

Copper, Chromium, and Arsenic Levels in Soil Near Highway Traffic Sound Barriers Built Using CCA Pressure-Treated Wood

D. E. Stilwell, T. J. Graetz

Department of Analytical Chemistry, The Connecticut Agricultural Experiment Station,
Post Office Box 1106, New Haven, CT 06504, USA

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Chromated Copper Arsenate (CCA) is the most popular water-born wood preservative in current use in the United States. It is commonly used for construction of such outdoor items as decks, porches, picnic tables, children's playscapes, docks, and sound barriers. However, due to the prevalence and extent of its use, concerns have been raised with regard to the dispersal of arsenic into the environment (Kelsall et al., 1999; Stilwell and Gorny 1997, Weis and Weis 1996). Indeed, the production of CCA wood accounts for about 90% of the arsenic used each year in the United States (Reese, 2000). The health hazards of acute arsenic poisoning are well documented (NRC 2000), and arsenic is a known human carcinogen, but the risk assessment at low levels is a matter of controversy (Guo and Valberg, 1997; NRC, 2000). Nonetheless, the US EPA has recently proposed lowering the drinking water standard for arsenic from 50 µg/L to 10 µg/L, and recommended a non-enforceable goal of zero (US EPA, 2000).

In this study we examine the leaching potential of the CCA preservative when used in wooden highway traffic sound barriers by measuring accumulation of the preserving elements, chromium, copper, and arsenic in soil. Highway traffic sound barriers are large vertical structures built on top of a 10-25 cm deep gravel underburden. Thus, any increase in the preserving elements found in the soil under the barriers would likely originate from a leaching mechanism, since any physical wearing of the wood would produce particles trapped by the gravel layer directly under the barriers. Previous studies both in the field and under laboratory conditions have shown that the CCA preservatives can leach to a varying degree both from the wood (Aceto and Fedele, 1994; Stilwell and Gorny, 1997; Warner and Solomon, 1990) and through soils (Allinson et al., 2000; Kelsall et al., 1999). For this study the Cu, Cr, and As levels in 35 soil samples taken under three sound barriers located in southern Connecticut are compared to soil samples taken at various distances from the barrier.

MATERIALS AND METHODS

All three sound barriers were located in southern Connecticut. Barrier 1 started at the Ferry Street Entrance to northbound interstate 91 in New Haven; barrier 2

Correspondence to: D. E. Stilwell

started at Entrance 4W, westbound interstate 691 in Meridan; and barrier 3 started at Entrance 30, westbound interstate 84W in Southington. Each “barrier unit” consisted of 24-40, 16 by 4 by 365 cm tongue and groove boards, stacked horizontally between posts (37 cm diameter), to a height between 400 to 630 cm. The wood in barrier 1 appeared in noticeably better condition than barrier 2 or 3, but the exact time of construction was not determined. All of the barriers were coated and were subsequently maintained by additional patch coatings. The soils under the barriers were all sandy loam. A total of 15 soil samples were taken under barrier 1, 10 under barrier 2, and 10 under barrier 3. Under barrier 1, the first 10 samples were taken over the first 20 barrier units, and 5 more were taken about 500 meters up from the entrance, over 5 barrier units. Under the second and third barriers, 10 samples were taken over 30 barrier units, starting with the first barrier unit at the interstate entrance.

Samples were taken midway under a barrier unit by first removing the gravel at the base and then taking a composite (ca 150 g) of the soil sample within a 25 cm wide by 25 cm long by 5-30cm deep volume. Five additional soil samples from each site, taken 80 cm laterally offset from the barriers, and at points that were subsequently determined to correspond to the 5 highest As levels at that site, were collected for analysis. For controls, 5 background soil samples were acquired 3-10 meters away from each barrier site.

All samples were dried at 95°C for 24 hours, and homogenized using a wrist action shaker, for four hours. Care was taken to exclude rocks and debris from the sample. The soil samples were prepared for analysis using microwave assisted acid digestion (MSP 1000, CEM Corp., Matthews NC, USA), as described previously (Stilwell 1993). Briefly, about 1.0 g portions (± 0.1 mg) were weighed into CEM Teflon microwave digestion vessels, 10mL of concentrated HNO_3 was added, the vessels were then capped and run on the digester following the manufactures EPA 3051 microwave program. After completion the digests were brought to 100mL and transferred to polypropylene containers. The digests were analyzed for Cu, Cr by Inductively Coupled Plasma Emission Spectroscopy (ICP-OES) using the Atom Scan 16 (Thermo-Jarrell Ash, Franklin, MA, USA). In those cases where the soil As concentrations were below 10ppm, the samples were analyzed using a PE 5100PC graphite furnace atomic absorption spectrometer (GFAAS) (Perkin Elmer Corp., Wellsley, MA, USA). Two replicate samples were digested and analyzed for each sampling site throughout the study. Both a blank and a reference soil (NIST, SRM-2709 San Joaquin Soil) were analyzed with each batch of five soils and their replicates. The blanks ($n=10$) were all below the solution detection limit of 0.01 mg/L. The amounts of Cu (30 ± 1 mg/kg, $n=10$) and Cr (74 ± 4 mg/kg, $n=10$) in the reference soil were within the reported range of 30-40 mg/kg (Cu) and 70-110 mg/kg (Cr) for this method (Rasberry, 1993). The amount of As (16 ± 3 mg/kg) was in agreement with the certified value of 17.7 ± 0.3 mg/kg. The percent recovery of fortified soil samples ($n=4$) were 92 ± 7 (Cu), 97 ± 6 (Cr), and 91 ± 9 (As).

Table 1. Copper, chromium and arsenic content in soils (mg/kg, dry weight).

Distance From Barrier		0 cm			80 cm			Background		
Element	Barrier*	Range	Average		Range	Average		Range	Average	
Copper	1	23-142	63 ± 34		18-31	26 ± 6		31-53	41 ± 12	
	2	30-243	99 ± 67		11-14	12 ± 1		11-12	11 ± 1	
	3	14-291	88 ± 86		9-15	11 ± 3		7-10	9 ± 1	
	1-3	13-291	80 ± 62		9-31	16 ± 8		7-53	20 ± 17	
Chromium	1	23-50	30 ± 7		15-21	18 ± 2		15-41	22 ± 10	
	2	20-95	45 ± 23		12-16	13 ± 2		9-15	13 ± 2	
	3	13-117	43 ± 33		9-17	13 ± 3		8-13	12 ± 1	
	1-3	13-117	38 ± 22		9-21	15 ± 3		8-41	15 ± 8	
Arsenic	1	10-104	43 ± 26		1.1-1.7	1.5 ± 0.2		1.6-2.2	1.9 ± 0.2	
	2	26-131	75 ± 34		1.6-2.9	2.1 ± 0.5		0.6-1.5	1.4 ± 0.2	
	3	7-228	95 ± 80		0.9-7.8	2.8 ± 2.8		0.6-1.6	1.1 ± 0.4	
	1-3	7-228	67 ± 52		0.9-7.8	2.1 ± 1.6		0.6-2.2	1.4 ± 0.5	

* 0 cm; n=15,10,10 (Barriers 1,2,3); 80 cm and Background, n=5.

Table 2. Comparison of overall amounts (mg/kg, dry weight) of copper, chromium, and arsenic in soils.

Element	Sample Location	Average	QUANTILES				
			MIN	25%	50%	75%	MAX
Copper	Under Barriers (n=35)	81 ± 62	13	34	69	112	291
	80 cm From Barriers (n=15) Background (n=15)	16 ± 8 20 ± 17	9 8	11 10	13 11	20 30	31 54
Chromium	Under Barriers (n=35)	38 ± 22	13	25	31	42	117
	80 cm From Barriers (n=15) Background (n=15)	15 ± 3 15 ± 8	9 8	12 11	15 12	18 16	21 41
Arsenic	Under Barriers (n=35)	67 ± 53	7	31	48	87	228
	80 cm From Barriers (n=15) Background (n=15)	2.1 ± 1.6 1.4 ± 0.5	0.9 0.6	1.6 0.9	1.7 1.4	2.0 1.7	7.8 2.2

RESULTS AND DISCUSSION

The results, shown in Table 1, is a comparison of the range, average and standard deviation in the Cu, Cr, and As contents in the soil samples taken directly under the barriers (0 cm), 80 cm laterally displaced from the barriers, and from the background locations. This comparison shows that the Cu, Cr, and As are noticeably elevated in the samples taken directly under the barriers. These increases are statistically different ($p < 0.05$) for each sample set for a particular barrier (barrier 1, 2, or 3) as well as the for the combined data (barriers 1-3) when compared to the samples taken 80 cm away and at background locations. In all cases the Cu and Cr levels in samples taken 80 cm away from the barriers were statistically equivalent compared to the background amounts. The differences in the arsenic levels were not significant in the sample set for barrier 3, and the combined sample set (barriers 1-3) taken at 80 cm and background. In the sample set at 80 cm for barrier 1 the arsenic level was less than the background. The difference in arsenic for the barrier 2 set at 80 cm compared to background was significantly different but minor in amount (2.1 ± 0.5 mg/kg and 1.4 ± 0.2 mg/kg). These results indicate that the observed elevation of the preserving elements may be localized to a very narrow zone beneath the barriers. In other words the lateral movement at the surface is minimal. Finally, statistical analysis of the amounts of each element (Cu, Cr, or As) between barriers showed that the As level under barrier 1 was significantly lower than that under barriers 2 or 3, and that amounts of Cu and Cr were not different under any of the barriers.

Also shown in Table 1 is the great deal of variability in the data between samples taken at 0 cm at a particular site as evidenced by the large range and standard deviation of the Cu, Cr, and As levels. The variability within a particular (replicate) sample was, however, $<5\%$ indicating that the sampling and mixing methods employed achieved good homogeneity. Some of causes for high intrabarrier variability could be caused by differences in the depth of the gravel overburden, the soil depth of the sample, in the water flow through the rock and into the soil. High variability within a sample site was also noted in soils under decks (Stilwell and Gorny, 1997).

Shown in Table 2 are the combined data for all soil samples (barriers 1-3) ranked by quartiles. These results further illustrate the local increases in the Cu, Cr, and As in samples under the barriers, compared to those taken nearby. The highest amounts of the Cu and Cr in the samples located 80 cm from the barrier are less than 75% of the amounts found under the barrier. Also the highest amount of arsenic in both the 80 cm and background samples are less than or nearly equal to the minimum amount of arsenic found in soils under the barrier.

Elemental ratio analysis can be used to suggest the major pathway responsible for the observed increases. If the background corrected ratio in the soil follows that in the wood, then physical wearing or sawdust generated during construction could be the cause. However, in leaching trials, Cu and As have been shown to leach out

much more readily than Cr (Aceto and Fedele, 1994; Warner and Solomon, 1990). So a relative depletion in Cr, all else equal, would suggest leaching (Stilwell and Gorny, 1997). The relative amounts of Cu, Cr, and As in pressure-treated wood is nominally 1: 1.7: 1.5 (Warner and Solomon, 1990), while the average background subtracted ratio in the soil samples directly under the barriers was 1: (0.4±0.3): (1.5±1.2). The background soil was 1:(0.9±0.3):(0.1±0.04). Thus, the suggested pathway for the observed increase is leaching, since the relative amount of Cr in the soil is less than that originally in the wood. This analysis confirms the hypothesis mentioned earlier that leaching was the most likely mechanism, since any particles of wood would be trapped by the gravel overburden.

Regardless of the pathway leading to the increase, the source of the variability in the data, and the rapid decrease in amount, the As level in 34 of the 35 samples taken directly under the barriers exceeded the State regulatory limit of 10 mg/kg (State of Connecticut, 1996), while in all of the samples taken 80 cm away and in all of the background samples the As levels did not exceed the 10 mg/kg limit. None of the samples exceeded the limit for Cu (2500 mg/kg) or for trivalent Cr (3900). The limit for hexavalent Cr, 100 mg/kg, was possibly exceeded in 1 of the 35 samples. However, under normal conditions any chromium leaching from the wood is expected to be, initially, in the trivalent oxidation state (Felton and DeGroot, 1996).

Though elevated in As, we believe that these soils present few health risks since the sound barriers, in many cases, are away from residential areas and the soil under the gravel overburden (6-12" of gravel) would be unlikely to be disturbed.

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