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# Linking the Agricultural Landscape of the Midwest to Stream Health with Structural Equation Modeling

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  - Supporting Information

ABSTRACT: Multiple physical and chemical stressors can simultaneously affect the biological condition of streams. To better understand the complex interactions of land-use practices, water quality, and ecological integrity of streams, the U.S. Geological Survey National Water Quality Assessment Project is conducting regional-scale assessments of stream condition across the United States. In the summer of 2013, weekly water samples were collected from 100 streams in the Midwestern United States. Employing watershed theory, we used structural equation modeling (SEM) to represent a general hypothesis for how 16 variables (previously identified to be important to stream condition) might be inter-related. Again, using SEM, we evaluated the ability of this "stressor network" to explain variations in multimetrics of algal, invertebrate, and fish community health, trimming away any environmental variables not contributing to an explanation of the ecological responses. Seven environmental variables—agricultural and urban land use, sand content of soils, basin area, percent riparian area as forest, channel erosion, and relative bed stability—were found to be important for all three-community metrics. The algal and invertebrate models included water-chemistry variables not included in the fish model. Results suggest that ecological integrity of Midwest streams are affected by both agricultural and urban land uses and by the natural geologic setting, as indicated by the sand content of soils. Chemicals related



to crops (pesticides and nutrients) and residential uses (pyrethroids) were found to be more strongly related to ecological integrity than were natural factors (riparian forest, watershed soil character).

#### INTRODUCTION

Human actions on the landscape propagate numerous and complex pathways by which stressors threaten the ecological integrity of river ecosystems. Understanding the effects of different land uses on stream habitat and water quality, and the subsequent effects of stream habitat and water quality on stream biology, is a fundamental goal of stream ecology<sup>2</sup> and is necessary for the effective management of our freshwater resources. Gaining this understanding typically is done with statistical models that require comprehensive data on stressors (e.g., habitat alteration, synthetic chemicals, and excess nutrients) and biology (e.g., toxicological and ecological responses) for a large number of sites.<sup>3-5</sup> Structural equation modeling (SEM) is one statistical modeling approach that has gained interest among ecologists in recent years. SEM seeks to explicitly connect empirical data to a theoretical model of interconnected factors. It can represent complex causal networks mathematically and permit the testing of the hypothesized interconnections using observed data, thereby relating data to theory.6

Intensive agricultural practices and urbanization in the Midwestern United States have adversely affected water quality and biological condition in streams. 7-10 Streams in the Midwestern United States (Illinois, Indiana, Iowa, Kansas, Kentucky, Michigan, Minnesota, Nebraska, Ohio, and Wisconsin) have some of the highest concentrations of nutrients in the country. 11,12 Complex mixtures of pesticides

are common; a median of 54 pesticides and pesticide degradates were detected in 99 small streams in the Corn Belt sampled during the growing season in 2013, and 183 unique compounds were detected at least once. 13 Further, more than one-half (54%) of the total stream length in the Temperate Plains Ecoregion (an area that includes the Midwest) was found to be in biologically poor condition.

In 2013, the U.S. Geological Survey (USGS) National Water Quality Assessment (NAWQA) Project began a series of five regional-scale studies (Regional Stream Quality Assessments, RSQA) to quantify how multiple stressors affect stream ecosystems. The goals of the studies were to evaluate contaminants, nutrients, sediment, and streamflow alteration as potential stressors to aquatic life and to quantify how these stressors relate to ecological conditions in streams at the regional scale.<sup>14</sup> In the first regional study (2013), USGS scientists collaborated with the United States Environmental Protection Agency (EPA) National River and Stream Assessment (NRSA) to assess stream quality across the Midwestern United States. This regional-scale Midwest Stream Quality Assessment (MSQA) covered about 600 000 km<sup>2</sup> in parts of 11 states. 15 Extensive data were collected to characterize

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habitat, water and sediment chemistry, and biological communities (algae, invertebrates, and fish) in 100 small streams, 50 of which were shared with the NRSA data collection.<sup>7</sup>

Several reports have described various aspects of the physical and chemical conditions from the MSQA study, 16-19 examined toxicological stressors, 20,21 and related land use and instream stressors to biological variables.<sup>8–10</sup> Although these reports identified stressors that likely influence biological communities, they did not develop meta-models (Figure S1 of the Supporting Information, SI) and test conceptual models of how land management (e.g., urban and agricultural development), chemical and physical factors (e.g., pesticides and substrate size), and natural landscape factors (e.g., soil characteristics, stream size) interactively influence the integrity of biological communities. Here we investigate hypothesized causal linkages between human development, physical and chemical stressors in streams, and stream ecological health using SEM. Our specific objectives in applying SEM were 3fold. First, we wanted to account for the interconnected effects among variables that were not otherwise addressed through previous interpretations of these data, and thus provide a more complete representation of how agriculture and urban land uses affect streams of the Midwestern United States. 8-10,13,16,21 Second, we wanted to account for both direct and indirect effects of variables and use a calculation of total effects as a means of determining variable importance to ecological health. Finally, we wanted to take advantage of the ability of SEM to represent latent variables. Latent variables are included in structural equation models to represent hypothesized responses associated with some general characteristic, quality, or concept, in our case, stream health. In our investigation we are specifically interested in how stream health, as indicated by biological community integrity metrics, is responding to the multiple stressors resulting from urban and agricultural land

## METHODS

**Study Design and Setting.** The design of the RSQA study relies on the concept of a water-quality index period assumed to extend for weeks to months prior to the ecological assessment, and corresponding to the time that researchers have observed is necessary for stream invertebrate communities to recover from stressor effects. <sup>15,22</sup> Of the 100 wadable stream sites selected for the MSQA study, 98 were included in this analysis. Of the 98 sites, 37 were selected across a gradient of agricultural land use and 12 across a gradient of urban land use by the RSQA study, whereas the remaining 49 were NRSA probabilistic (randomly selected) sites. <sup>7,23</sup>

The MSQA study region covered part or all of six USEPA level 3 ecoregions (SI Figure S2). Land use in the study region is mainly crop land, primarily composed of corn and soybeans. Because of the land-use distribution in the region, the 49 random sites spanned an agricultural gradient but did not include any sites with >8% urban land use. The 12 targeted urban sites (32–100% urban land use) were proximate to the cities: Chicago, Illinois; Dayton and Cincinnati, Ohio; Indianapolis, Indiana; Kansas City, Missouri; Milwaukee, Wisconsin; and Omaha, Nebraska. Two of the 100 streams sampled for water quality were dropped from this analysis because one stream was not wadable (all streams were sampled using wading protocols for ecological surveys), and the other stream had a basin area (>6000 km²) much larger than the

other sites (median = 167 km<sup>2</sup>) and was located on the far western edge of the region.

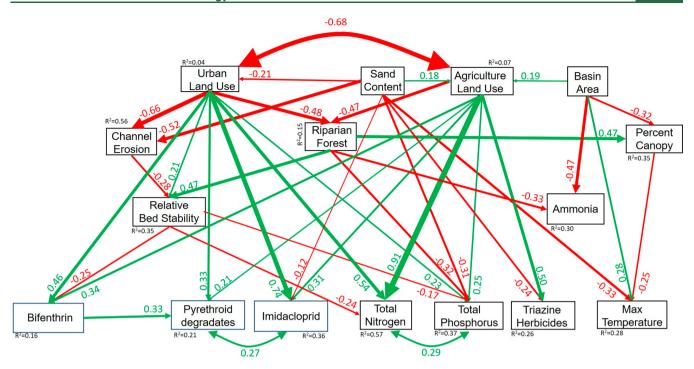
Collection and Analysis of Water and Sediment Chemistry and Ecology Data. Details of data collection and chemical analyses are given in Garrett et al. 15 and are briefly summarized here for constituents used in SEM development. Also, all the data used in this manuscript are available here, https://www.sciencebase.gov/catalog/item/ 5b463148e4b060350a15a836 and associated data can be found in citations provided throughout this manuscript. Twelve water samples were collected on weekly sampling intervals (May 6-August 9, 2013) except for two 2-week periods (May 27-June 7 and July 1-12) when only one sample was collected. The sampling period coincided with the season of high agrochemical use and runoff. 13,24 Water samples were collected typically by using a depth-integrating sampler at multiple vertical locations in the stream cross section composited into a Teflon churn. Subsamples were split from the churn for analyses of pesticides, nutrients, chloride, sulfate, suspended-sediment concentration (SSC), and dissolved organic carbon (DOC). Water samples were chilled and maintained at about 4 °C until chemical analysis. Polar organic compound integrative samplers (POCIS), designed to collect pesticides of moderate to high solubility, were deployed for about 7 weeks (mean  $37 \pm 6.7$  days) at each site and analyzed for pesticides using a similar method to that used for water samples.<sup>17</sup> Temperature and water levels were monitored continuously at all sites during the sampling index period.

Sampling of bed-sediment and ecological surveys, described in detail elsewhere, <sup>15</sup> was done at 98 sites in July and August 2013, coincident with the end of the water quality index period and retrieval of the POCIS. Sediment samples were composites of up to 40 surficial (top 2 cm) grab samples from depositional areas along the stream reach, similar to the approach described by Shelton et al. <sup>25</sup> Samples were chilled pending analyses of chemical and physical characteristics and for laboratory toxicity testing. <sup>21</sup>

Analyses of major ions, nutrients, and pesticides in water were done at the USGS National Water Quality Laboratory in Denver, Colorado. Pesticides in water and in POCIS extracts were analyzed using direct aqueous injection liquid chromatography tandem mass spectrometry (DAI LC–MS/MS). Samples for nutrients and major ions were analyzed as described by Fishman. Bed-sediment samples were analyzed for 118 pesticides following accelerated solvent extraction at the USGS California Water Science Center Pesticide Fate Research Laboratory (Sacramento, California); analyses were by gas chromatography-tandem mass spectrometry.

**Stressor and Biological Metrics.** Geospatial characteristics—e.g., land use and land cover, soils, precipitation—of each watershed and for a buffered reach of the stream (50 m on each side of the stream centerline for  $2.2 \pm 0.6$  km upstream from the sampling reach, depending on watershed size) representing the riparian zone were computed using a Geographic Information System (GIS) and nationally available GIS data sets. 9,15,29 Chemical and habitat stressor metrics and biological community metrics were computed as described by others and references therein. Variables used in SEM development and their sources are summarized in SI Table S1.

Multimetric indices for invertebrate<sup>9</sup> and fish<sup>10</sup> communities developed by EPA were used for the purpose of assessing the degree to which the observed community—based on a standardized sample—differed from natural expectations



**Figure 1.** Graphical representation of the structural equation model of relations among variables of streams of the Midwestern United States. A green arrow depicts a positive standardized path coefficient while a red arrow depicts a negative standardized path coefficient and (*p*-value < 0.100). Arrows are scaled to the size of path coefficients. Standard errors of path coefficients and other summary statistics can be seen in Table S2. Double-headed arrow indicates a covariance between observed variables. Coefficients of determination are provided for all endogenous variables. Variable name abbreviations. Sand Content = Sand Content in Soil, Riparian Forest = Percent Riparian Area as Forest, Percent Canopy = Percent Riparian Canopy Cover, Max Temperature = Maximum Temperature, Bifenthrin = Bifenthrin in Sediment, Pyrethroid degradates = Pyrethroid degradates in water, Triazine Herbicides = Sum of Triazine Herbicides.

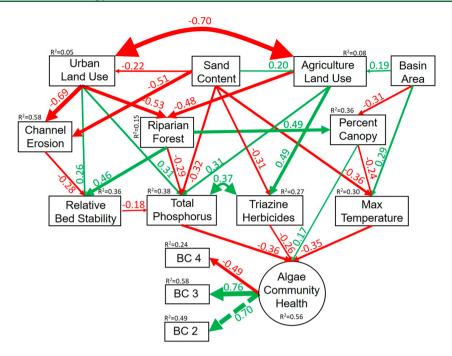
derived from regional reference sites. These biological indicators are widely used to assess the integrity of biological communities. However, there was no equivalent indicator for the integrity of algal communities. We therefore developed a latent variable comprising three metrics that represent the tolerance/sensitivity of three diatom taxon groups to a wide range of disturbances.<sup>30</sup> The metrics considered were derived by applying a Biological Condition Gradient approach to develop five metrics of Biological Condition (BC1-5) that split species of diatoms into groups of sensitive to BC1 to tolerant of stress and presented as the relative abundance of each group. 30-33 By employing multiple metrics to develop a latent variable we assume that the three metrics are descriptive of a similar property of the algal community, but make no assumption as to how the individual metrics relate to indicator variables. In this case the latent construct is named Algal Community Health because we used BC2-4 as indicators of the algal community. BC2 is a sensitive taxon group and used to scale the other two more tolerant indicators of algal health, thus this latent construct is scaled to indicate the response of sensitive taxa but is described by both sensitive and moderately tolerant (BC4) diatoms.

**Model Development.** SEM is a form of statistical modeling that allows for specification of networks of predictor and response variables. It is commonly used to test multivariate theoretical hypotheses. Here we employ SEM to evaluate ideas explaining associations between agricultural and urban land uses in terms of pathway effects (land use  $\rightarrow$  upland/riparian area  $\rightarrow$  instream habitat  $\rightarrow$  water/sediment quality) that collectively explain variations in ecological health of Midwest streams. Thus, we applied theory and empirical

evidence to assemble a meta-model (Figure S1) and a list of variables (Table S1) to investigate the combined effects of agricultural and urban land uses and their environmental consequences on stream ecosystems.

Because we did not have a finite set of a priori models we did not explore model structure or compare alternative models using d-separation or model selection approaches.<sup>35</sup> Our use of SEM can be considered to be "model building" modeling because of the many possible interrelations among variables reported in the literature. First, we evaluated how land use and natural landscape features, upland/riparian, instream habitat, nutrients, and synthetic chemicals were interrelated exclusive of ecological response metrics. In doing so, we explored all possible interconnections among these variables that were consistent with their spatial and temporal sequencing (i.e., plausible causal logic). This "stressor model" was optimized for fit using procedures described below. Second, we applied the optimized stressor model to each of three ecological health metrics (algae, invertebrate, and fish biological response variables) and further simplified each model as described below in this section. Finally, we used robust estimation methods to address deviations from normality and potential issues with model complexity and sample size for each of the final stressor-ecology models. In the end, missing links or missing variable interactions are not statements of conditional independence, rather they were just determined to be statistically insignificant at the alpha 0.10 level.<sup>35</sup>

All modeling was performed in R software (version 3.4.4) using the packages psych, data.table, lavaan, and semplot.  $^{36-40}$  All variables were assessed for skewness and kurtosis. Transformations (e.g.,  $\log 10(x + 1)$ , arcsin) were chosen on



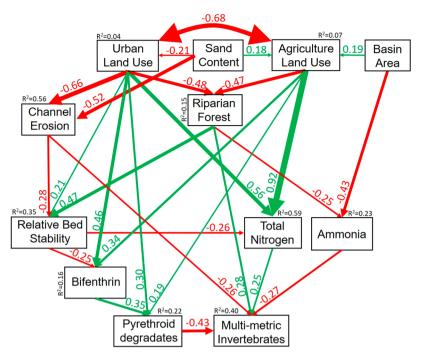
**Figure 2.** Graphical representation of the structural equation model relating stressors to algal community responses observed in streams of the Midwestern United States. A green arrow depicts a positive standardized path coefficient while a red arrow depicts a negative standardized path coefficient and (*p*-value < 0.100). Arrows are scaled to the size of path coefficients. Standard errors of path coefficients and other summary statistics can be seen in Table S3. Double-headed arrow indicates a covariance between observed variables. Circle indicates a latent variable. Dotted one-way arrow indicates scaling factor for latent variable. Coefficients of determination are provided for all endogenous variables. Variable abbreviations are defined in Figure 1.

the basis of data type (e.g., count, percent) to minimize skewness < abs (3), and kurtosis < abs(10)41, and the data were then centered and standardized by subtracting the mean value for each variable from each observation and then dividing by the standard deviation of all observations for that variable. Specific transformations for predictor variables are listed in Table S1 while for the ecology variables, only the algae variables were transformed as follows; BC 2 (4th root) and BC 3 and BC 4 were square root transformed. Structural equation models were fit in lavaan, using listwise deletion of missing values, with exogenous (causally independent variables) means, variances, and covariances treated as random. Model fit and parameter estimation was done using maximum likelihood estimation with robust errors. Models were iteratively evaluated trimming path coefficients that were not significant (p-value < 0.100). Modification indices, a measure of distance between fitted and implied covariance matrixes suggesting additional paths that could improve model fit (modification index >4), were then evaluated to assess if new pathways should be considered as just described. 42 Model fit was evaluated using the Robust chi-square global test (p-value >0.05) and Satorra-Bentler correction factor (near 1), Comparative Fit Index >0.95, Relative Noncentrality Index >0.95, Robust Root Mean Square Error of Approximation <0.05 and 90% confidence interval >0, Robust Standardized Root Mean Square Residual <0.05, and Incremental Fit Index >0.95. Once a model met these criteria it was once again evaluated with a global fit  $\chi^2$  and path coefficient estimates made by Bollen-Stine bootstrap (n = 1000). If a path had a pvalue >0.10, then the path coefficient was trimmed and the above modeling approach repeated. Any variable that did not have a direct or indirect effect on the ecological response metrics was trimmed from the model. All path estimates

(standardized or not) reported here were derived from the Bollen-Stine bootstrap estimation. Only standardized path coefficients are presented in figures and tables and used to represent the relative effect of one variable on another.<sup>41</sup> We then used Cohen's interpretations of correlation coefficients( $(\pm)$  0.1 (weak), 0.3 (moderate), and  $\geq$ 0.5 (strong)) to interpret the relative size of effects among standardized path coefficients. Finally, we assessed each variable's total, direct, and indirect effects on each of the three measures of ecological community integrity. Total effects are defined as the sum of all direct and indirect effects (standardized path coefficients) between variables, where direct effects are measured using path coefficients, and indirect effects—those propagated through a mediating variable—were calculated as the product of sequential path coefficients. Variables were grouped to determine total cumulative effects on ecological health by variable class (defined in Table S1) by taking the absolute value of total effect and calculating the percent total effect for each class. Finally, the covariance matrices needed to recreate these results are provided in SI Tables S7-S10.

# RESULTS

Stressor Model. Four major landscape-scale variables—agricultural land use (agriculture), urban land use (urban), basin area, and sand content of soil (sand content)—reasonably explained numerous instream stressors (Figure 1, Tables S2 and S7). Basin area was included to scale the influence of variables that can be affected by the size of a river or stream or the location of the sampling site within the stream network. Agriculture was a strong predictor of total nitrogen (TN, 0.91 standardized path coefficient) and triazine herbicides (0.50, herbicides), a moderately strong predictor of percent riparian area as forest (-0.47, riparian forest),



**Figure 3.** Graphical representation of the structural equation model relating stressors to invertebrate community responses observed in streams of the Midwestern United States. A green arrow depicts a positive standardized path coefficient while a red arrow depicts a negative standardized path coefficient and (*p*-value < 0.100). Arrows are scaled to the size of path coefficients. Standard errors of path coefficients and other summary statistics can be seen in Table S4. Double headed arrow indicates a covariance between observed variables. Dotted one-way arrow indicates scaling factor for latent variable. Coefficients of determination are provided for all endogenous variables. Multimetric Invertebrates = Multimetric Index of Macroinvertebrate Community, other variable abbreviations are defined in Figure 1.

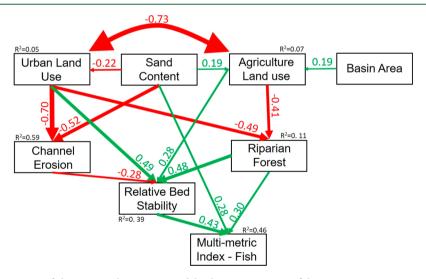


Figure 4. Graphical representation of the structural equation model relating stressors to fish community responses observed in streams of the Midwestern United States. A green arrow depicts a positive standardized path coefficient while a red arrow depicts a negative standardized path coefficient and (*p*-value < 0.100). Arrows are scaled to the size of path coefficients. Standard errors of path coefficients and other summary statistics can be seen in Table S5. Double headed arrow indicates a covariance between observed variables. Dotted one-way arrow indicates scaling factor for latent variable. Coefficients of determination are provided for all endogenous variables. Multimetric Index – Fish = Multimetric Index of Fish Community, other variable abbreviations are defined in Figure 1.

bifenthrin in sediment (0.34, bifenthrin), and imidacloprid (0.31), and a weak predictor of total phosphorus (0.25, TP) and pyrethroid degradates in water (0.21, pyrethroids). Urban land use was a strong predictor of imidacloprid (0.74), channel erosion (-0.66), and TN (0.54), a moderately strong predictor of riparian forest (-0.48), bifenthrin (0.46), and pyrethroids (0.33), and a weak predictor of TP (0.23) and relative bed stability (RBS, 0.21). Model fit was deemed good based on the

global model fit statistic robust  $\chi^2$  (65.368, *p*-value = 0.328, df = 61, n = 90, Table S2). Other model details including metrics of model fit and variance explained for endogenous variables can be found in Table S2.

**Algal Model.** Four instream stressor variables had significant direct effects on algal communities: TP (-0.36), maximum temperature (-0.35), triazine herbicides (-0.26), and percent riparian canopy cover (0.17) (Figure 2, Tables S3

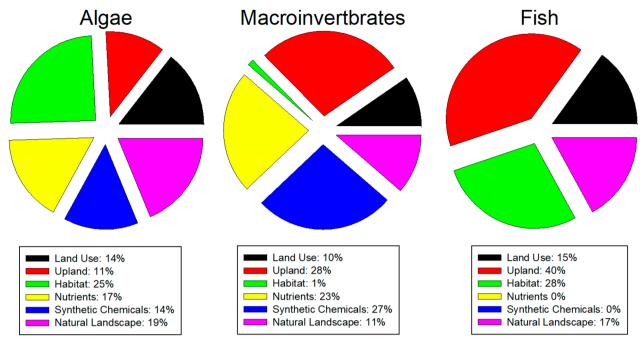


Figure 5. Pie charts illustrating the percent total effects for each class of variable for each of three structural equation models describing the stressors to ecological communities in small streams of the Midwestern United States. See Table S1 for a description of the variables included into each of the six classes described.

and S8). These instream stressors were directly and indirectly affected by the major landscape-scale variables: agriculture, urban, and sand content. Basin area was included to scale the variables agriculture, percent riparian canopy cover, and temperature. Some pathways by which landscape-scale factors influence instream stressors and algae were complex; for example, results imply urban (-0.69) and sand content (-0.51) influence channel erosion, which in turn influences RBS (-0.28) and TP (-0.18). Thus, sand content and urban have indirect influences on TP, herbicides, and algae in the model. Agriculture influenced algae through a different pathway; it was negatively related to riparian forest (-0.48), which was positively associated with percent riparian canopy cover (0.49), which in turn directly influenced the algal community (0.17). During model fitting, modification indices suggested that adding a covariance between herbicides and phosphorus (0.37) would improve model fit (suggesting some omitted common influence). The algae latent variable (Algae Community Health) had an  $R^2 = 0.56$  with indicator values of  $0.70 (R^2 = 0.49), 0.76 (R^2 = 0.58), \text{ and } -0.49 (R^2 = 0.24) \text{ for }$ each component metric (Biological Condition (BC) 2-4), respectively. The global fit metric  $\gamma^2$  was 63.215 (p-value = 0.330, df = 59, n = 93) and the other fit metrics were satisfactory (Table S3).

Invertebrate Model. Five environmental variables had direct effects on invertebrate community (multimetric index of macroinvertebrate community) integrity in the model, the most important of which was the pyrethroid insecticides as indicated by pyrethroid degradates (in water) (Figure 3, Tables S4 and S9). Pyrethroids (-0.43), ammonia (-0.27), and channel erosion (-0.26) had negative direct effects on invertebrate communities whereas TN (0.25) and riparian forest (0.28) had positive direct effects on invertebrate communities. These five variables completely mediated (i.e., completely explain) the effects of the three landscape-scale variables—agriculture, urban, and sand content—on the

invertebrate communities. The addition of basin area was key to this model and without it a spurious negative relationship existed between agriculture and ammonia. The global model fit metric  $\chi^2$  was = 35.930 (p-value = 0.566, df = 38, n = 90), the other model fit statistics are found in Table S4.

**Fish Model.** The fish model is the simplest of the three community models, as only habitat and landscape-scale variables remained (no chemical variables) in the final model (Tables S5 and S10, Figure 4). Three environmental variables had direct effects on the fish community (multimetric index of fish community), and all other variables had indirect effects. Unlike agriculture and urban, sand content (0.28) had a direct effect on the fish communities, whereas RBS and riparian forest mediated the effects of all the other variables. RBS (0.43) had a moderate direct effect on the fish community, mediating the influences of agriculture (0.28) and urban (0.49) as well as channel erosion (-0.28) and riparian forest (0.48) effects. Riparian forest mediated the effects of agriculture (-0.41) and urban (-0.49) land uses, and channel erosion and RBS mediated the indirect effects of sand content. Basin area helped scale the effect of agriculture but otherwise had little effect on this model. The global model fit metric  $\chi^2$  was = 6.615 (p-value = 0.882, df = 12, n = 91) and other model details are provided

Direct, Indirect, and Total Effects. The three models of biological integrity varied in degree of complexity as reflected by the number of direct and indirect pathways (algae = 4 direct, 10 indirect; macroinvertebrates = 5 direct, 8 indirect; fish = 3 direct, 6 indirect; Table S6) and a summary of total effects by each class (see Table S1 for a list of which variables belong to each class) of variable (Figure 5). The habitat class of environmental variables had the largest cumulative total effect on the algal community (25%), followed by natural landscape (19%), nutrients (17%), land use and synthetic chemicals (14% each), and upland (11%). For invertebrates, upland (28%), synthetic chemicals (27%), and nutrients (23%)

had similar total effects. Upland (40%), habitat (28%), natural landscape (17%), and land use (15%) collectively described all the effects on fish. Seven variables (agricultural, urban, sand content, basin area, channel erosion, riparian forest, and RBS) were common to all three models, and described 47% (algae), 50% (invertebrates), and 100% (fish) of total effects. The top three environmental variables affecting each of the ecological indicators were as follows: algae: TP (total effect = -0.46), herbicides (-0.39), and temperature (-0.35); invertebrates: pyrethroids (-0.43), riparian forest (0.35), and ammonia (-0.27); and fish: riparian forest (0.50), RBS (0.43), and sand content (0.24).

# DISCUSSION

Our findings support the concept that consideration of multiple biological communities is necessary to assess anthropogenic influences on ecological health. Although the natural landscape and land-use drivers (urban, agriculture, sand content, and basin area) were important in all community models, the specific mix of stressor variables influencing each community was different. Notably, chemical variables from multiple classes (herbicides, insecticides, and nutrients) and temperature were important in the algal and (or) invertebrate models but not in the fish model. Algae are known to be sensitive to herbicides and herbicides concentrations exceeded acute-plant benchmarks (either vascular or nonvascular) in one or more samples at 75% of the sites sampled. 13 Bifenthrin, a widely used pyrethroid insecticide, is highly toxic to aquatic invertebrates such as Hyalella azteca and occurs in some MSQA streams at levels shown to affect larval and adult invertebrates.<sup>20</sup> In contrast, concentrations of chemicals that exceeded acute or chronic benchmarks for fish were rarely measured (<10% of sites). 13 Differential sensitivity to stressors among biological communities is also consistent with differences in species traits. For example, algal model results are consistent with the short (days to weeks) life span of algal species and well-known sensitivity to nutrients and herbicides. 45,46 Similarly, fish community model results are consistent with the longer (years) life span and high mobility of fish species relative to algal or invertebrate communities, and hence greater sensitivity to reach-scale factors such as habitat quality and structure. Given the complementary nature of the biological community models, it may seem tempting to combine them into a single "ecological health" latent construct. However, our attempts to do so were unsuccessful because there was so little covariance among the three community indicators, a result of their unique associations with different sets of stress variables. This is an important finding because it suggests that each community embodies unique aspects of ecological health that cannot be quantified by simplifying ecological health into a single metric.

Channel erosion and RBS were found to be important influences in all three biological communities, indicating the importance of sediment to ecological health in Midwest streams. Channel erosion indicates the percentage of fine sediments in the active channel bed that originated from the erosion and collapse of stream banks, as opposed to sediment that originated from erosion of surface soils in the watershed. 16 All models suggest that high levels of stream bank erosion lead to excess fine-grained sediment in the stream (i.e., low RBS), which further influences ecological communities via direct and indirect pathways. We can only speculate why channel erosion was less pronounced in watersheds with higher amounts of sandy soils. Higher sand content is also associated with higher soil permeability, groundwater contributions to streamflow, and more stable and presumably less erosive flows. 16,47 The finding of increased channel erosion in increasingly urban watersheds has been well documented, 48 and is due to erosive flows generated by impervious surfaces. Channel erosion was not related to agricultural land use in our models (Figures 1-4), possibly because most sites were dominated by this land use (median agricultural land cover was 75%), making it difficult to distinguish the effect of agricultural land use on erosion in the presence of other processes. In addition to the physical stress caused by sediment, the links between channel erosion and sediment-associated contaminants (TP and pyrethroids) indicate sediment as a contaminant vector. The associations of channel erosion and contaminants were negative and mediated by RBS. The negative association indicates that erosion of surface soil, the alternative to channel erosion, is positively associated with TP<sup>49-51</sup> and pyrethroids (specifically bifenthrin), as demonstrated for bifenthrin by Gellis et al. 16

Pesticide associations in the models—triazine herbicides influence algae whereas pyrethroid insecticides influence invertebrates—provide evidence that assessments of stream health in the Midwest are incomplete without an assessment of pesticide exposure. Mesocosm experiments were done in association with the field assessment to provide additional causal evidence.<sup>20</sup> These experiments demonstrated that multiple ecological responses to bifenthrin in sediment occurred at bifenthrin concentrations similar to those measured in sediments in the MSQA study. Low levels of bifenthrin altered the timing of adult insect emergence while higher levels eliminated emergence all together, disrupting reproduction of aquatic insects and severing ecological linkages with terrestrial food webs.<sup>52</sup> Moderate and high levels of bifenthrin were lethal to many species of aquatic insect larvae, particularly grazers. Experimental results were consistent with observations in the MSQA study that showed a decrease in herbivorous mayflies with higher bifenthrin concentrations in streams. Pyrethroid degradates (in water), an alternative measure of bifenthrin (in sediment) and possibly other pyrethroids in sediment, was a significant variable in models of invertebrate metrics for Midwest streams. Taken together, these studies (experimental and observational) suggest that pyrethroids are having a measurable adverse effect on invertebrate communities in Midwest streams.

Nutrients appeared to influence biological communities in dissimilar ways. Total phosphorus, thought to be limiting relative to nitrogen in 60% of the streams, was negatively associated with the algae latent variable (Algae Community Health) primarily because of positive associations with BC2 and BC3 (negative TP x positive BC2 or BC3 = negative). Examination of existing trait databases 31,32 revealed that many taxa in BC2 and BC3 are associated with lower TP environments. Nitrogen, however, appeared to have contradictory influences on invertebrate communities. Ammonia was negatively associated with invertebrate community condition although observed ammonia concentrations were well below established levels of toxicity. In contrast, TN was positively associated with invertebrate community condition despite the fact that dissolved nitrate concentrations observed in this study approached acutely toxic thresholds in many streams.<sup>29</sup> One explanation of this finding is the possibility of interactions with other stressors. For example, a mesocosm study<sup>53</sup> identified

that moderate levels of nutrients in the presence of insecticides mitigate the effect of those insecticides on the community. Thus, it is possible that TN is providing a subsidy to invertebrate communities exposed to insecticides in Midwest streams.

The findings presented here highlight the importance of natural context,  $^{54-56}$  such as watershed soil characteristics and stream size, to the influence of land use on stream ecological health. Soil sand content in the Corn Belt is a surrogate for geologic and glacial history<sup>41,57</sup> and their potential effects on water quality and stream habitat. 47,58,59 The MSQA sites, with minor overlap in a few watersheds, are roughly split between sites in areas of pre-Wisconsin glaciation (Illinoisan and Kansan glaciation; 48 sites) and late-Wisconsin glaciation (43 sites; 7 sites are south of the glacial extent).60 Generally, the pre-Wisconsin sites are across the southern half of the region and the late-Wisconsin sites are across the northern half. Late-Wisconsin glaciated sites, compared to pre-Wisconsin sites, have, on average, higher sand content, stream base flow (more stable flows), and RBS (coarser sediment), accompanied by lower basin slope, channel erosion, and riparian area as forest (Table S11). Late-Wisconsin sites have more area farmed as row crops (74% versus 58% for the pre-Wisconsin sites), yet pre-Wisconsin sites have higher concentrations of herbicides, pyrethroid degredates, and TP. One reason that pre-Wisconsin sites might be more vulnerable to contamination by synthetic chemicals is the existence of low-permeability "restrictive" layers in their soils; these soil restrictive layers were a significant variable in modeling the occurrence of atrazine in Midwest streams.<sup>61</sup> As a result, generally higher levels of atrazine occur across the southern, pre-Wisconsin part of the region, even though row crop intensity is lower than in the northern part of the region.<sup>62</sup> Thus, ecological communities in pre-Wisconsin streams are more at risk to chemical exposure, while communities in late-Wisconsin streams have better instream physical habitat (e.g., temperature, substrate, base

Another natural factor, stream size, interacts with anthropogenic practices in the Midwest to affect stream condition. As streams and rivers became larger (larger basin area), they tended to have higher percent area as agricultural land use, warmer water, and less riparian canopy cover. Conversely, smaller basins were associated with higher ammonia levels. The associations with temperature and cover are likely natural processes influencing the ecological indicators of stream health. The reason for the association of stream size and ammonia is not known, but because ammonia is quickly assimilated in surface waters, 63 its occurrence in smaller streams might indicate proximity to sources (e.g., animal facilities, septic tanks) and lack of time for assimilation. Additionally, many small streams in the Midwest have been channelized (straightened), which might affect ammonia assimilation by increasing depth and reducing aeration in the stream. Thus, basin area was found to have important controls on natural characteristics of instream and near-stream physical habitat and on anthropogenic practices (farming) and nutrients in the streams. In the Midwest, the natural setting interacts with anthropogenic practices to influence the chemistry, habitat, and ecological health of the streams. This implies that stream conservation and restoration efforts would benefit by accounting for the influence of these natural factors. 54,64

In the structural modeling context both sand content and basin area are moderating variables. 41,57 Moderator variables

work to affect the relationship of another predictor on a response variable. While moderator effects (interaction terms) could have been explored, we had no a priori hypotheses that either sand content or basin area would have interactive term effects in our models and did not explore these types of effects. However, such interactions are possible. These effects are distinguishable from mediated effects. In our models many landscape-scale variable effects were mediated through upland/riparian, instream habitat, and water-quality variable effects on the ecological response variables. These type of effects (moderation, mediation) are accounted for in structural equation models making this approach to ecological modeling a unique and powerful approach to understanding how land use culminates in effects on freshwater ecosystems.

This assessment is the most comprehensive study of the effects of agricultural and urban land use on stream health in the Midwest to date. Historically, studies have been conducted at much smaller scales with a narrower focus 65,66 or did not include synthetic chemicals. 58,59,67 The MSQA study is the first to include pesticides as a stressor and to consider multiple communities at the large regional scale (but see<sup>68</sup>). In this study, we have quantified how these assemblages appear to respond to the multitude of stressors observed in Midwest streams and ranked the relative importance of sediment, nutrients, and pesticide impacts on all three ecological communities, filling an important knowledge gap. Our findings, however, do not deviate substantially from previous studies in areas where our data overlap. For example, agricultural land use dominates in this region and causes significant delivery of nutrients and sediment to streams 66,69 and that native plants 66 and riparian zones<sup>67,69</sup> are important to protecting stream health. Also, glaciation is an important natural factor to consider in this region that can affect water quality, ecological integrity, and stream restoration outcomes, independent of land-use change. 58,69 Although urban land-use impacts to stream health were perhaps more prominent in our study than in many other studies (an exception 65), population growth in the Midwest, in particular in the seven large metropolitan areas sampled, may have increased to the point that urban land-use impacts should be considered a growing concern in this region.

The SEM presented here has extended our understanding of relations between natural and human landscape factors and their effects on reach-scale conditions, instream stressors, and ecological condition for small Midwest streams. Although previous analyses using other model approaches had identified many of the same instream stressors, 8-10 they had not provided any understanding on how those stressors were related to each other or to landscape drivers. Pyrethroids were, for example, identified as a significant variable for invertebrates by Waite and Van Meter, however, the understanding that pyrethroids were primarily from urban land use but mediated by channel erosion and bed stability, indicating erosion and transport of fine sediment as a vector, was achieved. Ammonia also was identified as a significant stressor by Waite and Van Meter, but the inverse relation of ammonia to basin area combined with the positive relation of basin area to agriculture was not. These types of relations provide important understanding of the complex mechanisms driving the instream stressors. The complexity of relations among factors that affect water quality and ecological health of streams identified by this study presents a challenge to resource managers interested in stream conservation and restoration. There is not a single answer to the question, "Which stressor is the most

important?" Many stressors—physical habitat, nutrients, and pesticides—affect the different biological communities in the streams in different combinations and under the influences of different land uses and natural settings. In addition, no single biomonitoring end point (e.g., invertebrates) can represent the overall ecological health of the streams.

There is information in the SEM models that might help guide conservation efforts by revealing intervention points. Despite the depleted riparian zones in the Midwest, for example, these areas appear to be important to all ecological end points. Healthy riparian forests seem to be an effective countermeasure to more intensive agricultural and urban land uses. Channel erosion and its effect on streambed-sediment characteristics and occurrence of sediment-associated contaminants suggests that sediment management efforts might also be effective. Channel erosion is adversely affecting physical habitat and soil erosion is a vector for sediment-associated contaminants, meaning that both are important for stream health. Chemical exposure also appears to affect the condition of biological communities, indicating that reducing nutrient and pesticide loading to the streams will have a positive effect on stream health both locally and likely in downstream receiving waters. 70-72

### ASSOCIATED CONTENT

# **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b04381.

Figure S1, Meta-model generalizing relationships between land use, habitat, contaminates, and ecological health; Figure S2, map of the Midwest Stream Quality Assessment study area; Table S1, variables considered and why they were considered for use in this analysis; Table S2, regression coeffects and summary statistics of the stressor model; Table S3, regression coeffects and summary statistics of the algae model; Table S4, regression coeffects and summary statistics of the invertebrate model; Table S5, regression coeffects and summary statistics of the fish model; Table S6, direct, indirect, and total effects of predictors in the algae, invertebrate, and fish models; Table S7, covariance matrix and variable means used for the stressor model development; Table S8, covariance matrix and variable means used for the algae model development; Table S9, covariance matrix and variable means used for the invertebrate model development; Table S10, covariance matrix and variable means used for the fish model development; Table S11, model variable medians based on classification as either Pre-Wisconsin or Late-Wisconsin glacial history; and Table S12, summary statistics based on raw data values of each variable used in the structural equation modeling (PDF)

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# **Author Contributions**

T.S.S. helped collect the data, conducted the SEM analysis, and led writing of the manuscript. P.C.V.M. led the Regional Stream Quality Assessment studies and contributed to all

aspects of this manuscript including study design, data collection, interpretation, and writing of the manuscript. D.M.C. coordinated all ecological data for the Regional Stream Quality Assessment studies and the NAWQA project and contributed to all aspects of this manuscript including study design, data collection, interpretation, and writing of the manuscript. The work described in this article represents the combined efforts of study-team members from the US Geological Survey (USGS), U.S. Environmental Protection Agency, and State agencies and contractors supporting the National Rivers and Streams Assessment (NRSA) program in the Midwest region. The authors recognize the efforts and contributions of USGS scientists in Water Science Centers in the Midwest region and in numerous USGS laboratories across the country. The authors further recognize the contribution to the successful completion of the study of collaborators in the EPA, state environmental science agencies in the region, and EPA contractors supporting the NRSA program in the MSQA study area, including EPA Office of Pesticide Programs, Illinois, Indiana, Iowa Department of Natural Resources, Iowa State Hygienic Laboratory, and each of the individual states in the region. Scott Morton proofed calculations on direct and indirect effects.

#### Notes

The authors declare no competing financial interest.

#### REFERENCES

- (1) Coles, J. F.; McMahon, G.; Bell, A. H.; Brown, L. R.; Fitzpatrick, F. A.; Scudder Eikenberry, B. C.; M.D Woodside, M. D.; Cuffney, T. F.; Bryant, W. L.; Cappiella, K.; Fraley-McNeal, L.; Stack, W. P. Effects of Urban Development on Stream Ecosystems in Nine Metropolitan Study Areas Across the United States. U.S. Geological Survey Circular 1373.; U.S. Geological Survey: Reston, VA., 2012; p 138.
- (2) Allan, J. D. Landscapes and Riverscapes: The Influence of Land Use on Stream Ecosystems. *Annual Review of Ecology, Evolution, and Systematics* **2004**, 35 (1), 257–284.
- (3) Clapcott, J. E.; Collier, K. J.; Death, R. G.; Goodwin, E. O.; Harding, J. S.; Kelly, D.; Leathwick, J. R.; Young, R. G. Quantifying relationships between land-use gradients and structural and functional indicators of stream ecological integrity. *Freshwater Biol.* **2012**, *57* (1), 74–90.
- (4) Waite, I. R. Agricultural disturbance response models for invertebrate and algal metrics from streams at two spatial scales within the U.S. *Hydrobiologia* **2014**, 726 (1), 285–303.
- (5) Sundermann, A.; Gerhardt, M.; Kappes, H.; Haase, P. Stressor prioritisation in riverine ecosystems: Which environmental factors shape benthic invertebrate assemblage metrics? *Ecol. Indic.* **2013**, 27, 83–96.
- (6) Grace, J. B.; Anderson, T. M.; Olff, H.; Scheiner, S. M. On the specification of structural equation models for ecological systems. *Ecol. Monogr.* **2010**, *80* (1), *67*–87.
- (7) EPA. National Rivers and Streams Assessment; Office of Water and Office of Research and Development: Washington, DC, 2016; p 116.
- (8) Munn, M. D.; Waite, I.; Konrad, C. P. Assessing the influence of multiple stressors on stream diatom metrics in the upper Midwest, USA. *Ecol. Indic.* **2018**, *85*, 1239–1248.
- (9) Waite, I. R.; Van Metre, P. C. Multistressor predictive models of invertebrate condition in the Corn Belt, USA. *Freshw Sci.* **2017**, *36* (4), 901–914.
- (10) Meador, M. R.; Frey, J. W. Relative Importance of Water-Quality Stressors in Predicting Fish Community Responses in Midwestern Streams. J. Am. Water Resour. Assoc. 2018, 54, 708.
- (11) Dubrovsky, N. M.; Burow, K. R.; Clark, G. M.; Gronberg, J. M.; P.A, H.; Hitt, K. J.; Mueller, D. K.; Munn, M. D.; Nolan, B. T.; Puckett, L. J.; Rupert, M. G.; Short, T. M.; Spahr, N. E.; Sprague, L. A.; Wilber, W. G. The Quality of Our Nation'S Waters—nutrients in the

- Nation'S Streams and Groundwater; U.S. Geological Survey Circular 1350; U.S. Geological Survey: Reston, VA, 2010; p 174.
- (12) Ruddy, B. C.; Lorenz, D. L.; Mueller, D. K. County-Level Estimates of Nutrient Inputs to the Land Surface of the Conterminous United States, 1982–2001. Scientific Investigations Report 2006–5012; U.S. Geological Survey: Reston, VA., 2006; p 17.
- (13) Nowell, L. H.; Moran, P. W.; Schmidt, T. S.; Norman, J. E.; Nakagaki, N.; Shoda, M. E.; Mahler, B. J.; Van Metre, P. C.; Stone, W. W.; Sandstrom, M. W.; Hladik, M. L. Complex mixtures of dissolved pesticides show potential aquatic toxicity in a synoptic study of Midwestern U.S. streams. *Sci. Total Environ.* **2018**, *613–614*, 1469–1488.
- (14) Van Metre, P. C.; Mahler, B. J.; Carlisle, D. M.; Coles, J. F. The Midwest Stream Quality Assessment—Influences of Human Activities on Streams. Fact Sheet 2017–3087.; 2017–3087; U.S. Geological Survey: Reston, VA, 2018; p 6.
- (15) Garrett, J. D.; Frey, J. W.; Van Metre, P. C.; Journey, C. A.; Nakagaki, N.; Button, D. T.; Nowell, L. H. *Design and Methods of the Midwest Stream Quality Assessment (MSQA)*, 2013. Open-File Report 2017–1073; 2017–1073; U.S. Geological Survey: Reston, VA, 2017; p. 59.
- (16) Gellis, A. C.; Fuller, C. C.; Van Metre, P. C. Sources and ages of fine-grained sediment to streams using fallout radionuclides in the Midwestern United States. *J. Environ. Manage.* **2017**, *194*, 73–85.
- (17) Van Metre, P. C.; Alvarez, D. A.; Mahler, B. J.; Nowell, L.; Sandstrom, M.; Moran, P. Complex mixtures of Pesticides in Midwest U.S. streams indicated by POCIS time-integrating samplers. *Environ. Pollut.* **2017**, 220, 431–440.
- (18) Shoda, M. E.; Stone, W. W.; Nowell, L. H. Prediction of Pesticide Toxicity in Midwest Streams. *Journal of Environmental Quality* **2016**, *45* (6), 1856–1864.
- (19) Mahler, B. J.; Van Metre, P. C.; Burley, T. E.; Loftin, K. A.; Meyer, M. T.; Nowell, L. H. Similarities and differences in occurrence and temporal fluctuations in glyphosate and atrazine in small Midwestern streams (USA) during the 2013 growing season. *Sci. Total Environ.* **2017**, *579*, 149–158.
- (20) Rogers, H. A.; Schmidt, T. S.; Dabney, B. L.; Hladik, M. L.; Mahler, B. J.; Van Metre, P. C. Bifenthrin causes trophic cascade and altered insect emergence in mesocosms: Implications for small streams. *Environ. Sci. Technol.* **2016**, *50* (21), 11974–11983.
- (21) Moran, P. W.; Nowell, L. H.; Kemble, N. E.; Mahler, B. J.; Waite, I. R.; Van Metre, P. C. Influence of sediment chemistry and sediment toxicity on macroinvertebrate communities across 99 wadable streams of the Midwestern USA. *Sci. Total Environ.* **2017**, 599–600, 1469–1478.
- (22) Moulton, S. R., II; Kennen, J.; Goldstein, R. M.; Hambrook, J. A. Revised Protocols for Sampling Algal, Invertebrate, and Fish Communities as Part of the National Water-Quality Assessment Program, USGS Open-File Report 02–150; U.S. Geological Survey: Reston, VA, 2002; p 87.
- (23) Olsen, A. R.; Sedransk, J.; Edwards, D.; Gotway, C. A.; Liggett, W.; Rathbun, S.; Reckhow, K. H.; Yyoung, L. J. Statistical Issues for Monitoring Ecological and Natural Resources in the United States. *Environ. Monit. Assess.* 1999, 54 (1), 1–45.
- (24) Gilliom, R. J.; Barbash, J. E.; Crawford, C. G.; Hamilton, P. A.; Martin, J. D.; Nakagaki, N.; Nowell, L. H.; Scott, J. C.; Stackelberg, P. E.; Thelin, G. P.; Wolock, D. M. *Pesticides in the Nation's Streams and Ground Water*, 1992–2001, U.S. Geological Survey Circular 1291.; 1291; U.S. Geological Survey: Reston, VA, 2006; p 180.
- (25) Shelton, L. R.; Capel, P. D. Guidelines for Collecting and Processing Samples of Stream Bed Sediment for Analysis of Trace Elements and Organic Contaminants for the National Water-Quality Assessment Program, Open-File Report 94–458; U.S. Geological Survey: Sacromento, CA., 1994; p 27.
- (26) Sandstrom, M. W.; Kanagy, L. K.; Anderson, C. A.; Kanagy, C. J. Determination of Pesticides and Pesticide Degradates in Filtered Water by Direct Aqueous-Injection Liquid Chromatography-Tandem Mass Spectrometry, Techniques and Methods 5-B11; U.S. Geological Survey: Reston, VA, 2016; p 73.

- (27) Fishman, M. J. Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory; Determination of Inorganic and Organic Constituents in Water and Fluvial Sediments, Open-File Reports 93–125; U.S. Geological Survey: Denver, CO., 1993; p 216.
- (28) Hladik, M. L.; McWayne, M. M. Methods of Analysis-Determination of Pesticides in Sediment Using Gas Chromatography/ Mass Spectrometry, Techniques and Methods 5-C3; U.S. Geological Survey: Reston, VA, 2012.
- (29) Van Metre, P. C.; Frey, J. W.; Musgrove, M.; Nakagaki, N.; Qi, S.; Mahler, B. J.; Wieczorek, M. E.; Button, D. T. High Nitrate Concentrations in Some Midwest United States Streams in 2013 after the 2012 Drought. *Journal of Environmental Quality* **2016**, 45 (5), 1696–1704.
- (30) US EPA. A Practitioner'S Guide to the Biological Condition Gradient: A Framework to Describe Incremental Change in Aquatic Ecosystems; U.S. Environmental Protection Agency: Washington, DC, 2016
- (31) Potapova, M. G.; Charles, D. F.; Ponader, K. C.; Winter, D. M. Quantifying species indicator values for trophic diatom indices: a comparison of approaches. *Hydrobiologia* **2004**, *517* (1), 25–41.
- (32) Potapova, M.; Carlisle, D. M. Development and Application of Indices to Assess the Condition of Benthic Algal Communities in U.S. Streams and Rivers, Open File Report 2011–1126; 2011–1126; U.S. Geological Survey: Reston, VA, 2011; p 44.
- (33) Davies, S. P.; Jackson, S. K. The biological condition gradient: A descriptive model for interpreting change in aquatic ecosystems. *Ecological Applications* **2006**, *16* (4), 1251–1266.
- (34) Fausch, K. D.; Torgersen, C. E.; Baxter, C. V.; Li, H. W. Landscapes to riverscapes: Bridging the gap between research and conservation of stream fishes. *BioScience* **2002**, *52* (6), 483–498.
- (35) Shipley, B. The AIC model selection method applied to path analytic models compared using a d-separation test. *Ecology* **2013**, *94* (3), 560–564.
- (36) R: A Language and Environment for Statistical Computing; R Foundation for Statistical Computing., Vienna, Austria, 2016.
- (37) Revelle, W. Proceedures for Psychological, Psychometric, And Personality Research, 2018.
- (38) Dowle, M.; Srinivasan, A. Extension of "data.frame", 2018.
- (39) Rosseel, Y. lavaan: An R Package for Structural Equation Modeling. *Journal of Statistical Software* **2012**, 48 (2), 1–36.
- (40) Epskamp, S.; Stuber, S. Path Diagram and Visual Analysis of Various SEM Packages' Output, 2017.
- (41) Kline, R. B. Principles and Practice of Structural Equation Modeling, 2<sup>nd</sup> ed.; The Guilford Press: New York, NY, 2005.
- (42) Grace, J. B. Structural Equation Modeling and Natural Systems; Cambridge University Press: Cambridge, U.K., 2006.
- (43) Cohen, J., CHAPTER 9 F Tests of Variance Proportions in Multiple Regression/Correlation Analysis. In *Statistical Power Analysis for the Behavioral Sciences*; Cohen, J., Ed.; Academic Press: 1977; pp 407–453.
- (44) Fairchild, J. F.; Ruessler, D. S.; Carlson, A. R. Comparative sensitivity of five species of macrophytes and six species of algae to atrazine, metribuzin, alachlor, and metolachlor. *Environ. Toxicol. Chem.* 1998, 17 (9), 1830–1834.
- (45) Biggs, B. J. F. Eutrophication of streams and rivers: dissolved nutrient-chlorophyll relationships for benthic algae. *Journal of the North American Benthological Society* **2000**, *19* (1), 17–31.
- (46) Kosinski, R. J. The effect of terrestrial herbicides on the community structure of stream periphyton. *Environ. Pollut., Ser. A* **1984**, 36 (2), 165–189.
- (47) Konrad, C.; Gellis, A. Factors Influencing Fine Sediment on Stream Beds in the Midwestern United States. *Journal of Environmental Quality* **2018**, 47 (5), 1214–1222.
- (48) Leopold, L. B. Hydrology for Urban Land Planning: A Guidebook on the Hydrologic Effects of Urban Land Use, U.S. Geological Survey Circular 554; U.S. Geological Survey: Washington, D.C., 1968; p 21.
- (49) Sekely, A. C.; Mulla, D. J.; Bauer, D. W. Streambank slumping and its contribution to the phosphorus and suspended sediment loads

- of the blue earth river, minnesota. J. Soil Water Conserv. 2002, 57 (5), 243–250.
- (50) Noonan, B. J. Stream Channel Erosion As a Source of Sediment and Phosphorus in a Central Iowa Stream; Iowa State University, 2016.
- (51) Zaimes, G. N.; Schultz, R. C.; Isenhart, T. M. Streambank Soil and Phosphorus Losses Under Different Riparian Land-Uses in Iowa. *J. Am. Water Resour. Assoc.* **2008**, *44* (4), 935–947.
- (52) Kraus, J. M.; Schmidt, T. S.; Walters, D. M.; Wanty, R. B.; Zuellig, R. E.; Wolf, R. E. Cross-ecosystem impacts of stream pollution reduce resource and contaminant flux to riparian food webs. *Ecol. Appl.* **2014**, *24* (2), 235–43.
- (53) Alexander, A. C.; Luis, A. T.; Culp, J. M.; Baird, D. J.; Cessna, A. J. Can nutrients mask community responses to insecticide mixtures? *Ecotoxicology* **2013**, 22 (7), 1085–100.
- (54) Van Sickle, J. Estimating the risks of multiple, covarying stressors in the National Lakes Assessment. *Freshw Sci.* **2013**, 32 (1), 204–216.
- (55) Herlihy, A. T.; Paulsen, S. G.; Sickle, J. V.; Stoddard, J. L.; Hawkins, C. P.; Yuan, L. L. Striving for consistency in a national assessment: the challenges of applying a reference-condition approach at a continental scale. *Journal of the North American Benthological Society* **2008**, 27 (4), 860–877.
- (56) Clements, W. H.; Hickey, C. W.; Kidd, K. A. How do aquatic communities respond to contaminants? It depends on the ecological context. *Environ. Toxicol. Chem.* **2012**, *31* (9), 1932–40.
- (57) Irvine, K. M.; Miller, S. W.; Al-Chokhachy, R. K.; Archer, E. K.; Roper, B. B.; Kershner, J. L. Empirical evaluation of the conceptual model underpinning a regional aquatic long-term monitoring program using causal modelling. *Ecol. Indic.* **2015**, *50*, 8–23.
- (58) Johnson, L.; Richards, C.; Host, G. E.; Arthur, J. Landscape influences on water chemistry in Midwestern stream ecosystems. *Freshwater Biol.* **1997**, *37* (1), 193–208.
- (59) Richards, C.; Johnson, L. B.; Host, G. E. Landscape-scale influences on stream habitats and biota. *Can. J. Fish. Aquat. Sci.* **1996**, 53 (S1), 295–311.
- (60) Soller, D. R.; Packard, P. H.; Garrity, C. P. Database for USGS Map I-1970—Map Showing the Thickness and Character of Quaternary Sediments in the Glaciated United States East of the Rocky Mountains, U.S. Geological Survey Data Series 656; U.S. Geological Survey: Reston, VA, 2012.
- (61) Stone, W. W.; Gilliom, R. J. Watershed Regressions for Pesticides (warp) Models for Predicting Atrazine Concentrations in Corn Belt Streams. *J. Am. Water Resour. Assoc.* **2012**, 48 (5), 970–986.
- (62) Mahler, B. J.; Van Metre, P. C.; Burley, T. E.; Loftin, K. A.; Meyer, M. T.; Nowell, L. H. Similarities and differences in occurrence and temporal fluctuations in glyphosate and atrazine in small Midwestern streams (USA) during the 2013 growing season. *Sci. Total Environ.* **2017**, *579*, 149–158.
- (63) Peterson, B. J.; Wollheim, W. M.; Mulholland, P. J.; Webster, J. R.; Meyer, J. L.; Tank, J. L.; Martí, E.; Bowden, W. B.; Valett, H. M.; Hershey, A. E.; McDowell, W. H.; Dodds, W. K.; Hamilton, S. K.; Gregory, S.; Morrall, D. D. Control of Nitrogen Export from Watersheds by Headwater Streams. *Science* **2001**, 292 (5514), 86–90.
- (64) Suter, G. W., 2nd; Cormier, S. M. A method for assessing the potential for confounding applied to ionic strength in central Appalachian streams. *Environ. Toxicol. Chem.* **2013**, 32 (2), 288–95.
- (65) Wiley, M. J.; Hyndman, D. W.; Pijanowski, B. C.; Kendall, A. D.; Riseng, C.; Rutherford, E. S.; Cheng, S. T.; Carlson, M. L.; Tyler, J. A.; Stevenson, R. J.; Steen, P. J.; Richards, P. L.; Seelbach, P. W.; Koches, J. M.; Rediske, R. R. A multi-modeling approach to evaluating climate and land use change impacts in a Great Lakes River Basin. *Hydrobiologia* **2010**, *657* (1), 243–262.
- (66) Einheuser, M. D.; Nejadhashemi, A. P.; Sowa, S. P.; Wang, L.; Hamaamin, Y. A.; Woznicki, S. A. Modeling the effects of conservation practices on stream health. *Sci. Total Environ.* **2012**, 435–436, 380–91.

- (67) Riseng, C. M.; Wiley, M. J.; Black, R. W.; Munn, M. D. Impacts of agricultural land use on biological integrity: a causal analysis. *Ecological Applications* **2011**, *21* (8), 3128–3146.
- (68) Norton, S. B.; Cormier, S. M.; Smith, M.; Jones, R. C.; Schubauer-Berigan, M. Predicting levels of stress from biological assessment data: Empirical models from the Eastern Corn Belt Plains, Ohio, Usa. *Environ. Toxicol. Chem.* **2002**, 21 (6), 1168–1175.
- (69) C.A.S.T. Assessing the Health of Streams in Agricultural Landscapes: The Impacts of Land Mangement Change on Water Quality; Aimes, IA, 2012.
- (70) Scavia, D.; David Allan, J.; Arend, K. K.; Bartell, S.; Beletsky, D.; Bosch, N. S.; Brandt, S. B.; Briland, R. D.; Daloğlu, I.; DePinto, J. V.; Dolan, D. M.; Evans, M. A.; Farmer, T. M.; Goto, D.; Han, H.; Höök, T. O.; Knight, R.; Ludsin, S. A.; Mason, D.; Michalak, A. M.; Peter Richards, R.; Roberts, J. J.; Rucinski, D. K.; Rutherford, E.; Schwab, D. J.; Sesterhenn, T. M.; Zhang, H.; Zhou, Y. Assessing and addressing the re-eutrophication of Lake Erie: Central basin hypoxia. *J. Great Lakes Res.* **2014**, *40* (2), 226–246.
- (71) Goolsby, D. A.; Battaglin, W. A.; Lawrence, G. B.; Artz, R. S.; Aulenbach, B. T.; Hooper, R. P.; Keeney, D. R.; Stensland, G. J. Flux and Sources of Nutrients in the Mississippi-Atchafalaya River Basin: Topic 3 Report for the Integrated Assessment on Hypoxia in the Gulf of Mexico; United States National Ocean Service: Silver Spring, MD, 1999.
- (72) Michalak, A. M.; Anderson, E. J.; Beletsky, D.; Boland, S.; Bosch, N. S.; Bridgeman, T. B.; Chaffin, J. D.; Cho, K.; Confesor, R.; Daloglu, I.; Depinto, J. V.; Evans, M. A.; Fahnenstiel, G. L.; He, L.; Ho, J. C.; Jenkins, L.; Johengen, T. H.; Kuo, K. C.; Laporte, E.; Liu, X.; McWilliams, M. R.; Moore, M. R.; Posselt, D. J.; Richards, R. P.; Scavia, D.; Steiner, A. L.; Verhamme, E.; Wright, D. M.; Zagorski, M. A. Record-setting algal bloom in Lake Erie caused by agricultural and meteorological trends consistent with expected future conditions. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110* (16), 6448–52.