UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

Release of trace elements from a burning bituminous culm bank

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Open-file report 78-864
1978

This report is preliminary and has not been edited or reviewed for conformity with U.S. Geological Survey standards and nomemclature.

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from a burning bituminous culm bank

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Abstract

A burning bituminous coal waste-bank at Mather, PA was studied in order to determine if trace elements are being released into the environment in substantial concentrations. Samples of the minerals forming on the surface of the bank, the gases escaping from vents, and the water and sediment from a nearby stream were analyzed to determine the presence of these elements.

The output of trace elements from the Mather bank, as is evidenced by the minerals forming on the surface, is relatively low compared to the output from actively burning anthracite culm-banks.

Copper was the only element of potential environmental significance found accumulating on the Mather bank. However, the sediment in the vicinity of the bank and the waters immediately downstream did not have anomolously high concentrations of copper.

Relatively high concentrations of arsenic were found in the organic matter at the base of the bank but no evidence of high As values were found downstream.

No potentially toxic elements, other than sulfur, were detected in the gases being emitted from the culm-bank.

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Because of the quiescent condition of the Mather culm-bank the question of the fate of trace elements released in the burning process remains unanswered.

Introduction

An attempt was made to determine the fate of trace elements being released into the environment by a burning bituminous culm bank. Samples of the minerals forming on the surface of the bank, the gases escaping from vents, and the water and sediment from a nearby stream were analyzed to determine the presence of these elements.

The present study is an outgrowth of an investigation of the minerals forming on the surfaces of burning culm banks in the anthracite region of Pennsylvania (Finkelman, et al., 1974, Barnes, et al., in prep.). Those studies showed that, in addition to elemental sulfur and various ammonium, aluminum, magnesium, and calcium sulfates forming on the burning banks, minerals containing fluorine, selenium, tin, bismuth, lead, copper, arsenic, and germanium were also present (Table 1). Many of these compounds are highly soluble in water, raising the possibility that they are periodically flushed into the surrounding environment. No attempt was made to assess the environmental impact of these compounds.

The culm bank at Mather, Pennsylvania, was selected as the subject for this study primarily because of its size. This bank is reported (McNay, 1971) to be the largest burning coal refuse pile in the United States (21,000,000 cubic yards of material covering 45 acres). It is located about 7 miles east of Waynesburg in southwestern Pennsylvania (Figure 1). The South Fork of Tenmile Creek passes by the full length of the Mather bank ($\sim$3000 ft.), and enters the

Monongahela River about 10 miles downstream from Mather. The Mather bank is a byproduct from mining the high volatile, bituminous Pittsburgh coal bed (R. Stanton, personal communication).

Local residents indicated that mining operations ended about 1965. However, the bank is being used as a garbage dump and as a source of road metal. Only a few localized "hot spots" were detected: two distinct areas at the northeast end of the bank (Site A); one near the southwest end (Site B); and perhaps a small area at stream level in mid-bank. Thin puffs of smoke and the characteristic acrid odor emanating from the vents can only be detected within a few feet of the vent. Numerous large pockets of clinker, locally called "red dog", are evidence of more extensive burning in the past (Figure 2).

The Mather bank was revisited 5-1/2 months after the initial visit. Both Sites A and B were covered by fresh debris, perhaps due to a cave-in or to intentional moving of culm material by bulldozers.

From a distance there appeared to be a patch of white efflorescent material in the vicinity of Site A. There was much white efflorescent material on rubble scattered along the shore of Tenmile Creek, although there was no sign of active burning.

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In addition to studying the culm bank at Mather several other burning banks reported by McNay (1971) were visited. A bank at Chartiers, about 2 miles north of Mather, is no longer burning. A culm bank on State Route 88, east of Chartiers (not listed in McNay) is smoldering. Numerous small sulfur domes (Figure 3) were present on the surface of the bank. The sulfur crystals and some white efflorescent material appear to be moist. Several months prior to my visit, Ron Stanton of the U. S. Geological Survey collected clusters of sal ammoniac crystals and reported that the bank on State Route 88, as well as the one at Chartiers, were actively burning. A culm bank at Nemacolon, reported by McNay (1971) to be the second largest burning bank in the U.S. showed no signs of a recent fire.

Several small culm banks near Kingwood and Albright, West Virginia, were also observed but, here too, there was no evidence of current burning.

Site A

Several distinct vents were observed in a 200 sq. ft. area of loose rubble at the northeast end of the bank (Figure 4). A second, somewhat smaller area about 200 feet to the southwest had several "hot spots". All of the data for Site A were obtained from the larger area. The vents at this site were all relatively small and were covered by rubble; no open flames were observed. Temperatures of the gases emanating from vents only a few feet apart vary from $\sim$65°C to >360°C (upper limit of the mercury thermometer used). Arborescent sulfur crystals were present around the low temperature vent; molten sulfur was observed several inches below the surface. Only a few scattered sulfur crystals were found at the higher temperature vents. Whitish acicular crystals and arborescent sulfur (Figure 5) were scattered on the surface of the rubble 1-3 ft. from most vents. One vent was located at the base of a dead tree (Figure 4). A four inch wide mineral growth, reminiscent of flowstone, was collected from the tree about 6" above its emergence from the rubble.

Site B

At the southwest end of the bank there is evidence of recent reworking, perhaps to obtain "red dog" or to put out a smoldering fire. The characteristic acrid aroma of burning culm material was mild. Thin wispy vapors were seen emanating from the vents. Some rubble at the surface is coated with specular hematite. Similar material has been found in the burning anthracite culm banks and at the Clinker formation in the Powder River Basin, Wyoming, an ancient burned-out coal seam (Finkelman, unpublished data). Sulfur and white acicular crystals appearing moist were common at the site, much of it on vertical faces of the clinker material. On an overhang above the most active vent(s) were about a dozen white stalactites up to 12" long (Figure 6). About 20 feet laterally from the stalactites was a patch of turquoise-blue material (Figure 7). Both the stalactites and the blue material were moist.

During the second visit several patches and some scattered clusters of the turquoise-blue material were noted. They were on a vertical face of rubble about 25 feet above ground level. The zone had a vertical spread of about 10 feet and a horizontal spread of about 2 feet. This zone appears to be directly above the area of the first occurrence which was now covered by freshly fallen rubble. Scattered areas of the rubble surface totalling several square feet were coated with crusts of a white efflorescent material.

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Although only a very faint acrid odor was detectable, the presence of the copper phase, considerable stalactitic material (though not well developed morphologically), and sulfur on the fresh surfaces of the rubble suggest that low-level burning is continuing.

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Sampling

1. Gas samples

Two gas samples were collected from the two most active vents at Site A. The sampling device consisted of a portable hand vacuum pump attached to a high vacuum stopcock with an evacuated hollow stopper plug (∿8cc capacity). This was attached to a length of tygon tubing and this in turn to a 12" stainless steel pipe. The pipe was inserted into the smoking vent, the hand pump was then worked to remove air from the pipe, tubing, and stopcock. When smoke was seen coming out of the vacuum pump vent, the stopper plug was turned 180° to allow the gas sample to enter the evacuated chamber.

2. Water samples

All eight water samples were collected in 500 ml. plastic jars. The jars were hand held at the water surface with the mouth facing upstream (Table 2). A few drops of dilute HCl were added to each sample to keep the metal ions in suspension.

The water at Sites 1, 2A, B, and C was tested with pH paper. No reactions were observed for papers sensitive to pH less than 5.5 or greater than 9.0.

Between Kingwood and a point several miles north of Albright, W. Virginia, State Route 26 parallels a stream that is a bright reddish-brown color very similar in appearance to material leaching from the base of the bank at Mather (Figure 8). In Figure 9 the West Virginia stream is viewed as it passes by a

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small culm bank (note "red dog"). Sample 6A was taken from this stream.

3. Sediment samples

These four samples were scooped up from the stream bed with wide-mouth glass jars (Table 2).

4. Mineral samples

Specimens of efflorescent material were collected in the vicinity of the vents at sites A and B.

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Results

1. Gas samples - (Analyses by John E. Mclane)

The hollow stopcocks containing the gas samples were attached directly to a gas mass spectrometer. Both samples were analyzed at room temperature, then one stopcock was heated to ∿360°C and re-analyzed, (Table 3). The argon : nitrogen ratio of the samples is similar to the atmospheric ratio, suggesting that the combustion within the culm bank is supported by air. Most of the difference between the gas samples collected and air is attributable to combustion. Oxygen apparently was depleted in the sample by combining with carbon to form CO and CO_2. However, the oxygen tied up in these compounds is insufficient to account for the total oxygen depletion and it is assumed that some oxygen reacted with the stainless steel pipe. Sulfur dioxide is present, presumably from oxidation of sulfur in the burning coal. Several other small peaks were observed in the mass spectrum may be due to heavier elements such as As or Se, or to hydrocarbons.

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2. Water samples

The water samples were analyzed by Danold Golightly using an optical emission spectrograph with a rotating carbon disk to bring the water into the arc, (Kopp, 1971). This relatively rapid qualitative spectrographic technique was used to determine the major elements present in these samples. As can be seen in Table 4, all the samples contain Mg, Ca and Fe. Samples 2C and 6A, which undoubtedly contained some particulate material had the largest number of elements detected and generally the highest concentrations of each element.

Atomic absorption analyses of these samples were conducted by Philip Aruscavage. All values obtained were below the limit of detection (approximately 1 ppb) except those noted in Table 5.

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3. Sediments

Samples 1B and 3B are fine-grained stream sediments. Sample 2C is very fine-grained reddish-orange residue from a stagnant pool at the base of the Mather bank. This material gives the appearance of having leached out from the base of the bank and into Tenmile Creek (Figure 8). Sample 6A is similar in color and texture to 2C. The initial impression, that the material in samples 2C and 6A was predominantly iron oxides, was not substantiated by the optical emission spectrographic analyses which indicated the presence in sample 2C of only 7.4 weight percent Fe_2O_3 and 8.4 weight percent in sample 6A (Table 6A). Both samples had oxide totals of less than 25 weight percent indicating the presence substantial quantities of organic matter. The fine-grained material from sample 6A was dispersed on mylar-covered electron microscope grids and examined with a transmission electron microscope. It consisted of irregular clumps of fine filaments (Figure10). At magnifications up to 160,000X no evidence of crystal form was noted nor was any coherent diffraction of the electron beam obtained thus indicating a non-crystalline substance. The material appears to be similar to bacterial residues found in the leachate of sulfide mines (E. Dwornik, personal communication).

X-ray diffractograms (Ni filtered Cu radiation) for samples 1B and 3B indicate only the presence of quartz. The X-ray pattern obtained from sample 2C could not be identified. Sample 6A was

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not analyzed.

Semiquantitative optical emission spectrographic data on the sediment appear in Table 6A. X-ray fluorescence analysis of samples 1B and 3B appear in Table 6B.

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4. Mineral samples

Site A

The flowstone - like material proved to be a mixture of tschermigite [$(NH_4)Al(SO_4)_2.12H_2O$] and $Al_2(SO_4)_3$. It is virtually identical to material described by Barnes, Lapham and Downey (Barnes, personal comm.) from a burning anthracite culm bank near Williamstown, Pa. Their material contained some alunogen [$Al_2(SO_4)_3.18H_2O$]. However, they report that the $Al_2(SO_4)_3$ is readily soluble in water and under normal atmospheric conditions hydrates slowly to alunogen. The absence of X-ray powder lines attributable to alunogen in the Mather material suggests that the flowstone is relatively fresh. The whitish acicular material encrusting the rubble is primarily sal ammoniac (NH_4Cl) admixed with minor gypsum ($CaSO_4.2H_2O$) and mascagnite $(NH_4)_2SO_4$. One cluster of white fibers apparently consists of voltaite [$K_2Fe_5Fe_4(SO_4)_{12}.18H_2O$] and tschermigite or $Al_2(SO_4)_3$.

Site B

The stalactitic material is a complex mixture of sulfates and halite. Thenardite (Na_2SO_4), halite (NaCl), and Li_2SO_4 (quantitative optical emission spec. analysis showed 0.29 weight percent Li) have been identified from X-ray powder patterns; however, several strong lines remain unidentified. The stalactitic material is readily soluble in cold H_2O and does not

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react with dilute HCl. On evaporation the aqueous solution recrystallizes to form the original phases. Energy dispersive X-ray analysis indicated the presence of major Na, S, K, variable Al, minor Mg, and a trace of P. Results of optical emission spectrographic analysis are presented in Table 7. Gas chromatographic analysis (C/H/N Analyzer) indicated that this material contained approximately 0.07 weight percent C and 0.1 to 0.2 weight percent N. Thus, the stalactitic material does not contain any appreciable carbonates, nitrates, borates, organic material, or ammonia compounds. Chromatographic analysis also indicated a very high water content (∿20 weight percent). The high water content is corroborated by the rapid discoloration of the dessicant in contact with the stalactitic material. It thus appears that the three anhydrous phases detected are probable artifacts of sample preparation, created during the grinding procedure.

The turquoise-colored material (Fig 7) consisted of clusters of syngenite, $[K_2Ca(SO_4)_2.H_2O]$, needles and deep-blue crystals of copper acetate monohydrate $[Cu(CH_3COO)_2.H_2O]$ covered by a transparent film of picromerite, $[K_2Mg(SO_4)_2.6H_2O]$. In general this copper phase is so fine that it cannot be resolved with a binocular microscope. However, several relatively large (∿100μm) euhedral crystals have been observed. Further work on this new mineral is being conducted.

The white efflorescent material proved to be silky fibers of calcium acetate [$Ca(CH_3COO)_2 0.5H_2O$] admixed with halite. Preliminary X-ray powder data indicate that two hydrated forms of calcium acetate may be present.

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Formation of sublimates

Although burning culm banks are exceedingly heterogeneous conglomerations of coal, rock, and man-made material in various stages of combustion, some similarities were noted. These observations, based on studies of both bituminous and anthracite culm banks, are listed below:

1. Mineralization occurs around distinct vents - except for mascagnite [$(NH_4)_2SO_4$] and perhaps sulfur which behave as exhilates. This suggests that most of the mineralizing vapors are transported through conduits to the vents.
2. No condensation occurs around high temperature vents (T greater than $\sim 500^{\circ}C$). This suggests that the formation of the condensates is temperature dependent and not a primary function of oxygen fugacity.
3. Gaseous elements (O, N, H, F, Cl) and volatile elements (Si, Se, As, Pb, Ge, Bi, Cu, Sn) are generally the only elements to be observed in the condensates. The Si, Al, Mg, Fe, Ca, K and Li observed on the culm surface are probably derived from reactions of the vapors with the silicates in the culm. It appears that the volatility of the elements and not their concentration in the culm material is the principal factor in controlling their abundance in the condensates. An element as rare as germanium ($\sim$1 ppm in earth's crust; Turekian and Wedepohl, 1961) can exist as a discreet mineral species only if it has been concentrated by several orders of magnitude.

4. Minerals occur as clusters about each vent rather than as aureoles. That is, there is not an observable sequence of minerals containing increasingly volatile elements as one moves away from the vents. In many instances minerals of varying volatility are found intimately intergrown.

5. Mineralization around a particular vent changes with time.

6. Aside from the substitution of Se for S there are little or no solid solution effects. This suggests that the concentrating process differentiates the various elements to a significant degree.

The mechanism that is envisioned to account for these observations is depicted in Figure 11.

Each burning bank has one or more large central burns. As the organic meterial is consumed by the fire the volatile elements occuring in the mineral matter, organic material, and man-made material are vaporized and pass out through the conduits toward the vents (perhaps as organic complexes). During transport the vapors pass through a significant thermal gradient ($\sim$1800°F to $\sim$100°F). The culm material may act as a chromatographic column; as the vapors pass over, around and under the fine-grained material the various elements in the vapor are deposited in accordance with their volatility. The more volatile elements precipitate out closest to the vent, the least volatile nearest the burn. Thus the elements would be concentrated in pockets along the conduit. As the fire expands the temperature rises and the preconcentrated pockets would migrate outward eventually being

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expelled at the vent where the concentrated element is precipitated as clusters of crystals. If the burn is sufficiently active other elements may be concentrated and expelled from the vent to precipitate on the previously formed crystals before they have a chance to dissipate. If the fires subside, the concentrated pockets of these elements can be regenerated, within the bank thus several generations of the same minerals can be formed.

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Discussion

It is recognized that certain trace elements such as As, Sb, Pb, Se, Cd, Hg, F, Cu, and Li are potential environmental hazards (Asilomar Workshop, 1974). It must be emphasized that although the concentrations of these elements, in the samples analyzed for this report, are generally below the limits of detection, this does not imply that these elements are present in environmentally insignificant concentrations. The analytical techniques used for this study are not necessarily the most sensitive techniques, nor is any claim made of a knowledge of the environmentally significant concentrations for these trace elements.

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The question as to whether burning culm banks release high concentrations of trace elements into the environment remains largely unresolved. Copper and Lithium were the only elements with potentially adverse environmental impact found accumulating on the Mather bank. However, the sediments in the vicinity of the bank and the waters immediately downstream did not have anomolously high concentrations of copper. Indeed, the only water sample with detectable Cu (sample 1B, table 5) was upstream. The source of the copper at the Mather bank may be merely a piece of machinery or metal discarded during the development of the culm bank, a very common practice. The fact that the copper acetate occurs in only one narrow vertical zone supports this conclusion. Lithium is the only trace element found both on the bank (as Li_2SO_4 in the stalactites) and concentrated in the sediments (160 ppm in 2C). The high solubility of the stalactites and the liklihood of absorption by clays probably accounts for this observation.

The relatively high arsenic values apparently associated with the organic sediments at 2C may be due to selective absorption onto the organic matter in the stagnant pools over a period of time. Thus it may not indicate dangerously high release of arsenic by the burning culm. The arsenic values of the water downstream from this site are no more than background levels suggesting that the arsenic does not migrate far from the source. Perhaps the arsenic is absorbed onto the organic matter or clay minerals in the stream and concentrated there.

The higher As values for the undecanted sample (table 5) support this view. Frost and Griffen (1977) note that As^{+5} is strongly removed from landfill leachate by clay minerals at pH 7. Data from the vicinity of the burning bank at Burnside, Pa., may be much more illuminating since abundant arsenic bearing minerals such as realgar, orpiment, arsenolite, and an arsenic selenide have been found at that site (Finkelman and Downey, unpublished information).

The mineral assemblage forming on the Mather bank is distinct from the assemblages formed on the anthracite refuse banks. This, in part, reflects differences in the trace element concentration of the source materials and, in part, reflects the different stages in the burning process. Since bituminous and anthracite coals contain similar assemblage of trace elements (Zubovic, oral communication) it is likely that the different stage of burning is the dominant cause of the differences in the mineral assemblages. Most of the Mather minerals are alteration products, whereas, many of the minerals observed at the anthracite banks (table 1) are direct sublimates from the vapors escaping from actively burning banks. Undoubtedly the more hygroscopic compounds could not exist for long in the relatively low-temperature Mather environment. For example, Finkelman and Mrose (1976) note that downeyite (SeO_2), found on a number of anthracite banks, deliquesces in a few minutes when removed from the vicinity of an active vent, where temperatures were in excess of 200° C. Surface temperatures over extensive areas of the burning anthracite banks exceeded 100° C, this temperature was reached only in the immediate

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vicinity of several vents at Mather.

Many minerals on the anthracite culm banks apparently condensed from a vapor phase, this is indicated by the small, perfectly formed crystals, the hollow crystals, and the vapor-liquid-solid (VLS) growth (Finkelman et at., 1974). Presumably a similar situation existed at Mather, however, the attempt to detect toxic elements in the gases at Mather was inconclusive. This perhaps indicates that the temperatures at Mather may have been too low to volatilize the trace elements or that, in this relatively low temperature regime at Mather, the trace elements precipitated from the gases before they reached the surface.

Finally, the observable leachate from the Mather bank extended no more than a few feet into Tenmile Creek from the base of the bank (Figure 8). In contrast, a stream along State Route 26 near Albright, West Virginia (sample 6A) which is similar in appearance and composition to the leachate, extended for some 10's of miles from an unknown source. The volume of this reddish-brown residue is suggestive of a large coal mining operation rather than a burning culm bank.

It is clear from the conditions of the culm banks and from conversations with mine foremen and local inhabitants that statewide efforts to put out the fires have been successful. Virtually every culm bank fire in western Pennsylvania and Maryland and northern West West Virginia has been or will be extinguished in the near future. Obviously the environmental impact of these burning banks is greatly diminished (Figure 12). However, the danger of potentially toxic elements from these banks entering the surrounding environment may still exist. These elements may be slowly leached from these banks as is suggested by the As value of sample 2C. No doubt the burning process facilitates the mobilization of these elements by concentrating many of them on the surfaces of the banks in water soluble forms. The important question remains as to whether these water soluble toxic compounds are washed off the banks and then regenerated at the surface or are absorbed by the porous substrate and then recycled.

In one sense it is unfortunate that a bank releasing potentially toxic elements could not be located in the area investigated. Nevertheless, this study might serve as a baseline for future studies on the release of potentially toxic elements by burning culm banks.

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ACKNOWLEDGEMENTS

This report would not have been possible without the generous assistance of several colleagues at the U.S. Geological Survey in particular, Philip J. Aruscavage, Irving A. Breger, Ted Callender, C. Blaine Cecil, John C. Chandler, Edward J. Dwornik, William E. Davies, Danold W. Golightly, John E. Mclane and Ronald W. Stanton. John Barnes of the Pennsylvania Geological Survey improved the manuscript with a thorough review.

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Table 1

Culm bank minerals containing potentially

dangerous trace elements

(Finkelman, et al., 1974, Barnes, et al., in prep.)

elemental selenium	Se
realgar	AsS
orpiment	As_2S_3
------*	As_2Se_3
galena	PbS
------	GeS_2
berndtite	SnS_2
ottemanite	Sn_2S_3
herzenbergite	SnS
bismuthinite	Bi_2S_3
cassiterite	SnO_2
downeyite	SeO_2
arsenolite	As_2O_3
------	$KAlF_4$
cryptohalite	$(NH_4)_2SiF_6$
bararite	$(NH_4)_2SiF_6$
------	Cu acetate

* compounds not previously found in nature

Table 2

List of water and sediment samples

Water samples

Sample	
1A	Gaging station about 1 mile upstream from Mather, ∿3' from shore
2A	Mather bank, upstream from leachate, midstream
2B	Mather bank, downstream from leachate, ∿10' from shore
2C	Mather bank, midbank stagnant pool
3A	Bridge downstream from bank, ∿5' from shore
4A	Bridge at State Route 88, ∿1½' from shore
5A	Cheat River, downstream from Albright, W. Virginia, ∿1½ ' from shore
6A	Small River, paralleling State Route 26, several miles N. of Albright, contains reddish-brown sediment, ∿1½' from shore

Sediment

1B	Gaging station upstream from Mather, ∿1½' from shore
2C	Mather bank, reddish-brown fine sediment from stagnant pool
3B	Bridge downstream from bank, ∿1' from shore
6A	Small River paralleling State Route 26, several miles N. of Albright, West Virginia, Reddish-brown sediment

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Table 3

Results of mass spectrometric analyses of gases
(Analyst--J.E. Mclane)

Mass No.	Probable Constituent	Sample 727 Mole percent	Sample 241* Mole percent
64	SO_2	0.5	0.5
44	CO_2	0.28	0.32
40	Ar	0.96	0.95
32	O_2	10.4	9.1
28	CO, N_2	Trace	Trace
18	H_2O	3.5	3.2
17	NH_3,OH	Present	Present
16	CH_4,O	Present	Present
14	N	77.7	85.2
12	C	Trace	Trace
2	H_2	Trace	Trace
Collection Temp.		>360°C	∿210°C

*There was no significant difference between the heated and unheated runs.

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Table 4

Results of Optical Emission Spectrographic Analyses of Water Samples

(Analyst--D. Golightly)

Sample	Element detected
1A	Mg, Ca, Fe, Cu, (1-10 ppm)
2A	Mg, Ca, Fe
2B	Mg, Ca, Fe
2C	Mg*, Ca, Fe, Mn, Si, Na, Sr + several unidentified lines
3A	Mg, Ca, Fe
4A	Mg, Ca, Fe, Sr
5A	Mg, Ca, Fe
6A	Mg, Ca, Fe, Mn, Si, Al

*underscoring indicates relatively high concentration

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Table 5

Atomic Absorption Analysis of Water Samples
(Analyst--P. Aruscavage)

Element	Sample - Concentration	Ave. trace element composition of streams (ppb) (Turekian, 1969)
Sb	All - <1ppb	1
Pb	6A - 2.5 ppb	3
	All others - <1ppb	
Cr	6A - 10ppb	1
	All others - <1ppb	
Cu	6A - 30ppb	7
	All others - <1ppb	
As	Before decanting	2
	2C - 18ppb	
	6A - 3ppb	
	All others - <1ppb	
	After decanting	
	All - <1ppb	

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Table 6A

Optical emission spectrographic analyses of sediment samples

(Analyst - L. Mei; values in ppm except as noted)

	1B	2C	3B	6A
SiO_2 (%)	64.	1.5	54.	11.
AR_2O_3 (%)	7.7	0.72	9.3	2.5
Fe_2O_3 (%)	2.9	7.4	3.0	8.4
MgO (%)	0.45	2.7	0.71	0.16
CaO (%)	0.48	4.5	0.80	0.36
Na_2O (%)	0.30	>1.3	0.33	0.05
K_2O (%)	0.94	0.61	1.3	0.65
TiO_2 (%)	0.50	<0.01	0.43	0.10
P_2O_5 (%)	0.30	<0.16	0.32	0.84
MnO (%)	0.09	0.03	0.09	0.02
Ag(ppm)	<0.10	<0.10	<0.10	0.11
B	45	100	49	15
Ba	280	19	350	120
Be	2.2	2.7	2.8	1.7
Ce	120	<93	92	65
Co	12	5.8	13	5.9
Cr	26	4.0	39	16
Cu	17	17	21	11
Eu	<1.5	1.8	1.7	<1.5
Ga	8.0	<2.2	12	5.7

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	1B	2C	3B	6A
Gd	7.2	7.0	<6.8	<6.8
La	45	<10	37	13
Li	<68	160	<68	<68
Mn	710	250	710	130
Mo	2.6	<3.2	<2.2	7.2
Nb	12	<3.2	9.9	<3.2
Ni	22	9.2	27	13
Pb	26	<10	35	<10
Sc	9.3	2.3	11	6.1
Sr	94	710	130	19
V	45	<3.2	51	51
Y	41	30	21	6.6
Yb	6.7	1.6	2.6	0.83
Zn	71	110	96	72
Zr	510	7.9	250	39

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Table 6B

X-ray Fluorescence Analyses of sediment samples

(Analyst - R. Finkelman; values in weight percent)

	1B	3B
SiO_2	68.5	62.4
Al_2O_3	7.4	10.2
Fe_2O_3	4.48	5.03
MgO	0.43	0.58
CaO	0.52	0.93
Na_2O	0.36	0.40
K_2O	1.33	1.71
TiO_2	0.74	0.88
P_2O_5	0.04	0.08
MnO	0.12	0.11
Total*	83.94	82.33

*low totals due to admixed organic matter and volatiles such as H_2O and CO_2.

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Table 7

Optical Emission Spectrographic Analysis

of the Stalactitic Material

(Analyst - J. Fletcher)

Si	0.016	weight percent
Mg	3.3	weight percent
Ca	0.0051	weight percent
Na	>4.6	weight percent
K	4.5	weight percent
Mn	0.082	weight percent
B	69	ppm
Co	53	ppm
Cr	2.9	ppm
Cu	15	ppm
La	21	ppm
Li	4700	ppm
Ni	45	ppm
Sc	2.4	ppm
V	7.4	ppm
Y	2.4	ppm
Yb	0.14	ppm
Zn	24	ppm

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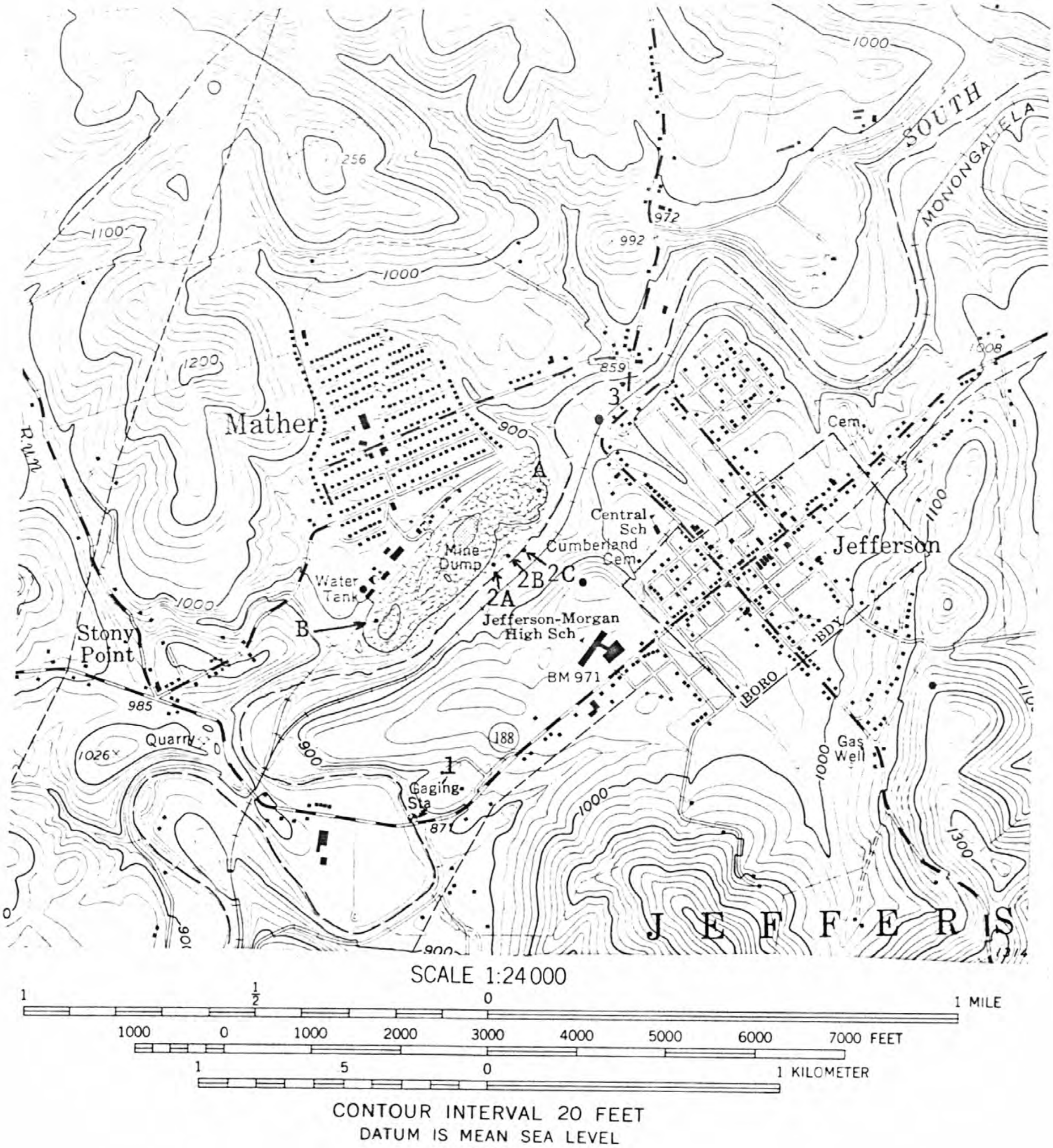
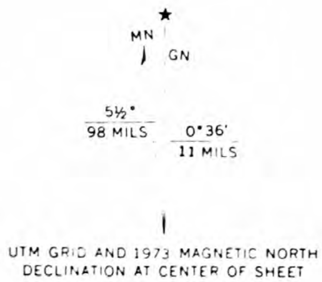


Figure 1. Mather, PA and adjacent culm bank numbers correspond to sample locations listed in Table 2. Letters refer to site locations described on pages 6 and 7.



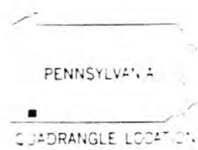


Figure 3. Sulfur domes on surface of burning culm bank.

Figure 4. Smoke escaping from a vent, Mather culm bank.

Scale 1" = 10"

Figure 5. Efflorescent crystals on rubble, Mather culm bank.

Scale 1" = 36"

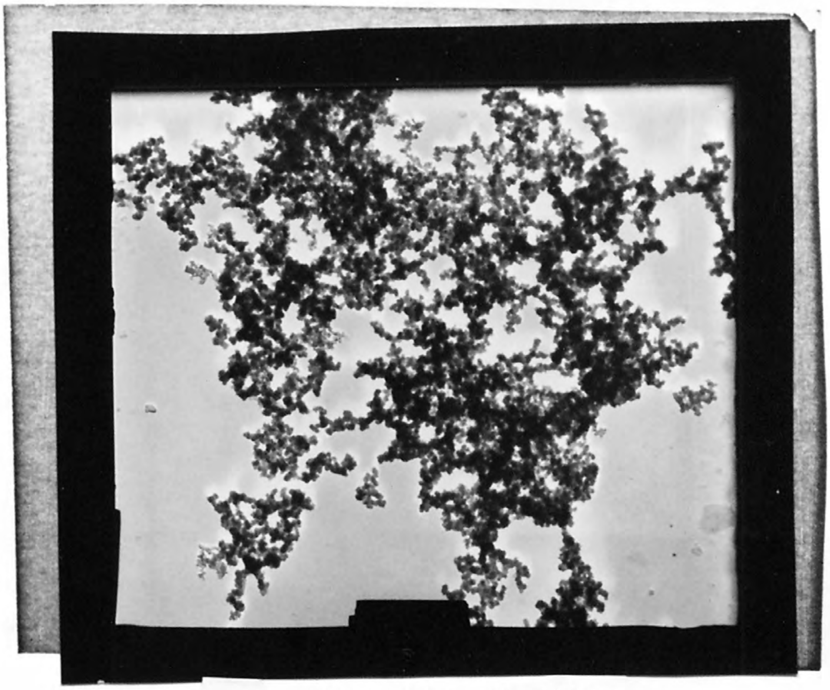
Figure 6. Stalactites on verticle wall, Mather culm bank.

Scale 1" = 4"

Figure 7. Blue copper acetate monohydrate, Mather culm bank.

Figure 8. Reddish-brown organic debris at base of Mather culm bank. Tenmile Creek on the right.

Figure 9 . Reddish-brown organic residue laden stream passing by culm bank near Albright, West Virginia.



Magnification 10,000X

Figure 10. Transmission electron photomicrograph of organic debris.

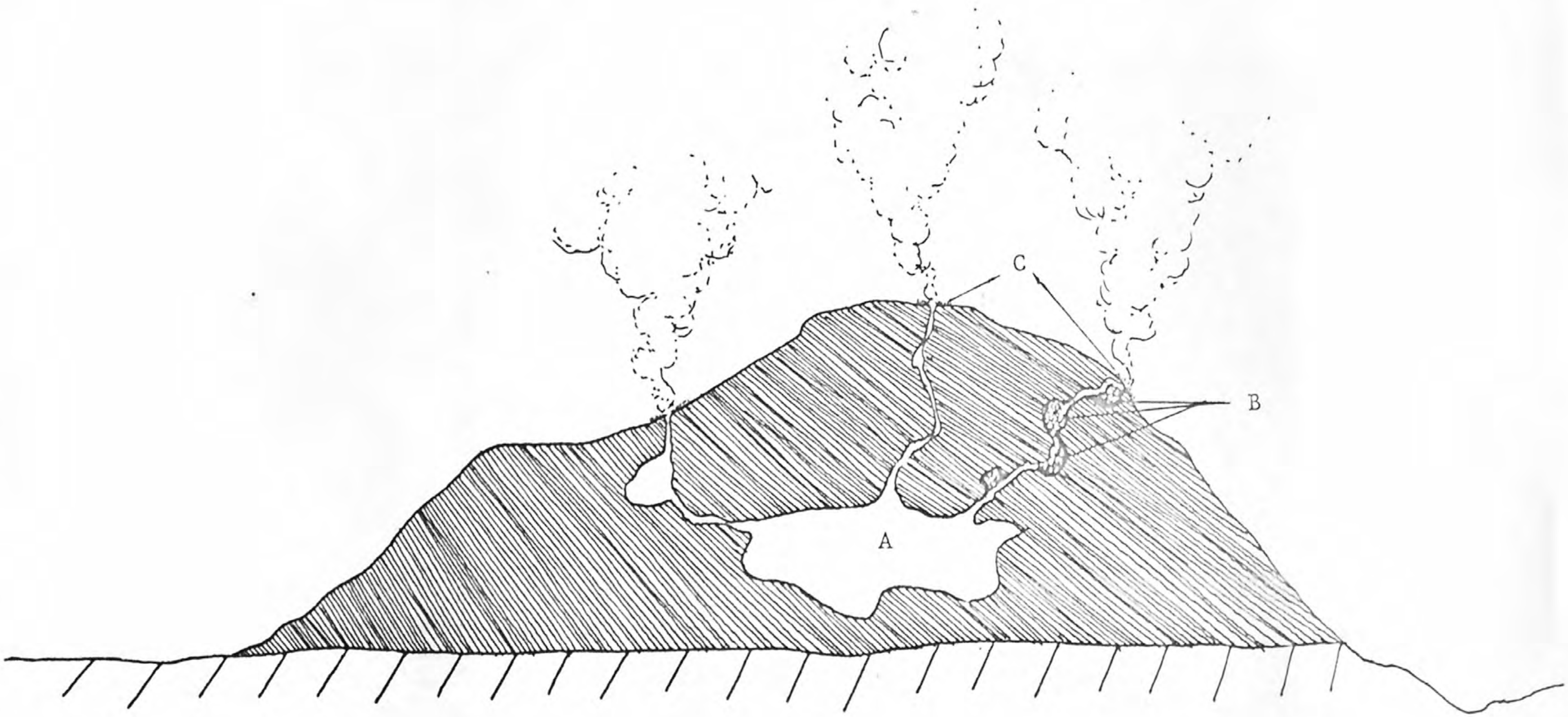


Figure 11. Theoretical cross-section of a burning culm bank. A=central burn; B=pockets of preconcentrated trace elements; C=mineral condensing around vents.

Figure 12. Burning trash on Chartiers culm bank. The chance of burning culm banks still exist as long as practices such as this continue.