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Effects of season and sediment-water exchange processes on the partitioning of pesticides in the catchment environment: implications for pesticides monitoring

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Abstract

Current and historic pesticide use has potential to compromise e.g. drinking water sources due to both primary and secondary emission sources. Understanding the spatial and temporal dynamics of emissions might help inform management decisions. To explore this potential; water, sediment and soil samples were concurrently collected from the River Ugie, Scotland over four seasons. Occurrence and fate of nine pesticides including four historic-use pesticides (HUPs): simazine, atrazine, isoproturon and permethrin, and five current-use pesticides (CUPs): metaldehyde, chlorpyrifos, chlortoluron, epoxiconazole and cypermethrin were analysed. Concentrations of target pesticides in water, sediments and soils were 4.5 - 45.6 $ng \cdot L^{-1}$, 0.9 - 4.6 $ng \cdot g^{-1}$ dw (dry weight) and 1.7 - 8.0 $ng \cdot g^{-1}$ dw, respectively. Concentrations of pesticides in water were found to significantly differ between seasons ($p<0.05$). Significant differences in pesticide concentrations also occurred spatially within sediments ($p<0.01$), indicating spatial and temporal associations with pesticide use. Sediment-water exchange showed that the sediment acts as an important secondary emission source particularly for the HUPs, while current local application and sediment emission are both major driving forces for CUPs in the riverine environment. These findings were supported by concentration ratios between different media, which showed potential as a preliminary assessment tool for identifying the source of pollutants in aquatic environments.

Key words: pesticides, partitioning, compartment, sediment-water exchange

1. Introduction

Pesticides are widely used throughout the world as part of agricultural production practices, primarily to protect crops and enhance yields (Panuwet et al., 2012; Liu et al., 2018). Although pesticides play a positive role in the control of pests and diseases, their use has also been implicated in loss of biodiversity including significant impacts on the aquatic ecosystem (Vörösmarty et al., 2010; Pimm et al., 2014; Song et al., 2016; Zhang et al., 2019; Song et al., 2019; Yi et al., 2019). Both historic-use pesticides (HUPs) and current-use pesticides (CUPs) have been detected in a range of environmental media located within agricultural, urban or remote regions (Gouin et al., 2008; Kuivila and Hladik, 2008; Zhong et al., 2011; Zhong et al., 2014; Zhong et al., 2015). Therefore, understanding the levels, transport and fate of pesticides in the environment has potential to inform management practices to mitigate against deleterious human and animal exposures (Fernandez et al., 2014; Stehle and Schulz, 2015; Zhang et al., 2016).

The composition of pesticides within riverine environments tend to reflect the land use of the catchment. Where the land use is dominated by agricultural activities, concentrations of pesticides in air, soil, river water and sediments tend to be elevated. The fate and transport of these pesticides is influenced by a number of processes including runoff and leaching, and dry or wet deposition from atmospheric transport (van Dijk and Guicherit, 1999; Zhong et al., 2014; Carratala et al., 2017). In order to reduce hazards, risks and dependence on chemical control for crop protection, the European Union (EU) has established policies including Integrated Pest Management (IPM) and the Water Framework Directive (WFD) for managing pesticides and monitoring water quality (EU, 2000; ECPA, 2010; Hillocks, 2012). Prior to this, the UK introduced a pesticide monitoring program in 1985, which included monitoring of surface and ground waters (Croll, 1991; Skinner et al., 1997; Ferrier et al., 2002; Bloomfield et al., 2006; Bloodworth et al., 2014). Under the auspices of this program, HUPs and/or CUPs in e.g. the Rivers Thames, Dee, Ugie, Wyre, Severn, etc. were observed and investigated (Loos et al., 2009; Gillman et al., 2012; Bloodworth et al., 2014; Jürgens et al., 2015; Zhang et al., 2016; Lu et al., 2017; Castle et al., 2018). However, these studies mainly focused on the occurrence and distribution of pesticides in water only. Few studies have included the wider multi-media environment, especially for the catchment environment from the perspective of concurrent seasonal monitoring of pesticides in various matrices including water, sediment and soil to elucidate environmental behavior, transport and fate. Some rivers, such as the River Ugie (Aberdeenshire, UK) provide a source of drinking water for the local population, as such has been designated as a priority catchment in Scotland for protection (SEPA, 2010). Therefore, understanding the environmental processes and identifying the sources and pathways of pesticides in these riverine ecological systems is very important for managing pesticide use and protecting the quality of the aquatic environment and raw water quality.

The objectives of this study were (1) to investigate the level and exhange dynamics of nine target pesticides in water, sediment and soil within the catchment environment using the River Ugie as a test case; (2) to evaluate the spatio-temporal distribution and the influence of total organic carbon (TOC) on pesticides in sediment and soil; and (3) to identify the source-sink relationship and input pathways for pesticides in the aquatic environment using fugacity fraction between sediment and water and concentration ratio of pesticides. The significance and heterogeneity of concentrations of pesticides in water, sediment, and soil will be examined through a monitoring network in catchment environment, which could be influenced by seasonal and spatial factors. Whether the sediment acts as a secondary release source of pesticides, as well as their input pathway in the riverine environment also need to be identified for managing and controlling agricultural production practices and eco-environmental safety. Results from the present study will provide the scientific knowledge and agricultural management practice for pesticides that is needed for better designing the monitoring networks containing seasonal or temporal variations at a catchment scale.

2. Materials and methods

2.1 Study area and sample collection

The River Ugie catchment (with a catchment area of 335 km^2) in the North East of Scotland. The Ugie is utilized by Scottish Water (a statutory corporation that provides water and sewerage services across Scotland, and is accountable to the public through the Scottish Government) as a drinking water source for the town of Peterhead and its surrounding area, supplying a population of approximately 40,000 people. Water, sediment and soil samples were collected at 3 different sites from the River Ugie catchment (**Fig. 1**) every three months from July 2013 to April 2014. Sodium azide (0.01 M, Sigma-Aldrich, Dorset, UK) was added to each water sample as a general biocide to eliminate bacteria and prevent sample degradation during storage and processing. Water samples were stored in a refrigerator below 4 ^{o}C until filtration. Soil and sediment samples were stored at -20 ^{o}C prior to analysis. A series of water quality measurements were also taken at each site including pH, conductivity, dissolved oxygen, temperature and water depth.

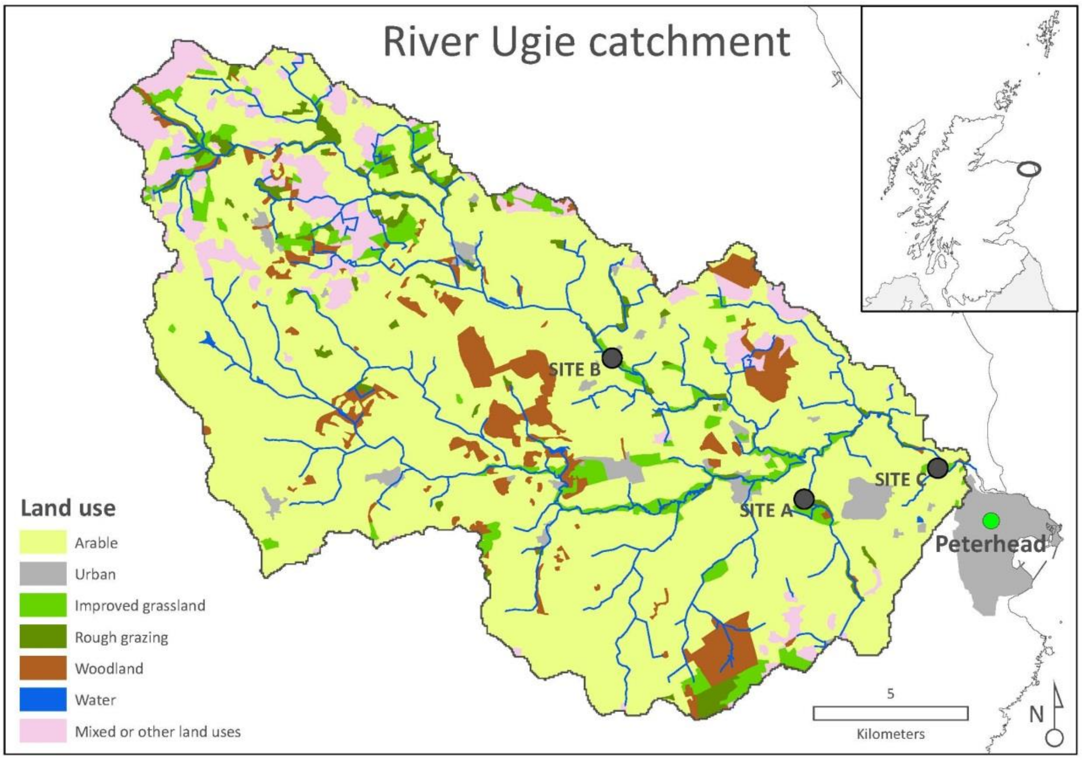


Fig. **1** Sampling sites in the River Ugie Catchment, Scotland

2.2 Sample extraction

Water samples (500 mL) were filtered under vacuum through pre-ashed glass-fibre filters (GF/F, 0.7 µm, Whatman, Camlab, Cambridge, UK). The filtrates were spiked with 20 ng of internal standards prior to solid phase extraction (SPE). Briefly, SPE cartridges (Strata-X) were first conditioned with 10 mL of dichloromethane, followed by 10 mL of methanol and ultrapure water (2×5 mL) passing through the cartridges at a rate of 1-2 mL/min. Then, water samples were extracted at a flow rate of 5-10 mL/min. After extraction, the cartridges were dried under vacuum for 30 min, with the analytes eluted into 20 mL vials from the sorbents with 12 mL of ethyl acetate: dichloromethane: acetone (45:10:45) followed by additional elution with 6 mL of dichloromethane at a flow rate of 1 mL/min.

Soil and sediment samples were extracted by Selective Pressurized liquid extraction (SPLE) using an ASE200 system (Dionex). Cell loading was conducted in the following sequence: an 11 mL extraction cell was loaded by inserting two filter papers (Dionex, Leeds, UK) into the cell outlet followed by silica (e.g. 3 g), topped by 1 g of sodium sulfate for in-cell clean-up, followed by another filter paper. 1 g (dry mass) of soil or sediment sample spiked with organic standard was added, followed by 0.5 g sand which had been heated in a muffle furnace at 550^{o}C overnight to remove traces of organic matter. The extraction solvent for SPLE was ethyl acetate: dichloromethane: acetone (45:10:45). Extraction temperature was 80 °C with 2 cycles.

Other settings were constant: preheating time of 5 min, heating time of 5 min, static time of 5 min, flushing volume of 60% of the cell, purge time of 60 sec and pressure at 1500 psi. All the extracts (including SPE, soil and sediment) were reduced to near dryness under a gentle flow of nitrogen at less than 30 ^{o}C. The sample was transferred to 0.1 mL ethyl acetate and analysed by gas chromatography - mass spectrometry (GC-MS) (Zhang et al., 2014). Total Organic Carbon (TOC) of soil and sediment samples was determined by loss on ignition method (Heiri et al., 2010).

2.3 Instrumental analysis

An Agilent 5975C MSD (mass spectrometer detector) linked to 7890 A GC with an autosampler (7683B), was used for pesticides analysis with selected ion mode (SIM). The capillary column was ZB-SemiVolatiles (30 m x 0.25 mm i.d. x 0.25 µm film thickness, Phenomenex, Macclesfield, UK). The operating temperature for pesticides was programmed from 40 ^{o}C (1 min) to 110 ^{o}C at 10 ^{o}C/min, then ramped to 200 ^{o}C at 20 ^{o}C/min, 200 ^{o}C to 310 ^{o}C at 5 ^{o}C/min and held for 12 minutes. Helium was used as the carrier gas at a constant flow of 1 mL/min. Samples were injected in splitless mode. The injector and mass spectrometer (ion source) were held at 250 oC and 200oC, respectively. The electron impact energy was set 70 eV for mass spectrometer.

2.4 Quality assurance and quality control

Before sample analysis, relevant standards were analyzed to check instrumental performance, peak height and resolution. With each set of samples to be analysed, reference standard mixtures, quality control samples, and procedural blanks were run in sequence to check for contamination, instrumental performance, peak identification and quantification. Compounds were identified mainly by selected ion and by their retention times. The percentage recovery range for nine target compounds in this study was 70-111%. All results for soil and sediment were reported on a dry weight (dw) basis.

2.5 Sediment-water exchange

In this study, a fugacity approach was employed to assess and understand the sediment-water exchange processes of pesticides. Fugacity, which governs the transfer of chemicals between media, was used as an indicator of the propensity for compounds to move from one medium to another (Mackay, 2001). The fugacity of a specific compound is related to the concentration of that compound in a particular environmental medium, as well as the fugacity capacity of that medium. A detailed derivation processes of sediment-water exchange is presented in the supplementary information (SI) as well as in our previous study (Cui et al., 2016).

The fugacity fraction (*ff*) was used to assess the exchange behaviors of pesticides between the sediment and water.

$$ff = \frac{f_{\mathrm{sedi}}}{f_{\mathrm{sedi}} + f_{\mathrm{water}}} = \frac{1000C_{\mathrm{s}} \times f_{\mathrm{oc}}K_{\mathrm{oW}}/0.41}{1000C_{\mathrm{s}} \times f_{\mathrm{oc}}K_{\mathrm{oW}}/0.41 + C_{\mathrm{W}}} \quad (1)$$

where f_{sedi} and f_{water} is the fugacity (Pa) of the organic pollutant in sediment and water, respectively. C_{s} is the measured mass concentration in the sediment in $\mathrm{ng \cdot g^{-1}}$ dw (dry weight), C_{w} is the measured mass concentration in the water in $\mathrm{ng \cdot L^{-1}}$. K_{ow} is the dimensionless partition coefficient of octanol-water; f_{oc} is the organic carbon fraction in the sediment. Values of $ff < 0.5$ indicate that the pesticide of interest has a greater propensity to partition to the sediment than remain within the water phase, in which case the sediment will act as a sink. Values of $ff > 0.5$ are indicative of migration of the pesticide from the sediment to the water, with the sediment acting as a secondary release source. The latter is an especially important factor with longer-term implications for water quality. For example, pesticides that have been banned or have restricted use can be stored in stable media (such as sediment or soil) for a prolonged time post-application and then re-released into the environment at a later point in time. Thus, there is potential for environmental fluxes of even banned products to occur on occasion. Application of Equation 1 can help inform under what conditions such fluxes are most likely to occur; which may aid management decisions.

2.6 Data analysis

Statistical analyses were performed using SPSS 20.0 for one-way analysis of variance (ANOVA). Data were tested for normality by Kolmogorov-Smirnov. The significant differences between variables were adopted by one-way ANOVA with Dunnett's T3 post hoc test. The statistical significance of the differences between two groups was determined by independent-samples T test. A *p*-value less than 0.05 was considered to be statistically significant. Correlation analysis was used for examining the relationship between sediment/soil and TOC.

3. Results and discussion

3.1 Concentrations of pesticides in water, sediment and soil

The nine pesticides were determined in water, sediment and soil at three sampling sites (**Fig. 1**) over four different seasons. The results obtained are summarized in **Table S2 to S4**. Among the target pesticides, seven were detected in the water samples, namely, metaldehyde, simazine, atrazine, isoproturon, chlorpyrifos, chlortoluron, and epoxiconazole; of which chlorpyrifos was only observed at site C during summer. Permethrin and cypermethrin were below the limit of detection (LOD) in all water samples. Chlortoluron, metaldehyde, isoproturon, and atrazine were the predominant pesticides in water, and the greatest concentrations were 31.1, 10.5, 5.3 and 2.7 $ng \cdot L^{-1}$, respectively (**Table S2**). Chlortoluron was detected at the greatest concentrations compared to the other target pesticides, which could reflect the dominance of cereal production within the River Ugie catchment (Zhang et al., 2016). The concentration of total detected pesticides (i.e., $\Sigma_7$pesticides) at individual sites ranged from 4.5 to 45.6 $ng \cdot L^{-1}$, with a mean of 19.0 $ng \cdot L^{-1}$, and showed moderate variability (coefficient of variation (C_V): 0.7). Metaldehyde is used by approximately 80 % of arable operations in Great Britain (FERA, 2018). Levels of metaldehyde were lower in the Ugie compared to available data for other rivers in the UK including the River Dee (<10~100 $ng \cdot L^{-1}$) and River Thames (<9~4200 $ng \cdot L^{-1}$) (Castle et al., 2018). However, the most directly comparable study is that of Bloodworth et al. (2014) which undertook a sampling campaign in the River Ugie (at a site corresponding to Site C in this study) between June 2011 and June 2013. They reported that the highest concentrations of chlortoluron and metaldehyde were 1.31 $\mu g \cdot L^{-1}$ and 0.2 $\mu g \cdot L^{-1}$, much higher than those (31.1 $ng \cdot L^{-1}$ and 10.5 $ng \cdot L^{-1}$) reported in the current study

(**Fig. 2**). However, Bloodworth et al. (2014) does not report on the exchange dynamics between sediment and water or on the surrounding concentrations of pesticides in the wider catchment. Despite these limitations, the comparison with Bloodworth et al (2014) does suggest that the Sustainable Land Management (SLM) strategy of Scottish Water has played a positive role for protecting the water quality and, by inference, the wider environment. However, these pesticides should be still considered for continuous monitoring and identifying risk in riverine systems, especially those that are used as a source of drinking or irrigation water.

Concentrations of chlortoluron, metaldehyde, isoproturon, and atrazine were detected in sediment samples while all other pesticides were below the LOD (**Fig. 2** and **Table S3**). The total concentrations of detectable pesticides (i.e. $\Sigma_4$pesticides) in sediment from each sampling site ranged from 0.9 to 4.6 ng·g^{-1} dw with an average of 2.7 ng·g^{-1} dw, indicating moderate variability (C_V: 0.5). Considering the contribution of each individual pesticide, the herbicide atrazine was measured at relatively high concentrations (average: 1.5 ng·g^{-1} dw; maximum: 3.2 ng·g^{-1} dw) (**Fig. 2**), which accounted for 54.1 % of the total target pesticides, followed by metaldehyde (18.6 %), chlortoluron (15.5 %) and isoproturon (11.8 %). Given that metaldehyde has a relatively low K_{OW} value (Log K_{OW}: 0.12) and therefore is more likely to remain in solution, the relative higher concentration found in sediment in this study is an indication of high intensity usage of metaldehyde in the catchment. It was observed that concentrations of atrazine in sediment samples taken from the Ugie were lower than those reported by Radović et al. (2015) from sediment of the Danube River in Serbia (24-392 ng·g^{-1} dw), and were higher than those reported by Fairbairn et al. (2015) in sediment of the Zumbro River watershed in Minnesota (0.06-0.28 ng·g^{-1} dw, with a mean of 0.13 ng·g^{-1} dw). Atrazine has been banned in the EU since 2004 and is easily degraded, however this study was not only able to detect it in the sediment of the River Ugie, but it also accounted for a large proportion (54%) of the total concentration of target compounds in the sediment. This indicates that there was widespread usage of atrazine in this area historically that has ended up being stored in the sediment fraction. There is therefore significant potential for the sediment to act as a secondary pollution source e.g. during storm events.

The concentrations of pesticides in the soil samples over the different seasons are summarized in **Table S4**. Six of the nine target pesticides were detected, namely metaldehyde, simazine, atrazine, isoproturon, chlorpyrifos, and epoxiconazole, of which epoxiconazole was observed only at site A. Chlortoluron, permethrin and cypermethrin were not detected above the LOD (**Fig. 2)**. The total concentrations of detectable pesticides (i.e. $\Sigma_6$pesticides) in soils ranged from 1.7 to 8.0 ng·g^{-1} dw, with a mean value of 4.7 ng·g^{-1} dw, indicating moderate variability (C_V: 0.4). The relative composition of the detected pesticides in soil was similar to that found in sediment with atrazine (59.7 %) and metaldehyde (19.5 %) dominating the mixture.

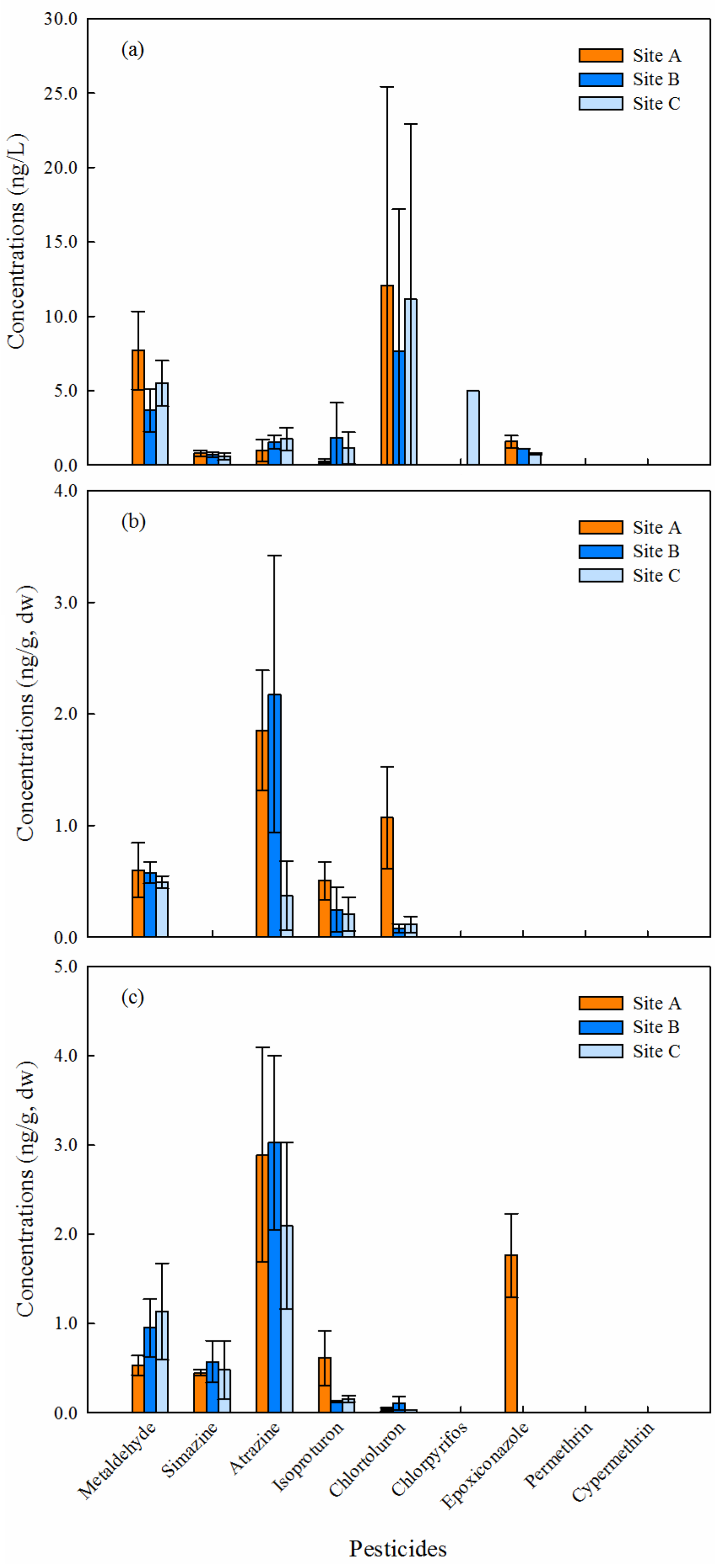


Fig. 2 Concentrations (mean of four seasons, error bar: standard deviation) of nine pesticides in

water (a), sediment (b) and soil (c) of River Ugie, Scotland

3.2 Spatio-temporal distribution of pesticides

Table S2 to S4 describe the seasonal and spatial distribution of the concentrations of target pesticides in water, sediments and soils. The highest total concentrations of pesticides in water were measured at site A (45.6 ng·L^{-1}, in winter), site C (38.2 ng·L^{-1}, in autumn), and site B (32.2 ng·L^{-1}, in autumn). Seasonal variability was most pronounced in water samples. The pesticides had higher concentrations in autumn and winter (mean: 28.7 ng·L^{-1}) than those in spring and summer (mean: 9.4 ng·L^{-1}). This seems to reflect the agricultural calendar and when large application of CUPs are likely to occur, as well as increased run-off from land during periods of wetter weather (autumn/winter). However, it should be noted that measured concentrations are influenced by flow rate and therefore may not reflect the likely flux of pesticides. For example, the average flow rate in autumn and winter was 2.7 m^3·s^{-1} and 10.1 m^3·s^{-1}, respectively, compared to spring and summer (2.8 m^3·s^{-1} and 1.6 m^3·s^{-1}, respectively). The higher flow rates in the winter time are likely to reduce measured pesticide concentrations as a result of dilution, while increased rates of precipitation are likely to facilitate the transfer of pesticides from where they are applied (soils) to the water courses via runoff. However, these inferred explanations require validation using monitoring or modeling tools. The independent-samples T test confirmed the significant difference in pesticide concentrations in river water between autumn-winter and spring-summer seasons ($p<0.05$), the inference being that pesticide application associated with typical agricultural practice is likely to cause the relatively high concentrations measured in the river water.

There is a different distribution pattern of pesticides in sediment samples for both seasonal variations and sampling sites compared to the water samples. The highest total concentrations were observed at site A (4.6 ng·g^{-1} dw in spring and 4.3 ng·g^{-1} dw in autumn) and site B (4.1 ng·g^{-1} dw in autumn). While concentrations at sites A were shown to be significantly greater to those at site C ($p<0.01$) using one-way ANOVA with Dunnett's T3 post hoc test, no significant difference between different seasons was established ($p>0.05$).

Similarly, the spatial distribution of pesticides in soil samples, showed limited seasonal variation. The highest concentrations were observed at site A (8.2 ng·g^{-1} dw in summer and 6.7 ng·g^{-1} dw in spring) and site B (5.7 ng·g^{-1} dw in summer). This indicated that the greatest concentrations of pesticides in soil were related to stable weather conditions, suggesting that soil runoff associated with precipitation events (most common in autumn/winter) is likely to be moving pesticides to the river channel (reflected in the seasonal variation in the concentrations of pesticides measured in water). There was no significant difference between seasons ($p>0.05$) or sampling sites ($p>0.05$).

The relationship between pesticide concentration and sediment/soil organic carbon were examined by Pearson correlation analysis. The correlations between individual detected pesticide and TOC in sediment and soil are presented in **Table 1** and **2**. Significant positive correlations were found between chlortoluron or atrazine and TOC in sediment; while no significant correlation was found between metaldehyde or isoproturon and TOC. The only significant correlation found between pesticide concentration and TOC in soils was chlortoluron. These results suggested that local application and secondary emissions and residues of HUPs and CUPs, precipitation and physico-chemical properties play a more important role than TOC in the spatio-temporal distribution of pesticides in the catchment. This inference is reflected in the differences seen between the individual pesticides measured in sediments and soils. Meanwhile the partitioning between chlortoluron and TOC is a major driving process in sediments and soils with higher TOC content. The results may be related to the physico-chemical properties, content of TOC, precipitation and runoff condition in this study area. This is especially relevant for metaldehyde, which is a polar organic pollutant with high water solubility and hence mobile in soil. Post application, under wet conditions, metaldehyde is readily transported via run-off and leaching with potential to adversely impact the aquatic environment (Castle et al., 2018); i.e. metaldehyde is weakly adsorbed to TOC and thus it is readily transported from the site of application and can impact adversely on water quality and the aquatic environment.

3.3 Sediment-water exchange and the concentration ratios

3.3.1 Sediment-water exchange

Sediment-water exchange is considered as an important environmental process for affecting aquatic environment quality, especially through the role of this process in secondary emissions and residues of organic pollutants. When exploring the sediment-water exchange of pesticides, we have mainly focused on four pesticides; metaldehyde, chlortoluron, isoproturon, and atrazine as they have been concurrently detected in sediment and water from the study site. The fugacity fractions (*ff*) of chlortoluron, isoproturon, and atrazine were greater than 0.9 indicating the sediment acts as a sink and potential secondary emission source for these pesticides (**Fig. S1**). Values of *ff* for metaldehyde reflected the seasonal and spatial variations described above. The role of sediments (i.e. as a sink and secondary source) is less relevant to metaldehyde given its relatively low K_{OW} value and higher water solubility. However, seasonal variations in values of *ff* for metaldehyde do reflect the temporal nature of agricultural practices, with values of *ff* lower during the period of usage (autumn and winter) compared to the non-usage period (spring and summer). Such temporal information could prove useful when designing countermeasures for pesticides or more general water quality protection protocols, especially as deploying temporary mitigation at the correct time is likely to be more cost-effective than permanent solutions. In addition, a previous study of the River Ugie also observed a dependent relationship between pesticide applications and temporal trends of pesticide concentrations in the river water (Bloodworth et al., 2014), but the study did not extend to include sediment. Given sediment can act as a secondary emission source introducing contemporary inputs of even legacy HUPs into the riverine environment, it should not be ignored.

3.3.2 Concentration ratios of pesticides in water, sediment and soil

Generally, sediment-water exchange was affected by benthic boundary layer transport. While the concentration of a pesticide in water and sediment is one important factor, and is regularly monitored by e.g. regulators, it is dependent to some extent on the sorption potential of the sediment and the physico-chemical properties of the compounds, as well as the pre-existing levels of pesticides in the sediments and the receiving water itself that determines the distribution dynamics of the pesticide between the different phases (Koelmans et al., 2010). The concentration ratio of pesticides between water and sediment ($C_{\text{water}}/C_{\text{sediment}}$) could therefore be a more appropriate monitoring tool than simple concentrations alone as this ratio should provide an indication of exchange behavior and potential for re-suspension of pesticides e.g. during storm events (Cui et al., 2016). **Fig. 3** illustrates the significant negative correlations between *ff* and $C_{\text{water}}/C_{\text{sediment}}$, except for metaldehyde. The simplified qualitative method by means of $C_{\text{water}}/C_{\text{sediment}}$ coupled to the value of *ff* is useful for preliminary assessment of the exchange variations between sediment and water. However, it should be noted that ratios of $C_{\text{water}}/C_{\text{sediment}}$ in this study showed significant variability ranging from 0 to 150 for chlortoluron, from 0 to 70 for isoproturon, and from 0 to 25 for atrazine, i.e. the pesticides have been released from sediment and elevated their concentration in water, and then led to the high ratio of $C_{\text{water}}/C_{\text{sediment}}$. The Values of $ff > 0.5$ also confirmed the migration of the pesticide from the sediment to the water. In other words, this phenomenon suggests that the dominant transport pathway of these pesticides is from sediment to water as secondary emission sources and they have strong release capacity compared to other organic pollutants, such as PAHs (Cui et al., 2016), and the physic-chemical properties (e.g. relatively low K_{OW}) could be the important factor influencing migration capacity of pesticides in aquatic environment. While it is a useful screening tool, it is not suitable for determining the equilibrium status of polar organic compounds (such as pesticides), which are strongly governed and driven by physico-chemical properties and concentrations in sediment and water, and weakly driven by TOC content in sediment.

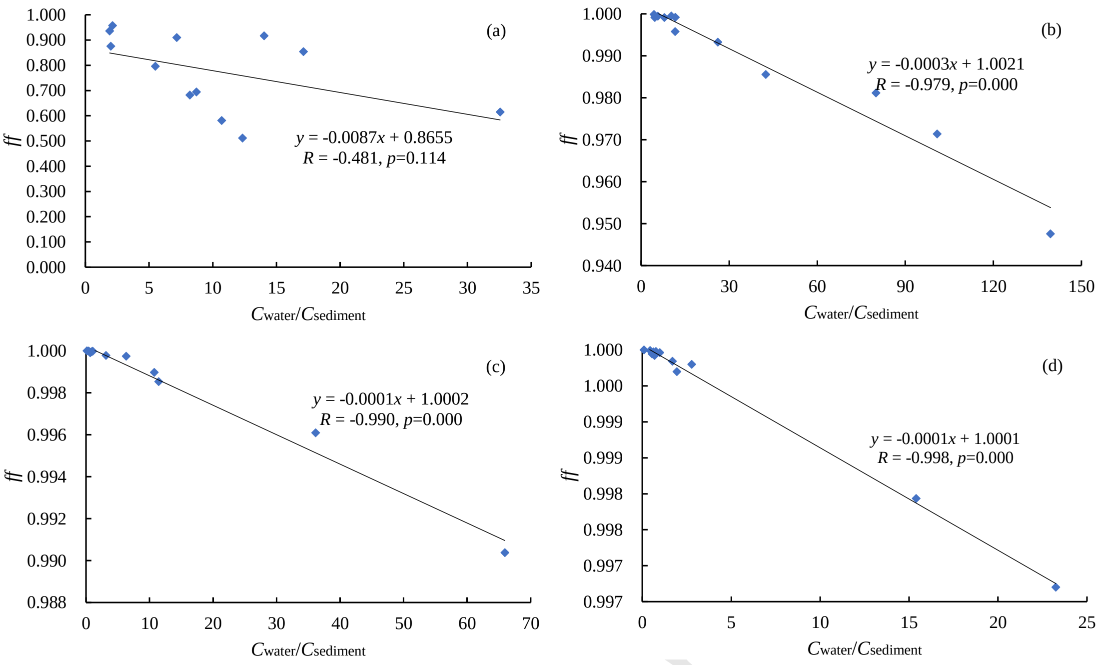
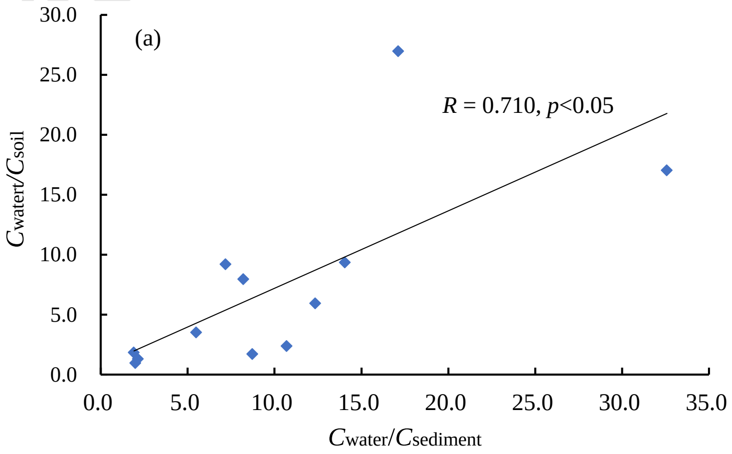


Fig. 3 The relationship between the value of *ff* and the concentration ratio of water and sediment ($C_{water}/C_{sediment}$): (a) metaldehyde; (b) chlortoluron; (c) isoproturon; and (d) atrazine

The concentration ratios between the two media have been used to identify the steady state for semi-volatile organic compounds (Kim et al., 2016). As for concurrently detected pesticides in water, sediment and soil for the River Ugie catchment, the concentration ratios were calculated and their pair relationships are illustrated in **Fig. 4**. Levels of pesticides in riverine water generally originated from runoff from cultivated soil during precipitation events, as well as re-emissions from previously-contaminated sediment. Some evidence was also found for the existence of point sources of discharge. Significant positive correlations were found between C_{Water}/C_{Soil} and $C_{Water}/C_{Sediment}$ for metaldehyde (R=0.710, $p<0.05$), and between $C_{Soil}/C_{Sediment}$ and $C_{Water}/C_{Sediment}$ for atrazine (R=0.972, $p<0.01$), respectively (**Fig. 4**). The pairs of concentration ratios exhibited consistent trends in variation, for example, the metaldehyde in sediment is more likely to be indirectly affected by soil runoff, and the contaminated sediment has minimal influence on the concentrations found in soil other than where the river water is used for agricultural irrigation, i.e. we can say that this effect is essentially irreversible. Although these concentration ratios of compounds between different media have various limitations of interpretation, the ratios do seem to provide a practicable and cost-effective assessment method for identifying the source of pollutants in the riverine environment based on interpreting the correlations between them. Such an approach would enhance current monitoring practices that tend to focus on concentrations of pesticides present only in the water phase with limited ability to make inferences about sources which in turn limits the ability to design management approaches. As already discussed, variability in flow rate limits the interpretation of using water concentrations in isolation of other forms of information.



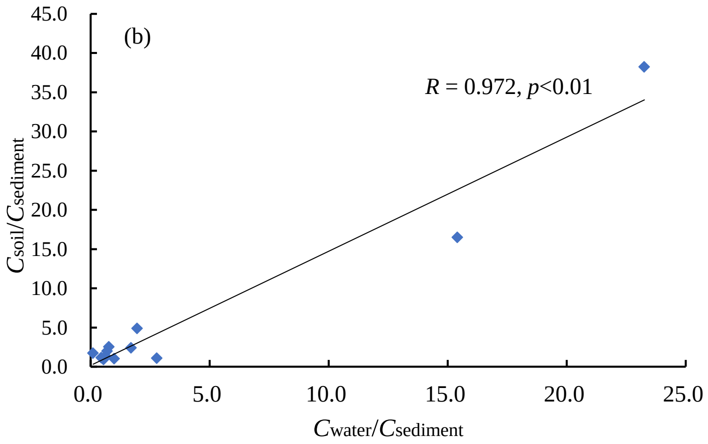


Fig. 4 Concentration ratio of pesticides in different environmental medium (a) metaldehyde and (b) atrazine

4. Conclusions

The concentrations and environmental processes of nine pesticides including HUPs and CUPs were investigated in a catchment environment. Concentrations of pesticides in water were found to be significantly influenced by season, while concentrations of pesticides in riverine sediments showed significant spatial heterogeneity. Some of these differences could be attributed to timing of pesticide usage as well as re-emission of pesticides present in sediments. While sediments do act as a secondary emission source in the riverine environment, the levels of pesticides present in water at a given moment in time are affected by a wider range of factors, including runoff from treated soil, pesticides usage, and (re)release from sediments. These processes were confirmed by sediment-water exchange and concentration ratios between different media. This approach has potential to enhance current monitoring schemes to enable more informed management decisions to be made. This can be achieved with relatively little further investment. However, while an improvement, there are still a number of limitations to the proposed approach, particularly with the sophistication of interpretation afforded. Therefore, the establishment of concurrent monitoring that looks ‘beyond the river’ at the wider environment (air, soil, water and sediment), and then identifying the input pathway of pesticides in riverine systems and quantifying the exchange flux between air-water and air-soil, as well as investigating the distribution and contribution ratio of dissolve and particle phase, and risk assessment of pesticides should be considered as the future evolutions in pesticides monitoring. These would help us to further understand the environmental behavior of pesticides on river catchment scale and to better serve the agricultural production practices and eco-environmental safety.

Acknowledgments

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Table 1 Pearson correlation coefficients between TOC and pesticides in sediment

	TOC	Metaldehyde	Chlortoluron	Isoproturon	Atrazine
TOC	1.000				
Metaldehyde	-.028	1.000			
Chlortoluron	.793**	-.337	1.000		
Isoproturon	.554	-.189	.498	1.000	
Atrazine	.629*	-.357	.400	.221	1.000

**. Correlation is significant at the 0.01 level (2-tailed).

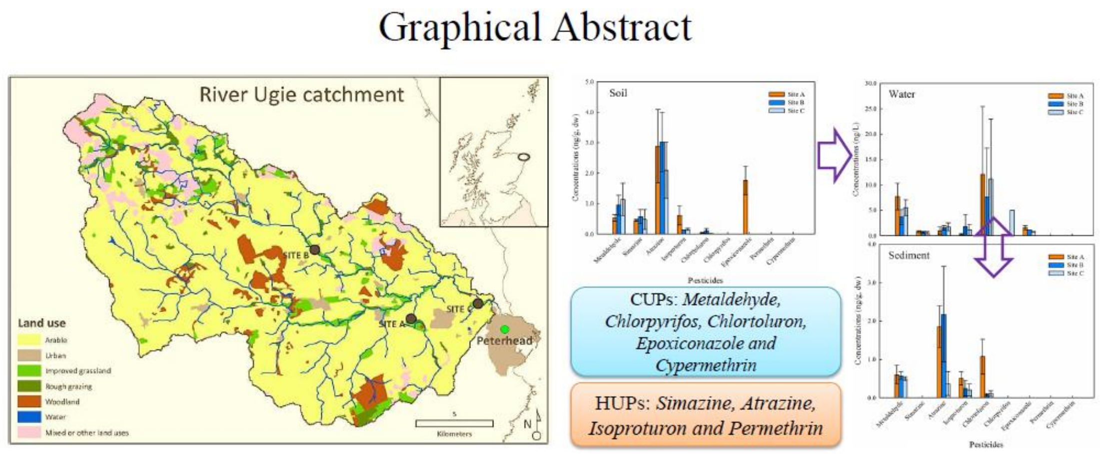
*. Correlation is significant at the 0.05 level (2-tailed).

Table 2 Pearson correlation coefficients between TOC and pesticides in soil

	TOC	Metaldehyde	Chlortoluron	Isoproturon	Atrazine
TOC	1.000				
Metaldehyde	-.119	1.000			
Chlortoluron	.704*	.387	1.000		
Isoproturon	-.204	-.500	-.199	1.000	
Atrazine	.308	.175	.345	.042	1.000

*. Correlation is significant at the 0.05 level (2-tailed).

Graphical abstract



- Highlights
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- Nine pesticides in a Scottish priority catchment were investigated.
- Concentrations of CUPs and HUPs in water, sediment and soil were determined.
- Seasonal and temporal variations were associated with pesticides use.
- Sediment-water exchange can be used to identify the source or sink of pesticides.
- Concentration ratios between different media were used to trace the input pathway.

Supplementary Information

Effects of season and sediment-water exchange processes on the partitioning of pesticides in the catchment environment: implications for pesticides monitoring

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Table S1 Total organic carbon in sediments and soils, rainfall, and flow rate in River Ugie

	Sediment (%)			Soil (%)			Rainfall (mm)
	site A	site B	site C	site A	site B	site C	
summer	2.25	1.47	0.86	4.56	4.34	1.54	52.3
autumn	1.61	0.62	0.46	2.89	5.82	1.02	74.3
winter	3.10	0.55	0.40	3.74	6.08	1.49	123.1
spring	4.79	0.66	0.44	3.09	5.58	2.04	69.9

Table S2 Concentrations of pesticides in water (ng/L) from the River Ugie of Scotland in different seasons.

		Metaldehyde	Simazine	Atrazine	Isoproturon	Chlortoluron	Chlorpyrifos	Epoxiconazole	Permethrin	Cypermethrin
	LOD	2.01	0.02	0.03	0.01	0.01	0.02	0.14	0.06	1.35
Summer	Site A	6.04	0.57	1.01	0.28	4.42	<LOD	1.16	<LOD	<LOD
	Site B	<LOD	0.55	2.04	1.10	5.50	<LOD	1.09	<LOD	<LOD
	Site C	<LOD	0.34	2.01	0.61	3.86	4.97	0.69	<LOD	<LOD
Autumn	Site A	9.33	<LOD	1.98	0.31	11.40	<LOD	1.36	<LOD	<LOD
	Site B	2.38	<LOD	1.77	5.31	21.69	<LOD	1.10	<LOD	<LOD
	Site C	4.40	<LOD	2.72	2.64	27.65	<LOD	0.78	<LOD	<LOD
Winter	Site A	10.49	0.82	0.69	0.40	31.10	<LOD	2.09	<LOD	<LOD
	Site B	5.23	0.88	1.02	0.79	2.67	<LOD	<LOD	<LOD	<LOD
	Site C	6.57	0.83	1.04	1.08	11.45	<LOD	<LOD	<LOD	<LOD
Spring	Site A	4.94	0.98	0.26	0.09	1.40	<LOD	1.70	<LOD	<LOD
	Site B	3.46	0.68	1.36	0.18	0.68	<LOD	<LOD	<LOD	<LOD
	Site C	<LOD	0.59	1.27	0.25	1.57	<LOD	0.80	<LOD	<LOD
Average	Site A	7.70	0.79	0.99	0.27	12.08	-	1.58	-	-
	Site B	3.69	0.70	1.55	1.84	7.63	-	1.09	-	-
	Site C	5.49	0.59	1.76	1.15	11.13	4.97	0.76	-	-

Table S3 Concentrations of pesticides in sediment (ng/g, dw) from the River Ugie of Scotland in different seasons.

		Metaldehyde	Simazine	Atrazine	Isoproturon	Chlortoluron	Chlorpyrifos	Epoxiconazole	Permethrin	Cypermethrin
	LOD	0.46	0.01	0.01	0.004	0.004	0.01	0.06	0.03	0.31
Summer	Site A	0.84	<LOD	1.32	0.67	0.52	<LOD	<LOD	<LOD	<LOD
	Site B	0.47	<LOD	3.23	0.17	0.13	<LOD	<LOD	<LOD	<LOD
	Site C	0.52	<LOD	0.72	0.19	0.22	<LOD	<LOD	<LOD	<LOD
Autumn	Site A	0.29	<LOD	2.01	0.34	1.63	<LOD	<LOD	<LOD	<LOD
	Site B	0.27	<LOD	3.22	0.49	0.09	<LOD	<LOD	<LOD	<LOD
	Site C	0.41	<LOD	0.18	0.23	0.10	<LOD	<LOD	<LOD	<LOD
Winter	Site A	0.61	<LOD	1.55	0.38	1.02	<LOD	<LOD	<LOD	<LOD
	Site B	0.64	<LOD	1.46	0.02	0.05	<LOD	<LOD	<LOD	<LOD
	Site C	0.53	<LOD	0.53	0.02	0.05	<LOD	<LOD	<LOD	<LOD
Spring	Site A	0.35	<LOD	2.54	0.63	1.12	<LOD	<LOD	<LOD	<LOD
	Site B	0.63	<LOD	0.80	0.30	0.04	<LOD	<LOD	<LOD	<LOD
	Site C	0.50	<LOD	0.05	0.38	0.09	<LOD	<LOD	<LOD	<LOD
Average	Site A	0.52	-	1.85	0.50	1.07	-	-	-	-
	Site B	0.50	-	2.18	0.25	0.08	-	-	-	-
	Site C	0.49	-	0.37	0.21	0.11	-	-	-	-

Table S4 Concentrations of pesticides in soil (ng/g, dw) from the River Ugie of Scotland in different seasons.

		Metaldehyde	Simazine	Atrazine	Isoproturon	Chlortoluron	Chlorpyrifos	Epoxiconazole	Permethrin	Cypermethrin
	LOD	0.46	0.01	0.01	0.004	0.004	0.01	0.06	0.03	0.31
Summer	Site A	0.66	0.43	3.36	1.06	0.05	<LOD	2.45	<LOD	<LOD
	Site B	0.77	0.46	4.29	0.12	0.04	<LOD	<LOD	<LOD	<LOD
	Site C	0.55	0.25	0.79	0.14	<LOD	<LOD	<LOD	<LOD	<LOD
Autumn	Site A	0.55	<LOD	2.03	0.48	0.04	<LOD	1.50	<LOD	<LOD
	Site B	1.39	0.84	2.99	0.13	0.21	<LOD	<LOD	<LOD	<LOD
	Site C	1.85	<LOD	2.91	0.20	0.03	<LOD	<LOD	<LOD	<LOD
Winter	Site A	0.39	0.47	1.80	0.52	<LOD	<LOD	1.65	<LOD	<LOD
	Site B	0.66	0.41	2.92	<LOD	0.08	<LOD	<LOD	<LOD	<LOD
	Site C	1.11	0.71	2.60	0.13	0.03	<LOD	<LOD	<LOD	<LOD
Spring	Site A	0.53	<LOD	4.37	0.38	0.02	<LOD	1.44	<LOD	<LOD
	Site B	0.99	<LOD	1.91	<LOD	0.10	<LOD	<LOD	<LOD	<LOD
	Site C	1.04	<LOD	2.09	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Average	Site A	0.95	0.57	3.03	0.13	0.11	-	-	-	-
	Site B	1.14	0.48	2.10	0.16	0.03	-	-	-	-
	Site C	0.49	0.47	2.73	0.46	0.03	-	1.53	-	-

Sediment-water exchange method

A fugacity approach was used to evaluate the equilibrium states of the organic pollutants and to better understand the sediment–water exchange processes of Pesticides. Generally, the movement of chemicals from one medium to another is represented by fugacity, which controls the transfer of chemicals between media (Mackay, 2001). The fugacity is related to the concentrations of organic pollutants and the fugacity capacity of the corresponding environmental medium:

$$f = C_{\mathrm{mol}}/Z \tag{1}$$

where f is the fugacity of the organic pollutant in Pa, Z is the fugacity capacity of the specific medium in mol·m^{-3}·Pa^{-1}, and C_{mol} is the molar concentration of the organic pollutant in mol·m^{-3}. However, the concentrations of organic pollutants in the sediments and water were monitored in ng·g^{-1} and ng·L^{-1}, respectively. Hence, the quality concentrations were converted to the corresponding molar concentrations as follows:

$$C_{\mathrm{sedi,mol}} = 10^6 C_s \rho_{s1}/P_{\mathrm{mol}} \tag{2}$$

$$C_{\mathrm{water,mol}} = 10^6 C_w/P_{\mathrm{mol}} \tag{3}$$

where $C_{\mathrm{sedi,mol}}$ and $C_{\mathrm{water,mol}}$ are the molar concentrations of organic pollutants in the sediment and water, respectively. C_s is the measured mass concentration in the sediment in ng·g^{-1} dw (dry weight), C_w is the measured mass concentration in the water in ng·L^{-1}, ρ_{s1} is the density of the sediments in kg·m^{-3}, and P_{mol} is the molar mass of an organic pollutant in g·mol^{-1}.

The fugacity capacities of the sediment (Z_{sedi}) and water (Z_{water}) can be expressed as follows:

$$Z_{\mathrm{sedi}} = K_p \times \rho_{s2}/H = 0.41 \times f_{oc} K_{ow}\, \rho_{s2}/H \tag{4}$$

$$Z_{\mathrm{water}} = 1/H \tag{5}$$

$$K_p = 0.41 \times f_{oc} K_{ow} \tag{6}$$

where H is the Henry's law constant in Pa·m^3·mol^{-1}, K_{ow} is the dimensionless partition coefficient of octanol-water (Log K_{ow}: 0.12 for Metaldehyde, 2.41 for Chlortoluron, 2.84 for Isoproturon, and 2.82 for Atrazine), f_{oc} is the organic carbon fraction in the sediment, ρ_{s2} is the density of the sediment in kg·L^{-1}, and K_p is the partition coefficient in L·kg^{-1}.

The fugacities of the sediment (f_{sedi}) and water (f_{water}) can be expressed as follows:

$$f_{\text{sedi}} = C_{\text{sedi,mol}}/Z_{\text{sedi}} = \frac{10^6 C_{\text{s}}\rho_{\text{s1}}/P_{\text{mol}}}{0.41 \times f_{\text{oc}}K_{\text{ow}}\rho_{\text{s2}}/H} \tag{7}$$

$$f_{\text{water}} = C_{\text{water,mol}}/Z_{\text{water}} = \frac{10^6 C_{\text{W}}/P_{\text{mol}}}{1/H} \tag{8}$$

The numerical relationship between ρ_{s1} and ρ_{s2} can be simplified as $\rho_{\text{s1}} = 1000\rho_{\text{s2}}$.

The fugacity fraction (*ff*) is used to assess the equilibrium states and exchange behaviors of chemicals or Pesticides between the sediment and water (Cui et al., 2016).

$$\begin{aligned} ff = \frac{f_{\text{sedi}}}{f_{\text{sedi}} + f_{\text{water}}} &= \frac{C_{\text{s}}\rho_{\text{s1}} \times f_{\text{oc}}K_{\text{oW}}\rho_{\text{s2}}/0.41}{C_{\text{s}}\rho_{\text{s1}} \times f_{\text{oc}}K_{\text{oW}}\rho_{\text{s2}}/0.41 + C_{\text{W}}} \\ &= \frac{1000C_{\text{s}} \times f_{\text{oc}}K_{\text{oW}}/0.41}{1000C_{\text{s}} \times f_{\text{oc}}K_{\text{oW}}/0.41 + C_{\text{W}}} \end{aligned} \tag{9}$$

Sediment-water equilibrium suggests that the values of *ff* are equal to 0.5; thus, the net diffusion flux is zero. Values of *ff* > 0.5 indicate migration from the sediment to the water. In this case, the sediment acts as a secondary emission source. Values of *ff* < 0.5 indicate the deposition of Pesticides from the water to the sediment. In this case, the sediment acts as a sink.

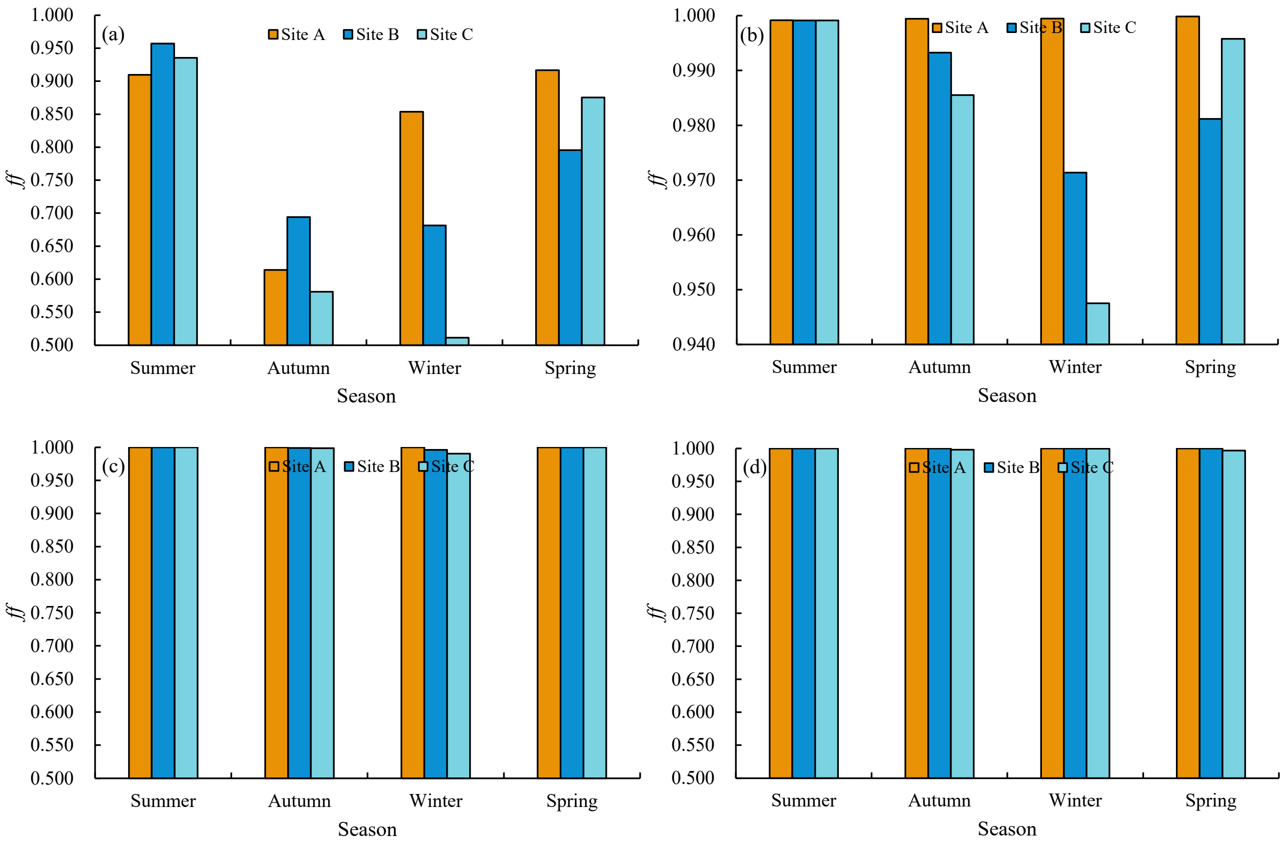

Fig. S1 Seasonal and spatial variations in the fugacity fraction of pesticides (a) metaldehyde; (b) chlortoluron; (c) isoproturon; and (d) atrazine

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