

Cadmium in Forest Ecosystems Around Lead Smelters in Missouri

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The development of Missouri's new lead belt within the past decade has provided an excellent opportunity to study the dissemination and effects of heavy metals in a deciduous forest ecosystem. Primary lead smelters within the new lead belt have been identified as potential sources of cadmium as well as lead, zinc, and copper. Sintering and blast furnace operations tend to produce significant quantities of small particulates highly enriched in cadmium and other heavy metals. At one smelter, samples of stack particulate emissions indicate that as much as 0.21 lb of cadmium may be released to the atmosphere per hour. This is accompanied by 0.44 lb zinc, 4.66 lb lead, and 0.01 lb copper/hr. These point-source emissions, as well as a number of other sources of fugitive (wind blown) and waterborne emissions contribute to a significant deposition of cadmium in the surrounding forest and stream beds. Mobilization of vagrant heavy metals may be significantly increased by contact of baghouse dusts or scrubber slurries with acidic effluents emanating from acid plants designed to produce H_2SO_4 as a smelter by-product. Two separate drainage forks within the Crooked Creek watershed permit some comparisons of the relative contributions of cadmium by air-borne versus water-borne contaminants. Cadmium and other heavy metals have been found to accumulate in the forest litter and partially decomposed litter along stream beds. Greater solubility, lower levels of complexation with organic ligands in the litter, and greater overall mobility of cadmium compared with lead, zinc, and copper result in appreciable contributions of dissolved cadmium to the watershed runoff. The present paper attempts to define the principle sources and current levels of heavy metal contamination and summarizes the efforts undertaken by the industry to curtail the problem.

Introduction

During the First International Cadmium Conference held in San Francisco, California in February 1977 (1), the principal sources of environmental cadmium were identified as: (a) the primary mining, milling and smelting of nonferrous metals and (b) secondary processing and recycling operations. Several reports (2-4) emphasized that cadmium is primarily a by-product of zinc production, with minor recovery during lead smelting. Dugdale and Hummel (5) presented data on the dissemination of cadmium and other heavy metals from the primary lead smelter at Belledune Harbor in New Brunswick, and discussed the metallurgy of cadmium within the conventional Imperial lead smelting process.

For the past ten years, a team of investigators (6) has studied the dissemination of heavy metals from the mines, mills and smelters of Missouri's new lead

belt (Fig. 1). The recent and rapid industrial development within the Clark National Forest, a vast deciduous oak-hickory forest, has offered a unique opportunity to study the dissemination of heavy metals and environmental effects within this type of

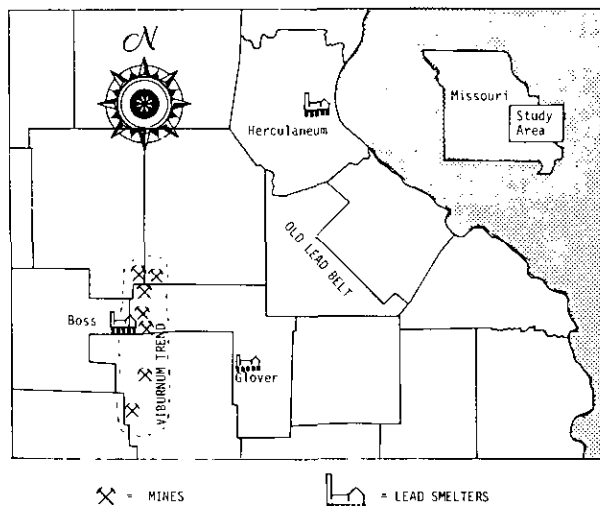


FIGURE 1. Missouri's new lead belt: the "Viburnum Trend."

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ecosystem. Presentation of data relative to the emission, deposition, and transport of cadmium in this geographic setting offers a useful comparison with past research efforts already cited, and, hopefully, may be useful in assessing the current environmental status of this potentially hazardous metal.

Industrial production within the "Viburnum Trend" or new lead belt of Missouri began in 1967. By 1976 there were seven mine-mill complexes and two smelters in production. Annual production of lead concentrates by the mines and mills now exceeds 500,000 tons, making this area the largest lead producing region in the world, accounting for approximately 82% of the total U. S. lead production (according to U. S. Bureau of Mines statistics) (6). Considerable quantities of zinc and copper ore concentrates are produced as by-products, and are shipped elsewhere for smelting. The combined design capacity of the two new lead belt smelters approaches 260,000 tons annually, necessitating ship-

ment of much of the lead concentrate to smelters outside the area.

Environmental Cadmium

There is little basis for environmental concern about vagrant cadmium from either the mines or mills of the new lead belt (6). Cadmium content of lead ore concentrates produced by the mills ranges from 0.005 to 0.2%, and current levels of exposure to workers or to aquatic ecosystems receiving process waters are not deemed hazardous. Lead smelters, on the other hand, have a more serious problem with cadmium and must deal with its control along with the more obvious emissions of lead and zinc. Figure 2 presents a flow sheet diagram for a typical primary lead smelter. Initially, a mixture of ore concentrate, sand, and limestone is ignited and roasted in the sintering or desulfurizing operation. PbS is converted to PbO in this process, and the latter is taken to a blast furnace and subsequently

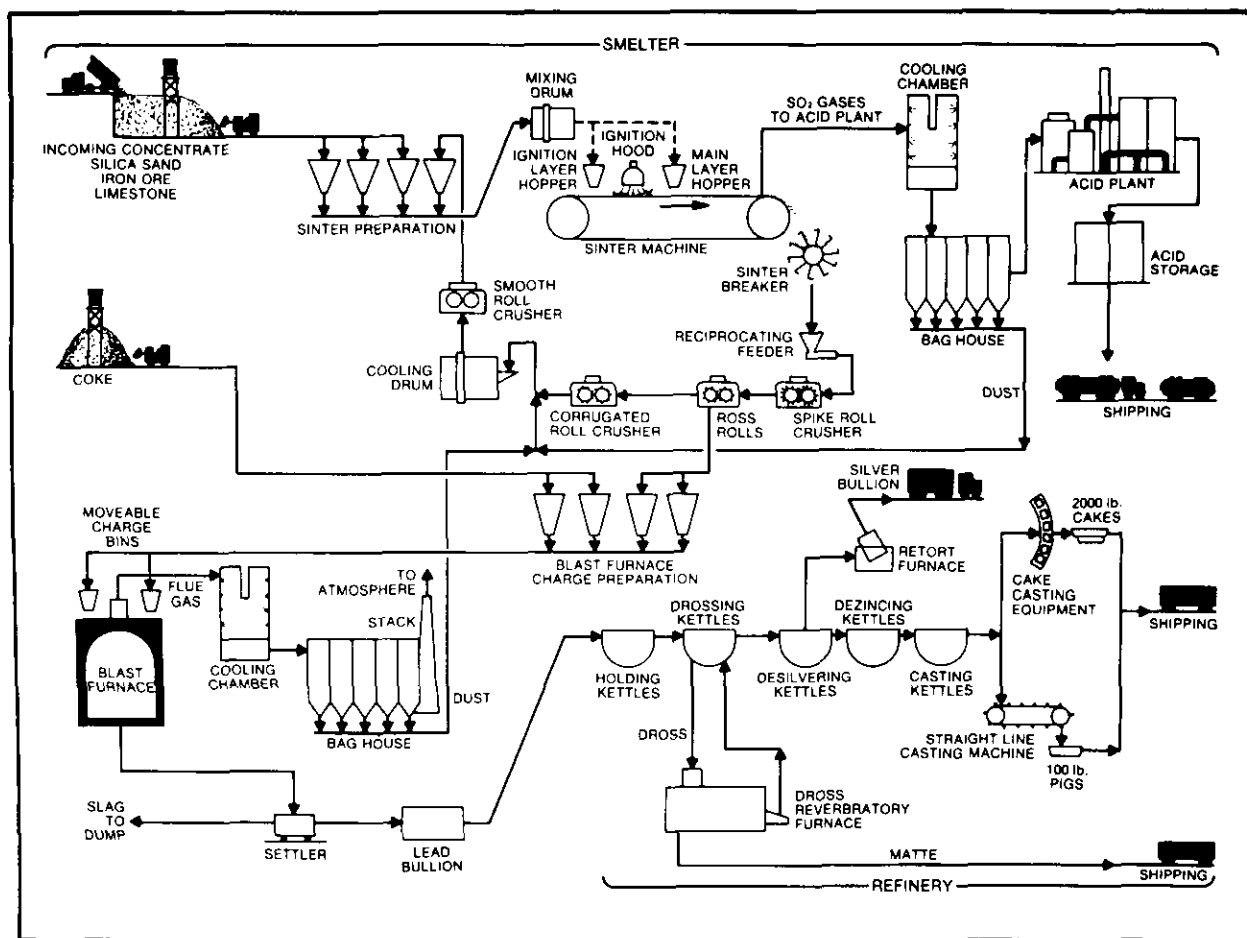


FIGURE 2. Flow sheet diagram for a typical lead smelter. Courtesy of AMAX-Homestake Lead Tollers.

reduced to produce metallic lead. Sulfur present in the ore concentrate is converted to SO₂ which is swept, along with strong updraft currents of air and suspended fine particulates, toward a cooling chamber and baghouse filter or Venturi scrubbers. Some smelters pelletize the sinter feed prior to roasting to reduce the quantity of fine particulate material suspended by updraft air currents.

Electrostatic precipitators may also participate with baghouse filters in removing particulates from sinter gases. The cleaned and cooled sinter gases are either released through a tall stack into the atmosphere, or in some smelters, the SO₂ is converted to sulfuric acid in a single or double-absorption contact acid plant.

The majority (75%) of the cadmium present in ore concentrates is volatilized at the temperatures employed during sintering, along with considerable quantities of lead (3). Particulate matter collected in the baghouse or scrubber slurry, enriched in cadmium, is periodically removed and cycled back to the sinter preparation area. A similar baghouse filter serves the blast furnace operation during which residual cadmium present in the PbO charge may be volatilized and subsequently condensed to form baghouse dusts. These trapped particulates are also routinely cycled back to the sinter preparation area. As others have already pointed out (5), there are no sinks for cadmium in this process, and its accumulation over an extended period will produce recycle dusts of relatively high cadmium concentration. A certain portion of finely divided particulates is not retained by the baghouse filters and escapes via the stack to the atmosphere, depending on the collection efficiency of the sinter gas filtering system.

Bolter's (7) analyses of baghouse dusts collected from new lead belt smelters illustrate this concentrating phenomenon (Table 1). Bolter showed that the ratio of Pb to Cd in ore concentrate is 4000:1,

and baghouse dusts may show cadmium enrichment by a factor of approximately 42 to 300-fold. Further size fraction of flue dusts indicated that cadmium concentrations are 10 to 15 times higher in the very fine particulates than in the coarser particulates present. Unfortunately, these very fine particles are those most likely to escape the baghouse and be swept to the stack for discharge to the atmosphere.

The concentrations of cadmium in the baghouse dust dictate special consideration of these hazardous materials. Concentrations of accumulated cadmium in baghouse dusts of zinc smelters are sufficient to permit recovery of the cadmium with some economic benefit. Baghouse material from lead smelters is only seldom treated to recover the concentrated cadmium. Accumulated cadmium is, for the most part, allowed to escape in the form of fine particulate matter from the stack scattered by fugitive emission during the handling, storing, and recycling of baghouse materials, or appears as impurities in smelter drosses. When old worn bag filters are removed and replaced, considerable dust adhering to the cloth material accompanies the bags to disposal sites. Each bag is approximately 25 to 30 ft long and may have as much as 10 to 20 lb of adhering dust. In some cases, the bags are cycled back through the sintering process, while some smelters haul them to land disposal sites. Careless selection of disposal sites or prolonged storage prior to recycling, subjecting such wastes to the leaching and erosion of rain and wind, may present a significant source of cadmium contamination to the surrounding environment.

Amax Lead Smelter

The larger of the two smelters now operating in the new lead belt is located at Boss, Missouri and is owned and operated by AMAX-Homestake Lead

Table 1. Heavy metals in baghouse dust from AMAX and ASARCO smelters.^a

Source of particulate material	Metal concn, ppm				Cd concentration factor
	Pb	Zn	Cu	Cd	
ASARCO					
Blast furnace, 3/74	268,000	126,000	3,150	59,500	298
Blast furnace, 2/73	352,000	105,500	4,440	47,000	235
Sinter plant, 3/74	272,000	12,480	13,100	30,700	154
Sinter plant, 2/73	248,000	11,900	7,300	32,000	160
AMAX					
Blast furnace, 2/73	666,000	56,000	4,200	8,300	42
Sinter plant, 2/73	619,700	4,100	400	9,400	47
Flue dust 2/73	623,000	62,200	5,500	19,500	98
Lead concentrate	783,400	23,000	4,900	200	1

^a Data of Bolter (7).

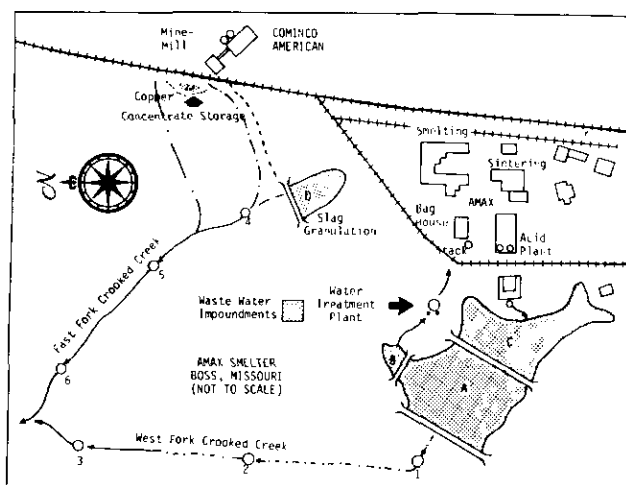


FIGURE 3. General layout of AMAX-Homestake Smelter and Crooked Creek watershed. Numbered circles indicate sampling sites on Crooked Creek.

Tollers, Inc. The general layout of the smelter and surrounding area is shown diagrammatically in Figure 3. Design capacity allows production of approximately 140,000 tons of lead annually. This smelter is located on a natural divide, at the extreme headwater area of the Crooked Creek watershed. Drainage from the area occurs through the east and west forks of Crooked Creek as shown in the diagram, flowing toward a confluence approximately 1 1/4 mile to the northwest. Crooked Creek continues to the north, joining the Huzzah Creek approximately 6 miles downstream, and eventually discharges to the Meramec River at a point approximately 30 miles from the smelter. Proposed construction of a dam across the Meramec River would create a reservoir which would possibly be affected by heavy metals in runoff from Crooked Creek.

The east fork of Crooked Creek drains an area which may receive runoff from the adjoining property of the Cominco American Mine-Mill complex as well as the AMAX smelter. Heavy metals may enter East Fork from a number of identified sources, including the overflow from the slag granulation pond, leachate from the industrial trash heap (where in the past many baghouse bags have been discarded), runoff from the railroad track (a major haulage route for ore concentrates), runoff from exposed copper concentrate piles stored on the adjoining Cominco American mine property, as well as stack and other fugitive particulate emissions. Past contributions of heavy metals and rock flour to East Fork have also been traced to seepage from Cominco American's mill tails piled near the tracks as a source of commercial agricultural lime.

Despite relatively high exposure to heavy metals,

the waters of East Fork generally support a fairly diverse biological community. Though the stream may be classified as a wet weather and disappearing stream, there are good stands of cattails in the marshy area immediately adjacent to the smelter trash pile, and during periods of flow, consistent algal growth extending some distance downstream. Further downstream, beyond the sampling station #5 (Fig. 3) as stream flow is somewhat consistent, standing populations of aquatic insects, tadpoles, and minnows are an indication of reasonable stream diversity.

Modification in the design of the agricultural lime storage area in 1975 eliminated an earlier problem. In 1977, the ore concentrate storage area at Cominco American was modified to contain all runoff and eliminate that source of heavy metals to East Fork. Much of the water flowing under the track and past the industrial trash heap has been diverted to flow southward into tailings lagoons designed to treat the mill effluents. Policies regarding disposal of baghouse materials by the smelter are currently under discussion to alleviate the obvious problems stemming from improper disposal of hazardous wastes.

The west fork of Crooked Creek receives effluents from the sanitary lagoon and the acid plant, as well as runoff from the concentrate storage area, the railroad tracks, and much of the smelter yard. Impoundment C was created in 1970, and existed until 1977 as the only sedimentation lagoon to treat industrial effluents and runoff.

Impoundments A and B and the water treatment facility were completed in 1977, with the ultimate goal of total recycle for all industrial effluent and runoff. However, total recycling has not yet been achieved. The acid plant has a relatively constant effluent with pH commonly between 2.2 to 3. Inefficient neutralization of this effluent has been a persistent problem, resulting in a long history of acidic effluents from impoundment C into the headwaters of Crooked Creek. The problem has been compounded by the extremely high heavy metal content of sediments in the impoundment. Sediments reflect significant runoff and erosion of concentrate storage piles. Recycling of the baghouse materials is usually achieved by truck (supersucker vacuum truck), as the accumulated dusts are periodically transferred from the baghouse to designated storage piles in the concentrate storage area. Cleanup of contaminated equipment was usually done at a convenient fire hydrant located immediately adjacent to the acid plant. Fugitive effluents from this procedure have contributed heavy metals to soils. Analyses of soil samples from the haulage route for these baghouse materials have shown evidence of fugitive heavy

Table 2. Heavy metals in soils and sediments near AMAX smelter acid plant.

Material analyzed	Metal concn. ppm			
	Pb	Zn	Cu	Cd
AMAX smelter yard soil sample near acid plant	274,000	65,000	9,860	4,930
AMAX smelter yard soil sample near acid plant	137,000	2,200	6,710	5,530
AMAX smelter yard soil sample near acid plant	25,150	1,490	3,370	9,010
Sediments from impoundment C taken near spillway. (average of 9 separate slices taken from 18 in. core sample) ^a	137,400	20,700	—	29,000
Dust adhering to baghouse bag in refuse pile	37,700	81,700	1,939	6,460

^a Data of McAllister (8).

Table 3. Stack particulate emissions from the AMAX lead smelter under normal operating conditions.^a

Test date	Emission rate ^b									
	Particulates		Lead		Zinc		Cadmium		Copper	
	Gr/DSCF	lb/hr	Gr/DSCF	lb/hr	Gr/DSCF	lb/hr	Gr/DSCF	lb/hr	Gr/DSCF	lb/hr
2/6/73	0.0122	20.87	0.0029	4.95	0.00027	0.47	0.00011	0.193	8.2×10^{-6}	0.0140
2/7/73	0.0240	38.69	0.0026	4.18	0.00016	0.339	0.00010	0.157	8.3×10^{-6}	0.0134
2/11/73	0.0111	25.80	0.0021	4.85	0.00021	0.495	0.00012	0.281	5.2×10^{-6}	0.0120
1973 avg. ^c	0.0158	28.45	0.0025	4.66	0.00021	0.435	0.00011	0.210	7.2×10^{-6}	0.0131
1975 avg. ^c	0.014	33.3								
1977 avg. ^c	0.037	87.0								

^a Data of Lowsley (9).

^b As grains per dry standard cubic ft and as lb/hr.

^c Unpublished data courtesy AMAX-Homestake Lead Tollers.

metals, including hazardous levels of cadmium (Table 2). Table 2 also shows heavy metals concentrations observed in a typical sediment core collected in the shallow waters near the effluent of impoundment C. The range of cadmium values in samples taken from different levels of the reported 18-in. core was 7,700 to 45,000 ppm. Combined conditions of high heavy metals in the sediments coupled with low pH of effluent has resulted in extraordinary levels of exposure of West Fork to adverse conditions.

As a consequence of industrial effluents, the headwaters of the west fork of Crooked Creek are devoid of biological activity for some distance downstream. Below sampling station #2, or within approximately 1/2 mile, the stream begins to recover, and persistent growths of algae have been observed. Dominant algal forms were of the genus *Hormidium*, renowned for its resistance to heavy metals, especially zinc.

Both forks of Crooked Creek also receive undetermined quantities of heavy metals resulting from horizontal transport of aerially deposited particulates collected and concentrated in forest litter, but originally emanating from the stack and other fugitive sources within the workyard.

Cadmium and other heavy metals may escape the baghouses and be released to the atmosphere. Early studies involving actual stack sampling procedures gave some indication of the quantities of lead, zinc,

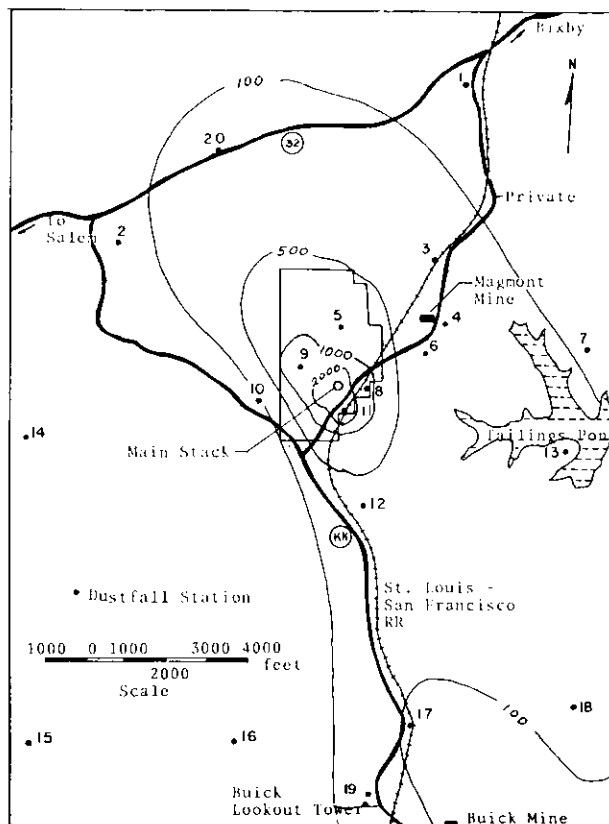


FIGURE 4. Radial distribution of settleable particulate lead in the vicinity of the AMAX smelter. Deposition rate is expressed as milligrams per square meter per month. After Lowsley (9).

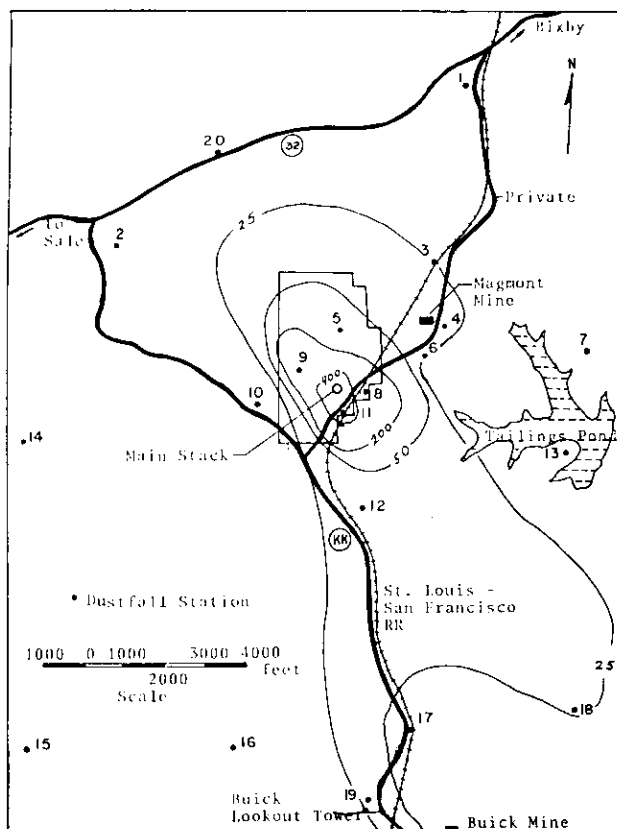


FIGURE 5. Radial distribution of particulate zinc in the vicinity of the AMAX smelter. Deposition rate is expressed as milligrams per square meter per month. After Lowsley (9).

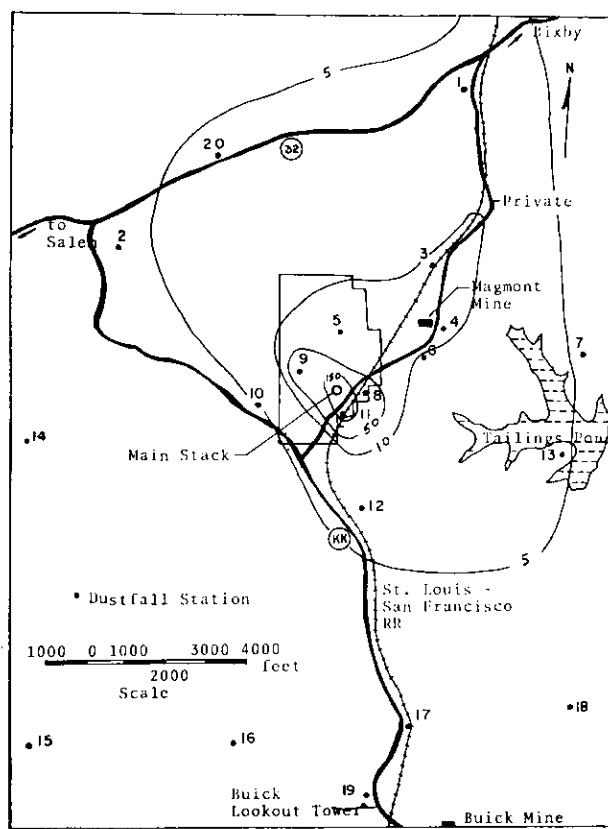


FIGURE 6. Radial distribution of settleable particulate copper in the vicinity of the AMAX smelter. Deposition rate is expressed in milligrams per square meter per month. After Lowsley (9).

cadmium and copper released to the atmosphere by the AMAX smelter. The results of these studies are summarized in Table 3. Size fractionation of these particulates confirmed the earlier studies that indicate that cadmium tends to be most highly concentrated in the finer particulate fractions with effective cutoff diameters less than $2 \mu\text{m}$. Actual deposition of heavy metals was measured at 35 established dustfall stations in the vicinity of the smelter. The results of these measurements are plotted as isopleths in Figures 4-7. These data must be considered as composite samples of air-borne particulates emanating from the stack and fugitive (wind-blown) resuspended particulates.

In 1974-1975, extensive modifications in the baghouse and acid plant were made to improve the efficiency of particulate retention. More recent dustfall data have shown some improvement in the amounts of cadmium and copper detected in air-borne particulates (Table 4).

Heavy metals emanating from industrial operations have resulted in appreciable accumulation in the surrounding forest. Studies on heavy metal con-

centrations in leaves of selected indicator plant species have been reported by Hemphill (11). Extracted data representing heavy metal concentrations found in white oak and blueberry leaves are shown in Figure 8. Low metal concentrations in the leaves of deciduous plants are not as impressive as those found for soils and forest litter.

Bolter (12) concluded from his studies of soils and forest litter, that heavy metals tended to be highly concentrated in the decomposing litter of the forest floor. Soil profiles taken to a depth of several feet indicate very little downward migration of heavy metals. Organic ligands present in the partially decomposed leaf litter as small particles of debris or more soluble humic and fulvic acids may act as vehicles for transport of heavy metals throughout the litter layer and horizontally into area streams. Concentrations of heavy metals in leaf litter specimens taken along a transect between the two smelters of the new lead belt are shown in Figure 9. Absolute values of cadmium concentrations approached 100 ppm at that time (1974) in specimens closest to the AMAX smelter, dropping down to

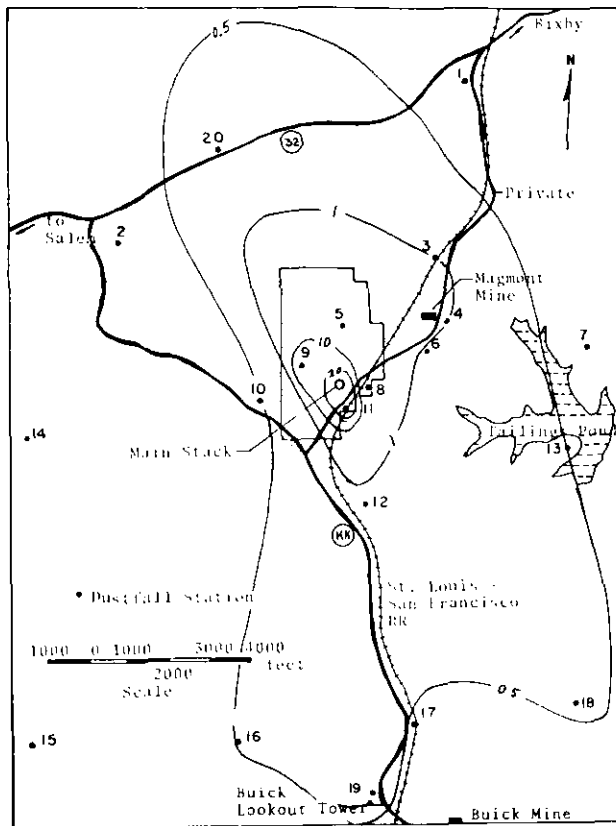


FIGURE 7. Radial distribution of settleable particulate cadmium in the vicinity of the AMAX smelter. Deposition rate is expressed as milligrams per square meter per month. After Lowsley (9).

Table 4. Settleable particulate material: geometric mean of 19 dustfall stations.^a

	Particulates, mg/m ² -mo			
	Pb	Zn	Cu	Cd
Prior to 1976	35.01	8.24	4.19	0.266
1976-1977	36.37	8.39	2.61	0.176

^a Data of Lowsley (9, 10).

background levels within 10 to 15 miles. On the particular transect shown in Figure 9, the contribution of heavy metals from industrial operations of the two smelters are shown to overlap.

Horizontal distribution of aerially deposited heavy metals in the affected watersheds is confused and compounded by episodes of heavy metals released in wastewater effluents and yard runoff. Therefore, heavy metal content of stream sediments (Table 5) (13, 14), leaf litter, mosses, and bracket fungi (Table 6) (15) must be considered the result of accumulation from all the various sources. Furthermore, horizontal transport of materials down the stream

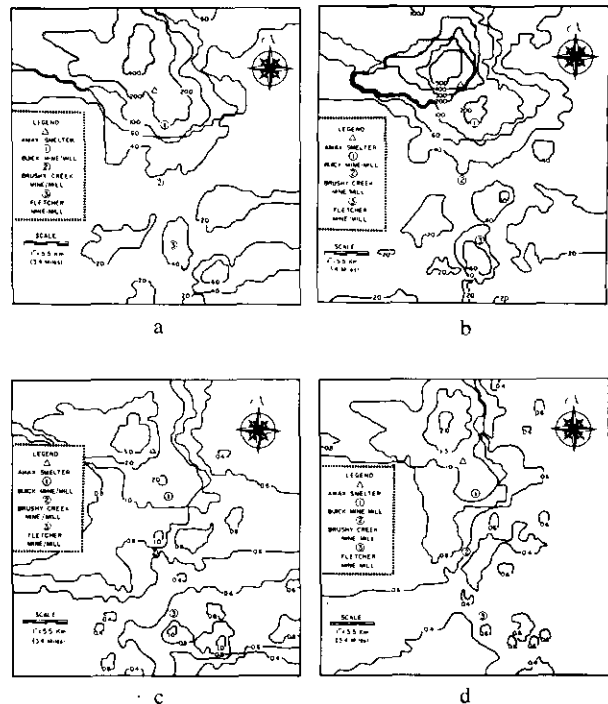


FIGURE 8. Heavy metals in white oak and blueberry leaves near the AMAX smelter: (a) lead in white oak; (b) lead in blueberry leaves; (c) cadmium in white oak; (d) cadmium in blueberry leaves. Values in ppm (dry weight). After Hemp-hill (11).

beds occurs as a result of dissolution by acid stream water or saltation and mass transport during storm runoff. Such factors cause considerable variation in metal content of collected specimens, and undoubtedly influence the rate and level of metal accumulation observed. Observed episodes of released industrial sediments high in cadmium and other heavy metal contamination are known to dissipate gradually, and represent a continual source of heavy metal contaminants to downstream sites. The east fork experiences a greater burden of lead, zinc, and copper than the west fork. But without the pH problems characteristic of the west fork, and despite the observed elevated concentration of heavy metals, biological activity within the east fork remains reasonably normal. Water quality parameters, as indicated in Figure 10, are significantly different in the two forks of Crooked Creek (16). The most obvious differences are largely attributable to the mentioned pH problem in the west fork.

An automatic water sampling station located at the confluence of the east and west forks of Crooked Creek was arranged to take a series of samples during 21 separate storm events. Results obtained from two relatively large storms are summarized in Figure 11. The first depicted storm event

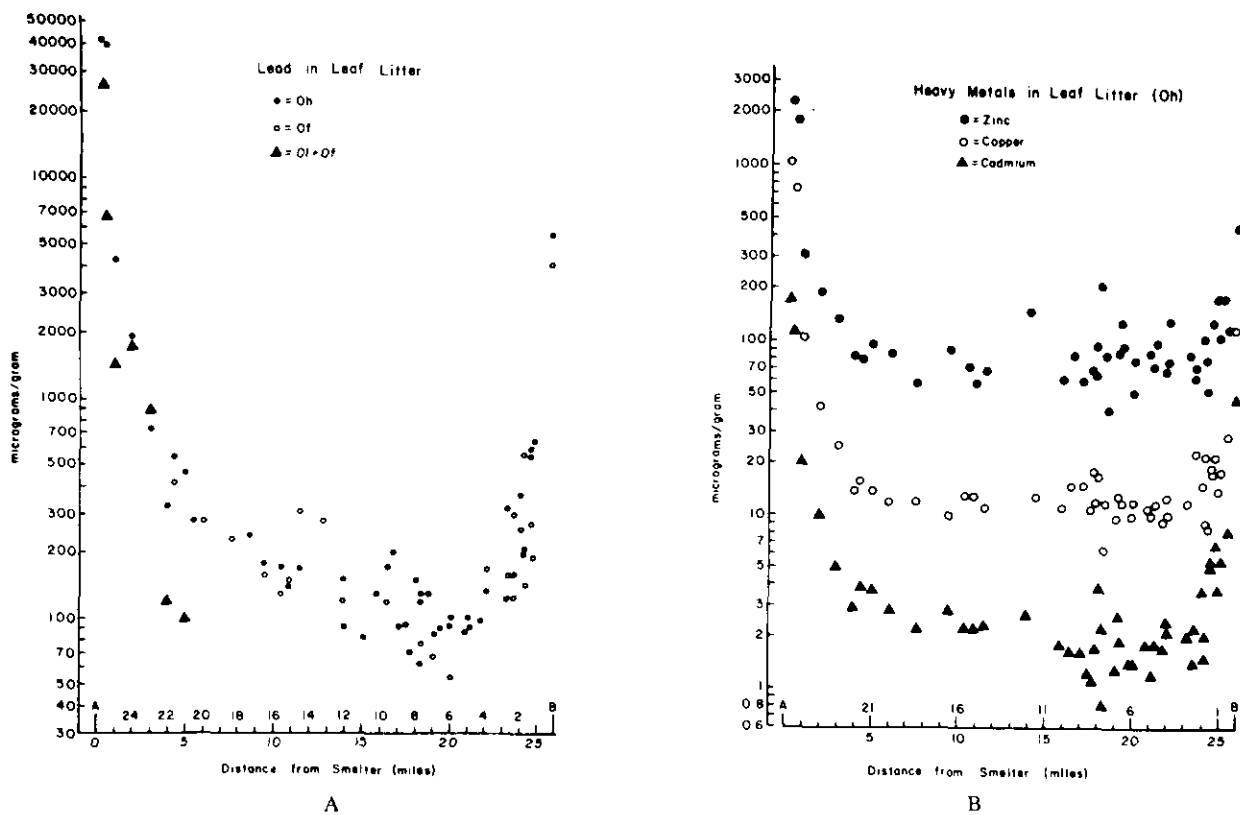


FIGURE 9. Heavy metals in leaf litter on transect between AMAX smelter (A) and ASARCO smelters (B): Oh = partially decomposed leaf litter; Of = top layer, recently fallen leaves. After Bolter (12).

Table 5. Stream sediment profiles in Crooked Creek watershed.

Station	Distance from confluence	Pb, $\mu\text{g/g}$	Zn, $\mu\text{g/g}$	Cu, $\mu\text{g/g}$	Cd, $\mu\text{g/g}$
Forks of Crooked Creek ^a					
East fork	6300 ft. (impoundment D overflow)	69,056	12,238	839	150
	5900 ft	12,250	5,350	2,050	46
	5350 ft	227,700	46,948	1,455	1,133
	4000 ft	14,500	3,800	390	57
	1600 ft	13,333	2,867	500	39
100 ft		3,750	1,500	225	32
	6300 ft (impoundment C overflow)	7,874	283	220	45
West fork	5900 ft	28,000	1,100	500	110
	4950 ft	21,667	567	267	57
	4850 ft	1,250	240	80	133
	4750 ft	8,350	480	185	55
	1400 ft	819	97	51	25
Downstream from confluence ^b					
Downstream Crooked Creek	6 miles	283	180	19	2.7
Huzzah Creek	8 miles	35	61	8	8.7
Huzzah Creek	13 miles	64	58	15	3.7
Huzzah Creek	18 miles	31	57	7	0.3

^a 200-325 mesh fractions; data of Jennett (13).

^b Reported values are maximum observed concentrations; data of Proctor (14).

Table 6. Average heavy metals concentrations in selected specimens in Crooked Creek, 1973-1976.

	Metal concn, ppm					
	West Fork ^a			East Fork ^a		
	1	2	3	4	5	6
Decomposing leaves						
Pb	39,636	17,821	5,622	44,430	18,768	13,370
Zn	4,192	1,045	1,571	7,608	4,093	4,655
Cu	742	251	228	1,093	723	408
Cd	684	359	629	164	152	185
Composite old and new leaves						
Pb	31,616	13,869	4,339	35,052	20,058	10,814
Zn	3,183	1,016	1,050	5,366	3,190	3,793
Cu	701	335	185	793	514	390
Cd	765	332	368	199	103	177
Moss						
Pb	20,892	9,262	3,686	30,627	21,457	9,980
Zn	1,136	359	267	5,397	2,178	1,971
Cu	384	174	135	951	485	304
Cd	70	41	37	74	73	57
Bracket fungi (<i>Fomes</i> and <i>Stereum</i>)						
Pb	10,661	2,458	880	5,844	2,664	4,115
Zn	925	519	97	533	672	275
Cu	117	150	38	178	160	98
Cd	70	22	28	31	43	20

^a See Figure 3 for location of sampling sites.

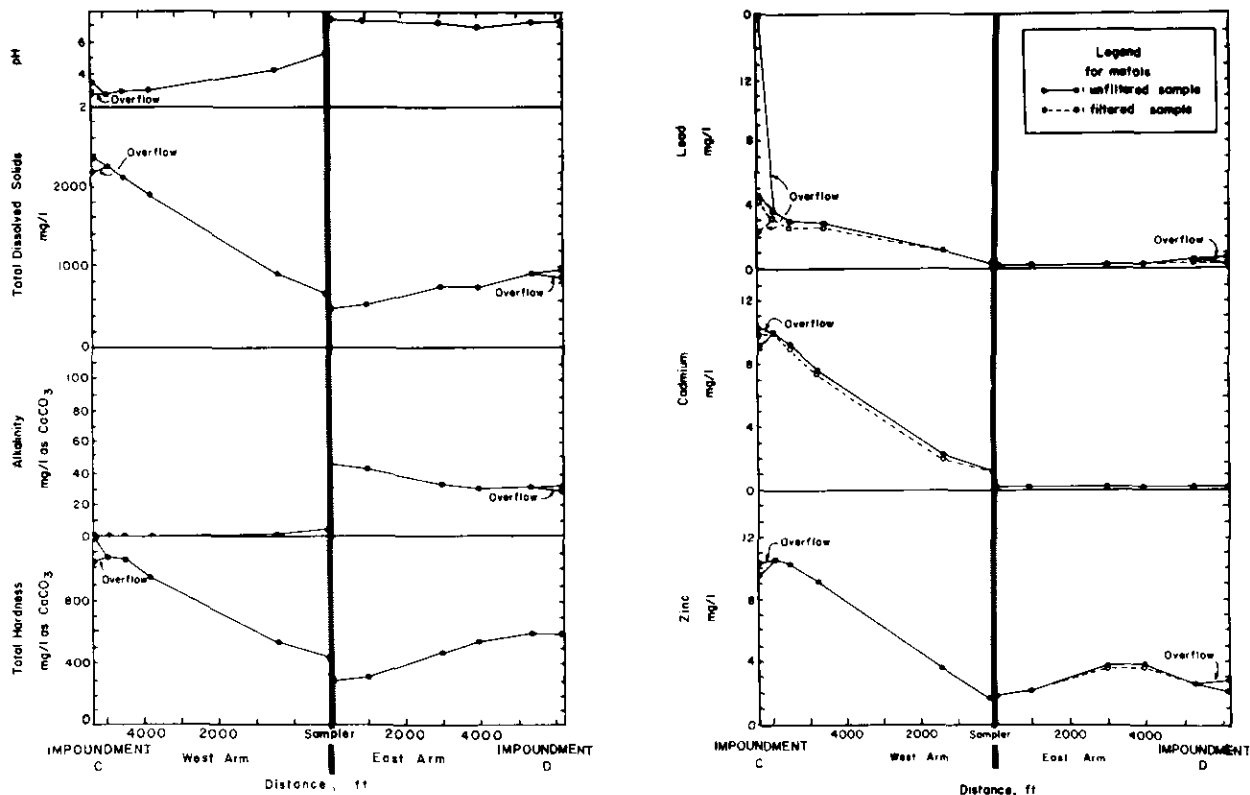


FIGURE 10. Water quality profiles of east and west forks of Crooked Creek near AMAX smelter. After Jennett and Foil (16).

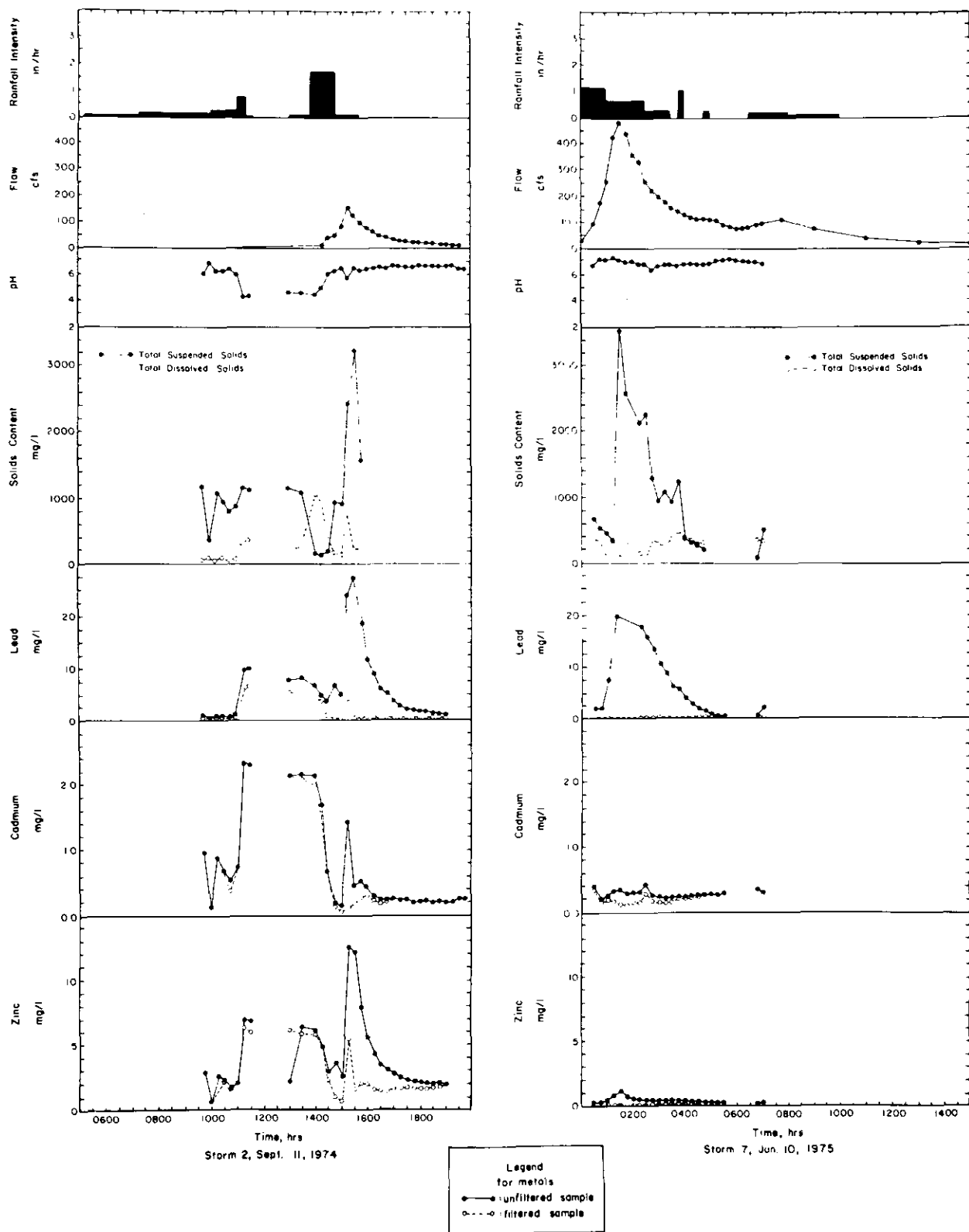


FIGURE 11. Water quality of Crooked Creek during storm runoff. Storm dates: Sept. 11, 1974 and Jan. 10, 1975; automatic water sampler located at confluence of east and west forks. After Jennett and Foil (16).

(September 11, 1974) resulted in a total rainfall of 2.25 in., producing a peak flow of 155 cfs approximately 1 hr after the peak rainfall intensity had occurred. There had been a smaller (0.21 in.) rainstorm two days earlier which produced runoff, and rain was detected on eight of the 14 days prior to that sampled storm.

A comparison of these two recorded storm events reveals some interesting points relative to the transport of heavy metals from the Crooked Creek watershed. Following a period of relatively little precipitation, the storm runoff from the watershed displayed a drop in pH. The bulk of Cd flow occurred during the period of low pH and was apparently in a dissolved state. Significant quantities of Pb and Zn were also present in these initial stages of storm runoff in the dissolved state. As the storm continued, all metal concentrations remained elevated in runoff waters, but they were predominantly in a particulate state which was not detectable in filtered water samples. Absolute concentrations of Pb and Zn were far greater than Cd concentrations. The storm event recorded shortly after previous intense runoff activity shows no acidic portion in the hydrograph. Yet, the suspended particulate matter shows significant transport of heavy metals, especially lead, under these conditions of sustained runoff.

In other recorded storm events not shown in the present figure, Cd was found to be present predominantly in the dissolved state, while Pb and Zn were consistently transported during periods of intense runoff in a particulate, filterable state. These findings are consistent with data from Butz (17) showing greater solubility of Cd salts and lower tendency of Cd to form organic complexes. Water quality data collected by Proctor et al. (14) for sampling stations for the downstream (Table 7) indicates only nominal concentrations of heavy metals during normal stream flow.

During the summer of 1977 a program was initiated to improve neutralization of effluent waters from impoundment A at the AMAX smelter. Despite daily addition of lime to the impoundments resulting in pH values above 10 observed in effluents at the point of discharge, the pH of the

waters of the west fork measured at the point of confluence with the east fork of Crooked Creek remained low, between 4.5 to 5.5 throughout the summer, fall, and most of the winter. It is possible that large reservoirs of acidic materials had accumulated along the creek bed in subterranean aquifers. Such reservoirs may have been established over a period of several years, having exhausted local supplies of neutralizing carbonates present in natural rocks of the area. Alternatively, the persistent pH problem may indicate leakage of acidic materials through fissures into the stream's underground aquifers at a point above or within the impoundment system upstream from zones of lime addition. Low alkalinity of the waters of the west fork creates a situation where radical changes in pH may occur upon addition of small amounts of acid. Further studies are required to determine the cause of persistent pH problems in the west fork of Crooked Creek. Fortunately, as the waters of the west fork merge with those of the east fork, the pH rapidly rises to normal values for typical Ozark streams.

Available data suggest that there is a region of contamination in the vicinity of the AMAX smelter. Observed concentrations of heavy metals in water, leaf litter, sediments and stream biota drop off rapidly with distance from the smelter. Because of its greater solubility under existing physical conditions, cadmium is apparently more mobile under normal stream flow conditions than lead or zinc. However, during periods of intense rainfall and runoff, considerable quantities of all mentioned heavy metals may be flushed into the storm flow as suspended particulates. Affinity of decomposing leaf litter for cationic materials permits the association of all mentioned heavy metals with organic ligands, providing temporary residence of metals and a vehicle for suspension and transport as decomposition proceeds.

ASARCO Smelter

The ASARCO smelter is located at Glover, Missouri and has a design capacity of 120,000 tons of lead per year. The general layout of the plant is

Table 7. Heavy metals concentrations in stream waters of Crooked and Huzzah Creeks, 1975.^a

Sampling site	Distance from smelter, mi	Metal concn, ppm			
		Pb	Zn	Cu	Cd
Crooked Creek	6	<0.001	0.012	0.001	0.007
Huzzah Creek	8	0.001	0.007	0.010	0.003
Huzzah Creek	13	0.003	0.001	0.010	0.003
Huzzah Creek	18	0.001	0.028	0.004	<0.001

^a Data of Proctor (14). Reported values are maximum observed concentrations.

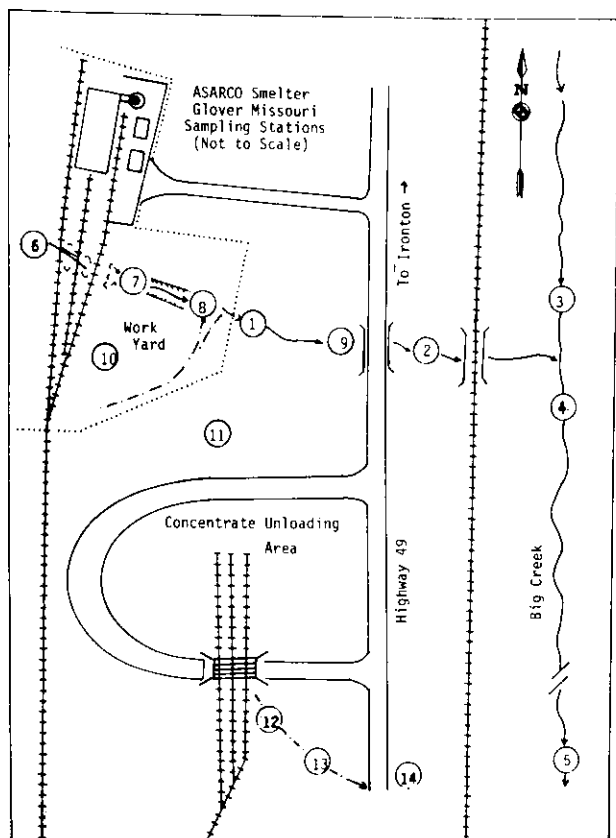


FIGURE 12. General layout of ASARCO smelter and adjacent Big Creek. Numbered circles indicate sampling sites.

indicated in Figure 12. Ore concentrates from the new lead belt, and other mining areas are delivered to the smelter by rail or truck. The truck dumping ramp is located at the south end of the work yard, where all concentrates are transferred to rail cars for eventual delivery to the sinter preparation area. In this smelter, sinter feed is initially moistened and pelletized prior to roasting. This procedure seems to reduce the quantity of galena particles blown by updraft air currents toward the baghouse. Separate baghouses are maintained for sintering and blast furnace operations. Mineralogical analyses by Arseneau (18) confirmed the presence of greater proportions of PbO and $PbSO_4$ in baghouse dusts from ASARCO, while AMAX baghouse dusts, without the benefit of the pelletizing procedures, contain much greater proportions of PbS . Cooled and cleaned sinter and blast furnace gases are passed to the atmosphere through a 602-ft stack. A weather station and a number of SO_2 monitors serve to warn plant operators of unfavorable weather conditions or excessive ambient SO_2 , and operations are scheduled to maintain acceptable levels of atmospheric pollutants.

The accumulation of cadmium in the baghouse materials at ASARCO has already been indicated previously (Table 1). On at least one occasion, when smelting ores of particularly elevated cadmium concentrations, cadmium content of baghouse materials approached 7%. At that time, the entire lot of baghouse dust was collected and shipped to El Paso, Texas for recovery of the cadmium. Baghouse dusts and worn out bags were routinely cycled to the blast furnace. In early operation of the plant, some of the old baghouse bags were hauled to a trash disposal site located to the west of the yard area, a situation perhaps responsible for some vagrant cadmium problems (personal communication, C. F. Bates, ASARCO).

The ASARCO smelter is situated alongside Big Creek. A tributary branch cuts directly through the south side of the work yard, under several sets of railroad tracks serving the facility, and alongside the slag storage area. It receives effluent from the plant sewage treatment system at the highway and joins Big Creek approximately 100 yd further downstream. This tributary branch is subject to contamination by heavy metals from a number of recognized sources: spillage from rail cars, erosion from the track area, old trash disposal area, and the slag storage yard. Excessive loss of ore concentrates from rail cars is evident along the entire route from the truck dumping ramp to the smelter, representing a source of fugitive metals entering this tributary and also the storm drainage ditch leading from the truck unloading ramp to Big Creek.

In 1975, Hemphill et al. (19) studied the extent of environmental contamination by heavy metals from ASARCO and offered the following observations.

Concentrations of lead in leaves from standing white oak trees (Fig. 13) ranged from $340 \mu\text{g/g}$ dry weight near the smelter to a low of $5.6 \mu\text{g/g}$ at 7 miles in a southeasterly direction. Levels of cadmium (Fig. 13) ranged from a high of $3.2 \mu\text{g/g}$, with only a few samples greater than $1.0 \mu\text{g/g}$.

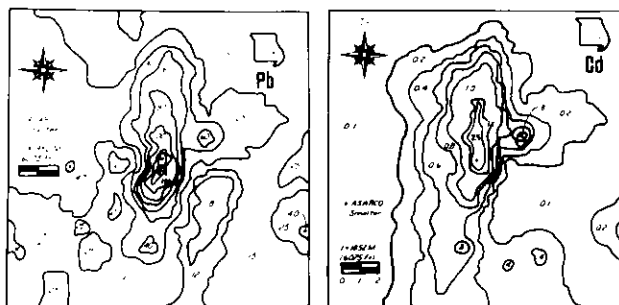


FIGURE 13. Lead and cadmium in white oak leaves near ASARCO smelter. After Hemphill et al. (19).

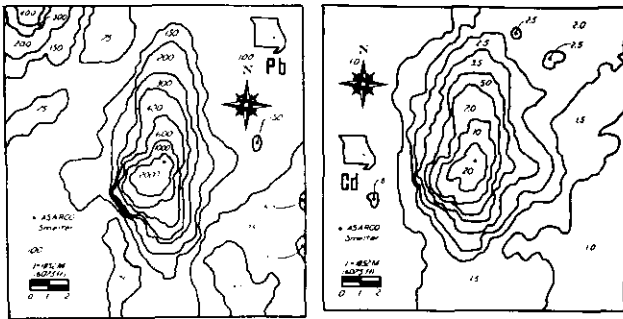


FIGURE 14. Lead and cadmium in decomposing forest litter near the ASARCO smelter. After Hemphill et al. (19).

Distribution patterns for lead and cadmium in the decomposing forest litter in the vicinity of the ASARCO smelter are shown in Figure 14. The influence of the AMAX smelter is seen clearly in the northwestern portion of the area.

A comparison of metal content of standing and matted pasture grasses showed markedly higher concentrations in the latter. Lead and cadmium concentrations in matted pasture grass from a

number of sampling sites near ASARCO smelter are summarized in Figure 15.

Industrial effluents and storm runoff waters from the workyard area were shown to have periodic pulses of heavy metals in excess of the guidelines set by the Missouri Department of Natural Resources. It is evident from the report that fugitive sediments and dusts in the work yard area frequently contributed significant quantities of heavy metals via the drainage ditches and tributary streams into Big Creek.

Big Creek has had a history of undesirable alterations due to industrial effluents with decreasing benthic diversity and undesirable algal blooms at various times extending as far downstream as Annapolis, approximately 8 miles from the smelter. A report prepared by Midwest Research Institute [see Hemphill (19)] in 1974 for the Environmental Protection Agency indicated that in the absence of any air pollution control equipment, the ASARCO smelter would emit over 5600 lb/hr particulate matter, approximately 11% of this emission being lead. With current air pollution equipment, however, total particulate emissions have been reduced to

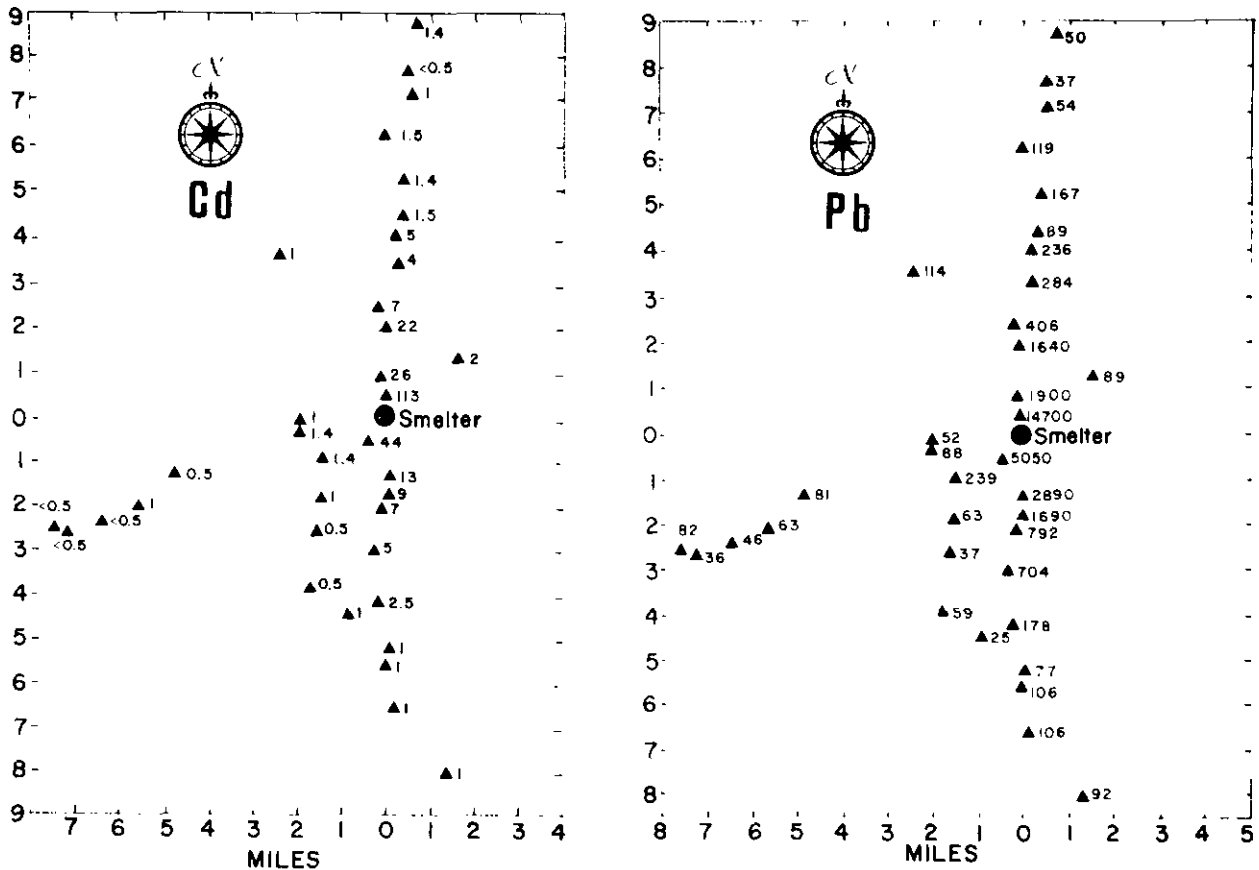


FIGURE 15. Lead and cadmium in matted pasture grasses near the ASARCO smelter. After Hemphill et al. (19).

Table 8. Representative heavy metals content of water, stream sediments, and leaf litter from sampling sites near ASARCO smelter, 1976-77.

Station	Material	Metals concn, ppm			
		Pb	Zn	Cu	Cd
6	Sediment, 80 mesh	147,000	29,000	7,170	450
	Sediment, 80 mesh	26,700	28,500	421	2,990
	Leaf litter	6,211	6,790	171	769
1, 8	Water	<0.2	0.4	<0.02	0.12
	Sediment, 80 mesh	29,300	23,670	1,206	9,400
	Leaf litter	18,400	16,800	531	1,780
2	Water	0.3	0.45	<.02	0.12
	Sediment, 80 mesh	32,300	22,660	1,086	3,330
	Leaf litter	12,510	10,800	416	911
3	Water	<0.2	0.13	<0.02	0.04
	Sediment, 80 mesh	19,600	20,900	588	592
	Leaf litter	8,520	1,400	127	312
4	Water	<0.2	0.08	<0.02	<0.02
	Sediment, 80 mesh	2,480	890	223	37
	Leaf litter	6,767	3,050	156	236
5	Water	<0.2	<0.03	<0.02	<0.02
	Sediment	13,080	12,600	238	696
	Leaf litter	4,450	1,490	114	325
13	Sediments	28,800	10,600	573	136
	Leaf litter	34,600	4,580	338	145
14	Sediments	11,600	3,400	266	29
	Leaf litter	17,240	3,480	424	78

approximately 39 lb/hr approximately 6.6 lb being lead.

Samples of water, stream sediments and leaf litter along the stream beds collected during 1976-1977 were recently analyzed for purposes of comparison with earlier data and evaluation of current control measures. These current data are shown in Table 8 and reflect residual heavy metals or those continually entering the stream system from established fugitive sources. During the summer of 1977, Big Creek displayed a dense diatomaceous mat which covered more than 80% of the stream bottom for more than a mile downstream from the smelter. Dominant algal forms included the diatom, *Cymbella*, and unidentified blue-green filamentous algae. Populations of normal consumer organisms were sharply reduced compared with regions of the stream upstream from the smelter. Similar algal blooms have been reported in new lead belt streams receiving effluents from mine-mill complexes with histories of elevated dissolved zinc and residual milling reagents (20).

Conclusions

Primary lead smelters in Missouri's new lead belt were recognized as potential sources of environmental cadmium as well as lead, zinc, and copper. Cadmium tends to concentrate in the baghouse

dusts and slurries associated with sintering and blast furnace gases. The handling and processing of these baghouse materials and slurries as well as disposal of old worn-out bags requires special consideration as sources of potentially hazardous levels of cadmium. Where possible, the industry should be encouraged to recover the cadmium present in such materials, since there is no other satisfactory sink for its removal other than fugitive emissions.

The lead industries have supported a number of studies to determine sources of fugitive heavy metals and has responded to correct environmental problems as these have become known. However, despite consistent efforts by the industry to curtail fugitive metals and to avoid and minimize environmental effects of their operations, there remains the constant potential of environmental contamination in close proximity to lead smelters. Current levels of cadmium contamination are obviously high in the vicinity of the smelters. These facts emphasize the obvious necessity of establishing a safe "green belt" or buffer around such operations. The smelters should be located, when possible, in sparsely populated areas.

Under present control conditions, environmental contamination by heavy metals, including cadmium, drops off rapidly with increasing distance from the smelters. Cadmium, lead, zinc, and copper present in the deciduous forest of the new lead belt

appear to have an affinity for the organic debris or decomposing forest litter and tend to accumulate there. Transport of these heavy metals may occur during storm events, as metal-laden organic particulates are swept into regional streams. The presence of mineral or organic acids, originating from natural processes of decomposition or from industrial sources may accelerate the dissolution of metal salts or complexes and contribute to transport of the metals in the dissolved state. Because of the characteristics of cadmium with regard to solubility and complexing ability, it tends to be more mobile than lead, zinc, or copper.

Much remains to be known about the possible toxic effects cadmium and associated heavy metals may have on the normal biota of a deciduous forest ecosystem. The continued survival of diverse and typical biological communities in areas known to be contaminated by heavy metals indicates a need for the scientific community to gain further insight into the problems of bioavailability, cellular transport mechanisms, and resistance characteristics in natural biological communities.

More precise definitions of toxic effects and hazardous levels for normal terrestrial and aquatic organisms are badly needed. Industry should be encouraged to continue their self-evaluation and monitoring efforts and to employ the best possible means of limiting or eliminating release of potentially hazardous materials into the environment. Many of the problems associated with heavy metal contamination may be avoided or certainly improved by proper and consistent housekeeping procedures. In a large industrial operation, however, such housekeeping details are perhaps easily observed, but difficult to correct. Nevertheless, the cooperative and professional attitude of industry representatives is appreciated.

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