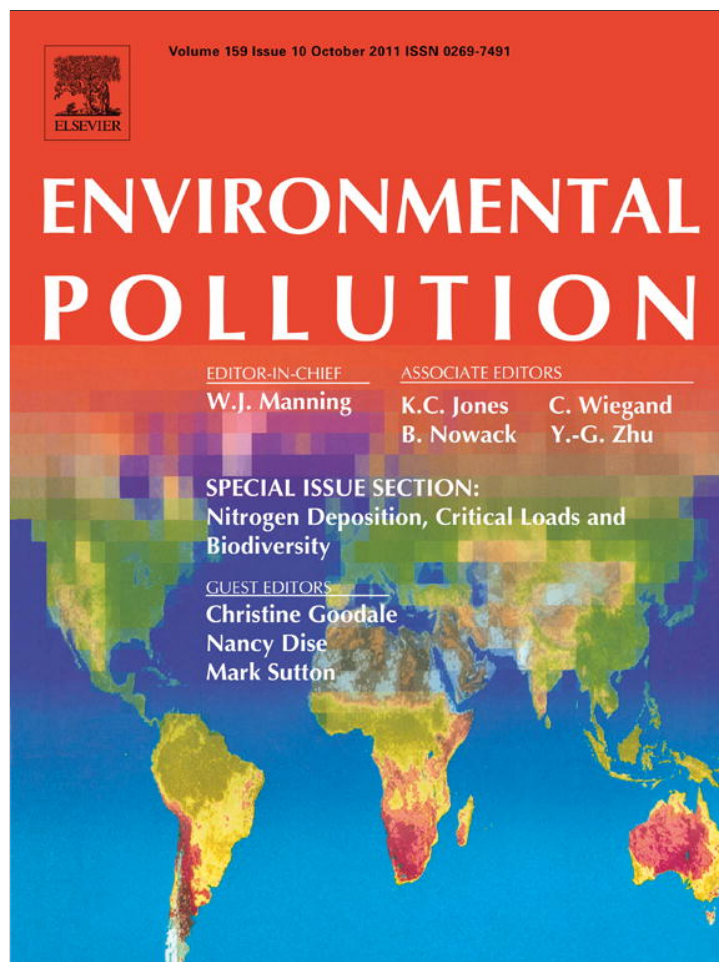


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## Floodplain methylmercury biomagnification factor higher than that of the contiguous river (South River, Virginia USA)

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### ABSTRACT

Mercury biomagnification on the South River floodplain (Virginia, USA) was modeled at two locations along a river reach previously modeled for methylmercury movement through the aquatic trophic web. This provided an opportunity to compare biomagnification in adjoining trophic webs. Like the aquatic modeling results, methylmercury-based models provided better prediction than those for total mercury. Total mercury Food Web Magnification Factors (FWMF, fold per trophic level) for the two locations were 4.9 and 9.5. Methylmercury FWMF for the floodplain locations were higher (9.3 and 25.1) than that of the adjacent river (4.6). Previous speculation was not resolved regarding whether the high mercury concentrations observed in floodplain birds was materially influenced by river prey consumption by riparian spiders and subsequent spider movement into the trophic web of the adjacent floodplains. Results were consistent with a gradual methylmercury concentration increase from contaminated floodplain soil, to arthropod prey, and finally, to avian predators.

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### 1. Introduction

Mercury in contaminated food can result in harmful exposures of humans (Grandjean et al., 1997; Crump et al., 2000; Van Wijngaarden et al., 2006) and wildlife (Bouton et al., 1999; Kenow et al., 2007a,b; Scheuhammer et al., 2007; Evers et al., 2008). Because mercury exhibits biomagnification, the trophic ecology of a species in a contaminated food web strongly influences whether its exposure exceeds safe levels. Consequently, quantitative trophic transfer models have become valuable tools for predicting species exposures. Many take advantage of the relationship between trophic position and the relative amounts of <sup>15</sup>N and <sup>14</sup>N in an organism's tissues (expressed as  $\delta^{15}\text{N}$ ) (Kidd et al., 1995; Jardine et al., 2006). As a germane example, Tom et al. (2010) successfully predicted mercury and methylmercury concentrations in members of the aquatic trophic web of the South River, Virginia using tissue  $\delta^{15}\text{N}$ .

The most common subjects of mercury biomagnification modeling are aquatic communities because many harmful human or wildlife exposures involve fish consumption. However, mercury discharged into flowing waters can move onto the floodplain

during periodic flooding and perhaps by trophic flux (Akamatsu et al., 2005; Cristol et al., 2008). Mercury deposited on the floodplain is then subject to trophic transfer. It follows that optimal risk management and remediation planning for a contaminated watershed requires biomagnification models for both the aquatic and floodplain food webs.

Methylmercury biomagnification models for a contaminated reach of the South River (Virginia, USA) (Tom et al., 2010) had enough predictive potential to support river management decision making. However, biomagnification models for the floodplain were deemed necessary because mercury concentrations in floodplain soils, birds, and mammals were elevated relative to those of reference sites. Four questions were addressed in the resulting study. Firstly, are methylmercury-based models for the floodplain superior to total mercury-based models as was found to be the case during river trophic web modeling? Secondly, can models useful for prediction be developed for the floodplain despite the higher habitat heterogeneity and perceived complexity of trophic web interactions relative to the adjacent river? Thirdly, does the magnitude of biomagnification in the floodplain trophic web differ substantially from that of the adjacent river? Fourthly, is there evidence of substantial methylmercury movement into the floodplain trophic web via aquatic insect consumption by riparian spiders or floodplain songbird predation on emergent aquatic insects as speculated by Cristol et al. (2008)?

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## 2. Materials and methods

### 2.1. Sampling

The study reach of the South River below Waynesboro, Virginia USA received elemental and ionic mercury from a DuPont acetate fiber production facility from 1929 until 1950 (Cocking et al., 1991). The released mercury contaminated the river below Waynesboro and the adjacent floodplain. Samples were taken at two locations within the twenty-three mile river reach previously modeled for aquatic biomagnification of methylmercury (Tom et al., 2010). The locations were 11.8 and 22.4 river miles (RM) below the point of historical mercury discharge and correspond to the RM 11.6 and RM 22.2 sampling sites of our previous studies (Tom et al., 2010). The RM 22.4 location was also used in another mercury bioaccumulation study of songbirds (Condon and Cristol, 2009).

Most samples were taken during the first two weeks of May 2009; however, additional emerging adult insects were taken during the second week of August 2009. (See Supplemental data for details.) The emergent insects (mayfly, midge, and caddisfly) moved into the floodplain trophic web from the aquatic, predominantly detritivory-based trophic web. Samples from the terrestrial detritivory trophic web component included slugs, isopods (Microcerberidae), and red marsh worms (*Lumbricus rubellus*). Most samples were associated with the terrestrial herbivory (folivory)-based trophic web component. They included greens tissues of plants (*Festuca elatior*, *Viola striata*, and *Lonicera japonica*), whole insects (eastern tent caterpillar, *Malacosoma americanum*, and ladybug (Coccinellidae)), whole wolf spiders (Lycosidae), liver and muscle of small mammals (deer mice, *Peromyscus maniculatus*, pine vole, *Microtus pinetorum*, and short tailed shrew, *Balarina brevicauda*), blood and feathers of songbirds (Carolina wren, *Thryothorus ludovicianus*, eastern song sparrow, *Melospiza melodia*, gray catbird, *Dumetella carolinensis*, northern cardinal, *Cardinalis cardinalis*, rufous-sided towhee, *Pipilo erythrophthalmus*, eastern phoebe, *Sayornis phoebe*, eastern tufted titmouse, *Baeolophus bicolor*, and eastern bluebird, *Sialia sialis*), and blood and feathers of the eastern screech owl, *Megascops asio*. Mice, voles and shrews captured by baited snap trap were frozen until tissues could be removed. Birds were caught with mist nets, sampled and banded prior to release to ensure that no bird was resampled.

### 2.2. Sample analyses

Freeze dried samples were sent to CEBAM (Seattle, WA, USA) for total mercury and methylmercury analyses, and to the University of California – Davis Stable Isotope Facility (Davis, CA, USA) for stable isotope analyses ( $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$ ). Mercury analytical quality was gauged with laboratory sample splits, laboratory spiked samples and standard reference materials. The mean differences between sample splits were 3.5% (SD = 2.9%,  $n = 22$ ) for total mercury and 5.0% (SD = 4.3%,  $n = 19$ ) for methylmercury, indicating excellent results for the intended use. The mean total mercury and methylmercury spiked-matrix recoveries were 100.7% (SD = 3.5%,  $n = 21$ ) and 99.3% (SD = 4.3%,  $n = 24$ ), respectively. The mean total mercury and methylmercury recoveries from the standard materials were 96.4% (SD = 2.8%,  $n = 5$ ) and 98.4% (SD = 3.5%,  $n = 6$ ), respectively. The stable isotope analyses were assessed using recoveries and associated standard deviations for replicate analyses of four standard reference materials, G-7 peach leaves, G-8 nylon, G-9 glutamic acid, and G-11 nylon standards. The  $\delta^{13}\text{C}$  recoveries for G-7 peach leaves, G-8 nylon, G-9 glutamic acid, and G-11 nylon standards were 101.1% (SD = 0.4%,  $n = 6$ ), 100.0% (SD = 0.2%,  $n = 44$ ), 100.5% (SD = 0.2,  $n = 20$ ), and 100.0% (SD = 0.2%,  $n = 17$ ), respectively. The  $\delta^{15}\text{N}$  recoveries for G-7 peach leaves, G-8 nylon, G-9 glutamic acid, and G-11 nylon standards were 94.9% (SD = 6.8%,  $n = 6$ ), 100.0% (SD = 3.0%,  $n = 43$ ), 99.1% (SD = 10.8%,  $n = 20$ ), and 100.0% (SD = 0.6%,  $n = 17$ ), respectively.

### 2.3. Model construction and selection

Biomagnification models were built using the SAS<sup>®</sup> 9.2 package general linear model procedures (PROC GLM and SELECTGLM, SAS Institute, Cary, NC) to predict mercury or methylmercury concentrations for members of the trophic web based on tissue  $\delta^{15}\text{N}$  as done in numerous other studies, e.g., Cabana and Rasmussen (1994),

$$\log_{10}[\text{Hg or MHg}] = a + b \delta^{15}\text{N} + \varepsilon$$

where  $a$  = intercept,  $b$  = coefficient for the influence of  $\delta^{15}\text{N}$ , and  $\varepsilon$  = error term. Unlike the river trophic web sampling, the floodplain trophic web sampling included homeotherms whose bioenergetics differed from sampled poikilotherms in ways that influence bioaccumulation (Hop et al., 2002; Fisk et al., 2001). The potential influence of metabolic status differences among sampled biota was determined by estimating an additional parameter ( $c$ ). Poikilotherms were established as the reference class by setting this parameter for them to 0 (Metabolic Status = 0). The parameter for homeotherms (Metabolic Status = 1) was then estimated relative to 0.

$$\log_{10}[\text{Hg or MHg}] = a + b \delta^{15}\text{N} + c(\text{Metabolic Status}) + \varepsilon$$

The  $c$  estimates also included probable tissue effects on concentrations. The poikilotherm samples used for modeling were whole bodies but the homeotherm samples were either, blood, liver, or muscle tissue.

After the best model was selected, a related model was generated that linked trophic level (TL), instead of  $\delta^{15}\text{N}$ , to  $\log_{10}[\text{Hg or MHg}]$ . This permitted estimation of the Food Web Magnification Factor (FWMF, mean rate of mercury increase per trophic level),  $\text{FWMF} = 10^b$ . Trophic level of a member of the food web was defined as the following,

$$\text{TL}_i = \frac{(\delta^{15}\text{N}_i - \delta^{15}\text{N}_{pp})}{3.4} + 1$$

where  $\delta^{15}\text{N}_i$  and  $\delta^{15}\text{N}_{pp}$  = the  $\delta^{15}\text{N}$  values for sample  $i$  and primary producers, respectively, and 3.4 = the average increase in  $\delta^{15}\text{N}$  per trophic level ( $\Delta\delta^{15}\text{N}$ ).

Biomagnification models are often backtransformed to predict mean contaminant concentration instead of mean logarithm of concentration. A back-transformation bias is introduced that can be corrected using the model mean square error (MSE) (Newman, 1993),

$$\log_{10}[\text{Hg or MHg}] = a + b \delta^{15}\text{N} + c(\text{Metabolic Status}) + \varepsilon$$

$$[\text{Hg or MHg}] = 10^a 10^{b(\delta^{15}\text{N})} 10^{c(\text{Metabolic Status})} 10^\varepsilon$$

where  $\varepsilon = \text{MSE}/2$ .

Modeling was done for each location because there was no reason to assume that the locations were similar enough to justify mercury data pooling. Notionally, factors that could potentially influence results were trophic web component affiliation (aquatic predominantly detritivory-based, floodplain detritivory-based, or floodplain herbivory-based), position within the trophic web ( $\delta^{15}\text{N}$  or TL), metabolic status (poikilothermic/homeothermic), and sample type (whole body, blood, feather, liver or muscle). General trophic affiliation was initially assigned using feeding ecology knowledge from published literature and confirmed a posteriori with  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  information. Similarly, position in a particular trophic web component was assigned based on feeding ecology knowledge during field sampling design and then quantified with  $\delta^{15}\text{N}$ . The usefulness of different tissues, e.g., bird blood versus feather, for reflecting a species' mercury or methylmercury accumulation was explored by an initial literature review and again during modeling.

Selecting the best of candidate models and deciding whether the chosen model was useful for predictions involved several steps that were established a priori (Tom et al., 2010). Selection of the best model was based on Akaike's Information Criterion (AIC) which quantifies the amount of explanatory information contained in each estimated parameter of a candidate model. Applying Minimum AIC Estimation (MAICE), models with different numbers of explanatory variables were built and the model with the lowest AIC selected as the best.

Whether a model selected by MAICE was capable of adequate prediction for management purposes was judged by establishing an a priori criterion. A prediction  $r^2$  or cross-validity coefficient ( $r^2_{\text{prediction}}$ ) in the range of 0.80 was deemed sufficient in this and our previous aquatic food web study (Tom et al., 2010). An  $r^2_{\text{prediction}}$  was calculated with the prediction residual sum of squares (PRESS) and the model total sum of squares ( $SS_T$ ). The PRESS was generated as done for the regression residual sum of squares except the  $y_i$  point for which a prediction was to be made ( $\hat{y}_i$ ) was omitted during model construction,

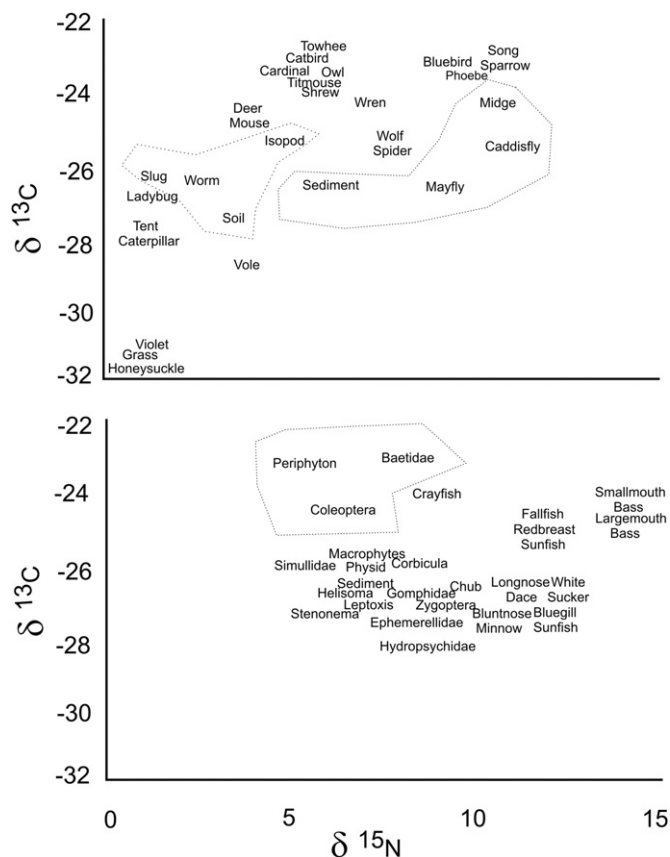
$$\text{PRESS} = \sum_{i=1}^n (y_i - \hat{y}_i)^2$$

$$r^2_{\text{prediction}} = 1 - \frac{\text{PRESS}}{SS_T}$$

With the  $r^2_{\text{prediction}}$ , the variation expected in any prediction is estimated for a model built without the observation for which prediction was being made. Importantly, the cross-validity coefficient differs from the conventional coefficient of determination,  $r^2$ , which only indicates how much of the total variance in the data is accounted for by the model. The coefficient of determination does not estimate the predictive adequacy of a model.

## 3. Results

Stable isotope trends were obtained for the samples that were consistent with the a priori sample categorization (Fig. 1, top panel). The  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  for those samples associated with the floodplain herbivory-based web component increased steadily with trophic status. The  $\delta^{13}\text{C}$  values for insects emerging from the aquatic detritivory-dominated component were slightly below the trend seen for the floodplain herbivory-based component, reflecting the isotopic signature of the adjacent river (Fig. 1, bottom panel). The number of trophic levels approximated by dividing the  $\delta^{15}\text{N}$  increase from plant to top avian predator by the generally applied



**Fig. 1.** Isotopic patterns for samples pooled from both locations. Averages for each floodplain sample type were plotted (top panel) as were those for the adjacent river segment (bottom panel). In the top panel, dotted lines define the trophic web members emerging from the adjacent river and also the detritivory-related members of the terrestrial trophic web. The remaining members were associated with the herbivory-based component of the terrestrial trophic web. In the bottom panel, a dotted line was used to define periphyton and trophic web members that scrape periphyton from hard surfaces. The remaining members were associated with the primarily detritivory-based aquatic trophic web although the gastropods also scrape material from submerged surfaces that contain algae. Taxonomic names in the bottom panel identify mayfly (Stenonema, Zygoptera), caddisfly (Hydropsychidae), waterpenny (Coleoptera), black fly (Simuliidae), dragonfly (Gomphidae), damselfly (Zygoptera), and gastropod (*Helisoma*, *Leptoxis*, Physid) members. Macrophytes were randomly selected submerged aquatic vascular vegetation.

increase of 3.4‰ per trophic level (TL) (Cabana et al., 1994) was consistent with the expectation of 3 to 4 trophic levels (Thompson et al., 2007; Newman and Clements, 2008).

Omission of feather samples improved predictions during model exploration and was consistent with recent literature (Bond and Diamond, 2008; Bond, 2010). Regardless of their limitations in this modeling effort, feathers remain central in many studies of bird exposure to mercury. To facilitate comparison of our results to those of studies employing feathers, feather and other data were included as Supplemental data to this publication. Pooling samples from all bird species, the percentage of total mercury in the blood that was methylmercury ( $n = 30$ , mean = 87%, 95% CI = 82–93%) was generally higher than that in the feathers ( $n = 30$ , mean = 65%, 95% CI = 60–71%). The percentages of feather mercury that was methylmercury were generally lower than those reported in the literature. Bond and Diamond (2009) reported percentages in feathers of 82–133% for seabirds, and Kenow et al. (2007a,b) reported 87–107% for captive juvenile common loons. Nearly all mercury in thrush (Rimmer et al., 2005) and swallow (Gerrard and St. Louis, 2001)

feathers was stated as being methylmercury. Our unpublished 2010 results for South River birds sampled from two other locations had mean percentages of 89% ( $n = 50$ , 95% CI = 86–91%), suggesting that methylmercury estimates for feathers were less reliable than blood estimates for modeling purposes.

Models based on  $\delta^{15}\text{N}$ , and also calculated TL, are summarized in Table 1 for the terrestrial, herbivory-associated members. Also included for comparison are models for the adjacent river (reanalyzed from Tom et al., 2010). Total mercury models were not considered further because they failed to meet the a priori  $r^2_{\text{prediction}}$  criterion. The total mercury FWMF calculated from  $b$  estimates (95% CI) for the RM 11.8 and RM 22.4 locations were 4.9 (3.0–8.1) and 9.5 (5.0–18.2), respectively. In contrast to the total mercury models, the methylmercury models had high  $r^2_{\text{prediction}}$  values indicating acceptable predictive capability. The methylmercury FWMF for the adjacent river trophic web was 4.6 (95% CI of 3.6–5.7 as estimated from the  $b$ -value CI). The FWMF for the RM 11.8 location was 9.3 (95% CI of 5.4–16.2) and that for the RM 22.4 locations was 25.1 (95% CI of 12.6–50.1). The methylmercury FWMF values were higher in the terrestrial trophic webs than the trophic web of the adjacent river. Methylmercury model predictions based the herbivory-associated biota samples and the relative trophic positions of all sampled biota are depicted in Fig. 2 for both locations.

#### 4. Discussion

The four questions posed in the introduction can be addressed with the study results. Relative to the first question, methylmercury-based models were superior to those based on total mercury as was the case during the aquatic biomagnification modeling. The percentage of total mercury that was methylmercury did increase with trophic level but the variation in the floodplain percentage methylmercury data was much wider than that in the aquatic study (Supplemental data).

As judged with the  $r^2_{\text{prediction}}$ , methylmercury biomagnification models useful for prediction can be developed for these floodplain locations. The differences between the two floodplain locations resulted in distinct FWMF values. Such a large difference was not noted for six locations modeled for the adjacent aquatic food web or another Virginia river, the Holston River (Tom et al., 2010). The interlocation difference was not explicable solely by differences in total mercury and methylmercury soil concentrations at these locations (Supplemental data). Nor could differences in potential prey linked to the adjacent aquatic system (Supplemental data) explain the contrasting results for the two locations. The RM 11.8 data set, but not the RM 22.4 data set, had several bird species with high methylmercury concentrations, i.e., bluebird, song sparrow and phoebe. Exclusion of these species during TL-based modeling generated the following parameter estimates:  $a$ : -3.76 (95% CI of -4.29 to -3.23);  $b$ : 1.17 (95% CI of 0.87–1.47);  $c$ : 0.80 (95% CI of 0.34–1.26);  $r^2$ : 0.82; MSE: 0.336. The corresponding methylmercury FWMF for RM 11.8 increased from the original estimated 9.3 to 14.8 (95% CI: 2.2–18.2) after omission of these three extreme species. This new FWMF of 14.8 was closer to that of the RM 22.4 location (25.1). Regardless, the best advice to a manager at this time would be to use the model for a specific floodplain location to make sound quantitative predictions about trophic web members of that location. Two additional South River floodplain locations (RM 2.0 and RM 20.0) are currently being sampled and modeled to ascertain factors most influencing interlocation differences in biomagnification.

Biomagnification (FWMF) was substantially higher for the terrestrial floodplain trophic webs than for the adjacent aquatic

**Table 1**  
Summary of total mercury and methylmercury models (terrestrial herbivory-related samples after exclusion of feathers).

	$r^2$	$a$ (95% CI)	$b$ (95% CI)	$c$ (95% CI) <sup>a</sup>	MSE	$r^2_{\text{prediction}}$
<b>Total mercury<sup>b</sup></b>						
$\delta^{15}\text{N}$						
RM 11.8	0.70	-1.47 (-1.76 to -1.18)	0.20 (0.14–0.27)	0.37 (-0.04 to 0.78)	0.274	0.53
RM 22.4	0.75	-1.82 (-2.11 to -1.54)	0.29 (0.21–0.37)	0.14 (-0.31 to 0.58)	0.241	0.62
Trophic level						
RM 11.8	0.70	-2.03 (-2.44 to -1.62)	0.69 (0.48–0.91)	0.37 (-0.04 to 0.78)	0.274	0.53
RM 22.4	0.75	-2.63 (-3.08 to -2.17)	0.98 (0.70–1.26)	0.14 (-0.30 to 0.58)	0.241	0.62
<b>Methylmercury<sup>b</sup></b>						
$\delta^{15}\text{N}$						
RM 11.8	0.83	-2.66 (-2.99 to -2.34)	0.29 (0.21–0.36)	0.89 (0.43–1.34)	0.343	0.79
RM 22.4	0.87	-3.11 (-3.42 to -2.82)	0.41 (0.32–0.50)	0.55 (0.08–1.03)	0.273	0.85
Aquatic (River)	0.78	-2.26 (-2.55 to -1.98)	0.19 (0.16–0.22)	0.02 (0.01–0.03)	0.100	0.76
Trophic level						
RM 11.8	0.83	-3.45 (-3.91 to -3.00)	0.97 (0.73–1.21)	0.89 (0.43–1.35)	0.343	0.79
RM 22.4	0.87	-4.26 (-4.74 to -3.77)	1.40 (1.10–1.70)	0.55 (0.08–1.03)	0.273	0.85
Aquatic (River)	0.78	-1.09 (-1.23 to -0.94)	0.66 (0.56–0.76)	0.02 (0.01–0.03)	0.100	0.76

<sup>a</sup> For the terrestrial models,  $c = 0$  for poikilotherms and  $c =$  the tabulated parameter estimate for homeotherms. For the river model,  $c =$  the effect of downriver distance from the historic source (Tom et al., 2010).

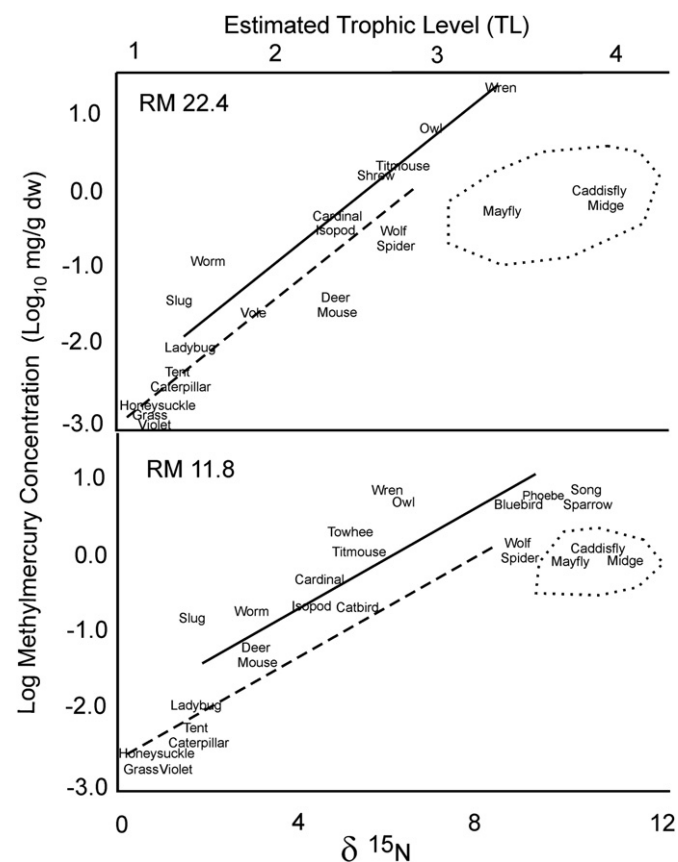
<sup>b</sup> The number of observations in the river, RM 11.8, and RM 22.4 models was 66, 43, and 40, respectively, for total and methylmercury models. The river (Aquatic (River)) model was generated using samples from six locations between RM 0.6 and 22.4.

trophic web or the aquatic trophic web of another Virginia river (Tom et al., 2010). The prominence of homeotherms in the terrestrial trophic web contributed to these higher FWMF (Fisk et al., 2001) but, because the same estimated coefficient for  $\delta^{15}\text{N}$  was

applicable for homeotherms and poikilotherms, it was not the only factor causing these differences.

Our findings provided no definitive answer regarding speculation that substantial amounts of mercury move out of the river and into the South River floodplain trophic web via spider consumption of river prey and consequent spider movement into the adjacent land trophic web (Cristol et al., 2008). There was evidence of substantial amounts of aquatic biota being consumed by several floodplain members. The position of the wolf spiders in Figs. 1 and 2 tended to be slightly off the herbivory-based model predictions and closer to the adult aquatic insects. This was consistent with Akamatsu et al. (2005) who documented the importance of aquatic insects in the diets of many riparian spiders. The diet of these South River songbirds, including that of the Carolina wren, contained 20–30% spiders (Cristol et al., 2008). As another piece of evidence, the large increase in  $\delta^{13}\text{C}$  with trophic level (Mean  $\Delta\delta^{13}\text{C} \pm \text{SD}$ :  $2.6 \pm 0.4\text{‰}$ ) (Fig. 1, top panel) was higher than expected. The average  $\Delta\delta^{13}\text{C}$  is generally given as  $0.8\text{‰}/\text{TL}$  (Jardine et al., 2006) and a review of forty-two studies reported a mean ( $\pm\text{SD}$ ) for  $\Delta\delta^{13}\text{C}$  was  $0.47 \pm 1.23\text{‰}$  (Vander Zanden and Rasmussen, 2001). The  $\Delta\delta^{13}\text{C}$  for the river food web was in this range (Fig. 1) but those of the two floodplain food webs were much higher. The high  $\Delta\delta^{13}\text{C}$  for the floodplain could reflect consumption of the aquatic biota by floodplain biota. The aquatic biota had generally more negative  $\delta^{13}\text{C}$  values and higher  $\delta^{15}\text{N}$  values than the corresponding terrestrial herbivory-associated biota.

Regardless of the above speculation, the gradual and consistent progression from low mercury concentrations in land plants through the herbivory-based trophic web to realized high concentrations in apex avian predators provided the simplest conceptual and computational models for high mercury found in birds. Mercury was deposited in soil during past flooding with contaminated waters and the deposited mercury moved progressively through the floodplain trophic web to apex avian predators. Certainly some floodplain species do take in mercury from prey coming from the river. For example, the screech owl frequently consumes crayfish from the river. Carolina wrens consume spiders (Cristol et al., 2008) and riparian spiders consume aquatic prey (Akamatsu et al., 2005). However, the elevated mercury in apex avian predators can be predicted from the herbivory-based model alone.



**Fig. 2.** Mean  $\log_{10}$  methylmercury concentration and  $\delta^{15}\text{N}$  values for each trophic web member were plotted for the RM 22.4 (top panel) and RM 11.8 (bottom panel) locations. Adult insects emerging from the river were defined with a dashed line and model predictions shown for poikilotherm (dashed line) and homeotherm (solid line) members of the floodplain herbivory-based trophic web. A trophic level scale x-axis was also provided at the top of the figure.

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## Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.envpol.2011.04.045.

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