Sediment-Associated Contaminants in Urban Streams: I. Characterization and Distribution of Synthetic Organics and Trace Elements in Relation to Urbanization

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Introduction

The goals-

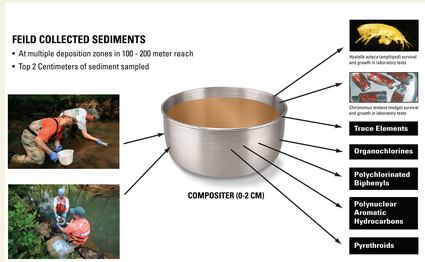
- Assess bed sediment contaminants in urban streams in different regions of the United States. Conduct the first broad-scale assessment of pyrethroids in relation to urbanization in different regions (see Hladik et al. #182).
- Evaluate the relationship between increasing urbanization in a region and the sediment contaminant profile.
- Characterize toxicity of sediments to sediment dwelling organisms (Kemble et al. #180) and assess relations between toxicity, contaminant profiles, and urbanization.

Sites and samples-

- 98 stream reaches, in unique watersheds, in 7 metropolitan areas across the US.
- Spanned a range of urbanization within each metropolitan area.
- Wadeable streams in typically small to moderate watersheds, (median drainage area of 58 sq. km).
- Co-located with sites in larger, ongoing study on the Effects of Urbanization on Stream Ecosystems (http://water.usgs.gov/nawqa/urban/)
- Composited multiple grab samples of the top 2 cm in depositional zones within each stream reach.
- Homogenized samples on site, sieved (trace elements < 63 µm, organics <2 mm) and sub-samples taken for multiple analyses.

Analysis-

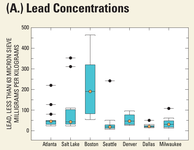
- Trace elements: strong acid digestion, then hydride generation atomic absorption spectrometry (AAS) for As; cold vapor AAS for Hg; and inductively-coupled plasma-atomic emission spectrometry for others;
- Organochlorine pesticides (OCs), Polychlorinated Biphenyls (PCBs): gas chromatography (GC) with electron-capture detection;
- Polynuclear Aromatic Hydrocarbons (PAHs), Pyrethroids: GC with mass spectrometric detection, see (Hladik et al #180);
- Toxicity, whole sediment tests with Hyalella azteca (28 day) and Chironomus dilutus (10 day) see (Kemble et al. #182).



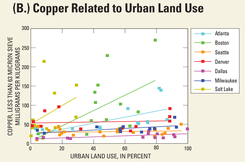
Trace Elements

- Trace element concentrations varied largely across the 7 metropolitan areas; (A).
- Relationships to urbanization were limited, and when present, were not found at all sites. Copper was significantly ($p<0.05$) related* to Urban at 4 sites (B).
- Local geochemistry, such as manganese, appears to be as important as carbon in controlling total metal content in sediments.

(A.) Lead Concentrations



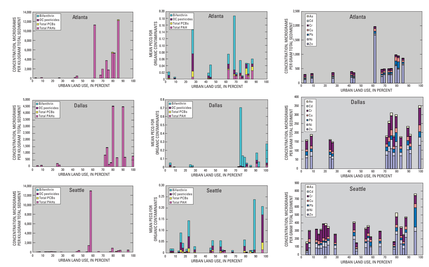
(B.) Copper Related to Urban Land Use



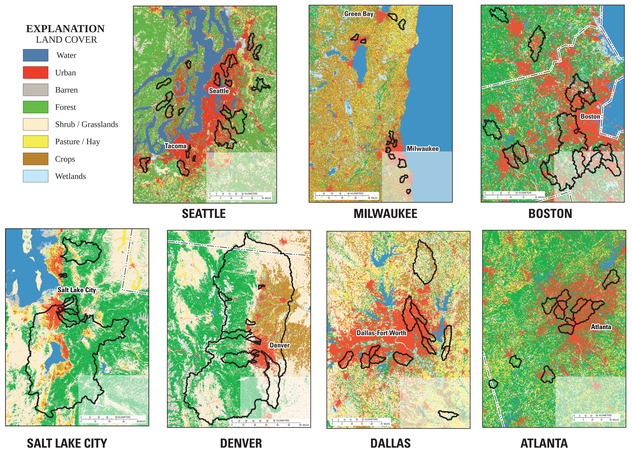
National Land Use Comparisons

- Trace elements (TEs) were detected in all samples because of the sediment extraction-method used (strong acid digestion).
- Organic contaminants were detected
  a) less often than trace elements and at 100 to 1,000-fold lower concentrations
  b) more often at urban than undeveloped sites.
- Weighting concentrations by their toxicity (see box on Predicted Toxicity) changes the relative importance of both sites and contaminants.
- For example, PAHs dominate organic contaminant concentration in all 7 study areas. However, bifenthrin and OC pesticides make proportionally larger contributions to predicted toxicity (mean PECQ).

(A) Organic Concentrations (B) mean PECQ organics (C) Trace Elements

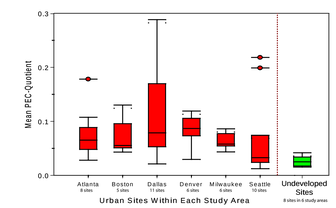


- Zn has high concentrations relative to most other trace elements, but Ni, As and (or) Pb become relatively more important in Atlanta, Dallas, and Seattle whenconcentrations are toxicity-weighted.
- Trace elements (largely from natural sources) account for about 2/3 of the mean PECQ (on average) at undeveloped sites (fig. F).

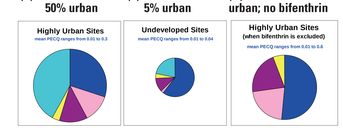


- Overall, mean PECQ increased as urbanization in basin increased ($p<0.01$) (not shown).
- Highly urban sites (>50% urban) in Dallas and Denver had the highest predicted toxicity (mean PECQ) and undeveloped sites the lowest. (Salt Lake City is excluded because it had no sites with >50% urban land.)
- At highly urban sites (>50% urban), organic contaminants—especially bifenthrin—are proportionally greater contributors to predicted toxicity (mean PECQ) than trace elements, although trace elementconcentrations are 100 to 1,000 times higher (fig E).

(D) Mean PEC Quotient by study area



(E) Greater than 50% urban (F) Less than 5% urban (G) Greater than 50% urban; no bifenthrin



- Pie charts show average contribution to predicted toxicity of contaminant classes analyzed. Size of pie is proportional to the average mean PECQ value (fig E, F, G).
- Analyzing pyrethroids changes our understanding of which contaminants contribute to potential toxicity at urban sites. When only traditional sediment contaminants are analyzed (not bifenthrin), as fig G, both trace elements and organic contaminants are about equally important contributors to predicted toxicity.

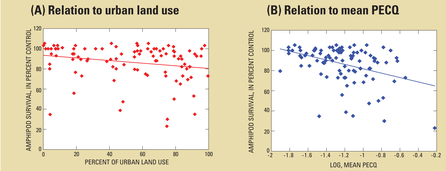
Do Urbanization and Mean PEC-Quotient Explain Amphipod Toxicity?

Detailed results of these and additional sediment toxicity tests are in Kemble et al. #180. Some highlights related to urbanization follow:

In 28-day toxicity tests, (A) survival of the amphipod Hyalella azteca was inversely related to urban land use in the basins ($p<0.05$). Overall, the percent of variance in survival explained by urban land was very low (5%). Other measures of toxicity (such as amphipod length and biomass) were not significantly related to urbanization.

Both amphipod survival (B) and amphipod length decreased significantly as the mean PECQ increased. Mean PECQ explained 15% of the variance in survival. Although quite low, this is more variance than was explained by urbanization.

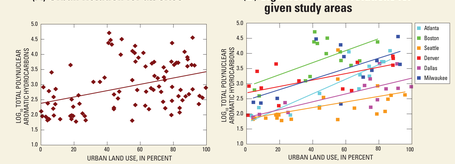
(A) Relation to urban land use (B) Relation to mean PECQ



Polynuclear Aromatic Hydrocarbons (PAH)

- Total PAH concentrations increased with urban land use ($p<0.01$) (see A below).
- Same urban relation was significant for combustion PAHs, nonalkylated PAHs, and alkylated PAHs ($p<0.01$), and for 6 of 7 individual study areas ($p<0.05$) (B below).
- Total PAH concentrations increased with sediment organic carbon ($p<0.05$).
- PAHs were predominantly from combustion sources, as suggested by several diagnostic PAH ratios. For example, 98% of samples have a ratio of (anthracene/anthracene+phenanthrene) > 0.1, which is characteristic of combustion sources (Budzinski et al., 1997).

(A) Urban Relation for all sites (B) Significant Urban relations for given study areas



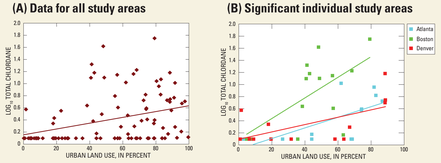
The Predicted Toxicity and Mean PEC-Quotient

- The relative importance of contaminants to aquatic organisms was assessed by comparing toxicity-weighted concentrations by dividing measured concentration by Probable Effect Concentration (PEC)- to get PEC-Quotients (PECQ). PEC values (above which adverse effects are expected to occur more often than not) were obtained from MacDonald et al. (2000), except bifenthrin, which was based on literature values.
- Predicted toxicity of mixtures was assessed using the Mean PECQ technique (following MacDonald et al., 2000; Ingersoll et al., 2001), which assumes joint additive toxicity. Simple additivity is unlikely to strictly apply for complex mixtures, however, an additive model predicted effects concentrations correctly, within a factor of two, for 90% of contaminant mixtures (in water) reviewed by Deneer (2000) and Belden et al. (2007).
- The Mean PECQ method is empirical—a mean PECQ >0.5 was associated with high likelihood of toxicity in studies evaluated by MacDonald et al. (2000) when mean PECQs were computed for trace elements, PAHs, and PCBs.
- In the present study, the mean PECQ was determined by averaging PECQs for five contaminant classes—trace elements (mean of PECQs for As, Cd, Cr, Cu, Pb, Ni, Zn), total PAHs, total PCBs, organochlorine pesticides (mean of PECQs for DDE, chlordane, dieldrin), and bifenthrin. Because more contaminants were quantified than in the original method (MacDonald et al., 2000) and PECQs were sediment organic carbon-normalized, a mean PECQ of 0.5 may underestimate the threshold of toxicity in the present study (Kemble et al. #180).

Organochlorine Pesticides and PCBs

- Total DDT, total chlordane, dieldrin, and total PCB concentrations increased with urban land use ($p<0.05$)—see Chlordane example (A).
- Relation with urban land use was significant for 1–3 study areas (depending on the compound) —see Chlordane (B).
- Organochlorine pesticide concentrations increased with sediment organic carbon ($p<0.05$).
- Urbanized sites had significantly ($p<0.01$) higher concentration ratios of [DDT/total DDT], which indicate recently deposited sediments, and lower ratios of [trans-nonachlor/ total chlordane], which indicate less weathered sediments (Nowell et al., 1999).

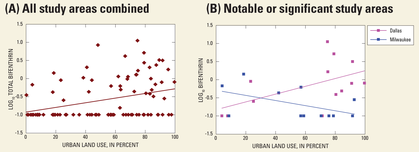
(A) Data for all study areas (B) Significant individual study areas



Pyrethroid and Current-use Insecticides

- Pyrethroid insecticides were detected at 45% of sites, including all 7 study areas. Bifenthrin was most commonly detected (41% of sites) and resmethrin had the highest maximum concentration (38 µg/kg).
- Fipronil degradates were detected at 5% of sites overall, in 2 study areas.
- Bifenthrin concentration increased with urban land use ($p<0.05$) (A).
- Only Dallas had a significant urban relationship ($p<0.05$) (■ in B). Milwaukee's relationship was inverse (not significant, ■ in B)—probably due to agricultural sources. Milwaukee's background (non-urban) land use is agriculture (see Map), and residuals from Milwaukee's urban relation were significantly related to agricultural land in the basin ($p<0.05$).
- Overall, bifenthrin concentration was not related to agricultural or undeveloped land use, or (unlike other organic contaminants) to sediment organic carbon.

(A) All study areas combined (B) Notable or significant study areas



Conclusions

- Trace elements make the largest average contribution to predicted toxicity at undeveloped sites, whereas organic contaminants make the largest contribution at urbanized sites when bifenthrin is included.
- Bifenthrin, OC pesticides and PAHs are the greatest contributors to predicted toxicity due to organic contaminants.
- Trace element concentrations are much higher than organic contaminants, and don't vary as much with urbanization.
- Trace elements need to account for underlying geochemistry.
- Concentrations of OC pesticides, PAHs, and PCBs all increased with urbanization and with sediment organic carbon.
- Bifenthrin concentrations increased with urbanization, but was not significantly related to sediment organic carbon.
- PAHs have the highest concentrations and detection frequencies of the organics, and most appear to be from combustion sources.
- Amphipod survival decreased with urbanization and with mean PECQ, but mean PECQ explained more of the variance in survival than urbanization.

References

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