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Natural estrogen emissions to subsurface tile drains from experimental grassland fields in Switzerland after application of livestock slurries and free compounds

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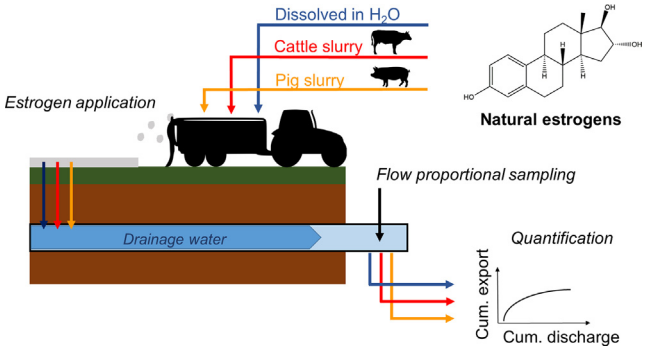
HIGHLIGHTS

- A dozen of close-to-practice field experiments were conducted over 1.5 years.
- Slurry types influenced natural estrogen export dynamics to tile drains.
- Preferential flow of estrogens accentuated through particle facilitated transport.
- Estrogen fractions exported <0.5% and no long-term critical stream concentrations.
- Groundwater ubiquity score underestimated exported natural estrogen fractions.

GRAPHICAL ABSTRACT



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ABSTRACT

Natural estrogens are present in high concentrations in livestock slurries, which are often applied to agricultural fields in large quantities. As such, the export of slurry-derived natural estrogens from tile-drained fields is a potential source for estrogenic pollution in surface waters. Yet despite the abundance of tile-drained fields in Central Europe, export of natural estrogens from agricultural fields receiving livestock slurries is rarely studied in this region. In an effort to fill this knowledge gap, here we applied natural estrogens to Swiss experimental fields in the form of cattle slurry, pig slurry or dissolved in water, and quantified them in flow-proportionally collected drainage water over 18 months. After pig and cattle slurry applications, concentration maxima in drainage water of 73, 8, 37, and 60 ng L^{-1} for 17α-estradiol (E2α), 17β-estradiol (E2β), estrone (E1), and estriol (E3), respectively, were observed shortly after rain events. The exported fractions of individual natural estrogens to tile drains were on average 0.26% (ranging from 0.08 to 0.41%) after cattle, and 0.18% (0.03–0.40%) after pig slurry applications. Such numbers were higher than expected from the leaching potential based on substance properties, and comparable to those of more mobile micropollutants previously studied on the same fields. Natural estrogens were mainly exported to tile drains through preferential flow. Exported fractions were lower when applied in aqueous solution than when applied in slurry, pointing to particle-facilitated transport to tile drains when applied in slurry. In Switzerland, the estimated 6.3, 0.6, 7.4, and 7.7 g of E2α, E2β, E1, and E3, respectively, exported through the tile-drained agricultural area per year contribute little to the total natural estrogen load received by surface waters. However, after slurry applications in highly drained catchments, natural estrogen emissions to tile drains can cause short term (i.e. less than 1 week) estrogenic exposure in nearby streams.

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1. Introduction

In Swiss agricultural systems, livestock slurry is applied in large quantities as a fertilizer source. In addition to key crop nutrients, these slurries also contain a variety of natural estrogens, including 17α-estradiol (E2α), 17β-estradiol (E2β), estrone (E1), and estriol (E3), in concentrations up to 74,700 ng L^{-1} (Combalbert et al., 2012; Raman et al., 2004; Rechsteiner et al., 2020a). In particular, drained agricultural areas have an elevated risk of exporting slurry related contaminants such as steroid hormones (Gall et al., 2014), nutrients (Stamm et al., 1998), or veterinary antibiotics (Boxall et al., 2002), as well as other types of micropollutants such as pesticides (Kladivko et al., 1999; Wettstein et al., 2016) and natural toxins (Hoerger et al., 2011; Schenzel et al., 2012) to surface waters. Furthermore, natural estrogens were found in surface waters with agriculturally dominated catchments (Alvarez et al., 2013; Kolodziej and Sedlak, 2007; Rechsteiner et al., 2020b; Tremblay et al., 2018) and wells in agricultural areas (Casey et al., 2019a). Moreover, in some of the investigated streams and wells, natural estrogen concentrations were even above critical concentrations for aquatic organisms according to the European Union environmental quality standards (EU EQS) of 0.4 ng L^{-1} for E2β and 3.6 ng L^{-1} for E1 (Commission Implementing Decision (EU) 2018/840, 2018). Exposure of fish to natural estrogens at such levels has led to various adverse effects including the feminization of male fish (Routledge et al., 1998). As slurry is a source of natural estrogens in the environment that potentially contaminates surface waters, the fate of slurry-derived natural estrogens from different livestock species after application on agricultural areas needs to be examined. Furthermore, in Switzerland the number of wastewater treatment plants (WWTPs) with an advanced treatment step that eliminates estrogens in wastewater is increasing (Maurer and Herlyn, 2006). Consequently, in terms of relative contribution, agriculture will gain in importance as a source for estrogens in surface waters.

Several studies ranging from pot trials, lysimeters, and even field scale have investigated emissions of E2β from manured grasslands to adjacent water bodies through surface run-off (Dutta et al., 2010; Havens et al., 2019), percolation (Lægdsmand et al., 2009; Steiner et al., 2010), and tile drains (Gall et al., 2014; Kjær et al., 2007). However, where reported or deducible, both the loads of E2β applied on soil (ranging from <1 mg ha^{-1} (Thompson et al., 2009) to 0.3 kg ha^{-1} (Steiner et al., 2010)), and the exported fractions found in eluting waters varied widely, from less than 1% (Gall et al., 2015; Kjær et al., 2007; Lægdsmand et al., 2009; Steiner et al., 2010) up to greater than 30% (Casey et al., 2019b; Thompson et al., 2009), which was explained by mobilized antecedent E2β in soils.

In this study, we focused on estrogen emissions from tile-drained agricultural areas, which cover 34% of the agricultural areas in northwestern Europe (Blann et al., 2009). Based on a modelling approach, it was estimated that in Switzerland around 25% of the total agricultural area, i.e. 230,000 ha, has a moderate to high potential to be drained (Kobierska et al., 2020). Even though drainage systems are widespread, the fate of slurry-derived natural estrogens applied to tile-drained fields has rarely been studied. Among them, only the experimental designs of Gall et al. (2011), Schoenborn et al. (2015), and Kjær et al. (2007) allowed monitoring of natural estrogen concentrations as well as fluxes in tile drains after slurry applications. Natural estrogens were mainly exported to tile drains through preferential flow after rain events (Gall et al., 2014; Kjær et al., 2007; Schoenborn et al., 2015). Concentration maxima in drainage water ranged from non-detected (E3) to 68 ng L^{-1} (E1) among all individual natural estrogens (Gall et al., 2011; Kjær et al., 2007). In the United States, less than 0.5% of the applied natural estrogens were measured in drainage water of agricultural fields receiving animal wastes (Gall et al., 2014). So far, only Gall et al. (2011) differentiated among emissions of natural estrogens from cattle and mixed pig and poultry slurry.

For the first time in Europe, we studied E2α, E2β, E1, and E3 emissions from tile-drained grassland fields on which cattle and pig slurries and estrogens dissolved in water were applied consecutively over two vegetation periods. In contrast to the Danish study of Kjær et al. (2007), slurry was applied with drag hoses and not through slurry injection. Natural estrogen concentrations and loads were quantified in drainage water and in different slurry types applied on the agricultural test fields to derive natural estrogen fractions exported to tile drains. To the best of our knowledge, a comparison between export dynamics and exported fractions of individual estrogens applied in matrices with solids (cattle and pig slurry) and those applied in a solid-free matrix (estrogens dissolved in water) is novel. Potentially influencing factors were evaluated, such as hydrology, as well as fate processes such as degradation and adsorption. In addition, we are able to compare exported fractions of different agricultural micropollutants such as mycotoxins (Hartmann et al., 2008; Schenzel et al., 2012), isoflavones (Hoerger et al., 2011), and pesticides (Wettstein et al., 2016), determined on the very same agricultural test fields. To this end, the groundwater ubiquity score (GUS) (Gustafson, 1989; Navarro et al., 2012), which classifies the leaching potential of pesticides to groundwater, was determined for each of these agricultural micropollutants. As far as we are aware, this is the first study to test the applicability of the GUS for compound classes other than pesticides to assess their emission behavior and fractions exported to tile drains. In a final step, determined fractions of natural estrogens exported to drainage water were extrapolated to annual slurry-derived estrogen loads exported to Swiss surface waters through tile drains and related to well-known human estrogen emissions (Arlos et al., 2018; Kostich et al., 2013; Margot et al., 2013).

2. Materials and methods

2.1. Chemicals

17α-Estradiol-16,16,17-d_3 (E2α-d_3) was purchased from BOC Sciences (Shirley, U.S.A.). Estriol-3,16,17-d_3 (E3-d_3) was acquired from Toronto Research Chemicals Inc. (North York, Canada). Additionally, E2α, E2β, 17β-estradiol-16,16,17-d3 (E2β-d_3), E1, Estrone-2,4,16,16-d4 (E1-d_4), and E3, all in 1000 μg mL^{-1} methanol, were bought from A2S (Saint Jean d'Illac, France). A list with all other chemicals used for chemical analyses is presented in the Supporting Information (SI), Chapter S2.

2.2. Study site

This study site has previously been described in Hartmann et al. (2008), Schenzel et al. (2012), Hoerger et al. (2011), and Wettstein et al. (2016). It is located in Zurich Affoltern, Switzerland (47°25′74"N, 8°30′85″E or 47.428899, 8.516591). The altitude is 444 m above sea level (a.s.l.). The experiments were conducted on two tile-drained agricultural test fields, named here as field 1 and field 2. The area of each field was 0.2 ha and the slope was between 1° and 2° from north-east to south-west (Fig. 1). According to the World Reference Base for Soil Resources, the soil was classified as a gleyic Cambisol (World Reference Base for Soil Resources, 2014). A list with additional soil parameters is presented in Table S1. At the study site, the mean annual precipitation was 1054 mm and the mean annual temperature was 9.4 °C from 1981 to 2010 (MeteoSwiss, 2020). The meteorological station (Reckenholz, 443 m a.s.l., 47°25′40″N, 8°31′04″E, MeteoSwiss, 2020), which is in 300 m distance from the study site, collected hourly the following meteorological variables: precipitation 1.5 m above soil surface, air temperature, relative humidity, global radiation and hours of sunshine 2 m above soil surface, and wind speed 10 m above soil surface. The daily mean values were calculated for all variables. The reference potential evapotranspiration for well-watered short grass cover with an albedo of 0.23 was determined with the Penman-Monteith equation (Smith, 1992). The calculations were conducted in a submodule

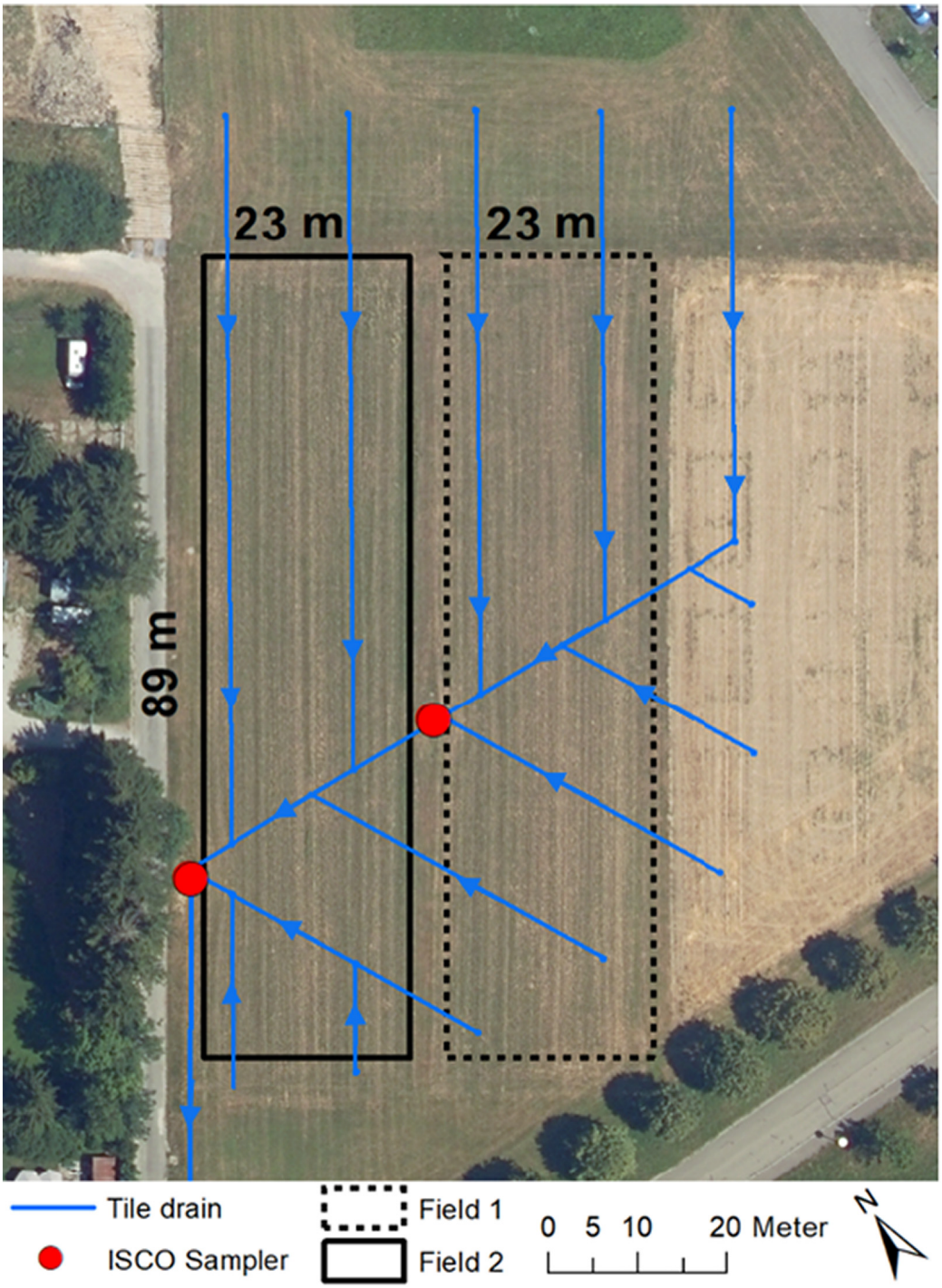

Fig. 1. Aerial image of the tile-drained agricultural test field 1 (framed with a black dotted line) and field 2 (framed with a black bold line). The tile drains are shown in blue. The arrows indicate the flow direction of the drainage water in the tile drains. The locations of the ISCO samplers are indicated with red dots. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of the HYDRUS-1D software package (Šimůnek et al., 2012). Net radiation from solar radiation was derived with the model's default values.

2.3. Natural estrogen application

Optimally, at the day of slurry application temperatures are moderate (10–25 °C) and after slurry application a small rain event (10–25 mm d^{-1}) takes place to reduce ammonia emissions and to assure infiltration of the nutrients to the top soil layer (Reidy and Menzi, 2007). To simulate optimal conditions, the fields were artificially irrigated after natural estrogen application with a dedicated irrigation system (Rainstar T32, Röhren- und Pumpenwerk Bauer GmbH, Voitsberg, Austria). The irrigation water was 70% filtered, ozonated, and with active carbon treated water from Lake Zurich and 30% groundwater (City of Zurich, 2020). Most estrogen applications were conducted on sown grassland. An exception were three estrogen applications on field 1, which was cultivated with oat from end of August to December 2019. The time intervals between the estrogen applications corresponded to common Swiss agricultural practices for slurry applications on grassland (Richner et al., 2017). All application dates, matrices in which natural estrogens were applied,

cultivation of the agricultural test fields and amounts, and date of artificial irrigation after natural estrogen application are listed in Table S2.

Both the cattle slurries and pig slurries were provided by local farms representative of the corresponding livestock farming system in Switzerland and comply with common agricultural practices. To study natural estrogen emissions from agricultural test fields, in total four cattle slurry and five pig slurry applications were conducted on both agricultural test fields (Table S2). The volume of slurry applied per application on the agricultural test fields ranged from 9.0 to 10.5 m^3. According to Swiss regulations, it is allowed to apply up to 315 kg of total nitrogen and 45 kg of phosphorus in the form of slurry per hectare agricultural area annually (Federal Act on the Protection of Waters, 2020). Considering the amount of total nitrogen and phosphorus contained in one cubic metre cattle and pig slurry (Richner et al., 2017), this corresponds to approximately 60 to 80 m^3 cattle slurry and 30 to 50 m^3 pig slurry per hectare per year. As we wanted to simulate a worst case scenario, the amount of slurry applied on the test fields exceeded these volumes on average by a factor of 1.8 and 2.5 for cattle and pig slurry, respectively. The slurry was spread on the fields with a slurry tanker equipped with drag hoses. Estriol (20 mg; September 2019) and E2α (4.4 mg; November 2019) (Table 1, Table S2) were dissolved in 20 mL ethanol, spiked in 200 L water in a tractor mounted pesticide sprayer, mixed, equally distributed on the fields, and the resulting estrogen concentrations in the sprayer were analytically confirmed (Table 1). To ensure there was no contamination from previous pesticide applications, the pesticide sprayer was rinsed with soap and water. For all experiments, the amount of individual natural estrogens applied in cattle slurry, pig slurry or dissolved in water is shown in Table 1 and Table S7.

2.4. Drainage system and water sampling

Lateral drains merge into a main drain with an inner diameter of 15 cm (blue lines Fig. 1, polyvinyl chloride tubes). The drains are 80 to 100 cm below the soil surface. For each field, the main drainage tube ends in a sampling duct in which we installed a flow meter and an automated ISCO sampler (6712 Full-size Portable Sampler with a 730 bubbler module and vinyl and silicone tubes from Teledyne Isco Inc., Lincoln NE, USA, Fig. 1 red dots) to conduct flow-proportional sampling of discharged drainage water. An artificial irrigation experiment showed that for both fields only half of the field area contributed to the drainage flow. In the sub-fields contributing to the drainage flow, 41.5% and 14.5% of the applied water was found in the tile drains of field 1 and field 2, respectively (Wettstein et al., 2016). The pH of the drainage water was between 6.8 and 7.5, i. e., in the same range as in Hoerger et al. (2011).

The ISCO sampler was programmed to take five subsamples of 200 mL and merge them in a plastic bottle (1 L) to one sample. As in former studies with the same experimental design (Gall et al., 2014; Wettstein et al., 2016), it was assumed that the estrogen concentration in the flown through drainage water between the first and the last subsample equalled the estrogen concentration determined in the merged drainage water sample. Depending on the elapsed time after slurry application, the ISCO samplers were programmed to take a subsample after different drainage water volumes, i.e. every 200 L during day one, 500 L from day two to seven, and 1000 L for all further days. When natural estrogens were applied dissolved in water in September and November 2019, the following flow through volumes in the tile drain to take a subsample were programmed: 50 L during the first 24 h after natural estrogen application, 100 L two to seven days after estrogen application and 500 L for every subsequent day. In 90% of the samples, the time interval between the first and the last subsample was less than 24 h. The maximal time interval between the first and the last subsample was 10 days (field 2, November 2019). When all natural estrogen concentrations in the analysed samples were below the limit of quantification (LOQ), the experiment was stopped. Maximally 2 days after the last subsample was collected, the samples were transferred into aluminium bottles (pure aluminium bottle with polypropylene screw cap with internal aluminium seal, Faust Laborbedarf, Schaffhausen, Switzerland) and transported to the laboratory or freezer. The samples were either immediately analysed or stored at −20 °C for no longer than 2 weeks. The estrogen load export was the product of the estrogen concentration in the drainage water and the cumulative drainage water discharge volume during the sampling period. The relative cumulative estrogen load export equalled the estrogen load export at a given cumulative discharge volume divided by the total estrogen load export during an experiment (Fig. 2).

2.5. Analytical procedures and method validations

Natural estrogens in drainage water were extracted with a method adapted from Backe (2015). After the samples were completely thawed and shaken, an aliquot of unfiltered drainage water (30 mL) was transferred to a 50 mL cylindrical (12 cm × 2.5 cm i.d.) borosilicate vial (Supelco, Sigma-Aldrich, Buchs, Switzerland). Subsequently, 0.5 g of NaCl

Table 1
Summary of experimental results obtained for estrogen application experiments on tile-drained grassland, grouped by estrogen input matrices (cattle and pig slurry, dissolved in water), and the recipient matrix drainage water. The letter *n* refers to the number of samples. The number of estrogen applications is indicated with the letter *a*.

		Matrix	E2α	E2β	E1	E3
Matrix	Mean concentration [ng L^{-1}]	cattle slurry ($n = 4$)	1338 ± 599	149 ± 40	132 ± 31	422 ± 194
		pig slurry (n = 4)	321 ± 141	482 ± 240	786 ± 322	705 ± 149
		dissolved in water ($n = 2$)	2.2×10^4			1×10^5
	Load applied (min. – max.) [mg ha^{-1}]	cattle slurry (a = 4)	64.0–558.0	4.5–91.5	5.0–20.5	11.5–344.5
		pig slurry (a = 4)	8.0–28.0	10.5–47.5	20.5–70.0	28.0–40.0
		dissolved in water (a = 2)	11.0			50.0
Drainage water	Samples > LOQ [%]	cattle (n = 184, a = 4)	32	7	45	16
		pig (n = 113, a = 5)	47	13	79	60
		dissolved in water (E2α: $n = 100$, a = 2; E3: $n = 140$, a = 2)	28			42
	Experimental time > LOQ [%]	cattle (a = 4)	22	0.3	63	20
		pig (a = 5)	40	4	76	31
		dissolved in water (a = 2)	7			69
	Maximal concentration [ng L^{-1}]	cattle (n = 184, a = 4)	73	8	29	60
		pig (n = 113, a = 5)	3	7	37	22
		dissolved in water (E2α: n = 100, a = 2; E3: n = 140, a = 2)	8			6
	Maximal load exported [μg ha^{-1}]	cattle (a = 4)	24.3	2.3	10.9	14.5
		pig (a = 5)	3.7	1.5	46.7	15.5
		dissolved in water (a = 2)	1.7			9.4
	Mean exported fractions [%]	cattle (a = 4)	0.15	0.08	0.41	0.39
		pig (a = 5)	0.09	0.03	0.40	0.18
		dissolved in water (a = 2)	0.08			0.15

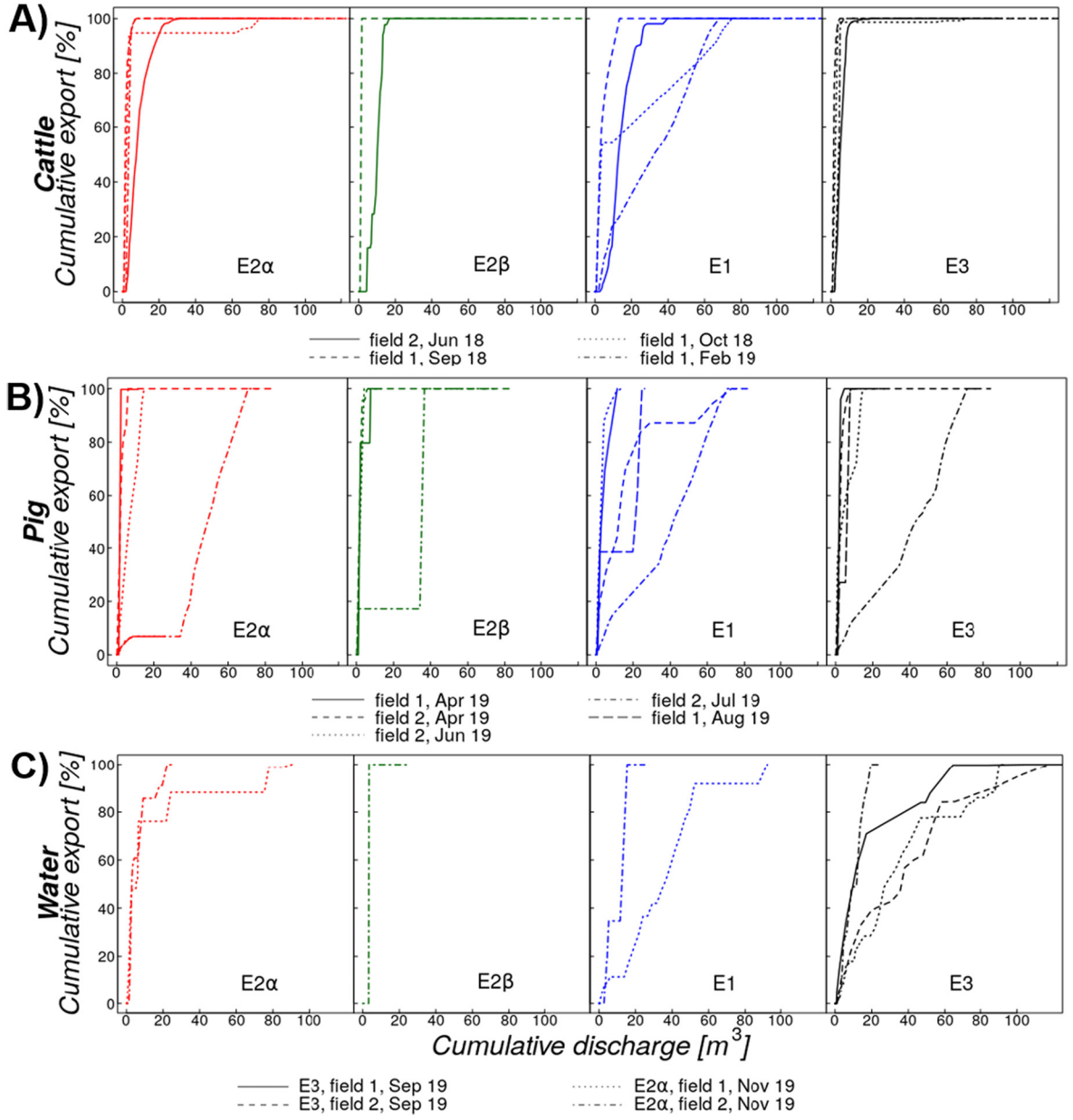

Fig. 2. Cumulative 17α-estradiol (E2α, red lines), 17β-estradiol (E2β, green lines), estrone (E1, blue lines), and estriol (E3, black lines) drainage water exports (% of total load) after application of natural estrogen in cattle slurry (panel A), pig slurry (panel B), and dissolved in water (panel C) as a function of cumulative discharge volume. Individual types of lines represent different experiments. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and 0.05 ng of deuterated internal standard (50 μL of 1000 ng L^{-1} internal standard mixture of E2α-d_3, E2β-d_3, E1-d_4, and E3-d_3 in acetonitrile, 50 ng L^{-1} final concentration) was added to every sample. Subsequently, natural estrogens in drainage water were liquid-liquid extracted with 2:5 methanol:MTBE as outlined in Rechsteiner et al. (2020b). Extraction of natural estrogens from liquid slurry took place with an adapted QuEChERS method as previously described in Rechsteiner et al. (2020a).

Natural estrogens in drainage water and slurry extracts were derivatized with dansyl chloride. Derivatized natural estrogens were measured by dynamic multiple reaction monitoring with liquid chromatography coupled with a triple-quadrupole mass spectrometer (LC-MS/MS). The LC-MS/MS operated in positive ionization mode. Internal standard calibration was used to quantify target analytes. Data processing was conducted with Agilent MassHunter QQQ Quantitative Analysis program version B.09.00 (Rechsteiner et al., 2020a).

Determination of limits of detection (LOD), LOQ, ion suppression, instrument and method precision, and relative and absolute recovery is described and shown more detailed in the SI, Chapter S3. The following ranges for these quality assurance and quality control parameters for drainage water were determined: LOD: 0.05–0.08 ng L^{-1}; LOQ: 0.15–0.28 ng L^{-1}; Ion suppression/enhancement: −45–13%; Method precision: 2–8%; absolute recovery: 100–127%; relative recovery: 94–121%. Detailed quality assurance and quality control parameters for quantification of natural estrogen in slurry are shown in Rechsteiner et al. (2020a) and in Table S4.

3. Results and discussion

3.1. Natural estrogen emissions to subsurface tile drains

3.1.1. Drainage hydrographs

The hydrographs in the tile drains during the monitoring periods after natural estrogen applications are presented in Fig. S1–3E. In periods with no or little precipitation (Fig. S1–3F), there was no drainage

water discharge. When running, mean discharge in the tile drain was 0.06 L s^{-1} (range: 0–6.8 L s^{-1}, median = 0.009 L s^{-1}). The cumulative volume of water that drained until estrogens were no longer detectable, ranged from 15 m^3 (July 2019) to 362 m^3 (October 2018) (Fig. S4-6E) for the individual application experiments. Maximal drainage discharges were caused by highest cumulative amounts of precipitation during the experiment and highest water excess during the experiment (cattle slurry: from October 10, 2018 until December 17, 2018 (191 mm of precipitation and 168 mm of water excess), pig slurry: from April 15, 2019 until May 22, 2019 (129 mm of precipitation and 32 mm of water excess), dissolved in water: from September 16, 2019 until November 12, 2019 (216 mm of precipitation and 156 mm of water excess); Table S6). Water excess was defined as precipitation minus potential evapotranspiration (Klaus et al., 2014). Rainfall on wet soil caused a particularly fast drainage hydrograph response. Similar observations were made in former studies on the same agricultural test fields (Hartmann et al., 2008; Hoerger et al., 2011; Schenzel et al., 2012; Wettstein et al., 2016).

3.1.2. Natural estrogens in slurry

From June 11, 2018 until August 27, 2019 four cattle slurry and five pig slurry applications were conducted on the agricultural test fields (Table S2). All natural estrogens were detected in all slurry samples. The mean individual estrogen concentrations in cattle slurries applied on the agricultural test fields were between 132 and 1338 ng L^{-1} (Table 1). The mean dry matter content in applied cattle slurries was 4.5%. As observed in previous studies (Noguera-Oviedo and Aga, 2016; Rechsteiner et al., 2020a), E2α was the predominant hormone in cattle slurry. Natural estrogen concentrations in cattle slurry applied in this study were in the same range as those determined as part of a nationwide Swiss slurry pit monitoring (Rechsteiner et al., 2020a).

In this study, the mean concentrations of individual estrogens in pig slurries ranged from 321 to 786 ng L^{-1} (Table 1). The mean dry matter content in applied pig slurries was 1.5%. Estrone followed by E3 were the most abundant natural estrogens in pig slurries applied on the agricultural test fields, in line with literature (Hutchins et al., 2007; Rechsteiner et al., 2020a). These concentrations were three to nine fold higher than those of a nationwide Swiss slurry pit monitoring (Rechsteiner et al., 2020a). However, the nationwide monitoring assessed only nine pig slurry samples, which likely accounted for the less representative values for pig slurries compared to cattle slurries ($n = 17$). Furthermore, slurry storage and management, such as frequency of slurry mixing, might have differed among the farms from which the slurry was obtained in this study and those in the nationwide slurry pit monitoring. Additionally, pig slurry applied in this study was transported in a slurry tanker usually used for cattle slurry. The slurry tanker was completely emptied, but not rinsed prior to pig slurry transports, and hence pig slurry mixed with cattle slurry residues. Whereas dry matter content in cattle slurry (4.5% in this study) was comparable to previous studies (4.5–9.0% in (Rechsteiner et al., 2020a; Richner et al., 2017)), dry matter content in pig slurry (1.5% in this study) was higher in literature (4.1–5.0%).

Total natural estrogen loads (estrogen concentrations in slurry multiplied with the volume of slurry applied; sum of all estrogens) applied in cattle and pig slurries per application ranged from 17.4 to 202.9 mg and from 18.3 to 25.9 mg, respectively. Individual compound loads applied on the agricultural test fields are presented in Table 1 and in Table S7.

3.1.3. Natural estrogens in drainage water

Natural estrogens were regularly measured in drainage water as a result of slurry applications. After cattle slurry applications, E1 was most frequently quantified in drainage water (45% of the samples ($n = 184$); 63% of the experimental time > LOQ). 17α-Estradiol, E2β, and E3 were above LOQ in 32%, 7%, and 16% of the samples (n = 184), and in 22%, 0.3%, and 20% of the experimental time, respectively (Table 1, Fig. S1). Similarly, E1 occurred most frequently in drainage water after pig slurry applications (79% of the samples ($n = 113$); above LOQ in 76% of the experimental time). Estriol was the second most abundant natural estrogen in drainage water samples after pig slurry applications (60%, n = 113), but for less of the experimental time (31% experimental time > LOQ) than E2α (47%, n = 113; 40% of the experimental time > LOQ). 17β-Estradiol was least abundant (13%, n = 113; 4% of the experimental time > LOQ) (Table 1, Fig. S2).

Natural estrogen concentration maxima in drainage water after cattle slurry applications were 73 ng L^{-1} E2α (field 1, February 2019), 8 ng L^{-1} E2β (field 2, June 2018), 29 ng L^{-1} E1 (field 1, October 2018), and 60 ng L^{-1} E3 (field 1, October 2018) (Table 1, Fig. S1A—D). The measured maximal natural estrogen concentrations in drainage water after pig slurry applications were 3 ng L^{-1} E2α (field 2, June 2019), 7 ng L^{-1} E2β (field 2, April 2019), 37 ng L^{-1} E1 (field 2, June 2019), and 22 ng L^{-1} E3 (field 2, April 2019) (Table 1, Fig. S2A–D). The application of E2α and E3 dissolved in water led to maximal concentrations of 8 ng L^{-1} E2α (field 2, November 2019) and 6 ng L^{-1} E3 (field 2, September 2019) in drainage water (Table 1, Fig. S3A–D). All natural estrogen concentrations in drainage water peaked immediately after the first rain event that followed the application. This immediate concentration peak in drainage water after the first rain event was independent of the matrix, i.e. cattle slurry, pig slurry or water, in which the natural estrogens were applied. The tailing period of these concentration maxima ranged from less than a day to several days. Concentrations in drainage water dropped below LOQ within one day to weeks after natural estrogen applications (Fig. S1–3A-D). Even after a strong rain event (>30 mm d^{-1}) two months after application, natural estrogens were no longer detectable in drainage water probably mainly due to degradation (see below).

After cattle slurry applications, the maximal individual natural estrogen loads exported to tile drains were between 2.3 and 24.3 μg ha^{-1} (Table 1, Fig. S4A–D, Table S7). In succession to pig slurry applications, the maximal loads found in drainage water ranged from 1.5 to 46.7 μg ha^{-1} (Table 1, Fig. S5A–D, Table S7) for individual compounds. When E2α and E3 were applied dissolved in water on the agricultural test fields, maximally 1.7 μg ha^{-1} of E2α (field 1, November 2019) and 9.4 μg ha^{-1} of E3 (field 2, September 2019) were exported to tile drains (Table 1, Fig. S6A–D, Table S7). Due to the limited hydrological capacity of the drainage water sampling device (2.5 L s^{-1}), exported estrogen loads were slightly underestimated. This was the case in 0.03% of the total experimental time. The exported fractions of individual natural estrogens to tile drains were on average 0.26% (ranging from 0.08% for E2β to 0.41% for E1) after cattle slurry applications, 0.18% (ranging from 0.03% for E2β to 0.40% for E1) after pig slurry applications, and 0.12% (ranging from 0.08% for E2α to 0.15% for E3) for estrogens applied dissolved in water (Table 1, Fig. 4, Table S7) (for calculations see SI, Chapter S4.2). The exported fractions were irrespective of the applied amount of natural estrogens. On field 1, drainage water from an uphill site provoked a dilution of the concentrations in the tile drains by a factor 1.3 to 3 (Wettstein et al., 2016). Consequently, natural estrogen prevalence, concentrations, and loads were potentially underestimated in drainage water of field 1.

Here, as well as in former studies conducted in the US and in Denmark (Gall et al., 2015; Kjær et al., 2007), E1 was the most frequently detected natural estrogen in drainage water after application of livestock animal wastes. In Denmark, maximal E1 and E2β concentrations in drainage water after pig slurry applications (Kjær et al., 2007) were in the same order of magnitude as in this study. Compared to Gall et al. (2011), maximal concentrations in drainage water were nearly the same for cattle slurry-derived E2β and E1 and for E3 from pig slurry. Note that Gall et al. (2011) applied pig slurry in combination with poultry slurry. Nevertheless in this study, E2α and E3 concentrations in drainage water originating from cattle slurry were by a factor of 1.4 and 17 higher than in the study by Gall et al. (2011), respectively, and pig slurry-derived E2α concentrations in drainage water were by a

factor of 4 lower. Similarly to our study, concentration maxima in drainage water coincided with the first discharge peaks after slurry applications (Gall et al., 2011; Kjær et al., 2007; Schoenborn et al., 2015). In contrast to our study, natural estrogens were reported in drainage water months after slurry applications (Gall et al., 2011; Kjær et al., 2007). Favoured accumulation and reduced degradation of natural estrogens in soil in former studies compared to this study may be explained as follows. First, the fields were more frequently irrigated with slurry lagoon effluents (Gall et al., 2011). Second, average soil temperatures at slurry application were lower (7 °C) (Kjær et al., 2007) (mean soil temperature 10 cm below ground in our study: 13 °C). Third, a different slurry application method was used in the study by Kjær et al. (2007), i.e. slurry injection. Similar fractions (0.25–0.37%) of natural estrogens from animal wastes were measured in tile drains in the United States (Gall et al., 2011). Exported fractions of natural estrogens were within the range of exported fractions of mycotoxins (Hartmann et al., 2008; Schenzel et al., 2012), pesticides (Wettstein et al., 2016), and isoflavones (Hoerger et al., 2011) determined on the same agricultural test fields (0.002–1.19%) (Fig. 4).

3.2. Factors influencing natural estrogen transport to subsurface tile drains

Various factors concomitantly influence natural estrogen emissions from tile-drained agricultural areas. While these factors and their complex interactions are difficult to disentangle at the field scale, we will discuss our results from different perspectives in the following subchapters. Physical and chemical soil properties (Table S1) and drainage systems (Fig. 1) remained the same over all experiments. Topography, vegetation on the fields (Table S2), and meteorological variables were considered to be identical or similar on both fields.

3.2.1. Hydrological aspects

Hydrology played a dominant role in the export of natural estrogens to tile drains. During flow rates above the 80th percentile (>0.04 L s^{-1}) in tile drains, on average 64% of the natural estrogen loads were exported to tile drains (Table S5). Gall et al. (2015) support this finding, reporting that approximately 80% of applied natural estrogens was exported during high flow events (flow rates above the 80th percentile), which they propose was potentially due to the prevalence of soil types with higher permeabilities or better drainage efficiencies.

According to Hendrickx and Flury (2001), preferential flow includes "all phenomena where water and solutes move along certain pathways, while bypassing a fraction of the porous matrix". Furthermore, Stone and Wilson (2006) found that water flow through preferential pathways largely contributes to peak flows in tile drains (40% to 81% of the peak flow). Although no direct preferential flow measurements were conducted in the study presented here, several factors circumstantially evidence that preferential flow was the major transport process for natural estrogens. First, in all cases, the drainage hydrographs peaked within hours after a rain event (Fig. S1–3E-F). Secondly, independent of the physicochemical properties, all natural estrogens appeared in tile drains within less than a day after application. The highest natural estrogen concentrations in drainage water were attained nearly simultaneously to the initial drainage water peak flow in the tile drain after slurry application (Fig. S1–3), which is in line with Ulén et al. (2014). Thirdly, the curve of the relative cumulative load export was upward and convex (Fig. 2), which was similar to those in Wettstein et al. (2016). Lastly, preferential flow was identified as the main transport process to tile drains for other organic micropollutants (mycotoxins, phytoestrogens, pesticides), as well as the conservative tracer bromide, studied previously on our agricultural test field (Hartmann et al., 2008; Hoerger et al., 2011; Wettstein et al., 2016) and for natural estrogens elsewhere (Gall et al., 2014; Kjær et al., 2007; Schoenborn et al., 2015).

Antecedent soil water and precipitation characteristics govern initiation and intensity of preferential flow processes (Klaus et al., 2014). The water balance, which is defined as precipitation minus potential evapotranspiration, is an approach to estimate water excess or deficit in soil (Klaus et al., 2014) (Table S6). A positive water balance represents a water excess in soil. The water balance in soil was determined for the period 10 days before estrogen application (see SI, Chapter S4.1). With this, we aimed to explain differences in natural estrogen export dynamics. Mean water excess before slurry applications was 21 mm (ranging from 4 mm (from July 30, 2019 until August 08, 2019) to 41 mm (from August 27, 2019 until September 15, 2019)). All slurry applications with a positive water balance between 20 and 41 mm showed similar and immediate upward curvatures of cumulative E2α and E2β load exports, which are parent compounds of E1 and E3 (Fig. 2AB). Among all slurry applications, the lowest water excess in soil before a slurry application (4 mm) caused the slowest natural estrogen export dynamics to tile drains. It is reflected in the least pronounced convex upward curvature of cumulative E2α and E2β load exports for the pig slurry application in July 2019 (Fig. 2B). Under very dry conditions, as in July 2019, the water table is very low in the soil profile. The precipitating water, which percolates through preferential flow pathways in the dry soil matrix, first needs to fill up the water table to the depth of the tile drain. Drain flow is only activated once the water table reaches the depth of the tile drain.

3.2.2. Dissolved versus solids bound natural estrogens

Characteristics of the different slurries applied on our agricultural test fields influenced natural estrogens measured in drainage water. After cattle slurry applications, we found the highest maximal natural estrogen concentrations in drainage water, and mean exported natural estrogen fractions to tile drains were higher than those after pig slurry applications (Table 1, Fig. S1–3, Table S7). Strongly sorbing compounds are prone to particle-facilitated transport. Especially when transported through preferential flow, particle bound compounds contribute to total losses to tile drains (de Jonge et al., 1998; Klaus et al., 2014; Larsson and Jarvis, 2000). Referring to Schwarzenbach et al. (2003), we used the dry matter content of the slurries and distribution coefficients (Kd) for E2β in sediments (Holthaus et al., 2002) to calculate that around 40% to 80% of the natural estrogens in slurry were sorbed to slurry solids. Presumably, the higher dry matter content in cattle slurry compared to pig slurry in this study, led to a higher fraction of natural estrogens bound to solids in cattle slurry. Consequently, natural estrogen export to tile drains through preferential flow was increased in cattle slurry.

To better understand the role of particle-facilitated natural estrogen transport, we applied E2α and E3 dissolved in water to simulate a solid-free matrix. Although water excesses before and after application of natural estrogens dissolved in water were among the highest of all experiments (Table S6), meaning conditions for preferential flow were favoured (see Section 3.2.1), export dynamics for natural estrogens applied dissolved in water were generally slower than after cattle and pig slurry applications (Fig. 2C). From a phase distribution mechanistic point of view, it seems plausible to assume that in absence of slurry-derived solids, a much higher fraction of the initially applied natural estrogens was available for sorption to the soil matrix. Furthermore, slurry seemed to reduce the infiltration capacity of the soil, for example by physically blocking smaller soil pores. Therefore, preferential flow would be more pronounced for natural estrogens applied in slurry (Fig. 2). Among experiments conducted on both fields in parallel, curvature differences of cumulative exported E2α and E3 applied dissolved in water (Fig. 2C), were most likely attributable to differences in field characteristics.

3.2.3. Influence of adsorption, degradation, and deconjugation on estrogen exports to tile drains

Without adsorption, degradation and deconjugation of natural estrogens, identical natural estrogen patterns were expected in the input matrices (cattle and pig slurry, as well as aqueous solution) and in corresponding drainage water. In reality, however, these patterns

slightly differed (Fig. 3). The decline of median relative E2α and E2β concentrations by 24% and 8%, and by 6% and 13% from cattle and pig slurry, respectively, to drainage water was accompanied by an increase in relative E1 concentrations from cattle and pig slurries to drainage water by 18% and 16%, respectively. Relative concentrations of E3 remained stable in both matrices. Independent of the matrix, the convex upward curves of the relative cumulative mass exports were less pronounced for E1 than for the parent compounds E2α and E2β (Fig. 2). When E2α was applied dissolved in water, E1 and E3 were measured retarded in drainage water (Fig. 2C, Fig. 3G). Shortly after cattle and pig slurry applications, mainly E2α, E2β and E3 contributed to the total natural estrogen concentration in drainage water. With increasing cumulative discharge volumes, relative concentrations of E1 and in one experiment of E3 increased after slurry applications (Fig. S7). 17α-Estradiol and E2β are degraded to E1 and E3 in slurry (Hutchins et al., 2007), soil (Caron et al., 2010; Ma and Yates, 2017; Mashtare et al., 2013), and water (Jürgens et al., 2002). Based on our data and findings of former studies, we presume that measured E1 and E3 originate to a certain extent from E2α and E2β, which degraded after slurry application in slurry, soil or drainage water, or in soil or drainage water when applied dissolved in water (Fig. 3). No E1 was detected after the application of E3 dissolved in water. Consequently, desorption or mobilization of E1 from former slurry applications can be excluded. Natural estrogens in slurry are partly conjugated (Hutchins et al., 2007). Once applied on agricultural area, conjugated estrogens accumulate in soil (Ma and Yates, 2017). Their deconjugation in soil and drainage water remains unclear, but it might further contribute to the total natural estrogen load found in drainage water. Adsorption to soil is less relevant for substance transport through preferential flow (Kung et al., 2000), which seemed to apply for natural estrogens in this study, as well as in the literature (Gall et al., 2014). Overall, degradation processes were probably more important than adsorption in the present study.

3.2.4. Groundwater ubiquity score for synoptic micropollutant assessment

Exported fractions of pesticides, determined on the same agricultural test fields as in this study, were positively correlated to the GUS (Wettstein et al., 2016) (Fig. 4). The GUS combines dissipation and adsorption properties of pesticides to classify their leaching potential to groundwater (Gustafson, 1989; Navarro et al., 2012). It is defined as $\log(DT_{50})\times(4-\log(K_{OC}))$, where DT_{50} is the time needed until 50% of the applied mass dissipated and K_{OC} represents the solid-water distribution coefficient normalized by the organic carbon content. As such, GUS may serve as an overarching tool to compare and evaluate emission behavior and exported fractions of different classes of (differently speciated) organic agricultural micropollutants (Fig. 4). A list with literature-based DT_{50} and K_{OC} values used to calculate worst and best case scenarios for the GUS values of natural estrogens is presented in the SI (Table S8). Natural estrogens have on average, relative to most

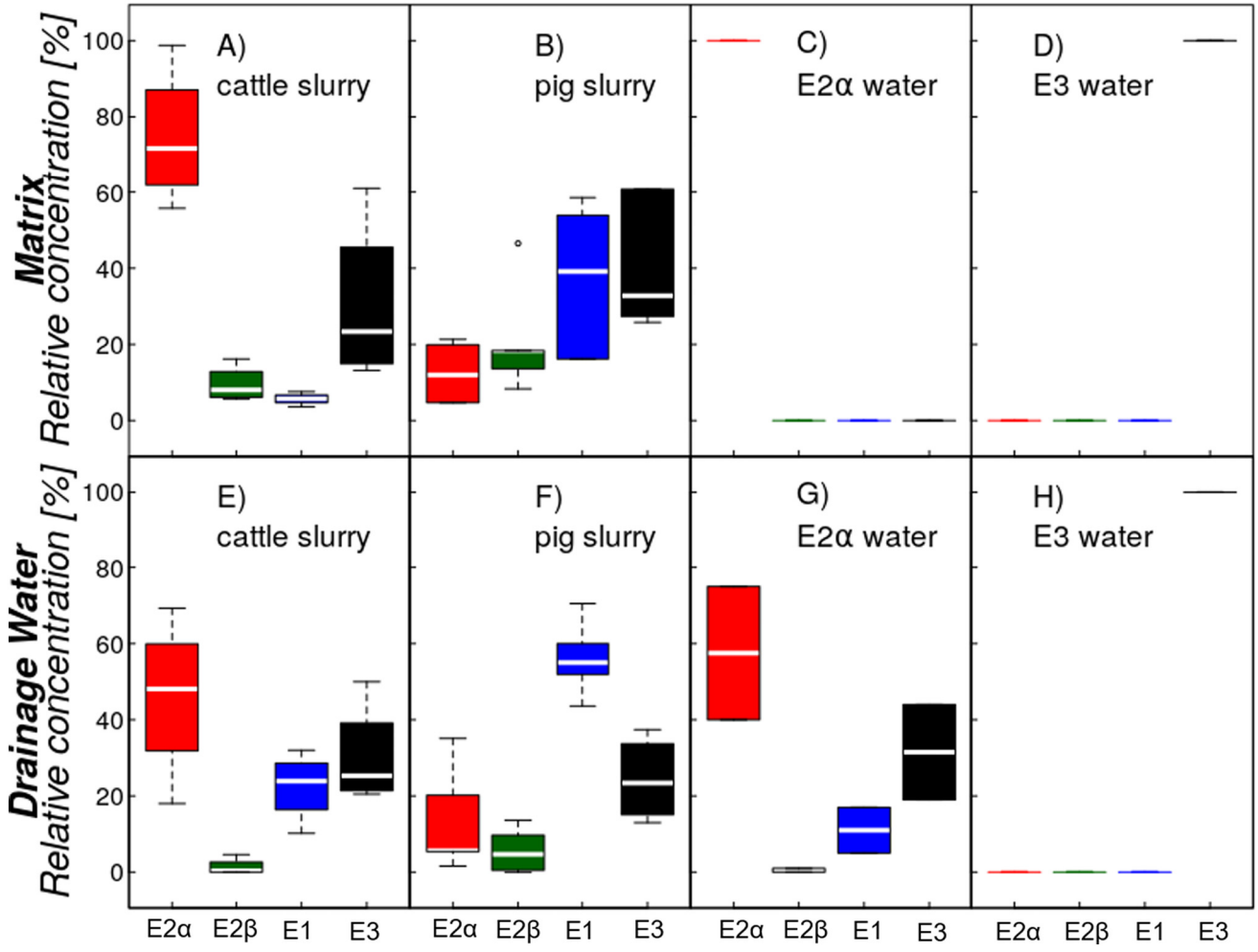

Fig. 3. Fractions of 17α-estradiol (E2α, red), 17β-estradiol (E2β, green), estrone (E1, blue), and estriol (E3, black) contributing to the total natural estrogen concentration (E2α + E2β + E1 + E3) in different matrices, i.e. cattle (panel A) and pig (panel B) slurries and dissolved in water (panel C and D), as well as in drainage water after corresponding applications (panels *E*-H). The white segment inside the rectangle indicates the median, and whiskers above and below the box minimal and maximal relative natural estrogen concentrations excluding any outliers. First and third quartile are linked through a central rectangle. The empty circle represents an outlier. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

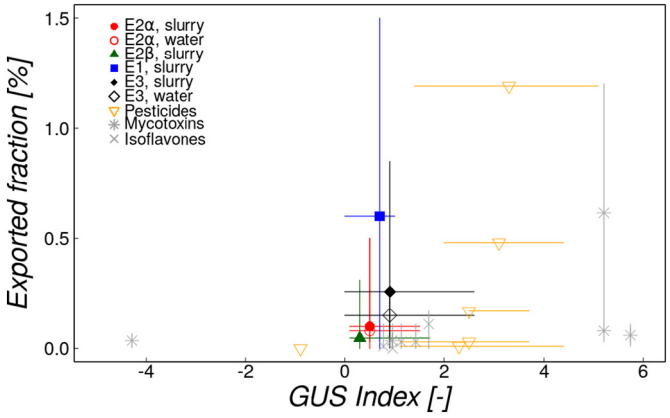

Fig. 4. Mean exported fractions of natural estrogens applied in slurry (17α-estradiol (E2α): filled red circle, 17β-estradiol (E2β): filled green triangle, estrone (E1): filled blue square, and estriol (E3): filled black diamond) and dissolved in water (E2α: open red circle and E3: open black diamond), pesticides (open top down orange triangles, Wettstein et al., 2016), mycotoxins (grey asterisk, Schenzel et al., 2012), and isoflavones (grey cross, Hoerger et al., 2011) plotted against groundwater ubiquity score (GUS). The GUS values were derived based on literature-based values for adsorption and degradation (for details see text). Horizontal lines present the range of possible GUS values based on their best-case and worst-case scenarios and vertical lines show the range between minimal and maximal determined exported compound fraction to drainage water. Substances with a GUS value below 0 have a very low leaching potential. Above a GUS value of 4, the leaching potential is extremely high. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

pesticides covered in Wettstein et al. (2016), lower GUS values, i.e. between 0.3 and 0.9. This implies that their leaching potential is very low both in absolute terms (Gustafson, 1989), and relative to that of pesticides. Nevertheless, exported fractions of natural estrogens applied in slurry (Fig. 4, filled symbols) were in the range of pesticides (Fig. 4, open top down orange triangles). While preferential flow may falsify the underlying assumption of matrix flow in the GUS approach (Lindahl and Bockstaller, 2012), this would be the same for both compound classes. Relative differences between them might point to particle-facilitated transport of estrogens, as indicated above. Particularly, the exported fractions of E1 were higher than those of pesticides more prone to leaching. As outlined above, formation of E1 in soils and increased estrogen export through particle-facilitated transport could explain higher exported natural estrogen fractions than expected. A better correspondence between exported fractions of E2α and E3 and the GUS values (of other compounds) was obtained, when they were applied in aqueous solution (Fig. 4, open red circle and open black diamond). In aqueous solution, they are immediately available for degradation and sorption. In further comparison, the exported fractions of mycotoxins and isoflavones (Fig. 4, grey asterisk and cross) were, relative to pesticides, underestimated, and overestimated, respectively. A possible explanation for such differences is that these compounds are fungal and plant-derived, respectively. Similar to estrogens, they do not enter the environment as free (or formulated) molecules, but primarily incorporated into the producing organisms' matrix. Apart from such obvious speciation differences, deviations in the exported fraction-GUS correlation among compound classes could also originate from differences in sample preparation and analysis, i.e. analysis of filtered vs. unfiltered water samples.

3.3. Environmental relevance

Environmental relevance can be assessed in terms of exposure concentrations as part of a risk assessment, and in terms of a general environmental mass balance to identify major emission sources. Among the natural estrogens investigated here, E2β, which is the most potent natural estrogen (Thorpe et al., 2003), was least abundant and had the lowest concentrations in drainage water. Furthermore, relative E2β concentrations, meaning the E2β concentration divided by the total natural estrogen concentration (E2α + E2β + E1 + E3), from slurry to drainage water decreased (Fig. 3). The maximal E2β equivalent concentration (EEQ) in drainage water was 14.1 ng L^{-1} (for calculations see SI, Chapter S5). In comparison, in small to medium sized Swiss Lake Baldegg tributaries with intensive agriculture in the catchment, EEQs were mostly below 0.5 ng L^{-1} (<0.5–2 ng L^{-1} EEQ; EU EQS of E2β = 0.4 ng L^{-1} (Commission Implementing Decision (EU) 2018/840, 2018)) (Rechsteiner et al., 2020b). Presumably, a combination of natural estrogen degradation in drainage and surface water ($t_{1/2}$ = 0.2–9 d) (Jürgens et al., 2002), dilution of drainage water once discharged into small to medium sized streams (diluted by a factor five to 82 in case of Lake Baldegg tributaries, which would result in estimated EEQs ranging from 0.2–2.8 ng L^{-1}; for calculations see SI, Chapter S5), and below-average abundance of tile-drained agricultural areas in a given catchment (11% of the total agricultural area tile-drained in Lake Baldegg catchment) (Stoll et al., 2019) explain such concentration decreases. Nevertheless, our data suggests that under certain circumstances, such as low flow rates in receiving water bodies and extreme rain events shortly after slurry applications in highly drained catchments, emissions of natural estrogens from tile drains plausibly cause temporally critical concentrations for fish in surface waters.

The mean monthly estrogen concentrations in streams with intensive livestock farming in their catchment were recently estimated with a Monte Carlo simulation (Rechsteiner et al., 2020b). There, the exported fractions determined here served as an approximation for the fraction of slurry-derived estrogens exported to surface waters. The resulting estimated mean estrogen concentrations underestimated the actually measured estrogen concentrations by a factor of three to eleven (Rechsteiner et al., 2020b). Comparably, both Hoerger et al. (2011) and Schenzel et al. (2012) indicate that emissions from our experimental fields can be used to predict micropollutant loads at larger scales within a factor of two to six. To estimate the annual exported estrogen loads from tile-drained agricultural areas, we multiplied the livestock animal densities (Federal Statistical Office, 2019) by the annual load of estrogens produced per livestock animal (Rechsteiner et al., 2020a) and the here determined exported natural estrogen fractions. Thereby, we obtained the amount of natural estrogens exported per hectare tile-drained agricultural area, which was then multiplied with the corresponding total tile-drained agricultural area of Switzerland. Our estimation showed that about 6.3 g of E2α, 0.6 g of E2β, 7.4 g of E1 and 7.7 g of E3 would be annually exported to Swiss surface waters through tile drains (the underlying assumptions of this estimation are explained more detailed in the SI, Chapter S5). In comparison, the annual loads of natural estrogens emitted through Swiss WWTPs were estimated to be three to four orders of magnitude higher, i.e. 1.5 kg of E2β, 9.7 kg of E1, and 51.1 kg of E3 (Rechsteiner et al., 2020a; Rechsteiner et al., 2020b).

4. Conclusions and outlook

This study confirmed that agriculturally derived natural estrogens are exported to surface waters through tile drains, mainly through preferential flow. The majority of the applied natural estrogens (>98%) dissipated or were retained in soil rather than being exported to tile drains. We showed that the matrix in which natural estrogens are applied is relevant for the fraction of natural estrogens exported to tile drains. Higher dry matter content in slurry seemed to favour particle-facilitated transport of natural estrogens to drains. To study the influence of particle-facilitated transport more specifically, the effective portion of free and solid-bound natural estrogens in slurry and drainage water samples could be determined by filtration and analysis of both fractions. In addition, slurry-derived conjugated natural estrogens exported to tile drains and their contribution to the total estrogen load merit further investigation. In contrast to pesticides, a positive correlation between GUS and exported fractions was not observed for natural estrogens, mycotoxins,

and isoflavones. Compared to natural estrogen emissions from WWTPs, the natural estrogen loads exported through tile drains were low. After slurry applications, natural estrogen concentrations in drainage water of the investigated agricultural test fields exceeded critical estrogen concentrations, but never for long periods of time.

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CRediT authorship contribution statement

Daniela Rechsteiner: Conceptualization, Data curation, Formal analysis, Investigation, Visualization, Writing – original draft. **Felix E. Wettstein:** Methodology, Validation, Writing – review & editing. **Nicolas Pfeiffer:** Data curation, Formal analysis, Investigation, Visualization, Writing – review & editing. **Juliane Hollender:** Conceptualization, Supervision, Writing – review & editing. **Thomas D. Bucheli:** Conceptualization, Investigation, Funding acquisition, Project administration, Resources, Writing – review & editing.

Declaration of competing interest

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

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Appendix A. Supplementary data

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