool foil and chapter 3 describes the studies with the stonewool mats collected at the end of the growing cycle.

2 Batch sorption studies with stonewool, pipe materials and stonewool foil

2.1 Materials and methods

2.1.1 Procedures of batch sorption studies with clean stonewool

The aim of the batch experiments was to measure sorption of pymetrozine and dimethomorph to clean stonewool in a system where there is perfect mixing of the water. The principle of the measurement procedure is to add an aqueous pesticide solution to the stonewool and to measure the decrease in the pesticide concentration caused by the sorption. However, it was expected that the sorption of pymetrozine and dimethomorph to the stonewool is low. Thus the decrease was expected to be small and the accuracy of the sorption measurement was expected to be low. Therefore an alternative measurement procedure was applied in parallel. In this procedure the solution is removed from the stonewool as much as possible after the sorption equilibration and the stonewool plus remaining solution is extracted with organic solvent. This is expected to give a more accurate result (Boesten, 1990).

Experiments were conducted with stonewool from two manufacturers (Cultilene and Grotop). Stonewool mats were placed in buckets and pre-equilibrated for 1 h and 15 min in a solution of distilled water containing 0.02 mol/L $Ca(NO_3)_2$ (further called '$Ca(NO_3)_2$ solution'). This pre-equilibration was done because fresh stonewool is expected to increase the pH of the solution (Matser & Leistra, 1997) because it is made of limestone for 20%. The upper limit of the pH in standard water for substrate cultures is 6 (van Ruiven et al. 2016) so it was the intention that this pre-equilibration resulted in lowering of the pH to 6. The buckets were not closed so in contact with air. The pH of the $Ca(NO_3)_2$ solution had decreased to below 6 after this pre-equilibration. Some ten pieces of moist stonewool (in total 3-4 g of dry stonewool) were put into a glass centrifuge tube (four replicates for Cultilene and four replicates for Grotop). About 60 mL of pesticide-free $Ca(NO_3)_2$ solution was added, the tubes were closed with a stopper and were rotated on a wheel (Figure 1) for 1 h at a rotation frequency of 6 min^{-1}.

The pH of the solution was measured and ranged between 6.0 and 6.6 (except one tube which had a pH of 5.5). Probably the closer contact between stonewool and solution caused by rotating the tubes led to an increase of the pH. The solution was decanted which left about 20 mL of $Ca(NO_3)_2$ solution in the tubes. To three of the four replicates 0.1 mL of a buffer (pH = 4 based on potassium hydrogen phthalate) was added; this was not added to the fourth replicate to be able to detect a possible effect of adding the buffer.

A volume of about 50 mL of $Ca(NO_3)_2$ solution containing either pymetrozine or dimethomorph at a concentration of about 0.1 mg/L was added. The concentrations in this solution were measured. Both for pymetrozine and dimethomorph two centrifuge tubes were added which contained only the pesticide solutions (so without stonewool). All tubes were rotated on the wheel (Figure 1) for 1 h at a rotation frequency of 6 min^{-1} and at a room temperature of about 20^{o}C.

It was the intention to use a solid-liquid ratio (i.e. mass of dry stonewool divided by volume of $Ca(NO_3)_2$ solution) that was as high as possible because the measurement error of sorption coefficients decreases with increasing solid-liquid ratio (Boesten, 1990). However, some 70 mL of $Ca(NO_3)_2$ solution appeared to be needed to ensure a good mixing of the liquid phased during the rotation. Thus the experiments were carried out at a solid-liquid ratio of about 0.05 g/mL (which is very low compared to sorption studies with soil where ratios of about 1 g/mL can be used).

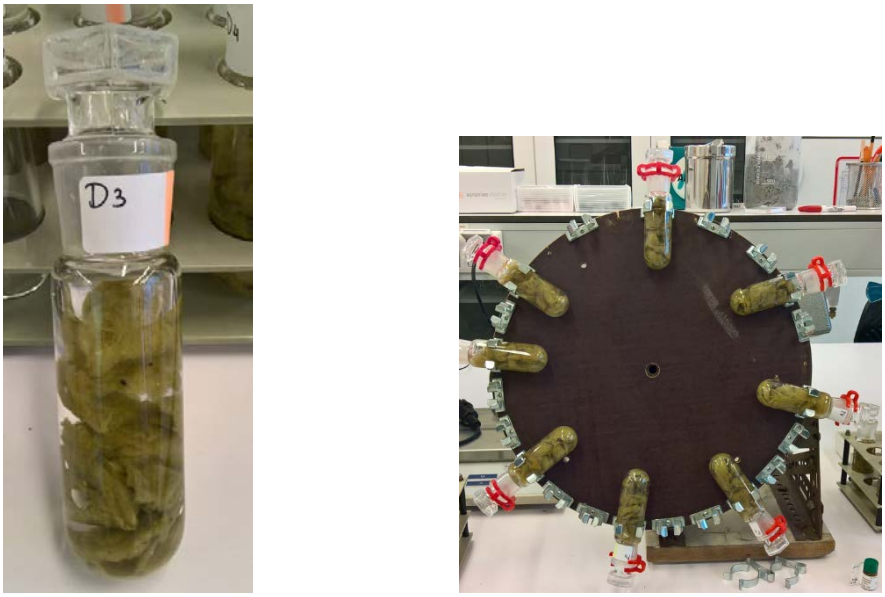

Figure 1 *Photographs of one of the batch stonewool systems and of the rotation wheel used for equilibration.*

After the 1-h rotation with pesticide solution, the tubes were centrifuged and a sample of the supernatant was taken for pesticide analysis. Then the pH of the supernatant of each tube that contained stonewool was measured. In the experiment with pymetrozine, the pH of the tubes with the buffer ranged from 5.6 to 5.7 for the Grotop and was 5.9 for Cultilene. The tube without buffer had a pH of 5.9 (Grotop) and 6.0 (Cultilene). In the experiment with dimethomorph the pH of the tubes with the buffer ranged from 5.8 to 5.9 for the Grotop and from 6.0-6.1 for Cultilene. The tube without buffer had a pH of 6.0 (Grotop) and 6.1 (Cultilene).

After the measurement of the pH as much solution as possible was removed. In the experiment with pymetrozine, this left 22-25 g solution in the system for Grotop and 18-22 g for Cultilene. In the experiment with dimethomorph, this left 17-20 g solution in the system for Grotop and 18-21 g for Cultilene. Methanol (a volume of about 36 mL for pymetrozine and about 50 mL for dimethomorph) was added to each tube and the tubes were shaken horizontally for 1 h at 175 movements per minute. After settling of the batch system a sample of the supernatant was taken for pesticide analysis.

At the end of each experiment, the tubes were dried at 105^{o}C overnight to measure the mass of dry stonewool added to each tube.

Masses of the tubes were measured in all steps so the volume of the liquid phase just before adding the pesticide solutions could be calculated. This volume was used to calculate the initial concentration of the pesticides in the system. Thus also the volume of liquid phase just before adding the methanol could be calculated. The mass sorbed onto the solid phase was calculated from the difference between the mass extracted with methanol and the mass present in the liquid phase just before adding the methanol. From the mass extracted with methanol plus the mass in the removed supernatant solution also the recovery of the added mass of pesticide could be calculated.

The results of the sorption measurements were described in terms of the measured sorption coefficient assuming a linear sorption isotherm:

$$X = K\,c \qquad (1)$$

where X is the mass of pesticide sorbed per mass of solid phase (mg/kg), c is the concentration in the liquid phase (mg/L) and K is the linear sorption coefficient (L/kg).

2.1.2 Procedures of batch sorption studies with pipe materials and stonewool foil

The aim of the batch experiments was to measure sorption of pymetrozine and dimethomorph to pipe materials and stonewool foil. Also here low sorption was expected so both the decrease in the liquid phase was measured and the materials were extracted with methanol after the sorption equilibration.

Experiments were conducted with two pipe materials, i.e. drip-irrigation pipes (further abbreviated to 'DP') and transport pipes (further abbreviated to 'TP') and stonewool foil from Cultilene stonewool (further abbreviated to 'SF'). The transport pipes consisted of 2-mm thick PVC and had an outer diameter of 32 mm. These were cut in pieces that ranged in size between 5 × 5 mm and 10 × 10 mm (Figure 2).

The drip-irrigation pipes consisted of a black inner ring and a white outer ring. The outer diameter of the pipes was about 5 mm and the inner diameter about 4 mm. The pipes were cut in pieces of 2-4 mm (Figure 2). The foil consisted of PVC and was cut in pieces ranging in size between 5 × 5 mm and 10 × 10 mm (Figure 2).

The masses and two-sided surface areas of samples of these materials were measured and the surface area per mass was found to be 8, 21 and 281 cm^2/g for the TP, DP and SF materials, respectively (the cutting faces were not included in this measurement). The mass of the pipe materials per length of the pipe was 2.38 g/cm for TP and 0.147 g/cm for DP.

For the interpretation of the sorption coefficients of TP and DP it is meaningful to calculate the ratio between the mass of the pipe and the volume of liquid contained in it. Let us first consider 1 cm of drip-irrigation pipe; this had an inner diameter of about 4 mm, so an inner surface area of 12.6 mm^2 = 0.126 cm^2 so the volume of liquid in 1 cm of pipe is 0.126 cm^3 whereas the mass of 1 cm of pipe is 0.147 g: this gives a mass/volume ratio of 1.2 g/cm^3 = 1.2 kg/L for DP. The transport pipes had an inner diameter of 30 mm so an inner surface area of 7.07 cm^2, so the volume of liquid in 1 cm of pipe is 7.07 cm^3 whereas 1 cm of pipe has a mass of 2.38 g ; this gives a mass volume ratio of 0.34 g/cm^3 = 0.34 kg/L for TP.

For the interpretation of the sorption coefficients of SF it is meaningful to calculate the ratio between the mass of foil and the volume of liquid in the mat that is in contact with the foil. The height of a sample of Cultilene stonewool was 7.2 cm and its width was 11.8 cm; this gives a perimeter of the stonewool of 38 cm. The length of the surrounding piece of foil was 38.6 cm, so slightly wider. Let us consider a stonewool slice of 1 cm. This has a volume of 11.8 x 7.2 = 85 cm^3. The volume fraction of water in a mat is typically 0.6 (van der Maas et al., 2015) so this gives about 50 cm^3 of liquid. The surface area of 1 cm of surrounding foil is 38.6 cm^2. This corresponds with a mass of 38.6/281 = 0.14 g. So the mass volume ratio is 0.14 g / 50 cm^3 = 0.03 g/cm^3 = 0.03 kg/L. The properties of the sorption materials are summarized in Table 2.

Table 2 *Properties of the pipe materials and the stonewool foil. The mass per volume of liquid is estimated assuming that the pipes are 100% filled with water and that the volume fraction of liquid in the stonewool mat is 60%.*

	TP	DP	SF
surface area per mass (cm^2/g)	8	21	281
mass per length of pipe (g/cm)	2.4	0.15	
mass per volume of liquid (kg/L)	0.34	1.2	0.03

All experiments were conducted in 10-mL centrifuge tubes with about 5 mL of $Ca(NO_3)_2$ solution (0.02 mol/L) for the TP material. The solid phase was 2.6-2.7 g of TP material, 2.0 g of DP material, or 1.0-1.1 g of SF material. The mass of solid phase in each tube was measured with an accuracy of 0.01 g. The solution contained pymetrozine at a concentration of about 100 µg/L, E-dimethomorph at a concentration of about 30-40 µg/L and Z-dimethomorph at a concentration of about 50 µg/L. All tubes were rotated on a wheel for 1 h at a rotation frequency of 6 min^{-1} and at a room temperature of about 20°C.

Figure 2 *Photographs of the batch pipe materials: transport pipe (TP) left, drip irrigation pipes (DP) middle, and stonewool foil (SF) right.*

A sample of the supernatant was taken for pesticide analysis. The tubes were centrifuged and as much solution as possible was removed. This left 0.4-0.5 g solution in the system for the TP material, 0.5-0.7 g for the DP material and 1-2 g for the SF material. Methanol (4 g for the TP and DP material and 6 g for the SF material) was added to each tube and the tubes were shaken horizontally for 1 h at 200 movements per minute. Then a sample of the supernatant was taken for pesticide analysis. The mass of pesticide sorbed was calculated using the same procedure as described in the previous section.

2.1.3 Analysis of pymetrozine and dimethomorph in water, acetone and methanol samples

The LC-MS/MS method for pymetrozine and dimethomorph analysis was developed at the laboratory of Wageningen Environmental Research. See Annex 1 for details of the analytical procedure and a number of example chromatograms. Table 3 describes the reagents and solvents that were used.

Table 3 *Overview of reagents and solvents*

Reagent / solvent	Purity	Source
Water		prepared by Advantage A10 Milli-Q water system
Methanol	100%	HiPerSolv Chromanorm, VWR PROLABO, gradient grade, art.nr. 20864.420
Acetone	100%	HiPerSolv Chromanorm, VWR, art.nr. 20067.320
Ammonium acetate		5M Ammonium acetate solution in water, Fluka, product code 101310728
Formic acid	99 – 100%	AnalaR Normapur, VWR PROLABO, Product 20318.297
Analytical standard pymetrozine	99.0%	dr. Ehrenstorfer, product identification C16587000
Analytical standard dimethomorph (mixture of E and Z isomer)	98.0%	dr. Ehrenstorfer, product identification C12710000
Plenum	50%	Formulated product of pymetrozine, WG
Paraat	50%	Formulated product of dimethomorph, WG
Calcium nitrate tetrahydrate		AnalaR NORMAPUR, VWR, art. nr. 22388.292, Lot: 16D204102

Calibration standards were prepared using analytical standards received from dr. Ehrenstorfer, with purities of 99.0% and 98.0% for pymetrozine and dimethomorph.

A stock calibration standard of pymetrozine was prepared by dissolving 0.0106 g of the reference material in 79.0141 g methanol (density of 0.791 g/mL) to a final concentration of 105.05 µg/mL pymetrozine. This stock calibration standard was stored in the freezer at a temperature below -10 °C.

A stock calibration standard of dimethomorph was prepared by dissolving 0.0126 g of the reference material in 48.8965 g methanol (density of 0.791 g/mL) to an end concentration of 199.75 µg/mL

dimethomorph (mixture of E and Z isomer). This stock solution was stored in the freezer at temperature below -10 ^{o}C.

A stock calibration standard of a mixture of pymetrozine and dimethomorph was prepared by weighing 7.964 g pymetrozine in methanol with a concentration of 105.05 µg/mL and 3.955 g dimethomorph in methanol with a concentration of 199.75 µg/mL in a flask and fill-up to 100 mL with a mixture of methanol and Milli-Q water (15/85 by volume). The concentration pymetrozine and dimethomorph in de mix standard is resp. 9.9875 µg/mL and 10.5767 µg/mL. This stock solution was stored in the refrigerator. This solution is further called the 'mix standard'.

The calibration standards used for measuring the concentration in the samples were prepared from the mix standard by using a dilutor Hamilton 600. The mix standard was diluted with a mixture of methanol and Milli-Q water containing 0.02 mol/L $Ca(NO_3)_2$; the volume ratio of methanol and the water was 15/85. The concentration levels of the calibration standards were: 1000-500-250-100-50-25-10 ng/mL.

Water samples were taken in duplo with a glass pipette and approximately 3 mL of sample was added to a 4-mL glass vial containing 0.6 mL methanol. After homogenizing by vortex a sub-sample was taken from one of the duplicate samples and transferred to a 2-mL vial for LC-MS/MS analysis. If the concentration was expected to be too high, the sample was diluted with the mixture of methanol and Milli-Q water containing 0.02 mol/L $Ca(NO_3)_2$ by using the dilutor. Samples were stored in the refrigerator.

Subsamples of the methanol samples were evaporated to dryness and the substances were dissolved in 0.3 mL of methanol using ultrasonic vibration. The same procedure was used for the acetone samples (see Section 3.1.3). A volume of 1.7 mL of Milli-Q water containing 0.02 mol/L $Ca(NO_3)_2$ was added and the mixture was analysed by LC-MS/MS.

2.2 Results

2.2.1 Batch sorption studies with clean stonewool

Table 4 shows that all concentrations for pymetrozine in the tubes without stonewool were at the end of the experiment very close to the average concentration of pymetrozine added (109 µg/L). Somewhat surprisingly the concentrations of E-dimethomorph increased some 10% wherease the concentrations of Z-dimethomorph were close to the concentrations added. Thus the 10% increase for E-dimethomorph is possibly the result of an analytical artefact.

Table 4 *Pesticide concentrations in the solution added to tubes without solid materials and pesticide concentrations in these tubes at the end of experiment with the stonewool. All concentrations are expressed as percentages of the average initial concentrations (i.e. 109 µg/L pymetrozine, 28 µg/L E-dimethomorph, 72 µg/L Z-dimethomorph, and 100 µg/L for the sum of the E and Z isomers).*

		pymetrozine	dimethomorph		
			E-isomer	Z-isomer	sum
concentrations in duplicate samples of	nr 1	100	100	104	103
solution added (%)	nr 2	100	100	96	97
concentrations in duplicate systems without	nr 1	100	110	99	102
stonewool at end of experiment (%)	nr 2	101	109	100	103

As described in Section 2.1.1, two methods were applied for the measurement of the sorption of the pesticides onto the clean stonewool: (1) based on the decrease in the concentration in the liquid phase before and after sorption equilibration, and (2) based on the mass of pesticide extracted from the solid phase with methanol at the end of the experiment.

Detailed results of all sorption measurements with clean stonewool are given in Annex 2. A summary of these results in Table 5 show that the methanol extraction generated more consistent results than the concentration decrease. The recovery (based on the methanol extraction) was very close to 100% for pymetrozine, somewhat above 100% for E-dimethomorph and somewhat below 100% for Z-dimethomorph. It is a possibility that part of the Z-isomer was converted into the E-isomer during the sorption equilibration. This would explain the large difference between the sorption coefficients of the Z and E isomers derived from the decrease in the concentrations. The measurement based on the methanol extraction is less sensitive to conversion between the isomers because both the mass sorbed and the concentration in the liquid phase are measured at the end of the equilibration.

Figure 3 contains only the numbers based on the methanol extraction because these were considered more reliable (as described in previous paragraph). The figure shows that differences between the Z- and E-isomers are not significant and that also differences between Grotop and Cultilene were not significant. Thus the best estimate of the sorption coefficient of pymetrozine to clean stonewool is 0.2 L/kg and that of the two isomers of dimethomorph is 1.0 L/kg.

To assess the significance of these sorption coefficients, we consider the percentage sorbed in a system with a mass of solid phase M (kg) and a volume of liquid V (L). The mass balance of such a system reads:

$$m = V\ c + M\ X \tag{2}$$

where m is the mass of pesticide in the system (mg). By combining with Eqn 1, it can be derived that the percentage sorbed in the system S is given by:

$$S = 100 \frac{R\ K}{1 + R\ K} \tag{3}$$

where $R = M / V$ (so kg/L). The value of R in a stonewool system is typically 0.1 kg/L (based on a volume fraction of water of 0.6 and a dry bulk density of 80 g/L; van der Maas et al., 2015; Matser and Leistra, 1997). This gives for pymetrozine a percentage sorbed of 2% and for dimethomorph a percentage sorbed of 9%.

Table 5 *Sorption coefficients measured for the two types of stonewool with the two methods. Numbers after '±' indicate sample standard deviations.*

		K (L/kg)		recovery (%)
		decrease of concentrations	methanol extraction	
pymetrozine	Grotop	0.1 ± 0.4	0.2 ± 0.2	100 ± 1
	Cultilene	0.6 ± 0.4	0.2 ± 0.1	98 ± 2
E-dimethomorph	Grotop	0.4 ± 0.2	1.2 ± 0.5	104 ± 3
	Cultilene	-0.4 ± 0.2	1.0 ± 0.2	107 ± 2
Z-dimethomorph	Grotop	2.3 ± 0.2	1.5 ± 0.4	97 ± 1
	Cultilene	1.6 ± 0.4	0.9 ± 0.1	97 ± 2

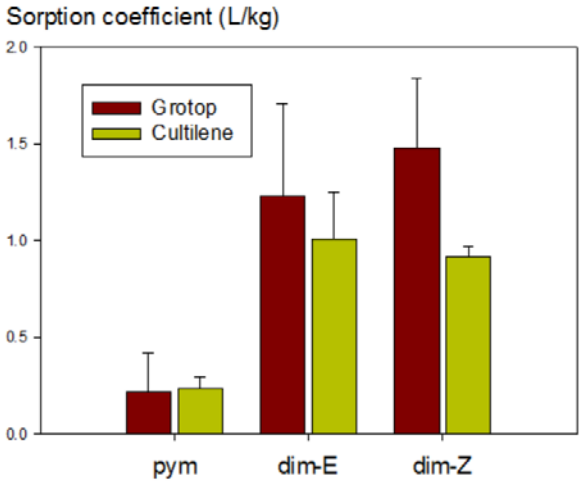

Figure 3 *Sorption coefficients of pymetrozine, E-dimethomorph, and Z-dimethomorph as measured for Grotop and Cultilene stonewool in batch experiments using the methanol extraction procedure. The vertical line segments indicate standard deviations.*

2.2.2 Batch sorption studies with pipe materials and stonewool foil

Table 6 and Table 7 show that all concentrations in the blank tubes were at the end of the experiment reasonably close to the concentrations added except one of the pymetrozine concentrations which was 109% of the added concentration. As described in Section 2.1.2, also for the pipe materials and the stonewool foil two methods were applied for the measurement of the sorption of the pesticides onto the clean stonewool: (1) based on the decrease in the concentration in the liquid phase before and after sorption equilibration, and (2) based on the mass of pesticide extracted from the solid phase with methanol at the end of the experiment.

Detailed results of all sorption measurements with pipe materials and stonewool foil are given in Annex 3. A summary of these results in Table 8 and Figure 4 shows that none of the measured sorption coefficients for pymetrozine differed significantly from zero, so it is concluded that this sorption was too low to be measured under these circumstances.

The measurement based on the methanol extraction is expected to generate more accurate results than that based on the concentration decrease unless the methanol extraction is incomplete for some reason: if this extraction is incomplete, the mass sorbed is underestimated because sorbed pesticide was not extracted. However, a recovery of less than 100% in Table 8 does not necessarily mean that the recovery was incomplete because there may have been some loss process other than sorption.

The summary of the results for dimethomorph in Table 8 and Figure 4 shows that the extraction for E-dimethomorph and the TP and DP materials was close to 100% and that the sorption coefficient based on the methanol extraction was much less variable than that based on the concentration decrease. So the best estimate for the sorption coefficient of E-dimethomorph is 0.07 L/kg for the TP material and 0.14 L/kg for the DP material. For the SF material the recovery of E-dimethomorph was only 86%; it is quite likely that this recovery was incomplete because the SF material is a very thin foil that was cut into pieces which may have been partly sticked to each other during the extraction. So for this material, the sorption coefficient based on the concentration decrease (1.5 L/kg) is considered more reliable than that based on the methanol extraction.

Following a similar reasoning, it is concluded for Z-dimethomorph that the sorption coefficients of TP and DP based on the methanol extraction (0.12 and 0.16 L/kg, respectively) are more reliable than those based on the concentration decrease and that for the SF material the coefficient based on the concentration decrease (1.2 L/kg) is more reliable than that based on the methanol extraction.

Using the mass-volume ratios from Table 2, the percentage sorbed to the pipe materials and the foil can be estimated with Eqn 3 assuming sorption equilibrium and perfect mixing of water in the pipes and in the mats. However, it should be realised that only the inner parts of the pipes and the foil is in contact with the pesticides in the actual system whereas also the outer parts of the pipes and the foil were included in the batch sorption studies. Let us assume that the sorption to outer and inner parts was equal. Then we have to take 50% of the measured sorption coefficients. This gave the following percentages sorbed for the isomers of dimethomorph: for TP 1-2% (using *K* range of 0.035-0.06 L/kg), for DP 8-9% (using *K* range of 0.07-0.08 L/kg) and for SF 2% (using *K* range of 0.6-0.75 L/kg). These are comparatively low percentages.

Table 6 *Pesticide concentrations in the solution added to tubes without solid materials and pesticide concentrations in these tubes at the end of experiment with the TP and DP materials. All concentrations are expressed as percentages of the average initial concentrations (i.e. 102 µg/L pymetrozine, 35 µg/L E-dimethomorph, 54 µg/L Z-dimethomorph, 89 µg/L for the sum of the isomers).*

		pymetrozine	dimethomorph		
			E-isomer	Z-isomer	sum
concentrations in triplicate samples of solution added (%)	nr 1	99	102	99	100
	nr 2	99	98	100	99
	nr 3	102	99	101	100
concentrations in duplicate systems without solid phase materials at end of experiment (%)	nr 1	109	102	100	101
	nr 2	101	98	96	97

Table 7 *Pesticide concentrations in the solution added to tubes without solid materials and pesticide concentrations in these tubes at the end of experiment with the SF material. All concentrations are expressed as percentages of the average initial concentrations (i.e. 104 µg/L pymetrozine, 39 µg/L E-dimethomorph, 53 µg/L Z-dimethomorph, 92 µg/L for the sum of the isomers).*

		pymetrozine	dimethomorph		
			E-isomer	Z-isomer	sum
concentrations in duplicate samples of solution added (%)	nr 1	104	101	99	99
	nr 2	96	99	101	101
concentrations in duplicate systems without solid phase materials at end of experiment (%)	nr 1	102	94	100	97
	nr 2	105	98	105	102

Table 8 *Overview of sorption coefficients measured for the TP, DP and SF materials with the two methods. Numbers after '±' indicate sample standard deviations.*

		K (L/kg)		recovery (%)
		decrease of concentrations	methanol extraction	
pymetrozine	TP	-0.09 ± 0.06	0.00 ± 0.01	105 ± 3
	DP	-0.05 ± 0.03	0.02 ± 0.02	103 ± 2
	SF	-0.16 ± 0.22	-0.09 ± 0.12	101 ± 4
E-dimethomorph	TP	0.11 ± 0.07	0.07 ± 0.00	98 ± 3
	DP	0.26 ± 0.07	0.14 ± 0.02	96 ± 3
	SF	1.49 ± 0.17	0.16 ± 0.05	86 ± 2
Z-dimethomorph	TP	0.26 ± 0.07	0.12 ± 0.02	94 ± 2
	DP	0.37 ± 0.07	0.16 ± 0.03	93 ± 3
	SF	1.20 ± 0.15	0.31 ± 0.16	90 ± 0

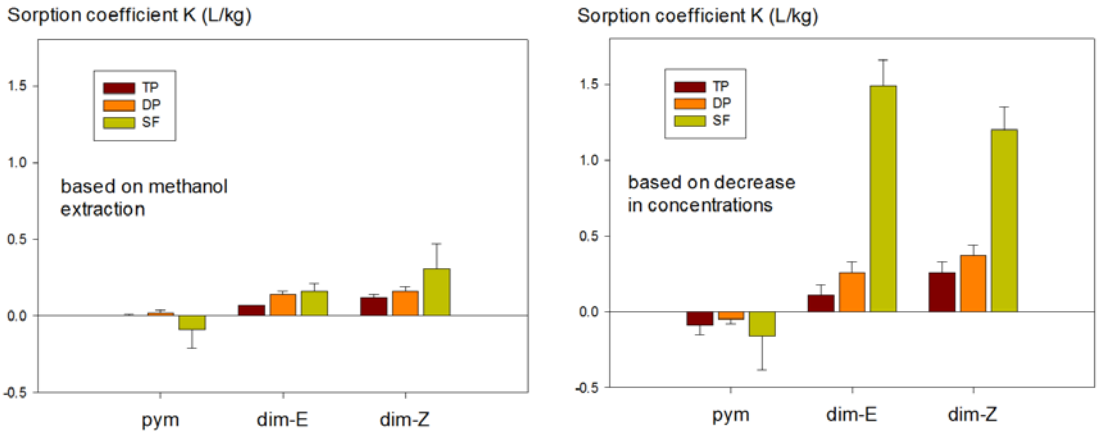

Figure 4 *Sorption coefficients of pymetrozine, E-dimethomorph, and Z-dimethomorph as measured for transport pipes (TP), drip pipes (DP) and stonewool foil (SF) in batch experiments. The vertical line segments indicate standard deviations.*

3 Circulation studies with stonewool mats

3.1 Materials and methods

3.1.1 Introduction

The purpose of the laboratory experiments was to test whether the sorption to an 'intact' stonewool system is higher than to the clean stonewool as reported in Chapter 2. An intact stonewool system contains also plant roots which may lead to some additional sorption. Furthermore during the cropping period some organic matter may be formed in the system that may also lead to additional sorption. Thus the experiments were done for a sweet-pepper system at the end of its growing cycle.

The principle of the experiments was to circulate a solution containing the pesticides through the system for approximately 6 h and to measure the course of time of the pesticide concentrations. If no sorption occurs (and no other loss processes), the concentration of each pesticide is expected to become equal after some time to the average initial concentration in the water in the system. If sorption occurs, the concentration is expected to decrease below this level.

3.1.2 Sampling of the plant systems

On 7 November 2016 mats of stonewool (Cultilene) were collected from a WUR greenhouse in Bleiswijk (the Netherlands). In this greenhouse sweet pepper was grown which was almost at the end of its growing cycle. Plants were 3-4 m high and the sweet peppers were located mostly in the upper metre of the plants (Figure 5).

Three pieces of mats were sampled with a length of about 30 cm in such a way that a plant was located in the centre of each mat. The plants were cut at a height of about 40 cm to enable transport and handling. Each mat was put into a plastic bucket (30 × 20 ×20 cm; Figure 5). The Cutilene stonewool mats were 10 cm wide and 7.5 cm deep. The mats were transferred to the laboratory and experiments with these mats were conducted on 8 and 10 November.

The greenhouse was treated with pymetrozine on 15 July, 5 October and 14 October to control aphids. No dimethomorph was applied.

Figure 5 *Photographs of the sweet pepper greenhouse and of one of the sampled plant systems.*

3.1.3 Procedures of the laboratory experiments

The system consisted of a stonewool mat in a sampling bucket through which $Ca(NO_3)_2$ solution containing the pesticides was circulated with help of a tube pump and Versilic tubes (silicon). Starting from the pump and going in the direction of water flow, the system consisted of (1) 2.5 m Versilic tube with inner- and outer diameters of 5 and 8 mm, (2) a valve to sample the inflow, (3) 0.9 m Versilic tube with inner- and outer diameters of 4 and 6 mm, (4) 0.3 m blue tube connected to syringes pierced into the mat (Figure 6), (5) the mat in the bucket, (6) 0.4-0.5 m Versilic tube with inner- and outer diameters of 4 and 6 mm, (7) a valve to sample the outflow, (8) 1.2 m Versilic tube with inner- and outer diameters of 4 and 6 mm, (9) a glass flask, (10) 1 m Versilic tube with inner- and outer diameters of 4 and 6 mm (see Annex 4 for a schematic representation of this system).

This solution was dripped on the mats from some ten needles pierced into the mats to promote an even distribution of the water flow through the mats (Figure 6). The solution was circulated at a speed of 86 mL/min (so about 5 L/h).

Experiments as described above were conducted with the three sampled plant systems. Furthermore one experiment was conducted with a system without stonewool (so with an empty bucket) and another experiment with a system with a 'clean' stonewool mat, i.e. as delivered from the factory. So there were five systems which will be further called 'empty bucket', 'clean stonewool', 'plant A', 'plant B' and 'plant C'. The experiments with plants A and B were conducted on 8 November and that with plant C was conducted on 10 November.

For each experiment 3.000 L of a solution was prepared using distilled water containing 0.02 mol/L $Ca(NO_3)_2$ and 5.0-6.0 mg/L pymetrozine (1.2 mg/L for the empty-bucket system) and 1.3-1.6 mg/L dimethomorph. The concentration of the Z-isomer of dimethomorph in the solution was about 1.7 times that of the E-isomer. For pymetrozine, a higher concentration was used for the experiments with the plant systems because pymetrozine had been applied to the sweet pepper so some background concentration of pymetrozine could be expected.

In the empty-bucket and the clean-stonewool systems, the water in the system was limited to the 3-L solution that was prepared. The plant systems contained of course some water at the start. Furthermore at the start of each plant experiment, a volume of 2.3 L of clean $Ca(NO_3)_2$ solution was circulated for 1-2 h through the systems to be able to detect a possible background level of the pesticides. After addition of the solution containing the pesticides, the solution in the systems was circulated for about 6 h and samples of inflow and outflow were taken at regular intervals. The concentrations of pymetrozine and dimethomorph was measured as described in Section 2.1.3.

Figure 6 *Photographs of a plant system in a bucket in the laboratory (left) and of the ten needles pierced into the mat used to distribute the solution on top of the system (right). Note the block with the plant on top of the mat (right). Four needles are placed in the block and six in the mat below.*

In the experiment with the empty-bucket system, the top of the bucket was covered with aluminium foil but with an opening of 10 × 10 cm to mimick the 10 × 10 cm surface area of the pots in the plant systems from which also water could evaporate (see Figure 6). The plant systems were loosely wrapped in aluminium foil during the pumping period.

At the end of the plant experiment, the above-ground parts of the plants were cut off and the masses of water and dry material in each mat was measured by drying during one week at 80 ^{o}C.

The organic matter contents of the mats of the plant systems were measured using the dried mats by first removing all plant roots present at the bottom of the mat, and then taking three subsamples of the mat (one in the middle and two at the ends). The mass of organic matter was measured by loss on ignition (overnight at 550^{o}C) both for the three subsamples and all plant-root material from each mat. As stonewool consist partly of $CaCO_3$, the ignition will also release some CO_2 from the stonewool. Therefore the loss on ignition of clean stonewool was measured as well in four subsamples. The mass lost divided by the remaining mass after ignition was found to be on average 0.069 with a standard deviation of 0.005. So the mass losses were lowered by 6.9% to derive the organic matter contents.

As will be described below, the empty-bucket experiment showed a significant decrease in the dimethomorph concentration. Extraction of a few pieces of the plastic tubes at the end of the experiment indicated that this was caused by sorption to these tubes. To be able to quantify the mass sorbed to the tubes, at the end of the other four experiments, the tubes were flushed with acetone or methanol (for 45 min with acetone for plants A and B and for 2 h with methanol for plant C and clean stonewool; see Table 9 for amounts of solvents). The problem with the acetone was that the tubes started to crack after some 45 min causing considerable leakage of acetone, so therefore methanol was used for the plant-C and clean-stonewool systems. The concentrations in the solvents and their volumes were measured and the masses extracted by the flushing were calculated based on the added masses of solvent.

Table 9 *Amounts of organic solvent used and recovered for the flushing of the tube systems at the end of the experiments.*

system	type of solvent	mass of solvent (g)		percentage solvent
		added	recovered	recovered
plant A	acetone	437	234	54
plant B	acetone	438	317	72
plant C	methanol	642	593	92
clean stonewool	methanol	730	694	95

Processing of the results
The aim of the study was to quantify the possible decrease in concentration of the pesticides resulting from sorption to materials in the mats. Therefore all concentrations will be presented as percentages of the so-called 'perfectly-mixed concentration' (acronym PMC). This concentration is defined as the concentration in the liquid phase of the systems assuming perfect mixing in the systems and assuming no sorption to the materials in the mats. However, the PMC does not include the mass recovered by flushing with organic solvent at the end of the study because this mass is of no interest for the processes in the mats.

This PMC was calculated for each pesticide (with separate calculations for the E- and Z-isomers of dimethomorph) as follows:
the total mass of water in the system was assumed to be equal to the total mass in the mats at the start plus the mass retained by the mats due to the circulation of the pesticide-free solution plus the total mass of the pesticide solution added to each system;
the total mass of each pesticide in the system was assumed to be equal to the mass of this pesticide in the pesticide solution that was added to each system minus the mass of this pesticide that was recovered by the flushing with organic solvent at the end of the study.

The calculation of the PMC as described above was impossible for the empty-bucket system because no flushing of tubes with solvent was performed. Therefore the concentrations for this system are given as percentage of initial concentrations.

3.2 Results

During the initial circulation of the pesticide-free solution, concentrations of pymetrozine up to 0.06, 0.01 and 0.03 mg/L were detected in the plant-A, plant-B and plant-C systems, respectively (resulting from the pymetrozine applications in the greenhouse described before). These were ignored in all calculations because they were no more than 1% of the concentration of pymetrozine in the added pesticide solution.

The overview of the elements of the water balance in the experiments (Table 10) shows that the masses of the dry mats in the plant systems ranged between about 200 and 260 g. The ratio of the mass of water divided by the mass of dry mat at the end of the experiment ranged between 9 and 11 for the plant systems and was only 7 for the clean-stonewool system. Obviously the presence of roots and some accumulation of organic matter led to an increased water retention. The loss of water from the systems ranged between 2 and 4% except for plant B which showed a much greater loss. This loss from plant B was caused by a leakage of the tubing system which led to loss of a considerable amount of water. The loss from the plant-A and plant-C systems was 100-130 g higher than the loss from the clean-stonewool system. This may have been the result of transpiration from the plant systems.

Table 10 *Wet and dry masses of the stonewool mats and the water balances of the circulation systems.*

	system				
	empty bucket	clean stonewool	plant A	plant B	plant C
mass (g) of dry mat without above ground parts		131	199	235	261
mass (g) of water in mat at start			1782	2060	1490
mass (g) of water retained in mat after circulation of pesticide-free solution			475	556	926
mass (g) of water in circulation system at start of circulation of pesticide solution	3000	3000	5257	5616	5417
mass of water in mat divided by mass of dry mat after circulation of pesticide-free solution			11.3	11.1	9.3
mass (g) of water in mat at end		907	2068	2643	2404
mass of water in mat divided by mass of dry mat at end		6.9	10.4	11.2	9.2
mass (g) of water lost from system	49	76	176	928	205
percentage of water lost from system based on total mass of water in system just after adding pesticide solution	2	3	3	17	4

Figure 7 shows that flushing with solvents released only 0.2-0.3% of the dosed mass of pymetrozine. However, it released 7-8% of the E- and Z-isomers of dimethomorph in the plant systems and 12% in the clean-stonewool system. The difference between the plant systems and the clean-stonewool system can be explained from the difference in the water volumes in these systems (on average 5.4 L for the plant systems based on Table 10 and 3 L for the clean-stonewool system). Assuming a linear sorption coefficient for the sorption to the plastic tubes and 8% of total mass sorbed to the plastic tubes for a volume of 5.4 L (using Eqns 1, 2 and 3), generated a predicted percentage of total mass sorbed to the plastic tubes of 13.5% for a volume of 3.0 L which is close to the observed 12% for the clean-stonewool system. The consistency in the results for dimethomorph for the different solvent systems and the different water volumes in Figure 7 suggest that the recovery of the dimethomorph from the plastic tubes was close to complete.

As described before, the calculation of the PMC was based on the masses of water added to the system. In view of the low loss percentages for all systems except plant B this seems justifiable. For the plant-B system this seems justifiable as well because the leakage occurred a few hours after the start of the experiment (so the water that leaked did sufficiently participate in the equilibration process). Table 11 gives the PMC values for all substance-system combinations.

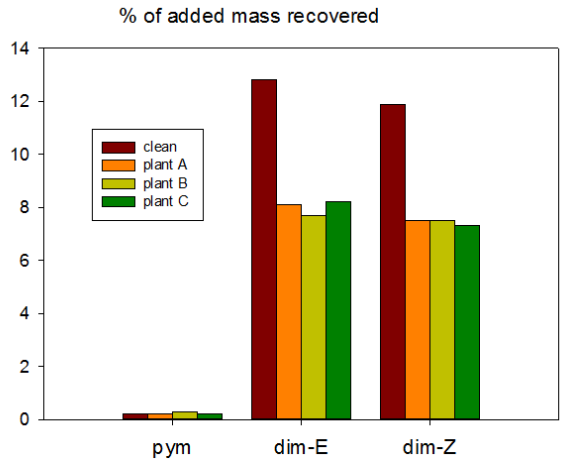

Figure 7 *Percentage of total added mass of pesticide (pymetrozine, E-dimethomorph, and Z-dimethomorph) hat was recovered by flushing the tube systems with acetone (plants A and B) and methanol (plant C and clean stonewool) at the end of the experiments.*

Table 11 *The 'perfectly-mixed concentration' (PMC) in mg/L of all substances for the plant and clean-stonewool systems and the initial concentration (mg/L) of all substances for the empty-bucket system.*

	system				
	empty bucket	clean stonewool	plant A	plant B	plant C
pymetrozine	1.17	4.96	3.40	3.06	2.82
E-dimethomorph	0.51	0.44	0.26	0.29	0.29
Z-dimethomorph	0.82	0.77	0.46	0.50	0.50

As shown in Figure 8, the concentration of pymetrozine in the empty-bucket system remained always close to the initial concentration. Obviously no measurable sorption of pymetrozine to the plastic tubes occurred (consistent with Figure 7). However, even the first inflow concentrations of E- and Z-dimethomorph were significantly below the initial concentration, indicating rapid sorption to the plastic tubes. The dimethomorph concentrations decreased gradually to about 75% of initial. From the water solubilities and the saturated vapour pressures in Table 1, an air-water partitioning coefficient (Henry coefficient) of about 10^{-9} can be calculated for pymetrozine and of about 10^{-8} for the isomers of dimethomorph, so volatilisation of these substances can be excluded as a loss process. Both pymetrozine and dimethomorph are hydrolytically stable according to the PPDB database so hydrolysis can also be excluded as a significant loss process. As described before, the plastic tubes were not flushed with solvent at the end of the experiment with the empty bucket so it is unknown how much was sorbed to these tubes. However, one would expect for this empty-bucket system about the same percentage sorbed to the tubes as in the clean-stonewool system which had 12% sorbed to the tubes (Figure 7).

In the clean-stonewool system, the concentration of pymetrozine remained mostly close to 100% of the PMC (Figure 8). The concentrations were usually slightly higher than 100% which may be the result of the 3% evaporation of water (Table 10). The concentration of the isomers of dimethomorph decreased after a few hours to about 90% of the PMC. However there was a clear outlier in an outflow sample (both the E and the Z isomer) around 13 h; probably something went wrong with this sample. This 90% of the PMC for the isomers of dimethomorph can be compared with a prediction from the batch experiments with stonewool. As described in Section 2.2.1, the sorption coefficient was estimated to be 1 L/kg. This system consisted of 131 g of stonewool (Table 10) and 3 L of water.

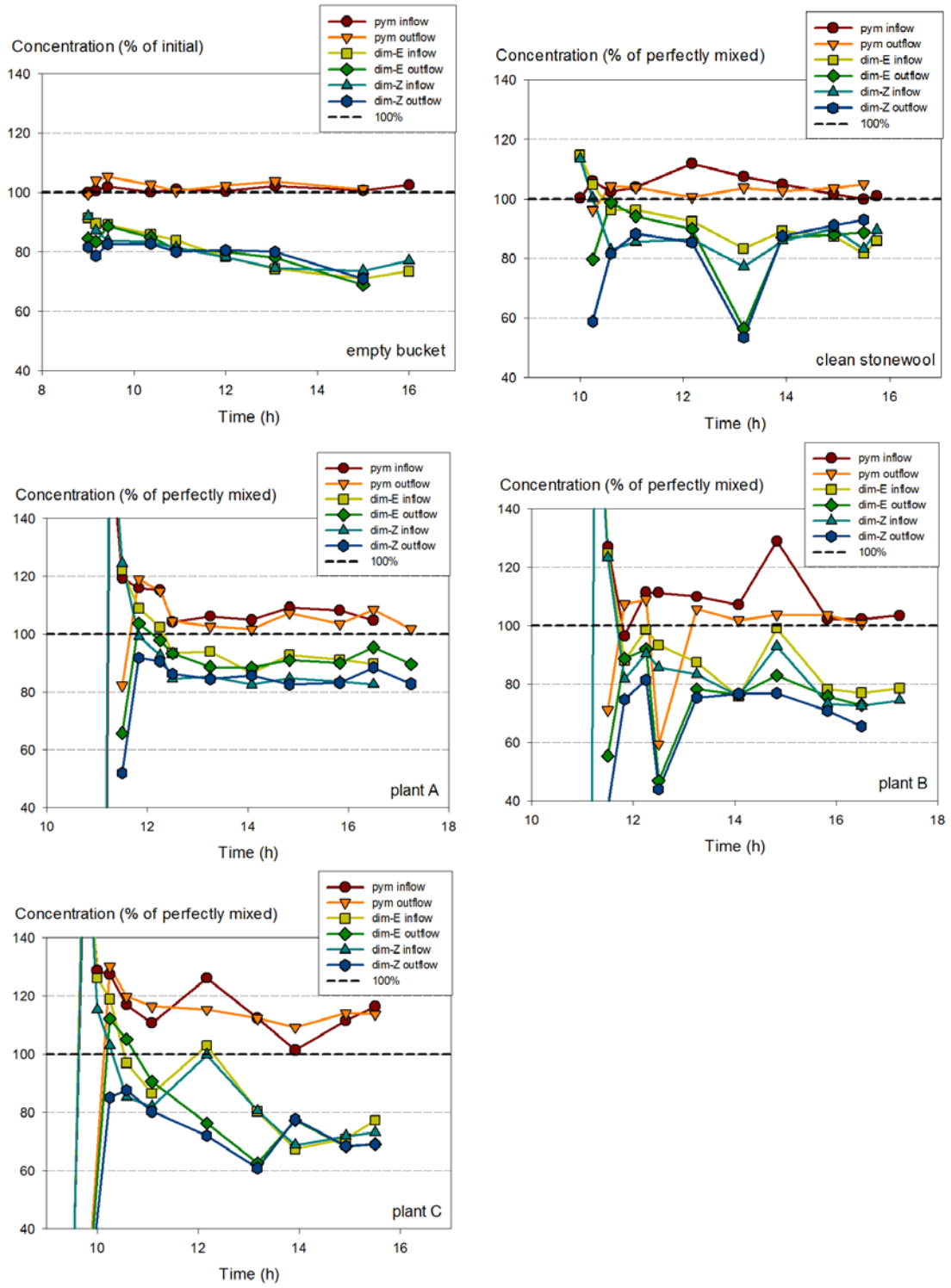

Figure 8 *Pesticide concentrations in the inflowing and outflowing water flows in the experiments with the empty-bucket, clean-stonewool, plant-A, plant-B and plant-C systems as a function of daytime. The concentrations of the empty-bucket system are in % of initial and those of the other systems in % of the PMC of each pesticide-system combination; pym= pymetrozine, dim-E = E-isomer of dimethomorph, dim-Z = Z-isomer of dimethomorph. Note that the vertical axis starts at 40%.*

Using Eqn 3, it then follows that the percentage sorbed is 4%. Considering the 3% evaporation of water, one would thus expect 99% of the PMC instead of the observed 90%. It is thus likely that there was a loss process of about 10% that was unaccounted for (possibly sorption of dimethomorph molecules to the plastic tubes that were not released by the flushing with organic solvent).

This conclusion for the clean-stonewool system is consistent with the result for the empty-bucket system: the loss from the clean-stonewool system was 12% as extracted with organic solvent (Figure 8) plus about 10% unaccounted loss, so in total 22% which is consistent with the dimethomorph concentrations decreasing to about 75% of initial in the empty-bucket system. So for the plant systems it has to be kept in mind that about 10% lowering of the PMC for the isomers of dimethomorph may be the result of an experimental artifact.

The concentrations of pymetrozine for the three plant systems in Figure 8 are mostly between 100 and 110%. Concentrations up to 103-104% could be expected because of the evaporation loss of the water (Table 10) if no pymetrozine would have been taken up by the plant. A possible explanation of the values of around 110% is that the mixing of the water in these mats was not perfect (especially for plant C; as described before, there was about 2-3 L of water in the mats at the start of the circulation experiments with the plant systems to which 3 L of solution containing the pesticides was added).

The concentrations of the isomers of dimethomorph in the plant-A, plant-B and plant-C systems at the end of the experiment were about 90, 75, and 70% for the E-isomer and about 85, 70 and 70% for the Z-isomer (Figure 8), so on average about 80%, i.e. 10% lower than expected on the basis of the experiments with the empty-bucket and the clean-stonewool system. This 10% may seem a low number. However, it should be realised that the percentage sorbed in this circulation system differs from the percentage sorbed in the real system in the greenhouse. Background is that in the circulation system the ratio of mass of solid phase to volume of liquid is about 0.2/5.4 = 0.04 kg/L whereas this ratio is about 0.1 kg/L in the real system. This is illustrated with Figure 9: some 10% sorbed at a ratio of 0.04 kg/L corresponds with a *K* of about 3 L/kg which gives about 20% sorbed for a ration of 0.1 kg/L. Based on Figure 9 this 10% can also be interpreted as an 'effective' sorption coefficient of about 3 L/kg for dimethomorph at the end of the sweet-pepper growing cycle, so three times the value measured in the batch experiments with clean stonewool.

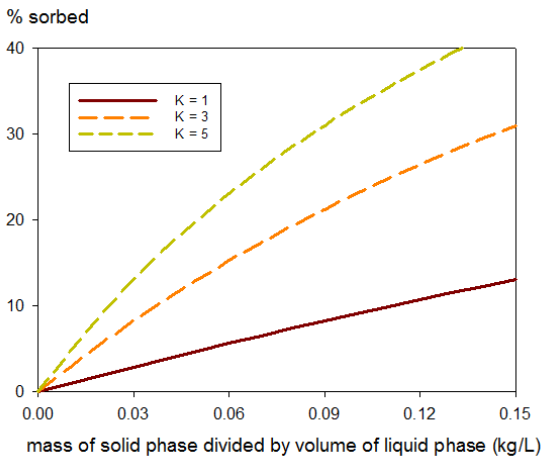

Figure 9 *Percentage sorbed in a solid-liquid system as a function of the solid-liquid ratio as calculated with Eqn 3 for three values of the sorption coefficient K as indicated in L/kg.*

The organic matter percentages of the mats varied strongly (Table 12). For each mat the highest percentage was found in the sample from the middle. This is understandable because the stem of the plant is located in the middle. Averages of each mat (based on the three subsamples) ranged between 13 and 22%. Table 12 shows also that the organic matter from the roots that were collected separately from the bottom of each mat (Section 3.1.3) corresponded only to an additional 2-3% of organic matter.

Table 12 *Measured mass fractions of organic matter (%) in the stonewool mats. This mass fraction is defined as 100 × the mass lost on ignition divided by the remaining mass after ignition. Mass fractions measured from stonewool samples were lowered by 6.9% to correct for the loss on ignition from clean stonewool.*

	plant system		
	A	B	C
sample from start of mat	13	19	7
sample from middle of mat	17	38	21
sample from end of mat	8	8	12
average from 3 samples	13	22	13
additional from roots	3	2	3

4 Discussion and conclusions

4.1 Batch sorption studies

Measuring the content sorbed by extraction with organic solvent after removing as much supernatant as possible has been considered a more accurate measurement method than the alternative procedure where the content sorbed is derived from the decrease in the concentration in the liquid phase (see Section 2.1.1 and Boesten, 1990). The batch adsorption studies with the stonewool foil and the isomers of dimethomorph showed that this is only true if the recovery of the extraction procedure is complete enough. So in any sorption study it seems advisable to check the plausibility of the recovery percentage.

In Section 2.2.1 we concluded to a sorption coefficient of 0.2 for pymetrozine and of 1.0 L/kg for the isomers of dimethomorph. Crum et al. (1985) and Matser & Leistra (1997) also measured sorption of pesticides to stonewool in batch experiments. Crum et al. used initial concentration levels of 2-17 mg/L, an equilibration time of 24 h and a solid-liquid ratio of 0.04 kg/L. They found a sorption coefficient of 1.8 L/kg for etridiazole and of 2.0 L/kg for tetrachlorvinphos; the sorption of ethoprophos was found to be too low to be measurable. The variation in the sorption coefficients between the replicates was considerable (CVs of 20-50%). Matser & Leistra measured sorption of oxamyl and metalaxyl at three concentration levels at equilibration times of 1 and 24 h using a solid-liquid ratio of 0.04 kg/L. For metalaxyl, they found a systematic difference between the concentration levels: the equilibrium concentration was on average 79%, 98% and 102% of the initial concentration for the three concentration levels (0.1, 1.1 and 9.23 mg/L). Matser & Leistra wrote 'possibly, only a limited number of interaction sites was available in the rockwool'. Based on the 79% we calculated a sorption coefficient of 8 L/kg which is very high given the log K_{ow} of 1.75 of metalaxyl as will be shown below. So we consider these measurements for metalaxyl not reliable. For oxamyl Matser & Leistra found rapid degradation during the batch equilibration (80%, 100% and 65% decline at the three concentration levels after 24 h). They showed that this was the result of transformation into the metabolite oxamyl-oxime so no sorption coefficient could be measured for oxamyl.

So the sorption coefficients of etridiazole and tetrachlorvinphos can be compared to our results. It can be expected that hydrophobic pesticides sorb stronger than lipophylic pesticides, so a positive correlation with the octanol-water partition coefficient can be expected. Figure 10 shows indeed a consistent relationship.

The K_{ow} of ethoprophos is about 1000, so based on Figure 10 a sorption coefficient above 1 L/kg could be expected. Crum et al. did not provide an upper limit for the sorption coefficient of ethoprophos so this cannot be checked further. Figure 10 indicates that a sorption coefficient for metalaxyl of 8 L/kg has to be considered very unlikely given the K_{ow} of metalaxyl of about 60 (corresponding to log K_{ow} of 1.75).

In Section 2.2.1 the concentration decrease in the stonewool system in the greenhouse was estimated at 9% for dimethomorph. In Section 2.2.2 the concentration decrease due to sorption to the drip irrigation pipes was estimated at 8-9% for dimethomorph. It is not clear whether these percentages sum up when estimating emission concentrations from greenhouses. Therefore, it is recommended to include sorption to stonewool and drip irrigation pipes in GEM to assess the combined effect of these processes on emission concentrations.

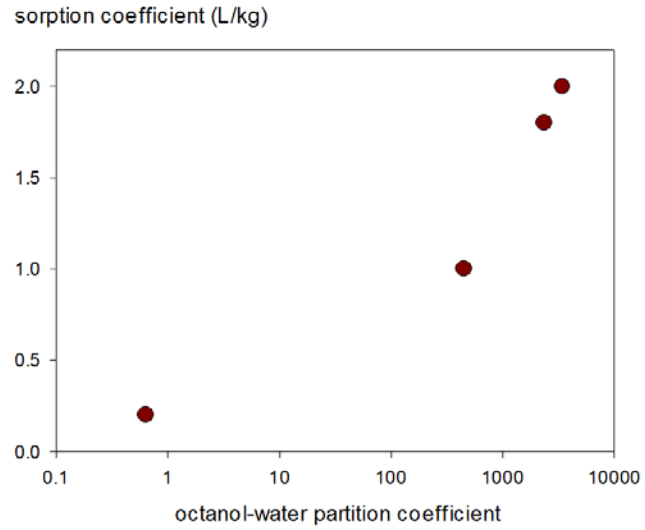

Figure 10 *The sorption coefficient of four pesticides (pymetrozine, dimethomorph, etridiazole and tetrachlorvinphos) to stonewool as a function of their octanol-water partition coefficient.*

4.2 Circulation studies

From the circulation studies we estimated that the concentration of the isomers of dimethomorph in the circulating solution was about 10% lower than expected from the experiments with the systems that did not contain roots. Roots are an important part of the organic matter in the stonewool mats. Briggs et al. (1982) established the following relationship between partitioning of pesticides into roots and the octanol-water partition coefficient:

$$\log(RCF - 0.82) = 0.77 \log(K_{ow}) - 1.52 \quad (4)$$

where RCF is the root concentration factor (L/kg) defined as the concentration in the roots divided by the concentration in the external solution (with concentration in roots defined as mass of pesticide in roots per mass of wet roots). It is worthwhile to test the hypothesis whether 10% lower concentration is consistent with the RCF predicted from Eqn 4. For dimethomorph (log K_{ow} = 2.6-2.7 from Table 1) Eqn 4 gives a RCF of about 4 L/kg. The stonewool mats of the plant systems had about 200 g of dry mass (Table 10). Let us assume that 10% of these 200 g were dry roots (based on Table 12, considering only the samples at the start and the end of the mat because the samples from the middle of the mat may have contained a considerable fraction of woody root parts). So we have 20 g of dry roots. The ratio between fresh and dry root mass is assumed to be 10, which gives 200 g wet root mass in each mat. Let us assume that the plant systems of the circulation studies consisted of 200 g of wet roots and 5.4 L of solution (this 5.4 L is the average water volume based on Table 10). The mass balance for such a system reads

$$m = V\ c + M_{roots}\ RCF\ c \quad (5)$$

where M_{roots} is the mass of wet roots (kg). Using Eqn 5, the percentage of total mass in the roots W is given by

$$W = 100 \frac{M_{roots}\ RCF}{V + M_{roots}\ RCF} \quad (6)$$

The parameters as described above give W = 13%, so in line with the observed 10% lower concentration. In a greenhouse system, a mass of 200 g of dry mat corresponds with a V of about 2 L (Table 10). For such a system W is estimated to be 29% which indicates a significant decrease of the

concentration due to partitioning into the roots. It is therefore concluded that partitioning into the roots should be included in the GEM model and that sensitivity of emission concentrations to this process should be assessed.

The log K_{ow} of pymetrozine is -0.2 (Table 1). Eqn 4 gives then a *RCF* of 0.84 L/kg and Eqn 6 gives then W = 3%. Such a low percentage could not be detected in the experiments with pymetrozine of Figure 8.

The *RCF* relationship of Eqn 4 is based on studies in which substances are taken up by the roots and transported to the shoots. In the circulation studies the water uptake by the roots was very limited (as indicated by the 3-4% loss of water in Table 10). It can be expected that contact between the solution and the roots is more intensive when water flows through the roots than when water passes the roots (i.e. the situation in the circulation experiments). So it is also possible that the additional 10% decrease in concentration is the result of sorption to organic matter formed during the course of the growing cycle.

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Annex 1 Details of analytical procedures

Analytical system

LC-MSMS	Agilent 1200 (Agilent Technologies, Germany)
– Binary pump	G1312A
– Column thermostat	G1316A
– Degasser unit	G1379B
– Autosampler	G1329A
– Triple quad mass spectrometer	G6410A
– ESI source	G1948A
– software	Agilent MassHunter

Separation

Injection volume:	50 µl or 100µl	
mobile phase:	A: Milli Q water with 5mM ammoniumacetate +0.1% formic acid	
	B: Methanol with 5mM ammoniumacetate +0.1% formic acid	
Gradient:	Time	Solvent Ratio B (%)
	0.0	10
	1.5	10
	4	60
	8	70
	11	100
	12	100
	12.01	10
	15	10
Flow:	0.7 mL min^{-1}	
Column:	Agilent Analytical Zorbax XDB-C18, 150*4.6 mm column, 5 micron	
Column temperature:	40 °C	
Retention time:	Pymetrozine	ca. 6.15 min
	E-Dimethomorph	ca. 12.51 min
	Z-Dimethomorph	ca. 12.86 min

QQQ Detection

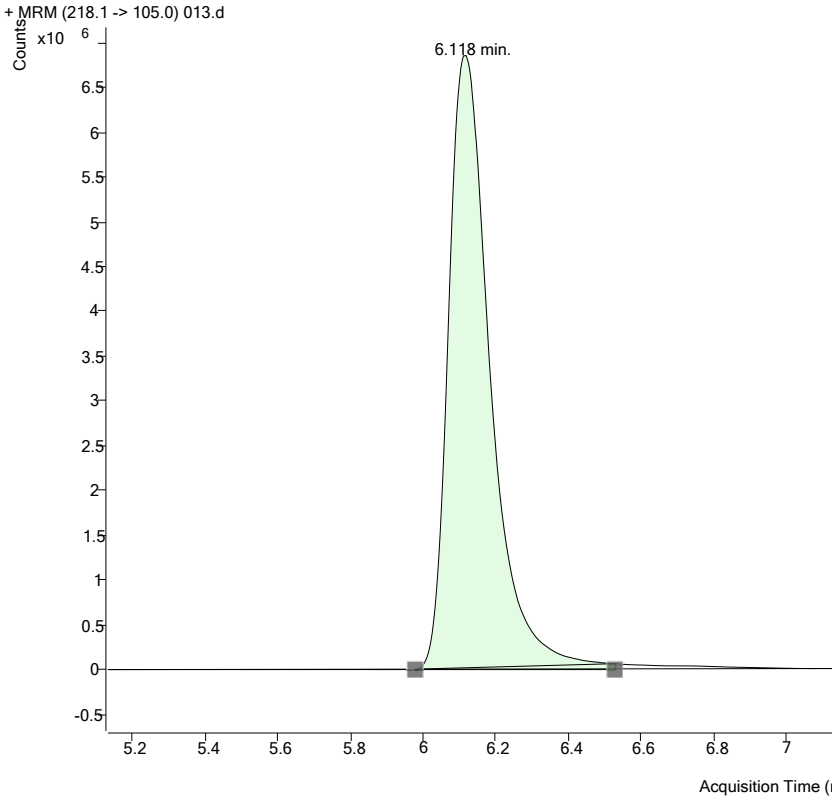
Ionization mode	: ESI	Gas flow	: 11 L/min
Polarity	: positive	Nebulizer pressure	: 50 psi
Capillary voltage	: 4000V	Nebulizer gas	: Nitrogen (98% purity)
Dry temperature	: 350 °C	Collission gas	: Nitrogen (99.99% purity)
Scan type	: MRM		

Compound	Precursor ion	Product ion	Type	Fragmentor Voltage	Collision energy
	(m/z)	(m/z)		(V)	(V)
Pymetrozine	218.1	105	quantifier	145	17
		78	qualifier		49
Dimethomorph	388.2	301.1	quantifier	85	10
		165.2	qualifier		10

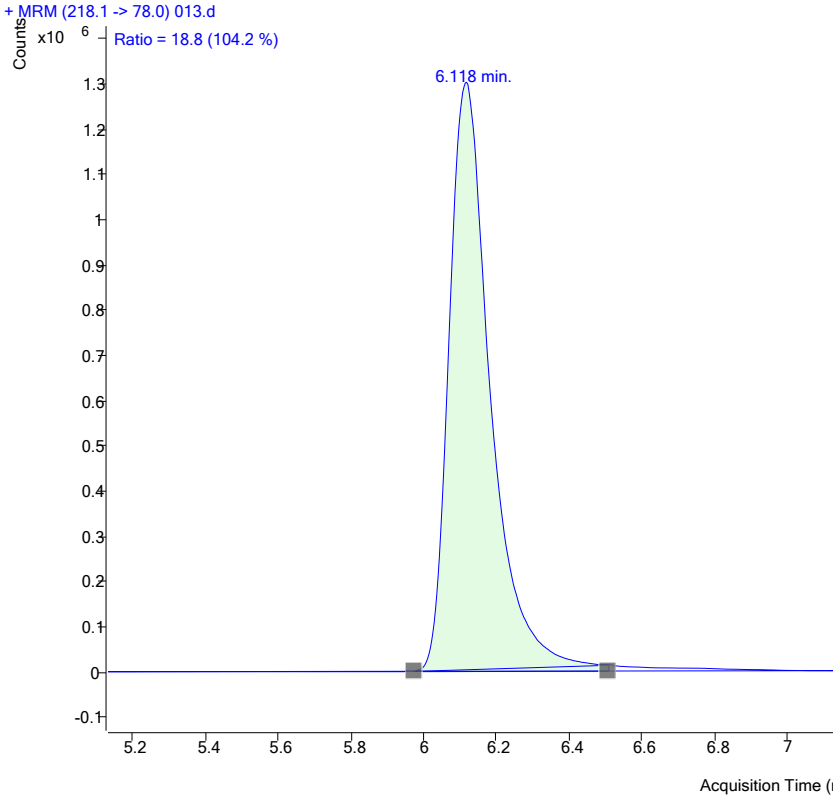
Injected samples were quantified by pymetrozine and E-dimethomorph and Z-dimethomorph peak area using the calibration curve constructed from calibration standards
The concentrations of the samples never exceeded the highest standard of the calibration curve. The curve fit was quadratic and forced through origin (x-axis zero; y-axis zero).

Chromatograms and calibration curves of pymetrozine and dimethomorph

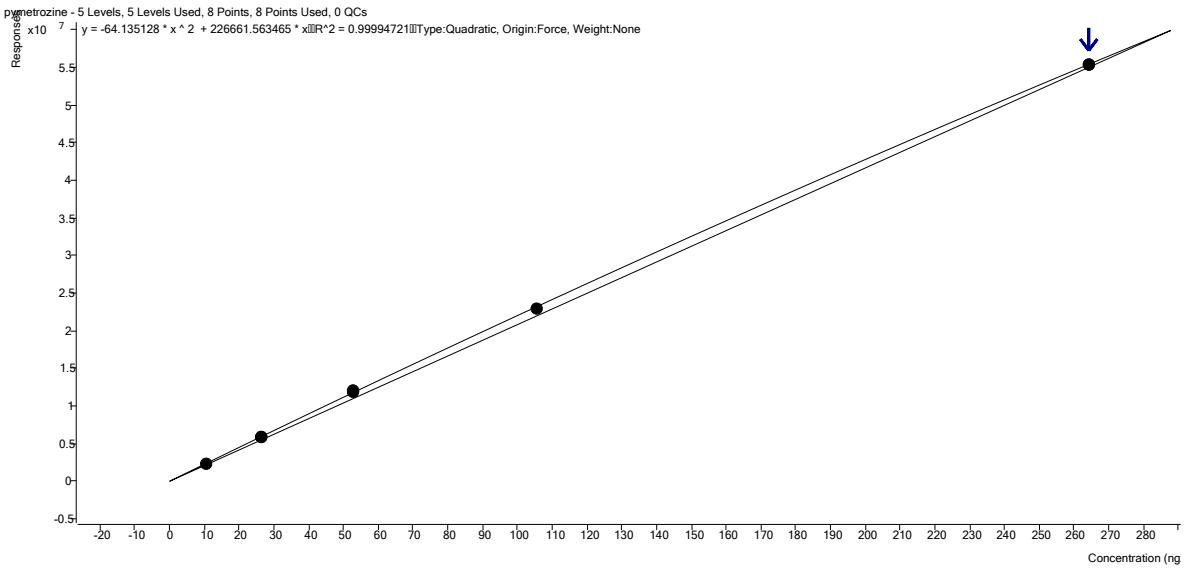
Standard Pymetrozine 264 ppb



Chromatogram of a 264 ng/ml pymetrozine standard (218.1---105.0); quantifier.



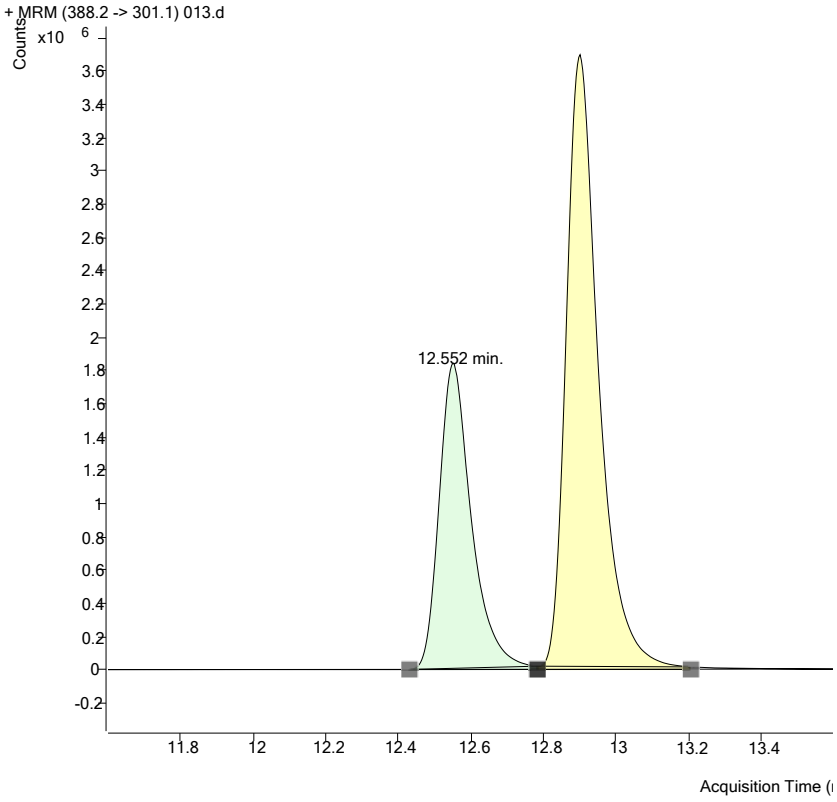
Chromatogram of a 264 ng/ml pymetrozine standard (218.1---78.0); qualifier.



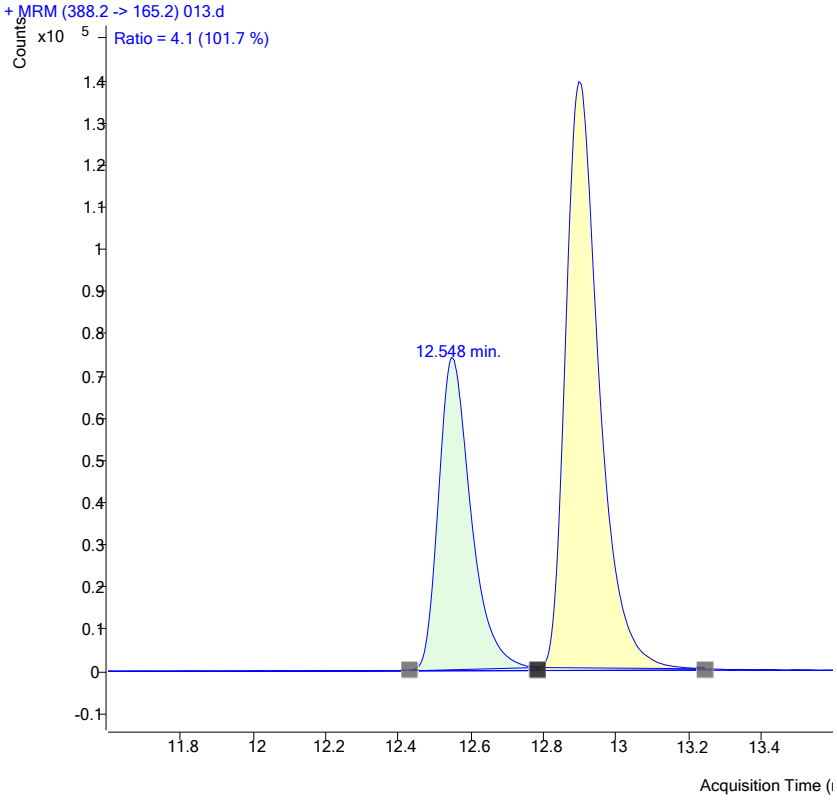
Calibration curve of pymetrozine.

Standard E-and Z-dimethomorph

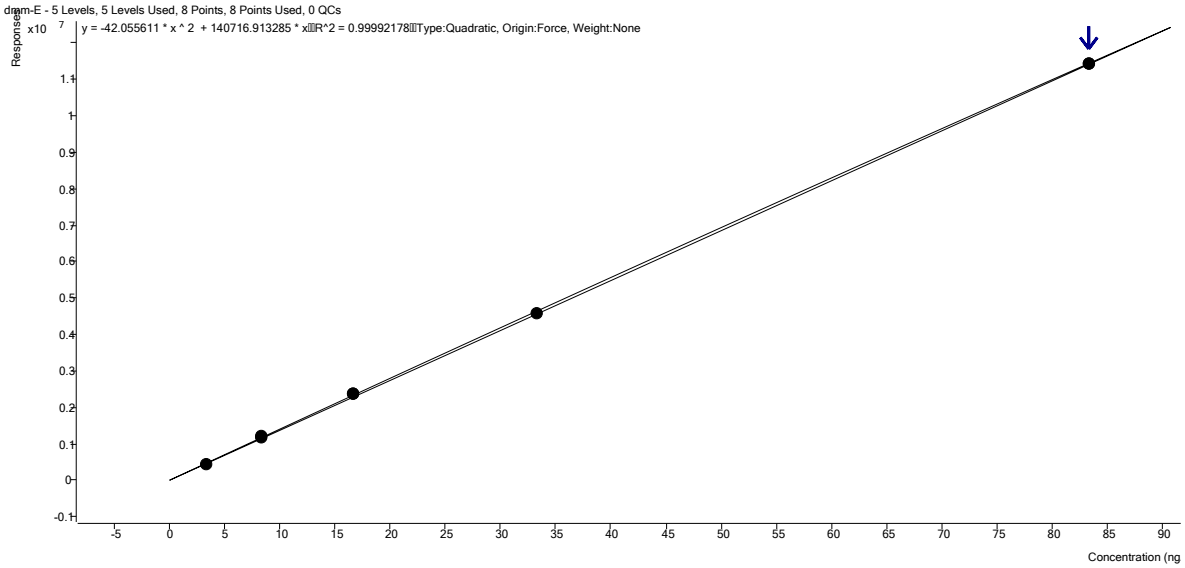
The total concentration of the standard dimethomorph is 250 ng/ml: 83.33 ng/ml E-dimethomorph and 166.66 ng/ml Z-dimethomorph.



Chromatogram of a 83.33 ng/ml E-dimethomorph standard (388.2---301.1); quantifier.

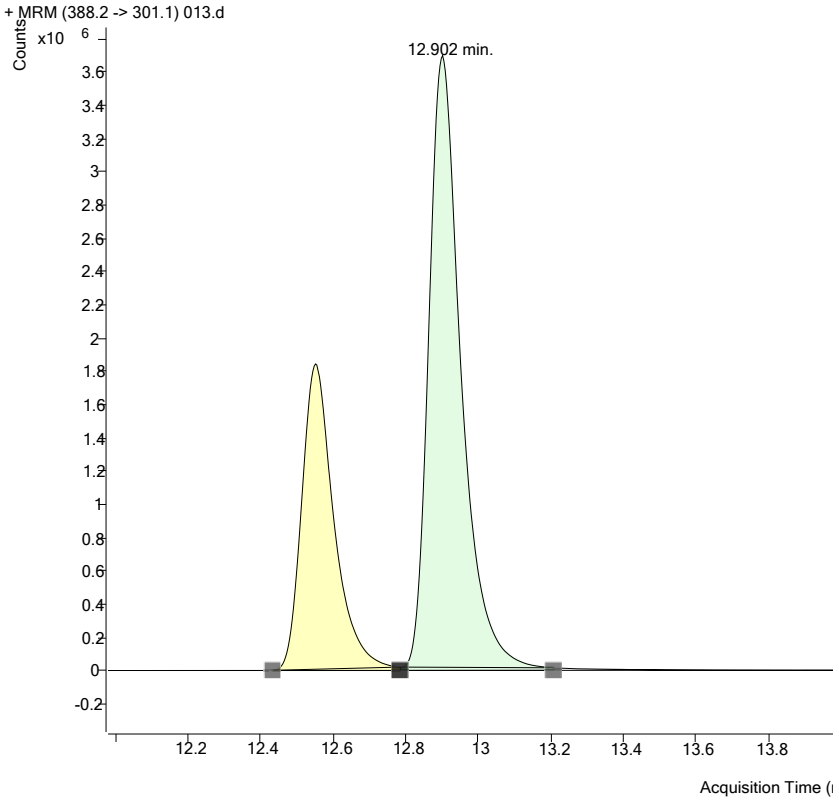


Chromatogram of a 83.33 ng/ml E-dimethomorph standard (388.2---165.2); qualifier.

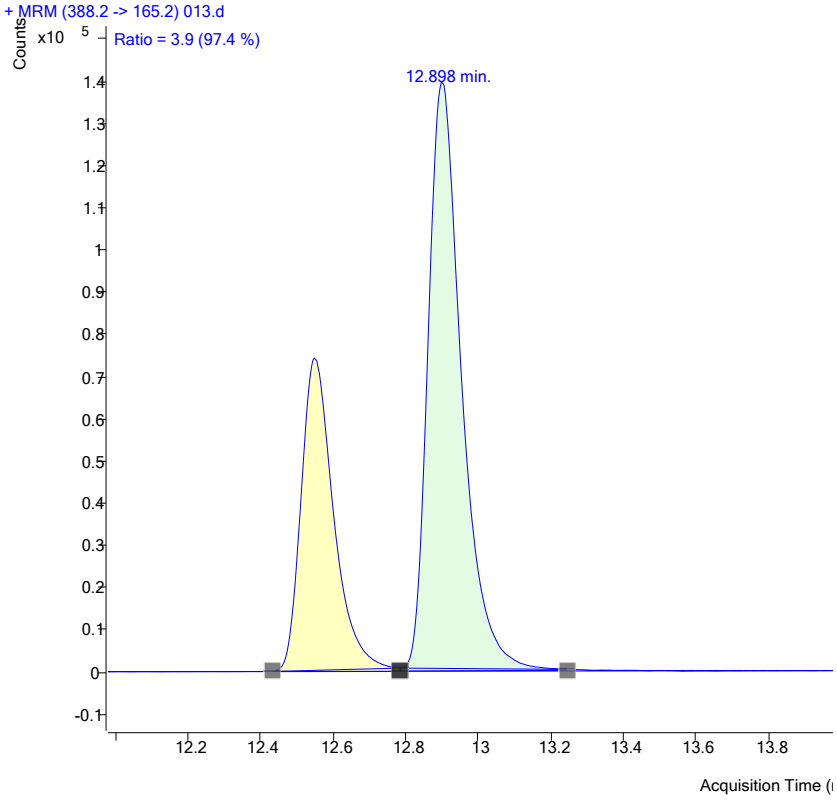


Calibration curve of E-dimethomorph.

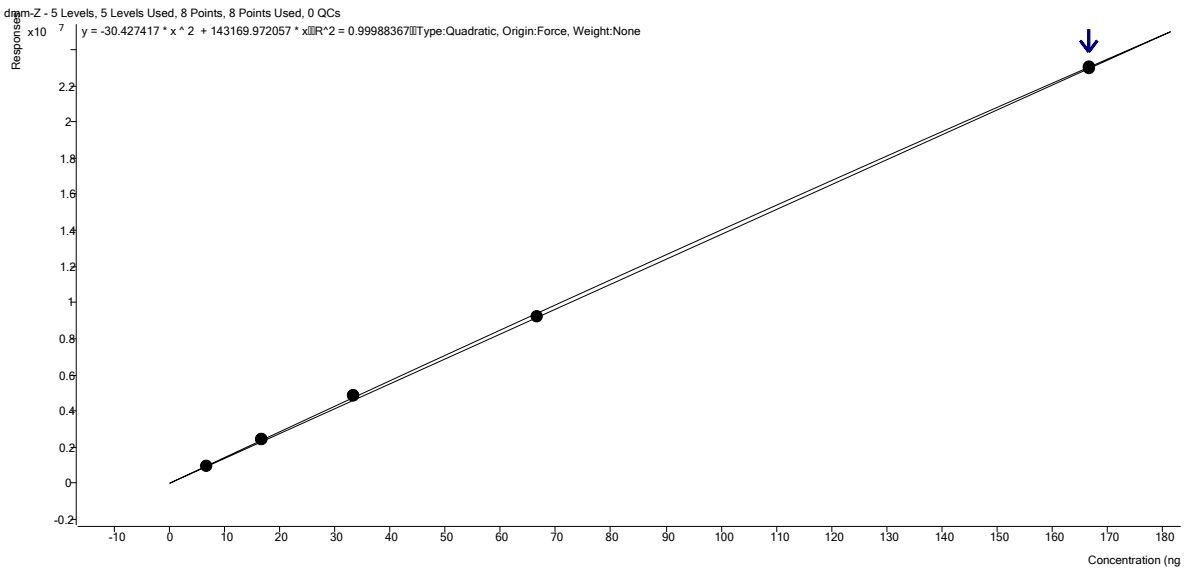
Z-dimethomorph



Chromatogram of a 166.66 ng/ml Z-dimethomorph standard (388.2---301.1); quantifier.



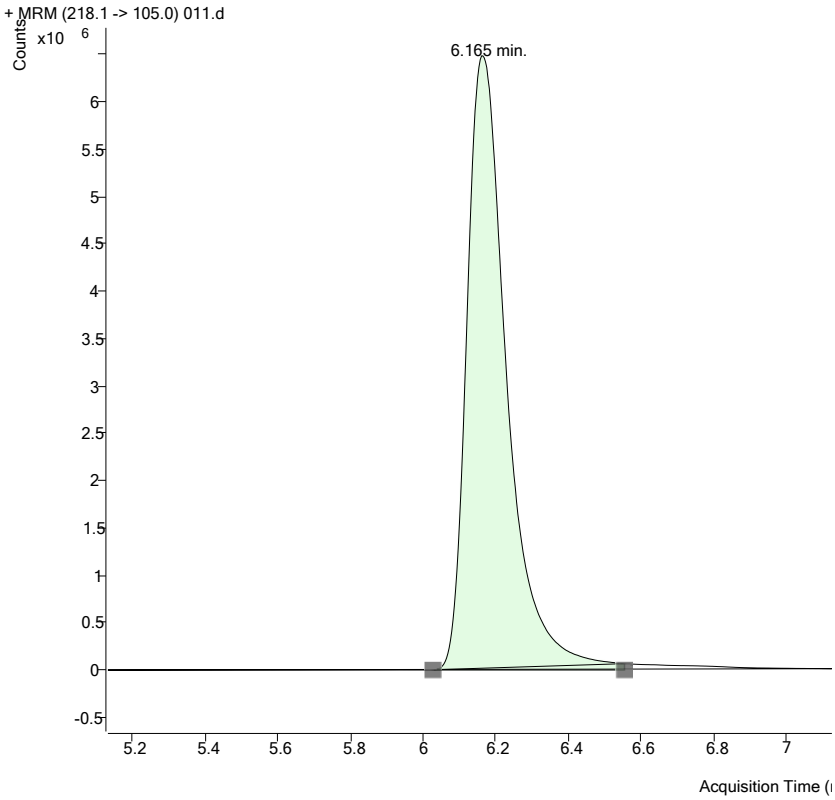
Chromatogram of a 166.66 ng/ml Z-dimethomorph standard (388.2---301.1); qualifier.



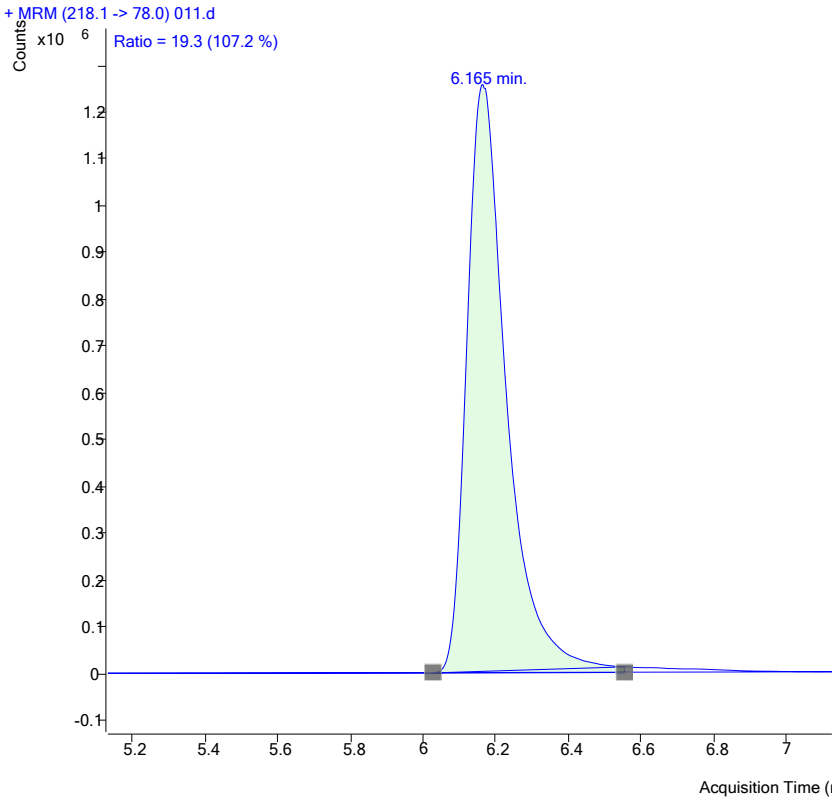
Calibration curve of Z-dimethomorph.

Chromatogram of a sample

Pymetrozine: measured concentration in LC-sample: 254.93 ng/ml



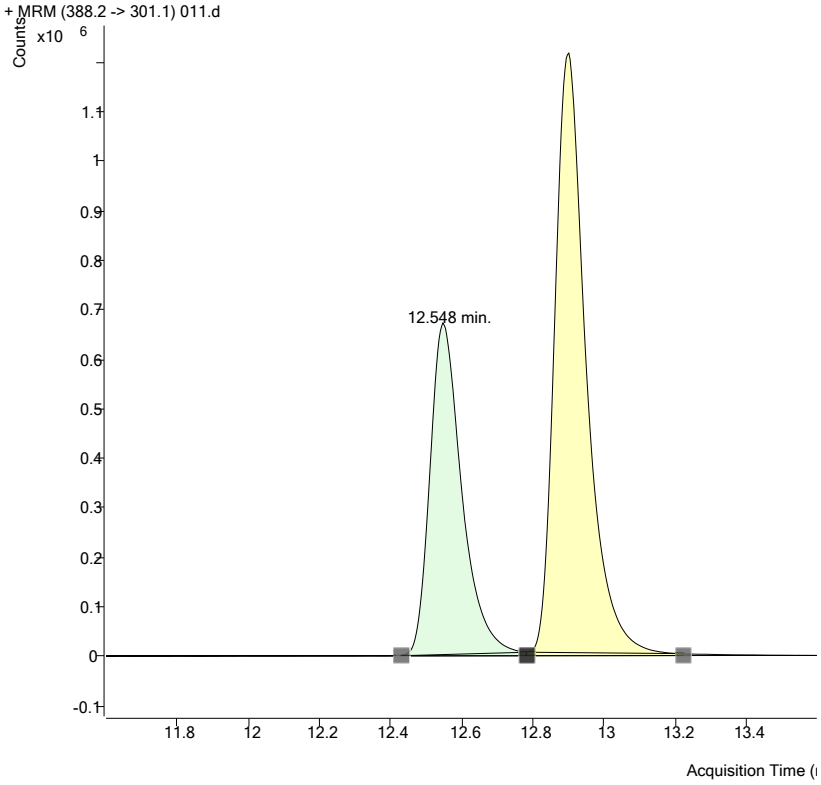
Chromatogram of sample D35 (10 times diluted) measured concentration 254.93 ng/ml pymetrozine standard (218.1---105.0); quantifier.



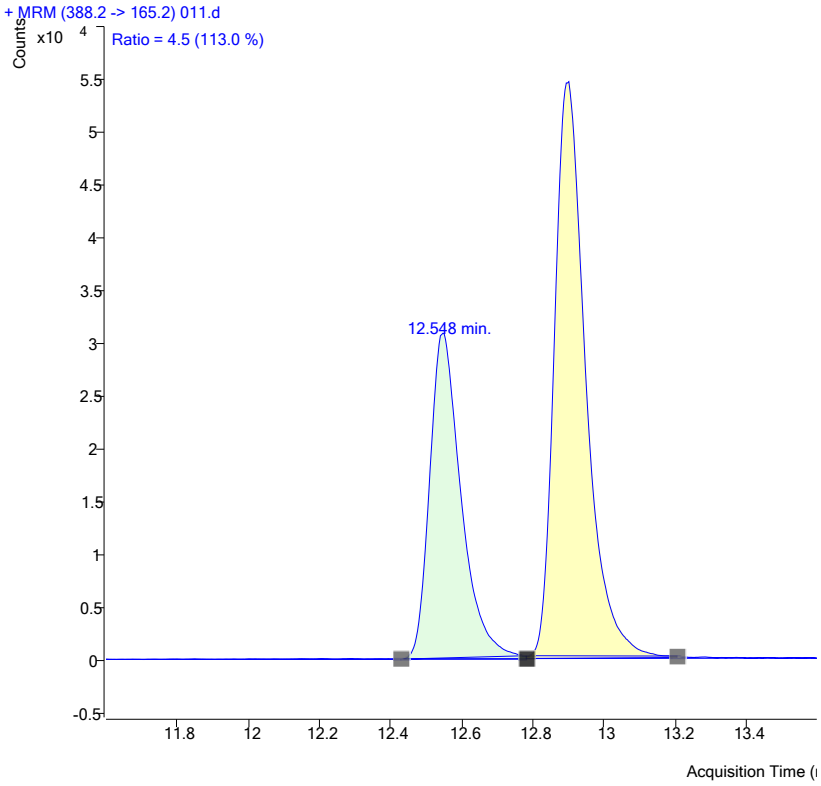
Chromatogram of sample D35 (10 times diluted) measured concentration 254.93 ng/ml pymetrozine standard (218.1---78.0); quantifier.

Chromatogram of a sample

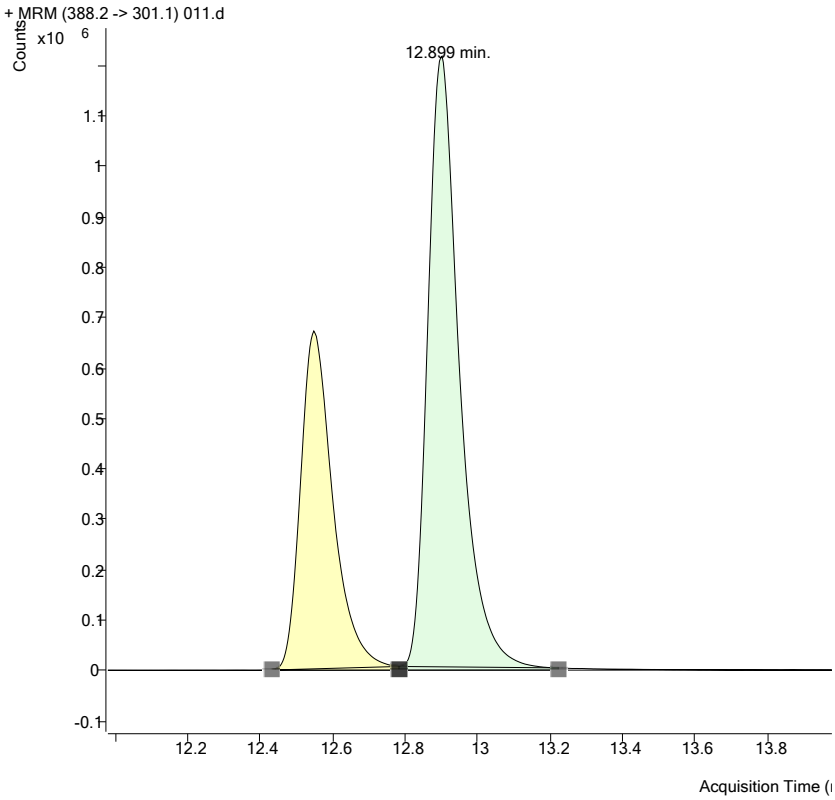
Dimethomorph: measured concentration in LC-sample (extract): 16.5663 ng/ml E-dimethomorph and 29.3448 ng/ml Z-methomorph.



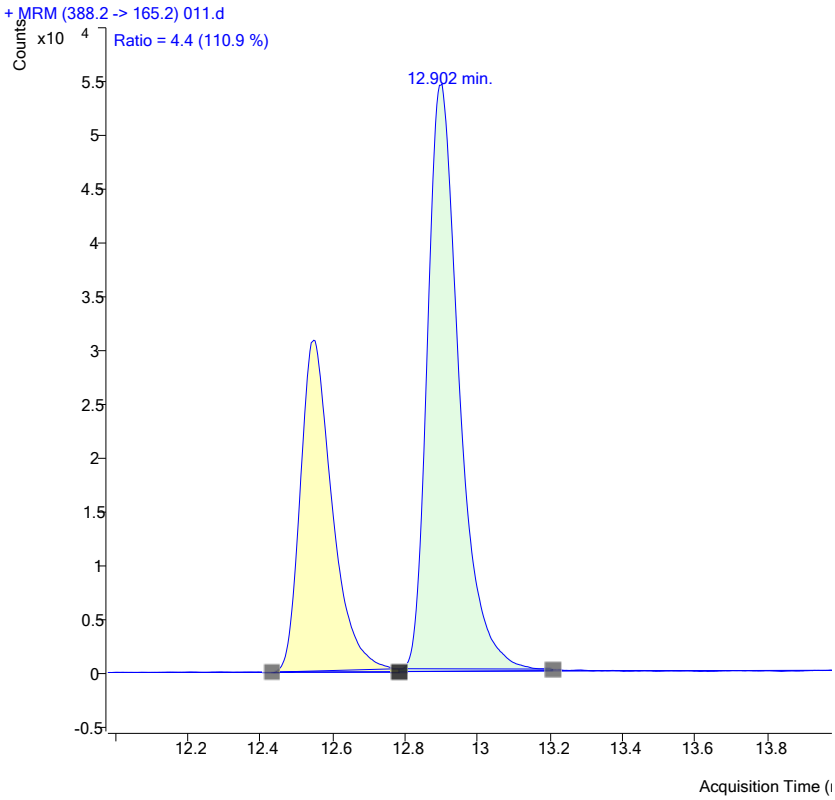
Chromatogram of sample D35 (10 times diluted) measured concentration 16.5663 ng/ml E-dimethomorph standard (388.1---301.1); qualifier.



Chromatogram of sample D35 (10 times diluted) measured concentration 16.5663 ng/ml E-dimethomorph standard (388.1---165.2); quantifier.



Chromatogram of sample D35 (10 times diluted) measured concentration 29.3448 ng/ml Z-dimethomorph standard (388.1---301.1); quantifier.



Chromatogram of sample D35 (10 times diluted) measured concentration 29.3448 ng/ml Z-dimethomorph standard (388.1---165.2); qualifier.

Annex 2 Detailed results of batch sorption experiments with clean stonewool

Table A2-1 *Results of sorption experiments with pymetrozine and Grotop stonewool. The buffer was added to samples 1-3 and not to sample 4.*

		nr of sample			
		1	2	3	4
mass of dry stonewool (g)		3.41	3.21	3.29	3.44
volume of $Ca(NO_3)_2$ solution during experiment (mL)		78	76	69	68
concentration (µg/L)	initial	71	71	80	79
	final	72	72	79	76
mass (µg)	in $Ca(NO_3)_2$ solution just before extraction with methanol	1.68	1.77	1.92	1.69
	extracted with methanol	1.67	1.83	1.97	1.80
sorption coefficient *K*	difference between initial and final concentrations	-0.13	-0.21	0.21	0.70
(L/kg) based on	methanol extraction	-0.05	0.29	0.21	0.43
recovery (%)		100	102	100	99

Table A2-2 *Results of sorption experiments with pymetrozine and Cultilene stonewool. The buffer was added to samples 1-3 and not to sample 4.*

		nr of sample			
		1	2	3	4
mass of dry stonewool (g)		3.19	3.61	3.20	3.21
volume of $Ca(NO_3)_2$ solution during experiment (mL)		70	73	69	66
concentration (µg/L)	initial	80	76	83	83
	final	77	74	79	83
mass (µg)	in $Ca(NO_3)_2$ solution just before extraction with methanol	1.43	1.58	1.44	1.68
	extracted with methanol	1.51	1.64	1.49	1.74
sorption coefficient *K*	difference between initial and final concentrations	0.97	0.56	0.94	0.04
(L/kg) based on	methanol extraction	0.32	0.23	0.18	0.24
recovery (%)		97	98	97	101

Table A2-3 *Results of sorption experiments with E-dimethomorph and Grotop stonewool. The buffer was added to samples 1-3 and not to sample 4.*

		nr of sample			
		1	2	3	4
mass of dry stonewool (g)		3.01	3.57	3.10	3.23
volume of $Ca(NO_3)_2$ solution during experiment (mL)		66	65	71	68
concentration (µg/L)	initial	22	19	21	19
	final	21	18	20	19
mass (µg)	in $Ca(NO_3)_2$ solution just before extraction with methanol	0.35	0.37	0.41	0.39
	extracted with methanol	0.41	0.50	0.48	0.45
sorption coefficient *K*	difference between initial and final concentrations	0.47	0.43	0.50	0.09
(L/kg) based on	methanol extraction	0.85	1.93	1.09	1.07
recovery (%)		102	108	103	105

Table A2-4 *Results of sorption experiments with E-dimethomorph and Cultilene stonewool. The buffer was added to samples 1-3 and not to sample 4.*

		nr of sample			
		1	2	3	4
mass of dry stonewool (g)		3.18	3.53	3.73	3.31
volume of $Ca(NO_3)_2$ solution during experiment (mL)		68	70	70	70
concentration (µg/L)	initial	18	19	20	21
	final	18	19	21	
mass (µg)	in $Ca(NO_3)_2$ solution just before extraction with methanol	0.37	0.40	0.41	
	extracted with methanol	0.44	0.45	0.50	
sorption coefficient *K*	difference between initial and final concentrations	-0.34	-0.25	-0.62	
(L/kg) based on	methanol extraction	1.16	0.72	1.13	
recovery (%)		107	105	110	

Table A2-5 *Results of sorption experiments with Z-dimethomorph and Grotop stonewool. The buffer was added to samples 1-3 and not to sample 4.*

		nr of sample			
		1	2	3	4
mass of dry stonewool (g)		3.01	3.57	3.10	3.23
volume of $Ca(NO_3)_2$ solution during experiment (mL)		66	65	71	68
concentration (µg/L)	initial	56	49	54	49
	final	51	43	49	45
mass (µg)	in $Ca(NO_3)_2$ solution just before extraction with methanol	0.85	0.88	0.99	0.91
	extracted with methanol	1.00	1.15	1.26	1.12
sorption coefficient *K*	difference between initial and final concentrations	2.20	2.24	2.54	2.25
(L/kg) based on	methanol extraction	0.99	1.74	1.78	1.42
recovery (%)		95	98	97	96

Table A2-6 *Results of sorption experiments with Z-dimethomorph and Cultilene stonewool. The buffer was added to samples 1-3 and not to sample 4.*

		nr of sample			
		1	2	3	4
mass of dry stonewool (g)		3.18	3.53	3.73	3.31
volume of $Ca(NO_3)_2$ solution during experiment (mL)		68	70	70	70
concentration (µg/L)	initial	47	50	52	
	final	43	47	48	
mass (µg)	in $Ca(NO_3)_2$ solution just before extraction with methanol	0.87	0.98	0.97	
	extracted with methanol	1.01	1.13	1.13	
sorption coefficient *K*	difference between initial and final concentrations	2.05	1.18	1.50	
(L/kg) based on	methanol extraction	0.98	0.88	0.90	
recovery (%)		95	99	97	

Annex 3 Detailed results of batch sorption experiments with pipe materials and stonewool foil

Table A3-1 *Results of sorption experiments with pymetrozine and TP material.*

		nr of sample			
		1	2	3	4
mass of TP material (g)		2.62	2.71	2.56	2.71
volume of $Ca(NO_3)_2$ solution during experiment (mL)		4.98	5.00	5.00	4.99
concentration (µg/L)	initial	102	102	102	102
	final	104	105	112	107
mass (ng)	in $Ca(NO_3)_2$ solution just before extraction with methanol	47	46	43	41
	extracted with methanol	49	50	40	41
sorption coefficient *K*	difference between initial and final concentrations	-0.04	-0.05	-0.17	-0.09
(L/kg) based on	methanol extraction	0.01	0.01	-0.01	0.00
recovery (%)		102	103	109	105

Table A3-2 *Results of sorption experiments with pymetrozine and DP material.*

		nr of sample			
		1	2	3	4
mass of DP material (g)		2.01	2.00	2.01	2.03
volume of $Ca(NO_3)_2$ solution during experiment (mL)		5.00	4.99	4.85	4.99
concentration (µg/L)	initial	102	102	102	102
	final	103	105	103	105
mass (ng)	in $Ca(NO_3)_2$ solution just before extraction with methanol	54	78	75	52
	extracted with methanol	61	86	74	52
sorption coefficient *K*	difference between initial and final concentrations	-0.02	-0.07	-0.02	-0.08
(L/kg) based on	methanol extraction	0.03	0.04	-0.01	0.00
recovery (%)		102	105	101	104

Table A3-3 *Results of sorption experiments with pymetrozine and SF material.*

		nr of sample			
		1	2	3	4
mass of SF material (g)		1.05	1.01	1.07	1.02
volume of $Ca(NO_3)_2$ solution during experiment (mL)		8.05	8.00	8.02	8.04
concentration (µg/L)	initial	104	104	104	104
	final	103	108	106	110
mass (ng)	in $Ca(NO_3)_2$ solution just before extraction with methanol	227	161	171	152
	extracted with methanol	204	162	152	155
sorption coefficient *K*	difference between initial and final concentrations	0.11	-0.24	-0.12	-0.40
(L/kg) based on	methanol extraction	-0.22	0.00	-0.17	0.03
recovery (%)		96	103	99	106

Table A3-4 *Results of sorption experiments with E-dimethomorph and TP material.*

		nr of sample			
		1	2	3	4
mass of TP material (g)		2.62	2.71	2.56	2.71
volume of $Ca(NO_3)_2$ solution during experiment (mL)		4.98	5.00	5.00	4.99
concentration (µg/L)	initial	35	35	35	35
	final	32	33	32	34
mass (ng)	in $Ca(NO_3)_2$ solution just before extraction with methanol	15	15	12	13
	extracted with methanol	20	21	18	20
sorption coefficient *K*	difference between initial and final concentrations	0.12	0.09	0.19	0.02
(L/kg) based on	methanol extraction	0.07	0.07	0.08	0.07
recovery (%)		97	99	95	103

Table A3-5 *Results of sorption experiments with E-dimethomorph and DP material.*

		nr of sample			
		1	2	3	4
mass of DP material (g)		2.01	2.00	2.01	2.03
volume of $Ca(NO_3)_2$ solution during experiment (mL)		5.00	4.99	4.85	4.99
concentration (µg/L)	initial	35	35	35	35
	final	32	31	30	31
mass (ng)	in $Ca(NO_3)_2$ solution just before extraction with methanol	17	23	22	15
	extracted with methanol	27	33	31	23
sorption coefficient *K*	difference between initial and final concentrations	0.17	0.28	0.34	0.25
(L/kg) based on	methanol extraction	0.15	0.16	0.14	0.11
recovery (%)		99	96	93	95

Table A3-6 *Results of sorption experiments with E-dimethomorph and SF material.*

		nr of sample			
		1	2	3	4
mass of SF material (g)		1.05	1.01	1.07	1.02
volume of $Ca(NO_3)_2$ solution during experiment (mL)		8.05	8.00	8.02	8.04
concentration (µg/L)	initial	39	39	39	39
	final	32	32	33	33
mass (ng)	in $Ca(NO_3)_2$ solution just before extraction with methanol	71	49	53	46
	extracted with methanol	74	55	58	52
sorption coefficient *K*	difference between initial and final concentrations	1.65	1.62	1.39	1.31
(L/kg) based on	methanol extraction	0.09	0.21	0.14	0.18
recovery (%)		87	88	88	89

Table A3-7 *Results of sorption experiments with Z-dimethomorph and TP material.*

		nr of sample			
		1	2	3	4
mass of TP material (g)		2.62	2.71	2.56	2.71
volume of $Ca(NO_3)_2$ solution during experiment (mL)		4.98	5.00	5.00	4.99
concentration (µg/L)	initial	54	54	54	54
	final	47	49	46	49
mass (ng)	in $Ca(NO_3)_2$ solution just before extraction with methanol	21	22	18	18
	extracted with methanol	36	37	34	32
sorption coefficient *K*	difference between initial and final concentrations	0.28	0.20	0.34	0.22
(L/kg) based on	methanol extraction	0.12	0.12	0.14	0.11
recovery (%)		93	96	91	95

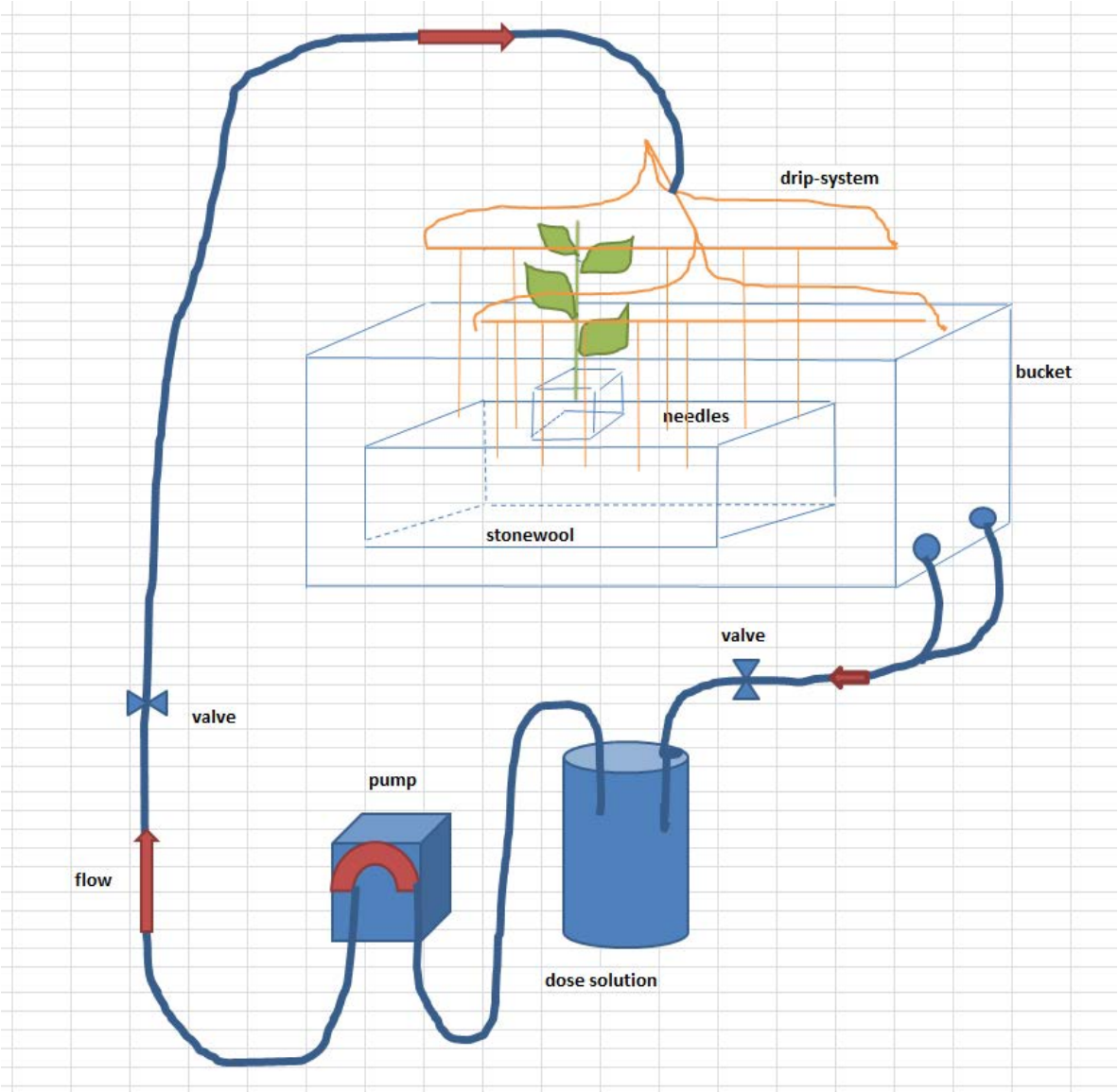
Table A3-8 *Results of sorption experiments with Z-dimethomorph and DP material.*

		nr of sample			
		1	2	3	4
mass of DP material (g)		2.01	2.00	2.01	2.03
volume of $Ca(NO_3)_2$ solution during experiment (mL)		5.00	4.99	4.85	4.99
concentration (µg/L)	initial	54	54	54	54
	final	49	47	46	47
mass (ng)	in $Ca(NO_3)_2$ solution just before extraction with methanol	26	35	33	23
	extracted with methanol	45	50	46	36
sorption coefficient *K*	difference between initial and final concentrations	0.28	0.38	0.45	0.37
(L/kg) based on	methanol extraction	0.19	0.16	0.14	0.14
recovery (%)		97	93	89	92

Table A3-9 *Results of sorption experiments with Z-dimethomorph and SF material.*

		nr of sample			
		1	2	3	4
mass of SF material (g)		1.05	1.01	1.07	1.02
volume of $Ca(NO_3)_2$ solution during experiment (mL)		8.05	8.00	8.02	8.04
concentration (µg/L)	initial	53	53	53	53
	final	47	45	46	46
mass (ng)	in $Ca(NO_3)_2$ solution just before extraction with methanol	103	68	74	63
	extracted with methanol	109	91	88	78
sorption coefficient *K*	difference between initial and final concentrations	1.01	1.37	1.16	1.26
(L/kg) based on	methanol extraction	0.13	0.51	0.28	0.31
recovery (%)		90	91	90	90

Annex 4 Schematic representation of the circulation systems of the mats with the plants



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