# Groundwater and Surface Water Contamination from Resource Extraction

#### INTRODUCTION

Groundwater and surface water may be contaminated by accident or by improper storage or disposal of wastes at the surface. Improper storage or disposal has occurred in many areas due to our ignorance about groundwater flow and potential health effects, the lack of concern for water supplies, and a short-term view of the behavior of groundwater and our future needs for water.

In this exercise we look at cases in which pits and holding ponds were used to dispose of or store liquid wastes. In the past it was expedient to create waste ponds, where the wastes decreased in volume through evaporation or infiltration. In this exercise we explore the cause and extent of contamination from oil field brines and runoff from a lead mine.

## PART A. GROUND WATER CONTAMINATION FROM OIL FIELD BRINES IN CENTRAL OHIO

In many oil-producing areas, severe problems of groundwater contamination were common. These were caused primarily by the infiltration of saltwater into the ground. Saltwater, or brine, is produced with the oil and, since the brine often is a by-product of little or no economic value, when unregulated it was commonly disposed of in the most economical manner possible. In most areas this is done by reinjection into the oil-producing zone by means of a well. In others it is accomplished by pumping the brine into holding ponds or pits, where a small percentage evaporates but most of it infiltrates. Infiltration can lead to severe groundwater pollution since the chloride concentrations of the brines may exceed 35,000 mg/L. In contrast many areas have groundwater with background or naturally occurring chloride concentrations of less

than 25 mg/L. Sea water is less salty than the brines, with a chlorinity of 19,000 mg/L, which makes up 55 percent of the total salt content of sea water.

Once the oil wells and pits are closed, the chemical quality of the groundwater tends to improve, usually very slowly, as the concentrated solutions migrate to areas of discharge such as springs, streams, or wells. The natural flushing of the groundwater system depends on the hydraulic conductivity of the rocks, the hydraulic gradient, the effective porosity, and the amount and rate of infiltration of rain and snowmelt. It may require decades for the groundwater system to return to its natural chemical state. The rate of flushing and the amount of time that the groundwater reservoir remains contaminated are of profound interest in legal cases.

The brines sterilize the soil, kill vegetation, and create an undesirable taste in drinking water. The concentration at which a brine becomes harmful to vegetation depends on the type of plant, the depth of the root system, the season, and the depth of the water table, to mention only a few factors. Dead trees and other vegetation, however, commonly mark areas where brine-contaminated groundwater discharges into streams or where it flows from springs. The USEPA recommends that drinking water contain no more than 250 mg/L of chloride, since higher concentrations cause a salty taste. Higher concentrations are not likely to cause illness in humans because the water is too salty for consumption.

Most of the problems developed prior to 1980; however, research on the fate of contaminant plumes continues to the present.

## **Groundwater Contamination near Delaware, Ohio**

In this part of the exercise we study the extent, movement, and changes in concentration of oil field brines that contaminated a site on the nearly flat floodplain of the Olentangy River in Ohio. Three oil wells were

drilled in this area in June 1964. The brine-to-oil ratio was about 10:1, and nearly 236,000 barrels of salt water were pumped into three ponds from June 1964 to July 1965. Dissolved solids in the brine averaged 60,000 mg/L, and of this about 35,000 mg/L consisted of the chloride ion (Pettyjohn, 1971).

The accompanying figures (Figures 15.1, 15.2, 15.3) show the location of four brine-disposal pits, three oil wells, 25 observation wells, and a water well. The observation wells averaged 25 feet in depth and were installed in late 1965, following cessation of brine disposal, to monitor the movement of the

contaminated groundwater. Shale bedrock is overlain by up to 30 feet of alluvial material consisting of a mixture of sand, silt, and clay. The average hydraulic conductivity (K) of the alluvial material, which contains the contaminated water, is about 25 ft/day, and the average effective porosity  $(n_e)$  is 0.15. The water table gradient (I) can be determined from a water-table map.

The objectives of the exercise are to determine the direction and rate of flow of the contaminants in the ground and to evaluate the possible contamination of a nearby water well.

7777

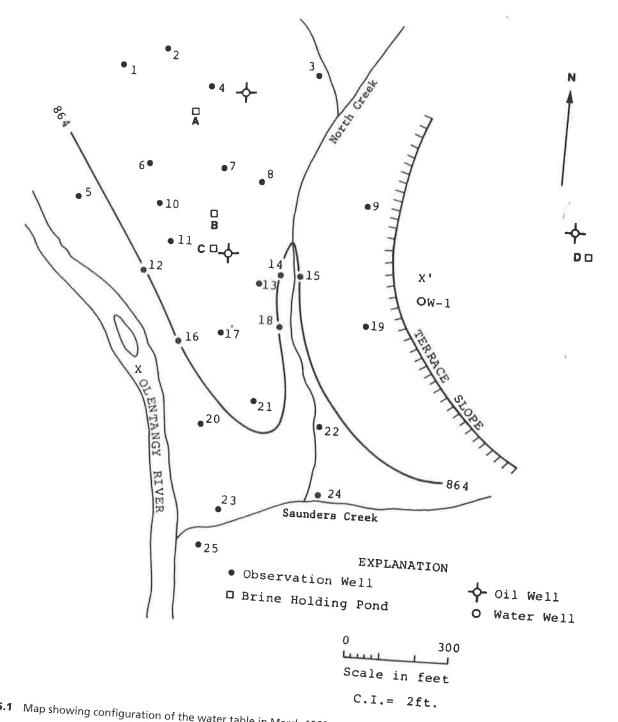


FIGURE 15.1 Map showing configuration of the water table in March 1969.

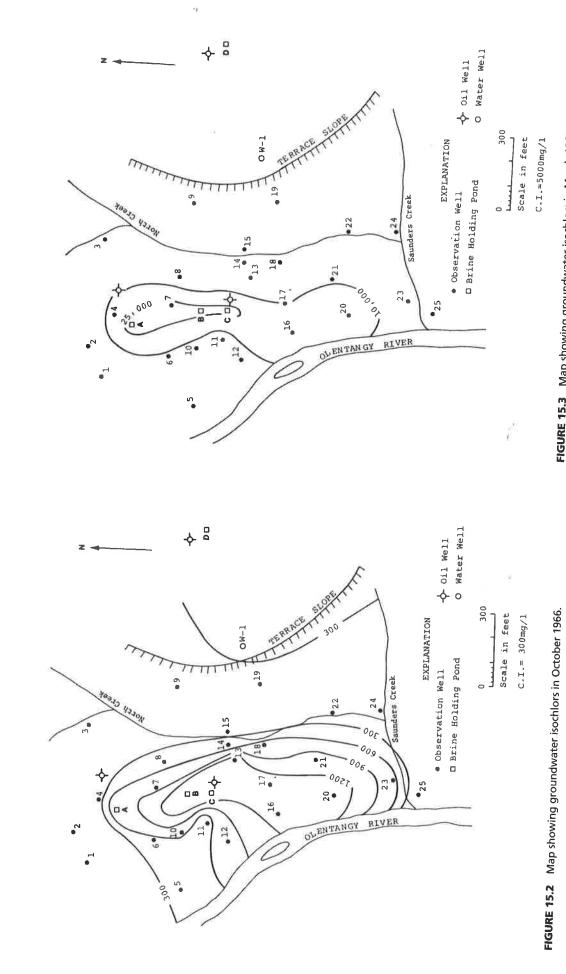


FIGURE 15.3 Map showing groundwater isochlors in March 1969.

#### **QUESTIONS 15, PART A**

- 1. Using the data in Table 15.1, construct a water-table map (Figure 15.1). Begin by transferring the water-table elevations from Table 15.1 to the appropriate test hole locations in Figure 15.1. Then contour the water-surface elevations using a contour interval of 2 feet. The contours should roughly parallel the 864-feet contour already drawn.
- 2. Draw several flow lines originating at the brine holding ponds to the most likely area of groundwater discharge. Remember that during dry weather streams flow only because groundwater discharges into them.
- 3. What is the gradient from pond C to the Olentangy River? ft/ft.

- 4. What is the gradient from pond C to Saunders Creek? ft/ft.
- **5.** Calculate the velocity of groundwater moving from pond C to the Olentangy River and from pond C to Saunders Creek using the following formula and the data given earlier in this exercise on the hydraulic characteristics of the unconsolidated material.

$$v = (KI)/(n_e)$$

where v = velocity (ft/day), K = hydraulic conductivity (ft/day) I = gradient, (ft/ft), and  $n_e = \text{effective porosity (% as a decimal)}$ 

**a.** The velocity of groundwater from pond C to the Olentangy River is about \_\_\_\_\_ft/day.

TABLE 15.1 Chloride Content of Wells and Water-Table Elevation in the Delaware Area

Water-Table Elevation (March 1969)	Chloride Content (mg/L)			
	Nov. 1965	Oct. 1966	March 1969	
867	4,500	288	24	
871		875	36	
866	12		1 12	
869	1==		200	
862	-		400	
868	18,000		407	
868			662	
865			490	
870	_		490 16	
868	25.500		917	
868	+			
864			550	
865			740	
864			1,355	
864			292	
864	22 750		302	
868			1,230	
864			1,300	
869			600	
862			300	
865			1,400	
			1,100	
			117	
			779	
			27	
	95		320	
	871 866 869 862 868 868 868 865 870 868 868 868 864 864 864 864 864 864 869	867       4,500         871       —         866       12         869       —         862       —         868       18,000         868       —         865       —         870       —         868       25,500         868       31,000         864       —         865       —         864       —         864       —         864       22,750         868       —         864       5,600         869       27         862       4,800         859       5,250         861       33         860       95	Nov. 1965         Oct. 1966           867         4,500         288           871         —         875           866         12         12           869         —         12,000           862         —         8,000           868         18,000         8,875           868         —         26,250           865         —         1,000           870         —         14           868         25,500         9,850           868         31,000         7,500           864         —         8,750           865         —         6,875           864         —         3,125           864         —         1,725           864         —         10,000           865         —         10,000           866         —         10,000           867         —         15,000           868         —         10,000           869         27         25           862         —         15,000           865         —         9,000           865         —         9,000	

b. The velocity of groundwater from pond C to Saunders Creek is about \_\_\_\_ ft/day.

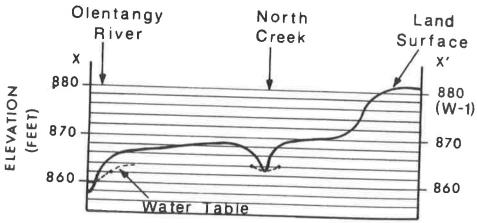
- 6. If we divide the distance of travel (measured along a flow line) by the rate of flow of groundwater, we obtain the travel time. What are the travel times for water from pond C to
  - a. Olentangy River:
  - b. Saunders Creek:
- 7. On another map (Figure 15.2) construct contours representing lines of equal chloride concentrations (isochlors). Use the data for October 1966 (Table 15.1) and a contour interval of 5,000 mg/L. Consider the direction of groundwater flow when drawing these contours. Thus isochlors are given in Figure 15.2.
- 8. Should the Olentangy River and Saunders and North Creeks contain higher than normal concentrations of chloride in the vicinity of the contaminated area? Why?
- 9. Wells 23 and 24 (Table 15.1) contain higher concentrations of chloride in October 1966 than in November 1965, while the other wells contained less. Consider your answer to question 6b in your explanation of why this is happened.
- 10. What do you think the chloride concentration of the groundwater was before brine-pit disposal began (i.e., what was the background concentration)?

- 11. What techniques might be used to increase the rate of flushing of the high-chloride water in the areas of contaminated
- 12. A second isochlor map, based on the March 1969 data, is shown in Figure 15.3. A contour interval of 300 mg/L was used. This map is useful in determining the change in contamination with time. Compare Figures 15.2 and 15.3 and describe the changes that have occurred.
- 13. The shallow farm well (12 ft deep) at W-1 increased in chloride concentration between 1966 and 1969 (Table 15.1). Has this contamination resulted from brine disposal into ponds A, B, C, or D? Explain your answer with the aid of the cross-section sketch (Figure 15.4), which goes from points X to X' in Figure 15.1. Complete the water table and indicate groundwater flow by arrows in Figure 15.4.

### PART B. SURFACE WATER CONTAMINATION FROM OIL FIELD BRINES IN CENTRAL OHIO

In this part of the exercise river pollution can be traced to techniques for disposing of saltwater (brine) that is pumped with oil. Regulations in most areas now require subsurface disposal of oil field brines and have significantly reduced groundwater and surface-water pollution.

Surface waters can be contaminated directly through effluent discharge and surface runoff or indirectly through discharge of contaminated groundwater. This exercise illustrates the effects on a drainage basin of poor waste-disposal practices of oil field



**FIGURE 15.4** Cross section from points X to X' in Figure 15.1.

brines; specifically we will look at a case where groundwater contamination has led to the deterioration of surface-water quality. A generalized diagram showing movement of groundwater into a stream is shown in Figure 15.5.

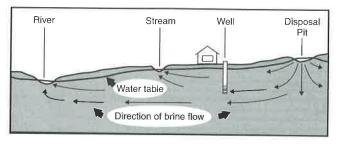
The water table usually lies at a depth of a few feet and follows the general topography of the land surface; that is, the water table is at a higher elevation under hills than it is in nearby low-lying areas. Groundwater moves in the direction of the water-table gradient, from higher pressure to lower pressure, which often may mean from higher elevation to lower elevation. Where the land surface is lower than the water table, such as at a swamp, lake, or stream, groundwater will flow onto the land surface.

Rainwater has a low mineral content, but as it slowly infiltrates soils and bedrock and perhaps flows great distances, its mineral content increases. The types and concentration of constituents in groundwater reflect the composition of the soils and rocks through which the water has moved. The naturally occurring concentrations of elements in groundwater are called background concentrations. If a water-soluble contaminant is allowed to infiltrate the ground, it will increase the concentrations of elements and compounds in the groundwater and may contaminate it so it is unusable.

In some parts of the world, an indirect but significant cause of surface-water contamination is disposal of oil-field brines. The brines, which are highly concentrated solutions consisting largely of sodium chloride (NaCl), are pumped from the ground with the oil. The mixture is routed through a separator which removes the oil from the brine. The oil flows to storage tanks while the brine most commonly is discharged to an unlined holding or evaporation pond (see Part A of this exercise) or is pumped back into the bedrock. In some climates where ponds are used, only a very small part of the brine evaporates; most of it infiltrates.

Brines sterilize soil, kill vegetation, and create an undesirable taste in water. The U.S. Environmental Protection Agency has recommended that drinking water should contain no more than 250 mg/L of chloride because higher concentrations cause a salty taste.

Even with careful regulation of the extractive industries, higher background readings of some



**FIGURE 15.5** Generalized diagram illustrating contamination of groundwater and surface water by pit disposal of oil field brines (Pettyjohn, 1972, p. 168).

components can be expected in some areas due to natural weathering and erosion. Before there was any human exploitation of oil in North America, natural brine seeps and springs degraded water quality in some areas.

#### **Alum Creek Basin, Ohio**

Low relief and a relatively high water table characterize this watershed in central Ohio. Much of the agricultural land is artificially drained. The region is underlain by a clayey glacial till that in many places contains thin layers of gravel. The till ranges from a few inches to several tens of feet in thickness. Oil-bearing reservoirs underlie much of the region at an average depth of about 3,500 feet.

Sixty-five water samples were collected in late autumn from streams in the upper part of the basin. Because there was no rain or surface runoff for several days prior to collection, and because groundwater discharges to the streams, the stream data represent the quality of the groundwater. The samples were analyzed to determine chloride ion concentrations. Chloride is a common constituent in oil field brines (Table 15.2). Stream sampling sites and locations of existing or abandoned gas or oil wells, including dry holes, are shown in Figure 15.6.

#### **QUESTIONS 15, PART B**

- 1. Using the data in Table 15.2 and Figure 15.6, construct a surface-water quality map. Assume that the chloride content at a station reflects the quality between that site and the next upstream station. Mark in blue the stream reaches that contain 25 mg/L or less of chloride. Use brown for reaches that contain more than 25 but less than 50 mg/L, and red for reaches that exceed 50 mg/L. A map of this type not only presents an obvious picture of the change in water quality from one area to the next, but it also can be used to determine the major source areas of contamination. Use only those data representing sample sites 1–41. Sites 42–65 on the other streams can be examined if you are interested or if the instructor assigns them. You may substitute other colors or patterns for the colors suggested above.
- **2.** Briefly describe the quality of the water in Alum Creek basin using the map you completed in Question 1.
- **3.** What areas are the major sources of chloride contamination in the drainage basin?
- 4. Why did the chloride concentration decrease between sites 21 and 25?

TABLE 15.2 Sample Site Numbers and Concentration of Chloride Ion, in mg/L, in Alum Creek Basin

Sito	Site CI (mg/L) Site CI (mg/L) Site CI (n				
		Site	CI (mg/L)	Site	CI (mg/L)
1	6	23	23	45	79
2	64	24	24	46	101
3	79	25	84	47	16
4	41	26	37	48	16
5	210	27	33	49	62
6	15	28	39	50	62
7	195	29	13	51	58
8	5	30	8	52	53
9	10	31	41	53	47
10	7	32	629	54	42
11	159	33	77	55	22
12	33	34	103	56	27
13	62	35	21	57	48
14	6	36	113	58	8
15	66	37	38	59	25
16	62	38	11	60	16
17	122	39	23	61	24
18	11	40	21	62	22
19	55	41	109	63	26
20	53	42	22	64	30
21	119	43	11	65	29
22	10	44	116		

**5.** Would you expect the stream's chloride concentration to be greater or less during the spring? Why?

**6.** Obviously, much of the groundwater in the basin is contaminated, at least locally. Do you think that all of the groundwater is contaminated? Explain.

7. Outline two areas in Figure 15.6 that should show background concentrations of chloride.

**8.** What are possible sources of chloride contamination in Alum Creek other than oil field brines?

9. In the upper part of the basin, many of the agricultural fields are underlain by drainage tile. The tiles intercept groundwater and divert it away from the fields. This causes the water table to remain at a lower elevation in fields with tile than in fields without tile. Ultimately, drainage from these tiles flows into a stream. How could you use data from water-quality samples taken from field tiles to aid in determining the areas of groundwater contamination by oil field drilling and extraction activities?

# PART C. SURFACE WATER CONTAMINATION FROM LEAD MINES IN SOUTHEASTERN MISSOURI

In this part we look at the impact of heavy metals from a lead-mining district on water and aquatic organisms. Similar impacts can be documented in other areas of North America; however, new mine operation and closing practices have lessened the environmental impact of mining.

In 1955 new deposits of copper, lead, silver, and zinc were discovered in southeastern Missouri. This

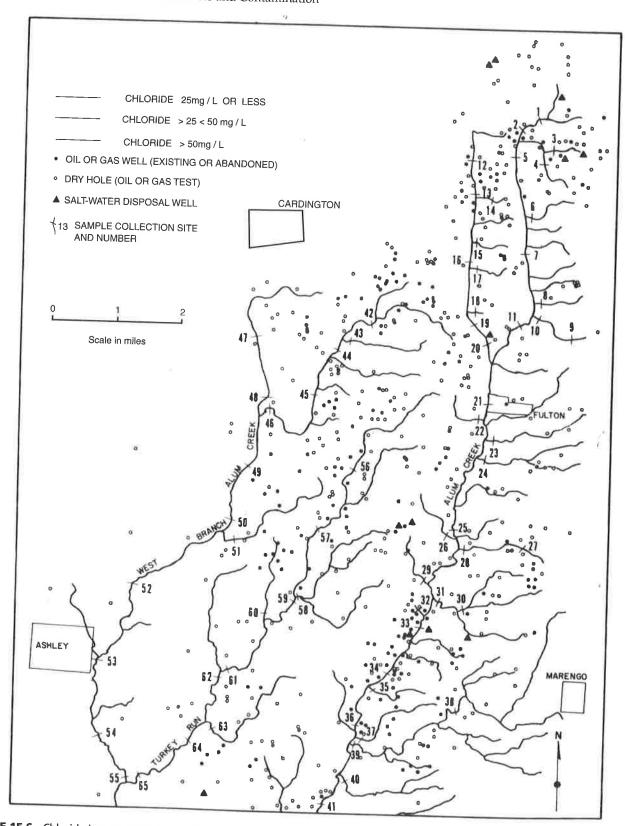


FIGURE 15.6 Chloride ion concentration in Alum Creek basin in the autumn.

region, known as the New Lead Belt, became one of the largest lead-producing areas in the world. It continues to be a primary producer of lead with secondary production of zinc, and small quantities of copper and silver (Brumbaugh et al., 2007). In order to evaluate the impact of mining on this sparsely populated,

heavily forested, and hilly region, a number of surfacewater and aquatic life forms were examined. Samples were collected from streams free of mining and milling operations (control samples) and from contaminated streams.

Changes in water quality and aquatic life in these streams since 1955 are related to the discharge of milling and mining wastes which include excess water pumped from mines, finely crushed rock, chemical reagents, and waste oils and fuel. These wastes are allowed to settle in holding ponds, and the effluent is either reused or allowed to discharge into streams. The greatest share of the noxious substances is retained in the settling basins.

Most of the heavy metals in the streams are in very fine particles; a minute amount is dissolved but most heavy metals travel on suspended sediment in the water. Where large excesses of groundwater have been pumped from mines and discharged into streams, significant algal blooms have occurred. They may be a result of the nutrients in the groundwater. The dense algal communities act as filters and remove many of the fine particles that escape the settling basins.

In this exercise we begin by investigating metal contamination of water and aquatic organisms on the West Fork Black River and tributaries Strother Creek, Neal Creek, and Bee Fork Creek (Figure 15.7) using data published in 1973 (Gale et al., 1973). We conclude with an assessment of conditions in this same area based on sampling of water and sediments between 2002 and 2005 (Brumbaugh et al., 2007).

#### **QUESTIONS 15, PART C**

1. Examine Figure 15.7 and Table 15.3. Sample sites 6, 9, 10, and 14 are in uncontaminated areas. What are the background concentrations of the following elements in surface water?

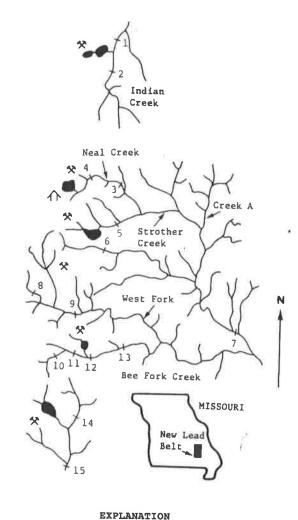
Lead:

Zinc:

Copper:

Manganese:

- 2. In Figure 15.7 mark in red (or use a pattern [e.g., dots] that you identify in the explanation) the stream reaches that exceed background concentrations of lead. Consider the most likely source of the lead as a guide in marking the stream reaches.
- 3. In Figure 15.7 mark in green (or with a dash pattern) the stream reaches that exceed 0.011 ppm of zinc.
- 4. What relationship appears to exist between settling basin location and the quality of water in the stream?



#### Settling Pond ↑ Smelter Sample Number ☆ Mine and Site

Scale in miles

FIGURE 15.7 Trace element sampling sites and lead and zinc concentrations in water in the New Lead Belt, southeastern Missouri (Gale et al., 1973).

- 5. On the basis of available data, would you expect background concentrations of the contamination in Creek A? Explain.
- 6. Examine the Mn concentrations in aquatic organisms in Strother Creek as shown in Table 15.4.
  - a. What general relationship is evident?

**TABLE 15.3** Mean Concentrations of Lead, Zinc, Copper, and Manganese in Water in the New Lead Belt

Site	Mean Concentrations					
	Flow (cfs)	Pb (ppm)	Zn (ppm)	Cu (nnus)		
1	11.22	.021	.034	Cu (ppm)	Mn (ppm)	
2	11.22	.011		.010	.077	
3	-		.017	.010	.049	
4	5.80	.010	.011	.011	.012	
5	8.70	.014	.069	.010	.035	
6		.090	.034	.011	.127	
	4.10	.011	.010	.010		
7	382.6	.014	.011	.010	.011	
8	33.8	.044	.011		.021	
9	33.8	.011	.010	.010	.013	
10	9.22	.011		.010	.013	
11	_	.035	.010	.010	,013	
12	-		140	,017	1.637	
13	9.22	,033	,134	.012	1.691	
14		.030	.038	.010	488	
	6.75	.012	.010	.010		
15	6.75	.019	.020	.018	.025	

TABLE 15.4 Mean Concentrations of Lead, Zinc, Copper, and Manganese in Aquatic Organisms of Strother Creek

Organism		Mean Concentrations (mg/g)			
	Miles Below Pond	Pb	Zn	Cu	
Snails	0.2	16			Mn
	1.3		54	57	1,770
	2.8	75	27	21	710
Tadpoles	0.2	44	18	16	59
		69	97	142	195
	1.3	24	92	130	
	2.8	38	86	86	750
	4.2	28	94		410
	0.2			97	485
	1.3	36	210	26	5,650
	2.8	780	265	44	4,560
		310	210	26	690
	4.2	1,590	160	17	500

**b.** Similar but less obvious trends exist for Pb, Zn, and Cu; however, Pb in tadpoles exhibits the opposite trend. What might account for this different trend?

b. How many times greater is the concentration of lead at the mine than 6.5 miles downstream from the mine?

7. Examine Figure 15.8.

a. What is the background concentration for lead in aquatic vegetation in the Bee Fork drainage basin?

c. How many times greater is the value for lead at 6.5miles downstream than the apparent background level?



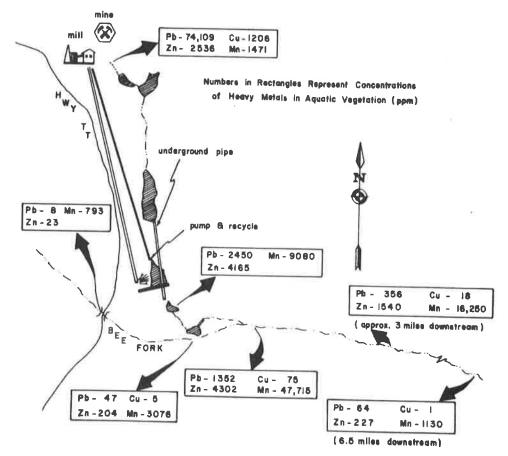


FIGURE 15.8 Trace element concentrations (ppm) in aquatic vegetation along Bee Fork and tributary, New Lead Belt (Gale et al., 1973).

8. The pollution load that a stream carries can be calculated if the stream discharge and the concentration of the specific contaminants are known.

Load (tons/day) = 
$$Q \times C \times 0.0027$$

where Q = stream discharge (cfs), C = concentration of specific contaminant (mg/L), and 0.0027 = constant to convert seconds and mg/L to days and tons

Using the available data and the formula given above, calculate how many pounds per day of lead and manganese were being transported past site 7 (Figure 15.7; refer to Appendix A for conversion of tons to pounds).

9. What techniques might be used to reduce the contamination of these streams in the New Lead Belt?

10. Using the above information from the USGS studies that began in 2000, briefly describe, in a bullet statement for each, the key findings or conclusions that you might make from this study of part of the New Lead Belt.

Concern about potential degradation of water quality and aquatic biota of nearby federally protected streams prompted a multidisciplinary study of the area that began in 2000. The results of the sediment and surface water analyses on samples collected between 2002 and 2005 have been published by the USGS (Brumbaugh et al., 2007). That publication is the source of much of the following environmental information.

The greatest concentrations in sediment collected in 2002 were from sites downstream from mines on Strother Creek and West Fork, with noticeable enrichment in lead in sediments from Bee Fork. Compared to reference sites, sediments downstream from mine areas were enriched "by factors as large as 75 for cadmium, 62 for cobalt, 171 for nickel, 95 for lead, and 150 for zinc."

The impact of mining was recorded at least 75 kilometers downstream in Clearwater Lake where metal concentrations were 1.5–2.1 times greater than in sediments in an area of the lake with no upstream mining. Sediment samples collected in 2004 on West Fork showed "dramatically lower" concentrations of metals, which was attributed to the closing of a mill on West Fork.

Concentrations of metals in surface water generally tracked those in sediments. Water samples from July 2005 on Strother Creek showed a "considerable increase in metal loadings" for a few days in which there was a moderate increase in stream discharge.

11. Using the online resources (or the actual publications) from the USGS study on the New Lead Belt that began in 2000, prepare two or three lab questions based on those reports that would be suitable for use by your fellow students. Include the full reference, any diagrams or tables, and the questions. Also include the answers that you expect for each of the questions. You can focus on either the geological or the biological data or use both. (The instructor might make this a take-home assignment, depending on available resources and time, and possibly a group assignment. Select

from suggested references below or others that you find that might be useful. Full references are in the Bibliography section of this manual.)

Besser et al. 2006 http://www.springerlink.com/content/r4t8q457354847t0/; Brumbaugh et al., 2007 http://pubs.usgs.gov/sir/2007/5057/, Schmitt et al., 2007a, 2007b.

### **Bibliography**

- Besser, J.M., Brumbaugh, W.G., May, T.W., and Schmitt, C.J., 2006, Biomonitoring of lead, zinc, and cadmium by streams draining lead-mining and non-mining areas, southeast Missouri, USA: *Environmental Monitoring and Assessment*. Retrieved October 2006 from http://www.springerlink.com/content/r4t8q457354847t0/
- Boster, R. S., 1967, A study of ground-water contamination due to oil-field brines in Morrow and Delaware Counties, Ohio, with emphasis on detection utilizing electrical resistivity techniques, M.Sc. thesis: Columbus, OH, The Ohio State University, 191 p.
- Brumbaugh, W.G., May, T.W., Besser, J.M., Allert, A.L., Schmitt, C.J., 2007, Assessment of elemental concentrations in streams of the New Lead Belt in Southeastern Missouri, 2002–05: U.S. Geological Survey Scientific Investigations Report 2007–5057, 57 p.
- Feth, J. H., 1973, Water facts and figures for planners and managers: U.S. Geological Survey Circular 601–1, 30 p.
- Gale, N. L., Wixson, B. G., Hardie, M. G., and Jennett, J. C., 1973, Aquatic organisms and heavy metals in Missouri's New Lead Belt: *Water Resources Bulletin*, v. 9, no. 4, p. 673–688.
- Pettyjohn, W. A., 1971, Water pollution by oil-field brines and related industrial wastes in Ohio: *Ohio Journal of Science*, v. 71, no. 5, p. 257–269.

- Pettyjohn, W. A., 1972, Water Quality in a Stressed Environment: Minneapolis, MN, Burgess, 309 p.
- Pettyjohn, W. A., 1973, Sources of chloride contamination in Alum Creek, Central Ohio: Columbus, OH, Ohio Department of Natural Resources, 54 p.
- Reiten, Jon C., 2006, Oil-field brine plumes in shallow ground water, Sheridan County, Montana: Sixteen years later: AAPG Rocky Mountain Section Annual Meeting, June 11–13, 2006, Billings, Montana.
- Sassen, Douglas S., 2004, Oil-field-brine-induced colloidal dispersion: A case study from southeast Texas: Geological Society of America *Abstracts with Programs*, vol. 36, no. 1, p. 24.
- Schmitt, C.J., Brumbaugh, W.G., and May. T.W., 2007a, Accumulation of metals in fish from lead-zinc mining areas of southeastern Missouri, USA: *Ecotoxicology and Environmental Safety*, v. 67, p. 14–30.
- Schmitt, C.J., Whyte, J.J., Roberts, A.P., Annis, M.L., and Tillitt, D.E., 2007b, Biomarkers of metals exposure in fish from lead-zinc mining in southeastern Missouri, USA: *Ecotoxicology and Environmental Safety*, v. 67, p. 31–47.
- Shaw, J. E., 1966, An investigation of ground-water contamination by oil-field brine disposal in Morrow and Delaware Counties, Ohio, M.Sc. thesis: Columbus, OH, The Ohio State University, 127 p.