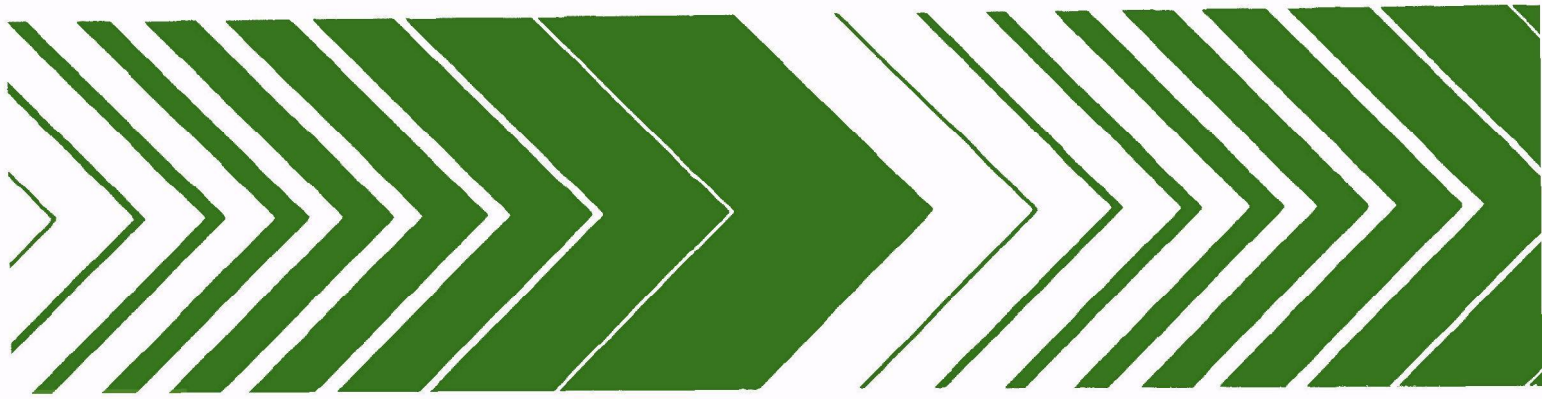


Research and Development



Environmental Effects of Western Coal Combustion

Part III The Water Quality of Rosebud Creek, Montana



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July 1980

ENVIRONMENTAL EFFECTS OF WESTERN COAL COMBUSTION:
PART III - THE WATER QUALITY OF ROSEBUD CREEK, MONTANA

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FOREWORD

This study, one of many examining impacts of energy development in the western U.S., documents pre and post operation contributions of a coal-fired power plant on a small stream. The role of snowfall and subsequent melt water as transport mechanisms from air to water is a finding of this study that merits more attention at other sites.

Norbert Jaworski, Ph.D
Director
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ABSTRACT

The results of a study on Rosebud Creek, Montana, designed to assess the impacts on water quality of surface coal mining and/or coal combustion at Colstrip are summarized herein. A general degradation of water quality has been observed along the stream course but direct impacts of groundwater from the mine areas have not been demonstrated. Influxes of arsenic, mercury, selenium, and polynuclear aromatic compounds during snow-melt periods have been linked by analyses of snow samples to their accumulation in snowfall via scavenging of the power plant plume and subsequent delivery to the stream via surface runoff. Although this contaminant transfer route may prove highly significant, it is emphasized that this will depend on site specific conditions.

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SECTION I

INTRODUCTION

Increased reliance on coal as an energy source is accompanied by potential environmental impacts due to coal mining and combustion. It now appears certain that mine-mouth power plants will become increasingly common for various economic reasons. Since many of these are, and will be, located in relatively fragile areas of the western states where water is scarce enough to be treated as a commodity, it is particularly pertinent to assess the potential impacts on the aquatic system.

The mining and combustion activities may affect the surrounding area in various ways. It is known that strip mining may alter the hydrologic cycle, and that backfilling, leveling, and revegetation are useful means of alleviating the associated problems (McWhorter *et al.* 1975; Dollhopf *et al.* 1977a,b, 1978; Van Hook and Shults 1977). Such studies have shown that drainage from western surface coal mines can have deleterious effects on surface water quality. An evaluation of such reports indicates that the disruptions caused by mining result in increases in the total dissolved solids and saline constituents in groundwaters and eventually the receiving surface waters. Although these investigations have also examined the influx to surface waters of numerous heavy metals from mine operations, these metals do not appear particularly significant in the western states. This is due, in part, to the basic characteristics of ground and surface waters in the western states. Such waters are typically buffered by carbonate-bicarbonate constituents leached from mine overburden as well as the undisturbed strata. This buffering controls heavy metal solubilities through metal carbonate precipitation (Skogerboe *et al.* 1979).

The possible impacts of coal combustion can be broadly assigned to two categories: (i) those associated with the furnace (bottom) and precipitator ash and the scrubber waters and (ii) those associated with the materials emitted to the atmosphere. An overview of the problems which may be associated with coal combustion has been presented by Van Hook and Shults (1977). This workshop summary drew the following consensus conclusions.

1. There is a considerable body of knowledge pertaining to trace elements released by coal combustion. This information needs to be evaluated in the context of source term characterization, dose-response, and ecological transport/transformation investigations. Understandings of the total problem will be significantly expedited by this integrated approach.
2. Occurrence of detectable ecological or health effects due to atmospheric releases of trace elements is unlikely in the near future.

The elements As, Be, Cd, Cr, F, Hg, Ni, and Pb were excepted from this generality and studies of the atmospheric transformations of sulfur and nitrogen oxides were singled out in terms of pressing importance.

3. There is little reason to expect acute effects from trace elements on the aquatic ecosystem, but there is a lack of knowledge regarding the impact(s) of ash, slag, and sludge disposal practices and associated aquatic discharges. A better understanding of the mobility of trace elements and the controlling factors was delineated as essential to the health and ecological effects assessment question.
4. A pressing need for more information regarding the organic contaminants produced and released in coal combustion technologies was emphasized.

Although these points or their emphasis may be subject to challenge, they represent the consensus opinions derived from intensive discussions by experts having widely variant interests and training. They serve as a general means of focusing on pertinent problem areas. The present research program, *in toto*, has dealt directly or indirectly with each of the four areas cited above.

Reports by Natusch (1976), Natusch *et al.* (1975), Natusch and Taylor (1980), Davison *et al.* (1974), and Linton *et al.* (1976) present a comprehensive overview of the chemical and physical characteristics of fly ash emitted from coal-fired power plants. The findings of that research indicate that the more volatile trace elements and many organic contaminants are emitted from a coal-fired power plant stack as gases and subsequently condense or "sorb" onto the fly ash particles as they cool. Such processes affect the atmospheric dispersion question, since particle rather than gaseous dispersion laws exert control (Friedlander 1977). The presence of contaminants on particle surfaces rather than within the relatively insoluble particle matrix sharply affects their accessibility to the environment and their solubility characteristics (Davison *et al.* 1974; Natusch *et al.* 1975; Natusch 1976; Natusch and Taylor 1980; Linton *et al.* 1976; Van Hook and Shults 1977). Finally, the coexistence of heavy metals and organics on fly ash particle surfaces raises a concern not just about the potential carcinogenic, mutagenic, and/or teratogenic hazards, but also about possible synergistic enhancements of health and ecological effects resulting from heavy metal/organic interactions (American Chemical Society 1969, National Academy of Sciences 1972, Federal Power Commission 1974, U.S. Environmental Protection Agency 1976, Van Hook and Shults 1977). Investigations in this last area will clearly require extensive efforts involving scientists from several disciplines. Meanwhile, the present efforts have concentrated on a general evaluation of the transfer of combustion emissions to surface waters.

Coal-fired power plants deliver both particulate matter and gaseous materials to the atmosphere. Atmospheric processes such as rainout, washout, and fallout may deliver these materials directly to surface waters; they may also be delivered indirectly via being incorporated into precipitation and surface or groundwater runoff. The determination of the extents of such

transfer processes is a difficult problem complicated by the fact that precipitator and bottom ash from the power plant must be disposed of. Such disposal typically involves burial and/or settling pond treatment such that the disposal site(s) may be accessible to surface and groundwaters and the settling pond waters may be cycled back to surface impoundments (American Chemical Society 1969, National Academy of Sciences 1972, Federal Power Commission 1974, U.S. Environmental Protection Agency 1976). Thus, field studies should ideally involve sites where the groundwater and surface impoundments directly associated with the coal combustion plant are reasonably isolated from the watershed(s) which may be affected by the atmospheric transfer processes. Only under such circumstances can the relative importance of these two general routes of surface water contamination be assessed.

This report summarizes the results of a study focusing on the water quality of Rosebud Creek, the major surface drainage immediately east of the power plant at Colstrip, Montana. The study was begun in October of 1975, about two months before initiation of power generation at this site, and continued through the spring of 1978. Concurrent with this study, separate studies were conducted on the distribution of fishes and aquatic macroinvertebrates in Rosebud Creek (Elser and Schreiber 1978; Baril *et al.* 1978). The results of all these studies address short-term effects of the Colstrip power plant operation and serve as references against which long-term effects may be assessed.

Although mining and power generation occur at Colstrip, the effects of mining on water quality have not been detected in eastward flowing creeks having headwaters in the mine area (Van Voast *et al.* 1977), e.g., Cow Creek (Figures 1 and 2). Rosebud Creek receives flow from intermittent Cow Creek, which contributes surface water to Rosebud Creek during the snowmelt season and in times of heavy rainfall (Figure 2). The location of Rosebud Creek in the primary downwind direction from the power plant (Heimbach and Super 1973) coupled with the reported lack of mining influence led to its selection as a site for the evaluation of possible impacts due to atmospheric transport of coal combustion emissions.

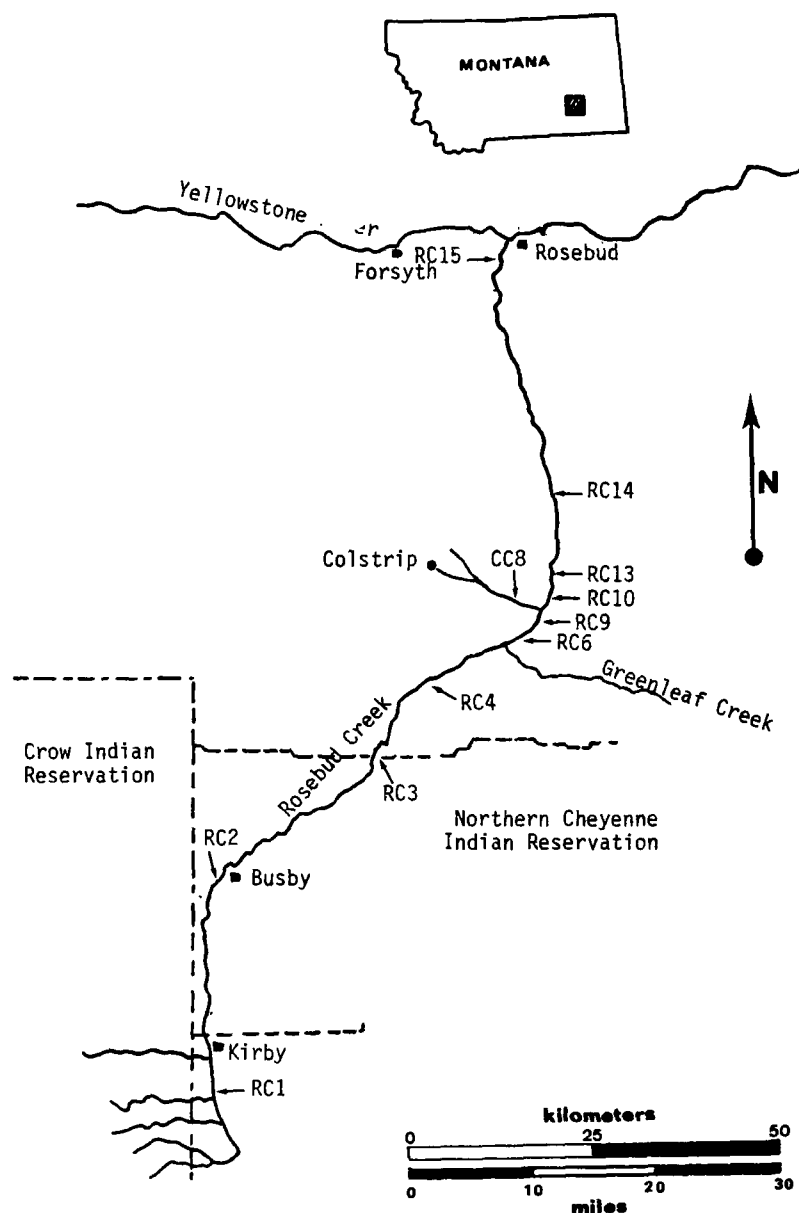


Figure 1. Location map of water quality monitoring stations sampled at least ten times.

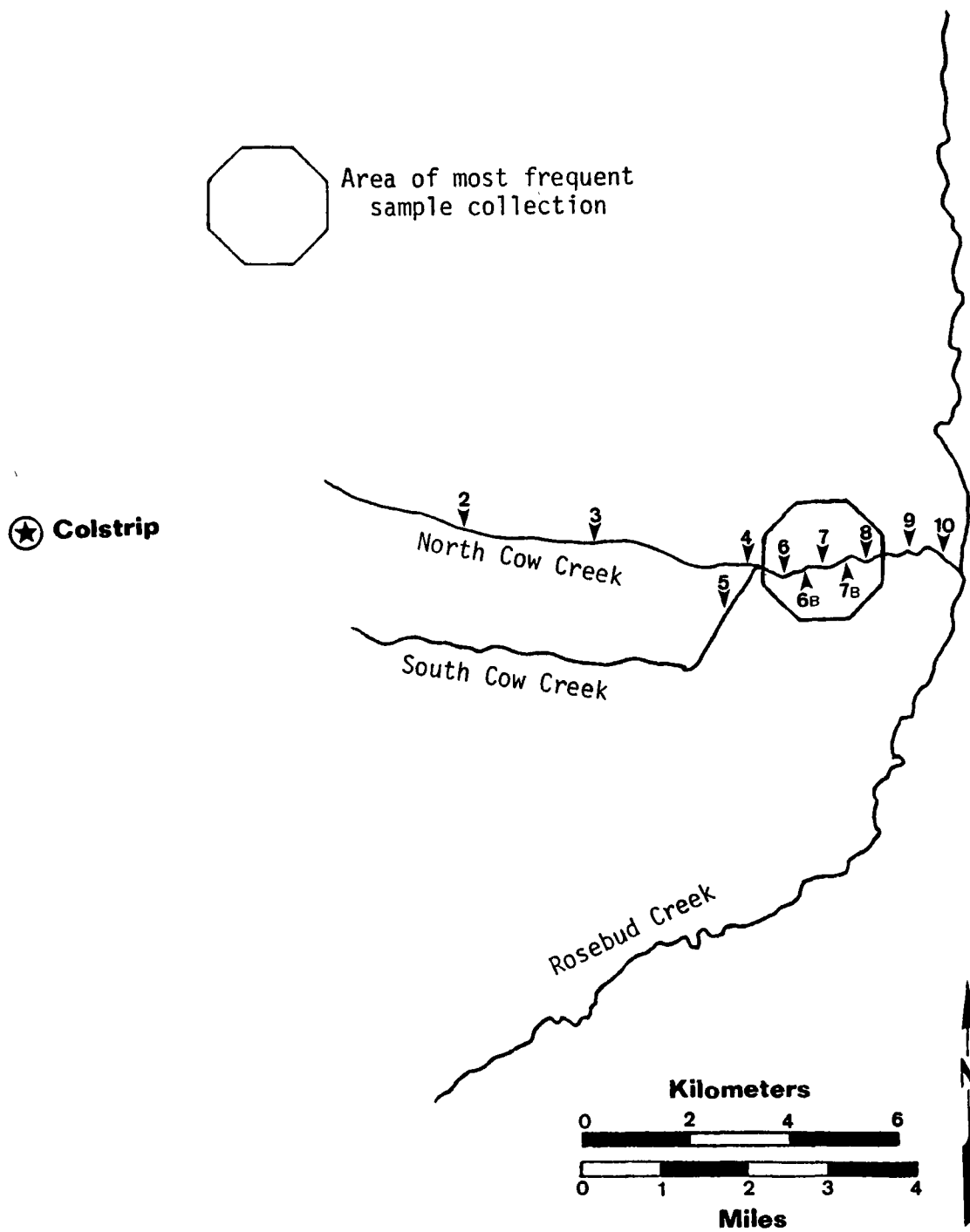


Figure 2. Cow Creek sampling sites.

SECTION II

CONCLUSIONS

1. Although the water quality characteristics of Rosebud Creek, Montana, degrade between the headwaters and its confluence with the Yellowstone River, the present study has not found changes directly attributable to surface coal mining in the region.
2. Influxes of arsenic, mercury, and polynuclear aromatic compounds occurring during snowmelt periods have been linked to scavenging of those contaminants from the plume of the power plant located at Colstrip, Montana. In general, snow cover tends to accumulate plume constituents, thereby semi-isolating them from the soil and terrestrial biota so that both are denied the extent of contaminant accumulation operative during warmer months. Soluble contaminants accumulating throughout the watershed may consequently be delivered to the stream via the surface runoff associated with snowmelt.
3. Influxes of contaminants delivered intermittently to surface streams via this general route are likely to accumulate in sediments due to normal sedimentation processes and the generally alkaline characteristics of streams in this region which will enhance precipitation of heavy metals.
4. Examination of the Rosebud Creek water quality data for the period of this study indicates that the average concentrations of constituents are at levels considered safe for maintenance of aquatic life.

SECTION III

RECOMMENDATIONS

The results of this investigation have provided data indicative of the water quality of Rosebud Creek for 3-4 months preceding and several months following the beginning of coal-fired power plant operations in the area of the watershed. These data should be used as reference points against which long-term changes can be assessed. Continued monitoring of the stream for this purpose is recommended.

This investigation has also demonstrated a route of transfer between a coal combustion power plant and a surface stream. This transfer route has heretofore not been widely studied but will surely be operative at other sites. The potential impacts on water quality and the aquatic biota derived from this means of transfer will be site specific to some extent. It is recommended that studies be undertaken at other sites to demonstrate the generality of the atmosphere-snowmelt transfer route and define the nature(s) and extent(s) of associated impacts.

SECTION IV

SITE DESCRIPTION

PHYSICAL FEATURES

Surface descriptions of the Rosebud Creek study area have been given by Renick (1929) and Pierce (1936). The region is semi-arid with hot summers, cold winters, and lasting snow cover. The average annual precipitation is 34.5 cm at Forsyth (north of Colstrip and west of the Rosebud Creek-Yellowstone River confluence) and 47 cm in the headwaters vicinity of Rosebud Creek (south of Colstrip). Highly dissected plateau-like uplands, terraces, and badlands are characteristic of the area. Irregular uplands, often with buttes along their margins, divide the Tongue River and Rosebud Creek watersheds. The uplands tend to be sharply separated by steeply descending slopes which flatten to irregularly dissected slopes that merge into valley bottoms.

Variations in vegetation occur in association with variations in soil and precipitation. Some pine is dispersed throughout the area. Lower elevation areas support various natural grasses with gramma predominating in the drier areas and wheat grass predominating in the lowlands where flooding may occur. The area along the creek supports hay meadows including alfalfa, but the rest of the area is naturally adaptable only for grazing.

HYDROLOGY

In its 300 km course, Rosebud Creek enhances the value and livelihood of the farms and ranches through which it flows. It is a meandering stream, deep and slow moving enough to raise the water tables and provide subirrigation in summer months. It is also used for flood irrigation, particularly during high runoff months. The flow at its confluence with the Yellowstone River varies significantly from year to year but all years show a common pattern of low flow from July through February and then sharp increases with two distinct maxima (see Figure 3) (Thom *et al.* 1938). The first maximum usually occurs between mid-March and early April due to snowmelt at lower elevations; the second and higher maximum occurs in June or July due to snowmelt at higher altitudes (headwaters) and enhanced by seasonal precipitation. The first maximum will most likely include fallout, rainout, and washout from the atmosphere that has accumulated in snowfall at the elevations near Colstrip; its effects on the water quality of Rosebud Creek may be most prominent. The second maximum is principally associated with melting of snowfall occurring at more remote locations; it may have less effect on water quality.

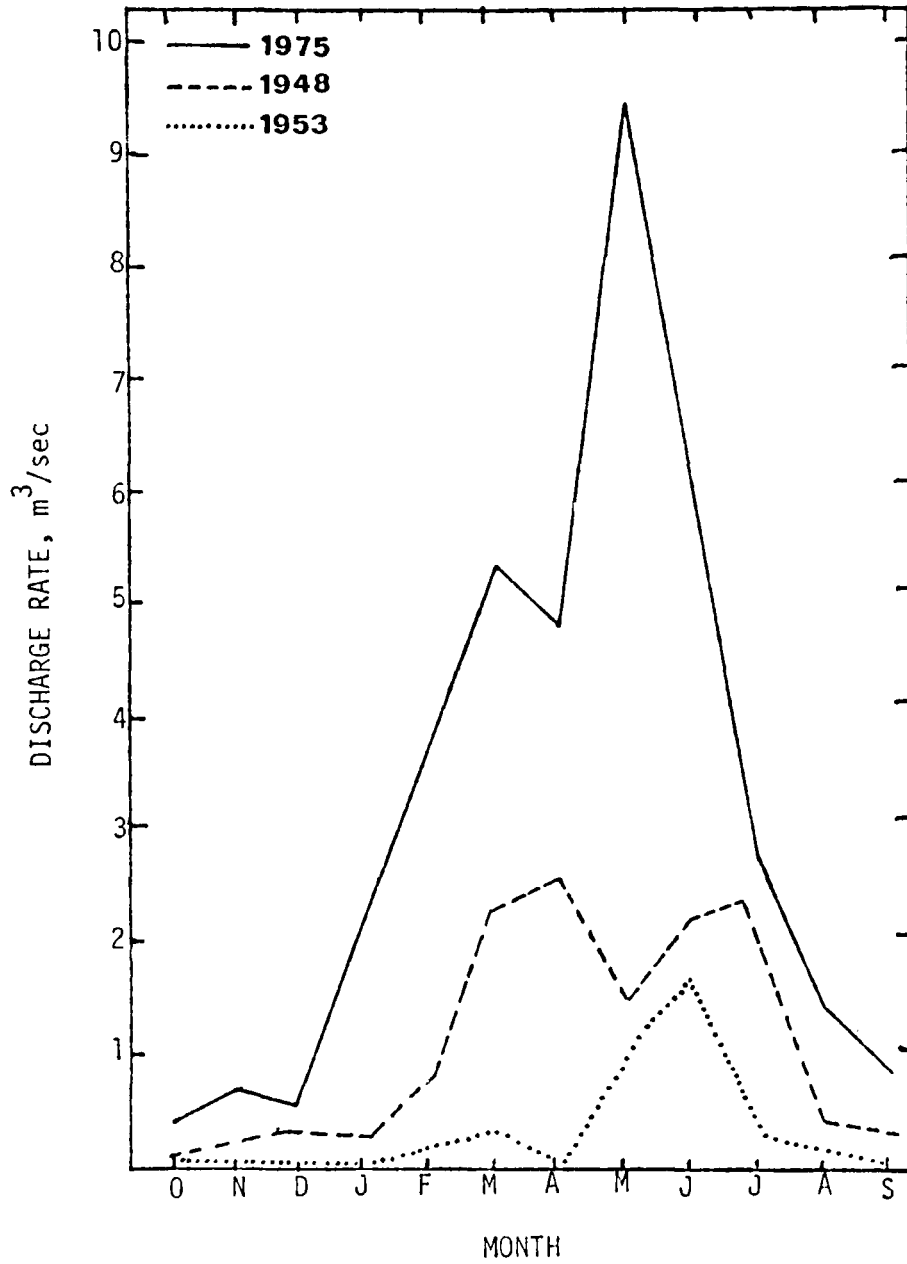


Figure 3. Average monthly flow of Rosebud Creek, 1948, 1953, and 1975. (Thom *et al.* 1938)

There are two primary aquifers in the region; they are associated with the Rosebud and the McKay coal beds and are separated by clay, silt, and sand (Van Hook and Shults 1977, Van Voast *et al.* 1977).

SAMPLING SITES

Ten sample collection stations were established along Rosebud Creek (Figure 1). All stations were sampled at least ten times during the course of this study; most were sampled monthly for an 18-month period. The collections were initiated in October 1975, approximately three months before the coal-fired power plant at Colstrip became fully operational. As noted in Figure 1, the collection stations along Rosebud Creek ranged from the headwaters, about 80 km S,SW of Colstrip, to its confluence with the Yellowstone River; the most intensive sampling centered around the region nearest Colstrip. A detailed description of the sampling sites and their locations is given in Table 1. Collection stations were also established along Cow Creek which intermittently drains the watershed immediately east of Colstrip; these are shown in Figure 2.

The Rosebud Creek sampling sites are shown in Figure 4 in relation to the "wind exposure" from Colstrip. The 10-year mean wind data (Heimbach and Super 1973) were used to construct this figure. Thus, stations RC-2 and RC-3 lie in a quadrant which is downwind of Colstrip less than 3% of the time (averaged over 10 years). Station RC-4 lies in a quadrant which is downwind ~3% of the time while RC-6, RC-9, and CC-8 lie in a quadrant which is downwind 11% of the time (see the differential plume exposure data in Figure 4). A cumulative plume (wind) exposure profile is also shown in Figure 4. The determination of this profile was based on linear addition of the differential exposures for each quadrant and was used to estimate the approximate exposure effect integrated over time. These data suggest that the wind from Colstrip is in the direction of the Rosebud watershed more than 70% of the time. This clearly indicates that any atmospheric emissions from the power plant are most likely to impact on the Rosebud watershed. It may also be noted that the mean wind directions are such that the areas of highest wind plume exposure are those immediately to the east of Colstrip where Rosebud Creek is nearest the power plant. A further rationale for considering the cumulative exposure data as presented in Figure 4 and Table 1 may be based on the fact that the stream flows north from a region of low plume exposure to regions of successively higher exposure. Thus, if a pollutant were delivered to the creek at RC-4, for example, and if that pollutant is capable of being transported in the natural water system, it would be carried northward into the region of higher exposure so that a "cumulative" effect would be possible in the downstream direction. The sites selected for the present study considered the above exposure factors.

The following points concerning the sample stations should be noted.

1. The RC-1 and RC-2 sites are basically reference point stations which lie upstream from all mining activity and outside the regions of most significant wind (plume) exposure. Water quality differences between these two stations probably reflect agricultural and ranching impacts.

Table 1. Description of Rosebud Creek water sampling sites and their cumulative plume exposures.

Station Number	Date Sampling Started	Site Description	Approximate Distance from Colstrip, km	†Cumulative Plume Exposure
*RC-1	10/75	Collected from a road culvert ~2 km south of Kirby township	80 S,SW	<3%
RC-2	10/75	Collected under a bridge ~2 km west of Busby township	50 S,SW	<3%
RC-3	10/75	Collected behind the Bailey house (Box 42), along Rosebud Creek	30 S	<3%
RC-4	10/75	Collected at the McRae Ranch (Box 28) ~100 m upstream from stables	15 S	3%
RC-6	10/75	Collected at the Kluver Ranch (Box 24) along Rosebud Creek ~300 m above RC-9	15 S,SE	14%
RC-9	7/76	Collected at the Kluver Ranch ~20 m upstream from the confluence of Cow Creek with Rosebud Creek	15 E,SE	14%
**CC-8	3/76	Collected at the Kluver Ranch ~200 m upstream from the Rosebud-Cow Creek confluence	13 E,SE	14%
RC-10	3/76	Collected at the Kluver Ranch ~10 m downstream from the confluence of Cow Creek with Rosebud Creek	15 E	25%
RC-13	10/75	Collected at the Kluver Ranch ~1 km below the confluence of Cow Creek with Rosebud Creek	19 E	25%
RC-14	10/75	Collected at the Polich Ranch (Box 14) along Rosebud Creek	24 NE	55%
RC-15	10/75	Collected ~400 m south of the confluence of Rosebud Creek with the Yellowstone River	40 N,NE	73%

* Rosebud Creek.

** Cow Creek (intermittent stream).

† It is assumed that the plume exposure will be cumulative since the stream flow is northerly and the water from each site, as it moves north, will reflect the plume exposure from each quadrant of the wind rose through which it has passed.

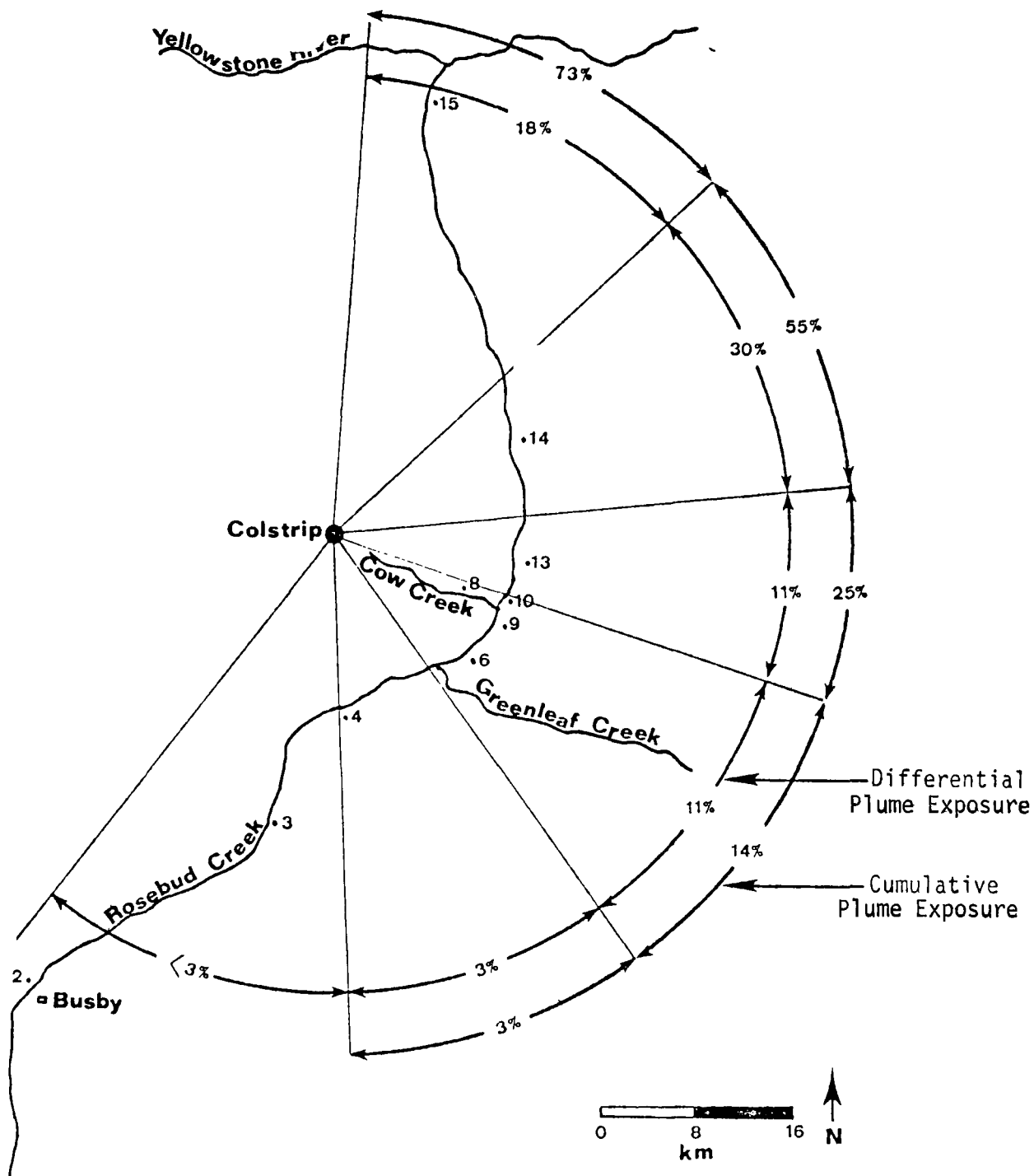


Figure 4. Rosebud Creek sampling stations in relation to wind exposure from Colstrip (Heimbach and Super 1973). (Station 1 located approximately 30 km south of Busby)

2. The Sites RC-3 and RC-4 are also not reflective of mining and/or plume exposure but generally indicative of the effects of agricultural activities which tend to increase in the downstream (northerly) direction. Each successive station should reflect increasing changes attributable to irrigation return flow, primarily during the June-October irrigation season.
3. Comparison of RC-6 and RC-9 with RC-13 *et seq.* should reflect changes which occur due to inputs from the Cow Creek drainage as well as impacts associated with the cumulative effects of plume exposure.

SECTION V

METHODS AND PROCEDURES

Water samples were collected at each sampling station on a monthly basis between October 1975 and April 1977. Samples were collected in acid-washed polyethylene or polypropylene bottles. Temperature was measured in the field. Dissolved oxygen was measured either in the field with a YSI Model 54-RC meter or by fixing samples in the field according to the azide modification of the idometric method (APHA *et al.* 1971) and subsequently titrating samples at Fisheries Bioassay Laboratory (FBL) with phenylarsine oxide substituted for sodium thiosulfate. Alkalinity, hardness, and conductivity were determined according to analytical procedures described in APHA *et al.* (1971, 1976) on samples that were chilled immediately upon collection and transported to FBL for analysis within 24 hours. All other analyses were performed on samples filtered at FBL through a 0.45 μ m glass filter and preserved according to recommended procedures described by the U. S. Environmental Protection Agency (1974) and shipped to Colorado State University for subsequent analysis according to standard procedures (U. S. EPA 1974). The precision of the metal analyses was typically $\pm 10\%$ of the amount present. The quality assurance check program of the analytical laboratory indicated analytical accuracies that were typically within the $\pm 10\%$ range.

The data obtained were keypunched and placed in permanent tape file in the Colorado State University computer system so that they could be summarized and evaluated via any of several available procedures.

SECTION VI

RESULTS AND DISCUSSION

STREAM WATER QUALITY

A synopsis of the general water quality characteristics at selected sites in Rosebud Creek is presented in Table 2; these show average changes which occur between the headwaters (RC-1) and the confluence with the Yellowstone River (RC-15). A complete tabulation of the water quality characteristics of Rosebud Creek has been presented for reference purposes in a report by Skogerboe *et al.* (1980). The general chemistry evidenced in Table 2 is very similar to that of numerous streams in southeastern Montana and the Rocky Mountain states in general. The water is quite basic, carbonate buffered, and relatively high in sulfate due to the presence of appreciable amounts of gypsum and epsomite in the region. Increases in these characteristics, and others evident in Table 2, may be largely attributed to groundwater and irrigation return flow influxes. The higher concentrations of several constituents which may be noted for the Cow Creek station (CC-8) reflect the fact that this stream is essentially stagnant for several months each year. As such, it reflects the rather poor quality of the ground water in shallow aquifers in the region.

A summary of data for several elements is presented for convenience in Figure 5. In this figure, data for stations RC-2 and RC-3 have been pooled to obtain upstream references; data for RC-4, RC-6, and RC-9 have been pooled to represent stream conditions above the Cow Creek confluence; pooled data for RC-10 and RC-13 reflect changes just downstream of Cow Creek; and the pooled data for RC-14 and RC-15 indicate concentration levels as Rosebud Creek approaches its confluence with the Yellowstone River. The lower end of the bar in each case (Figure 5) indicates either the detection limit of the analysis method or the lowest concentration measured for the element in question; the upper end of the bar indicates the maximum concentration measured at each site; the percentage given above each bar indicates the fraction of the total measurements for which the element was present above the detection limit; and the star (-*-) indicates the mean for each case. This was computed, however, using the detection limit as the actual concentration for those samples where a particular element could not be detected; since the concentrations were likely less than the detection limits, the averages should be taken as upper limit estimates.

Examination of the data summarized in the figure suggests the following general conclusions. The average concentrations of the elements are generally low and within the criteria limits established by EPA for protection of aquatic life (U.S. Environmental Protection Agency 1977). A previous report (Skogerboe *et al.* 1979) has shown that, even though such heavy

TABLE 2. SUMMARY OF MEAN VALUES AND RANGES OBSERVED AT SELECTED ROSEBUD CREEK STATIONS^{a/}

Water quality parameter	Mean values and ranges observed at station numbers ^{b/}				
	RC-1	RC-6	RC-13	RC-15	CC-8
pH	8.4 (8.0-8.8)	8.5 (8.0-8.8)	8.4 (8.0-8.7)	8.4 (8.1-8.8)	8.0 (7.8-8.2)
H ⁺ buffer capacity	0.71 (0.41-1.38)	0.71 (0.42-1.49)	0.75 (0.43-1.51)	0.74 (0.39-1.36)	1.66 (1.17-2.07)
Specific conductivity (μ siemens)	857 (647-979)	1244 (967-1450)	1266 (856-1496)	1352 (558-1798)	5870 (5410-6510)
Hardness (mg CaCO ₃ /liter)	445 (345-484)	556 (400-659)	560 (421-659)	542 (215-687)	2790 (2530-3060)
Alkalinity (mg CaCO ₃ /liter)	377 (270-425)	407 (326-488)	409 (244-480)	418 (313-492)	470 (451-528)
Chloride (mg/liter)	2.9 (1.0-7.0)	4.8 (2.5-8.0)	5.0 (2.8-8.0)	7.3 (2.1-28)	25 (22-29)
Sulfate (mg/liter)	145 (90-260)	316 (175-375)	332 (250-405)	388 (160-605)	2950 (710-3880)
Total dissolved solids (mg/liter)	535 (252-780)	808 (551-1000)	836 (610-980)	926 (431-1367)	5220 (4220-6220)
Ca (mg/liter)	88 (58-110)	84 (45-140)	86 (56-140)	81 (45-150)	199 (120-350)
Mg (mg/liter)	142 (54-930)	170 (50-1200)	180 (69-1200)	150 (30-900)	611 (350-810)

TABLE 2. CONTINUED

Water quality parameter	Mean values and ranges observed at station numbers ^{b/}				
	RC-1	RC-6	RC-13	RC-15	CC-8
Total Fe (mg/liter)	0.66 (0.26-1.68)	1.2 (0.25-3.8)	1.2 (0.19-4.4)	2.2 (0.33-24)	0.44 (0.1-1.3)
Suspended Fe (mg/liter)	0.63 (0.23-1.6)	1.1 (0.2-3.7)	1.1 (0.16-4.3)	2.1 (0.25-22)	0.41 (0.1-1.3)
Na (mg/liter)	21 (13-25)	68 (35-88)	68 (34-90)	130 (60-740)	570 (520-620)
K (mg/liter)	5.9 (3.0-9.2)	10 (3.3-22)	11 (0.9-22)	11 (4-23)	29 (19-40)

^{a/} See Figure 1

^{b/} Average over 18-month monitor period; ranges given for same period.

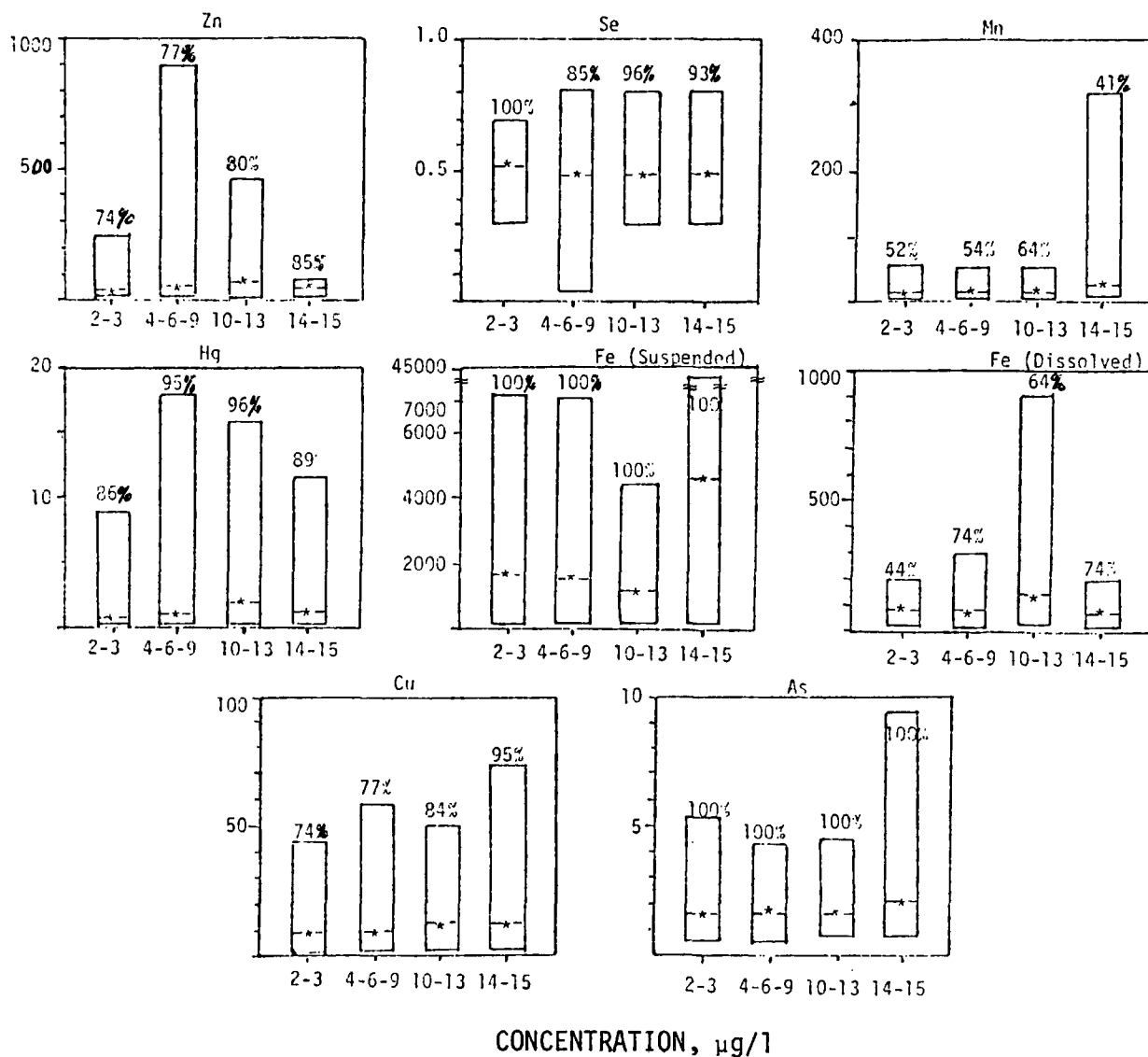


Figure 5. Comparisons of trace element concentrations in Rosebud Creek.

[Lower limits of bars indicate detection limits; upper limits of bars indicate maximum observed concentrations; *- indicates average concentration observed; and percentage numbers indicate frequency of occurrence above detection limit. Station numbers are given below respective bars (see text).]

metals may be available to the surface waters, the basic characteristics of such waters are likely to limit their solubilities through carbonate and/or hydroxide precipitation processes. Comparison of the averages for each element between the headwaters and downstream stations also suggests that prominent influxes of soluble heavy metals are absent. The solubility limitations mentioned above surely support this observation. Finally, possible influxes of dissolved Fe, Hg, and Zn in the region of the Cow Creek confluence are suggested by the upper limit excursions of the bar graphs; this is discussed below. It should also be noted that data are not presented for Al, Cd, Cr, Pb or Ni because the majority of samples had concentrations of these elements below the detection limits, i.e., generally less than 10 µg/liter.

Further indications of the general water quality features of Rosebud Creek and their implications are presented in three-dimensional graphs (Figures 6-15). The results have been temporally and spatially blocked on the basis of the following rationales.

A. Temporal blocks

1. January and February represent months of low stream flow and low surface and subsurface runoff.
2. March and April reflect stream flow increases generally caused by snowmelt at the elevations near Colstrip.
3. May and June are blocked to average the further stream flow increases associated with snowmelt at elevations nearer the headwaters and the increased spring precipitation.
4. July through September represent the average low flow summer months during which irrigation return flows may influence water quality.
5. October through December cover low stream flow periods during which precipitation, irrigation return flows, and ground water inflows should be generally minimal.

B. Spatial blocks

1. Sampling sites RC-1 through -3 serve as reasonable water quality references because they are located upstream nearest the headwaters above the primary regions of possible irrigation return flow impact, and where the Colstrip plume impact should be less than 3% of the total.
2. Site RC-4 is also in a region where possible plume impact should be small (~3%), but farming, ranching, and population (Busby, Montana) effects on water quality may be significant.

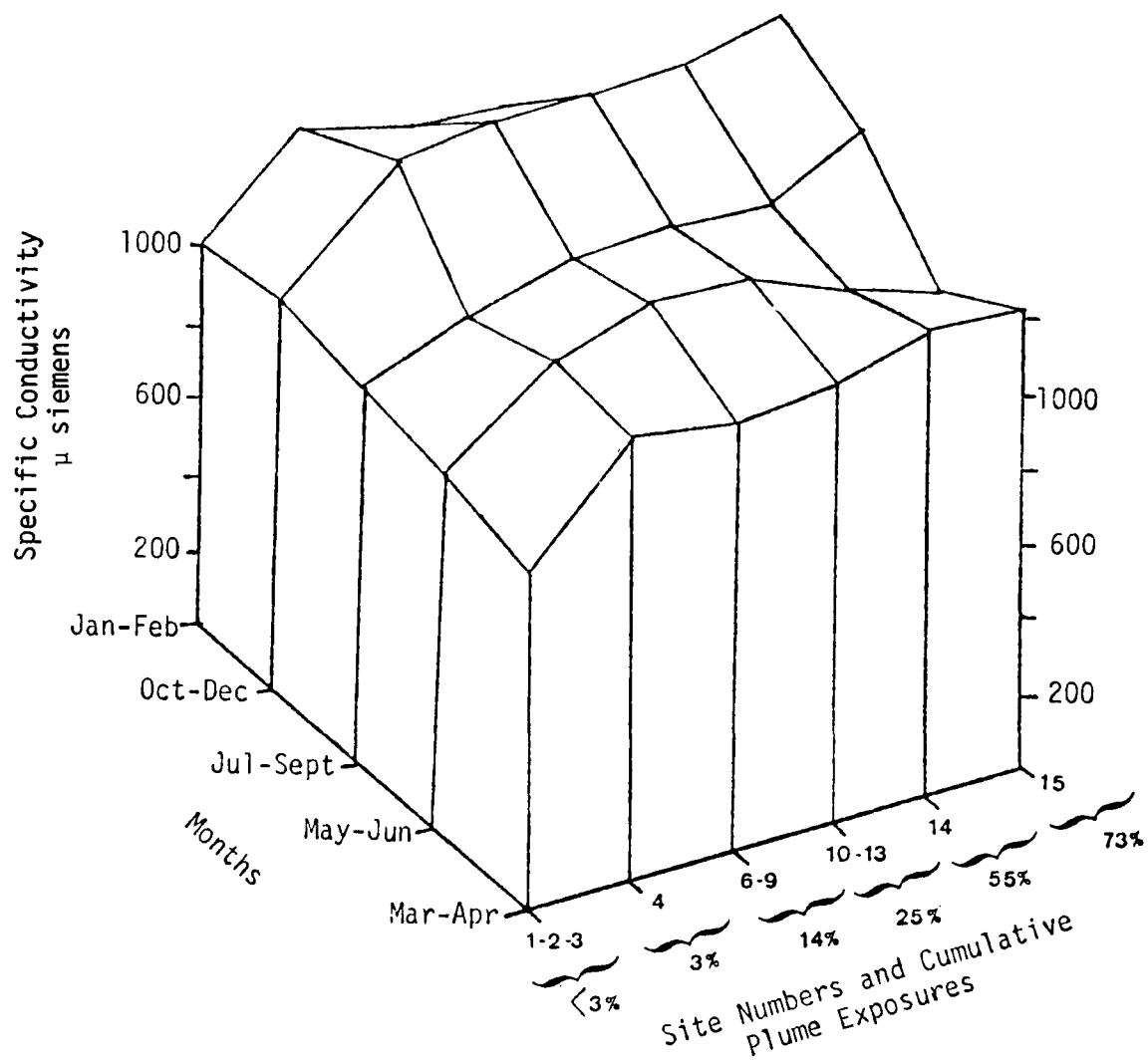


Figure 6. Spatial and temporal changes in specific conductivity. [Percentages indicate cumulative wind exposure (see Figure 4)].

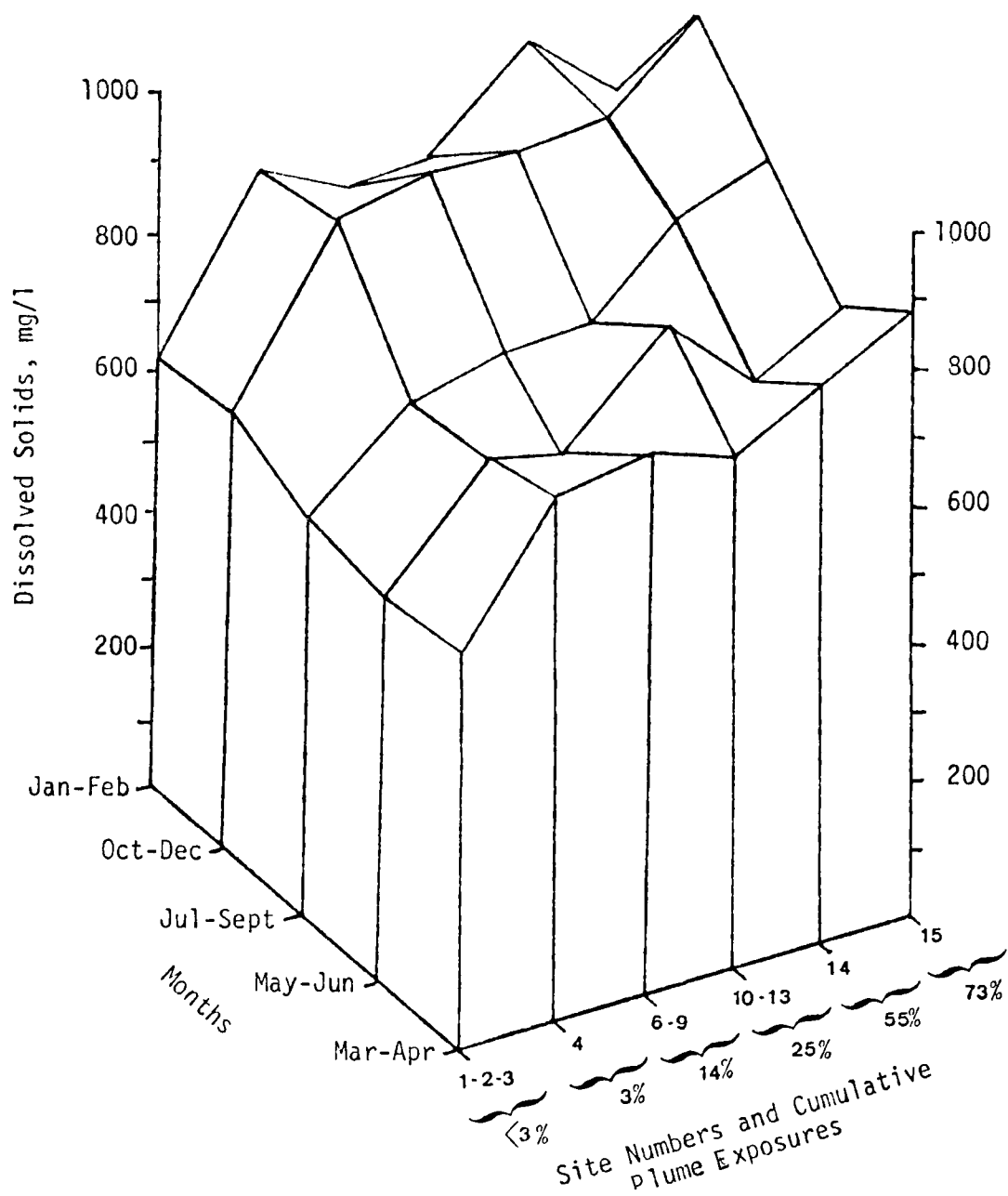


Figure 7. Spatial and temporal changes in dissolved solids. [Percentages indicate cumulative wind exposure (see Figure 4)].

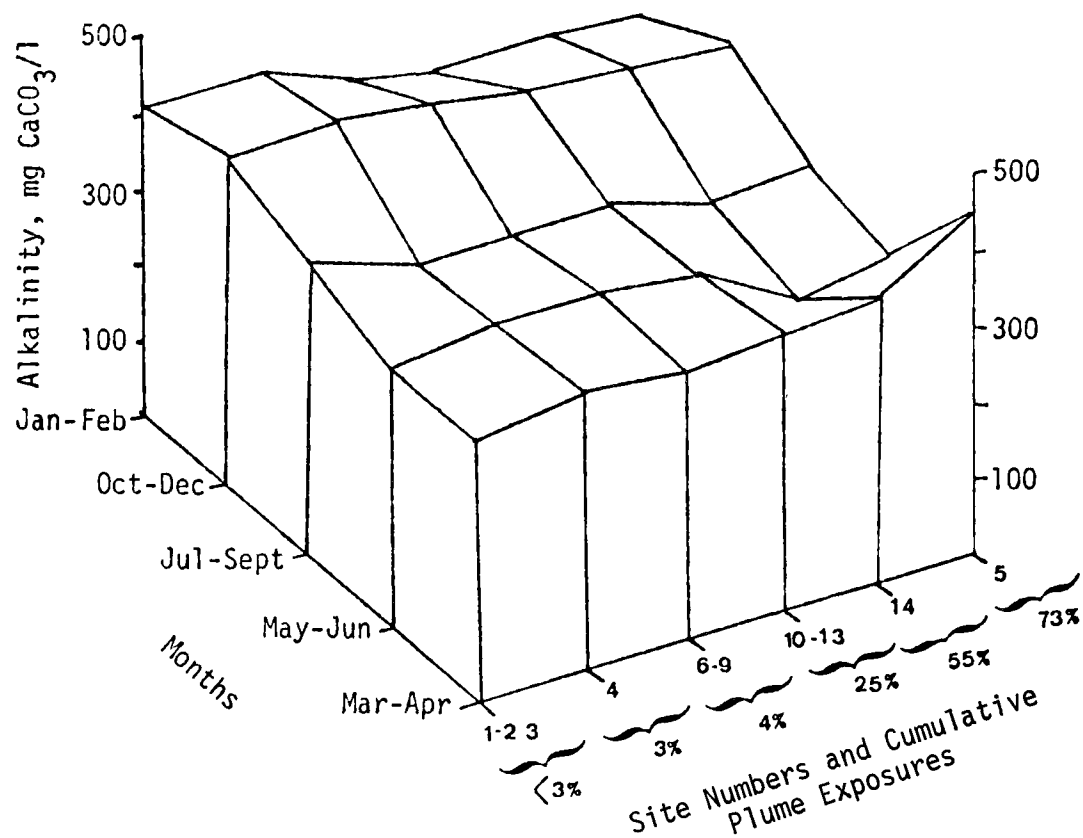


Figure 8. Spatial and temporal changes in alkalinity.
[Percentages indicate cumulative wind exposure
(see Figure 4).]

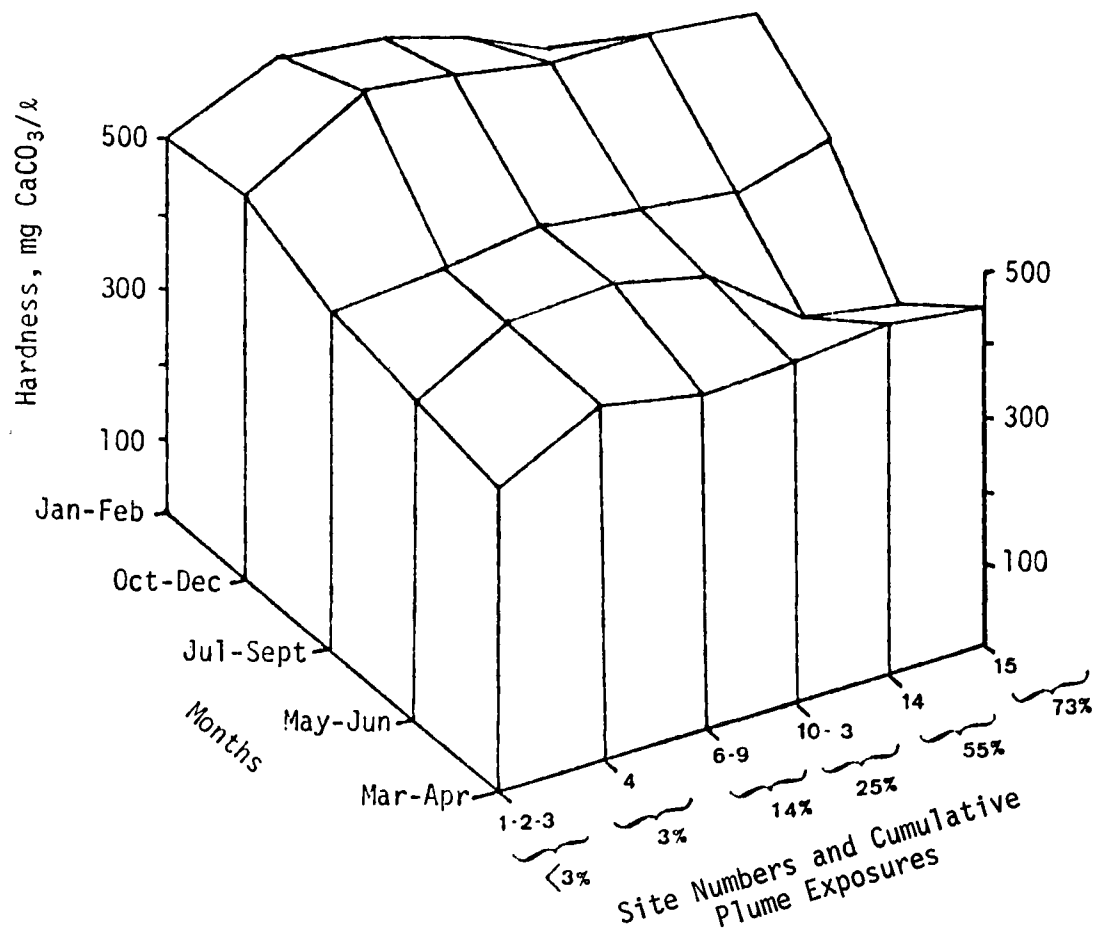


Figure 9. Spatial and temporal changes in hardness. [Percentages indicate cumulative wind exposure (see Figure 4).]

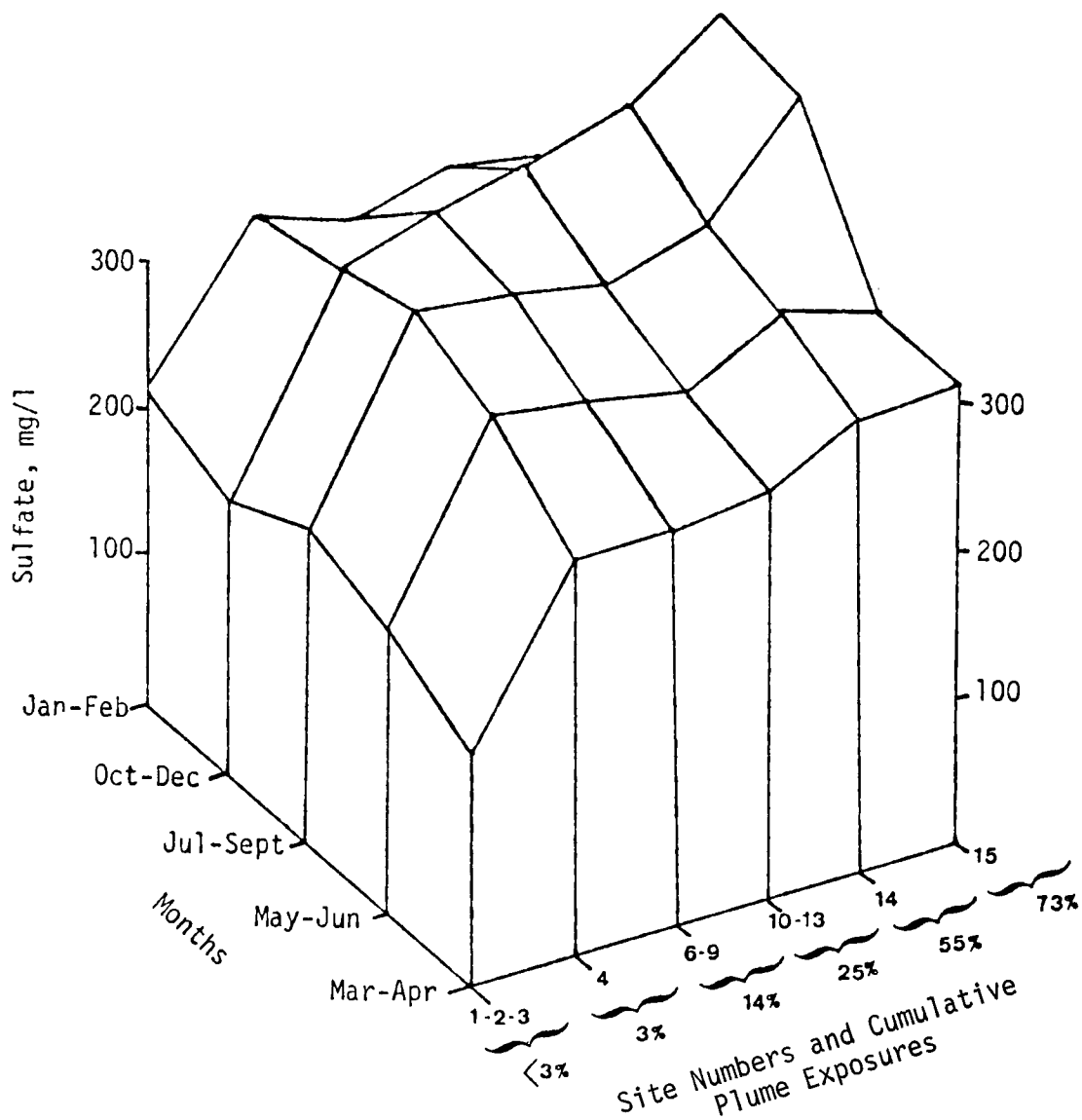


Figure 10. Spatial and temporal changes in sulfate. [Percentages indicate cumulative wind exposure (see Figure 4).]

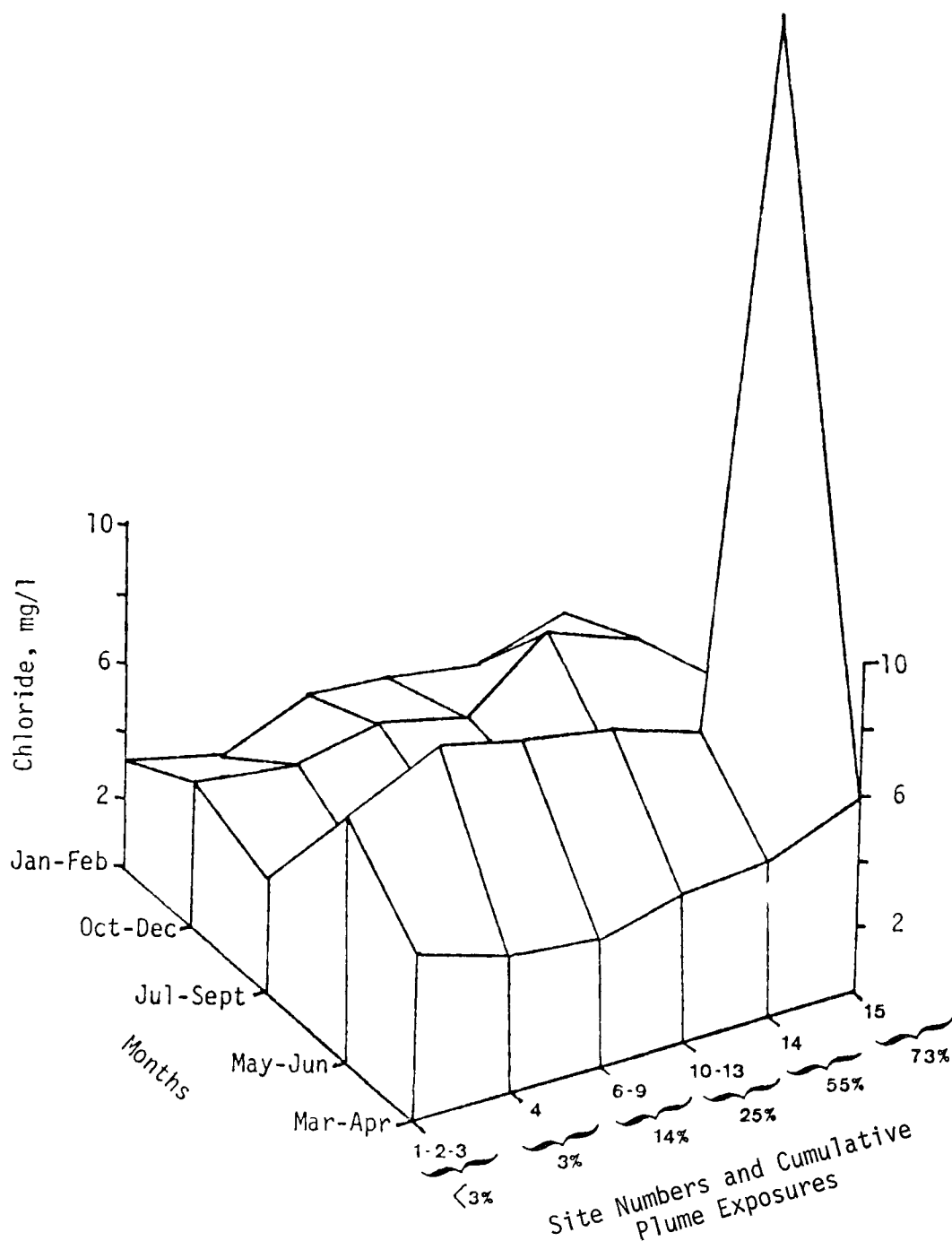


Figure 11. Spatial and temporal changes in chloride. [Percentages indicate cumulative wind exposure (see Figure 4).]

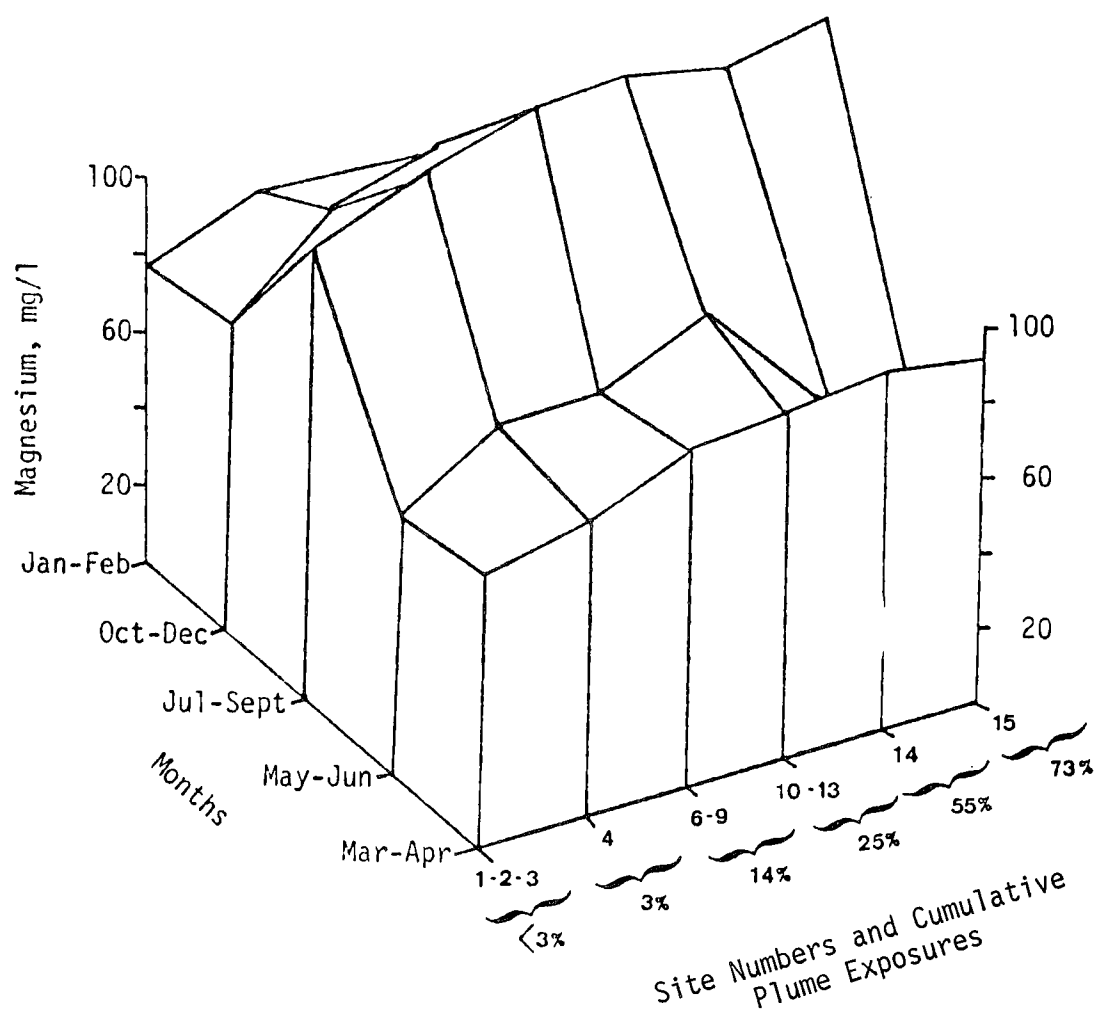


Figure 12. Spatial and temporal changes in magnesium. [Percentages indicate cumulative wind exposure (see Figure 4).]

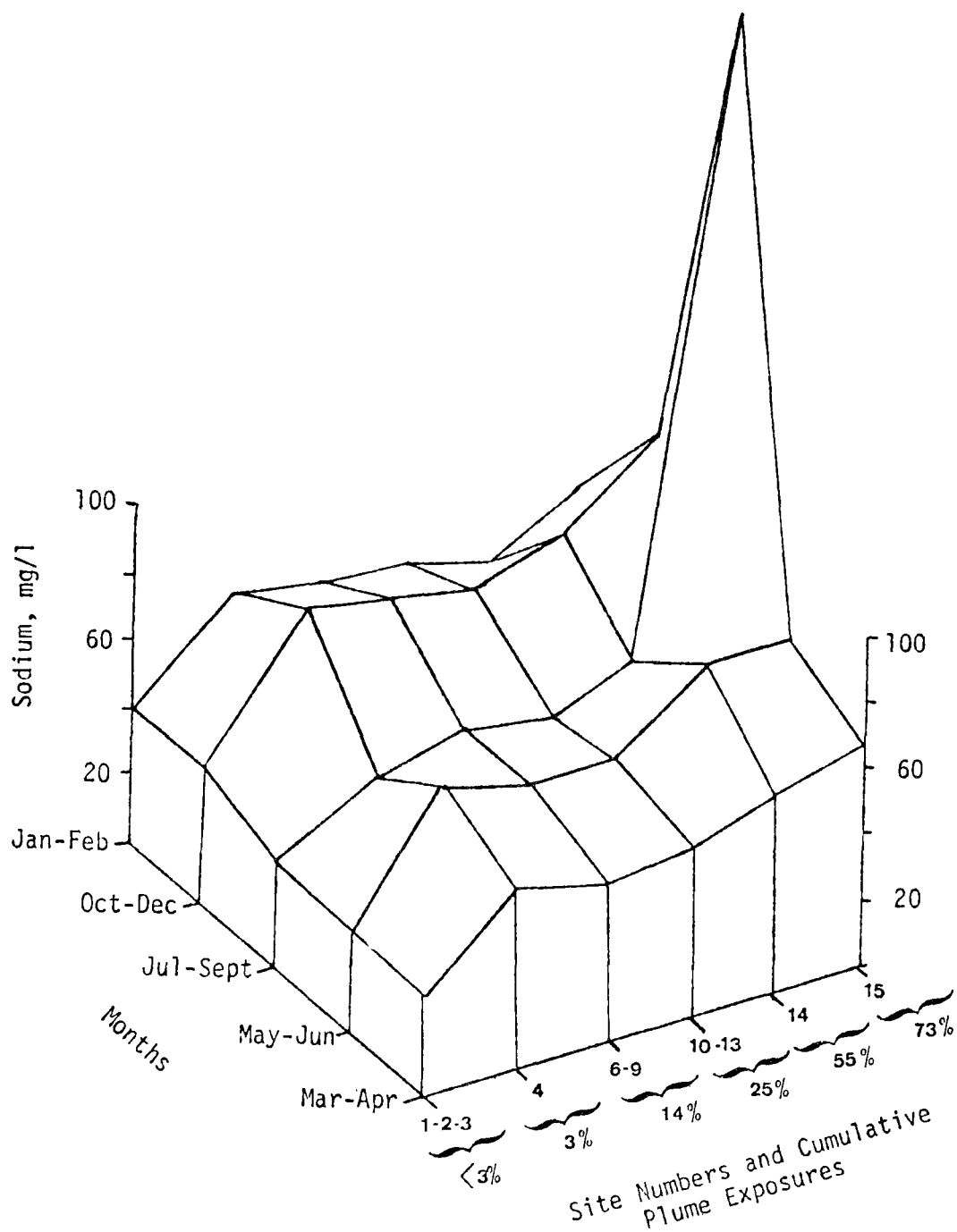


Figure 13. Spatial and temporal changes in sodium. [Percentages indicate cumulative wind exposure (see Figure 4).]

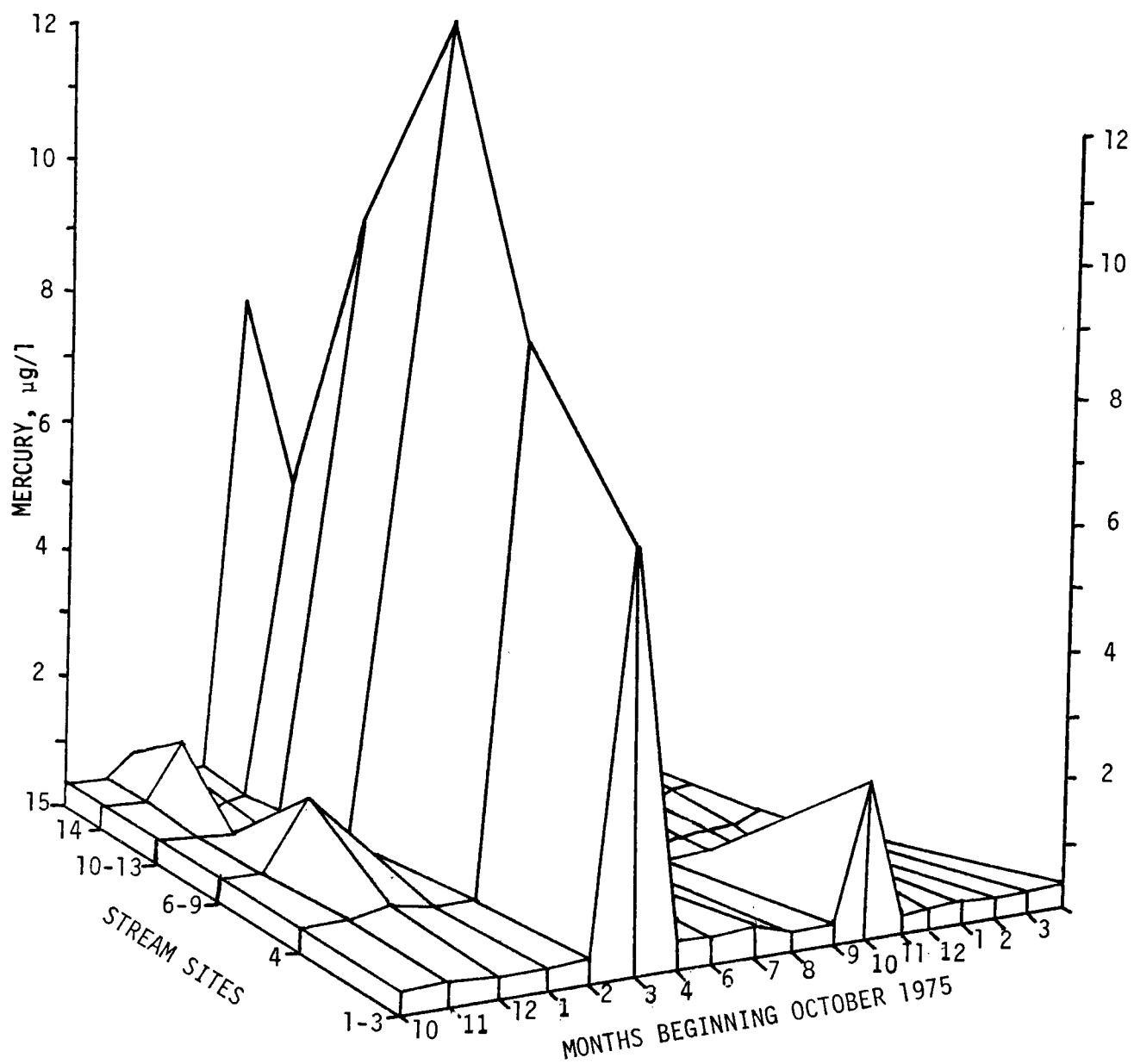


Figure 14. Spatial and temporal changes in mercury.

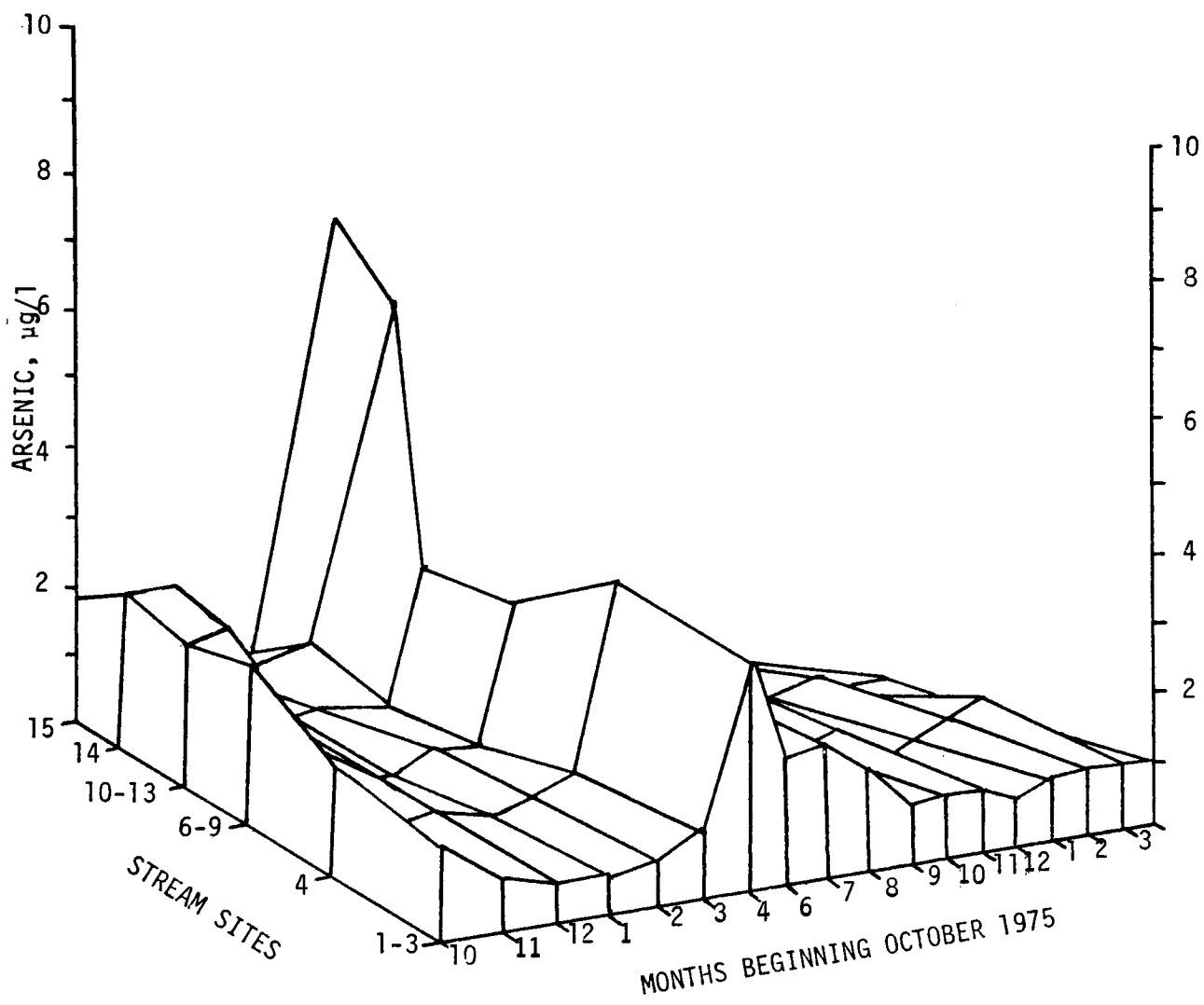


Figure 15. Spatial and temporal changes in arsenic.

3. Sites RC-6 through -9 may reflect enhanced plume impacts (~14%) and serve as a reference for water quality characteristics prior to inputs from the Cow Creek drainage.
4. Sites RC-10 through -13 should show further plume impacts combined with influx from the Cow Creek drainage.
5. Sites RC-14 and -15 should be indicative of the degree of transport of contaminants from the stream segment closest to Colstrip combined with further plume impacts from north of there on to the Yellowstone River.

The water quality parameter values presented in the following graphs (see Figure 6 *et seq.*) are therefore averages for the above temporal and spatial groupings. As such, they provide average indications of the temporal and spatial changes which occurred over the study period. It must be emphasized, however, that samples collected on a monthly basis can only be rough approximations of the averages and that interpretations based on them are also limited by the general validity of the monthly collections. Note that the temporal blocks are arranged progressing from the high to the low stream flow months.

The general water quality characteristics of Rosebud Creek may be inferred from Figures 6 through 13. The specific conductivity and dissolved solids (Figures 6 and 7) tended to increase in the downstream direction reaching highest values during the low streamflow months. The alkalinity and total hardness values (Figures 8 and 9) show the same general trends and tend to be reasonably constant (factors of 2 or better) due largely to the geology of the region in which carbonate and gypsum are quite ubiquitous. The pH (8.0-8.8) remained consistently in the range characteristic of carbonate-buffered natural water systems. The general influence of gypsum, and other sulfate minerals such as epsomite, may be inferred from the sulfate data (Figure 10) and parallel changes in sulfate-associated cations such as magnesium (Figure 12) and sodium (Figure 13). Indeed, sulfate was the principal anion (other than carbonate and bicarbonate) while chloride (Figure 11) was a minor anion and phosphate, nitrate, and nitrite were rarely observed and then only at levels approximating 0.1 mg/liter (Skogerboe *et al.* 1980).

Examination of these summary figures for these general water quality parameters does not indicate readily identified and/or definitive effects on water quality that can be directly associated with the mining or power plant operations at Colstrip. The changes observed can be rationalized on the basis of other probable causes including the increases in irrigation and population along the stream course.

As indicated above and in other reports (Mesmer and Baes 1975, Van Hook and Shults 1977, Van Voast *et al.* 1977, Skogerboe *et al.* 1979) the alkaline and carbonate buffer characteristics of western surface and groundwaters are likely to exert prominent influences on the heavy metal concentrations in streams such as Rosebud Creek. In essence, equilibrium calculations indicate that many heavy metals, even if available, will typically be precipitated as carbonate or hydroxide species under such conditions. Such computations

would, of course, be rendered invalid if certain chemical entities capable of forming soluble complexes with the heavy metals were present at significant concentrations in the stream or the influent groundwater. The characteristically low levels of chloride found (Figure 11) and the fact that checks on the total organic carbon produced values of 1-2 mg/liter or less tend to minimize the possibility of soluble entities being formed with chloride or organic ligands. Furthermore, evaluation of the heavy metal concentrations observed provides reason for accepting the model calculations as generally valid. The comparisons presented in Table 3 indicate that the maximum and the mean soluble concentrations observed at all stations were generally equivalent to or less than those predicted by calculation. This indicates, in a circumstantial context, that either these metals were not being delivered to the stream or that their concentrations were controlled by precipitation equilibria. If the latter is the case, the precipitate species indicated in Table 3 are those most likely to exert primary control.

The results for mercury presented in Figure 14 indicate the occurrence of sharp excursions in the dissolved concentrations observed. A similar profile was observed for arsenic (Figure 15). Although these increases were observed in varying extents along the entire stream course, they were most prominent in the region directly east of Colstrip (sites RC-6 through -15) and were apparent in a less pronounced way for selenium. Examination of precipitation and temperature records, as well as the stream flow data, indicated that the influx of mercury and arsenic coincided temporally with snowmelt and surface runoff periods. This is illustrated for mercury in Figure 16 where it may be noted that the primary influx was associated with the March 1976 snowmelt at the low elevations but not with that at high (headwaters) elevations (June 1976). These observations suggested a mechanistic possibility for impacts of the power plant on surface waters, i.e., accumulation of contaminants emitted in and on the relatively clean and nonreactive snowfall followed by delivery to surface waters during runoff (snowmelt) periods.

The routes via which this type of transfer may occur have been discussed (Van Hook and Shults 1977); these are shown in Figure 17. The focus of the present discussion is directed toward those routes involving the atmosphere as a transfer medium.

EMISSION LEVELS

The 750 megawatt plant at Colstrip began test operation in late 1975 and achieved essentially full-scale operations in early 1976. Emission test data for Unit No. 2 (Montana Power Co. 1976a, b) are summarized in Table 4; the values should be multiplied by two to estimate the emissions for both units. These indicate operation within state and federal emission standards. Calculations based on coal consumption and emission rates indicate that nominally 5-15% of the sulfur in the coal may be emitted as SO_2 . Limited data on the chemical composition of the fly ash (Montana Power Co. 1976b, Crecelius *et al.* 1978) are given in comparison to the concentrations of the same elements in the coal (Gluskoter *et al.* 1977) in Table 5. These data verify that the fly ash is primarily composed of "glassy" and relatively insoluble matrix constituents as previously shown (Davison *et al.* 1974; Natusch *et al.*

TABLE 3. COMPARISON OF CALCULATED AND OBSERVED METAL CONCENTRATIONS FOR ROSEBUD CREEK

Metal (oxidation state)	Concentrations ($\mu\text{g/l}$)			Chemical limiting the solubility ^{d/}
	Calculated ^{a/}	Mean value ^{b/}	Maximum observed ^{c/}	
Al(III)	3	<100	<100	Al(OH) ₃
Cd(II)	0.3	<5	<5	CdCO ₃
Cu(II)	350	5	10	Cu(OH) ₂
Fe(II)	140	<100 ^{e/}	190 ^{e/}	FeCO ₃
Fe(III)	100	<100 ^{e/}	190 ^{e/}	Fe(OH) ₃
Hg(II)	36,000	0.05	20	Hg(OH) ₂
Mn(II)	2,500	10	22	MnCO ₃
Pb(II)	1	<10	20	PbCO ₃
Zn(II)	0.1	6	10	ZnCO ₃

^{a/} Calculated for: pH = 7.8, alkalinity = 250 mg/l as CaCO₃, sulfate = 150 mg/l, chloride = 5 mg/l, and phosphate = 0.1 mg/l.

^{b/} Average of all values measured over study period.

^{c/} Maximum concentration observed at any sampling site over the 18-month study period.

^{d/} Precipitate which limits solubility as predicted by the equilibrium calculations for the above average stream conditions.

^{e/} Analysis technique used does not differentiate between Fe(II) and Fe(III).

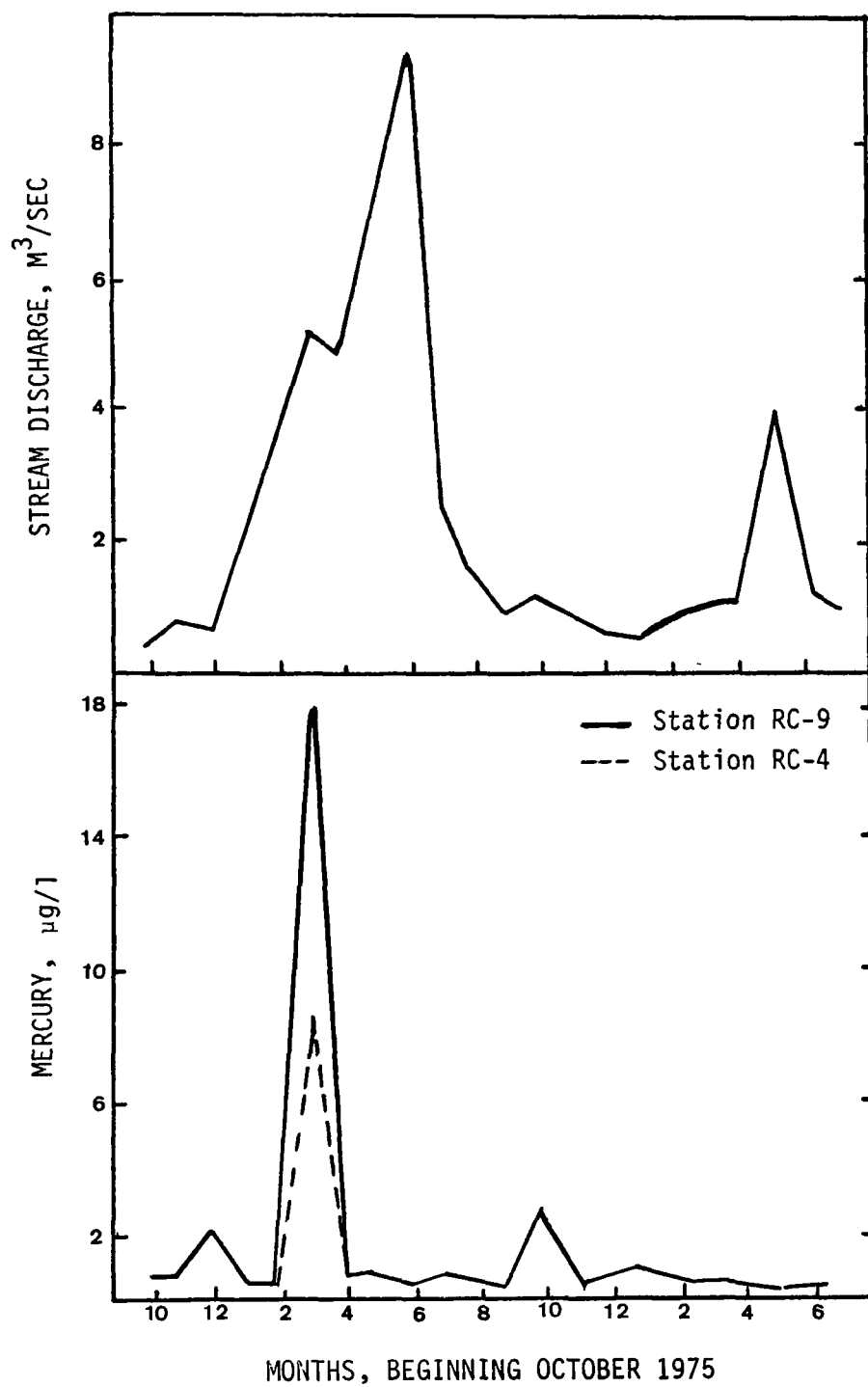


Figure 16. Comparison of mercury levels with stream flows.

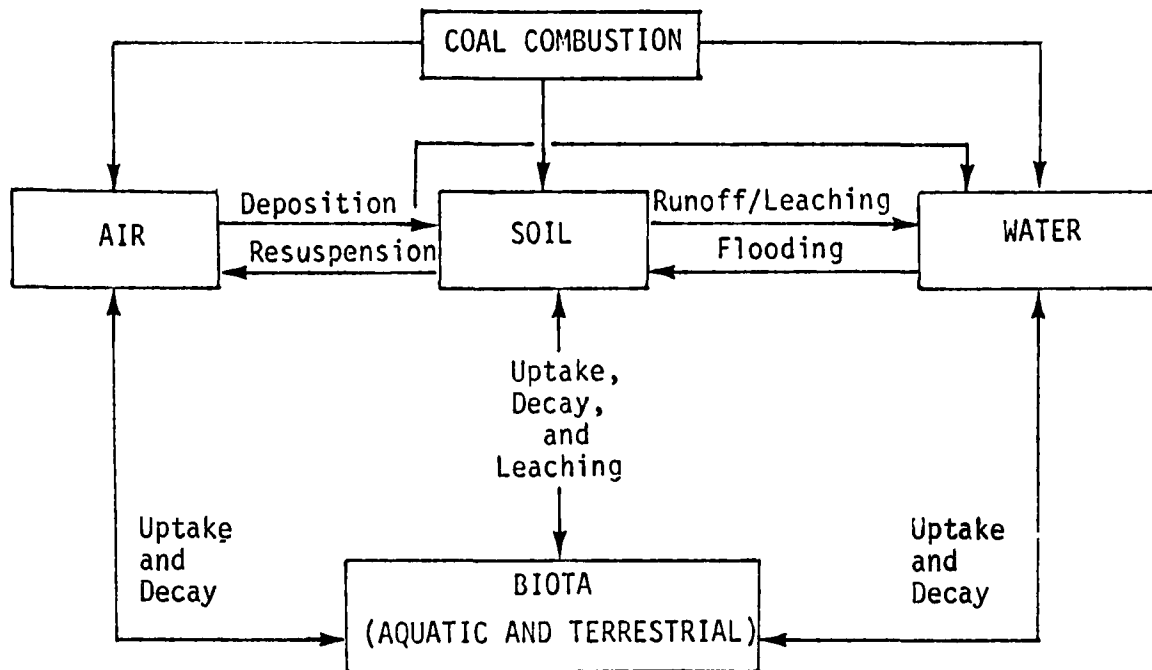


Figure 17. Schematic of transfer pathways between coal combustion sources and aquatic ecosystems (Van Hook and Shults 1977).

TABLE 4. EMISSION TEST DATA FOR COLSTRIP
UNIT NO. 2 (MONTANA POWER CO. 1976a, b)

Emitted species	Concentration ^{a/}		
	Kg/hr	μg/m ³	g/10 ⁶ BTU
Particulate matter	47.9	37,500	15.6
SO ₂	353.9	257,400	115.4
NO _x (as NO ₂)	355.7	278,600	115.5

^{a/} Stack concentrations based on the average of three tests; plant operating at 325 megawatts (3.08×10^8 BTU/min) gross load and using three scrubbers; coal use rate was 181 tons/hr; mean percent sulfur \approx 0.7.

TABLE 5. ELEMENT CONCENTRATIONS IN FLY ASH EMITTED
AT COLSTRIP COMPARED WITH CONCENTRATIONS IN COAL BURNED

Element	Mean concentration ($\mu\text{g/g}$)	
	Emitted fly ash ^{a,b/}	Coal ^{c/}
Al	15,400	17,800
As	N.D. ^{d/}	5.7
Ba	10,900	390
Br	72	17
Co	10	5.2
Cr	178	19
Fe	12,300	0.81
Mn	410	41
Se	370	3.3

^{a/} Fly ash samples collected April 19, 20, and 21, 1976. Averages of three samples reported. Analysis by neutron activation analysis (Crecelius *et al.* 1978).

^{b/} Federal Power Commission (1974), U.S. Environmental Protection Agency (1974).

^{c/} Crecelius *et al.* (1978).

^{d/} Elements not detected indicated by N.D. including Cd, Hg, and V; concentrations less than approximately 1 $\mu\text{g/g}$ fly ash.

1975, Natusch and Taylor 1980; Linton *et al.* 1976; Natusch 1976). It is significant to note that the more volatile elements, e.g., As, Cd, and Hg, were not detected. This is consistent with the typical size dependence results given in Table 6 (Davison *et al.* 1974) and indirectly supports the tendency of volatile elements to condense onto fly ash surfaces as the plume cools. The mean aerodynamic diameters of the particles emitted are less than 4-5 μm (usually around 1 μm) (Montana Power Co. 1976a,b); these are highly enriched in volatile elements (see Table 6). These smaller particles are also those which enter into long range transport (Friedlander 1977). In view of the fairly universal presence of significant concentrations of such elements in U.S. coals (Table 7) and their tendencies to be emitted and collect on aerodynamically small particles, the above observations are applicable on a widespread basis.

ATMOSPHERIC TRANSPORT AND DISPERSION

Current transport modeling techniques rely primarily on a Gaussian plume formulation which in turn relies on an *a priori* specification of the local wind velocity and turbulence levels (Turner 1974). The application of such models to transport calculations must take the following caveats into account (Hales 1973). First, the dispersion parameters used in the model were determined for open, flat terrain. Such parameters do not take into account the effects of rough terrain on dispersion; thus the calculations must be regarded as approximations only. Second, one cannot assume, in general, that power plant site measurements of wind speed, direction, and atmospheric stability are going to persist on a spatial or temporal basis beyond a few kilometers. As a result, dispersion calculations based on such data must be considered approximate for transport modeling over longer ranges.

In the present program, dispersion calculations based on the Gaussian model have been carried out for approximation purposes. The example results shown in Figure 18 are for emission and transport of mercury vapor to ground level along the plume centerline. In view of the stack temperatures, mercury is emitted in the vapor state. One report (Gluskoter *et al.* 1977) has shown that more than 90% of the mercury in coal was lost by vaporization when the coal was ashed at $\sim 100^\circ\text{C}$ in a low temperature ashing unit. Its vapor pressure is such that it is also transported in the vapor state at typical ambient temperatures. Mercury levels in the coal burned are nominally 0.05-0.1 $\mu\text{g/g}$ (Gluskoter *et al.* 1977). Based on the discharge and coal use rates characteristic of the Colstrip plants and the assumption of 85% emission for Hg, concentrations of 5-10 $\mu\text{g Hg/m}^3$ are estimated for stack exit emission levels. The calculations summarized in Figure 18 assumed a conservative level of 1 $\mu\text{g Hg/m}^3$ at the stack exit. The results indicate: (i) that the impact of the plume at ground level should occur at reasonable distances downwind of the plant and typically within the Rosebud Creek watershed when the wind is from westerly directions, and (ii) increasing wind velocity should result in ground level impact of the plume closer in to the plant. In addition, it should be noted that the presence of a temperature inversion will affect the dispersion and that Gaussian reductions in the concentrations are expected as a function of distance from the plume centerline (Turner 1974). Finally, even though these model calculations are for a gaseous entity, the fact that the particles emitted have aerodynamic diameters approximating 1-2 μm or less (Montana Power Co. 1976a, 1976b)

TABLE 6. TYPICAL DEPENDENCE OF THE CONCENTRATIONS OF SOME TRACE ELEMENTS ON THE AERODYNAMIC PARTICLE DIAMETER OF EMITTED COAL FLY ASH (DAVISON *ET AL.* 1974)

Aerodynamic diameter (μm)	Concentration ($\mu\text{g/g}$)										
	As	Cd	Cr	Mn	Ni	Pb	Sb	Se	Tl	V	Zn
>11.3	680	13	740	150	460	1100	17	13	29	150	8100
11.3-7.3	800	15	290	210	400	1200	27	11	40	240	9000
7.3-4.7	1000	18	460	230	440	1500	34	16	62	420	6600
4.7-3.3	900	22	470	200	540	1550	34	16	67	230	3800
3.3-2.1	1200	26	1500	240	900	1500	37	19	65	310	15000
2.1-1.1	1700	35	3300	470	1600	1600	53	59	76	480	13000

TABLE 7. MEAN CONCENTRATIONS OF TRACE ELEMENTS IN U.S. COALS
(GLUSKOTER *ET AL.* 1977)

Element	Mean concentration ($\mu\text{g/g}$ for indicated region)			
	Illinois ^{a/}	Appalachia ^{b/}	Western U.S. ^{c/}	Colstrip ^{d/}
Ag	0.03	0.02	0.03	0.06
As	14	25	2.3	5.7
B	110	42	56	--
Ba	100	200	500	390
Be	1.7	1.3	0.46	--
Br	13	12	4.7	17
Cd	2.2	0.24	0.18	--
Co	7.3	9.8	1.8	5.2
Cr	18	20	9.0	19
Cs	1.4	2.0	0.42	1.4
Cu	14	18	10	--
F	67	89	62	--
Hg	0.2	0.2	0.09	--
I	1.7	1.7	0.52	--
Mn	53	18	49	41
Mo	8.1	4.6	2.1	--
Ni	21	15	5.0	16
P	64	150	130	--
Pb	32	5.9	3.4	--
Sb	1.3	1.6	0.58	37
Se	2.2	4.0	1.4	3.3

TABLE 7. CONTINUED

Element	Mean concentration ($\mu\text{g/g}$ for indicated region)			
	Illinois ^{a/}	Appalachia ^{b/}	Western U.S. ^{c/}	Colstrip ^{d/}
Sn	3.8	2.0	1.9	--
Th	2.1	4.5	2.3	3.4
Tl	0.66	--	--	--
U	1.5	1.5	1.2	--
V	32	38	14	33
Zn	250	25	7.0	--

^{a/} 114 samples^{b/} 23 samples^{c/} 28 samples^{d/} Crecelius *et al.* (1978)

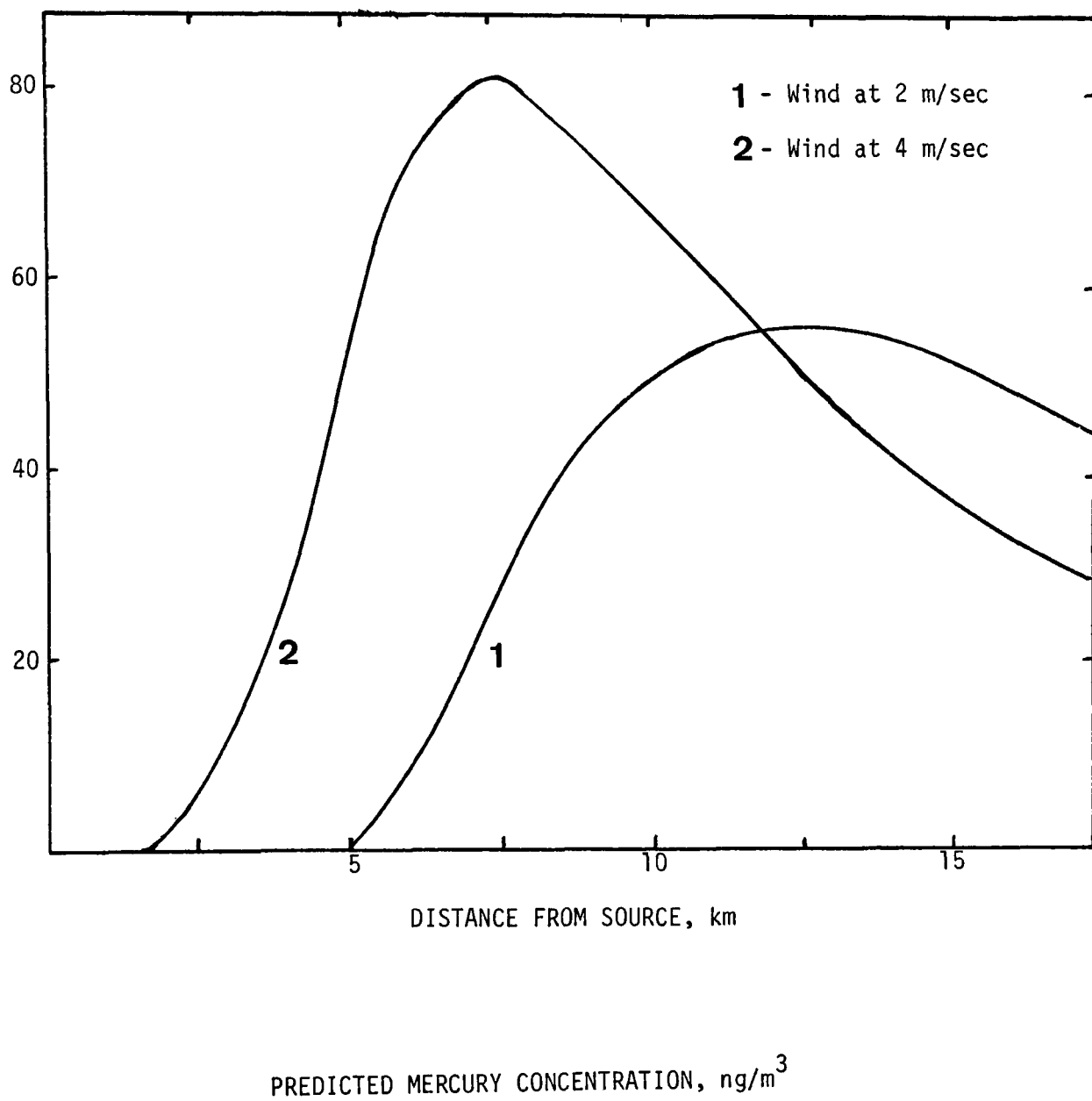


Figure 18. Model calculation of mercury. (Dispersion along the plume centerline at ground level.)

indicates that their settling velocities are quite low (Friedlander 1977). Consequently, these calculations also serve as approximations of the fallout profiles for particulates. The concentration scale in these instances must be considered only in qualitative terms, i.e., indicative of the fallout trend(s).

A two-day atmospheric sampling program was run at Colstrip in October 1976 to determine the levels of mercury along the plume direction, to evaluate the ratio of gaseous-to-particulate mercury characteristic of the plume, and to qualitatively check the model calculations. A 0.45 μm membrane filter was used to remove the particulates. This was backed by a graphite filter coated with a thin film of gold to collect gaseous Hg via formation of the Au:Hg amalgam. Two such sampling trains were run in parallel at each of several sites located at various distances downwind of the plant. A control site was also run upwind (~2 km). Winds were relatively constant in terms of direction and velocity on both sampling days so location of the samplers near the plume centerline was relatively simple. The atmospheric stability conditions were stable on the first day but moderately unstable the second.

The results plotted in Figure 19 summarize the ranges and means observed for the duplicate samples collected at each site ~2-3 km downwind. These data show high levels of gaseous Hg at the plume centerline which undergo the expected (Gaussian) dropoff in moving away from the centerline. The values near the plume centerline are clearly greater than the upwind control levels of $5.5 \pm 2.5 \text{ ng/m}^3$. The differences observed between the two days reflect the increase in the wind velocity on the second day as well as the increased atmospheric instability for that day. Analyses of the membrane filters also indicated that Hg associated with particulates was not detectable; the general conclusion based on the data was that more than 95% of the Hg remained in the gas phase during transport. This is consistent with the vapor pressure characteristic of Hg.

The membrane filters were also analyzed for As and Se but neither of these elements was detected. Based on the sampling and analysis conditions used, the atmospheric As and Se levels were generally less than 50 ng/m^3 . In view of the small aerodynamic size of the emitted particles, however, spatially defined concentration profiles for particle associated elements comparable to that observed for mercury can be anticipated.

DEPOSITION AND SCAVENGING FROM THE PLUME

Scavenging of particles and gases by precipitation has been measured in the neighborhood of coal-fired power plants; the best experimental results relate to total mass scavenged (Friedlander 1977). Rainfall scavenging of trace organics when the solubility coefficients are known has been theoretically modeled (Hales 1973). In effect, two types of wet deposition may be operative: (i) rainout refers to the inclusion of the constituents in the precipitation during its formation (nucleation) in the clouds; (ii) washout deals with the removal of the contaminants below cloud base during the fall of the precipitation. Junge (1963) and Gatz (1976) have evaluated the washout ratio, i.e., the ratio of the concentration of the pollutant in the

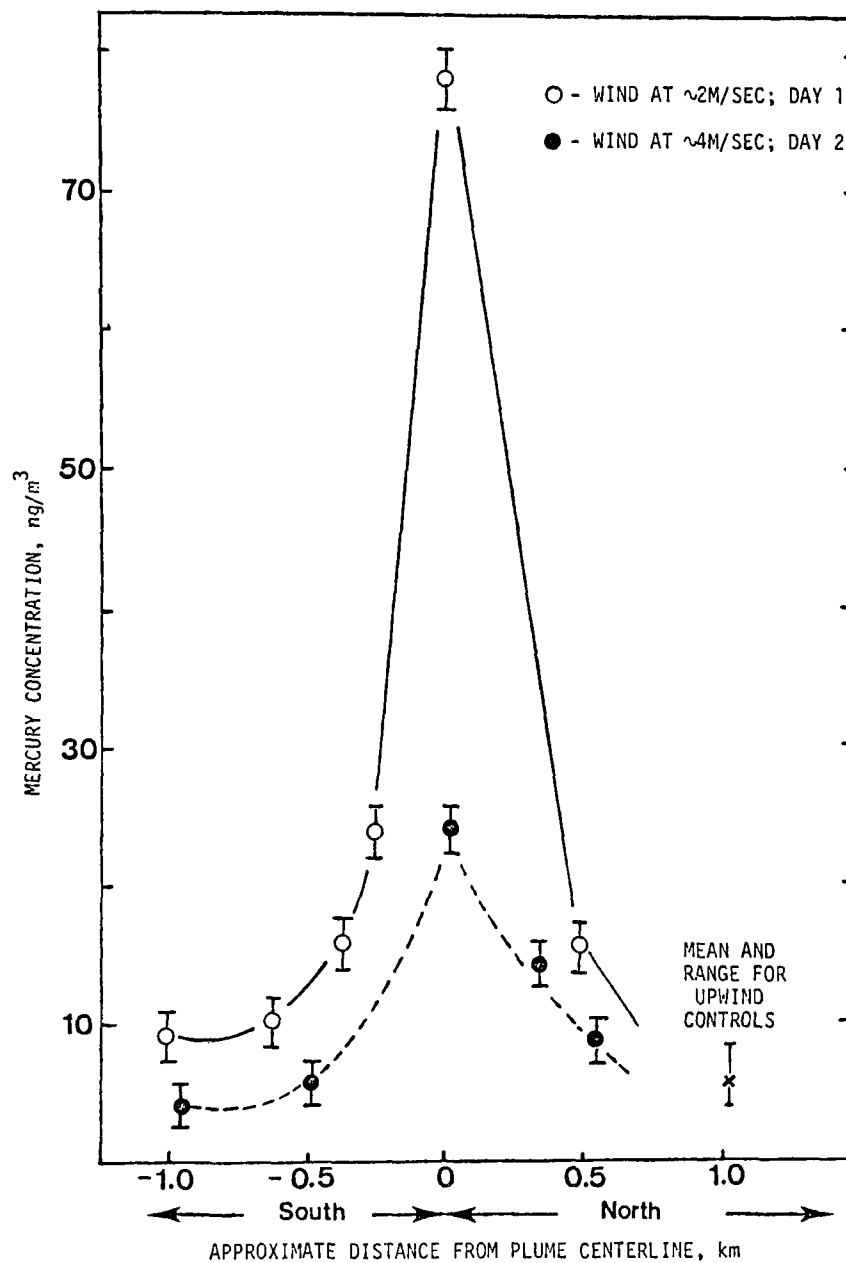


Figure 19. Measured atmospheric mercury concentrations. (Error bars indicate ranges for replicate samples.)

precipitation to its concentration in air. These ratios appear to be fairly constant for trace contaminants, and approximate 3×10^5 . Values this high indicate that precipitation can effectively remove contaminants from the atmosphere and that the process can "preconcentrate" the constituents in the precipitation.

Dry deposition of particles to ideal smooth surfaces as influenced by particle size and degree of atmospheric turbulence can be reasonably predicted but deviations from ideal conditions cause the predictions to be less reliable. Modeling of deposition of small particles to trees, grass, lakes, etc. is largely based on guesswork (Friedlander 1977). The matter is further complicated by the effects of rough terrain on meteorological conditions and atmospheric stability. As a result, a dry deposition velocity of 1 cm/sec for all particles being delivered to real surfaces is often applied to calculate the deposition flux (Friedlander 1977).

In spite of the uncertainties in models for wet and dry deposition, the fact remains that constituents in plumes are deposited on the terrestrial surface and may ultimately reach ground and surface waters. To estimate the extent of such possible impacts, snow samples were collected in the watershed areas lying in the mean winter wind direction from Colstrip and draining into Rosebud Creek. Primary rationales for the choice of snow samples have been: (i) snow serves as a relatively clean substrate for the accumulation of pollutants; (ii) snow cover reduces the fugitive dust and soil contamination problems so that the plume fallout can be more readily differentiated from other contamination sources; (iii) the snow cover serves as an integrator of the fallout flux over the time period(s) between successive snowfalls; (iv) the temperature regimes involved may operate to preserve the identities of the trace contaminants through the reduction of chemical transformations; and (v) some of the trace contaminants may be included in the snowflakes during the nucleation-growth and/or fallout processes. The latter may involve particulates serving as nuclei for snow formation, condensation of gaseous constituents with the nuclei at the low temperatures involved ($\leq -20^\circ\text{C}$), or adsorption onto the formed nuclei.

Snow samples collected in 1976, 1977, and 1978 were analyzed for mercury. The results summarized in Table 8 are generally indicative of the plume impacts which may be inferred from the profiles shown in Figures 18 and 19 and also suggest the integrative deposition of mercury over time. The 1978 snowfall collections were also analyzed for other constituents (Ca, Fe, Mn, Zn) considered likely to be indicative of the plume impact. The concentration patterns observed were not as pronounced as those for mercury, probably due to the occurrence of significant amounts of those elements in the soils and humic materials of the region.

Snow collections carried out during December 1977 and January 1978 were analyzed for water soluble As , Cl^- , F^- , Hg , NO_3^- , Se , and SO_4^{2-} . The results for mercury are summarized in Figures 20 and 21 using the mean easterly wind direction for December and January to estimate the mean centerline of the plume impact. The results are expressed in terms of $\mu\text{g Hg}$ per square meter of surface for a snow depth of 1 cm to provide an approximation of the mercury flux integrated over the time that the snow surface was exposed. Figure

TABLE 8. SUMMARY OF MERCURY LEVELS IN SNOW

Month and year	Sample Collection Locale (number of samples)	$\mu\text{g Hg/liter}$ snowmelt (mean value, range in parentheses)
February 1976	Upwind controls (4)	<0.02
	Downwind 4-6 km (4)	0.67 (0.38-0.78)
	Downwind 8-10 km (4)	0.16 (0.08-0.28)
March 1976	Upwind controls (4)	0.05 (<0.02-0.1)
	Downwind 4-6 km (6)	5.6 (4.3-6.8)
January 1977	Remote controls (5)	0.05 (0.04-0.07)
	Downwind 2-4 km (3)	0.22 (0.17-0.28)
	Downwind 4-6 km (3)	0.55 (0.44-0.67)
	Downwind 6-8 km (3)	0.15 (0.11-0.18)
	Downwind 8-12 km (4)	0.06 (0.04-0.08)
March 1978	Remote controls (5)	0.07 (0.04-0.09)
	Downwind 4-7 km (8)	0.12 (0.09-0.19)
	Downwind 10-12 km (5)	0.06 (0.04-0.08)

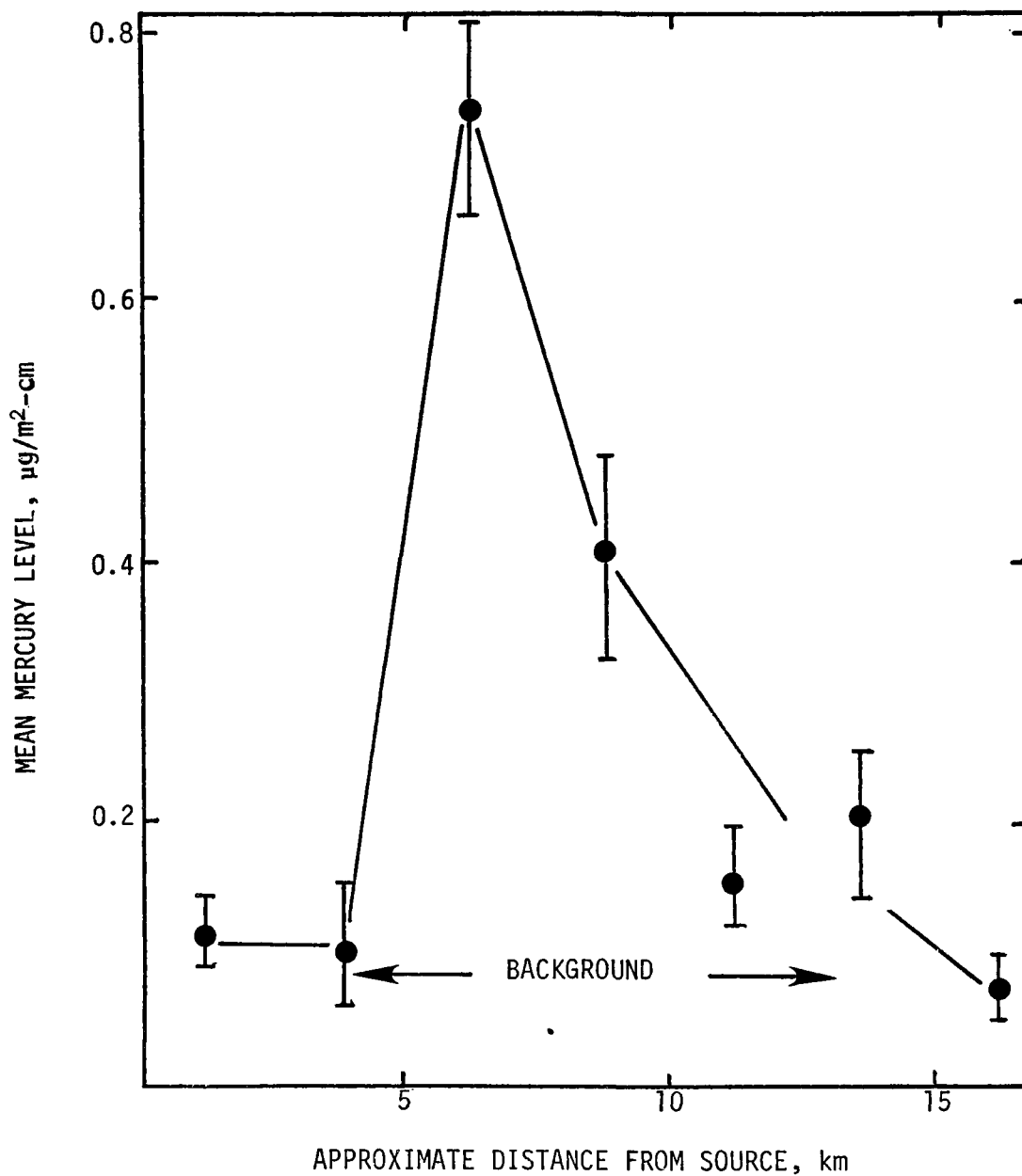


Figure 20. Mercury levels in snow versus downwind distance from the Colstrip plant. (Each point is the average of 3-5 samples; vertical bars indicate the standard deviations.)

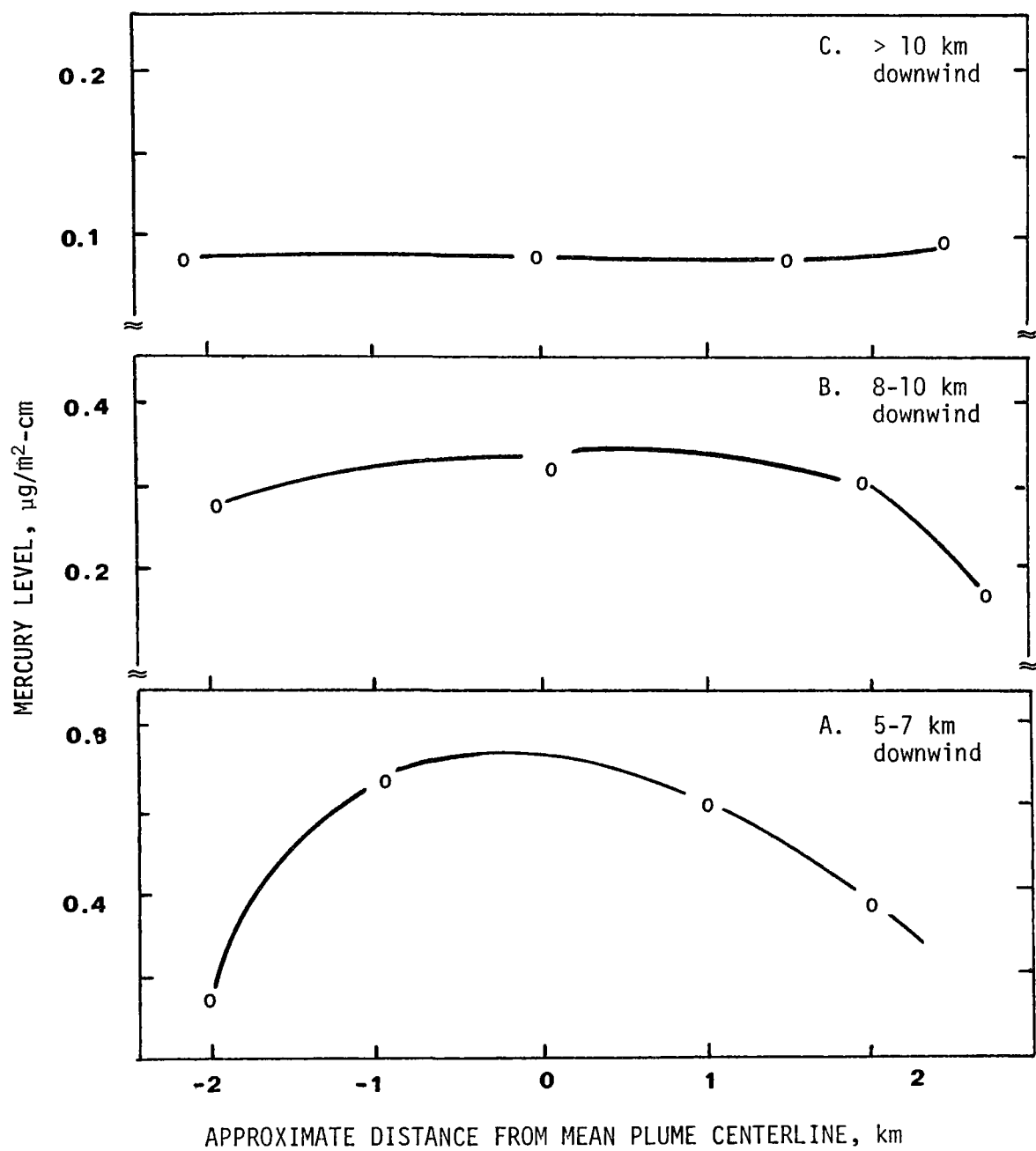


Figure 21. Mercury levels in snow versus distance from the mean plume centerline.

20 indicates the general accumulation of Hg in the snow along the mean plume direction dropping off with distance from the plant due to dilution and scavenging of the plume during transport. The plots also demonstrate the localization of the plume impact close in and dilution of its impact farther out due to its lateral expansion (Figure 21).

Comparable results were observed for As and Se, as shown in Figure 22. Finally, results for the anions determined are summarized in Table 9. These results suggest fairly significant levels of plume impact which also tend to drop off with distance.

It should be emphasized that the snow samples were allowed to melt at ambient temperature (20°C) with the melt water being immediately filtered, as it formed, through 0.45 μ m membrane filters to remove particulates before chemical preservatives were added to maintain the shelf lives of the solutions. Thus, the element concentrations found in the melt solutions are representative of only the water soluble fractions of each constituent and, consequently, of those fractions which might be transported to the stream via surface runoff. This is clearly an important distinction in considering potential impacts on surface waters.

STREAM IMPACTS

Analyses of water samples collected at the Rosebud Creek sampling stations have been discussed above. The results summarized in Figures 14 through 16 quite clearly show that increased concentrations of dissolved As and Hg occur concomitantly with snowmelt periods occurring near Colstrip but not with those occurring in the headwater regions remote from Colstrip. This clearly implies the importance of accumulation of plume constituents in snowfall and delivery to streams via surface runoff. The importance of other possible sources of snow contamination is largely minimized for the following reasons.

1. The snow and stream measurements have relied exclusively on determining soluble (dissolved) constituents. The As and Hg associated with soils, coal, and humic matter are generally insoluble.
2. Analyses for organic mercury indicated that more than 95-98% was present in inorganic forms. Thus, although the historical use of organic mercury to treat seeds might prove to be a source of mercury during runoff, the relatively long environmental lifetimes of such compounds and the failure to find them in surface waters suggest that such sources are not primary.
3. Analyses of snow and stream samples using a fluorescence technique (American Public Health Association Intersociety Committee 1977) to approximate total concentrations of dissolved polynuclear aromatic compounds (PNA) indicated their influx into Rosebud Creek in parallel with As and Hg during the March 1978 runoff (Figure 23) and (circumstantially) their deposition in snow downwind of Colstrip. Although these concentration estimates approximate total PNA concentrations, these observations coupled with the demonstration that

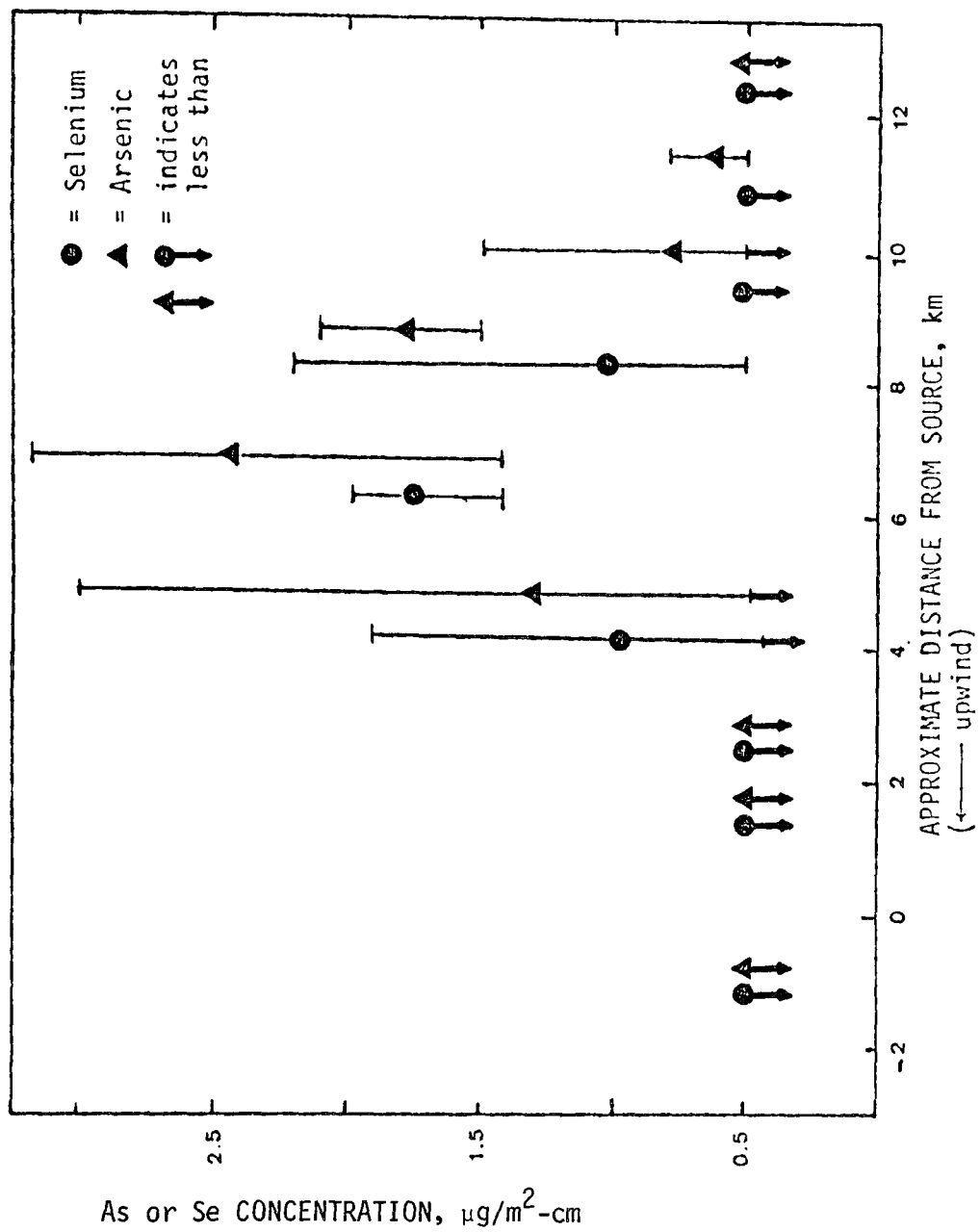


Figure 22. Concentrations of arsenic and selenium in snowfall as functions of distance from the source. (Each point is the average of 3-5 samples; vertical bars indicate the standard deviation; arrows downwind indicate less than concentration values.)

TABLE 9. SUMMARY OF SNOW ANALYSES FOR ANIONIC SPECIES WHICH MAY ORIGINATE FROM COAL COMBUSTION

Approximate distance from source (km)	Mean constituent concentration ^{a/} ($\mu\text{g/ml}$ snowmelt water)			
	Cl^-	F^-	NO_3^-	SO_4^{2-}
2.5-5	2.6	0.42	1.8	2.6
5-7.5	1.8	0.20	1.2	1.5
7.5-10	1.3	0.21	1.1	0.90
10-12.5	0.69	0.20	1.4	1.2
12.5-15	0.66	0.13	1.3	0.89
Controls ^{b/}	0.88	0.15	0.55	0.62

^{a/} Average of three to four samples; individual sample results usually consistent to $\pm 20\text{-}30\%$ of the mean concentration given.

^{b/} Collected approximately 80 km west of Colstrip near Red Lodge, Montana.

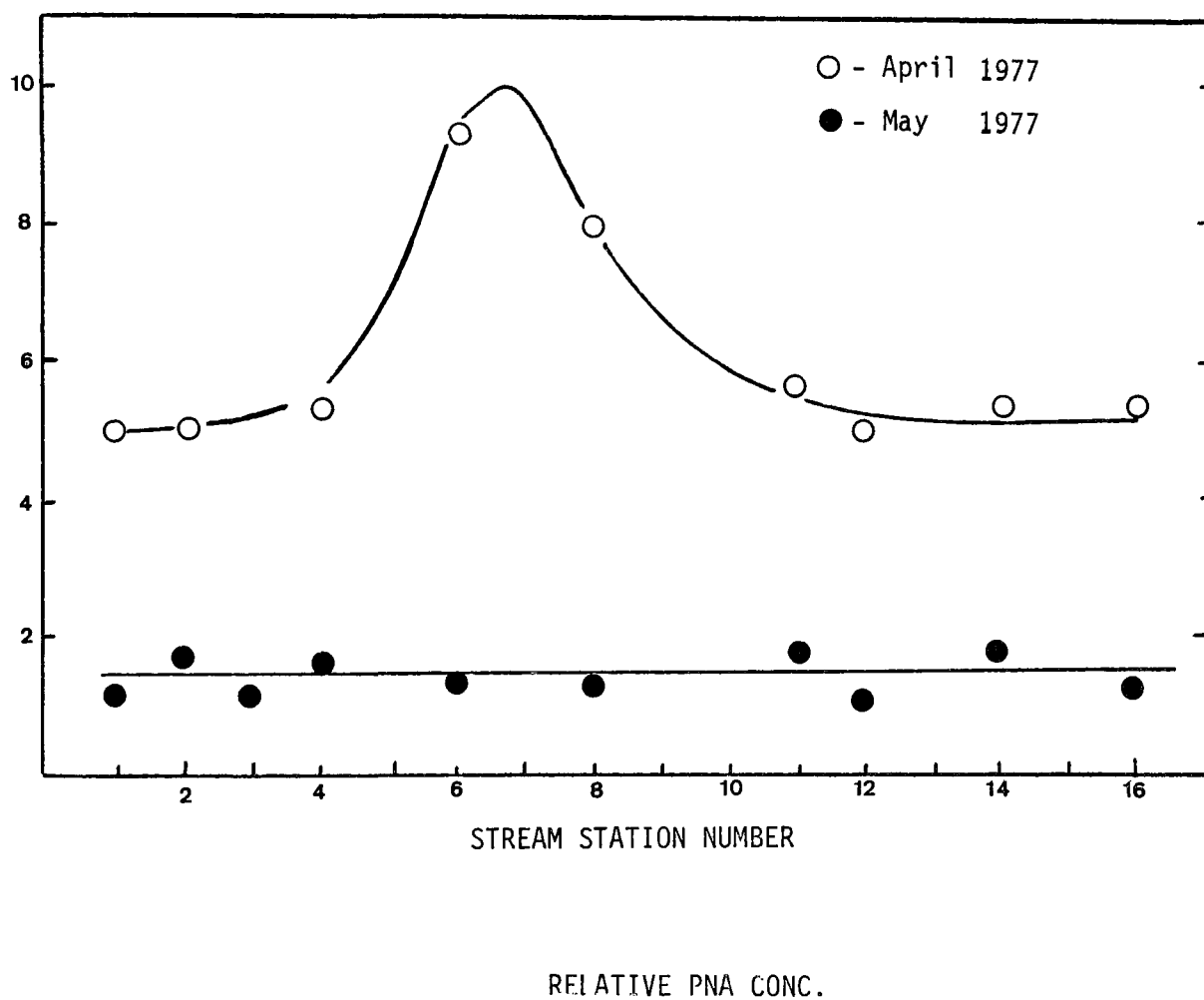


Figure 23. Relative concentrations of PNA compounds found in Rosebud Creek during and after snowmelt runoff.

PNA compounds tend to accumulate on the surfaces of emitted fly ash particles (National Academy of Sciences 1972, Davison *et al.* 1974, U.S. Environmental Protection Agency 1976, Van Hook and Shults 1977, Natusch and Taylor 1980) tend to emphasize the plume as their primary source.

The general rationale of the plume impact on Rosebud Creek via the snow accumulation-runoff mechanism may also be roughly inferred on the basis of mass balance calculations. The two coal-fired units at Colstrip consume nominally 360 tons of coal per hour (Montana Power Co. 1976a, 1976b) having a mean mercury concentration approximating 0.1 $\mu\text{g/g}$ (Gluskoter *et al.* 1977). Accepting 85% as a reasonable emission factor for mercury, it may be estimated that 780 g of mercury are emitted each day giving a total of 23 kg/month. Since the wind direction is toward Rosebud Creek about 70% of the time (Heimbach and Super 1973), about 16 kg of mercury may be transported in that direction each month.

It was noted (Figure 16) that the stream flow for February and March ranged from about 1-5 m^3/sec and may have averaged around 2 m^3/sec . The peak mercury concentration during this time approximated 18 $\mu\text{g/l}$. Use of this value and the mean stream flow, and assuming that the snow runoff and the peak mercury concentration was maintained for one week, it may be estimated that the total mercury discharge in the stream would be approximately 2.2 kg. This amounts to roughly 14% of the mercury transported in the direction of the Rosebud watershed during one month, i.e., 16 kg. If the mercury accumulated in the snowfall over a longer time period, a proportionately smaller percentage accumulation from the plant emissions would be determined.

Mass balance calculations of this type serve only as crude approximations. Although it is generally agreed that gaseous entities such as mercury and small particles are typically transported over distances approximating 50 kilometers or more (Friedlander 1977), it should be noted that the Rosebud Creek watershed extends 50 to 100 km to the east of Colstrip depending on the projection direction. Thus, atmospheric contaminants transported over distances in excess of 40-50 km may still impact on the stream during snowmelt runoff. In essence, these mass balance approximations suggest that the mechanism of impact presented above is reasonable.

A complete assessment of potential impacts of such plume constituents on surface waters via the snow collection-runoff route must take into account site-specific conditions which will affect the deposition and accumulation processes and the runoff transfer process. The results discussed above apply specifically to the Colstrip-Rosebud Creek site and the meteorological and watershed parameters for the time periods embraced by this study. Surely the effects observed and the magnitudes thereof will vary considerably from year to year. Consideration of factors which may affect the accumulation processes is germane to the present discussion.

ACCUMULATION OF ATMOSPHERIC CONSTITUENTS IN SNOWFALL

As previously indicated, the accumulation of gaseous pollutants with snow may occur via condensation, nucleation, or adsorption processes enhanced by the fact that snow tends to form at temperatures below $\sim -20^{\circ}\text{C}$. Particulate material can accumulate by serving as the nuclei for snow formation and growth, by gravitational settling, and by impactive removal under (micro- or macro-scale) turbulent atmospheric conditions.

The accumulation and retention of gaseous entities such as Hg vapor via snow will clearly depend on the operative temperature regime. To demonstrate this, known amounts of Hg vapor were generated in the lab by reduction of standard mercury solutions with stannous ion and passed through loosely packed columns of snow held at various temperature levels using a cryostatic chamber. At levels between -2 to -8°C , small fractions (10-25%) of the mercury vapor were absorbed by the melted water on the snow crystal surface(s). Mercury accumulated in this manner was retained when the snow was allowed to continue melting and reach ambient temperature. Between -0 and -15°C the retention of Hg vapor by the snow was essentially negligible ($<5\%$), but below this retention increased rapidly to 90-100%. In view of the fact that the vapor pressure of Hg drops from 185×10^{-6} to 18×10^{-6} to 4.8×10^{-6} mm as the temperature drops to 0, -20 , and -30°C , respectively, the condensation of Hg at these lower temperatures can be anticipated. After Hg was condensed on the snow at such temperatures, raising the temperature to 0°C resulted in the recovery of most of the Hg in the vapor state. These laboratory experiments verified that snow can serve as an accumulator for mercury vapor at low temperatures ($\sim -20^{\circ}\text{C}$) but that the mercury vapor may be released back to the atmosphere when the temperatures rise. If the snow melts rapidly, a fraction of the mercury may be "dissolved" in the product water.

The inclusion of gaseous constituents such as organics in rainfall has been demonstrated by Junge (1963) and Gatz (1976). This process may also occur in the cloud during the conversion of raindrops to snowflakes but data supporting this have not been found. By analogy with the Hg case discussed above, organic plume constituents having vapor pressures approaching 10^{-6} mm at temperatures characteristic of snow nucleation ($\sim -20^{\circ}\text{C}$) may condense onto snowflakes or be adsorbed onto the surfaces thereof. Most inorganic gases (e.g., NO_x , SO_x , and CO_x) exhibit much higher vapor pressures at such temperatures; the probability of these condensing during nucleation should be quite low. It is known, however, that gases such as SO_2 , NO_x , NH_3 , CO_2 , and Cl_2 dissolve in water and hydrolyze to produce a variety of ionic species including, for example, SO_4^{2-} and NO_3^- (Junge 1963, Gatz 1976, Friedlander 1977). The prominence of such gas-to-particle conversion reactions (both homogeneous and heterogeneous) in coal combustion plumes is widely accepted as highly significant. Their occurrence during nucleation and growth of snowflakes can also be readily rationalized.

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