Retention and distribution of pesticides in planted filter microcosms designed for treatment of agricultural surface runoff

Andrii Butkovskyi [a], Yuying Jing [a], Hege Bergheim [b], Diana Lazar [c], Ksenia Gulyaeva [b], Sven Roar Odenmarck [b], Hans Ragnar Norli [b], Karolina M. Nowak [d], Anja Miltner [a], Matthias Kästner [a,*], Trine Eggen [b]

[a] UFZ - Helmholtz Centre for Environmental Research, Department of Environmental Biotechnology, Permoserstr. 15, 04318 Leipzig, Germany
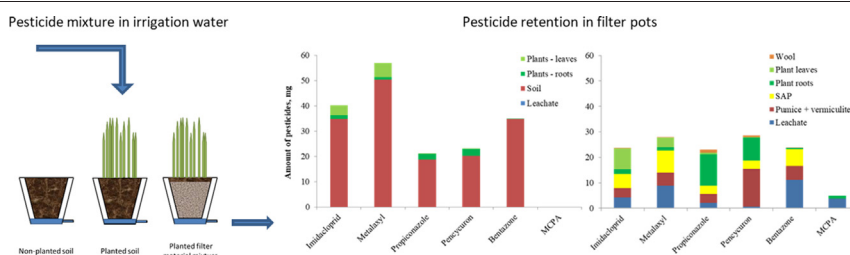[b] NIBIO Norwegian Institute of Bioeconomy Research, NIBIO, Fredrik A. Dahls vei 20, 1431 Ås, Norway
[c] National Institute for R&D on Isotopic and Molecular Technologies INCDTIM, 67-103 Donat, PO 5 Box 700, 400293 Cluj-Napoca, Romania
[d] Technische Universität Berlin, Institute of Biotechnology, Chair of Geobiotechnology, Ackerstraße 76, 13355 Berlin, Germany

HIGHLIGHTS

- Pesticide retention was shown in organic soil and various potential wetland filter materials.
- Water leaching occurs from all materials.
- Plants reduce leaching of water and pesticides by evapotranspiration with highest effect in organic soil.
- Water retention by super absorbent polymer accompanied by retention of dissolved pesticides
- Overall pesticide retention: organic soil > super absorbent polymer > pumice/ vermiculite

GRAPHICAL ABSTRACT

ABSTRACT

Pesticides in agricultural surface water runoff cause a major threat to freshwater systems. Installation of filter systems or constructed wetlands in areas of preferential run-off is a possible measure for pesticides abatement. To develop such systems, combinations of filter materials suitable for retention of both hydrophilic and hydrophobic organic pesticides were tested for pesticide removal in planted microcosms. The retention of six pesticides frequently detected in surface waters (bentazone, MCPA, metalaxyl, propiconazole, pencycuron, and imidacloprid) was evaluated in unplanted and planted pot experiments with novel bed material mixtures consisting of pumice, vermiculite, water super-absorbent polymer (SAP) for retention of ionic and water soluble pesticides, and synthetic hydrophobic wool for adsorption of hydrophobic pesticides. The novel materials were compared to soil with high organic matter content. The highest retention of the pesticides was observed in the soil, with a considerable translocation of pesticides into the plants, and low leaching potential, in particular for the hydrophobic compounds. However, due to the high retention of pesticides in soil, environmental risks related to their long term mobilization cannot be excluded. Mixtures of pumice and vermiculite with SAP resulted in high retention of i) water and ii) both hydrophilic and hydrophobic pesticides but with much lower leaching potential compared to the mineral systems without SAP. Mixtures of such materials may provide near natural treatment options in riparian strips and also for treatment of rainwater runoff without the need for water containment systems.

* Corresponding author.
E-mail address: matthias.kaestner@ufz.de (M. Kästner).

1. Introduction

Pesticides are substances that are used to enhance crop productivity and to reduce crop losses caused by pathogenic microorganisms, fungi, insects, weeds etc. (Aktar et al., 2009; Matthews, 2015). Their use in modern agriculture is inevitable to meet food requirements for the human population (Harlander, 2002; Hubert et al., 2010). However, pesticides are widely transferred in the environment and may cause negative effects on human health, ecosystem functions, and biodiversity (Goulson, 2014; Goulson et al., 2015; Hallmann et al., 2014; Whitehorn et al., 2012). Adverse effects on key species in surface water, soil, and sediments are of increasing concern (Bundschuh et al., 2014; Meffe and de Bustamante, 2014; Reichenberger et al., 2007).

Surface water runoff is one of the main pathways of pesticide discharge to the environment (Reichenberger et al., 2007; Riise et al., 2004; Sandin et al., 2018). Runoff from agricultural fields is the dominating process of freshwater contamination with global relevance (Lefrancq et al., 2017; Liess et al., 1999). It is estimated that up to 5% of the amount of pesticides applied may be lost via surface runoff (Vymazal and Březinová, 2015). Pesticides in subsurface runoff are often retained via sorption to soil particles and biodegradation, but their elimination from surface runoff is negligible, in particular after heavy rain events (Kladivko et al., 2001).

Pesticides often found in surface waters in Europe and U.S. are for example: i) the herbicides bentazone and MCPA, ii) the fungicides metalaxyl, propiconazole and pencycuron, and iii) the insecticide imidacloprid (Schreiner et al., 2016; Silva et al., 2019; Stenrød, 2015). These pesticides cover a wide range of physico-chemical properties (Table 1) (Lewis et al., 2016). They have often been detected above the EU drinking water limits in fresh and groundwater used for drinking water production, (0.1 µg L^{-1} for individual pesticide) (Hetland et al., 2014; Roseth, 2013). For example, in Norwegian surface waters, pesticide concentrations are sometimes high enough to exceed the Norwegian Environmental Risk Indicator for aquatic organisms (Stenrød, 2015). In addition, there are also indications that mixtures of pesticides exhibit higher toxicity at lower concentration (Lefrancq et al., 2013).
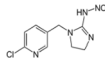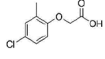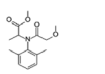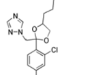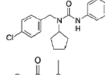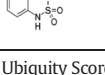
Options to prevent contamination of surface waters by pesticides from agricultural surface runoff are thus needed. Riparian strips are considered to be able to retain pesticide contaminations from agricultural fields, if they are properly organized (Arora et al., 2010; Cole et al., 2020). In general, near-natural technical solutions, such as subsurface drainage, vegetated ditches, and constructed wetlands are often used for treating pesticide containing water (Kladivko et al., 2001; Otto et al., 2016; Vymazal and Březinová, 2015). Physical retention is the main process which determines effectiveness of these measures for pesticide mitigation, resulting in low retention of highly water-soluble pesticides (Prosser et al., 2020; Reichenberger et al., 2007). Vegetated riparian strips, or buffer strips, are also frequently studied as a measure to decrease pesticide input to surface water from agricultural runoff (M. Boyd et al., 2003; Prosser et al., 2020). However, surface runoff following heavy rain events, which are the dominant driver for pesticide discharge, is poorly treated or retained (Lefrancq et al., 2017; Liess et al., 1999), in particular in soils with low porosity and a high potential for soil particle erosion with low water draining capacity. As a consequence, pesticides adsorbed to eroded soil particles and associated to dissolved organic matter (DOM) increase the pesticide load to the surface water bodies dramatically.

Measures to reduce pesticide emissions via agricultural surface runoff to surface waters should include retention of particle-sorbed as well as dissolved pesticides and their metabolites, preferably by a combination of sorbents and water retention. This would allow for retention times sufficiently long for microbial degradation of these pesticides, e.g. in the rhizosphere of wetlands or riparian strips, finally resulting in better removal of the pollutants. Solid media for pesticide sorption, filtration, and the establishment of plants that promote degradation of contaminants may include soil, gravel, carbonaceous materials, pumice, vermiculite, etc. (Dordio and Carvalho, 2013). Pumice and vermiculite are light-weight materials with high porosity and a high specific surface area that promote better aeration and biofilm formation as well as sorption of nutrients and pesticides. Pumice is a natural porous volcanic rock that has been used as a filter material in a field of water and wastewater treatment for adsorption of organic compounds and heavy metals (Çifçi and Meriç, 2016). Vermiculite is a clay mineral that has been used to promote root growth and enhance the cation exchange capacity of plant growth media (Abdelhakeem et al., 2016; Çifçi and Meriç, 2016). Both materials have been used in constructed wetlands, improving removal of COD, ammonium, organic dyes and pesticides (Dordio and Carvalho, 2013; Vymazal, 2013). In addition, hydrophobic wools and

Table 1
Properties of the studied pesticides according to Pesticide Properties DataBase (Lewis et al., 2016). However, there are inconsistencies with other data.

Active compound	Structure	Type	pKa	Water solubility, [mg L^{-1}]	log K_{ow} (at pH 7)	Potential for particle bound transport	GUS index[a]	Aerobic biodegradability DT_{50}, d[b]	Aqueous photolysis DT_{50}, d (at pH 7.0)	Hydrolysis, DT_{50}, d (at 20 °C, pH 7.0)
Imidacloprid		Insecticide	n.a. (no dissociation)	610	0.57	Medium	3.69	77–341	0.2	Stable
MCPA		Herbicide	3.73 (weak acid)	29,390	−0.8	Low	2.98	7–41	0.05	Stable
MCPA[c]			3.07	640	2.73					
Metalaxyl		Fungicide	n.a. (no dissociation)	8400	1.75	Low	2.84	33–42	Stable	106
Propiconazole		Fungicide	1.09 (very weak base)	150	3.72	Medium	1.58	26.6–115	Stable	53.5
Pencycuron		Fungicide	n.a. (no dissociation)	0.3	4.7	High	0.49	43.7–175	Stable	156
Bentazon		Herbicide	3.51 (weak acid)	7112	−0.46	Low	1.95	8–35	4	Stable
Bentazone[d]			3.3	500	2.34					

[a] Groundwater Ubiquity Score index; predicts pesticides leachability according to its Koc and DT_{50} (half-life time).
[b] DT_{50} range according to EU dossier lab studies in the PPDB.
[c] Vergili and Barlas (2009).
[d] Liu et al. (2011).

fibers that are well known materials for the retention of hydrophobic chemicals can be added to the filter medium in order to retain highly hydrophobic compounds (Carmody et al., 2007).

In contrast to carbonaceous and mineral filter materials, which retain dominantly hydrophobic pesticides based on sorption, materials for improved retention of ionic and highly water soluble pesticides and their metabolites are rarely available, in particular those for enhancing subsequent biodegradation by microbial communities. One innovative option is the use of superabsorbent polymers (SAP) that were developed to improve the water holding capacity of agricultural soils in arid climates (Hüttermann et al., 2009). SAP are natural or synthetic cross-linked hydrophilic polymers that form hydrogels; they can absorb and retain up to 100 times more aqueous solutions than their own weight (Zohuriaan and Kabiri, 2008). The unique properties of hydrogels, such as swelling ability and partial hydrophilicity, make these polymers suitable for removing a wide range of pollutants, including heavy metals and organic compounds with polar or ionic functional groups (for review see Khan and Lo, 2016). In addition, SAP were used in wastewater treatment to remove pollutants (mostly dyes) by adsorption (Dhiman et al., 2015; Fosso-Kankeu et al., 2015). Presumably, SAP can sorb pesticides in aqueous solution, and when SAP are applied in constructed wetlands (CW), they will not only support the growth of plants but also enhance the retention of water and pesticides. These materials or smart combinations of them may provide options for runoff filters, tree infiltration ditches, or the construction of `wetland´ conditions without the need of a built containment or for retention ditches within riparian strips in order to increase the buffering and retention capacities.

Therefore, the aim of this study was to test combinations of filter materials suitable for retention and elimination of both hydrophilic and hydrophobic organic pesticides as an option to improve pesticide removal. The retention of commercially available formulations of six pesticides (bentazone, MCPA, metalaxyl, propiconazole, pencycuron, and imidacloprid) was investigated in pot experiments with various bed materials. The pesticides were selected based on different physico-chemical properties (Table 1) and their frequent detection in the environment. The combined novel filter bed materials included pumice, vermiculite, SAP (for retention of water and ionic and water soluble pesticides), and synthetic hydrophobic wool (for sorption of lipophilic pesticides) and were compared to soil with high organic matter content. For comparison, dissipation and distribution of pesticides was also studied in unplanted soil microcosms to test for the effect of plants. Pesticide retention and elimination was determined by regular sampling of leachates; pesticide distribution in plants and filter materials after continuous application of pesticides for 4 weeks.

2. Materials and methods

2.1. Chemicals and filter materials

Commercial pesticides used as pesticide formulations were purchased from Felleskjøpet (Ås, Norway) and included Confidor WG70 (active compound: imidacloprid, 700 g L^{-1}), Bumper 25EC (propiconazole, 250 g L^{-1}), Monceren FS250 (pencycuron, 250 g L^{-1}), MCPA 750 (MCPA, 750 g L^{-1}), Basagran S6 (bentazone, 870 g L^{-1}), and Apron XL (metalaxyl M, 339 g L^{-1}). For standard solutions, imidacloprid, metalaxyl, propiconazole, bentazon-d6 and MCPA were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Imidachloprid-d4, metribuzin, pencycuron, and bentazone were purchased from Merck (Darmstadt, Germany). Purity of all standards was 99.5% or higher except for bentazone-d6 (98%). Stock solutions (1.0 mg mL^{-1}) were prepared in acetonitrile and stored at −20 °C. For preparation of working solutions, the stock solutions were further diluted with acetonitrile as appropriate.

Soil (Green Viking growth medium for vegetables, 23% total organic carbon [TOC]) was purchased from Felleskjøpet (Ås, Norway), pumice (particle size 4–8 mm) was obtained from Bergknapp (Sandnes, Norway), vermiculite (particle size 2–4 mm) from Pull Rhenen (the Netherlands), SAP Stockosorb medium 660 from Evonik GmbH (Essen, Germany), and synthetic hydrophobic wool "Deurex Pure" from Deurex (Elsteraue, Germany). To prepare pumice:vermiculite:SAP mixture (dry weight ratio 94:5:1), dry vermiculite and pumice were blended in a cement mixer; afterwards dry SAP was added in pre-calculated amounts to each pot and mixed manually. Hydrophobic wool was added to the respective pots (30 g per each pot).

2.2. Sorbent characterization

Specific surface area of the materials was analyzed and the details are provided in the SI section. Soil pH, loss on ignition (LOI) and cation exchange capacity (CEC) were measured in commercial service laboratory according to standard methods (ASTM D4972, EN 12879 and ISO 13536, respectively). Total organic carbon was calculated from loss of ignition (LOI).
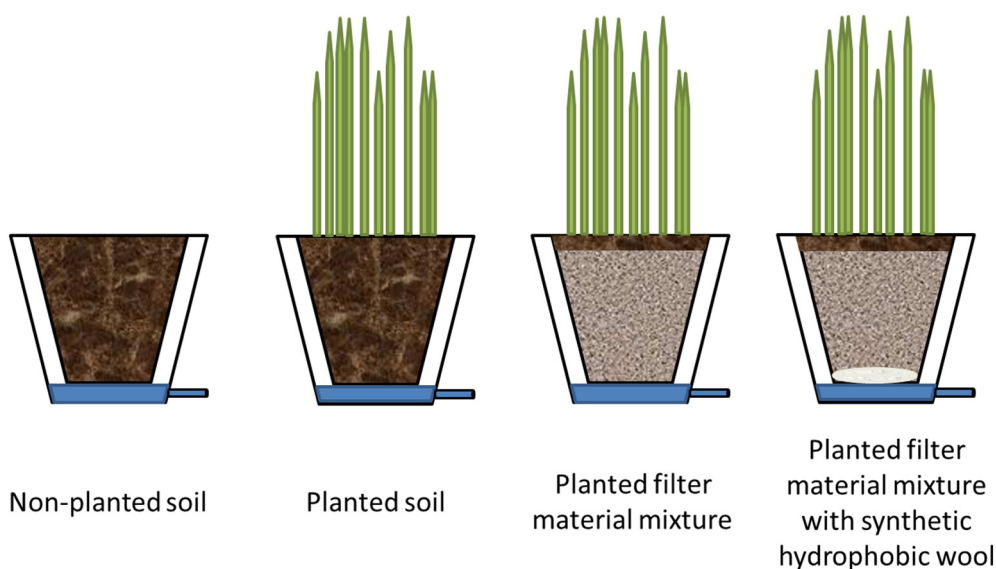
2.3. Experimental setup

The experiments were performed in Kick-Brauckmann plant culture pots (10-L; Stoma, Siegburg, Germany) that consist of an inner part (d = 22 cm) with an opening in the bottom and an outer part (d = 23.5 cm) with a tube for drainage of leachate.

On order to screen the efficiency of the filter materials in pesticide retention, the following treatments were performed in duplicates: non-planted soil, planted soil, planted filter material mixture, and planted filter material mixture with addition of hydrophobic wool (Fig. 1). The hydrophobic wool (30 g) was placed as a separate layer at the bottom of the inner pots and held in place with a metal grid. In pots with planted filter material mixture, with and without wool addition, a thin layer of soil (ca. 1–2 cm) was spread at the bottom and the top of the inner pot in order to provide optimal conditions for germination of seeds. In all planted treatments, seeds of *Phalaris arundinacea* sp. *Lara* (~24.5 mg seeds/pot which corresponds to 34 seeds/pot and 1.6 kg seeds/ha) were sown in the top soil layer. *P. arundinacea* was selected for this study because it is endemic in Norway and it is a fast-growing perennial bunchgrass with an early season growth and a wide physiological tolerance. It is also reported to promote aromatic compound degrading microorganisms in its rhizosphere (Vymazal, 2013).

The experiment was performed in a greenhouse at 23 °C with artificial illumination (Osram HQI-BT 400 W D Daylight E40, 16/8 h daylight/night cycle) in order to provide sufficient day light over the entire sampling period in autumn and winter 2018. The planted pots were irrigated daily with tap water and fertilized every third day with a commercial fertilizer solution (1.8‰ conductivity, Calcinit (N:Ca = 15.5:19) and Kristalon-plus (N:P:K = 7.9:3:26.5) from Yara (Porsgrunn, Norway). Prior to pesticide exposure, irrigation of the planted pots was adjusted to the water demand. Pots with soil were irrigated to keep the soil moisture near water holding capacity (WHC$_{max}$: 60%). The total amount of water added to planted pots was 800 mL d^{-1}; in the 1st week after the start of pesticide exposure it was increased to 1200 mL d^{-1} due to the high evapotranspiration rates of the plants. The non-planted soil was kept wet by irrigation with tap water without fertilizer at 300 mL d^{-1}.

Pesticides were added to the pots when the grass reached a stem length of approximately 40 cm. Planted pots were irrigated daily by adding 1.200 mL d^{-1} pesticide mixture with 1.67 mg L^{-1} of each active substance. In non-planted pots, the water supply was 300 mL d^{-1} with pesticide concentrations of 6.67 mg L^{-1}, ensuring the same pesticide load to each pot (2 mg d^{-1}). This is a high load compared to the field conditions, and it was chosen to ensure precise detection and quantification of all pesticides under study even after substantial elimination.

Leachates were collected from the outer pots into glass bottles every day before the new irrigation event. The volume of leachate from each

Fig. 1. Experimental setup of filter pots. Test soil matrix was organic soil material derived from compost. Filter material mixture comprise pumice, vermiculite, superabsorbent polymer, and hydrophobic woll; for more details see text.

pot was registered. After 4 weeks of pesticide exposure, the experiment was terminated and solid samples (soil, filter materials, roots and leaves) were collected. It was not possible to separate pumice and vermiculite; therefore, these sorbents were analyzed as a mixture. Dry weight was determined for soil and plant materials by drying them at 105 °C for 2 h. Liquid and solid samples were preserved at −20 °C prior to pesticide analysis. Each sample containing pesticide mixture was analyzed in triplicate.

2.4. Pesticide analysis

Daily leachate samples from seven consecutive days were pooled and stored at 4 °C to obtain weekly samples. Samples with high concentration of pesticides were diluted with milliQ water in order to fit the calibration range. Pure LC-MS grade methanol was added to the diluted samples at a 1:4 ratio. 50 μL of a mixture of isotopically labelled internal standards (imidacloprid-d4 and bentazon-d6, 2 mg L^{-1} each) were added to 1 mL of the diluted samples. The samples were rigorously mixed and filtered through a 0.2 μm filter to sample vials prior to direct injection into HPLC. Three subsamples were analyzed in order to evaluate the instrument precision.

Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) extraction of pesticides from solid samples was performed. Plant material was dried at 40 °C overnight prior to the extraction procedure. Pesticides from the filter materials were extracted without pre-drying. All samples were homogenized before extraction. Appropriate amounts of solid samples (leaves, roots, hydrophobic wool – 2 g, roots – 1 g, soil, pumice + vermiculite (not separated), SAP – 5 g, hydrophobic wool – 2 g) were amended with 10 mL of Milli-Q water and 10 mL of LC-MS grade acetonitrile. Samples were then extracted on a Heidolph Reax 2 Rotator (Merk, Darmstad, Germany) for 30 min at speed 6. Supelco salt mixture (citrate extraction tube) was added to achieve phase separation and the samples were shaken again vigorously in the rotator (20 min, speed 6). Extracted samples were then centrifuged (5 min, 3000 rpm), and the top acetonitrile layer was collected for analysis. Concentrated extracts were diluted with pure LC-MS grade acetonitrile to fit the calibration curve. Pesticides trapped in SAP were extracted from 5 g samples of wet SAP in a similar way and the concentrations were corrected by the average water absorption capacity of SAP in the pots of about 70 g H$_2$O/g SAP, which corresponds to 1.4 g dry weight per 100 g wet weight. The maximum water holding capacity of the SAP is up to 200 g of absorbed distilled water per gram of SAP (dw).

Pesticides in water and extracts from solid samples were analyzed using Alliance 2695 HPLC-system (Waters Corp., Milford, MA, USA) with a Micromass Quattro Ultima PT triple quadrupole mass spectrometer (Micromass, Manchester, UK) equipped with an electrospray interface. A Phenomenex Gemini® 3 μm C$_{18}$ LC Column (110 Å, 100 × 2 mm), was used for LC separation. The column oven temperature was 30 °C, the flow rate was 0.3 mL min^{-1}, and the injection volume was 5 μL. Methanol and water (Milli-Q) with 5 mM formic acid were used as mobile phases. Methanol was linearly increased from 10% to 95% within 5 min, and held for 6 min, finally brought back to 10% and held for 4 min until the next injection. The instrumental parameters are shown in Table S1. Pesticide standard mixtures with concentrations ranging between 0.02 and 1 mg l^{-1} were analyzed with each batch of LC-MS samples for calibration. Data acquisition and evaluation were performed with the MassLynx 4.0 software. The Limit of Quantification (LOQ) was <0.02 mg L^{-1}, 0.1 mg kg^{-1} and 0.25 mg kg^{-1} for water, soil and plant samples, respectively. Recoveries ranged between 85% and 127% (Table S2).

2.5. Calculations

The details of the calculations of the concentrations in each compartment of the filter system (soil, SAP, pumice and vermiculite, plant leaves and roots) as well as the total amounts retained in the pots are described in detail in the SI Section S.3. Mean values of the analyses were calculated with standard deviations or deviations from the means depending on the sampling regime as indicated for the respective analyses.

3. Results and discussion

3.1. Pesticides concentrations in leachates, retention, and elimination

The weekly time course of pesticide concentrations in leachate samples from the pots are shown in Fig. 2. The highest leaching potential was observed for bentazone and metalaxyl in all pots (Gluhar et al., 2019; Hiller et al., 2010; Morton et al., 2020). Concentrations of the other pesticides in the leachates from unplanted soil pots were either below (imidacloprid, propiconazole, pencycuron) or slightly above the LOQs (metalaxyl, MCPA) in the first week of pesticide exposure indicating high retention and transformation potential of soil with high organic matter (TOC 23%) even for highly mobile compounds,
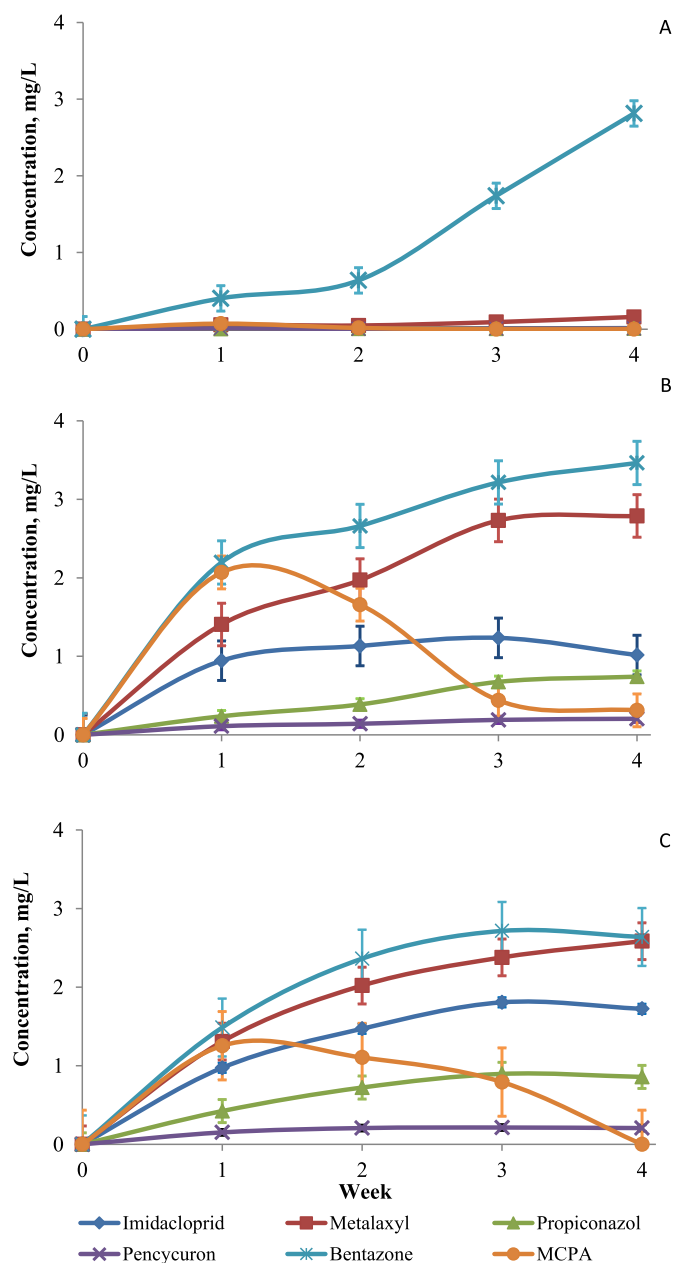
Fig. 2. Comparison of pesticide leaching from irrigated pots with non-planted soil (A), planted filter material with (B) and without (C) hydrophobic wool. Mean concentrations for duplicates are shown, for details see Materials and methods section.

such as metalaxyl, MCPA and imidacloprid (Fig. 2A). In other words, in soil the highest potential for retention and elimination was observed for pencycuron, followed by propiconazole and imidacloprid. The retention and elimination in planted filter materials can be attributed to uptake by plants, adsorption to filter materials or degradation (Stottmeister et al., 2003). Adsorption and plant uptake presumably accounted for the most of reduction of pesticide concentrations. In planted soil pots, no leachates could be collected due to the high evapotranspiration of water by the plants, therefore no pesticide analyses were performed. Plants thus contribute to the reduction of pesticide leaching but to an increase in concentrations within the pots at the same time. Therefore, we have to consider leachate concentrations as net effects of (1) enrichment due to evapotranspiration, (2) sorption/desorption, (3) microbial degradation and (4) downward movement of water in the pots incl. chromatographic effects.

In contrast to organic soil, all pesticides were found in the effluents of the pots with filter materials at substantial concentrations (Fig. 2B ad C). Concentrations of the more soluble and hydrophilic compounds bentazone, MCPA, metalaxyl and imidacloprid were in a similar range in the leachate collected after the first week of pesticide exposure, and higher than the concentrations of the hydrophobic pesticides propiconazole and pencycuron. For all pesticides, except for MCPA, there was an increase in concentrations during the first three weeks of exposure, presumably caused by saturation of the sorption sites. After 3 weeks, the elimination potential was large enough to compensate this increase presumably by microbial degradation of some compounds and a slight decline of the concentrations followed in the fourth week. In case of MCPA, this adaptation process seems to have been much faster.

The lower leaching of pesticides in soil is presumably attributed to its much higher TOC content compared to the mineral filter materials. Sorption of imidacloprid, metalaxyl and MCPA strongly depends on the soil organic carbon content (Cox et al., 1998; Fernandes et al., 2003; Nemeth-Konda et al., 2002; Sørensen et al., 2006). However, pH rather than TOC, is the main factor that controls bentazone and MCPA adsorption to soil (Boivin et al., 2005). This pesticide is a weak acid (pKa = 3.69), which is likely to be repelled from negatively charged soil particles (pH = 6.3) at near-neutral pH. It explains the different behavior of bentazone in the soil with high organic matter content compared to that of the other pesticides.

The leaching potential of the pesticides from filter materials after the first week of exposure followed the order bentazone > MCPA > metalaxyl > imidacloprid > propiconazole > pencycuron. The leaching potential thus decreased with increasing log K_{ow} and the potential for sorption to particles of these pesticides, but not with their Groundwater Ubiquity Score (GUS) index (Table 1). The GUS index predicts the leachability of the pesticides according to their K_{oc} (organic carbon-water partitioning coefficient) and DT_{50} (half-life time) and indicates the intrinsic leaching of pesticides in the water-soil system (Gustafson, 1989). The GUS index of imidacloprid (3.69) is much higher compared to the GUS index of bentazone (1.95), however, lower concentrations of imidacloprid were observed in the effluents of the pots with both soil and filter materials. These results indicate that the GUS index does not always correlate with the real mobility of pesticides. As described above, the weak acid bentazone may be repelled from soil particles (pH = 6.3), which are negatively charged at near-neutral pH. Imidacloprid, in contrast, is not charged, thus its tendency to adsorption is higher, particularly in the soils with high TOC (Clausen et al., 2001; Cox et al., 2001). However, the GUS index does not take into account electrostatic interactions. In addition, though imidacloprid is highly persistent under aerobic conditions (DT_{50} of 174 to 997 d are reported in the literature), its soil photolysis half-life in the upper 2 mm of soil is 39 d (Graebing and Chib, 2004). However, this study was performed in greenhouse under additional artificial illumination with lower energy as real sun light, thus, higher removal of imidacloprid in the upper layer of soil and filter systems is not very likely and the major part of this pesticide will not be photo-degraded in the system as long as the water infiltrates quickly.

Concentrations of MCPA in leachates decreased considerably with time. In pots with soil, MCPA was detected above LOQ (0.1 mg kg^{-1}) only in the leachate sampled at the week 1 (Fig. 2A), while in pots with filter material an obvious increase of MCPA concentrations (1.5–2.0 mg L^{-1}) were observed in the first week; thereafter concentrations gradually decreased to 0.3 mg L^{-1} (pots with hydrophobic wool; Fig. 2B) or <0.1 mg L^{-1} (pots without wool; Fig. 2C) by week 4. MCPA is not expected to be degraded much faster than metalaxyl based on the DT_{50} values (Table 1) (Braskerud and Haarstad, 2003) but is known to be easily degraded microbially (Bælum et al., 2006). In both soil and the filter system studied, MCPA was the only pesticide showing a strong decrease in concentration after 1 to 2 weeks of exposure, indicating a development of efficient biodegradation of MCPA over time. MCPA biodegradation is known to be preceded by a lag-phase, which

typically lasts from one to several weeks depending on the degree of adaptation of microbial community (Bælum et al., 2006) resulting in the low concentrations after one and two weeks.

3.2. Pesticide distribution in filter materials and soil

After 4 weeks of pesticide exposure the highest total concentrations of parent pesticide in soil were measured for bentazone and metalaxyl (average concentrations in the range of 36.9–53.4 mg kg^{-1} dw), followed by imidacloprid (average concentrations 27.2–36.9 mg kg^{-1} dw), while average concentrations of propiconazole and pencycuron were about 13.4–21.4 mg kg^{-1} dw (Fig. S1A) and this trend is also shown for the recovered amounts of pesticides per pot (Fig. 3). The pesticides concentrations in the planted soil were slightly higher in comparison to the non-planted soil except for bentazone. However, the average concentrations in the mixture of pumice and vermiculite were much lower, between 0.9 and 2.0 mg kg^{-1} dw for all pesticides, except of pencycuron with average concentrations around 4.5 mg kg^{-1} dw (Fig. S1B). MCPA concentrations were below 0.1 mg kg^{-1} both in the soil and in the mixture of pumice and vermiculite.
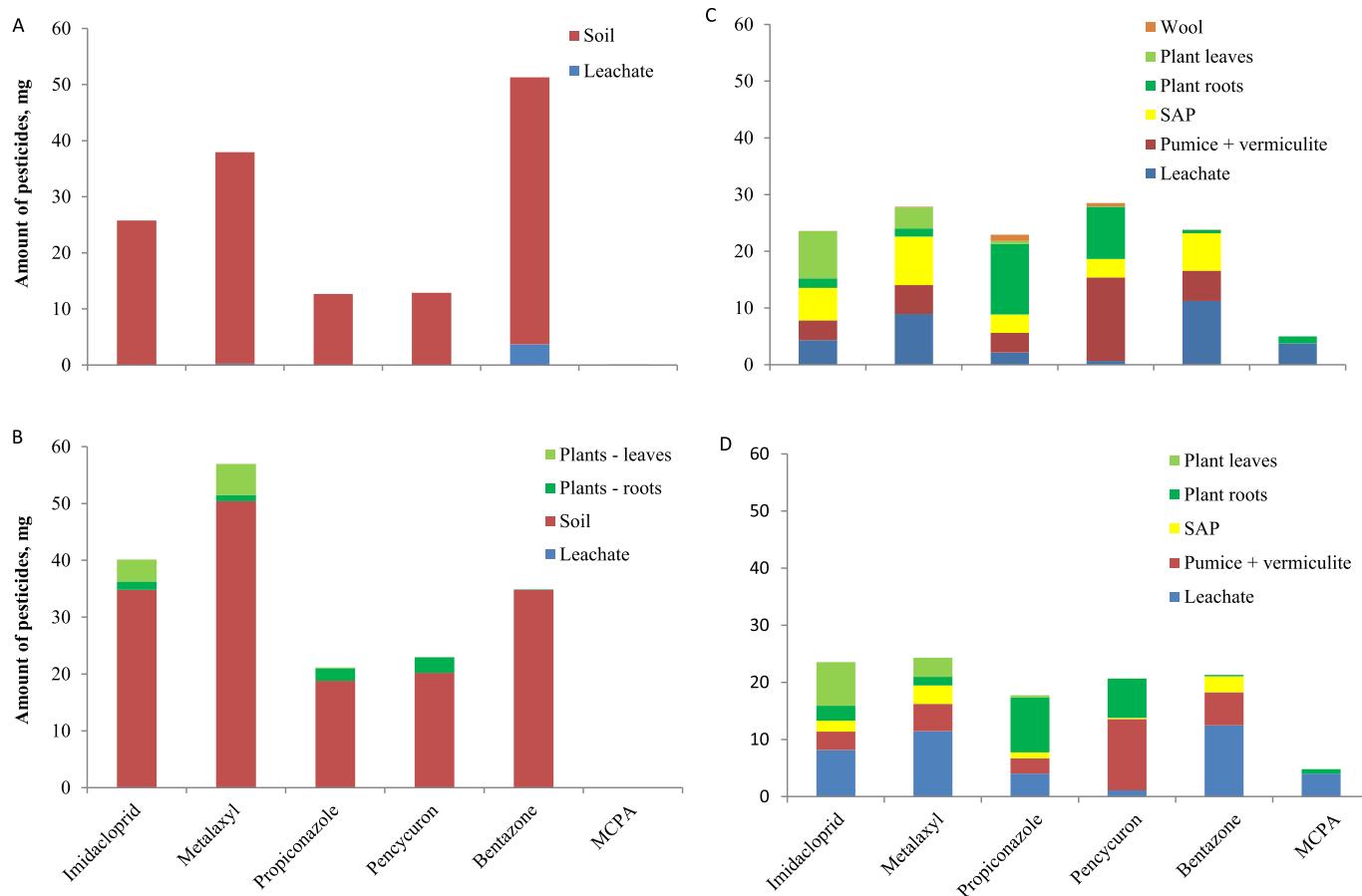
Notably, the concentrations of more hydrophobic pesticides (pencycuron, propiconazole) measured in the soil without and with plants (13.6 ± 6.6 and 21.4 ± 8.1 mg kg^{-1}, 13.4 ± 6.2 and 19.9 ± 9.8 mg kg^{-1}) were lower compared to the concentrations of hydrophilic pesticides (bentazone 50.4 ± 5.9 and 36.8 ± 9.5 mg kg^{-1}, metalaxyl 39.9 ± 8.8 and 53.4 ± 1.5 mg kg^{-1}, imidacloprid 27.3 ± 8.5 and 36.9 ± 8.9 mg kg^{-1}). Lower concentrations of propiconazole and pencycuron can be explained by strong sorption with the formation of so-called non-extractable residues as a result of incomplete extraction of propiconazole and pencycuron. On the other hand, more efficient

transformation of other organic pollutants in soils with high TOC content was described in a number of studies (Pal et al., 2005; Paszko and Jankowska, 2018), which may also explain effective biotransformation of sorbed pesticides in the soil with high TOC content.

Relatively high concentrations of hydrophilic metalaxyl (neutral) and bentazone (anionic) under the given conditions in the soil extracts without and with plants (50.4 ± 5.9 and 36.8 ± 9.5 mg kg^{-1}; 39.9 ± 8.8 and 53.4 ± 1.5 mg kg^{-1}) are explained by the residual water in the interstitial pores and by lipophilic as well as electrostatic interactions of their acidic molecules (pKa = 3.28 and 0, respectively) with negatively charged soil particles (soil pH = 6.3), as anion repulsion is relatively low and lipophilic interactions increase at lower soil pH (Franco et al., 2009). Negative correlation of bentazone sorption and soil pH was also reported previously (Boivin et al., 2005).

Electrostatic interactions also explain the retention of ionic mobile pesticides in the mixture of pumice and vermiculite. Pumice, being a main component of the mixture, has a pH of 8.15 (Table S3). Therefore, a lower sorption of acidic ionic and hydrophilic compounds, e.g. metalaxyl and bentazone, is expected. Sorption of propiconazole and pencycuron to the mixture of pumice and vermiculite (4.2 ± 1.0 and 0.9 ± 0.2 mg kg^{-1}) was also lower compared to soil (18.5 ± 11.3 and 19.6 ± 9.9 mg kg^{-1}), as TOC content of pumice and vermiculite is much lower than that in soil (Table S3). MCPA, which was extracted neither from soil, nor from filter materials, is the most hydrophilic compound among the six studied pesticides and is known to be easily biodegradable (see Table 1).

The hydrophobic wool had the highest sorption potential for the hydrophobic compounds propiconazole and pencycuron (Fig. S1; 28.2 ± 13.5 and 14.7 ± 9.2 mg kg^{-1} dw, respectively), followed by metalaxyl (3.1 ± 1.2 mg kg^{-1} dw) and bentazone (2.2 ± 1.2 mg kg^{-1} dw). Due

Fig. 3. Distribution of residual pesticides in the filter pots recovered from soil, filter materials, plant biomass, and leachates of non-planted soil (A), planted soil (B), planted filter materials with (C) and without (D) addition of hydrophobic wool. The total amount of each pesticide added to each system was 58 mg. Data and standard deviations are provided in the SI section.

to competing processes (sorption to soil particles, sorption to wool, biodegradation, etc.), sorption of pesticides to wool did not correlate with their hydrophobicity, e.g., bentazone (log K_{ow} − 0.46 or 2.34 depending on the reference, see Table 1) was extracted from wool, whereas concentrations of imidacloprid (log K_{ow} 0.57) were below detection limit. Further studies of the mechanisms that govern sorption of hydrophilic ionic and non-ionic organic compounds to hydrophobic wool are thus required.

Hydrophilic pesticides bentazone, imidacloprid, and metalaxyl were present in SAP in considerable concentrations (2.4 ± 1.7 mg kg^{-1}, 1.9 ± 1.5 mg kg^{-1}, 3.0 ± 2.3 mg kg^{-1}) compared to hydrophobic pencycuron (0.6 ± 0.9 mg kg^{-1}) and propiconazole (1.1 ± 0.9 mg kg^{-1}). This distribution pattern is similar to that in the effluent of the pots with filter materials (Fig. 2) Since average water holding capacity of SAP in the pots was 73 g H_2O/g SAP, it can be hypothesized that the high pesticide concentrations measured in SAP were dominantly attributed to the retention of water with dissolved pesticides, and to a much lesser extent to adsorption or other chemical interaction of pesticides with SAP. To test this hypothesis, the average theoretical amounts of pesticides that could be retained in SAP only by water uptake were estimated assuming that the pesticides concentrations in the effluent water from these pots were in equilibrium with their concentrations in water retained by SAP (Fig. S2). The calculated pesticides concentrations in water retained by SAP and the actual concentrations measured in SAP are in the same range. Therefore, water retention was the main, if not the only mechanism to enrich concentrations of highly water soluble compounds in filters with SAP. The advantage of this effect is that additional time for biodegradation of hydrophilic compounds is provided in SAP by increasing hydraulic retention times.

3.3. Accumulation of pesticides in plants

After 4 weeks of exposure, all pesticides except MCPA were detected in roots of plants grown in the soil pots. The highest concentrations in roots of plants grown in soil were measured for pencycuron (32.8 ± 20.2 mg kg^{-1} dw), propiconazole (26.0 ± 26.4 mg kg^{-1} dw) and imidacloprid (17.8 ± 10.0 mg kg^{-1} dw). Given the high variation between replicates in each pot, but also between replicate pots, there was no real difference between the concentrations of pencycuron, propiconazole and imidacloprid in roots of *P. arundinacea* grown in soil.

All pesticides were detected in the roots of plants grown in the filter material mixture. In contrast to roots in soil, the hydrophobic pesticides pencycuron (logKow = 4.7) and propiconazole (logKow = 3.7) were present at much higher concentrations (108.7 ± 18.3 and 146 ± 36.4 mg kg^{-1} dw) compared to imidacloprid (20.2 ± 6.0 mg kg^{-1} dw) (Figs. S3 and 3 for the overall recovered amounts in the pots). The higher concentrations of the hydrophobic pesticides in the roots of plants grown in filter materials, compared to those grown in soil, can be explained by the high organic matter content in soil (23.6%, Table S3). Concentrations of organic pesticides in plants are controlled by the equilibrium with their concentrations in soil pore water, which, in turn, depend on the pesticide concentrations in soil organic matter (Chiou et al., 2001). Therefore, partitioning of hydrophobic pesticides to plant roots is much stronger in filter materials with lower TOC content, which explains higher concentrations of the hydrophobic pesticides in the roots of plants grown in filter materials, compared to those grown in soil. The higher transfer of the hydrophilic pesticides to the plants in the SAP containing pots show a high bioavailability of these compounds contributing to the exchange.

In addition, the recovered amounts of pesticides in the plants corrected for their biomass content showed a higher pesticide retention by leaves and roots of the plants in the pots with the filter materials (Fig. 3). It is noteworthy that the total biomass of the plants in the pesticide exposed pots were ~ 20% lower than in the respective controls. Overall plant biomass in the filter materials reached only half of the amounts in comparison to the soil reactors (data not shown).

In the plant leaves, imidacloprid, metalaxyl and propiconazole were detected. Concentrations of imidacloprid in the leaves of plants grown in filter materials where 4 times higher compared to those grown in organic soil, 167 ± 14.1 and 36.4 ± 1.6 mg kg^{-1} dw, respectively. Notably, the concentration of imidacloprid and metalaxyl in plant leaves were much higher compared to their concentrations in plant roots. Metalaxyl concentrations were also higher in the leaves of plants grown in filter materials (74.2 ± 9.3 mg kg^{-1} dw vs 51.6 ± 4.6 mg kg^{-1} dw in the leaves of plants grown in soil) (Fig. S3B). The concentrations of more hydrophobic pesticide propiconazole in the leaves of *P. arundinacea* grown in soil were in the range of 0.1–1 mg kg^{-1} dw, while 8.5–10.5 mg kg^{-1} dw were measured in the leaves of plants grown in filter materials. In contrast to imidacloprid and metalaxyl, propiconazole had 10 times lower concentrations in the leaves of plants compared to the concentration in roots.

The obtained results are in accordance with the mode of action of selected pesticides and previous studies on their translocation in plants after subsurface application. Thus, imidacloprid, metalaxyl and propiconazole are systemic pesticides with potential for translocation in plant tissues, whereas bentazone, pencycuron and MCPA are nonsystemic pesticides. Ju et al. (2020) and Gong et al. (2020) have shown high upward translocation potential of imidacloprid and metalaxyl in wheat (*Triticum aestivum* L.) and greenhouse *Chrysanthemum* (Gong et al., 2020; Ju et al., 2020). High acropetal translocation of imidacloprid within the xylem and poor basipetal mobility within the phloem was also shown using ^{14}C-labelled imidacloprid (Sur and Stork, 2003). Hence translocation potential within the plant decreases with increasing hydrophobicity (Ju et al., 2020), which explains lower translocation potential of propiconazole compared to imidacloprid and metalaxyl.

Accumulation of imidacloprid in the above-ground biomass of plants grown in retention filters designed for pesticide elimination requires further studies. Translocation of this pesticide or its transformation products to the plant reproductive system may have negative effects e.g. on bees and other pollinators. (Butler, 2018; Wu et al., 2019).

3.4. Distribution of pesticides in microcosms with filter materials and soil: outcomes for pesticide retention strategies

Cumulated amounts of pesticides, adsorbed to filter media, retained in plants or leached from the pots after 4 weeks of exposure are shown in Fig. 3. The total amount of each pesticide, added to each pot during 4 weeks of exposure was 58 mg. The missing fraction of the compounds is either mineralized, partially transformed into mobile metabolites, which leave the pots with the leaching fraction, or incorporated to non-extractable residues (NER).

Less than 25 mg (~43%) of each added pesticide was recovered overall in leachates, filter materials and plants, except for bentazone and metalaxyl in planted and non-planted soil. The fraction of MCPA (>50 mg = 92–100%), which was not extracted from soil, filter materials, plant biomass or leachates, is much higher than the reported NER fraction for this compounds (~35%) (Barriuso et al., 2008) which indicates microbial degradation.

Bentazone and metalaxyl have shown very low mineralization in several studies (Hedegaard and Albrechtsen, 2014; Luo et al., 2019; Norgaard et al., 2015; Sukul and Spiteller, 2000). Therefore, it is likely that large fractions of these compounds remain in form of NER either as a parent non-extractable compound or as sorbed metabolites in soil and filter materials. However, the missing fractions of bentazone (3–27 mg = 5–46%) and metalaxyl (5–17 mg = 8–30%) are much lower than the percentages of NER reported for these compounds in agricultural soil (45–80% and 65–75%) (Barriuso et al., 2008). For these compounds higher aerobic biodegradability was observed in the literature (see Table 1), which may have triggered higher degradation and lower NER formation, in particular combined with the extended retention time in the filter material mixture. In contrast, the missing fractions

of imidacloprid (11–20 mg = 19–34%) and propiconazole (20–26 mg = 35–44%) were in the range of the reported NER fractions for these compounds (15–25% and 5–50% respectively) (Barriuso et al., 2008).

Notably, the amount of added pesticides extracted from non-planted soil pots was lowest for MCPA 0%, followed by propiconazole, and pencycuron (both <16 mg = 28%), Surprisingly, the overall recovery of pesticides were highest in planted soil pots, except for bentazone. Considerable amounts of imidacloprid, metalaxyl, and bentazone (>25 mg = 43%) were recovered either from soil or from plants and SAP. The presence of the plants affected the amount of pesticides leached from the soil, but a fraction of the recovered pesticide was also found in the plants. It has to be considered that the overall reduction of the water content by evapotranspiration of the plant may have led to a relative increase of the pesticide concentrations. The high retention of the pesticides in the organic soil used in this study shows that soil may be an important sink for pesticides from surface runoff. This, however, may result in pesticide levels exciding toxicity limits to soil biota or plants.

In contrast, the newly proposed filter materials have lower tendency for pesticide accumulation and showed a much lower overall recovery of the pesticides. Considerably lower fractions of pesticides were adsorbed to pumice, vermiculite and SAP than to soil material. As a consequence, larger fractions of the pesticides were lost with leachates and presumably mineralization or degradation.

In comparison to the mineral filter materials, pumice and vermiculite, the SAP was able to retain higher amounts (5–15%) of the more hydrophilic pesticides imidacloprid, metalaxyl and bentazone by retaining the water phase. In addition, the complete degradation of MCPA shows that this material enables microbial degradation activity. Hence SAP provides a promising option to increase pesticide retention and biodegradation in mineral matrices. In addition, SAP increases the water holding capacity of such matrices by orders of magnitude and thus the hydraulic retention time, enabling the growth of helophytes in such systems without defined water containments. On the other hand, the pure mineral filter materials would enhance leaching of pesticides considerably. Therefore, smart combinations of filter materials as growth medium for plants including the option for rapidly retaining high amounts of water by SAP may open perspectives of treating higher volumes of surface runoff owing to permeability and saturation capacity of the materials. Additional soil layers on the top or at the bottom may increase retention and provide the appropriate microbial inoculum. Such combinations of filter material may thus provide the most promising options for increased retention of pesticides derived from agricultural runoff.

The pesticide partitioning between different compartments of the system, water, filter materials, soil, and plants, change their concentrations in different compartments, and, thus, the driving forces which control their fate. More detailed assessment of the fate of the pesticide, in particular the biodegraded and mineralized fraction of pesticides should be studied in additional experiments with isotope labelled compounds in order to set up mass balances and to obtain more detailed information about transformation processes in the filter materials and their mixtures.

As pointed out in the introduction, surface water contamination by agricultural field runoff is an upcoming problem of increasing global relevance (Lefrancq et al., 2017; Liess et al., 1999). Therefore, near-natural treatment techniques are needed for the pesticide retention. The tested filter materials provide several options for application in vegetated ditches, in filtration ditches or constructed wetlands, for example at riparian strips (Arora et al., 2010; Cole et al., 2020). In addition, the application of SAP provides several advantages: i) the SAP used already has the approval for the application in agricultural field cropping systems and is thus without toxicological relevance, ii) is of relatively low price since it is used for the increase of the water holding capacity of agricultural fields in arid areas, and iii) provides the option for high water retention e.g. in constructed wetlands at riparian strips without the need for containment installations.

4. Conclusions

- Leaching was barely observed in the soil pots in particular with the evapotranspiration of the plants. Therefore, soils with high organic matter contents or mature composts will provide high retention potentials but the higher accumulation of pesticides in the soil may also result in a higher potential of remobilization and toxicity to plants.
- Pure mineral matrices have much higher leaching potentials than soil with high TOC content. However, the addition of SAP increases the water holding capacity accompanied by an increase of the hydraulic retention times which may promote microbial degradation.
- SAP-enriched mineral filter materials had less sorption capacity for hydrophobic pesticides than soil but caused a considerable enrichment of water soluble and ionic compounds.
- Therefore, a beneficial combination of filter materials may provide options for the treatment of agricultural surface water runoff events either by artificial treatment filters, wetlands, or by enforced retention within improved riparian strips by using nature-based solutions.

CRediT authorship contribution statement

AB and MK wrote and organized the manuscript; TE organized the project and provided the outline and contributed to writing the manuscript, plus YJ, KN, AM produced the data from UFZ and improved the manuscript and discussion; DL and CN characterized the surface properties of the materials and behavior of pesticides; TE and HB planned and performed the experiments in Norway; KG, SRO, and HRN developed the extractions and analytical procedures.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.146114.

References

Abdelhakeem, S.G., Aboulroos, S.A., Kamel, M.M., 2016. Performance of a vertical subsurface flow constructed wetland under different operational conditions. J. Adv. Res. 7, 803–814.

Aktar, W., Sengupta, D., Chowdhury, A., 2009. Impact of pesticides use in agriculture: their benefits and hazards. Interdiscip. Toxicol. 2, 1–12.

Arora, K., Mickelson, S.K., Helmers, M.J., Baker, J.L., 2010. j.1752-1688.2010.00438.x. Review of pesticide retention processes occurring in buffer strips receiving agricultural runoff. J. Am. Water Resour. Assoc. 46, 18–47.

Bælum, J., Henriksen, T., Hansen, H.C.B., Jacobsen, G.S., 2006. Degradation of 4-chloro-2-methylphenoxyacetic acid in top- and subsoil is quantitatively linked to the class III tfdA gene. Appl. Environ. Microbiol. 72, 1476–1786.

Barriuso, E., Benoit, P., Dubus, I.G., 2008. Formation of pesticide nonextractable (bound) residues in soil: magnitude, controlling factors and reversibility. Environmental Science & Technology 42, 1845–1854.

Boivin, A., Cherrier, R., Schiavon, M., 2005. A comparison of five pesticides adsorption and desorption processes in thirteen contrasting field soils. Chemosphere 61, 668–676.

PM. Boyd, JL. Baker, SK. Mickelson, SI. Ahmed. Pesticide transport with surface runoff and subsurface drainage through a vegetative filter strip. Transactions of the ASAE 2003; 46: 675.

Braskerud, B.C., Haarstad, K., 2003. Screening the retention of thirteen pesticides in a small constructed wetland. Water Sci. Technol. 48, 267–274.

Bundschuh, M., Goedkoop, W., Kreuger, J., 2014. Evaluation of pesticide monitoring strategies in agricultural streams based on the toxic-unit concept—experiences from long-term measurements. Sci. Total Environ. 484, 84–91.

Butler, D., 2018. EU pesticide review could lead to ban: major assessment concludes that neonicotinoids harm bees. Nature 555, 150–151.

Carmody, O., Frost, R., Xi, Y., Kokot, S., 2007. Surface characterisation of selected sorbent materials for common hydrocarbon fuels. Surf. Sci. 601, 2066–2076.

Chiou, C.T., Sheng, G., Manes, M., 2001. A partition-limited model for the plant uptake of organic contaminants from soil and water. Environ. Sci. Technol. 35, 1437–1444.

Çifçi, D.İ., Meriç, S., 2016. A review on pumice for water and wastewater treatment. Desalin. Water Treat. 57, 18131–18143.

Clausen, L., Fabricius, I., Madsen, L., 2001. Adsorption of pesticides onto quartz, calcite, kaolinite, and α-alumina. J. Environ. Qual. 30, 846–857.

Cole, L., Stockan, J., Helliwell, R., 2020. Managing riparian buffer strips to optimise ecosystem services: a review. Agric. Ecosyst. Environ. 296.

Cox, L., Koskinen, W.C., Celis, R., Yen, P.Y., Hermosin, M.C., Cornejo, J., 1998. Sorption of imidacloprid on soil clay mineral and organic components. Soil Sci. Soc. Am. J. 62, 911–915.

Cox, L., Hermosin, M.C., Koskinen, W.C., Cornejo, J., 2001. Interactions of imidacloprid with organic and inorganic-exchanged smectites. Clay Miner. 36, 267–274.

Dhiman J, Prasher S, Mannan A, ElSayed E, Nzediegwu C. " Use of Super Absorbent Polymers (Hydrogels) to Promote Safe Use of Wastewater in Agriculture. 22nd Canadian Hydrotechnical Conference, 2015.

Dordio, A.V., Carvalho, A.J.P., 2013. Organic xenobiotics removal in constructed wetlands, with emphasis on the importance of the support matrix. J. Hazard. Mater. 252-253, 272–292.

Fernandes, M.C., Cox, L., Hermosín, M.C., Cornejo, J., 2003. Adsorption–desorption of metalaxyl as affecting dissipation and leaching in soils: role of mineral and organic components. Pest Manag. Sci. 59, 545–552.

Fosso-Kankeu, E., Mittal, H., Mishra, S.B., Mishra, A.K., 2015. Gum ghatti and acrylic acid based biodegradable hydrogels for the effective adsorption of cationic dyes. J. Ind. Eng. Chem. 22, 171–178.

Franco, A., Fu, W., Trapp, S., 2009. Influence of soil pH on the sorption of ionizable chemicals: modeling advances. Environ. Toxicol. Chem. 28, 458–464.

Gluhar, S., Kaurin, A., Grubar, T., Prosen, H., Lestan, D., 2019. Dissipation of mecoprop-P, isoproturon, bentazon and S-metolachlor in heavy metal contaminated acidic and calcareous soil before and after EDTA-based remediation. Plant Soil Environ. 65, 273–281.

Gong, W., Jiang, M., Zhang, T., Zhang, W., Liang, G., Li, B., et al., 2020. Uptake and dissipation of metalaxyl-M, fludioxonil, cyantraniliprole and thiamethoxam in greenhouse chrysanthemum. Environ. Pollut. 257.

Goulson, D., 2014. Ecology: pesticides linked to bird declines. Nature 511, 295–296.

Goulson, D., Nicholls, E., Botías, C., Rotheray, E.L., 2015. Bee declines driven by combined stress from parasites, pesticides, and lack of flowers. Science 347.

Graebing, P., Chib, J.S., 2004. Soil photolysis in a moisture- and temperature-controlled environment. 2. Insecticides. J. Agric. Food Chem. 52, 2606–2614.

Gustafson, D.I., 1989. Groundwater ubiquity score: a simple method for assessing pesticide leachability. Environ. Toxicol. Chem. 8, 339–357.

Hallmann, C.A., Foppen, R.P.B., Van Turnhout, C.A.M., De Kroon, H., Jongejans, E., 2014. Declines in insectivorous birds are associated with high neonicotinoid concentrations. Nature 511, 341–343.

Harlander SK. The evolution of modern agriculture and its future with biotechnology. J Am Coll Nutr 2002; 21: 161s–165s.

Hedegaard, M.J., Albrechtsen, H.-J., 2014. Microbial pesticide removal in rapid sand filters for drinking water treatment – potential and kinetics. Water Res. 48, 71–81.

Hetland RB, Brunborg G, Dirven H, Gjølme N, Instanes C, Lindeman B. Intake of pesticides via drinking water related to drinking water limits. Report from Norwegian Health Institute. (in Norwegian) 2014.

Hiller E, Cernansky S, Zemanova. Sorption, degradation and leaching of the phenoxyacid herbicide MCPA in two agricultural soils. Polish J. of Environ. Stud. 2010; 19: 315–321.

Hubert B, Rosegrant M, van Boekel MAJS, Ortiz R. The future of food: scenarios for 2050. Crop Science 2010; 50: S-33-S-50.

Hüttermann, A., Orikiriza, L.J.B., Agaba, H., 2009. Application of superabsorbent polymers for improving the ecological chemistry of degraded or polluted lands. CLEAN – Soil, Air, Water 37, 517–526.

Ju, C., Dong, S., Zhang, H., Yao, S., Wang, F., Cao, D., et al., 2020. Subcellular distribution governing accumulation and translocation of pesticides in wheat (Triticum aestivum L.). Chemosphere 248.

Khan, M., Lo, I.M.C., 2016. A holistic review of hydrogel applications in the adsorptive removal of aqueous pollutants: recent progress, challenges, and perspectives. Water Res. 106, 259–271.

Kladivko, E.J., Brown, L.C., Baker, J.L., 2001. Pesticide transport to subsurface tile drains in humid regions of North America. Crit. Rev. Environ. Sci. Technol. 31, 1–62.

Lefrancq, M., Jadas-Hécart, A., La Jeunesse, I., Landry, D., Payraudeau, S., 2013. Estimating the toxicity of pesticide mixtures to aquatic organisms: a review. Hum. Ecol. Risk. Assess. 19, 1557–1575.

Lefrancq, M., Jadas-Hécart, A., La Jeunesse, I., Landry, D., Payraudeau, S., 2017. High frequency monitoring of pesticides in runoff water to improve understanding of their transport and environmental impacts. Sci. Total Environ. 587–588, 75–86.

Lewis, K.A., Tzilivakis, J., Warner, D.J., Green, A., 2016. An international database for pesticide risk assessments and management. Hum. Ecol. Risk. Assess. 22, 1050–1064.

Liess, M., Schulz, R., Liess, M.H.D., Rother, B., Kreuzig, R., 1999. Determination of insecticide contamination in agricultural headwater streams. Water Res. 33, 239–247.

Liu, Z., Yan, X., Drikas, M., Zhou, D., Wang, D., Yang, M., et al., 2011. Removal of bentazone from micro-polluted water using MIEX resin: kinetics, equilibrium, and mechanism. J. Environ. Sci. 23, 381–387.

Luo, Y., Atashgahi, S., Rijnaarts, H.H.M., Comans, R.N.J., Sutton, N.B., 2019. Influence of different redox conditions and dissolved organic matter on pesticide biodegradation in simulated groundwater systems. Sci. Total Environ. 677, 692–699.

Matthews, G.A., 2015. Pesticides: Health. Safety and the Environment, Second Edition.

Meffe, R., de Bustamante, I., 2014. Emerging organic contaminants in surface water and groundwater: a first overview of the situation in Italy. Sci. Total Environ. 481, 280–295.

Morton, P.A., Fennell, C., Cassidy, R., Doody, D., Fenton, O., Mellander, P.-E., et al., 2020. A review of the pesticide MCPA in the land-water environment and emerging research needs. Advanced review. WIREs Water 7.

Nemeth-Konda, L., Füleky, G., Morovjan, G., Csokan, P., 2002. Sorption behaviour of acetochlor, atrazine, carbendazim, diazinon, imidacloprid and isoproturon on Hungarian agricultural soil. Chemosphere 48, 545–552.

Norgaard T, de Jonge LW, Moldrup P, Olsen P, Johnsen AR. Can simple soil parameters explain field-scale variations in glyphosate-, bromoxyniloctanoate-, diflufenican-, and bentazone mineralization? Water, Air, & Soil Pollution 2015; 226: 262.

Otto, S., Pappalardo, S.E., Cardinali, A., Masin, R., Zanin, G., Borin, M., 2016. Vegetated ditches for the mitigation of pesticides runoff in the Po Valley. PLoS One 11, e0153287.

Pal, R., Chakrabarti, K., Chakraborty, A., Chowdhury, A., 2005. Pencycuron dissipation in soil: effect of application rate and soil conditions. Pest Manag. Sci. 61, 1220–1223.

Paszko, T., Jankowska, M., 2018. Modeling the effect of adsorption on the degradation rate of propiconazole in profiles of Polish Luvisols. Ecotoxicol. Environ. Saf. 161, 584–593.

Prosser, R.S., Hoekstra, P.F., Gene, S., Truman, C., White, M., Hanson, M.L., 2020. A review of the effectiveness of vegetated buffers to mitigate pesticide and nutrient transport into surface waters from agricultural areas. J. Environ. Manag. 261, 110210.

Reichenberger, S., Bach, M., Skitschak, A., Frede, H.-G., 2007. Mitigation strategies to reduce pesticide inputs into ground- and surface water and their effectiveness; a review. Sci. Total Environ. 384, 1–35.

Riise, G., Lundekvam, H., Wu, Q.L., Haugen, L.E., Mulder, J., 2004. Loss of pesticides from agricultural fields in SE Norway – runoff through surface and drainage water. Environ. Geochem. Health 26, 269–276.

Roseth R. Pesticides in Groundwater in Agriculture Areas. Bioforsk Report Vol. 8 Nr.46. (in Norwegian), 2013.

Sandin, M., Piikki, K., Jarvis, N., Larsbo, M., Bishop, K., Kreuger, J., 2018. Spatial and temporal patterns of pesticide concentrations in streamflow, drainage and runoff in a small Swedish agricultural catchment. Sci. Total Environ. 610-611, 623–634.

Schreiner, V.C., Szöcs, E., Bhowmik, A.K., Vijver, M.G., Schäfer, R.B., 2016. Pesticide mixtures in streams of several European countries and the USA. Sci. Total Environ. 573, 680–689.

Silva, V., Mol, H.G.J., Zomer, P., Tienstra, M., Ritsema, C.J., Geissen, V., 2019. Pesticide residues in European agricultural soils – a hidden reality unfolded. Sci. Total Environ. 653, 1532–1545.

Sørensen, S.R., Schultz, A., Jacobsen, O.S., Aamand, J., 2006. Sorption, desorption and mineralisation of the herbicides glyphosate and MCPA in samples from two Danish soil and subsurface profiles. Environ. Pollut. 141, 184–194.

Stenrød, M., 2015. Long-term trends of pesticides in Norwegian agricultural streams and potential future challenges in northern climate. Acta Agric. Scand. Sect. B 65, 199–216.

Stottmeister, U., Wießner, A., Kuschk, P., Kappelmeyer, U., Kästner, M., Baeder-Bederski-Anteda, O., Müller, R.A., Moormann, H., 2003. Effects of plants and microorganisms in constructed wetlands for wastewater treatment. Biotechnol. Adv. 22, 93–117.

Sukul, P., Spiteller, M., 2000. Metalaxyl: persistence, degradation, metabolism, and analytical methods. Rev. Environ. Contam. Toxicol. 164, 1–26.

Sur, R., Stork, A., 2003. Uptake, translocation and metabolism of imidacloprid in plants. Bulletin of Insectology 56, 35–40.

Vergili, I., Barlas, H., 2009. Removal of 2,4-D, MCPA and Metalaxyl from water using Lewatit VP OC 1163as sorbent. Desalination 249, 1107–1114.

Vymazal, J., 2013. Emergent plants used in free water surface constructed wetlands: a review. Ecol. Eng. 61, 582–592.

Vymazal, J., Březinová, T., 2015. The use of constructed wetlands for removal of pesticides from agricultural runoff and drainage: a review. Environ. Int. 75, 11–20.

Whitehorn, P.R., O'Connor, S., Wackers, F.L., Goulson, D., 2012. Neonicotinoid pesticide reduces bumble bee colony growth and queen production. Science 336, 351–352.

Wu, C., Dong, F., Mei, X., Ning, J., She, D., 2019. Distribution, dissipation, and metabolism of neonicotinoid insecticides in the cotton ecosystem under foliar spray and root irrigation. J. Agric. Food Chem. 67, 12374–12381.

Zohuriaan J, Kabiri K. Superabsorbent polymer materials: a review. Iranian Polymer Journal (English Edition) 2008; 17.