Environmental Pollution 316 (2023) 120493

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Atmospheric deposition of particulate matter from beef cattle feedlots is a likely contributor of pyrethroid occurrence in isolated wetland sediment: Source apportionment and ecological risk assessment

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ABSTRACT

Industrial cattle feeding operations (feedlots) have been subject to public scrutiny in recent decades regarding environmental impacts of site runoff and aerial dispersion of agrochemical-laden particulate matter (PM). However, source apportionment of multi-use pesticides is challenging in mixed agricultural settings. Beef cattle on feed and row crop production are heavily concentrated in the Southern Great Plains of North America, where playa wetlands are vulnerable to agrochemical inputs and sedimentation from surrounding land use. In the current study, playa basin sediment ($n = 33$) was analyzed via UHPLC-MS for 21 agrochemicals spanning eight classes (macrocyclic lactones, neonicotinoids, organophosphates, pyrethroids, triazoles, β-methoxyacrylates, a carboximide, and phenylpyrazole). Pyrethroids were detected most frequently (75.8% of basins). Sediment pyrethroid concentrations were also significantly correlated ($R^2 = 0.178$, $p = 0.007$) with feedlot proximity (<1–50 km). Principal component analysis (PCA) of land use metrics extracted three principal components (74.3% of total variance), with principal component regression (PCR) showing the greatest agrochemical occurrence in basins heavily weighted by cropland buffer acreage (≤1 km) and feedlot proximity. Sediment toxicity benchmarks protective of two benthic invertebrates (*Hyallela azteca* and *Chironomus* spp.) identified λ-cyhalothrin, fenvalerate, and esfenvalerate as individual compounds exceeding levels of acute (RQ > 0.5) and chronic (RQ > 1) concern in >5% and >50% of cases, respectively. However, additive toxicity of co-occurring pyrethroids represents an acute high risk (RI > 1; median RI; acute = 2.4, chronic = 38.6) to benthic invertebrates in >75% of cases, which may threaten higher-order wetland taxa via bioaccumulation and trophic transfer.

1. Introduction

Land application of livestock manure and drift from aerial pesticide application are well-documented sources of agrochemical transport (Anderson et al., 2013; Caldwell and Wolf, 2005; Chee-Sanford et al., 2009). However, in agroecosystems where beef cattle feedlots are heavily concentrated, use of insecticides to combat livestock pests and disease may disproportionately contribute to environmental dissemination of agrochemicals (Modernel et al., 2013). Beef cattle feedlots, hereafter "feedlots," utilize several classes of insecticides via direct animal treatment or area application including but not limited to carbamates, macrocyclic lactones (avermectins), neonicotinoids, organophosphates, and pyrethroids (Peterson et al., 2020). Fogging and spray applications of insecticides settle on pen floors, while direct treatments are metabolized and excreted in fecal waste and urine (Swiger, 2012; Wardhaugh, 2005). In addition to environmental contamination via waste runoff, feedlots are open-air facilities which facilitate transport of aerosolized feces, urine, and dust to offsite terrestrial and aquatic systems (Blackwell et al., 2015; McEachran et al., 2015; Peterson et al., 2017; Sandoz et al., 2018; Wooten et al., 2018). The complex nature of agrochemical mixtures in manure, PM, and feedlot effluent, as well as a scarcity of comprehensive data regarding operation-specific usage in the United States (U.S. GAO, 2008) has hindered efforts to determine the spatial extent of contaminant transport from feedlot facilities.

Two classes of pesticides comprise 97.9% of agrochemical use at feedlots in the US: avermectins (87.1%) and pyrethroids (10.8%; NAHMS, 2013). Avermectins are used as pour-on or injectable anthelmintic treatments in cattle, whereas pyrethroid formulations include both pour-on and premises applications that serve to manage and/or eliminate common feedlot-associated pests (Rotz et al., 2019) such as ticks, lice, mites, and various flying species within Order Diptera (i.e. mosquitoes, stable flies, horn flies, etc.). While veterinary grade avermectins are used almost exclusively for livestock and domestic household pets, pyrethroids are widely used for both animal and crop production and residential purposes. Overall, the use of pesticides

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https://doi.org/10.1016/j.envpol.2022.120493
Received 20 September 2022; Received in revised form 17 October 2022; Accepted 18 October 2022
Available online 1 November 2022
0269-7491/

benefits multiple economic sectors, not only in terms of increased revenue through avoided losses to pests (Tudi et al., 2021), but through socio-economic benefit of affordable food, secure farm income, and improved efficiency of natural resources when used at recommended application rates (Popp et al., 2013). Notably, however, improper use and overuse of pesticides carries the additional indirect costs (estimated USD 9.6 billion; Pimentel, 2005) of pest resistance, loss of native wildlife and pollinators, and public health impacts via contaminated natural resources and direct or indirect human exposure (Popp et al., 2013).

Commonly used feedlot agrochemicals have been detected on wildflowers (Peterson et al., 2017) and co-located native pollinators (Peterson et al., 2022, 2021) ≤1 km of feedlots, and in rural wetlands ≤15 km from feedlots (Sandoz et al., 2018; Wooten et al., 2018). Source apportionment in more remote ecosystems remains difficult due to land application of livestock manure on croplands, thereby complicating efforts to determine pathways driving agrochemical occurrence. Likewise, intersecting use of insecticides in both cropland farming and feedlots can further obscure origination from aerial transport versus overland flow and deposition from neighboring fields. Still, previously detected concentrations in ecological receptors have made deterministic risk characterizations for pollinator species possible. Wildflower hazard quotients (FHQ) and indices (FHI) developed based on agrochemical detections on wildflower species (Peterson et al., 2022) indicated that 30% of wildflower samples collected within 600 m of feedlots in the Southern Plains of North America posed elevated risk (FHQ, FHI >1) to pollinators. Additionally, Peterson et al. (2020) calculated honeybee death equivalencies and estimated that the bulk mass of permethrin alone released by U.S. feedlots have the theoretical potential to kill 1 billion honeybees each day. Nevertheless, further research is needed to identify the spatial extent and source contribution of agrochemical residues.

The Great Plains is the leading contributor to US total beef cattle on feed (82.4%) and second in row crop production (USDA NASS, 2017, 2021). Feedlots are heavily concentrated in the semi-arid Southern Great Plains (SGP; Colorado, Kansas, Oklahoma, New Mexico and Texas; 6.5 million head; 43.2% of Great Plains total; USDA NASS, 2017). Major crops produced annually in the SGP include winter wheat, corn, cotton, and sorghum (USDA NASS, 2021). Geographically isolated playa wetlands are the primary hydrological features of the SGP (Fig. 1), distributed as far east as the escarpment of the Llano Estacado caprock formation and west into eastern New Mexico (PLJV, 2016). The SGP is largely restricted to annual precipitation averages of 25–58 cm (Shafter et al., 2014), and playas rely solely on rain and surface water runoff for inundation. Infrequent precipitation facilitates increased PM deposition downwind of feedlots to surrounding playa basins and upland habitats (Sandoz et al., 2018).

Sandoz et al. (2018) and Wooten et al. (2018) previously sampled water and sediment from playa wetlands in the SGP to investigate potential for atmospheric deposition of veterinary pharmaceuticals ≤15 km from feedlots. Ractopamine, a β-adrenergic receptor agonist, was detected in 92% of PM samples, one water sample (271 ng/L), and six of 33 sediment samples (<0.05–5.2 ng/g; Wooten et al., 2018). Monensin, an ionophore antibiotic, was detected in 53% of water and 100% of sediment samples with increased concentrations in samples collected in

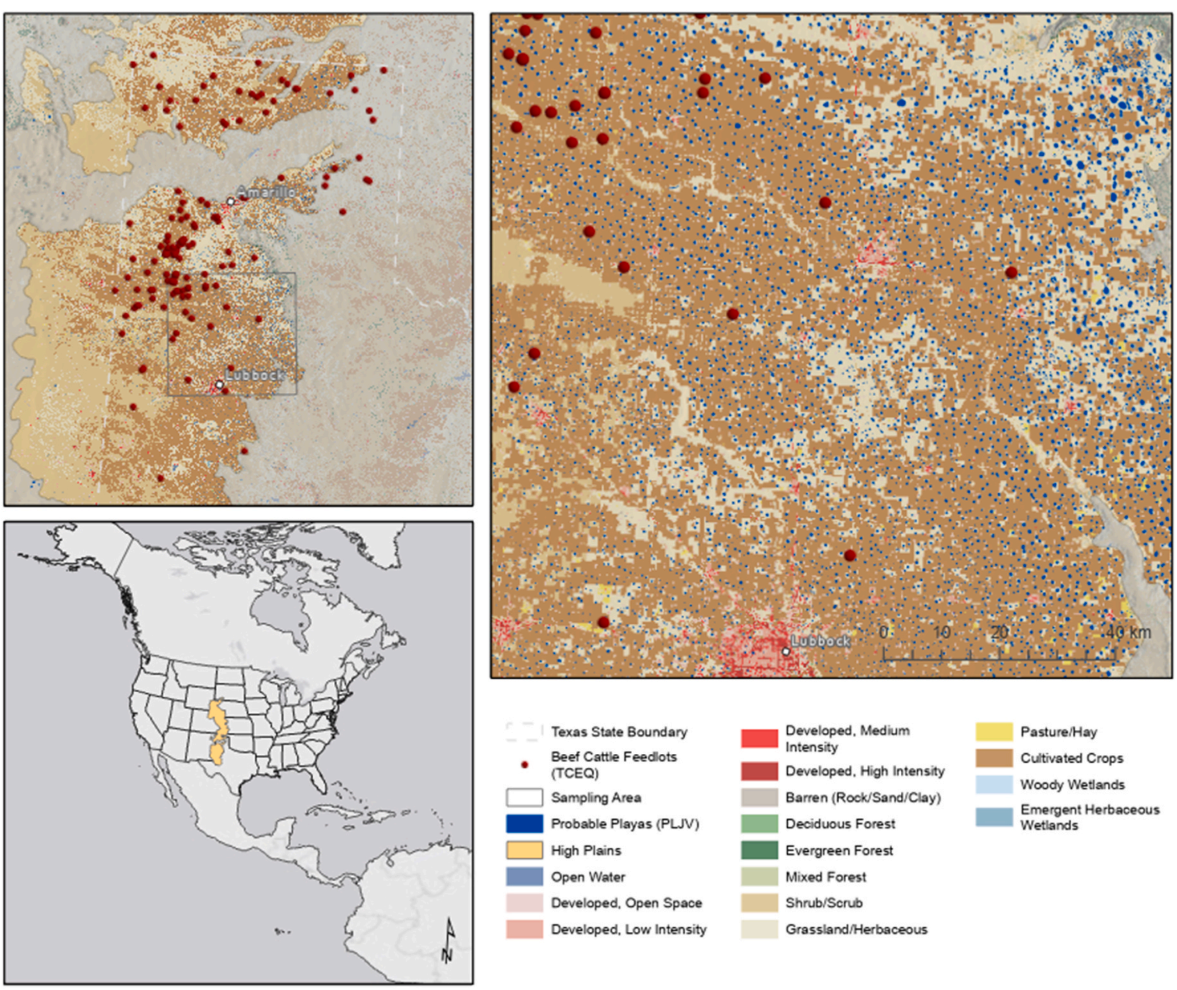

Fig. 1. Map of study area, Southern Great Plains, USA.

closer proximity to feedlots ($R^2 = 0.21$, $p = 0.0007$). Moreover, agrochemical profiles in both studies were similar to PM samples collected downwind of feedlots in the SGP over the same time frame (Wooten et al., 2018) and in previous years (Blackwell et al., 2015; McEachran et al., 2015). As previously noted, transport mechanisms are often obscured by multiple potential sources. Although, it can be reasonably hypothesized that feedlot-derived manure is largely an underlying source of veterinary pharmaceutical occurrence in rural playa basins and that aerial dispersion of PM plays some role in transport. Compared to insecticide applications, feedlot-associated pharmaceuticals are administered in targeted doses at lower overall concentrations through feed additives, topical, injectable, subdermal implant, and oral routes (Blackwell et al., 2015; Kumar et al., 2012; Tasho and Cho, 2016). This being the case, non-targeted application of insecticides is likely more amenable to long-range transport at higher concentrations.

Hence, there were three objectives in the current study: 1) to characterize spatial distribution of agrochemicals in playa wetland sediment, 2) determine source apportionment from agrochemical-associated land use, and 3) perform a refined ecological risk assessment of agrochemicals of interest on two benthic invertebrates. Within the context of agricultural use, analytes of interest were selected based on frequency of use and representation of classes with exclusive association to crop production (β-methoxyacrylates, carboximides), animal production (macrocyclic lactones), or dual-use (neonicotinoids, organophosphates, pyrethroids, phenylpyrazoles, and triazoles). Using this approach, we hypothesized that agrochemical classes with exclusive associations could be attributed to relevant land use classes using principal component analysis and regression of factor scores across sampled sites.

2. Methodology

2.1. Sample collection

Sediment samples were collected from playa wetland basins ($n = 33$) in the SGP, Texas, USA from May 25 to June 10, 2021, following a major precipitation event. Basins were selected based on inundation, road access, landowner permission, and varying proximity to feedlots. Field blanks were collected approximately once per day ($n = 8$). Sediment samples were collected in amber glass bottles from the top 10 cm near the playa basin edge, placed on ice immediately following collection, and transported to the Texas Tech University Institute Environmental and Human Health in Lubbock, TX where they were stored at −20 °C until processing.

Sample Extraction and Analysis

Since the original QuEChERS method (Anastassiades et al., 2003) was developed for the extraction of pesticides in fruit and vegetables, there has been a rapid expansion of modified QuEChERS methods for the application of environmental samples, including soil and sediment (Bruzzoniti et al., 2014). In the current study, sediment was extracted and analyzed for macrocyclic lactones (abamectin, doramectin, eprinomectin, ivermectin), neonicotinoids (clothianidin, imidacloprid, thiamethoxam), organophosphates (diazinon, malathion, temephos), pyrethroids (bifenthrin, λ-cyhalothrin, fenvalerate, esfenvalerate, permethrin), triazoles (propiconazole, tebuconazole), β-methoxyacrylates (azoxystrobin, pyraclostrobin), a carboxamide (boscalid), and a phenylpyrazole (fipronil) using QuEChERS extraction and instrumentation methods detailed in length in Peterson et al. (2021) and Peterson et al. (2017), respectively. Briefly, 4–5 g of sample were left to dry in 50-mL polypropylene centrifuge tubes under ambient air until mass stabilized. Once dry, sediment was homogenized with a glass stirring rod, spiked with internal standard, tris (1-chloro-2-propyl) phosphate (TCPP), and 15 mL acetonitrile:water (66:33) was added. Samples were then vortexed for 30 s followed by addition of QuEChERS salts (4 g $MgSO_4$ and 1 g NaCl) and vortexed again for 1 min. Sample tubes were centrifuged at 10 °C at 3000 rpm for 10 min and supernatant was poured into glass culture tubes and nitrogen evaporated to dryness at 35 °C. Extract was reconstituted in 1 mL of acetonitrile and filtered through 0.2 μm polytetrafluoroethylene (PTFE) syringe filters into 2 mL amber glass chromatography vials for subsequent analysis. Instrumental analysis was performed via triple-quadrupole ultra-high precision liquid chromatography tandem mass spectrometry with electrospray ionization (UHPLC-ESI-MS; Thermo TSQ Endura) using a Hypersil Gold AQ column (100 × 2.1 mm, 1.9 μm; Thermo Fisher Scientific).

2.2. Quality assurance and quality control

Matrix spikes and method blanks were co-extracted at a rate of approximately 10:1, and matrix-matched standards were used for calibration. Correlation coefficients (R^2) of all target analyte calibration curves were above the minimum acceptable limit for quality assurance ($R^2 > 0.995$). Limit of detection (LOD) and limit of quantitation (LOQ) were calculated as 3.3σ/S and 10σ/S, respectively (σ = standard deviation of response; S = slope of calibration curve; ICH, 2021). No analytes of interest were detected in method blanks and field blanks above LOQ. All sediment samples were extracted and analyzed <6 months of collection.

Geospatial Analysis

ArcGIS Pro (Version 2.9; Redlands, CA) was employed for all geostatistical operations and visualization. National Land Cover Data 2019 layer (Wickham et al., 2021) and ESRI World Light Gray Canvas basemap were used for broad visualization in Fig. 1. Playa basin polygons and attributes were imported from Playa Lakes Joint Venture (PLJV) probable playas shapefile (PLJV, 2022). Basin buffer land use characteristics were produced by clipping buffer polygons extending 1 km from the basin edge to USDA 2021 Cropscape Data layer (Supplemental Table S1; USDA-NASS, 2021). Cropscape land use classifications were reclassed into 6 categories: cropland, grassland/shrubland, fallow/idle cropland, developed, barren, and forest. Active feedlot coordinates in Region 1 (Amarillo) and Region 2 (Lubbock) were imported into ArcGIS Pro from Texas Commission on Environmental Quality's (TCEQ) central registry of General Water Quality Permits (TCEQ, 2021) for use in determining proximity to sampled playa basins.

Sediment Toxicity Benchmarks

Sediment toxicity benchmarks for two benthic invertebrates used in comparison with sediment concentrations from the current study were previously developed by Nowell et al. (2016; Supplemental Table S2). Briefly, benchmarks were based on median lethal concentrations (LC50) of spiked-sediment bioassays (SSB) compiled from the Pyrethroid Working Group (PWG) database. Sufficient SSB data were available for only two taxa, Hyalella azteca (n = 327) and Chironomus spp. (n = 389), and 48 currently used pesticides. Concentrations above which adverse effects are likely are indicated as Likely Effect Benchmarks (LEB) and concentrations below which adverse effects are not expected are indicated by Threshold Effect Benchmarks (TEB; Nowell et al., 2016). Benchmark terms are specific to sediment-dwelling organisms and correspond to those developed by MacDonald et al. (2000), published as one part of a series that were an earlier effort to resolve inconsistencies inherent in sediment quality guidelines. Along with LEB and TEB determined for each taxa individually, Nowell et al. (2016) generated a third integrated benchmark representing LEB and TEB values protective of both taxa. Sediment benchmarks are expressed in microgram per gram organic carbon (ug/g-oc) to account for impact of soil organic carbon (SOC) content on compound bioavailability.

Probabilistic Risk Assessment

Organic carbon-normalized sediment concentrations (Supplemental Information SI2) were used to generate acute and chronic risk quotients (RQ) and risk indices (RI) for benthic invertebrates in playa basins. Risk quotients were calculated as $EC/LEB_{integrated}$ (acute) or $EC/TEB_{integrated}$

(chronic) for each analyte of interest (Suter II, 2007), where RQ > 0.5 and RQ > 1 indicate sediment concentrations exceeding acute and chronic level of concern (LOC; U.S. EPA-OPP-EFED, 2007), respectively. Risk indices were calculated as $\sum$RQ in each sampled basin. Monte Carlo (MC) analysis was performed to determine probability distribution curves of RQ's and RI in playa sediment.

2.3. Statistical analysis

Statistical operations and analyses were performed in IBM SPSS Statistical Software for Windows (Version 28.0. Armonk, NY: IBM Corp). Varimax rotated principal component analysis (PCA) with Kaiser normalization was employed for unconstrained dimension reduction of relevant environmental variables. Longitude and latitude of collected samples, basin distance to the nearest feedlot and paved roads, and acreage of individual land use classes within a 1 km buffer of playa basins were included as predictor variables. Forest buffer acreage was excluded from PCA, only being detected at a single site (A5) and accounting for 0.3% of total buffer acreage at that site. All PCA variables were scaled using z-score standardization, and collinearity diagnostics were performed to confirm tolerance and variance inflation factors (VIF) (tolerance <1; VIF <10). Kaiser-Meyer-Olkin's (KMO) and Bartlett's Test of Sphericity were performed to determine factorial adequacy (KMO ≥0.60) and to establish that the component matrix was not an identity matrix (p < 0.05), respectively (Supplemental Table S3-4). Factor scores (FS) were generated through principle component regression (PCR) of each site. Communalities of predictor variables were considered acceptable at a combined mean of ≥0.7 (Maccallum et al., 2001; Supplemental Table S5). Eigenvalues were considered significant at values ≥ 1 (Hair et al., 2009) and eigenvectors were considered significant if absolute values were ≥0.80 (Tabachnick and Fidell, 2019). While only significant loading scores are interpreted, all loading scores were retained for PCR to preserve full variance in each factor score. Resampling was performed for uncertainty analysis of benthic invertebrate risk profiles (MC; n = 100,000) with RQ's and RI's including analyte NDs as zero.

3. Results

3.1. Agrochemical analysis

Of 21 compounds included in analysis, 14 were present in concentrations > LOQ (Table 1), ranging from 0.21 to 17.0 ng/g dw. Mean number of analytes detected per playa basin was 2.3 ± 0.4. No analytes of interest were detected at seven sites (A1, A3, A11, A13, A20, and A31) whereas the maximum number of detects (n = 11) occurred at site A24. Pyrethroids were detected most frequently across all basins (n = 25; grand mean = 3.1 ± 0.4 ng/g dw), with ≥2 pyrethroids detected in 57.6% of basins and ≥3 detected in 42.4% of basins. No avermectin, boscalid, diazinon, or temephos were detected > LOQ in any sampled basin.

Non-normal distribution and a large proportion of values below LOD are common in environmental data (Liu et al., 1997; Rathbun, 2006; Singh and Nocerino, 2002; Toscas, 2010), which can hinder spatial pattern analysis. Treatment of left-censored data as ½ LOD is suggested as an acceptable substitution method provided that non-detects are ≤70% (Antweiler and Taylor, 2008). Because pyrethroids were particularly abundant > LOQ in sediment, linear regression was performed on overall log (x + 1)-transformed concentrations including non-detects (n = 99; 60.0%) as ½ LOD. A significant correlation with feedlot proximity was established (R^2 = 0.178, p = 0.007; Fig. 2), whereas no significant correlation to cropland buffer acreage was observed (R^2 = 0.014, p = 0.259) during the sampling window.

3.2. PCA and PCR

Three principal components were extracted in PCA (Table 2) accounting for a cumulative 74.3% of overall variance between sites (Supplemental Table S6) with varimax rotation converging in five iterations. No individually significant loading scores were present on the PC2 axis. Fig. 3 highlights site regression scores along Factor Score 1 and 3 axes in four quadrants (Q1-Q4), and Fig. 4 displays agrochemical occurrence across individual playa basins.

Playa basins where cumulative agrochemical concentrations were

Table 1
Occurrence and mean concentrations of 21 agrochemicals in playa basin sediment (n = 33) in the Southern Great Plains, Texas, USA.

Compound	Class	Detection (%)	LOD[a]	LOQ[a]	Recovery (mean % ± SE)	Mean[a]	Median[a]	Min.[ae]	Max.[a]	SE[a]
clothianidin[b]	Neonicotinoid	3.0	0.50	1.51	68.3 ± 2.1	2.50	–	–	–	–
imidacloprid[b]	Neonicotinoid	9.1	0.12	0.36	69.6 ± 3.0	1.00	0.96	ND	1.60	0.3
thiamethoxam[b]	Neonicotinoid	3.0	0.19	0.58	59.1 ± 3.9	1.74	–	–	–	–
diazinon[b]	Organophosphate	0	0.22	0.68	81.8 ± 1.1	–	–	–	–	–
malathion[b]	Organophosphate	3.0	0.08	0.24	65.4 ± 3.2	0.38	–	–	–	–
temephos[b]	Organophosphate	0	0.51	1.70	40.2 ± 2.3	–	–	–	–	–
bifenthrin[b]	Pyrethroid	18.8	0.11	0.33	60.6 ± 4.7	0.53	0.52	ND	0.82	0.1
λ-cyhalothrin[b]	Pyrethroid	15.2	0.41	1.25	74.0 ± 4.1	2.84	1.82	ND	5.33	0.8
esfenvalerate[bf]	Pyrethroid	57.6	0.74	2.25	56.3 ± 5.7	4.43	3.78	ND	9.41	0.5
fenvalerate[b]	Pyrethroid	51.5	0.61	1.85	57.2 ± 6.7	5.29	4.16	ND	17.0	1.0
permethrin[b]	Pyrethroid	57.6	0.11	0.34	56.6 ± 5.1	1.06	0.83	ND	3.57	0.2
abamectin[c]	Macrocyclic lactone	0	1.04	3.14	33.8 ± 5.7	–	–	–	–	–
doramectin[c]	Macrocyclic lactone	0	0.68	2.05	32.7 ± 6.1	–	–	–	–	–
eprinomectin[c]	Macrocyclic lactone	0	1.19	5.80	27.1 ± 3.9	–	–	–	–	–
ivermectin[c]	Macrocyclic lactone	0	0.71	2.16	35.8 ± 6.7	–	–	–	–	–
azoxystrobin[d]	β-methoxyacrylate	3.0	0.01	0.20	47.5 ± 2.3	0.46	–	–	–	–
pyraclostrobin[d]	β-methoxyacrylate	3.0	0.01	0.20	45.1 ± 2.5	1.13	–	–	–	–
boscalid[d]	Carboximide	0	0.49	1.49	75.2 ± 2.4	–	–	–	–	–
fipronil[b]	Phenylpyrazole	3.0	0.03	0.20	38.4 ± 3.9	1.13	–	–	–	–
propiconazole[d]	Triazole	6.1	0.04	0.20	83.5 ± 2.9	0.84	0.84	ND	1.37	0.5
tebuconazole[d]	Triazole	6.1	0.02	0.20	86.4 ± 2.3	0.72	0.72	ND	1.22	0.5

[a] Values reported in ng/g, dry weight.
[b] Insecticide.
[c] Anthelmintic.
[d] Fungicide.
[e] ND = Not detected.

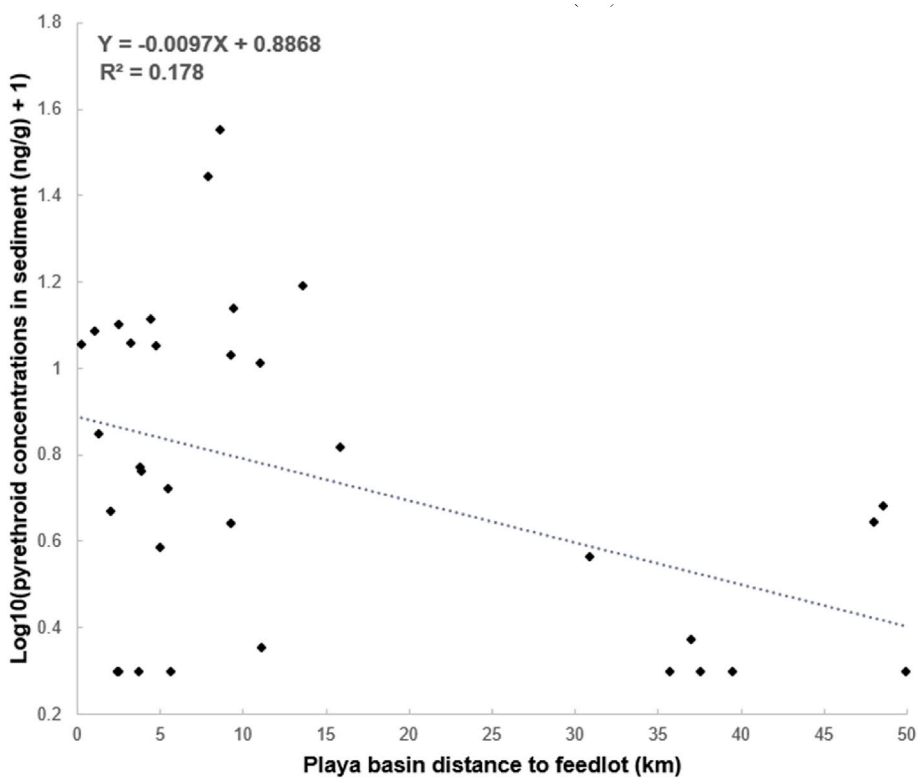

Fig. 2. Linear regression of overall log ($x + 1$)-transformed pyrethroid concentrations (ng/g) in playa basin sediment and basin distance to nearest beef cattle feedlot (km) with non-detects as ½ LOD.

Table 2
Rotated principal component loading and coefficient scores of sampled playa basins, Southern Great Plains, Texas, USA.

Predictors	PC1	R^2	PC2	R^2	PC3	R^2
Distance to beef cattle feedlot (km)	**0.90**[a]	0.348	0.30	−0.041	0.03	−0.010
Longitude	**0.83**[a]	0.295	0.39	0.028	0.10	0.026
Distance to paved roadway (km)	0.53	0.092	0.64	0.264	−0.17	−0.127
Grassland/ Shrubland (ac)[b]	0.14	0.016	0.16	0.025	**0.86**[a]	0.460
Fallow/Idle Cropland (ac)[b]	0.07	−0.156	0.77	0.450	−0.01	−0.040
Cropland (ac)[b]	0.02	−0.032	0.20	−0.158	**−0.89**[a]	−0.496
Barren (ac)[b]	−0.04	−0.191	0.67	0.391	0.52	0.255
Developed (ac)[b]	−0.38	−0.035	−0.59	−0.264	0.05	0.059
Latitude[b]	**−0.88**[a]	−0.438	0.11	0.284	−0.08	−0.038

[a] Bold values indicate significant loading score (≥|0.80|).
[b] Buffer acreage ≤1 km of basin.

>75th percentile primarily occurred in Q3 (55.6%) followed by Q2 (44.4%), while only one site in Q4 (A7) and two sites in Q3 (A12, A15) were >50th percentile of overall concentrations. Sites A24 and A28 were the only two basins in which tebuconazole was detected > LOQ, with an additional five agrochemicals detected at A24 not present > LOQ in any other basin (azoxystrobin, clothianidin, fipronil, pyraclostrobin, and thiamethoxam) indicating a higher likelihood of occurrence in more extreme cases of adjacent cropland conversion. While exclusive land use-occurrence patterns could not be established for fungicides, avermectins, neonicotinoids, and organophosphates due to sparse detections, feedlot proximity was a primary predictor of overall agrochemical occurrence in playa basins.

3.3. Outliers

Collinearity diagnostics determined that site A31 was an outlier contributing to variance inflation of distance to feedlot (49.9 km; VIF = 10.39; tolerance = 0.096). Due to its contribution to violation of VIF assumptions, the decision was made to exclude site A31 from PCA analysis. After exclusion of A31, distance to feedlot predictor was within limits of acceptable tolerance (0.11) and VIF (9.12). Therefore, reporting of statistical results are based on outlier excluded PCA.

3.4. Sediment toxicity benchmarks

Two soil types (Randall soil, n = 31; Mclean soil, n = 2; Supplemental Table S7) were underlying sampled basins and all basin buffers were cropland-dominated. Because pyrethroids were primarily detected across sites, only sediment toxicity exposure and effect profiles for bifenthrin, λ-cyhalothrin, fenvalerate, esfenvalerate, and permethrin are reported (Supplemental Table S8). Fenvalerate benchmarks were not available in Nowell et al. (2016). In cases where fenvalerate toxicity data are insufficient, esfenvalerate may be used as a proximate benchmark (Pohanish, 2014), which has been done for the current study. Esfenvalerate (S,S-fenvalerate) is the most insecticidally active of four fenvalerate stereoisomers and has largely replaced the latter's usage for agricultural purposes (Adelsbach and Tjeerdema, 2003). As such, fenvalerate toxicity benchmarks should be interpreted with caution.

3.5. Risk probability distributions

Probability distributions of integrated acute and chronic RI's are presented in Fig. 5a and b. Notably, MC-simulated RI's for pyrethroids in the current study exceeded acute and chronic LOC's in >75% and >95% of cases, respectively (Supplemental Table S9). Median acute and chronic pyrethroid RI's were 2.4 and 38.6, respectively. Pyrethroids identified as individual compounds of concern included λ-cyhalothrin,

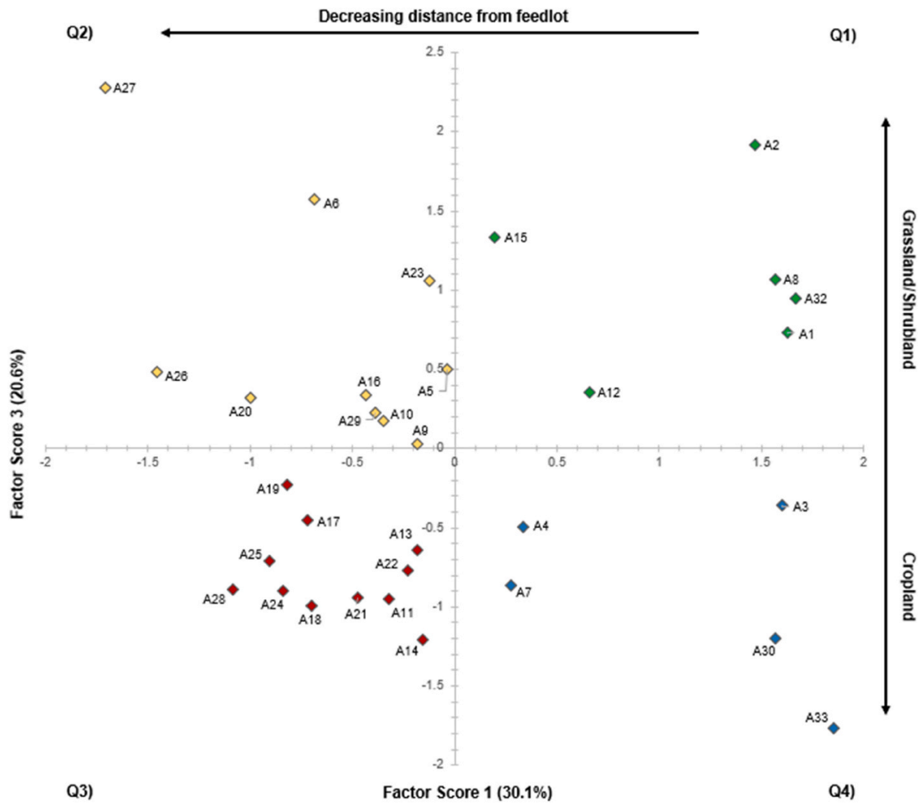

Fig. 3. Principle component regression of playa basins in four quadrants (Q1-Q4) along Factor Score 1 and Factor Score 3 axes; Factor Score 1 axis highlights sites in closer proximity to feedlots from right to left; Factor Score 3 axis highlights the site gradient as proportion of grassland/shrubland buffer acreage increases (top) or proportion of cropland buffer acreage increases (bottom).

esfenvalerate, and fenvalerate. Independently, λ-cyhalothrin exceeded acute and chronic RQ LOC's in >25% and >75% of cases, respectively. Esfenvalerate and fenvalerate contributed significantly to overall pyrethroid risk in sediment, exceeding acute RQ's in >75% and >50% of cases, respectively. Chronic risk of bifenthrin and permethrin to sediment-dwelling benthic invertebrates are unlikely based on the present study. Individual acute and chronic risk quotient distributions can be found in Supplemental Figures S1-2a-e.

4. Discussion

Atmospheric deposition of feedlot PM is a growing global concern as confined cattle finishing has become standard practice in many countries and is projected to increase in the coming decades (Kadarisman et al., 2021; Lam et al., 2019). U.S. EPA's most recent risk management evaluation of feedlots largely focused on contaminant loading from site runoff and land application, greenhouse gas emissions, bioaerosols, and nuisance odors (Barth et al., 2004), noting that there had not been any studies evaluating public health exposure beyond a reasonable distance from confined animal feeding operations. Feedlot PM generation received mention as a respiratory threat to workers and livestock but has yet to be recognized as a source of aerial transport of agrochemicals, likely due to underrepresentation in previous literature. Still, required federal reporting of hazardous air releases was eliminated in 2008 for feedlots <1000 head under the Emergency Planning and Community Right-to-Know Act (EPCRA), and all feedlots were exempted from reporting hazardous air releases under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA; U.S. EPA, 2022). The Fair Agricultural Reporting Method (FARM) act exempted air emissions reporting for all feedlots under CERCLA in 2018 (U.S. EPA, 2018), and in 2019, U.S. EPA eliminated EPCRA reporting requirements for all feedlots (U.S. EPA, 2019). Presently, there is no federal regulatory framework for basic reporting of air emissions, including PM, at feedlots in the U.S.

To our knowledge, this is the first study in which sediment pyrethroid concentrations have been linked to beef cattle feedlots well beyond the influence of direct site runoff. Pyrethroids have previously been detected in water, sediment, and suspended solids of rivers, estuaries, and lakes in the US and internationally (Tang et al., 2018; Li et al., 2017), though urban, residential, and/or cropland sources are often the focus of sampling campaigns. Since sampling occurred prior to typical foliar insecticide application on crops (July-October; Vyavhare and Kerns, 2022), overall pyrethroid mass from cropland buffers was likely lower compared to inputs later in the growing season, a trend observed in previous sampling campaigns (Belden et al., 2012; Thurman et al., 2000). Similarly, cropland manure application occurs relatively infrequently (5% of US cropland acreage; Macdonald et al., 2009) with application rate and timing depending on animal source, field nutrient requirements, and cover crop rotation (Liu et al., 2018). Precision agriculture technologies increasingly favor targeted, variable-rate fertilizer application, whereas inconsistent nutrient concentrations in livestock manure may further deter farm operators from fertilizing with manure as more economically viable strategies become widely accessible (de Rosa et al., 2022; Westerman and Bicuto, 2005). While sediment sampling early in the growing season does not fully encompass temporal dynamics of pyrethroid occurrence, lower source apportionment from cropland buffers elucidated a more apparent spatial relationship to feedlot proximity.

Pyrethroids pose a significant risk to aquatic life, but sediment bioavailability is largely dependent upon SOC content due to high organic carbon-water partition (K_{OC}) coefficients (K_{OC} > 4.5), which serves to mitigate uptake in aquatic vertebrate and sediment-dwelling invertebrate species. A distinguishing feature of playa basins is an underlying clay lens that facilitates higher SOC via accelerated organic

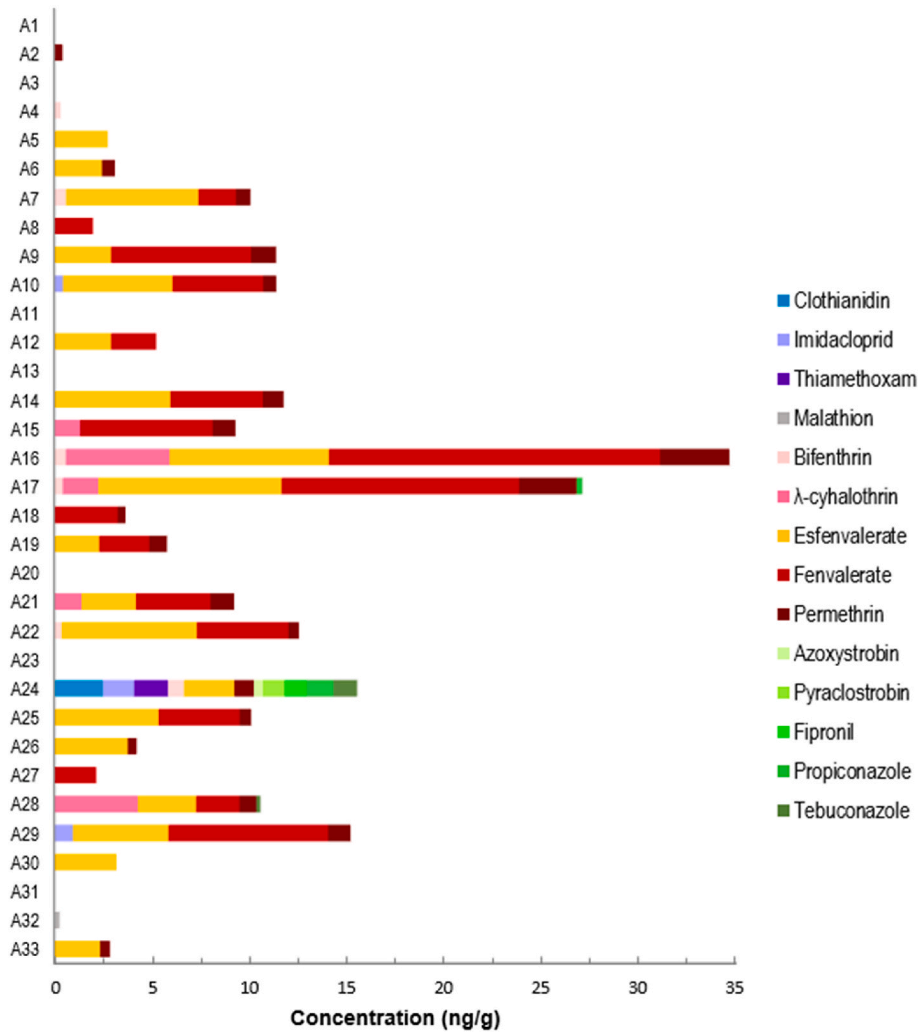

Fig. 4. Playa basin site distribution of agrochemical occurrence in the Southern Great Plains, Texas, USA.

matter decomposition relative to upland soils (Matus, 2021; Wei et al., 2014), as well as enhanced sediment detoxification through larger and more diverse microbial communities. Soil organic carbon is further enhanced in the top 50 cm in playas buffered by native vegetation versus cropland and CRP (O'Connell et al., 2016). While biotic and abiotic mechanisms of degradation including photodecomposition may lead to rapid dissipation of pyrethroids under field conditions (Gajendiran and Abraham, 2018), daily atmospheric PM deposition would provide a continuous source of agrochemicals potentially contributing to accumulation at rates exceeding degradation potential in air and wet sediment.

Native grassland buffers also mitigate agrochemical exposure by filtering sediment in surface water runoff (Haukos et al., 2016). Prior to cropland conversion, the Great Plains was dominated by temperate grasslands but has since been reduced to half of its historical range (WWF, 2021), being one of the most at-risk biomes on the planet. Alteration of land use patterns in the last century has increased erosion potential across the landscape causing a surge in agrochemical inputs to playa basins (Anderson et al., 2013; Belden et al., 2012). The loss of buffering vegetation has impaired the ability of playa wetlands to provide numerous ecosystem services such as carbon sequestration and groundwater recharge in the Ogallala aquifer, as well as providing critical migratory bird stopover and wintering habitat along the Central Flyway and breeding habitat for native amphibian communities (Bowen and Johnson, 2017). Since playa basins are low points of entire watersheds, they are heavily impacted by human activity in adjacent uplands. With >99% of playa wetlands located on private property, these largely unregulated keystone ecosystems are at high risk of habitat degradation (Haukos, 2003).

Insecticide-resistant biota in agroecosystems may also explain how aquatic and aquatic-dependent species can persist in heavily impacted wetlands. Studies have documented insecticide-resistant populations of wood frogs (*Lithobates sphenocephalus*; Bridges and Semlitsch, 2000; *L. sylvaticus*; Cothran et al., 2013), freshwater arthropods (*Daphnia pulex*; Bendis & Relyea, 2016; *H. azteca*; Muggelburg et al. 2017; *Thamnocephalus platyurus;* Brausch and Smith, 2009), and mayflies (*Stenacron* spp.; Rackliffe & Hoverman, 2020). Amphibians are the primary aquatic vertebrate taxa in isolated, ephemeral wetlands, with 43 species distributed throughout the Great Plains (Wishart, 2011). Aquatic-stage amphibian diets consist of algae, hydric plant material, and invertebrates, thus exposure can occur through oral routes and contact with contaminated media. Metamorphosed amphibians serve as a nexus between aquatic and terrestrial food chains (Ansley et al., *under review*), with continued bioaccumulation via cutaneous absorption in surviving adults (Brühl et al., 2011). Increased survival of resistant vertebrate and invertebrate organisms also facilitates greater bioaccumulation (Derby et al., 2021; Muggelburg et al. 2017), generating concerns of higher-order trophic transfer.

Monte Carlo uncertainty analysis serves to expand deterministic point estimates to probabilistic distributions, allowing for more realistic characterization of environmental exposure and effects. Risk quotient distributions in the current study highlight distinct compounds that a)

b)

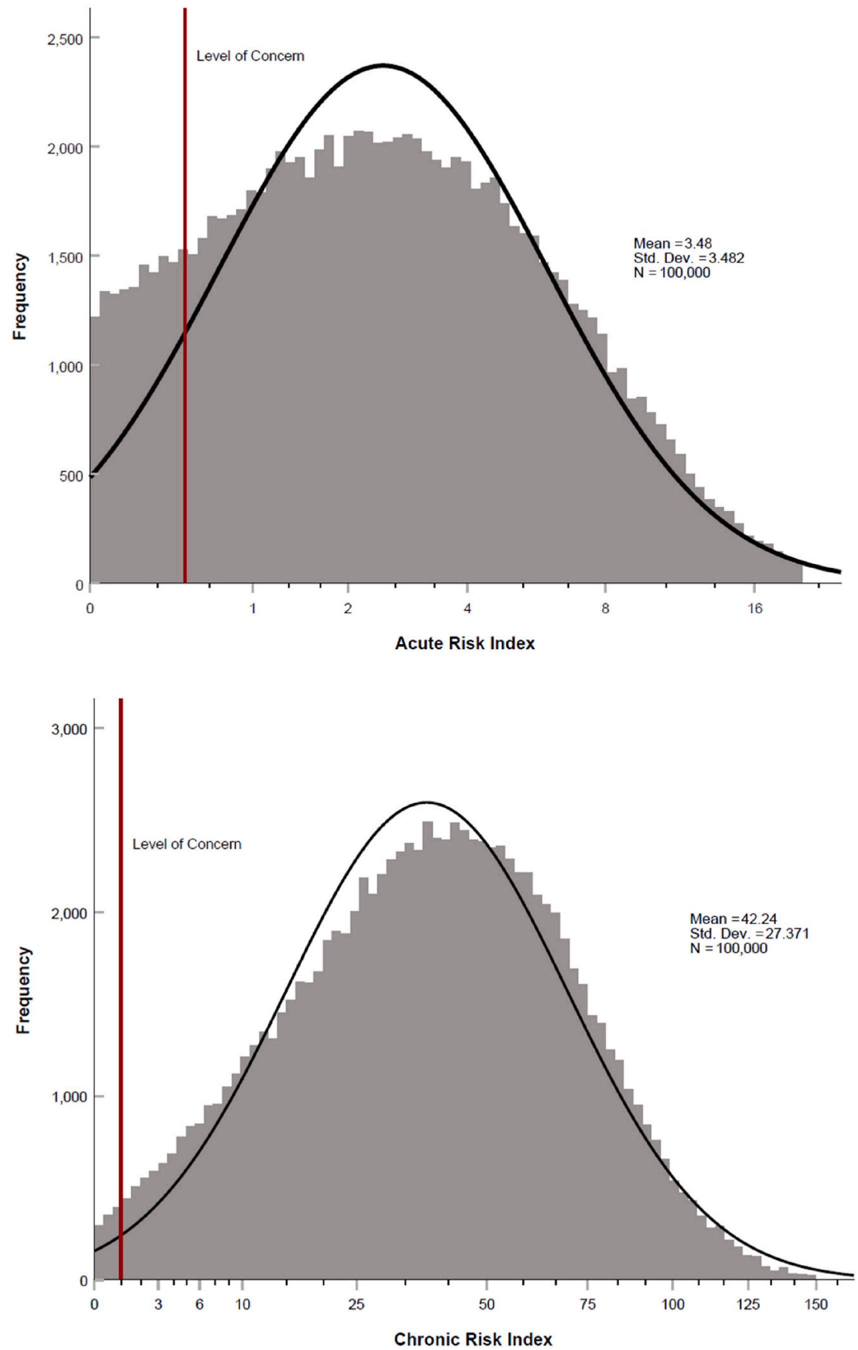

Fig. 5. a–b Monte Carlo-simulated acute and chronic probability distribution curve of risk indices for bifenthrin, λ-cyhalothrin, esfenvalerate, fenvalerate, and permethrin sediment concentrations (ug/g-oc).

disproportionately contribute to overall pyrethroid risk to benthic invertebrates. The considerable influence of fenvalerate isomers to pyrethroid RI's is likely a result of greater sediment partitioning relative to other pyrethroids included in analysis (Todd et al., 2003), facilitating greater persistence in sediment. Despite lower anticipated bioavailability, current organic carbon-normalized sediment concentrations indicate that esfenvalerate and fenvalerate are present in concentrations exceeding acceptable acute LOCs to sediment-dwelling invertebrates, even after higher soil adsorption tendency is considered. Esfenvalerate emulsifiable concentrate formulations, while enriched with the more insecticidally active S,S-isomer, may contain ≤25% of less insecticidally active fenvalerate isomers (Todd et al., 2003). U.S. EPA has indicated stereospecific fate properties are needed to adequately characterize ecological risk from pesticide formulations (U.S. EPA, 2000), though stereoisomerization of fenvalerate optical isomers in aquatic systems has not been well studied.

Results of the current risk probability distributions suggest regulatory action may be warranted to prevent mortality in non-target sediment-dwelling invertebrates. Benthic invertebrate risk profiles were generated following a pulse rainfall event to more accurately characterize agrochemical concentrations present during aquatic invertebrate emergence and growth. Temporal dynamics of agrochemical transport and fate were not explored in this study, restricting risk characterization to spatial dynamics at the date of collection. Moreover, generated RI's only consider those pyrethroids included in chemical analysis. Future studies should expand to include more analytes within the pyrethroid class of insecticides, as well as co-occurring potentiating compounds (e.g. piperonyl butoxide; Bradberry et al., 2005) to better assess additive and synergistic toxicity. As such, present RI's likely represent an underestimation of overall pyrethroid risk to SGP benthic invertebrates. Thus, a more conservative approach was adopted via use of integrated toxicity benchmarks.

5. Conclusion

This study highlights spatial distribution of agrochemicals in SGP playa wetland sediment. Despite growing evidence to the contrary, aerial dispersion of PM from beef cattle feedlots has not been recognized as a source of agrochemical transport to remote ecosystems. Pyrethroids used in both livestock and crop production represent a disproportionate frequency of agrochemical occurrence in playa sediment, which may have significant implications for aquatic wetland communities in agroecosystems. This work clearly demonstrates updated guidance for risk management of feedlots is warranted. Risk mitigation via ameliorating sediment loading in isolated wetlands is only a final point of control and more work is necessary to understand the underlying mechanisms of agrochemical release and transport. Sustainable livestock and cropping systems and judicious use of pesticides in the face of increasing strain on natural resources are essential for biodiversity and wildlife persistence in agroecosystems.

Data statement

Location-censored raw data tables are available by request to the corresponding author.

Author statement

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Declaration of competing interest

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

Data availability

Data will be made available on request.

Acknowledgement

This work was supported by the Texas Tech University Graduate School, the Texas Academy of Science Graduate Research Award, and the Sandy Land Underground Water Conservation Research Scholarship.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2022.120493.

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