Does sea-dyke construction affect the spatial distribution of pesticides in agricultural soils? – A case study from the Red River Delta, Vietnam

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Abstract

The Red River Delta is a major agricultural production area of Vietnam with year-round use of pesticides for paddy rice cultivation and other production systems. The delta is protected from flooding, storm surges and saline water intrusion by the construction of a sophisticated river and sea-dyke system. Little is known about the effects of such a dyke system on pesticide pollution in the enclosed landscape. Our aim was to address this gap by i) determining pesticide prevalence in soils and sediments within a dyked agricultural area, and by ii) assessing whether and to which degree this dyke system might affect the spatial distribution of pesticides. After sampling paddy rice fields (topsoil) and irrigation ditches (sediment) perpendicular to the dyke in Giao Thuy district, we analysed 12 of the most commonly used pesticides in this area. In soils, we detected most frequently isoprothiolane (100% detection frequency), chlorpyrifos (85%) and propiconazole (41%) while in sediments isoprothiolane (71%) and propiconazole (71%) were most frequently found. Maximum concentrations reached 42.6 µg isoprotiolane kg^{-1} in soil, and 35.1 µg azoxystrobin kg^{-1} in sediment. Our results supported the assumption that the dyke system influenced residue distribution of at least selected pesticides in that more polar substances increasingly accumulated in fields the closer they were allocated to the sea-dyke (R^2=0.92 for chlorpyrifos and 0.51 for isoprothiolane). We can thus support initiatives from local authorities to use the spatial distance to dykes as a measure for identifying zones of different environmental pollution; yet, the degree at which dykes are a sink for pesticides appear to be compound specific.

Capsule:

This study provides data on concentrations of recently and commonly used pesticides in soil and sediments and investigated possible effects of human dyke constructions on spatial pesticide distribution.

Keywords

Pesticide residues; irrigation system; soil; sediment; coastal protection construction

1. Introduction

Most coastal regions, including deltas, are densely populated and represent major agricultural production areas of the world (Kuenzer and Renaud, 2012). The Red River Delta is the second largest river delta in Vietnam, renowned for intensive monoculture paddy rice production, which, however, is often associated with elevated inputs of agrochemicals such as pesticides and fertilizers (Dang and Danh, 2008; Larsen, 2013). In Vietnam, ca. 19,000 tonnes of active ingredients were applied on agricultural land in 2001 (FAOSTAT, 2018), with an average pesticide application rate of 3.3 kg ha^{-1} in the Red River Delta (Thuy et al., 2012). The often-reported improper usage of pesticides by farmers poses a particular health risk for humans and the environment (Thuy et al., 2012). Even though there is an increasing awareness of these risks, there is still only limited information available about the concentrations of recently used pesticide in soil and sediments of such coastal delta regions. So far, only a few studies addressed this issue in Vietnam´s intensive agricultural lands (Lamers et al., 2011; Hoi et al., 2013; Toan et al., 2013; Chau et al., 2015). For the Mekong Delta, Toan et al. (2013) detected pesticide residues such as buprofezin, fenobucarb, isoprothiolane, cypermethrin in soil and sediment of arable land with a maximum concentration of up to 521 µg kg^{-1} for buprofezin. Chau et al. (2015) found that up to 12 different pesticides reached drinking water sources, often above the critical threshold values of 0.1 µg L^{-1} according to the European Commission (EC) parametric guideline values for individual pesticide in drinking water (EC, 1998). For the Red River Delta, Nishina et al. (2010) detected pesticide residues in vegetable fields (e.g., fenobucarb, isoprothiolane, metalaxyl, cypermethrin) within a concentration range of 0.4 to 121.9 µg kg^{-1}. However, to the best of our knowledge, there is currently no data available on the concentrations of recently used pesticides in soil and sediments of paddy rice systems of the coastal Red River Delta, and we are not aware of any study that even succeeded in identifying potential spatial controls.

Worldwide the vulnerability of agro-ecosystems in deltas is increasing due to climate change-related impacts (e.g., sea level rise) (Wong et al., 2014). As a combined result of sea level rise and concomitant low river discharge, many deltas are currently prone to salinity intrusion, as, e.g., reported for both the Mekong Delta (Smajgl et al., 2015) but also the Red River Delta in Vietnam (Nguyen et al., 2017). To protect fertile agricultural land from saline intrusion, dykes have become a preferable adaptation option in the past (Renaud et al., 2015). In the Red River Delta, they were built to mainly protect the land from extreme floods and storms coming from the Gulf of Tonkin, however with the additional benefit to protect the area for salinity intrusion.

However, the construction of dykes and sluice gates can alter the environment in several ways. For instance, Lie et al. (2009) reported a rapid change of the estuarine tidal system and negative consequences for the natural environment after sea-dyke construction. In South Korea, the construction of a dam in the Yeongsan estuary region led to accumulation of sediments, anthropogenic components and nutrient loads close to the dam (Lee et al., 2009). Aas much as similar processes also apply to the Red River Delta, it is likely that dyke construction also affects the fate and spatial distribution of commonly used pesticides.

The dyke and sluice gate system of the Red River Delta has been developed since the 1900s (Tuong et al., 2003). These constructions regulate the water discharge in irrigation ditches and fostered the intensification of agricultural production at reduced salinity intrusion and flooding (Own exploratory interview based data, 2015).

However, governmental institutions have already become aware of possible disadvantages of this regulated irrigation system, such as surface water pollution. Therefore, they classify the area inside the dyke into three surface water pollution zones: *i)* a highly polluted zone directly behind the sea-dyke close to the outflow, *ii)* a moderately polluted zone further away from the sea-dyke, and *iii)* a non-polluted zone close to the river where the fresh water enters the area (Own exploratory interview based data, 2015). At present, there is no empirical proof that these pollution zones also make sense for soils, as the latter are not yet explicitly considered. Besides, there are no data related to pollution by pesticides.

Concentrations of pesticides in irrigation or channel water can lead to an exposure of the local population to pesticides. However, pesticide concentrations in such water samples are highly influenced by, e.g., water flow direction and velocity, dwell time as well as rain events (Schäfer et al., 2011), i.e., they vary considerably on an hourly or daily timescale. Therefore, to determine the long-term impact of the sea-dyke and sluice gate system on the distribution and fate of pesticides, soil and sediment samples are better suited as they represent a longer-term archive of cumulative pesticide inputs. Some studies have already succeeded in linking seasonal or spatial pesticide distribution to agricultural land use (Toan et al., 2013; Zheng et al., 2016), to runoff behaviour from paddy fields (Anyusheva et al., 2012; Lamers et al., 2011), or simply assessed spatial pesticide patterns at field scale (Asami et al., 2003). However, the impact of sea-dykes on the spatial distribution of pesticides concentrations in coastal areas has not yet been elucidated.

The main aim of this research was, therefore, to investigate the influence of a sea-dyke on the fate and spatial distribution of pesticide in the Red River Delta. Our specific objectives were *i)* to determine pesticide concentrations in soil (paddy rice fields) and in sediments (from adjacent irrigation ditches) in a dyked agricultural area, as well as *ii)* to relate the occurrence of pesticide accumulations to the distance from the sea-dyke system and therewith, for the very first time for pesticides, also to test the validity of the governmental suggestion of different pollution zones near the dyke. These results will serve as first basis to derive recommendations for local farmers, irrigation officers and decision makers.

2. Material and Methods

2.1 Study site

The study site was located in the Giao Lac and Hong Thuan communes of the Giao Thuy district, Nam Dinh province, Red River Delta, Vietnam. The climate is sub-tropical with an annual average temperature of 23.5 °C (Nishina et al., 2010) and a mean annual rainfall of 1,667 mm (Minh et al., 2010). About 75% of this rain falls in the wet season from May to October (Duc and Umeyama, 2011). The discharge of the Red River varies between dry and wet season with an average flow of 2,640 m^3 s^{-1} (Anh and Shannon, 2010). The delta has a dense system of dykes and gates to control low and high tides of the Red River and minimize salinity intrusion. In total 8,000 km of dykes were built, 5,000 km of river-dyke and 3,000 km of sea-dyke (Anh and Shannon, 2010). The study site is surrounded by both types of dykes, which have several inlet and outlet gates to control the water level in the irrigation ditches (Fig.1). From the adjacent river the fresh water flows through inlet gates into the dyked area (Fig. 1). The outlet gate, ca. 7 km seawards from the inlet gate, controls the water discharge into the sea. The land area between both dykes is mostly under agricultural use with intensive paddy rice production in a double cropping system.

2.2 Explorative Interviews

In October 2015 nine interviews with local experts and farmers including the head of the irrigation company (responsible for the water management in the Giao Thuy district), the Department of Agriculture and Rural Development (DARD), officials at the commune level and local farmers were carried out to understand the local irrigation water management and reveal possible problems with salinity intrusion and the pollution problems with pesticides. The soil and sediment sampling strategy was developed based on the results of these interviews.

2.3 Sampling

Soil and sediment sampling was performed in January 2016. Sampling was done along a catena to represent the entire dyked area from the river-dyke (inlet) to the sea-dyke (outlet) consisting of seven catena points with five field replications each (Fig.1). Each catena point was separated by approximately 1 km, and there was a 500 m distance between the five field replications. The first catena point was located close to the inlet gate, where the fresh water of the river was allowed to enter the dyked area. The seventh catena points were located close to the outlet gate, where the water of the dyked area flow into the sea. This point was located 7 km from the river dyke (Fig.1). A main irrigation ditch cross the dyked area including the catena (Fig 1.). The sampled field of the catena point 4 were directly located at this ditch.

In total 35 topsoil samples of paddy rice fields and 16 sediment samples of irrigation ditches were collected. All sampled rice fields were fallow just before land preparation for the next cropping season at the time of sampling. Soil samples from paddy rice fields were taken from 0 to 15 cm by using a stainless steel shovel. Sediment cores (0 to 10 cm) were taken close to the catena points one, three, five and seven with four field replicates (n=16) using a sediment corer with 7 cm diameter (Hydro-Bios, Kiel, Germany). At least four cores with a distance of 100 m between each core were collected. All samples were taken as composites from at least five individual mixed and homogenized subsamples. Soil and sediment samples were wrapped in aluminium foil on site, cooled for short-distance transport (freezer, -4°C), transported frozen to Germany, and stored at -20 °C for further analysis.

2.4 Standard analysis of soil properties

Texture classes of soil and sediment samples were determined by finger test for fine earth fraction and classified after soil textural classes according to FAO (1990) (FAO, 2006). The pH value was determined in a water solution in a ratio of 1:2.5 (Sonmez et al., 2008). Total C was determined after dry combustion using a MicroCube elemental analyser (Elementar, Hanau, Germany) (according to DIN ISO 10694), and inorganic C was determined by the Scheibler method (DIN ISO 10693) by gasometric measurement of the developing CO_2 concentration

considering pressure and temperature effects. Soil organic carbon (SOC) was calculated by subtracting inorganic C from total C. Cation exchange capacity (potential CEC) was analysed with NH_4-acetate solution and percolation technique (according to Thomas, 1982).

2.5 Studied pesticides

Selection of target pesticides was based on the following criteria: *i)* pesticide use (frequency, amount) as derived from a survey of empty packages of pesticides found in the study fields and by former studies conducted in Southeast Asia; *ii)* fate in the environment (derived from physico-chemical properties, i.e., solubility in water, hydrolysis half-life, octanol– water partition coefficient, soil sorption, soil degradation half-life, and *iii)* eco-toxicological relevance. In total, 12 pesticides were selected; their main properties are listed in Tab.1. Pesticide standards had a purity > 97% and were purchased from LGC Standards (Wesel, Germany). All used solvents were of HPLC grade.

2.6 Pesticide analysis

All samples were lyophilized and sieved to grain size of < 2 mm. Extraction was performed after a modified method of Villaverde et al.,(2008) via accelerated solvent extraction (ASE; Dionex 350 with following conditions temp: 100°C, static time: 5 min, two extraction cycles) using a solvent solution of n-hexane: acetone (1:1, v/v). The surrogate standard delta-hexachlorcyclohexan (δ-HCH) was added to the sample prior extraction. After adding 300 µL toluene the extract volume was reduced to 1.5 mL via rotary-evaporation. Clean-up was conducted after the solid phase extraction method from Laabs et al. (2007). In detail, the sample was loaded on the column, which was filled with 1 g of aluminium oxide (Merck, Darmstadt, Germany) and 1 g florisil (Merck, Darmstadt, Germany). Samples were eluted from the column with 20 mL diethylether: n-hexane (1:1, v/v). After reducing the volume via rotary-evaporator close to dryness, the sample was spiked with fluorene-d_{10} as internal standard for quantification, dried under nitrogen and filled into 300 µl glass inlets before measurement.

Pesticides were analysed using a gas chromatograph (GC) (Agilent Technologies 6890N, Böblingen, Germany) coupled with a mass selective detector (MSD) (Agilent Technologies 5973, Böblingen, Germany) and equipped with an Agilent 7683 automatic sampler. The GC was equipped with Optima 5 MS column (30 m length x 0.25 mm ID x 0.5µm film thickness; Macherey & Nagel, Düren, Germany); helium with a constant flow rate of 1 mL min^{-1} was utilized as carrier gas. The injector block temperature was set at 250 °C. The oven temperature started with 85 °C initial temperature (hold for 2.5 min) increased to 220 °C with 15 °C min^{-1}; increased to 280 °C with 10 °C min^{-1} (held for 5 min), and increased to 300 °C with 10 °C min^{-1}(held for 5 min). The injection volume was 1 µL using splitless mode. The MSD operated in selected ion monitoring (SIM) mode.

2.7 Quality assurance and quality control

Blank samples were regularly handled for each analytical batch. To determine the extraction efficiency, recovery experiments at two concentration levels (0.2 and 2.5 µg for each pesticide in 15 g dry soil, n=2) were conducted, yielding 70 to 120% recovery for all studied pesticides. Determined concentrations were not corrected for the recovery of the surrogate standard. The lower limit of quantitation for each substance was defined by the routine limit of quantitation (RLOQ) of the calibration standard. The RLOQ for the majority of the pesticide was 3 µg kg^{-1} (lowest detected calibration standard: 0.01 µg kg^{-1}). For propiconazole, azoxystrobin,and pretilachlor RLOQ was 4 µg kg^{-1} (lowest detected calibration standard 0.05 µg kg^{-1}) and for difenconazole 6 µg kg^{-1} (lowest detected calibration standard 0.1 µg kg^{-1}).

2.8 Statistical analysis

Data were checked for normal distribution with Shapiro-Wilk Test at $p = 0.05$. For non-normal distributed data, the Friedman Test and Kruskal-Wallis Test were applied. For normal distributed data, univariate ANOVA with repeated measurements and with Mauchly´s test for sphericity were used. Individual pesticide concentrations were defined as the dependent variable and the distance from the river-dyke to the sea-dyke as the independent variable. Relation between pesticide concentration and distance to the sea-dyke were calculated with linear regression.

3. Results and Discussion

3.1 Soil and sediment properties

Texture of all soil samples was silty clay loam and silt loam for all sediment samples. The pH was in the range from 5.9 to 6.1 for soil samples and from 6.2 to 6.9 for sediment samples. The SOC ranged from 15.6 to 19.3 gkg^{-1} and organic carbon of sediment from 13.0 to 16.6 g kg^{-1}. The CEC ranged from 10.2 to 12.1 $cmol_c$ kg^{-1} in soil samples and from 9.5 to 11.7 $cmol_c$ kg^{-1} for sediment samples (detailed results given in SI in Tab. S1 and S2). The soil property data agree with findings of previous studies describing properties of soil under paddy rice cultivation. Pan et al. (2003) determined soil organic carbon concentrations in paddy rice soil in China in the range of 7.7 to 19.2 g kg^{-1}. Liu et al., (2011) determined a CEC of 14.6 $cmol_c$ kg^{-1} and a pH value of 5.9 in paddy soil of the Zhejiang province in China, and Lu et al. (2002) measured a CEC of 14.4 $cmol_c$ kg^{-1} and a pH of 6.3.

Noteworthy, the soil organic carbon concentrations of fields towards the sea-dyke was (catena points 6 and 7), contained up to 3 g kg^{-1} more SOC than fields of the catena point 1, close to the river-dyke (R^2=0.88, $p<0.01$; Fig. 2 and Tab. S1). These findings were in line with Lee et al (2012), who reported an enrichment of organic matter closer to the dyke in the Chonus Bay, Korea. Beside the SOC concentration, no other soil and sediment properties showed any trends in distribution pattern as related to the presence of the sea-dyke.

3.2 Pesticide residues in soil under rice monoculture

In soil, eight out of the 12 target pesticides were detected. At least three pesticides co-occurred in all samples, with a maximum of eight pesticides measured in one single sample. Among all pesticides the fungicide isoprothiolane was most frequently detected (in 100% of the samples), followed by chlorpyrifos (85%) and propiconazole (41%) (Tab.2). Concentrations of pesticides in soils ranged from 4.8 (pretilachlor) to 42.6 µg kg^{-1} (isoprothiolane). Chlorpyrifos was amongst the three pesticides with highest residue concentrations, exhibiting a maximum value of 31.2 µg kg^{-1} in addition to having a high detection frequency (Tab.2).

Isoprothiolane is used against rice blast – a fungal infestation diseases in paddy rice production (Kihoro et al., 2013). The recommended application dosage for isoprothiolane was 480 g ha^{-1} one of the highest among all target pesticides (Tab.1), which corresponded with the highest detection frequency (100%) and average residue concentration (21.6 µg kg^{-1}) of all pesticides (Tab. 2). Only Fenobucarb, with recommend 600 g ha^{-1} application amount was higher, however the detection of this pesticides was only 38%, which likely reflects the short half-life of this compound of 18 days (PPDB, 2017) (Tab 1 and 2). Several studies observed similar detection frequencies of isoprothiolane in soil of paddy rice fields (Toan et al., 2013), surface water (Chau et al., 2015) or floodwater of paddy fields (Trinh et al., 2017) in Vietnam. Average isoprothiolane concentration in this study was lower than reported by Toan et al. (2013), who determined an average of 182 µg isoprothiolane kg^{-1} in paddy rice soil in the Mekong Delta. In the Mekong Delta, climate conditions allow three cropping cycles per year, resulting in higher application frequencies. Our concentrations were thus closer to those of Nishina et al. (2010), who reported an average isorpothiolane concentration of 9.6 µg kg^{-1} in soil under vegetable production in the Red River Delta.

The recommended application dosage for chlorpyrifos was 150 g ha^{-1}, which corresponds to the second lowest application doses among the four most detected pesticides. Nevertheless, Chlorpyrifos was detected at high frequency (85%), which can be explained by its physico-

chemical properties (Fig. 3). The potential of a pesticide to accumulate in soil and the environment can be estimated by the octanol-water partition coefficient (log K_{ow}). Chlorpyrifos has one of the highest log K_{ow} of all target pesticides, which indicates stronger sorption to organic matter than for the other ingredients under study. As organic matter is the main binding partner for many pesticides in soil (Bollag et al., 1992) and specifically for chlorpyrifos (Álvarez et al., 2013), the enhanced accumulation of this insecticide is in line with the elevated SOC concentrations (15 to 19 g kg^{-1}) of the soil samples.

In all soil samples pesticide concentrations were below respective critical concentration values for soil and sediment dwelling organism (PPDB, 2018; Tab. S.3). However, all samples contained at least three or more pesticides with yet unknown effects due to multiple exposures (so-called “cocktail” effect).

3.3 Pesticide residues in sediment of irrigation ditches

Six out of 12 target pesticides were detected in sediments of the irrigation ditches. All samples contained at least two pesticides. Most frequently detected pesticides were isoprothiolane (71%) and propiconazole (71%), which was similar to the soil samples, followed by pretilachlor (43%) and azoxystrobin (26%) (Tab.2). Pesticide concentrations ranged from 5.5 (pretilachlor) to 35.0 µg kg^{-1} (azoxystrobin) (Tab.2).

Detection frequencies in the sediments of the irrigation ditches were lower than those of paddy soil samples, reflecting that only parts of the pesticides applied to the fields reached the ditches and that some of the pollutants might have already been washed away. However, pesticides can reach irrigation ditches via the discharge of irrigation water, either in dissolved form or bound to dissolved organic matter (DOM) (Boithias et al., 2014). A direct correlation between water drainage of paddy fields and an increase of pesticide concentrations in adjacent surface water was reported by Phong et al. (2010). Similar pesticides loads in soil, as the target area,

and in sediment, as the non-target area, strongly indicate a translocation of applied pesticides via irrigation water into the water environment.

The pesticide with the highest detected concentration in sediment was azoxystrobin (Tab.2). This finding contrasts that of the soil samples, where concentrations for this pesticide were amongst the lowest (Tab.2). The fungicide can be used against rice sheath blight, which is a similarly important disease as rice blast (Rice knowledge Bank of the IRRI, 2018). Due to its hydrophilic nature, azoxystrobin is more mobile in soil than the other target pesticides, i.e., it can also be more easily mobilized via irrigation water and transported into the ditches. In contrast, the immobile pesticide chlorpyrifos (high log K_{ow} value) with low application dosages (Tab.1 and Fig.3) was not detected frequently in the sediment of the irrigation ditches. These pesticide concentration patterns were in line with findings of Riise et al. (2004), who observed a transport of more mobile pesticides from agricultural fields through surface and drainage water. Additionally, Riise et al. (2004) found that high detection frequencies and concentrations of pesticides in non-target areas were controlled by the application dosage on the target area and by substance properties.

The low detection frequency of chlorpyrifos in sediment samples was consistent with findings of Haynes et al. (2000). They did not detect chlorpyrifos in intertidal sediments from an intensive coastal agricultural area of Queensland, Australia, although this pesticide had been commonly used. Hence, the fate of pesticides in the environment is highly influenced by the compound´s movement from paddy fields into the river and by individual log K_{ow} value of the substances (Nakano et al., 2004; Tab.1 and Fig. 3).

Individual pesticide concentrations in sediment samples of irrigation ditches did not exceed any critical value for soil and sediment organisms with the exception of chlorpyrifos; here maximum residue concentrations of 9.1 µg kg^{-1}(Tab. 2) were seven times larger than the critical value for fish (1.3ppb; Tab. S 3) and approximately twice as high for aquatic invertebrates (4.6ppb; Tab. S 3).We cannot easily translate a sediment concentration to that potentially occurring in animals; yet, at any contact with the sediment, biological damage should not be

a-priori excluded at such concentration levels. The elevated concentrations might thus also put local people at risk as *i)* chlorpyrifos has a high potential to accumulate in soil and environment, while *ii)* irrigation ditches are also used as a water source for freshwater aquaculture ponds and act as a natural habitat for fish and shrimps, which is utilized either for own consumption or for selling by local population (Klemick and Lichtenberg, 2008).

3.4 Influence of a dyke system on the spatial distribution of pesticides

To evaluate the influence of the dyke system on the spatial distribution of pesticides, we only considered pesticides with a detection frequency of > 50% in soil samples of the catena, i.e., isoprothiolane and chlorpyrifos. There was no overall relationship between the average concentrations of isoprothiolane and chlorpyrifos and distance to the sea-dyke along the entire sampled catena (Fig. S1)

We attribute the lack of clear spatial relationship of pesticide concentrations towards the sea-dyke to the presence of incoming irrigation ditches, which may lead to changes in pesticide loads from side channels. Based on these considerations, we thus further clustered the catena points to illustrate how the main irrigation ditch within the dyked area and the tidal effects on the outlet might influence the distribution pattern of pesticide concentrations (Fig.1). There has been one catena point (point 4), which was located on rice fields with a direct connection to the main irrigation ditch, and one catena point (point 7), which was located on rice fields with a close connection to the outlet gate (Fig.1). Pesticide concentrations at these catena points were lower than at other catena points, indicating that a connection with main irrigation ditches results in a washout of pesticides or in a dilution with less contaminated sediments relative to other sampling points (Fig. 4 and Tab. 3).

Toan et al. (2013) described 40% lower pesticide concentrations in canal water than in water of field outlets, in line with our observations. In addition, they reported significantly larger

pesticide concentrations in soils during the dry season than in the rainy season because of less water flow and consequently less dilution (Toan et al., 2013).

Pesticide concentrations in samples of the catena point next to the outlet (close to the sea-dyke; Catena point 7) might be affected by diurnal tidal effects. During every tidal cycle, fine sediments are eroded during ebb-tide, re-suspended and deposited flood-tide (Allen et al., 1980). The opening time of the outlet gate is aligned with tides: during flood-tide the gate is closed to prevent flooding and salinity intrusion and during ebb-tide the gate might be opened to discharge water (Own exploratory interview based data, 2015). However, the farmer's necessities determine the opening time of the gate, which is most of the time closed to keep the required water level for paddy rice production (Own exploratory interview based data, 2015). It seemed thus reasonable to hypothesize that the pesticide distribution pattern in soils is influenced by such water exchange. We therefore distinguished between fields at sites in close connection to the main irrigation ditch and to the outlet and fields at sites not in intermediate contact with the main irrigation ditch and the outlet.

Average isoprothiolane concentration in fields at sites in connection to the main irrigation ditch and the outlet did not exceed 20 µg kg^{-1}, whilst average concentrations in fields at sites not in intermediate contact with the main irrigation ditch and the outlet were not below 22 µg kg^{-1} (Fig. 4). Likewise, average chlorpyrifos concentrations were larger in fields at sites not in intermediate contact with the main irrigation ditch and the outlet than in fields at sites close in connection to the main irrigation ditch and the outlet (Fig. 4). Chlorpyrifos concentrations in fields direct located at the inlet gate is approximately 2 µg kg^{-1} lower than in fields in connection to the main irrigation ditch and the outlet (Tab. 3). However, these fields are closely located at the inlet gate and the concentration in these fields can be asses as baseline values.

A similar trend as observed for average concentrations, were for maximum pesticide concentrations (Fig. S2). In fields at sites connected to the main irrigation ditch and the outlet, the maximum pesticide concentrations were lower, compared to fields at sites not in intermediate contact with the main irrigation ditch and the outlet (Fig. S2). The lower pesticide

load in fields at sites in connection to the main irrigation ditch and the outlet support our assumption that elevated availability of water in these fields resulted in larger washout or increased dilution effects with less contaminated sediment or in both.

Due to above-mentioned dilution effects on-site, both the average and maximum isoprothiolane concentration did not increase from the river-dyke to the sea-dyke in fields at sites in connection to the main irrigation ditch and the outlet (Fig. 4 and Fig. S2). This was different to isoprothiolane concentrations in fields at sites without intermediate contact to the main irrigation ditch and the outlet: here the average concentrations of isoprothiolane increased with increasing distance from the river dyke, i.e., with increasing vicinity to the sea-dyke (Fig. 4 and Fig. S2). This trend was even more clear for chlorpyrifos (Fig. 4 and Fig. S2). Both, average and maximum concentrations of chlorpyrifos clearly increased with increasing vicinity to the sea-dyke in fields at sites not in intermediate contact with the main irrigation ditch and the outlet (catena points 1,2,3,5,6), while concentrations in fields at sites close in connection to the main irrigation ditch and the outlet remained similar (catena points 4,7) (Fig. 4 and Fig. S2). Consequently, these results clearly imply an impact of human dyke construction and water management on pesticide pollution patterns in the Red River Delta, and therewith support the assumption of local authorities that areas closer to the dyke are exposed to higher pesticide pollution levels. However, more research is needed to further explore the fate of pesticides with different physico-chemical properties and other pollutants typical for agricultural production areas in delta regions, such as e.g. antibiotics (Holmström et al., 2003) including also other dyked areas globally.

We can assume that the high recommended pesticide application dosage masks an even clearer spatial pattern for isoprothiolane accumulation in the dyked area. The application dosage has direct impact on pesticide load in surface water (Stover and Hamill, 1994) and therefore on residue concentrations in soils and sediments. Varca (2012) additionally demonstrated a correlation between pesticide load in surface water and application time on paddy fields, which was not controlled for here. In contrast, the distribution pattern of

chlorpyrifos, which is characterized by lower application dosage and high accumulation in soil and environment, is rather decoupled from recent application considerations. The correlation between average SOC concentration and the average chlorpyrifos concentration of the fields without connectivity to main irrigation ditch implies a coherence (Fig. 5. Increasing SOC concentration leads to enhanced sorption of chlorpyrifos to soils (Gebremariam et al., 2012).

Artificial dyke systems facilitate sediment deposition close to the dyke (Kim et al., 2006; Lee et al., 2012; Lee et al., 2009), which is known to transport and later deposit large amount of pesticides (Bergamaschi et al., 2001). Davis et al. (2012) determined high concentrations of diuron in sediments of catchment waterways of the Great Barrier Reef. The herbicide diuron is strongly hydrophobic (log *Kow*: 8.3), and Davis et al. (2012) as well as Spark and Swift (2002) thus related its fate to that of dissolved organic matter or suspended sediments. In addition, other pesticides with properties similar to chlorpyrifos, i.e., pretilachlor and fenoxaprop-p-ethyl, increased in average concentrations towards the sea-dyke (Tab. 3). Pesticides with strong affinity to organic matter seem to show the largest dependence to dyke construction.

The correlation between the concentrations of chlorpyrifos and SOC was limited to the catena points without connectivity to the main irrigation ditch and the outlet (Fig. 5), which we attribute to the higher dilution at these two catena points affecting the pesticide concentrations but affecting much less the concentration of SOC in the soil (Fig. 2).

In summary, the results imply that the dyke influences the spatial distribution of pesticides inside the dyked area, modulated by, e.g., dilution effects from first main irrigation ditches and the outlet gate nearby, the compound´s physiochemical properties and the application dosage.

4. Recommendations for stakeholders

There was no single sample, in which a number of pesticides did not co-occur. Although no threshold for sediment dwelling organism was exceeded, it has to be considered that all

detected pesticides were either moderately or slightly hazardous after WHO classification (WHO, 2010) and their toxicity effects might add-up when more than one pesticide is abundant. To limit pesticide pollution, one possible measure would be to prolong the water holding period within rice fields after pesticide application (Anyusheva et al., 2012), in order to avoid discharge into adjacent water bodies. Watanabe et al. (2006) recommend keeping the water in the field for at least 10 days after application.

Although we could show some patterns of spatial distribution of pesticides linked to the dyke and irrigation systems only, our data support the assumption that pesticide concentrations, for some compounds, are higher at the sea-dyke. Whether this finding also implies reduced pesticide loads reaching the ocean now warrants further attention. Care, however, should be be taken when the sea-dyke is opened and water and suspended sediment with respective pesticide load is discharged in one pulse to the coastal environment and mangrove systems, commonly used for clam production, for instance. The opening time of the outlet gate should thus be adjusted considering not only the pesticide application schedule of the paddy rice farmers, but also clam farming for instance, to prevent discharging irrigation water with high pesticide concentrations to the outside environment at critical times.

However, besides coping with pesticide pollution, it is even more important to reduce the overall pesticide input to the environment to a minimum. It is therefore critical to raise the awareness of farmers for the risk associated by pesticides, as several studies and our own observations showed inadequate pesticide handling and management (Chau et al., 2015; Toan et al., 2013). Although programs such as Integrated Pest Management (IPM) (Berg and Tam, 2012; Chi et al., 2004) has started in the 1980s in Southeast Asia, many farmers still practice the “the more, the better” principle, and they still need to be convinced to follow the good farming practices (Normile, 2017).

4. Conclusions and Outlook

This study was designed to evaluate pesticide concentrations in soil and sediments in rice monocultures and irrigation ditches and the influence of a dyke on spatial distribution of the detected pesticides in the Red River Delta, Vietnam. Residues of pesticides were frequently detected in soil and sediment of the dyke-protected area. Most frequently detected pesticides were isoprothiolane and chlorpyrifos in paddy rice soil and isoprothiolane and propiconazole in sediments of irrigation ditches, as explained by substance properties and application dosage. Our data indicate that the classification of different pollution zones within the dyked area as practiced by local authorities is not only meaningful for surface water but also applicable for the spatial distribution of at least hydrophobic pesticides in surface soil, which can be found at higher concentrations in fields closer to the sea-dyke.

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Tab. 1: Target pesticides, their physiochemical properties and toxicity classes (after WHO, 2010) as well as recommended application doses.

Pesticide Compound [a]	Solubility (20°C) [a] mg L^{-1}	Octanol-water partition coefficient log *Kow* [a]	Soil sorption Koc L kg^{-1} [a]	Half-life in soil DT_{50} (av., days) [a]	WHO toxicity classes [b]	Recommended application dose (g ha^{-1})[c]	Chemical formula [a]
Insecticide							
Chlorpyrifos	1.1	4.70	8,151	21	II	150	$C_9H_{11}Cl_3NO_3PS$
Quinalphos	17.8	4.44	1,465	21	II	375	$C_{12}H_{15}N_2O_3PS$
Fipronil	3.8	3.75	-	225	III	40	$C_{12}H_4Cl_2F_6N_4OS$
Fenobucarb	420.0	2.78	-	18	II	600	$C_{12}H_{17}NO_2$
Fungicide							
Difenconazole	15.0	5.44	-	130	II	63	$C_{19}H_{17}Cl_2N_3O_3$
Fludioxonil	1.8	4.12	145,600	20	U	4.6 ml kg^{-1}[d]	$C_{12}H_6F_2N_2O_2$
Tebuconazole	36	3.78	-	47	II	250	$C_{16}H_{22}ClN_3O$
Propiconazole	150.0	3.72	1,086	214	II	50	$C_{15}H_{17}Cl_2N_3O_2$
Isoprothiolane	54	3.30	1,352	320	II	480	$C_{12}H_{18}O_4S_2$
Azoxystrobin	6.7	2.50	589	180.7	III	100	$C_{22}H_{17}N_3O_5$
Herbicide							
Fenoxaprop-P-ethyl	0.7	4.60	11,354	0.4	U	28	$C_{18}H_{16}ClNO_5$
Pretilachlor	500	4.08	-	30	U	360	C_{17}H26ClNO2

[a] Source: The pesticide properties database (PPDB, 2017): [b]WHO toxicity classes: Class III: slightly hazardous, Class II: moderately hazardous, U: unlikely to present acute hazard (WHO, 2010);[c] Estimated via the prescribed highest dosage of the commercial products; [d] Dosage refer to seed treatment with ml per kg seed.

Tab. 2: Detection frequency (%), mean and maximum concentration (µg kg^{-1}) for soil (paddy rice fields) and sediments (irrigation ditches), standard deviation brackets.

Pesticide compound	Detection frequency (%)	Mean conc. (µg kg^{-1})	Max conc. (µg kg^{-1})
Paddy rice fields (Soil samples)(n=35)			
Isoprothiolane	100	21.6 (±7.7)	42.6
Chlorpyrifos	85	11.0 (±5.8)	31.2
Propiconazole	41	9.6 (±5.2)	18.8
Fenoxaprop-p-ethyl	38	18.1 (±9.1)	22.9
Fenobucarb	38	9.9 (±4.9)	10.6
Pretilachlor	28	14.9 (±8.6)	37.4
Azoxystrobin	15	14.5 (±5.6)	15.7
Difenconazole	2	18.4 (±0.0)	18.4
Irrigation ditches (Sediment samples)(n=16)			
Isoprothiolane	71	18.9 (±3.1)	23.3
Propiconazole	71	17.0 (±4.9)	28.6
Pretilachlor	43	14.1 (±4.5)	19.8
Azoxystrobin	26	21.0 (±8.1)	35.0
Chlorpyrifos	21	8.6 (±0.5)	9.1
Fenoxaprop-p-ethyl	7	17.3 (±0.0)	17.3

Tab. 3: Mean pesticide residue concentrations (µg kg^{-1}) with standard deviation in brackets (n = 5) of paddy rice soil of the individual catena point. Non-detected pesticide residue concentrations were set to the routine limit of quantification^{-2} (RLOQ^{-2}) for calculations of means. Catena points are defined as the sampling points perpendicular to the dyke with catena point 1 located at the inlet (river-dyke) to catena point 7 located at the outlet (sea-dyke).

	Close to river dyke						Close to sea dyke
Catena point	1	2	3	4*	5	6	7**
Pesticide							
Chlorpyrifos	5.6 (±3.8)	8.7 (±0.7)	10.4 (±2.3)	8.1 (±4.3)	12.3 (±4.3)	17.6 (±7.7)	7.2 (±3.3)
Fenobucarb	9.9 (±0.5)	6.7 (±4.7)	1.5 (±0.0)	3.2 (±3.7)	6.8 (±4.8)	6.3 (±4.4)	1.5 (±0.0)
Isoprothiolane	18.5 (±6.3)	24.6 (±11.1)	23.6 (±4.2)	17.7 (±3.4)	22.5 (±10.8)	28.2 (±11.5)	20.7 (±2.2)
Pretilachlor	3.6 (±2.4)	8.8 (±6.8)	3.1 (±2.5)	2.0 (±0.0)	5.1 (±5.0)	21.1 (±15.4)	2.0 (±0.0)
Propiconazole	6.4 (±2.5)	6.0 (±3.6)	7.2 (±3.0)	5.3 (±4.7)	6.0 (±3.6)	5.4 (±7.4)	4.9 (±6.2)
Fenoxaprop-p-Ethyl	1.5 (±0.0)	4.8 (±7.5)	5.1 (±8.0)	1.5 (±0.0)	4.1 (±5.7)	17.3 (±3.2)	18.7 (±1.7)
Azoxystrobin	2.0 (±0.0)	2.0 (±0.0)	6.8 (±6.5)	6.7 (±6.4)	7.3 (±7.3)	2.0 (±0.0)	4.7 (±6.1)

*Catena point in connectivity to the main irrigation ditch; ** Catena point in connectivity to the outlet

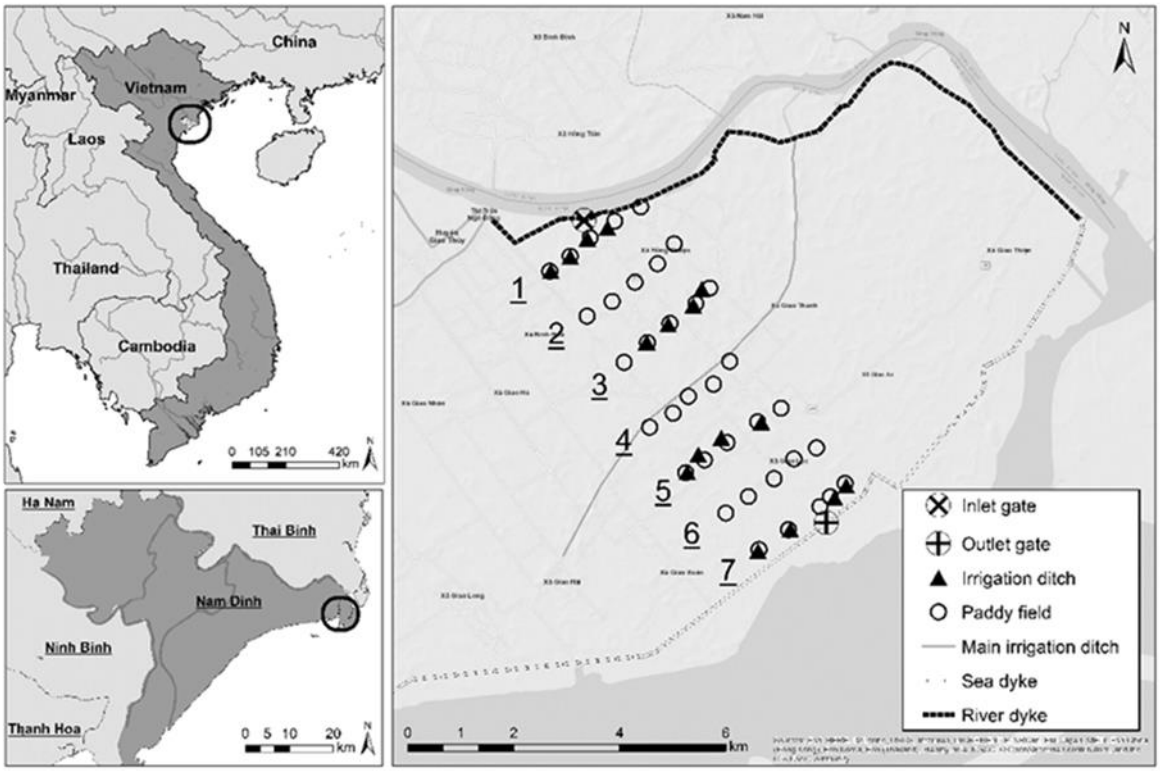


Fig. 1: Location of the study site and sampled catena; the irrigation system is not shown.

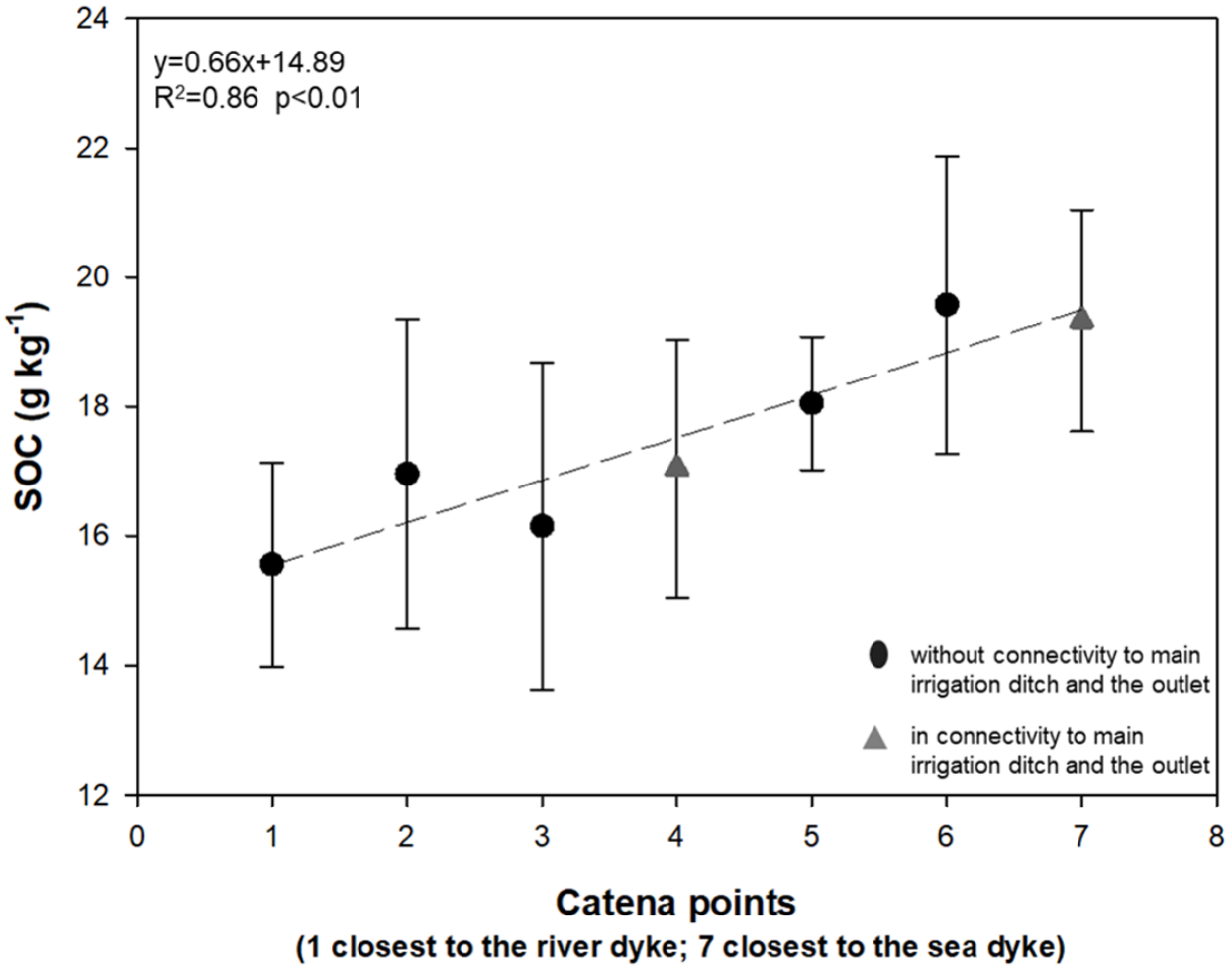


Fig: 2: Changes in mean SOC (g kg^{-1}) concentrations with standard deviation in the paddy rice fields with decreasing distance to the sea-dyke; values in filled circles represent catena points that are influenced by mass inputs and outputs of larger irrigation channels. For location of the catena points, refer to Fig. 1.

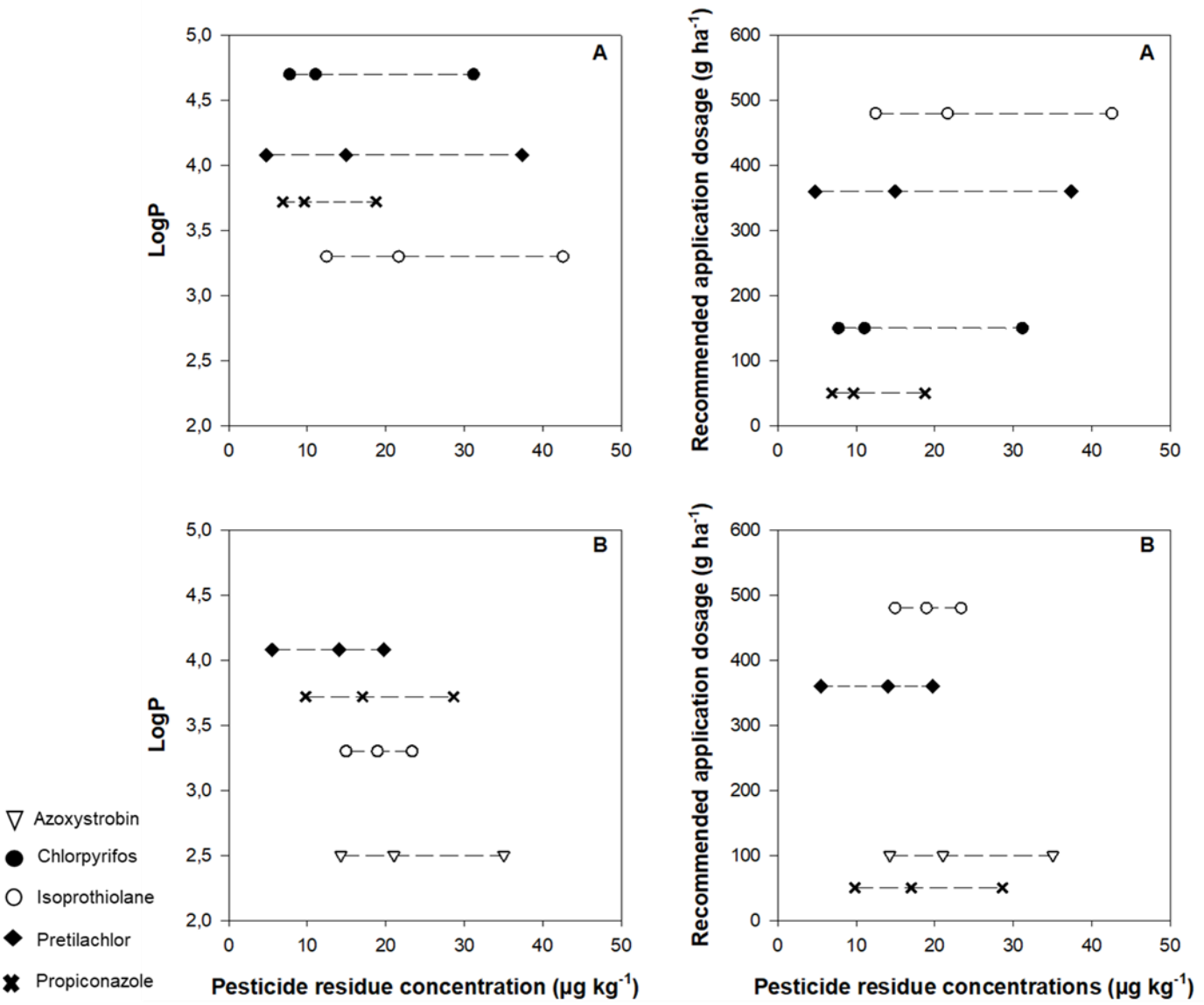


Fig. 3: Concentration ranges (minimum, mean, maximum) of pesticide residues in soil of paddy rice fields (A) and sediment of irrigation ditches (B); the concentrations are noted against log K_{ow} values and the recommended application dosage (g ha^{-1}) estimated via the prescribed dosage of the commercial products containing the respective active ingredient. Only pesticides with detection frequency ≥ 40% and the maximum detected pesticide in the soil and sediment were considered.

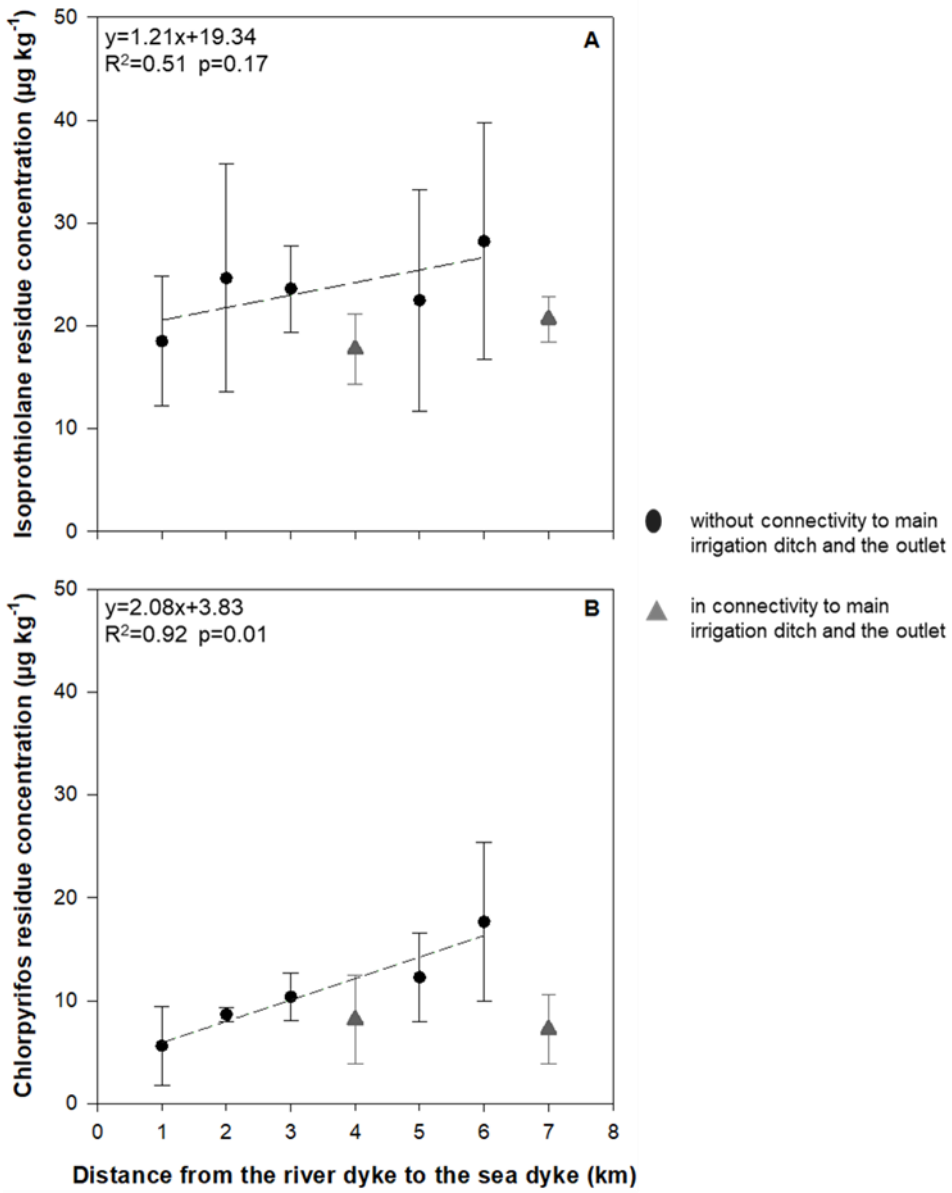


Fig. 4: Mean pesticide residue concentration distribution with standard deviation inside the dyked area. Detection frequency was 100% for Isoprothiolane (A) and 85% for Chlorpyrifos (B).

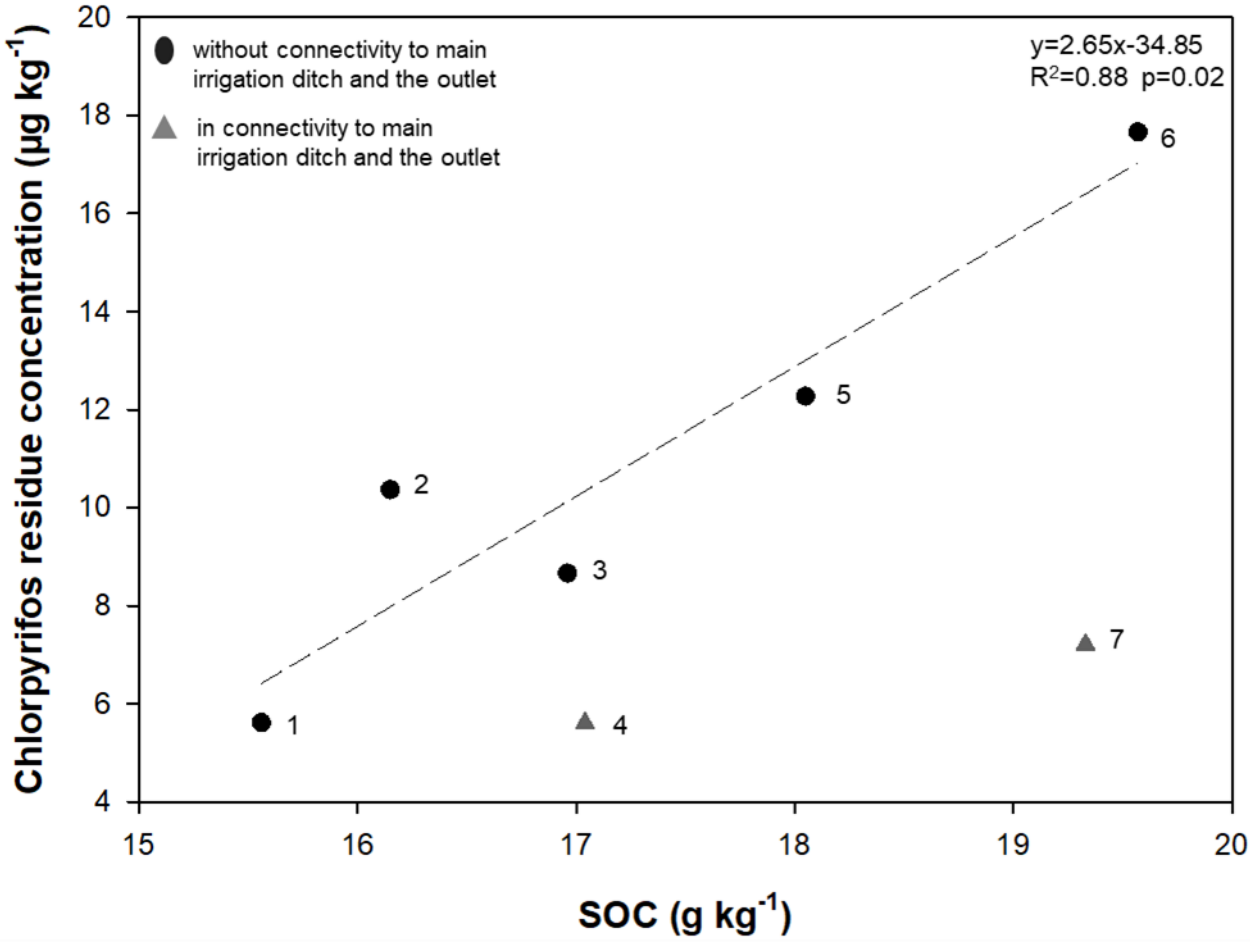


Fig. 5: Correlation between mean SOC (g kg^{-1}) concentration and mean chlorpyrifos concentration (µg kg^{-1}) of the catena points without connectivity to main irrigation ditch and the outlet; The numbers in the figure are the respective catena points.

Tab. S1: Summary of the estimated soil parameter; pH, SOC and CEC are mean values with standard variation in brackets; used methods are described in chapter 2.4

Catena point/ Distance to the sea dyke (km)	Texture (FAO classification)	pH	SOC (g kg^{-1})	Salinity (FAO classification)	CEC (cmolc kg^{-1})
1	SiCL-silty clay loam	6.0 (±0.19)	15.56 (±1.58)	Non saline	12.1 (±3.39)
2	SiCL-silty clay loam	6.2 (±0.28)	16.93 (±2.39)	Non saline	11.0 (±1.22)
3	SiCL-silty clay loam	6.1 (±0.31)	16.15 (±2.53)	Non saline	10.4 (±0.89)
4	SiCL-silty clay loam	6.1 (±0.32)	17.04 (±2.00)	Non saline	10.8 (±0.44)
5	SiCL-silty clay loam	5.9 (±0.30)	18.05 (±1.03)	Non saline	11.0 (±0.00)
6	SiCL-silty clay loam	5.8 (±0.01)	19.57 (±2.30)	Non saline	10.2 (±1.14)
7	SiCL-silty clay loam	6.1 (±0.21)	19.33 (±1.71)	Non saline	10.2 (±0.82)

FAO: Food and Agriculture Organization of the United Nations; SOC: soil organic carbon; CEC: cation exchange capacity

Tab. S2: Summary of the estimated sediment parameter; pH_{H2O}, C_{org} and CEC are mean values with standard variance in brackets; used methods are described in chapter 2.4.

Catena point	Texture (FAO classification)	pH_{H2O}	C_{org} (g kg^{-1})	Salinity (FAO classification)	CEC (cmolc kg^{-1})
1	Sil-silt loam	6.2 (±0.20)	15.95 (±5.31)	Non saline	9.5 (±0.57)
3	Sil-silt loam	6.3 (±0.49)	16.62 (±4.88)	Non saline	9.7 (±0.50)
5	Sil-silt loam	6.4 (±0.54)	13.00 (±1.17)	Non saline	9.7 (±0.95)
7	Sil-silt loam	6.9 (±0.53)	14.44 (±1.83)	Non saline	11.7 (±4.19)

FAO: Food and Agriculture Organization of the United Nations; C_{org}: organic carbon; CEC: cation exchange capacity

Tab. S 3: Critical values for risk assessment

Pesticide	Species	Test	Duration	Critical Value (ppb)
Isoprothiolane	Fish	LC50	96h	6,800
	Aquatic invertebrates	EC50	48h	62,000
	Earthworm	LC50	14d	>91,950
Chlorpyrifos	Fish	LC50	96h	1.3
	Aquatic invertebrates	NOEC	21d	4.6
	Earthworm	LC50	14d	129,000
Propiconazole	Fish	LC50	96h	3,400
	Aquatic invertebrates	NOEC	21d	310
	Soil dwelling organism	NOEC	28h	25,000
Fenoxaprop-p-Ethyl	Fish	NOEC	21d	36
	Aquatic invertebrates	NOEC	21d	220
	Sediment dwelling organism	NOEC	28d	200
Fenobucarb	Fish	LC50	96h	1,700
	Aquatic invertebrates	EC50	48h	100
	Earthworm	LC50	14d	10,700
Pretilachlor	Fish	LC50	96h	900
	Aquatic invertebrates	EC50	48h	13,000
	Earthworm	LC50	14d	93,000
Azoxystrobin	Fish	NOEC	21d	147
	Aquatic invertebrates	NOEC	21d	44
	Sediment dwelling organism	NOEC	28d	800
Difenconazole	Fish	NOEC	21d	23
	Aquatic invertebrates	NOEC	21d	5.6
	Sediment dwelling organism	NOEC	28d	10,000

Source: Pesticide Properties Database (The PPDB): https://sitem.herts.ac.uk/aeru/iupac/index.htm

Tab. S 4: Mean pesticide residue concentrations with standard derivation in sediment (n=5) of the irrigation ditches of the individual catena points. Non-detected pesticide residue concentrations were calculated as RLOQ $^{-2}$. Catena points are defined as the sampling points perpendicular to the dyke with one located at the inlet to seven located at the outlet

	Close to river-dyke			Close to sea dyke
Catena points	1	3	5	7
Pesticides		µg kg^{-1}		
Chlorpyrifos	1.41 (±0.00)	3.76 (±4.07)	3.09 (±3.35)	3.34 (±3.86)
Fenobucarb	1.55 (±0.00)	1.55 (±0.00)	5.65 (±8.20)	1.55 (±0.00)
Isoprothiolane	19.97 (±2.66)	19.12 (±3.98)	13.54 (±8.52)	6.02 (±8.44)
Pretilachlor	5.23 (±6.46)	12.75 (±6.32)	11.81 (±7.39)	2.00 (±0.00)
Propiconazole	12.12 (±6.78)	14.53 (±4.40)	13.62 (±8.38)	12.27 (±12.28)
Fenoxaprop-p-Ethyl	5.46 (±7.91)	1.50 (±0.00)	1.50 (±0.00)	1.50 (±0.00)
Azoxystrobin	13.33 (±5.59)	12.56 (±9.22)	6.55 (±9.09)	2.00 (±0.00)

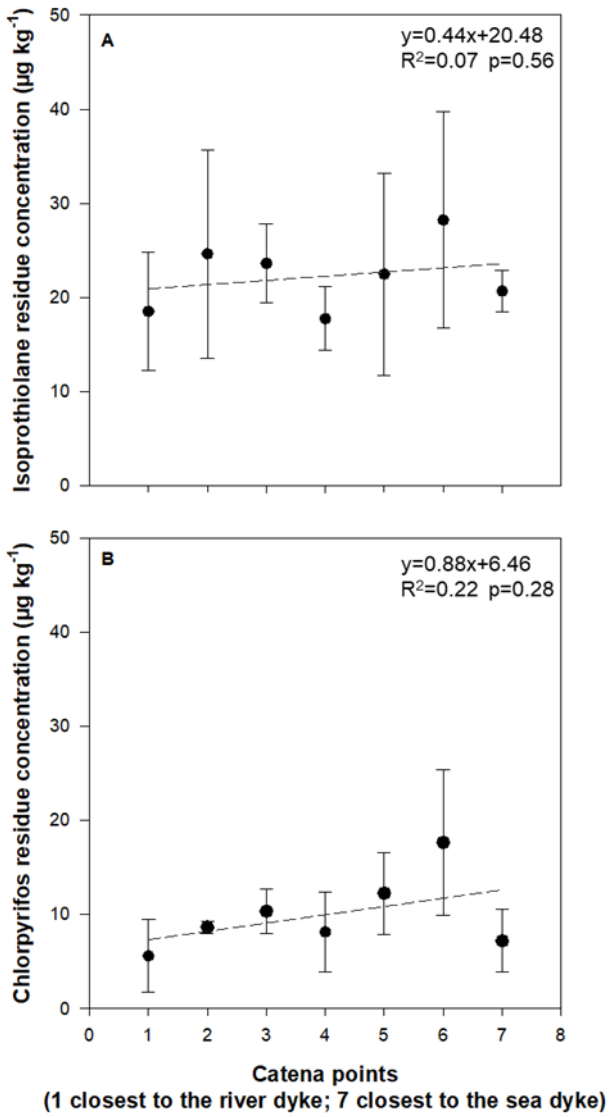
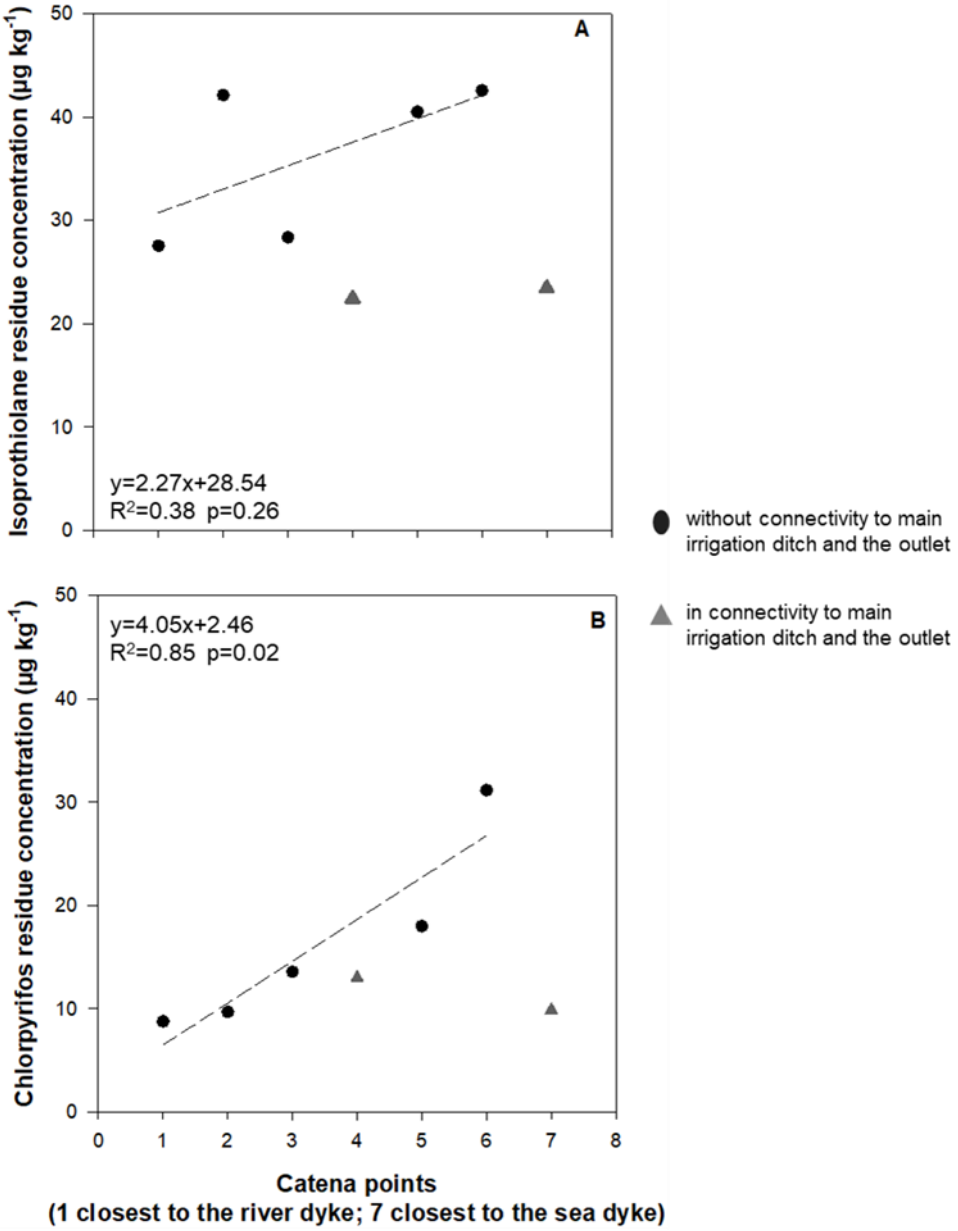


Fig. S1: Mean pesticide residue concentration distribution with standard deviation inside the dyked area. Detection frequency was 100% for Isoprothiolane (A) and 85% for Chlorpyrifos (B).



S 2: Maximum pesticide residue concentration distribution inside the dyked area. Detection frequency was 100% for Isoprothiolane (A) and 85% for Chlorpyrifos (B).