Ecotoxicology studies with sediment, pore water, and surface water from the Palmerton Zinc site

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BACKGROUND

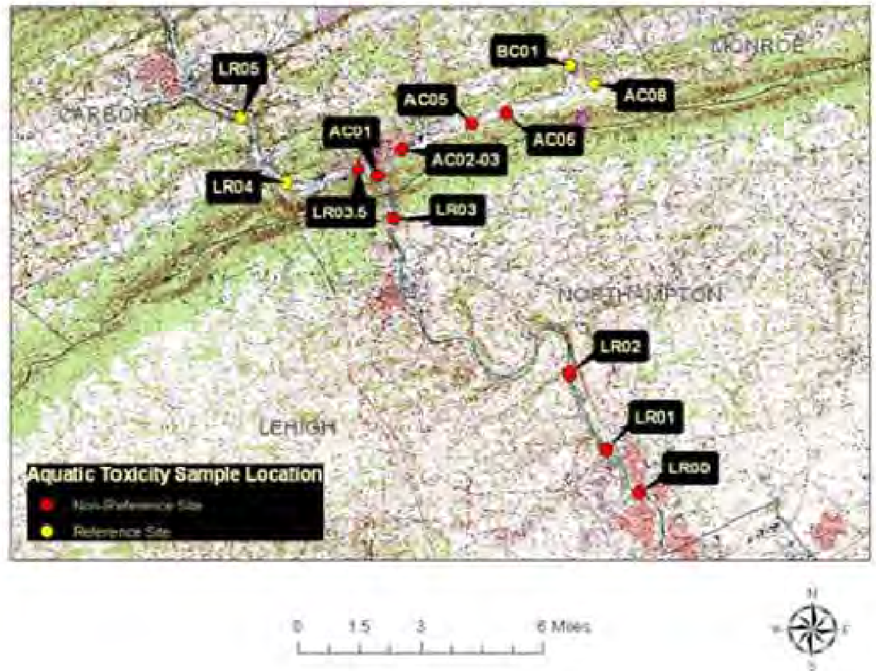
Zinc smelters operated in Palmerton, Carbon County, Pennsylvania between 1898 and 1980. Atmospheric emissions and solid waste (slag or cinders) from smelter operations resulted in deposition of toxic elements – including arsenic, copper, cadmium, lead, manganese, and zinc -- on the surrounding landscape, including surface and ground water. The smelter sites, waste piles, and the contaminated terrestrial and aquatic landscape around them are collectively referred to as the Palmerton Zinc Pile Site (Palmerton site).

The objective of this study was to update the findings of a 1997 study of the toxicity of surface water, pore water, and sediment in the vicinity of the Palmerton Site (U.S. Environmental Protection Agency, 2001. Final Draft Palmerton Zinc Site Ecological Risk Assessment, Volume 2: Aquatic Community Endpoints. USEPA Environmental Response Team Center, Edison NJ). Samples were collected August 12-13, 2008 to document current levels of metal concentrations and associated toxicity in stream water, sediment, and sediment pore water at sites in Aquashicola Creek (including an uncontaminated tributary, Buckwha Creek), and Lehigh River.

This study consisted of four tasks: (1) surface water sampling and analysis; (2) sediment sampling and analysis; (3) sediment porewater sampling and analysis; and (4) toxicity testing.

Table 1. Collection sites for surface water, pore water, and sediment for toxicity testing. BC=Buckwha Creek, AC=Aquashicola Creek, LR=Lehigh River. Ref = reference site.

BC1	Above covered bridge (Ref.)
AC8	Upper Aquashicola Cr (Ref.)
AC6	Near Ampal facility
AC5	Near PPL electric substation
AC2/3	Palmerton (6th St)
AC1	Near mouth
LR5	Parryville (Ref.)
LR4	Bowmanstown boat ramp (Ref.)
LR3.5	Above Aquashicola Cr
LR3	1 mile below Aquashicola Cr
LR2	Laury's Station
LR1	Upstream of Cementon Dam
LR0	Coplay



Photos of the Palmerton site: (top) Slag deposit and impacted hillside; (middle) Aquashicola Creek with slag deposit on bank (site AC5) ; (bottom) Lehigh River and partially-revegetated hillside above Lehigh Water Gap (site LR3.5).

METHODS

Water and Sediment Sampling

- Surface water was collected from ten sites in Buckwha Creek, Aquashicola Creek, and Lehigh River (Table 1) by compositing sub-surface grabs collected across the stream width.
- Pore water was collected from ten sites using a peristaltic pump attached to a push-point sampler (Geoprobe™ slotted sampling rod) driven into the stream bed at mid-channel (or at maximum wading depth).
- Sediment was collected from 14 sites, including four reference sites (Table 1). Surficial sediment (1-6 cm depth) was collected from depositional areas at each location using a plastic scoop.

Toxicity Testing

- Fathead minnow test. The toxicity of surface water and pore water was evaluated using a 7-d survival and growth test with larval fathead minnow, *Pimephales promelas,* using methods published by the U.S. Environmental Protection Agency (USEPA 2002. Short-term methods for estimating the chronic toxicity of effluents and receiving waters to freshwater organisms, 4th edition, EPA-821-R-02-013). These tests evaluated the toxicity of undiluted water samples under static conditions, with daily water replacement (Table 2).

- Amphipod water-only test. The toxicity of surface water and pore water was evaluated using a 10-d survival and growth test with the amphipod, *Hyalella azteca*. This test was conducted with static-renewal methods similar to those used for the fathead minnow tests (Table 2).
- Amphipod sediment test. The toxicity of whole sediment was evaluated using standard methods (USEPA 2000. Methods for measuring the toxicity and bioaccumulation of sediment-associated contaminants with freshwater invertebrates, EPA-600-R-99-064) for 10-d and 28-d survival and growth tests with *H. azteca* (Table 2). Overlying water was well water diluted with de-ionized water to a hardness 70 mg/L, typical of the hardness of water in Aquashicola Creek (Tables 3a, 3b).
- Data analysis. All controls met requirements for test acceptability (95-98%). Toxicity data were rank-transformed before analysis of variance, with differences between test samples and controls determined with Dunnett's test.

Chemical and Physical Analysis

- Water. Surface water and pore water were analyzed for routine water quality parameters, plus major cations, major anions, and dissolved organic carbon (DOC). Waters were analyzed for manganese and five trace metals (cadmium, copper, nickel, lead, and zinc) by inductively coupled plasma-mass spectrometry (ICPMS). One set of water samples was filtered (0.45 µm pore diameter) in the field and a second set at the start of toxicity tests. Passive diffusion samplers ('peepers') were used to sample dissolve metals in pore water during the sediment toxicity tests.

- Sediment. Sediment samples were analyzed for particle size distribution, total organic carbon (TOC) and acid-volatile sulfide (AVS). Sediment from each site was analyzed for total recoverable metals by a multi-element ICPMS scan (data not yet available). Extracts from the AVS digestion were analyzed for concentrations of simultaneously-extracted metals (SEM).

Table 2. Test conditions for toxicity tests with water and sediment.

Test Condition	**Water-only tests**	**Sediment Tests**
Test type:	Static-renewal test (100% site water)	Whole-sediment exposures with water renewal
General conditions:	Temperature, 23 ± 1^{o} C; Ambient laboratory light, 16 h light/8 h dark	
Test chamber:	300-mL beaker (5 mL silica sand for amphipods)	300-ml beakers
Test material:	150 mL test water	100 mL sediment and 175 ml water
Control water:	Diluted well water (nominal hardness = 70 mg/L as $CaCO_3$)	
Control sediment:	West Bearskin Lake, Minnesota (sand/silt/clay: 60/15/25 %; organic carbon, 5 %)	
Water renewal:	Minnows, daily replacement; Amphipods, 2 volume additions / d	
Age of organisms:	Minnows, 24 hr post-hatch; Amphipods, about 7-d old	
Stocking & Replication:	10 animals per chamber; 4 reps per treatment	
Feeding:	Minnows: brine shrimp, 0.15 g twice a day Amphipods: yeast-cereal leaf-trout chow suspension (USEPA 2000), 1.8 mg/d	
Test duration:	Minnows, 7 d; Amphipods, 10 d	10 d and 28 d
Endpoints:	Survival, growth (dry wt of minnows, length of amphipods), and total biomass.	
Test acceptability:	Control survival (both species) ≥80%. Control growth (minnows) >0.25 mg avg. dry weight	

RESULTS AND DISCUSSION

Physical and Chemical Characteristics of Water and Sediment

- Surface Water and Pore Water Quality. Water quality of surface waters and pore waters from toxicity tests were generally similar among sites (Table 3a,b). Surface water from Aquashicola Creek had greater hardness (60-90 mg/L) and alkalinity than water from Lehigh River (hardness 15-26 mg/L). Conductivity of surface water was also highest in lower Aquashicola Creek. Water quality of pore waters was generally similar to surface waters, except for high levels of conductivity, hardness, alkalinity, iron, and chloride in pore water from LR3.5.

- Sediment Characteristics. Sediments from most sites were dominated by sand-sized particles (61-84%), except the sediment from AC6 was dominated by fine particles (55% silt and clay; Table 3c). Organic matter content (loss on ignition) was greater in the lower Lehigh River sites (>20% at LR2, LR1, LR0) than at upstream sites in either stream. Acid-volatile sulfide concentrations varied widely, with lowest levels (<1 μmol/g) at AC5 and LR5 and highest (>20 μmol/g) at AC6, AC1, and LR1.

Table 3. Characteristics of water and sediment samples from the Palmerton site, August 2008: (a) surface water; (b) pore water; (c) sediment. R=reference site; LOI = loss on ignition.

(a) Surface water quality:

Site	pH	Conductivity (µS/cm)	Alkalinity (mg/L)	Hardness (mg/L)	Iron (ug/L)	Chloride (mg/L)	DOC (mg/L)
BC1 (R)	7.58	114	27	38	52	10	2.8
AC8 (R)	8.11	180	81	81	85	7	1.8
AC6	7.84	156	47	60	63	9	2.4
AC5	7.74	180	50	73	23	9	2.4
AC2/3	7.68	212	49	83	21	12	2.3
AC1	7.64	230	51	90	35	12	4.0
LR4 (R)	7.50	121	21	32	37	16	3.0
LR3.5	7.51	128	15	33	54	18	2.7
LR3	7.37	120	17	29	88	17	3.3
LR2	7.62	142	24	40	76	19	2.9
LR2-DUP	7.60	154	26	41	78	18	7.8

(b) Pore water quality:

Site	pH	Conductivity (µS/cm)	Alkalinity (mg/L)	Hardness (mg/L)	Iron (ug/L)	Chloride (mg/L)	DOC (mg/L)
BC1 (R)	7.50	102	26	36	46	10	1.5
AC8 (R)	7.78	175	76	86	253	8	1.1
AC6	8.07	177	65	86	77	11	2.9
AC5	7.94	186	58	89	<20	9	1.1
AC5-DUP	7.59	167	46	73	<20	9	1.6
AC2/3	7.84	227	51	88	41	12	1.7
AC1	7.54	202	43	82	<20	10	1.5
LR5 (R)	7.89	297	57	94	63	57	1.3
LR3.5	7.59	639	191	201	5,630	83	3.1
LR3	7.43	122	30	38	<20	19	2.0

Table 3 (continued).

(c) Sediment characteristics:

Site	Moisture (%)	Sand (%)	Silt (%)	Clay (%)	LOI (%)	AVS (μmol/g)
BC1 (R)	48	61	22	17	5.4	3.3
AC8 (R)	54	61	22	17	7.6	16.7
AC6	67	45	36	19	12.1	37.0
AC5	51	75	12	13	11.1	0.8
AC2/3	50	69	16	15	7.9	4.7
AC1	65	77	11	12	11.0	28.5
LR5 (R)	30	87	4	9	8.5	0.4
LR4 (R)	34	78	6	15	8.5	4.2
LR3.5	32	84	5	11	13.3	2.3
LR3	54	65	20	16	16.4	5.2
LR2	62	66	22	12	18.6	11.6
LR2-DUP	54	65	20	15	22.5	14.3
LR1	50	66	16	18	24.1	27.8
LR0	41	76	9	15	20.5	6.4

Toxicity of Water and Sediment

- Fathead minnow water-only test. Surface water from most sites caused little toxicity to fathead minnows. Survival differed significantly among sites and was lowest (67-80%) in surface water from several sites in lower Aquashicola Creek, but survival was significantly less than the control only in water from AC2/3 (Figure 1a). Growth of minnows in surface water followed similar trends among sites, but none of the site means were significantly different from controls (data not shown). Neither survival nor growth of minnows was significantly reduced by exposure to Palmerton pore waters, although survival was lowest (73%) in pore water from AC1 (Figure 1b).

- Amphipod water-only test. Both surface water and pore water from Palmerton sites caused significant toxicity to amphipods. Surface water from sites AC1, AC2/3, and AC5 in lower Aquashicola Creek caused 100% mortality (Figure 1a). Amphipod survival was 100% in the original AC5 pore water, but was significantly reduced in the duplicate pore water sample from AC5 and in pore water from AC2/3 (Figure 1b). Growth of surviving amphipods was not significantly reduced, relative to controls, by either surface waters or pore waters (data not shown).

- Amphipod sediment test. Sediment from Aquashicola Creek site AC5 had significant toxic effects on amphipods, with mean survival of 12.5% in the 10-d test and 0% in the 28-d test (Figure 1c). Survival in sediments from lower Aquashicola Creek (AC2/3 and AC1) caused small reductions in mean amphipod survival over time (from 93% on day 10 to 80% on day 28), but mean survival in these sediments did not differ significantly from controls in either test. Growth of amphipods was not significantly reduced in either sediment test relative to controls (data not shown).

- Differences between 2008 and 1997 tests. Results of tests with both surface water and pore water suggest that toxicity to fathead minnows has decreased in the affected reach of Aquashicola Creek (from AC5 downstream to AC1), where survival was close to 0% in 1997, but ranged from 67% to 93% in 2008. There was little change in sediment toxicity to amphipods between years (ranges of survival: 0-89% in 1997, 13-93% in 2008), but both surface water and pore water from lower Aquashicola Creek remained highly toxic in 2008 (0-3% survival).

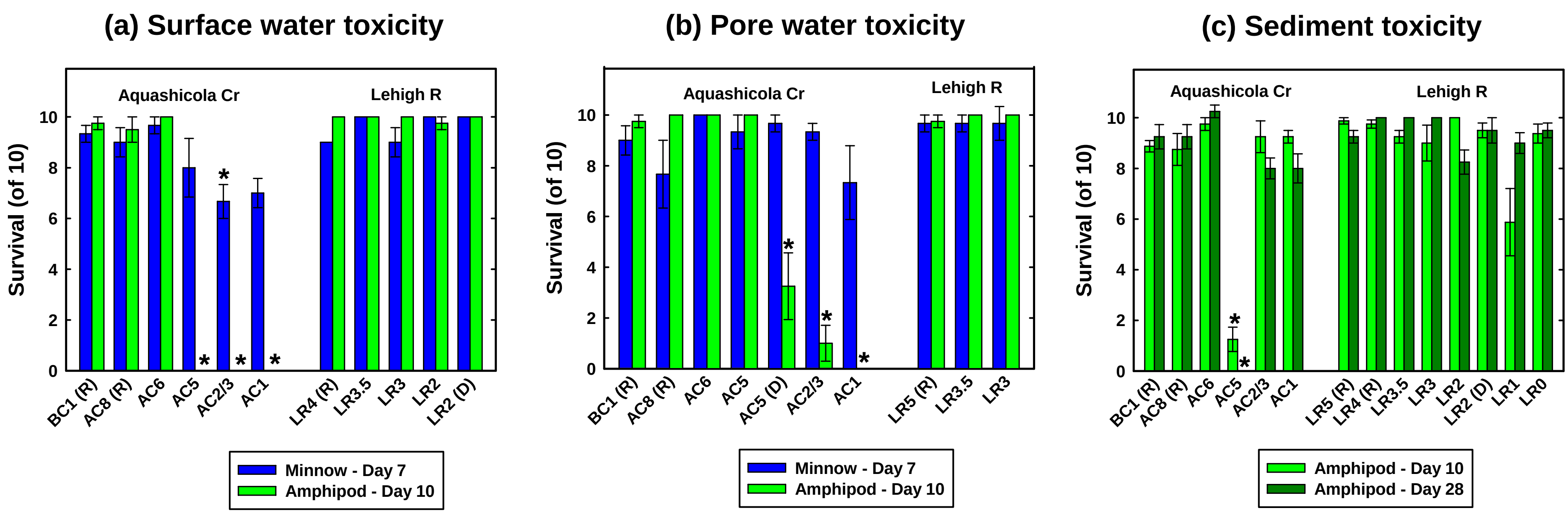


Figure 1. Toxicity of surface water, pore water, and whole sediment from the Palmerton site. Mean survival of fathead minnows and amphipods, with standard errors. Asterisks indicate means that are significantly reduced relative to controls. 'R'=reference site; 'D'=field duplicate.

Metals in Water and Sediment

- Dissolved metals. Metal concentrations in surface and pore waters were dominated by zinc (Figure 2a,b). Greatest Zn concentrations (>200 µg/L) occurred in samples of surface water and pore water from AC5, AC2/3, and AC1, although one of two duplicate pore water samples from AC5 had a low Zn concentration (42 µg/L). Samples that had greatest Zn concentrations also had elevated of cadmium (0.6-3.2 µg/L). Manganese concentrations were moderately high (84-104 µg/L) in several high-Zn samples, but greatest Mn concentrations occurred in pore waters from AC8, LR5. and LR3.5 (278-1885 µg/L), which did not have elevated Zn concentrations. Concentrations of lead, copper, and nickel were low (range: 0.5-6.2 µg/L) in all water samples.
- Sediment metals. Simultaneously-extracted metals also showed higher sediment zinc concentrations (>5000 µg/g) from lower Aquashicola Creek than from other sites (<1000 µg/g; Figure 2c). Sediments from lower Aquashicola Creek also had elevated levels of lead (>200 µg/g), and cadmium (>10 µg/L). Copper concentrations were only elevated (2450 µg/g) at AC5. Sediments from AC5 had highest concentrations of SEM metals (sum of 5 metals =125 µmol/g) and the lowest AVS, suggesting high metal bioavailability.

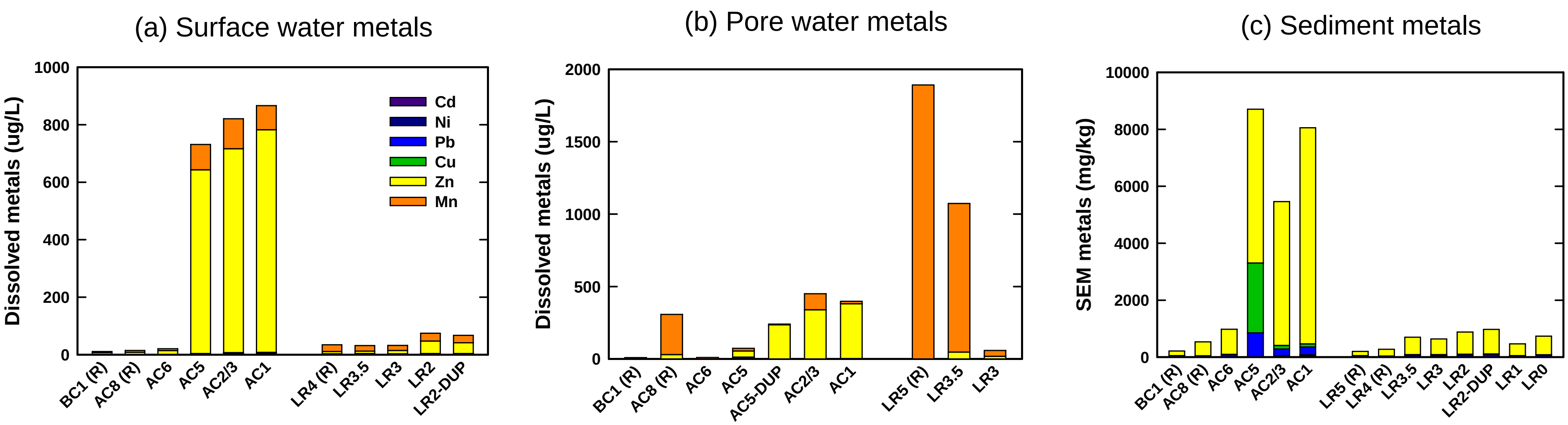


Figure 2. Metal concentrations in surface water, pore water, and whole sediment from the Palmerton site. For surface water and pore water, bars are means of two analyses. SEM=simultaneously-extracted metals (co-extracted with acid-volatile sulfides.) 'R'=reference; 'D'=duplicate.

Relationships Between Toxicity and Metal Concentrations

- Water. Zinc concentrations were most closely associated with toxicity in surface water and pore water from the Palmerton site. Combined data from the two amphipod surface water and pore water tests indicated a strong concentration-response relationship between dissolved zinc and amphipod survival (logistic regression, $r^2 = 0.99$; Figure 3). Estimation of a site-specific threshold for Zn toxicity is difficult, due to the absence of samples with intermediate levels of Zn. Non-toxic samples (98-100% survival) had dissolved Zn concentrations less than 50 µg/L and toxic samples (0-33% survival) had Zn concentrations greater than 230 µg/L. These observations are consistent with the current chronic water quality criterion for dissolved Zn, which ranges from 76 µg/l to 108 µg/l for the hardness of surface waters and pore waters from lower Aquashicola Creek (USEPA 2002. National recommended water quality criteria: 2002. EPA 822-R-02-047).
- Sediment. Associations of metals with toxicity in sediments from the Palmerton site are difficult to assess because sediments from only one site (AC5) were toxic to amphipods. Sediments from AC5, which caused 100% amphipod mortality after 28 d, had lower SEM zinc concentrations less than those in sediments from AC2/3 or AC1, which had 28-d amphipod survival of 80%. The toxicity of AC5 sediments apparently reflects toxic effects of zinc in combination with toxic effects of lead and copper, which both occurred at greatest concentrations in the AC5 sediment.

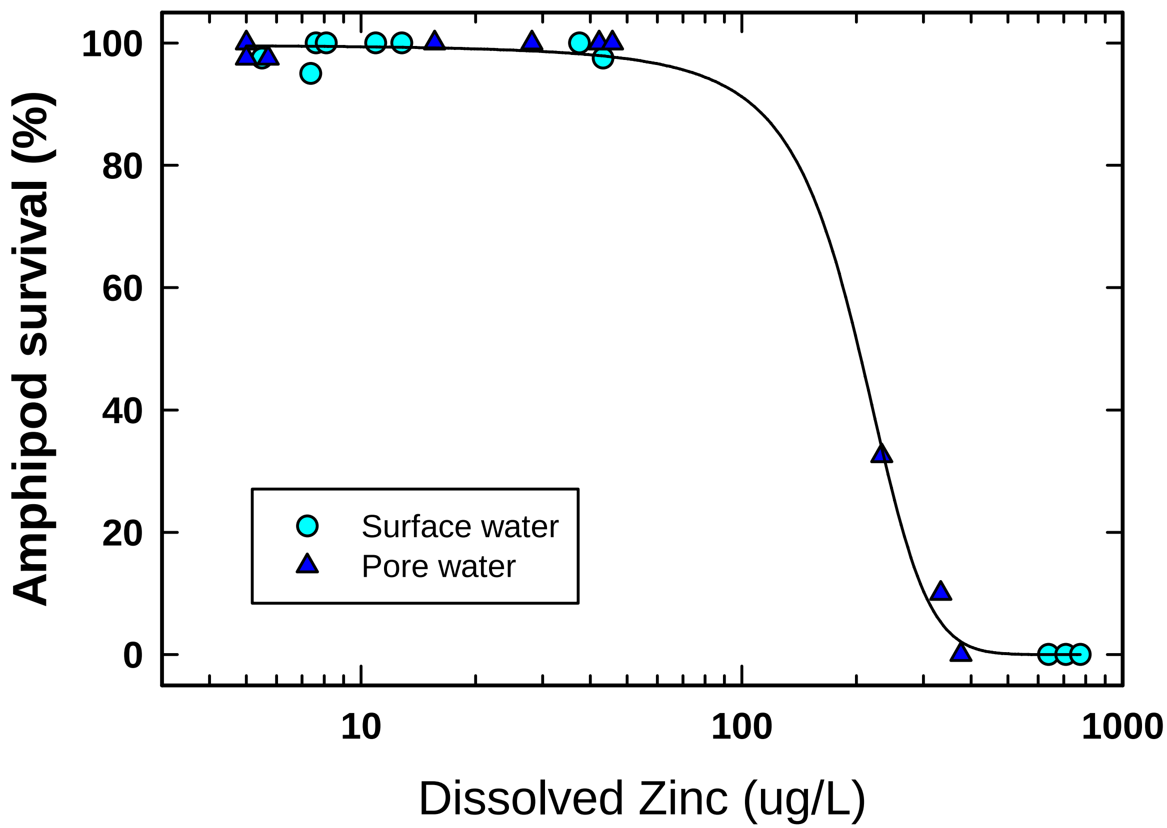


Figure 3. Relationship between amphipod survival and dissolved zinc concentrations in surface water and pore water from the Palmerton site.