EFFECT OF NON-VEHICULAR SOURCES ON HEAVY METAL CONCENTRATIONS OF ROADSIDE SOILS

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Abstract. Soils along highway environments typically contain high concentrations of heavy metals because of non-point contamination sources, most commonly vehicle exhaust and wear of vehicle parts. Pb, Zn, Cu, Cr, Sb, Ba and Ra concentrations of soils along roadways with very low traffic volumes in a rural portion of San Patricio County, Texas, have been studied in order to distinguish the effects of a point source (an industrial waste landfill) from the effects of traffic. The highest concentrations of Zn, Cr, Sb, Ba and Ra were detected in soils along the access road to the landfill. The association of high Ba values with high Ra values suggests that the most probable sources of this contamination were oilfield waste from storage tank bottoms, which were disposed of in landfill waste pits and were also spread over roads within the landfill to decrease dust. Outside the landfill along a different roadway, a second contamination area which was characterized by very high Ba but low Sb and Ra concentrations compared to background values, has been detected. Drilling mud spill is the most probable source of this contamination.

The contaminations caused by these two point sources differ from typical vehicle-sourced contamination in two ways: their areal extent was limited and contaminants were not typical for highway environments (like Ba and Ra). Like vehicular contamination, however, these areas were confined to the immediate vicinity of the roadways. Another difference is that Pb in most vehicle-contaminated areas is strongly bound to the soil constituents, mostly organic matter, whereas the point source Pb was found to be readily exchangeable and to have no association with organic matter.

Keywords: contamination, heavy metals, organic matter, point source, roadside soil

1. Introduction

The major source of high heavy metal concentrations in the soils can be metal rich source rock, atmospheric pollution from motor vehicles, combustion of fossil fuels, agricultural fertilizers and pesticides, organic manures, disposal of urban and industrial wastes, as well as mining and smelting processes (Alloway, 1990). There have been many studies reporting high concentrations of heavy metals especially in soils along highways (Vandenabeele and Wood, 1972; Ward *et al.*, 1975; Wheeler and Rolfe, 1979; Gratani *et al.*, 1992; Teichman *et al.*, 1993; Gibson and Farmer, 1984; Hamilton *et al.*, 1984; Harrison, 1987; Hewitt and Candy, 1990; Al-Chalabi and Hawker, 2000). It is generally assumed that these contaminants are of non-point source origin, coming mostly either from vehicle exhausts or from the abrasion of vehicle parts or tires (Sansalone and Buchberger, 1997). The concentrations can

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reach up to 1980 ppm (Pb) and 1426 ppm (Zn) in the top 15 cm of the soil immediately adjacent to the roadways (Turer *et al.*, 2001). These concentrations decrease with depth but increase as the amount of organic C increases in the soil. Since highway environments are a relatively constant source of anthropogenic organic matter (from vehicle exhaust emissions (Kleeman *et al.*, 2000) and asphalt paving materials (Faure *et al.*, 2000)) beside heavy metals, heavy metals will continue to remain bound to this insoluble organic matter *in situ* unless metals are re-mobilized mechanically, for example as wind-blown dust. Another mechanism could be surface run-off carrying the metals into surface drainage, bypassing the soil (Turer *et al.*, 2001). In lateral pavement sheet flow from an area of 15 m × 20 m on I-75 in Cincinnati, Zn, Cd, Cu were determined to be mostly in dissolved form while Pb, Fe and Al were particulate-bound (Sansalone and Buchberger, 1997).

In this paper, some characteristics of roadside soil contamination resulting from a point source are presented in order to show how this source can be discriminated from those associated with vehicles. For this purpose, a contaminated site near Corpus Christi, Texas, where a previous study on non-point source metal contamination had been carried out by Turer and Maynard (2003), was chosen. The study area has a traffic volume considered to be too low for a significant vehicular source, but with a potential industrial point source from a landfill that has accepted large amounts of oilfield waste. South Texas oilfield operations are characterized by high radioactivity (Fisher, 1995), which provided a potential fingerprint for tracking this source of contamination. In this study use of Ba concentrations, as a proxy for Pb as a tracer for vehicle emissions, as suggested by Monacı and Bargaglı (1997), was tested since oilfield wastes were accepted at the landfill and provided a possible point source for Ba contamination.

2. Study Area

The Sinton Waste Disposal Center (SWDC) landfill is located in San Patricio County north of Corpus Christi, Texas. It lies 1.75 miles west of the intersection of FM 1945 and Texas Highway 77, about 3 mi SW of the town of Sinton. Samples were collected along FM 1945, CR 36a, CR 39, CR 43, CR 43a, CR 43b and CR 38a as shown in Figure 1.

Such materials as municipal solid waste, paint wastes, oil and water based drilling muds, petroleum tank bottom wastes, and plant process wastes have been deposited in the SWDC over time (Woodward-Clyde Consultants, 1992).

2.1. OILFIELD WASTES

Oilfield wastes are known to contain NORM (naturally occurring radioactive materials) which are associated with Ba (Testa *et al.*, 1994; Hebert *et al.*, 1995; Spitz *et al.*, 1997). NORM occurs in produced water; in sludges, sands and mineral scale precipitated in pipes, valves or gauges; as thin platings on the inner surfaces of

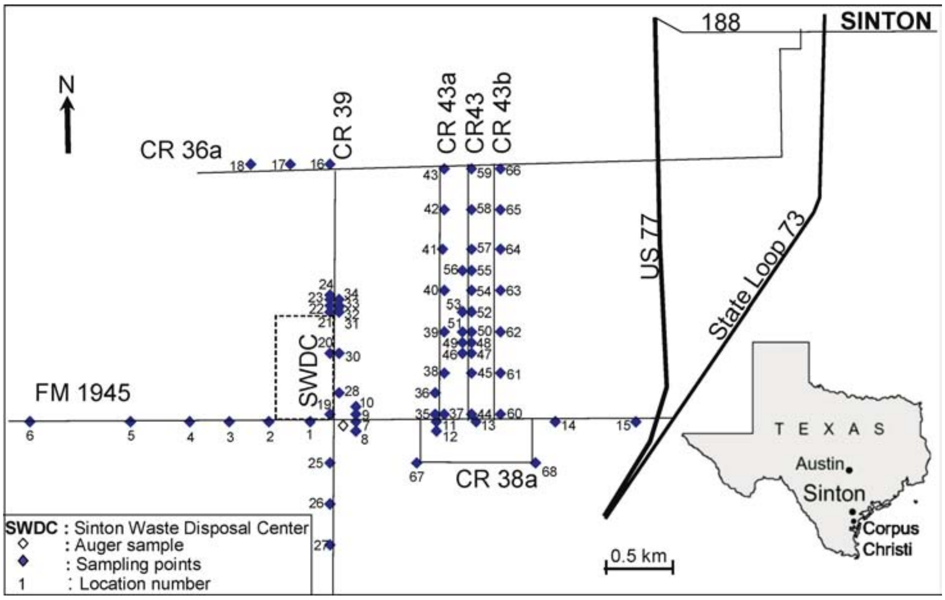

Figure 1. Location of the study area.

gas processing and transporting equipment; or as gas (Smith, 1987; Baird *et al.*, 1990; White, 1992). Because of their chemical similarity, Ba and Ra occur together in oilfield waste. In produced water, scale and sludge accumulations, most of the NORM radioactivity is caused by ^{226}Ra and ^{228}Ra. In gas processing facilities ^{210}Pb can accumulate as a thin plating on the inner surfaces of pipes. These radioactive isotopes are members of the ^{238}U and ^{232}Th decay series (Fisher, 1995).

To determine the likely mineral type of the scale that Ra would incorporate, Langmuir and Riese (1985) estimated the distribution coefficients for Ra in anhydrite ($CaSO_4$), celestite ($SrSO_4$), anglesite ($PbSO_4$), barite ($BaSO_4$), aragonite ($CaCO_3$), calcite ($CaCO_3$), strontianite ($SrCO_3$), and cerussite ($PbCO_3$). Based on the distribution coefficients and the Ca, Sr, Ba and Pb amounts in typical formation waters, two Ba minerals, barite and celestite, were shown to be the scale minerals that would preferentially incorporate significant amounts of Ra. Most of the Texas formation waters are reported as saturated with barite, rather than celestite, leaving barite as the most likely mineral to precipitate Ra in significant amounts (Fisher, 1995).

A study from a former well site in the Martha oil field in Kentucky by Spitz *et al.* (1997) showed that spreading sludge from the bottom of tank batteries used for separating water and sediment from crude oil and brine waste (produced during water injections to old wells to increase productivity) over the ground to encourage microbacterial digestion of the wastes is responsible for distributing Ra – bearing material in soil and streams. Ba/$RaSO_4$, which is known to be insoluble in pipe scale, was suggested as being in a more soluble form in soil and water where it will become available for uptake in the food chain. Also in this study high As and Pb values were measured in water samples (max: 84.9 and 16.2 ppb respectively) showing an association of these two elements with oilfield waste.

3. Methods

68 roadside soil samples were taken with a trowel at a depth of 0–5 cm and 1 auger sample was taken down to 55 cm. For the auger sample sampling intervals were 0–5, 5–15, 15–25, 25–35, 35–45 and 45–55 cm.

A variety of instrumentation methods were applied for various aspects of the research: C-S analyzer (LECO) was used to find the percentage of organic C in the soil. Organic C was measured on acidified samples: First, 50 mL of 1 N HCl was added to 0.5 g of sample. Next, the sample was left on a hot plate at 60 °C for 12 h. 50 mL of distilled water was then added to stop the reaction. The solution was filtered through a glass filter and the residue was rinsed with distilled water to remove all acid. Finally, the sample was dried for at least four hours and analyzed with LECO.

To determine the amount of heavy metals in different fractions of the soil 2 g of dry soil sample were placed into a labeled centrifuge tube and the following procedure was applied (Sposito *et al.*, 1982):

- 25 mL of 0.5 M KNO_3 was added and shaken for 16 h (Exchangeable fraction)
- 25 mL of distilled H_2O was added and shaken for 2 h (Adsorbed fraction)
- 25 mL of 0.5 M NaOH was added and shaken for 16–21 h (Organically bound fraction)
- 25 mL of 0.05 M Na_2EDTA was added and shaken for 6 h (Carbonate bound fraction)
- 25 mL 4 M HNO_3 added and heated (70–80 °C oven) for 16–21 h (Residual fraction)

After each step the sample was centrifuged and filtered through a Whatman # 42 into a nalgene bottle. The solutions were refrigerated and analyzed with Atomic Absorption Spectrometry (Perkin-Elmer 3110).

The heavy metal concentrations of the soils were determined with neutron activation and inductively coupled plasma by XRAL Laboratories of Toronto and Ra measurements were carried out by Envirotest (formerly Corelabs) of Casper WY by gamma-ray spectroscopy.

4. Results

The maximum heavy metal, Ba and Sb concentrations obtained from the study site were as follows: Cr: 73 ppm (along CR 39), Zn: 279 ppm (along FM 1945), Pb:

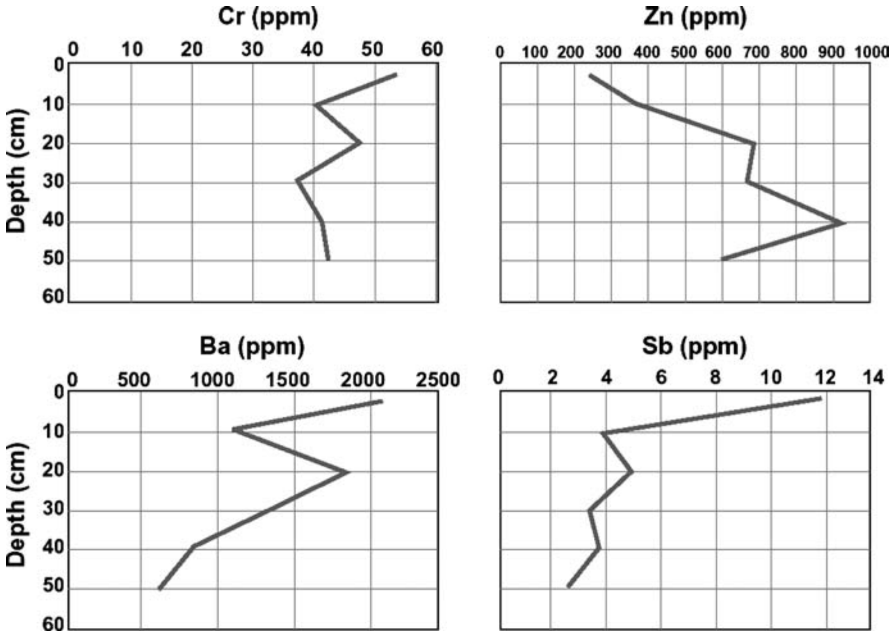

Figure 2. Depth vs. Cr, Zn, Ba and Sb for a sample from 1945-2.5 with 0–5, 5–15, 15–25, 25–35, 35–45 and 45–55 cm sampling intervals (for location see Figure 1).

70 ppm (along FM 1945), Ba: 15 800 ppm (along CR43) and Sb: 31 ppm (along FM 1945) (Table I). The depth profiles of Zn, Cr, Ba and Sb concentrations for an auger sample taken from FM 1945-2.5 (Figure 1), shows that, except for Zn, the metals decrease as depth increases (Figure 2). Zn, Cr, Ba and Sb concentrations obtained along the edge of FM 1945 also show a decreasing trend with distance from the road (exceptions were Zn concentrations at FM 1945-2.6 and Pb concentration at FM 1945-3) (Table II).

The highest concentrations of Zn and Sb were obtained from the samples collected along the SE corner of the landfill (Figures 3 and 4). The Ba concentrations at this location were also high, but the highest concentrations were at CR43 (Figure 5).

The Ba and Sb concentration maps indicate that there seems to be two different sources for these high concentrations. One of the sources is SWDC which is associated with high Ba, Sb and also Ra concentrations. The other source is associated with high Ba, but low Sb. Cluster analysis was applied to determine if there was any difference between the two sources regarding a relationship between the heavy metals, Ba and Sb. For this assessment, samples were grouped into three depending on their Ba and Sb concentrations. Samples having Sb concentrations greater than 5 ppm (9 samples) were named as Group I, samples with high Ba and low Sb concentrations (3 samples) were named as Group II and the remaining 46 samples were assumed to represent background values (Group III). Cluster analysis of Group I

TABLE I

Organic content, heavy metal, Ba and Ra concentrations around SWDC

Location #		Organic C	(ppm)						(pci/g)	
(Figure 1)	Sample name	(%)	Pb	Zn	Cu	Cr	Sb	Ba	Ra/226	Ra/228
1	*1945-1.0		24	63.6		48	1.4	280	<3.2	<2.5
2	*1945-1.5		29	70		42	1.2	590		
3	*1945-1.8		29	71.6		40	1.2	350	<0.6	3.8
4	*1945-2.0		51	130		42	1.5	560		
5	*1945-2.2		22	80.3		34	2.3	470		
6	*1945-2.4		37	165		51	9.6	910	2.6	2.2
7	*1945-2.6A		48	119		59	32	1300	<0.2	<1.3
8	*1945-2.6B		31	144		51	35	2200		
9	*1945-2.6F		40	183		65	18	2000	<0.2	1.6
10	*1945-2.6G		35	279		59	19	800		
11	*1945-3A		23	127		49	9.8	1500	<0.4	3.5
12	*1945-3B		70	106		27	0.9	410	<1.4	2.2
13	*1945-3.2		22	58.2		43	2.6	490		
14	*1945-3.6		23	72.9		47	3.2	690		
15	*1945-4		18	55		44	1.4	300	<0.2	3.9
16	CR36a-CR39 N	0.909	17	44	12	25	0.8	360		
17	CR36a02	0.809	11	25	8	19	0.6	490		
18	CR36A 0.4 0-5		12	32	9	24	0.7	510		
19	*CR39-0.0 05		33	121		73	13	1200	2.4	2.5
20	*CR39-0.3W		21	78.2		44	6	530	1	2.3
21	*CR39-0.5W		27	46		35	1.1	650	<0.3	2.3
22	*CR39-0.53W		14	28.3		38	1	220	<0.2	<0.3
23	*CR39-0.56W		21	46.3		32	1.1	320	<0.2	3.3
24	*CR39-0.58W		19	30.9		28	0.9	400	<0.2	2.7
25	CR3902-05	2.177	14	100	3	38	1.2	460		
26	CR3904-05	1.616	15	48	7	29	1.0	470		
27	CR3906-05	1.341	17	56	17	30	0.9	410		
28	CR39BFI-05	0.265	13	49	10	35	1.3	260		
29	CR39-0.0E								1.3 ± 0.3	
30	*CR39-0.3E		27	114		46	5.7	520	2.1	3.4
31	*CR39-0.5E		13	36.9		30	0.9	290		
32	*CR39-0.52E		14	39.3		22	0.9	290		
33	*CR39-0.53E		22	102		51	2.50	320	<0.5	4.6
34	*CR39-0.56E		19	42.4		32	1.10	280		
35	*CR43A-0.0		38	124		50	4.00	710	0.2	4.3
36	*CR43A-1.0		26	44.8		27	0.70	360		
37	CR43a-0.0		21	88	17	34	1.3	450		
38	CR43a-0.2	1.477	25	40	15	25	0.8	370		

(*Continued on next page*)

TABLE I

(*Continued*)

Location # (Figure 1)	Sample name	Organic C (%)	(ppm)						(pci/g)	
			Pb	Zn	Cu	Cr	Sb	Ba	Ra/226	Ra/228
39	CR43a-0.4	1.53	22	54	14	30	0.8	340		
40	CR43a-0.6	2.343	30	54	21	30	0.7	320		
41	CR43a-0.8	1.176	24	46	14	26	0.7	220		
42	CR43a-1	2.22	23	54	14	29	0.8	260		
43	CR43a-1.2	1.676	15	44	14	27	0.7	390		
44	CR43-0.0	2.218	19	67	22	42	2	370		
45	CR43-0.2	2.456	19	52	13	26	0.6	440.0		
46	CR43-0.3W		51	42	14	48		518		
47	CR43-0.3E		26	60	14	63		738		
48	CR43-0.35E		9	51	8	26		55173	1.7 ± 0.3	
49	CR43-0.35W		12	46	6	53		51114		
50	CR43-0.4	2.295	22	54	12	27	0.6	15800	1.0 ± 0.4	
51	CR43-0.4W		11	48	7	49		46520		
52	CR43-0.5E		19	44	10	75		1400	1.4 ± 0.3	
53	CR43-0.5W		21	58	11	52		1179		
54	CR43-06	1.423	18	56	13	31	0.8	990.0		
55	CR43-0.7E		20	56	14	68		485		
56	CR43-0.7W		33	68	14	44		774		
57	CR43-08		24	55	16	29	0.8	770.0		
58	CR43-1	2.642	22	54	13	29	0.8	380.0		
59	CR43-1.2	2.533	25	58	16	35	0.9	410.0		
60	CR43B-0.0	3.155	16	66	11	36	1.3	280		
61	CR43B-0.2	3.806	11	31	4	33	0.6	340		
62	CR43B-0.4	2.698	14	34	5	25	0.6	380		
63	CR43B-0.6	2.679	14	38	5	30	0.6	400		
64	CR43B-0.8	1.669	14	29	4	26	0.6	290		
65	CR43B-1.0	3.258	10	30	3	25	0.6	380		
66	CR43B-1.2	1.754	18	48	9	26	0.6	280		
67	CR38a-0.2	2.133	13	51	14	29	0.7	220.0		
68	CR38a SE	1 138	15	35	15	24	0.6	230.0		

[*] Cd < 1.

showed that there was an association between Pb and Zn (0.57) and with a lesser degree of clustering (0.47) between Ba and Sb. Cluster analysis of the Group III, background samples, did not show any strong association between heavy metals, Ba and Sb concentrations. Since there were not enough samples in Group II, it was not possible to apply cluster analysis to this group.

When organic C content of the soils cross plotted with the Pb, Zn, Ba, Sb, Ni and Cr concentrations of the soils, unlike the strong correlation found for Corpus

TABLE II

Change in concentrations with distance from the road

	(ppm)				
Sample name	Ba	Sb	Zn	Pb	Cr
1945-2.6A (South edge of the road)	1300	32	119	48	59
1945-2.6C (Ditch at south of the road)	670	5.3	127	23	45
1945-2.6F (North edge of the road)	2000	18	183	40	65
1945-2.6G (Ditch at north of the road)	800	19	279	35	59
1945-3A (South edge of the road)	1500	9.8	127	23	49
1945-3B (Field 10 m south of the road)	410	0.9	106	70	27

Ni < 50 ppm for all samples.

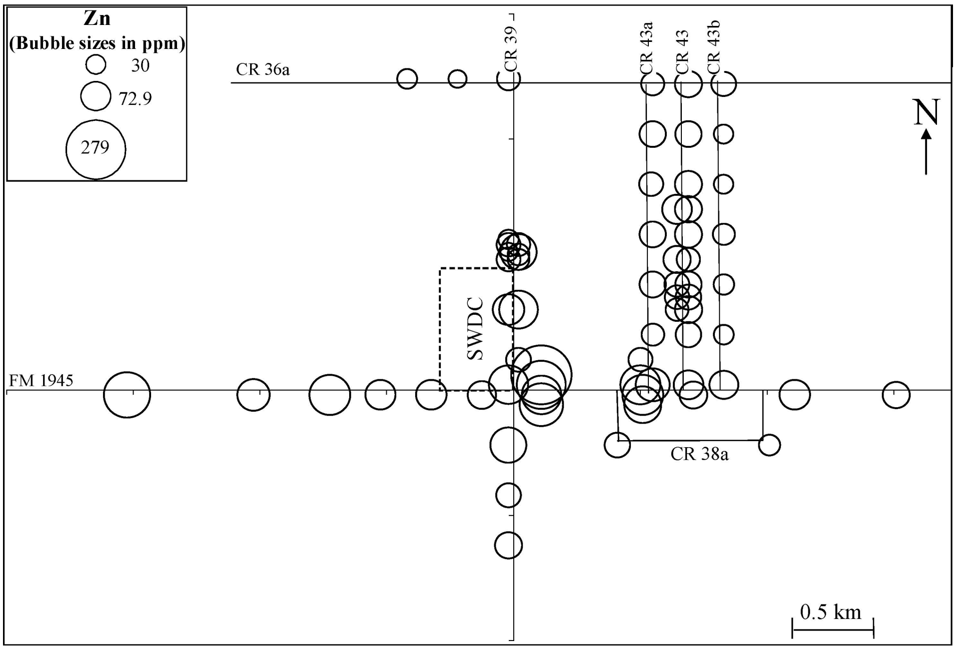

Figure 3. Map of Zn concentration.

Christi (Turer and Maynard, 2003), no relationship was found between organic C content and heavy metal concentrations of the soils in Sinton.

Sequential soil extraction procedure was applied to 5 soil samples. The metal amounts in exchangeable fractions (the most easily mobilized fraction) were low except for Pb. On average only 0.7% of Zn, 0.0% of Cu, 8.1% of Ni and 7.5% of Cr was exchangeable, but 83% of Pb was in exchangeable fraction. The percentages for the other fractions can also be seen in Table III.

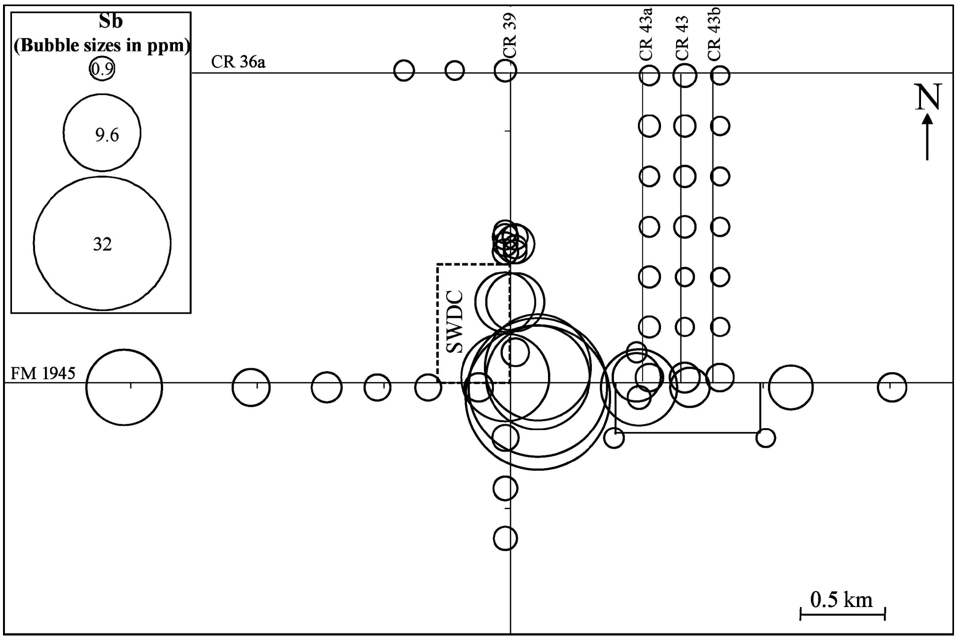

Figure 4. Map of Sb concentrations.

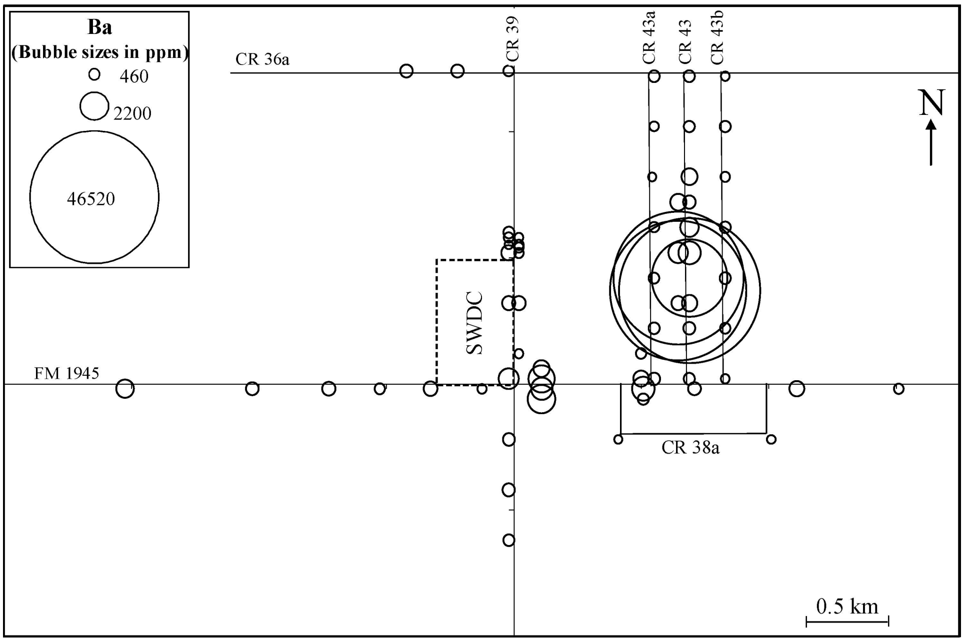

Figure 5. Map of Ba concentrations.

TABLE III

Results of sequential soil extraction

Sample name	Exchangeable	Absorbed	Organically bound	Carbonate bound	Residual
Pb (%)					
CR 39 NE CORN. 05	64.50	0.00	0.00	32.30	3.20
CR 39@ FM 1945 515	50.00	0.00	0.00	0.00	50.00
CR 43 04 05	100.00	0.00	0.00	0.00	0.00
CR 43 06 05	100.00	0.00	0.00	0.00	0.00
CR 43 08 05	100.00	0.00	0.00	0.00	0.00
Ni (%)					
CR 39 NE CORN. 05	3.70	3.70	29.60	14.80	48.10
CR 39 @ FM 1945 515	12.50	4.20	29.20	20.80	33.30
CR 43 04 05	7.10	0.00	35.70	21.40	35.70
CR 43 06 05	6.30	0.00	37.50	31.30	25.00
CR 43 08 05	11.10	5.60	33.30	22.20	27.80
Zn (%)					
CR 39 NE CORN. 05	0.60	0.60	4.60	26.30	68.00
CR 39 @ FM 1945 515	0.40	0.40	4.00	21.10	74.10
CR 43 04 05	0.00	0.00	7.30	14.60	78.00
CR 43 06 05	2.80	2.80	2.80	16.70	75.00
CR 43 08 05	0.00	0.00	3.00	12.10	84.80
Cr (%)					
CR 39 NE CORN. 05	5.30	0.00	5.30	15.80	73.70
CR 39 @ FM 1945 515	6.30	6.30	12.50	12.50	62.50
CR 43 04 05	7.70	7.70	15.40	15.40	53.80
CR 43 06 05	9.10	0.00	9.10	9.10	72.70
CR 43 08 05	9.10	0.00	9.10	9.10	72.70
Cu (%)					
CR 39 NE CORN. 05	0.00	0.00	36.40	9.10	54.50
CR 39 @ FM 1945 515	0.00	0.00	54.50	9.10	36.40
CR 43 04 05	0.00	0.00	33.30	0.00	66.70
CR 43 06 05	0.00	0.00	25.00	0.00	75.00
CR 43 08 05	0.00	0.00	20.00	0.00	80.00

5. Discussion

The soil samples collected along the main approach roadway to the SWDC (FM 1945), have higher Cr, Zn, Pb and Sb concentration than the ones collected along the smaller roadways that do not receive truck traffic (Table I), or those collected on FM 1945 beyond the landfill entrance. When the average heavy metal, Ba and

TABLE IV

Average heavy metal, Ba and Sb concentrations

	(ppm)				
	Ba	Sb	Zn	Pb	Cr
Group Name					
Group I	1218	16.5	148	33	55
Group II	5853	0.7	55	21	29
Group III	385	1.1	56	21	33
*Soils of United States (average)	580	0.66	60	19	54

*Shacklette, H.T. and Boerngen, J.G.: 1984.

Sb concentrations in these soils for the different groups are compared with corresponding average values for soils from the United States (Table IV) it can be seen that Group I had higher averages for all of the contaminants than U.S. averages. Group II had higher average Ba concentration and Group III had higher average Sb concentration than the U.S. average.

In the Sinton area, there is no relationship between heavy metal and organic C concentrations in the soil. Previous studies carried out on Corpus Christi (Turer and Maynard, 2003) and Cincinnati (Turer *et al.*, 2001) highway soils, however, showed a strong positive relationship between heavy metal and organic C concentrations: as the amount of organic C increased, heavy metal concentrations also increased. Also, in both Corpus Christi and Cincinnati soils, the mobility of Pb was found to be very low (Turer and Maynard, 2003). In the Sinton area, however, 83% Pb was exchangeable. The differences could be explained with the difference in the source of contamination. Pb in Corpus Christi and Cincinnati was vehicular in origin and was bound to insoluble organic matter. Pb in the Sinton area must have come from another source of contamination and was not bound to organic matter.

The increase in Zn concentrations as depth increases, opposite to that of Ba and Sb, could be explained with much higher solubility of $ZnSO_4$ compared to $BaSO_4$ (Brookins, 1988) and hence can leach further down profile than other heavy metals.

The high concentrations of Ba, Sb at the entrance of the SWDC suggests that the source of this contamination in SWDC. Association of high Ra values with Ba suggests that oilfield waste is responsible for these high concentrations. The common process of spreading tank bottoms on the road to decrease dust is known to have been applied at SWDC (letter of Oct 29, 1980 from Texas Dept of Health to operators of SWDC). These tank bottoms contain high Ra concentrations associated with $BaSO_4$ (Wascom, 1994). During transportation of the wastes to the SWDC, tires of the trucks may have picked up the contaminants from the roadways inside the facility, and carried them to the outside of the SWDC border. Why Sb is associated with Ba and Ra in this contamination area is not known, but may be related to the

TABLE V

Heavy metal, Ba and Sb concentrations in drilling mud barites (Turer, 2000)

	(ppm)					
Drilling mud barites	Ba	Sb	Zn	Pb	Cr	Ni
7460B (Nevada)	>10000	0.3	<0.5	<2	12	<50
7461A (Nevada)	>10000	0.8	2	<2	5.4	<50
7462 (Nevada)	>10000	0.3	<0.5	<2	12	<50
7353 (Arkansas)	>10000	<0.1	<0.5	<2	11	<50
7354 (Arkansas)	>10000	0.6	5	4	44	<50
7355 (Arkansas)	3400	1.6	145	16	160	120
7357 (Arkansas)	>10000	0.4	36.3	8	22	<50
7361 (Arkansas)	>10000	0.2	<0.5	<2	9.5	<50

paint waste disposed at the site along with the oilfield waste. The Zn contamination may have formed as a result of transport and disposal of smelter waste at SWDC.

The high Ba concentrations along CR43, however, may have come from a spill of barite-rich drilling mud on the road during a separate process, probably oil drilling operations unrelated to the SWDC operation. The heavy metal, Ba and Sb concentrations obtained from 9 drilling mud barite samples show high Ba, but low Sb values (Table V). In addition, these samples showed no detectable radiation from radium. Thus these barites seem quite distinct from those found within the landfill.

6. Conclusion

Heavy metal, Sb, Ba and Ra concentrations on roadways in a rural portion of San Patricio County, Texas, have been studied to discriminate effects of a point source (an industrial waste landfill) on roadside soils from effects of traffic. Ba, Sb, Zn, Cr and Ra concentrations obtained from the soils along the road leading to the landfill were particularly high near the entrance to the landfill. Association of high Ba and Ra values suggest that the most probable source of this contamination is sludge from tank bottoms, which were known to have been spread over the landfill to decrease dust. A second point source, outside the landfill, was characterized by very high Ba but low Sb and Ra values and was possibly a drilling mud spill.

The areas of contamination caused by these two point sources differ from typical vehicle-sourced contamination in two ways: their areal extent was limited and they contained high concentrations of contaminants which are not typical for highway environments. The two areas of contamination found were 1/2 and 1/4 mile across. Like vehicular contamination, however, these areas were confined to the immediate vicinity of the roadways. By contrast, vehicle-sourced contamination in the city of Corpus Christi extends along the roadways for several miles with only minor changes in concentration. The point sources that were studied were both characterized by much higher Ba concentrations than those found in vehicle-sourced contamination, and one source was also characterized by high Sb and Ra, neither of which was associated with vehicular contamination. Another difference was that Pb in the vehicle-contaminated areas was strongly bound to the soil constituents, mostly organic matter, whereas the point source Pb was found to be readily exchangeable and to show no correlation with organic carbon content.

Monaci and Bargagli (1997), on the basis of a very significant relationship between normalized concentrations of Pb and Ba and the presence of the latter element in diesel and unleaded gasoline, recognized Ba as a valuable tracer for vehicle emissions in place of Pb. Results of this study, however, show that caution must be taken when using Ba as a proxy for Pb especially in areas of petroleum operations (like Texas), since soil could have high Ba unrelated to vehicular emissions.

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