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Predictions of sediment toxicity in the Barton Springs watershed located in Texas using sediment quality guidelines

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Abstract. Elevated concentrations of polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides, and metals have been documented in bed sediments or in resuspended particles in water in the Barton Springs watershed located in Austin, Texas. The endangered Barton Springs salamander (*Eurycea sosorum*) inhabits the springs and concern has been expressed that sediments in the springs may be contaminated to concentrations that may be toxic to invertebrates that serve as a food source for these salamanders. Consensus-based probable effect concentrations (PECs) were used to predict the potential for toxicity in sediments collected from the springs. These PECs were developed to determine the concentration of contaminants above which adverse effects are likely to be observed to sediment-dwelling organisms. Mean PEC quotients (PEC-Q) were calculated to provide an overall measure of chemical contamination and to support an evaluation of the combined potential effects of multiple contaminants in sediments collected from the Barton Springs watershed. In addition, 28-d sediment toxicity tests were conducted with the amphipod *Hyalella azteca* with samples collected from Barton Springs Pool. Mean PEC-Q in sediments from the watershed were frequently elevated to levels that would be predicted to be toxic to sediment-dwelling organisms and elevated concentrations of PAHs contributed to these elevated quotients. Moreover, suspended particles collected from creek flow and spring discharge indicate that run-off during storm events is likely contributing to this contamination. Sediments from the Barton Springs watershed were toxic to *H. azteca* following exposure of amphipods to low irradiance of ultraviolet radiation (UV-B). Results of these evaluations indicate that sediments in watershed are contaminated with PAHs to concentrations that are likely toxic to invertebrates that serve as a food source for the endangered salamanders. Concentration of organochlorine pesticides are also elevated in sediment samples and may pose a risk to sediment-dwelling organisms inhabiting the watershed. However, organochlorine pesticides were not included in this evaluation because reliable PECs have not be developed for these compounds. Additional studies are needed to determine: (1) the depth of UV-B penetration into the water column within the watershed during different times of the year, (2) the contribution of UV-B to the toxicity of contaminants to organisms inhabiting the watershed, and (3) the risks of exposure to organochlorine pesticides to organisms inhabiting the watershed.

Introduction

During the past seven years, elevated concentrations of polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides, and metals have been documented in bed sediments or in resuspended particles in water in the Barton Springs watershed located in Austin, Texas (Leila Gosselink, City of Austin; personal communication). The endangered Barton Springs salamander (*Eurycea sosorum*) inhabits the springs and concern has been expressed that sediments in the springs may be contaminated to a concentrations that may be toxic to invertebrates that serve as a food source for these salamanders (Matt Lechner, USFWS, Austin, TX; personal communication).

Numerical sediment quality guidelines (SQGs) have been developed by a variety of federal, state, and provincial agencies across North America using matching sediment chemistry and laboratory toxicity data (MacDonald *et al.* 2000a). These SQGs have been routinely used to interpret historical data, identify potential problem chemicals or areas at a site, design monitoring programs, classify hot spots and rank sites, and make decisions for more detailed studies (Long and MacDonald 1998). Additional suggested uses for SQGs include identifying the need for controlling sources of problem chemicals before release, linking chemical sources to sediment contamination, triggering regulatory action, and establishing target remediation objectives (USEPA 1997). Numerical SQGs, when used with other tools such as sediment toxicity tests, bioaccumulation, and benthic community surveys, provide a powerful weight of evidence for assessing the hazards associated with contaminated sediments (Ingersoll *et al.* 1997).

MacDonald *et al.* (2000a) developed consensus-based probable effect concentrations (PECs) for use in determining concentration of contaminants above which adverse effects are likely to be observed to sediment-dwelling organisms. USEPA (2000a) evaluated the ability of these PECs to predict toxicity of sediment samples in a database developed from 92 published reports, which included a total of 1657 samples with high-quality matching sediment toxicity and chemistry data from across North America. The database was comprised primarily of 10- to 14-d or 28- to 42-d toxicity tests with the amphipod, *Hyalella azteca* and 10- to 14-d toxicity tests with the midges, *Chironomus tentans* or *C. riparius*. The results of that evaluation demonstrated that there was an overall increase in the incidence of toxicity with increasing mean PEC-Q in all three tests (USEPA 2000a). A consistent increase in the toxicity in all three tests occurred at a mean PEC-Q >0.5, however, the overall incidence of toxicity was greater in the long-term test with *H. azteca* compared to the short-term tests. The longer-term tests, in which survival and growth are measured, tend to be more sensitive than the shorter-term tests, with acute to chronic ratios on the order of 6 indicated for *H. azteca*. An increase in the incidence of toxicity was observed with increasing mean PEC-Q within most of the regions, basins, and areas in North America for all three toxicity tests. The results of these analyses indicate that the consensus-based PECs can be used to reliably predict the toxicity of sediments on both a regional and national basis (USEPA 2000a, Ingersoll *et al.* 2001). USEPA (2000a) concluded that these SQGs provide a unifying synthesis of the existing guidelines, account for the effects of contaminant mixtures in sediment, and reflect causal rather than correlative effects (i.e., based on correspondence between SQGs and either sediment-spiking studies or equilibrium partitioning estimates of sediment toxicity; Swartz 1999, Di Toro and McGrath 2000, MacDonald *et al.* 2000a,b).

In the current report, PECs were used to predict the potential for toxicity in sediments collected

from the Barton Springs watershed. Mean PEC quotients (PEC-Q) were calculated to provide an overall measure of chemical contamination and to support an evaluation of the combined potential effects of multiple contaminants in sediments collected from the Barton Springs watershed. In addition, 28-d sediment toxicity tests (ASTM 2000, USEPA 2000b, Ingersoll *et al.* 1998) were conducted with the amphipod *Hyalella azteca* with eight samples collected from Barton Springs Pool (Jeannie Hayward, USGS, Columbia, MO; unpublished data).

Methods

A historic database maintained by the City of Austin was used as the source of information on the chemical composition of sediment samples from the Barton Springs watershed. Samples of bed sediments or suspended particulates in water collected over the past seven years have been included in this database. Chemical analyses of sediments reported in this database included PAHs, polychlorinated biphenyls (PCBs), organochlorine pesticides, or metals. In the current report, concentrations total PAH in each sample was calculated by summing the dry-weight concentrations of up to seven lower molecular weight (LMW) PAHs (acenaphthene, acenaphthylene, anthracene, fluorene, 2-methylnaphthalene, naphthalene, phenanthrene) and up to six higher molecular weight (HMW) PAHs (benz(a)anthracene, dibenz(a,h)anthracene, benzo(a)pyrene, chrysene, fluoranthene, and pyrene). In calculation of PEC-Qs, half the detection limit was used for compounds reported below the detection limit.

In an effort to focus on the agreement among various published SQGs, consensus-based PECs were developed by MacDonald *et al.* (2000a) for 28 chemicals of concern in freshwater sediments (i.e., metals, PAHs, PCBs, and pesticides). These PECs were derived by compiling effects-based SQGs that define the concentration of contaminants above which adverse effects are likely to be observed in sediment-dwelling organisms. USEPA (2000a) and Ingersoll *et al.* (2001) evaluated the ability of mean PEC-Qs to predict sediment toxicity using only reliable PECs (i.e., more than 75% of the samples with concentrations exceeding the PEC were toxic and more than 20 samples exceeding the PEC; MacDonald *et al.* 2000a). These reliable dry-weight normalized PECs included: arsenic (33.0 µg/g), cadmium (4.98 µg/g), chromium (111 µg/g), copper (149 µg/g), lead (128 µg/g), nickel (48.6 µg/g), zinc (459 µg/g), total PAHs (22.8 µg/g), total PCBs (0.676 µg/g), and sum DDE (0.0313 µg/g). Evaluations using PECs are based on dry-weight concentrations because previous studies have demonstrated that normalization of SQGs for PAHs or PCBs to total organic carbon (Barrick *et al.* 1988, Long *et al.* 1995, USEPA 1996) or normalization of metals to acid-volatile sulfides (Long *et al.* 1998) did not improve the predictions of toxicity in field-collected sediments.

The initial evaluation of predictive ability by MacDonald *et al.* (2000a) focused primarily on determining the ability of each PEC, when applied alone, to correctly classify samples as toxic or not toxic. Because field-collected sediments typically contain complex mixtures of contaminants, the predictive ability of these tools is likely to increase when SQGs are used in combination to classify toxicity of sediments. For this reason, the evaluation of the predictive ability of the PECs in USEPA (2000a) and Ingersoll *et al.* (2001) was conducted to determine the probability of observing sediment toxicity above and below various mean PEC-Qs (mean quotients of 0.1, 0.5, 1.0, and 5.0).

In the current report, a PEC-Q was calculated for each chemical in each sample in the database by dividing the measured concentration of the chemical by the reliable PEC for that chemical.

The PEC for total PAHs, instead of the PECs for the individual PAHs, was used in the calculation to avoid double accounting of the PAH data (MacDonald *et al.* 2000a). To equally weight the contribution of metals and PAHs in the evaluation of sediment chemistry and toxicity (assuming these two diverse groups of chemicals exert some form of joint toxic action), an average PEC-Q for up to seven metals in a sample was first calculated. A mean PEC-Q was then calculated for each sample by summing the average quotient for metals and the quotient for total PAHs, and then dividing this sum by two (except for the sample of Highway 71 collected on 6/9/00, where metals were not measured). The predicted probability of toxicity was calculated for each sediment sample based on the mean PEC-Q and the logistic regression model developed from the survival or growth data for 28- to 42-d tests with *H. azteca* (Figure 1; $y=a/[1+(x/x_0)^b]$; $a=111.803$, $b=-1.247$, $x_0=0.745$; USEPA 2000a, Ingersoll *et al.* 2001). Total PCBs was not included in the calculation of mean quotients because the concentrations of PCBs were below the detection limit in all but one sample (Sunken Garden on 3/22/99). Sum DDE was not included the calculations of mean quotients because there was limited number of samples with measured concentrations of sum DDE and because sum DDE was not used to develop the regression model illustrated in Figure 1. Concentration of other organochlorine pesticides were not included in this evaluation because reliable PECs have not be developed for these compounds (MacDonald *et al.* 2000a).

Results and Discussion

The mean quotients calculated for 22 grab samples of sediments collected upstream from Barton Springs Pool are summarized in Table 1. In these bed samples, mean PEC-Qs ranged from 0.06 to 2.2 and PAHs were the compounds that primarily contributed to the elevated quotients. The predicted probability of toxicity ranged from 0.04 to 0.89 and exceeded 0.5 in 32% of these samples.

The mean quotients calculated for 16 samples of resuspended particles collected from creek flow and spring discharge are summarized in Table 2. Mean PEC-Qs ranged from 0.004 to 0.49 in these samples and PAHs and metals both contributed to the elevated quotients. The predicted probability of toxicity in these samples ranged from 0.0 to 0.41.

The mean quotients calculated for 11 grab samples of sediments collected from Barton Springs Pool are summarized in Table 3. In these bed samples, mean PEC-Qs ranged from 0.07 to 1.5 and elevated concentrations of PAHs primarily contributed to the elevated quotients. The predicted probability of toxicity ranged from 0.06 to 0.79 and exceeded 0.5 in 36% of these samples.

Sediment chemistry and toxicity were determined for 8 grab samples of sediments collected from Barton Springs Pool in the fall of 2000 (Table 4). In these bed samples, mean PEC-Qs ranged from 0.04 to 11.4 and elevated concentrations of PAHs primarily contributed to the elevated quotients. The predicted probability of toxicity ranged from 0.03 to 1.0 and exceeded 0.5 in 38% of these samples. None of the samples significantly reduced survival or growth of *H. azteca* after the 28-d exposure to the sediments. However, reduced survival of amphipods was observed in three treatments following exposure to low irradiance to ultraviolet radiation after the completion of the initial sediment exposures ($4 \mu\text{W}/\text{cm}^2$ of UV-B; 4-h exposure/d to UV-B for 2 d; Table 4; Figure 1).

The importance of evaluating photoinduced toxicity of PAHs and other compounds by ultraviolet radiation has been recognized for many years (Oris and Giesy 1985, Davenport and Spacie 1991, Ankley *et al.* 1994, Cleveland *et al.* 1997). Moreover, standard toxicity testing methods provide guidance to support the design of experiments to assess photoinduced toxicity (ASTM 2000, USEPA 2000a). Therefore, the influence of ultraviolet radiation should be considered when evaluating the toxicity of compounds expressed by this mode of action. Photoinduced toxicity is particularly important when evaluating sediments in clear, shallow water systems. No data are available on the irradiance of UV-B that penetrate the water column in the Barton Springs watershed. Therefore, the irradiance of UV-B used in the exposures summarized in Table 4 were selected to represent about 1% of incidence light at water depth of 10 cm at other sites in North America (Hurtubise *et al.* 1998, Barron *et al.* 2000).

The lack of toxicity of sediments collected from Barton Springs Pool to *H. azteca* at the end of the 28-d exposure was unexpected (i.e., before the exposure to UV-B). Based on calculated mean PEC-Qs, a probability of toxicity exceeding 0.5 was predicted for three of these samples (1279, 1234, and 1266; Table 4). The source of PAHs in these sediments is thought to include asphalt from older parking areas deposited during storm events (Leila Gosselink, City of Austin, personal communication). The percentage of lower molecular weight (LMW) PAHs relative to total PAH in these samples was quite low in the samples from Barton Springs Pool (only about 10 to 13%; Table 4) as might be expected for PAHs from combustion sources such as asphalt. In contrast, the proportion of LMW PAHs tended to be much higher (i.e., 15 to 95%) in the samples that were previously evaluated in the assessment of PECs (USEPA 2000a) suggesting that petroleum-based sources of PAHs were predominant (Van Meter *et al.* 2000). Van Meter *et al.* (2000) described an approach that can be used to distinguish between combustion- and petroleum-based PAHs in sediments (a ratio of the sum two- and three-ring PAHs to the sum combustion PAHs). These ratios were ≤ 0.12 for all of the samples listed in Table 4 and were less than or equal to the lowest ratios reported in Van Meter *et al.* (2000) for a range of sediment samples collected from across the United States. Results of these analyses support the conclusion that the PAHs in Barton Springs Pool are primarily from combustion sources.

Preliminary analyses of the USEPA (2000a) database indicate a trend of lower correct classification of the toxicity attributed to PAHs in samples with a lower percentage of LMW PAHs (<40%) compared to samples with a higher percentage of LMW PAHs (>40%). Therefore, PEC-Qs described in MacDonald *et al.* (2000a) may over predict the toxicity of samples with PAHs primarily from combustion sources (i.e., with PAHs dominated by HMW PAHs). However, the samples evaluated from Barton Springs Pools with a low percentage of LMW PAHs were toxic to *H. azteca* following subsequent exposure of amphipods to low irradiance of UV-B (Table 4). Additional analyses of the USEPA (2000a) database are ongoing to evaluate the toxicity associated with LMW and HMW PAHs to sediment-dwelling organisms (i.e., using the approach used by Van Meter *et al.* 2000 for classifying combustion- vs. petroleum based sources of PAHs in sediment).

Concentration of organochlorine pesticides are also elevated in sediment samples and may pose a risk to sediment-dwelling organisms inhabiting the watershed. However, organochlorine pesticides were not included in this evaluation because reliable PECs have not be developed for these compounds (MacDonald *et al.* 2000a). While the current report has evaluate the potential

for toxicity of sediment in the Barton Springs watershed to invertebrates, the influence of UV-B on the direct toxicity of PAHs to salamanders should also be further investigated. Specifically, Dwyer (2001) observed that accumulation of PAHs (fluoranthene) from water following 4-d laboratory exposures were not highly toxic to *Eurycea sosorum*. However, subsequent exposure of these salamanders to low irradiance of UV-B resulted in high toxicity of fluoranthene. Therefore, it is also important to determine the amount of UV-B the salamanders may be exposed to in order to determine the potential for photoactivation of PAH residues in these organisms. The following research is needed to generate information that could be used help to further address the toxicity of sediments to organisms inhabiting the Barton Springs watershed:

1. Site-specific measurements of irradiance of UV-B at the sediment-water interface should be performed across the watershed. These measurements are needed to determine the depth of UV-B penetration in the water column during various conditions (i.e., during time of sediment resuspension, during different times of the year).
2. Additional studies are needed to determine if UV-B contributes to the toxicity of contaminants to salamanders and other organisms inhabiting the watershed. These studies should include additional exposures of organisms in laboratory to contaminants alone or in combination with UV-B or exposures of organisms collected from the watershed.
3. Additional studies are needed to evaluate the risk of organochlorine pesticides to organisms inhabiting the watershed.
4. Additional analyses of the USEPA (2000a) database are needed to further evaluate the contribution of LMW PAHs to the toxicity of sediment samples.

Conclusions

Sediments from the Barton Springs watershed are contaminated with elevated concentrations of PAHs and some of these samples were observed to be toxic to the amphipod *H. azteca* following subsequent exposure of amphipods to low irradiance of UV-B. These sediments are frequently contaminated with PAHs to concentrations that are likely toxic to invertebrates that serve as a food source for the endangered salamanders. Moreover, suspended particles collected from creek flow and spring discharge indicate that run-off during storm events is likely contributing to this contamination and associated effects. Additional studies are needed to determine: (1) the depth of UV-B penetration into the water column within the watershed during different times of the year, (2) the contribution of UV-B to the toxicity of contaminants to organisms inhabiting the watershed, and (3) the risks of exposure to organochlorine pesticides to organisms inhabiting the watershed. Additional analyses of the USEPA (2000a) database are also needed to further evaluate the contribution of LMW PAHs to the toxicity of the sediment samples.

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Table 1. Predicted probability of toxicity in grab samples of sediment collected upstream of Barton Springs Pool using mean PEC quotients.

Location	Date	Mean PEC-Q	Predicted probability of toxicity
Cambell Hole Pool	9/26/00	0.14	0.13
Below Spyglass	6/17/99	0.2	0.18
Above Spyglass	6/17/99	0.13	0.11
Recharge Pool	7/20/00	0.14	0.12
Lost Creek Blvd.	8/26/00	0.09	0.08
Short Spring	4/17/00	0.24	0.22
Johnson Pool	7/19/00	0.15	0.13
Below BCT	2/23/99	0.15	0.13
Above BCT	2/23/99	0.13	0.11
Shield Pool	5/20/94	0.7	0.53
Stark Pool	7/19/00	0.06	0.04
Upper Sunken Garden	3/22/99	0.19	0.17
Barton Creek above Barton Pool	11/21/94	2.2	0.89
	4/20/95	0.94	0.64
	4/20/95	1.1	0.68
	9/4/97	0.83	0.60

	4/28/98	0.2	0.18
Barton Creek Between Dams above Pool	7/9/96	0.55	0.46
	9/4/97	0.87	0.61
	4/28/98	0.19	0.17
	8/26/99	0.29	0.26
	7/6/00	0.37	0.33

Table 2. Predicted probability of toxicity in samples of suspended particles collected from creek flow and spring discharge (when flow was turbid) during storm events from Barton Springs Pool and Barton Creek using mean PEC quotients.

Location	Date	Mean PEC-Q	Predicted probability of toxicity
Barton Creek at Highway 71	5/26/99	0.17	0.15
	5/1/00	0.18	0.17
	6/9/00	0.1	0.09
	11/3/00	0.12	0.11
Barton Creek above Barton Pool	5/18/99	0.26	0.24
	5/26/99	0.41	0.36
	5/2/00	0.49	0.41
	6/9/00	0.26	0.24

	11/3/00	0.34	0.30
Barton Springs	5/26/99	0.46	0.39
	5/1/00	0.22	0.20
	5/2/00	0.19	0.17
	6/9/00	0.004	0.0
	6/10/00	0.2	0.18
	11/3/00	0.19	0.17
Eliza Springs	11/3/00	0.24	0.22

Table 3. Predicted probability of toxicity in grab samples of sediment collected from Barton Springs Pool using mean PEC quotients.

Date	Mean PEC-Q	Predicted probability of toxicity
4/20/95	1.5	0.79
4/20/95	1.5	0.79
7/25/95	0.09	0.08
3/22/99	0.08	0.06
3/22/99	0.07	0.06
5/5/99	0.25	0.23
11/19/99	0.28	0.25
5/3/00	0.08	0.07
11/8/00	1.1	0.68
11/14/00	0.89	0.62
2/8/01	0.2	0.18

Table 4. Predicted probability of toxicity in grab samples of sediment collected from Barton Springs in the fall of 2000 and results of 28-d toxicity tests with the amphipod *Hyaella azteca* (Jeannie Hayward, USGS, Columbia, MO; unpublished data).

Sample	Control	879-1	879-2	219	1279	1234	35	463	1266
Metals (mg/kg)									
Cadmium	0.07	0.18	0.18	0.09	0.28	0.18	0.18	0.20	0.45
Copper	0.08	<0.19	0.56	<0.19	5.16	6.23	1.25	0.34	33.2
Lead	0.06	13.20	12.10	10.20	20.10	17.50	12.70	9.58	40.1
Nickel	0.20	6.33	5.51	3.29	6.81	4.73	5.90	6.70	5.24
Zinc	0.09	36.2	38.8	20.10	64.40	53.20	23.90	30.30	93.3
PAH (ug/kg)									
Acenaphthene	<100	<309	<309	<426	375	726	<282	<18	1042
Acenaphthylene	<100	<309	<309	<426	<198	178	<282	<18	305
Anthracene	<100	<309	<309	<426	355	2166	<282	<18	4320
2-methylnaphthalene	<100	<309	<309	<426	<198	<128	<282	<18	<128
Benz(a)anthracene	<100	2099	1692	<426	5128	20382	621	48	49555
Benzo(a)pyrene	<100	4938	5231	596	8679	25478	1469	78	69886
Chrysene	<100	2716	2985	723	8087	24204	537	104	80051
Dibenz(a,h)anthracene	<100	1667	1815	<426	2959	8535	621	45	25413
Fluoranthene	<100	4630	4923	894	10651	58599	1158	108	132147
Fluorene	<100	<309	<309	<426	375	1006	<282	<18	1525
Naphthalene	<100	<309	<309	<426	<198	<128	<282	<18	<128
Phenanthrene	<100	1173	1200	<426	4734	22930	311	39	43202
Pyrene	<100	3395	4000	468	8087	44586	904	91	108005
LMW PAHs	350	2099	2123	1489	6134	27134	1158	95	50521
HMW PAHs	300	19444	20646	3106	43590	181783	5311	473	465057
Total PAHs	650	21543	22769	4596	49724	208917	6469	568	515578

% LMW of Total PAHs	54	10	9	32	12	13	18	17	10
Mean PEC-Q	0.06	0.51	0.53	0.12	1.14	4.62	0.17	0.04	11.4
Predicted probability of toxicity	0.05	0.43	0.44	0.11	0.70	1.0	0.16	0.03	1.0
Observed survival (%) after UV exposure	95	98	95	100	84	0	95	90	0