ORGANIC GEOCHEMISTRY OF OKEFENOKEE PEATS: METAL CONSTITUENTS

by Daniel J. Casagrande and Leo D. Erchull
Governors State University
Park Forest South, Illinois  60466

ABSTRACT

Distributions of 17 major and trace metals were studied in two peat-forming environments in the Okefenokee Swamp. Samples of plant, water, and peat cores (at various levels) were analyzed. Distributions of metals were related to processes occurring in the origin(s) of coal and to constituents eventually found in coal. One of the major findings was that virtually all metals in fresh water coals could be accounted for in the peat-forming stage of coal formation.

INTRODUCTION

Over the past few years there has been a renewed interest in the metal constituents of coals (Ruch and others, 1974, and numerous others). The interest has changed from metals being viewed as potential commercial accumulations (Zubovic and others, 1961, 1966, 1967) to their being viewed as major environmental problems (Rao and Gluskoter, 1973; O'Gorman and Walker, 1972; Ruch and others, 1971, 1974).

Recently, an investigation was initiated on organic geochemical processes occurring in the peat-forming areas of the Okefenokee Swamp in Georgia. The overall purpose of the study was to investigate peat as the first member of the coalification sequence: peat → lignite → bituminous coal → anthracite coal. By understanding diagenetic processes occurring in the peat-forming system, one could perhaps begin to understand how coal became chemically what it is.

Because of the renewed interest in metal constituents in coal and the authors' interest in studying organic geochemical processes leading to coal formation, a study was undertaken to investigate metals in peat-forming systems in the Okefenokee Swamp. There are a number of questions that require study: (1) How do metal concentrations in a contemporary fresh-water peat-forming system relate to those found in coals? (2) What interactions involving trace elements are there between plants and an organic rich soil? (3) What role do metal constituents in water play? (4) Do organic fractions in the peat selectively concentrate certain metals? (5) What influence does bedrock have on constituents found in peat? (6) Are metals concentrated to different extents as a function of depth? (7) What role(s) do fires play in the cycling of metals in the swamp? (8) Is the Okefenokee Swamp a relatively pristine environment?
The peat-forming system is indeed a complex one to investigate; the system is dynamic, being composed of a living vegetational cover, water, minerals, peat, microorganisms, and surface litter. Thus, to study metal constituents with the above questions in mind, it is necessary to understand the geology and botany as well as the chemistry of the system.

GEOLGY AND BOTANY OF THE OKEFENOKEE SWAMP

The Okefenokee Swamp (Figure 1, next frame) with an area of over 400,000 acres is the second largest swamp in the U. S. It is a paludal region of both swamps and marshes and is developed upon a broad, gently sloping Pleistocene terrace situated in the eastern part of the Atlantic Coastal Plain at an elevation between 100 and 160 ft. above sea level (Mac-Neil, 1950). It is bordered on the east by Trail Ridge, a narrow, elongated sand ridge. This physiographic feature is believed to have been an offshore barrier island (or bar) that formerly separated the marine Pleistocene "Okefenokee Lagoon" from the open ocean (Cohen, 1974a).

The numerous sand islands within the swamp (such as Billy's Island, The Pocket, and Floyd's Island) are believed to be remnants of bars that probably formed during lagoonal time. Considering the nature and thickness of the underlying Pleistocene and recent sediments, it is unlikely that the lagoon was deeper than 30 ft.

Sometime after regression of the Pleistocene Sea, this basin developed into a fresh-water marsh-swamp complex in which partially decomposed plant debris (peat) began to accumulate. Peat depths range from less than 1 ft. near the edges of the swamp to 14 or 15 ft. in some portions of the interior. There is no fossil evidence for previous existence of the sea; the area during geologic time appears to have been thoroughly cleansed with fresh-water before peat-formation started (Cohen, 1974a). The swamp is drained by the Suwannee River to the southwest and the St. Mary's River to the east.

For an area the size of the Okefenokee, the watershed appears to be small. Along the east and northeast sides of the drainage area, which extends from Trail Ridge to the swamp, the area is about 1 mi. wide. The sandy soil of Trail Ridge erodes very little and consequently deposits little silt into the swamp. On the north and northwest sides, about 300,000 acres drain into the swamp; this is flat, sandy land with very little, if any, erosion.

While some people feel that the swamp waters are derived from ground waters or precipitation, with very little coming from the watershed, others, such as Reuter and Beck (1974) indicate that the drainage area of the Suwannee River extends west of the Okefenokee, approximately doubling the area of the swamp, and that the water from this area is delivered to the Okefenokee by surface and subsurface flow.

The Okefenokee was selected as a suitable model system because of (1) the above geologic considerations, (2) Cohen's work (1974a) indicating
that the vegetation in the Okefenokee is similar to the flora that gave rise
to the Lower Rhine Brown Coals and Dakota Lignites, and (3) the probability
of past peat-forming systems being laid down in subtropical environments.

While it would have been desirable to take numerous samples from all
areas of the swamp and an equal number of plant samples for metal analyses,
two areas were sampled which represent major environmental types.

From Cohen's (1974b) work it has been established that there are two
major peat-forming systems in the Okefenokee; a swamp environment (covering
85% of the Okefenokee) and a marsh environment. The vegetation in the swamp
environment consists primarily of Taxodium or Myriaria; also Gordonia, Magnolia,
Persea and Cyrilla are found. The open marsh consists of prairies that are
open-water areas dominated by Nymphaea, Orotetum, Panicum, and Utricularia.
Peat depth is generally greater in the prairies than in the swamp areas and
the basal peats are dated at around 6500 B.P. \(^{14}C\) data not corrected by den-
drochronologic methods).

Sampled were:

1. The Minnie's Lake area as an example of the swamp environment. The
area is dominated by Taxodium, Figure 2 (next frame). The pH of the water
was 4.1 and the Eh was +350 mv. At the time of sampling, no surface water
was present; however, on other occasions surface water to a depth of a few
inches was present. A series of plant, water and peat-core samples was taken.

A core taken from this area measured 350 cm. Cohen (1974a) recognized,
on the basis of his work on oriented thin sections at various depths of peat,
that a major vegetational change took place at the 90 cm level, when the pre-
sent Taxodium dominated environment succeeded a Nymphaea or open water environ-
ment. Fires have also played a major role in the ecology of the area and thus
a certain amount of charcoal was found at certain levels.

2. Chesser Prairie as an example of a marsh environment, dominated by
the aquatic plants named above (see Figure 3, next frame); the pH and Eh in
this area were similar to the values reported for the Minnie's Lake site.
Chesser Prairie is covered by water and remains so except for times of severe
drought. A core taken from this area measured about 180 cm. Cohen showed
that here also a major vegetational change in the source of the peat is ob-
served at the 90 cm level, but the succession was the reverse of that ob-
served in the Minnie's Lake core.

Both coring sites are underlain by a relatively pure white sand (Cohen,
1974a).

EXPERIMENTAL

In the Minnie's Lake area a series of ten plant samples was collected
and the core of peat was sampled at 13 levels. In the Chesser Prairie area,
a total of 7 levels of peat were selected along with 14 plant samples. Water
samples were also collected. Coring techniques were as described by Cohen and Spackman (1972).

All samples upon collection in the field were frozen in dry ice and subsequently kept frozen. The water samples were preserved by adding redistilled concentrated HNO₃ to a pH of 1.

Analyses of 17 metals were carried out on water, plant and sediment samples collected from both areas. The analytical procedure used for mercury and other metals can be seen in Figure 4 (next frame). Mercury analysis was done by the manual cold vapor technique (Hatch, 1968). Results for the major metals are within 5% accuracy and 2% precision. Figures for the trace element data are similar except in the few cases where values were approaching detection limits.

RESULTS

Figure 5 (next frame) shows the mean distributions of the major metals in peat, plants and water from the Minnie's Lake site; these values represent means for 13 levels of peat, 10 plant samples and 4 water samples. The important observations are the following: (1) Plants act as major concentrators in the peat-forming system for calcium, magnesium, sodium and potassium. (2) Iron appears to be a major metal in the peat, but not in the plants. (3) The levels of metals in the waters are low. Figure 6 (next frame) shows the mean distributions of major metals in peat, plants and water from the Chesser Prairie site; these values represent means for 7 levels of peat, 14 plants and 4 water samples. The important observations include the following: (1) as in the Minnie's Lake area, the plants are concentrators for calcium, magnesium, potassium and sodium while the level of iron in peat is high; (2) the levels of major elements in plants from the marsh environment of Chesser Prairie are, in many cases, twice as high as those in the tree-type vegetation in Minnie's Lake, but the ratios of Ca to K are similar; (3) levels of metals in the water are relatively low but somewhat higher than at Minnie's Lake; and (4) while the metal levels are higher in plants from Chesser Prairie, the levels are quite similar in peats derived from the two different systems.

Figure 7 (next frame) shows the ash yield of each core as a function of depth. High sand contents are evidenced in the basal sections of both cores by the high ash values. The steady decrease in ash down to the 210 cm level is noteworthy in the Minnie's Lake core.

In Figures 8 and 9 (next frames) the distributions of major metals as a function of depth of peat are given for both sampling sites. The levels of sodium and potassium change little with depth, no doubt because diffusion in solution is easily possible. The widest variations are seen with iron. There seems no reason to doubt the very high figures for calcium and magnesium at the 50 cm level in both cores. The atomic ratio of the two elements is close to unity, but one can hardly suggest that a layer of dolomite was formed in this kind of sedimentary environment. It was at this level that Cohen (1974a)
PROCEDURE FOR ALL METALS EXCEPT Hg.

1. Thaw, oven dry at 105°C, 24 hrs.
2. Grind in mortar.
3. Pass through 100 mesh screen.
4. Heat to constant weight at 105°C.

(0.5 g)

1. Five ml 48% HF into polypropylene beaker.
2. Heat at 100°C for 8-12 hrs.
3. Dry in oven at 105°C, weigh.

1. Quan. transfer to Kjeldahl flask.
2. Five ml conc. HNO₃ + 60% HClO₄.
3. Digest for 2 hrs.
4. Filter through What. No. 2 filter paper into 100 ml vol. flask.

PROCEDURE FOR Hg

1. Thaw sample, 12 hr. minimum.
2. Homogenize in a blender.
3. Weigh 2.5 g wet sample into beaker.
   a. Dry 1 g sample in oven at 100°C for 24 hrs.
4. Add 1 g KMnO₄, 50 ml HOH, 10 ml 1:1 H₂SO₄.
5. Boil, minimum 15 min., add excess KMnO₄ if necessary.
6. Cool to room temperature.
7. Filter through What. No. 42 filter paper into 100 ml vol. flask.
observed large amounts of charcoal in the peat at both areas, suggesting that a major forest fire occurred when this level constituted the surface. A result of the fire would be to concentrate the metals in the plants with the charcoal (sodium and potassium, with no common insoluble salts, would subsequently diffuse away from the zone of concentration). There is no obvious break in the curves at 90 cm, where the vegetational changes occurred.

In Figure 10 (next frame), the distributions of trace metals in the Minnie's Lake core are presented. The following points should be noted: (1) Zn, Ba and Mn appear to be concentrated by plants, particularly the latter; (2) Cu, Cr, Pb and Co are decidedly lower in plants; (3) Ni is quite similar in plants and peat; and (4) the levels of metals in the water are low.

Figure 11 (next frame) presents the distributions of trace metals in the Chesser Prairie area. As in the Minnie's Lake area, Zn and Mn appear to be concentrated in plants, but Ba is not. Ni was not found in any plants sampled in Chesser Prairie, but it was found in the sediment at levels similar to those in the Minnie's Lake peat. Co was observed in the peat from Chesser Prairie but not from that at the Minnie's Lake site.

In both cores V, Ag and Cd were not observed above the lower limits of detection which were 5, 2 and 1 ppm respectively. Mercury values were lower than the measurable amounts of the other trace metals and thus were not included in the histograms. Overall, Hg values ranged from 0.01 to 1.09 ppm in peats and 0.05 to 2.04 ppm in plants. Utricularia seemed to concentrate Hg to 2 ppm. The plants appeared to have more Hg associated with them relative to peat in the Chesser Prairie area, while the reverse was true for Minnie's Lake.

DISCUSSION AND CONCLUSION

Surely any discussion with regard to data the authors observed in peat must be put into proper perspective by saying that two cores from two major peat-forming areas were sampled; the same is true for the plants. However, on the basis of what has been presented here, along with other data the authors have presented elsewhere (Casagrande and Erchull, 1975), a number of points can be made.

1. The levels of major and trace metals in the peat-forming stage of coal formation - assuming the Okefenokee is a suitable model - are similar to those found in coals from the Great Plains and Rocky Mountain Provinces; this is especially true with regard to major metals and such minor metals as Ba, Cr, Cu, Hg, Mn, Ni, Pb and Zn. Thus metal distributions found in coals could be largely syngenetically derived, without need for postulating epigenetic processes. Furthermore, levels of metals except for Hg and Pb were far below Clarke values, as is true of most coals.

2. The levels of certain metals such as K and Na did not change with depth; others such as Ca, Fe and Mg did change, but in no particular trend.
Observations in channel samples of coal seams have produced similar results - distributions are as erratic as those observed in the peat.

3. While plants serve as concentrators of certain metals and show variations from the marsh to swamp areas, the levels in the peats do not reflect these changes. It will be recalled that the top 90 cm of peat in the Chesser Prairie core is derived from the same plants as the lower section (below 90 cm) of the Minnie’s Lake core. Also the lower section at Chesser Prairie and the upper section at Minnie’s Lake are both derived principally from Taxodium. A comparison of distributions of metals in pairs of sections of similar origin shows no great differences. That is, plants do not appear to leave trace element signatures in the peats studied (but see also Cameron and Wright, this Symposium, where plant signatures were seen in some trace elements).

4. No significant correlation was seen between metal distributions and ash yields; a similar lack of correlation was noted by Ruch and others (1974) for many metals in coals. In the lower sections of the cores, where ash yields were high because of admixture of sand with the peat, the concentrations of the metals studied remained low. Therefore this sand is unlikely to be the principal source of the metals. A factor determining the low level of many elements in the peats is no doubt the low concentrations in the surface waters. Where and how the elements get into the waters is not clear. To clarify this, additional samples are being taken from the far reaches of the northwestern section of the swamp and from Trail Ridge.

5. Fires have played a major role in the ecology of the swamp. They no doubt act as concentrators of metals, and some of the erratic trends observed for metal distributions in the peat cores may be due to this.

6. Most metals in water samples were observed in the dissolved state (<0.45µ); exceptions to this included Zn at both sites. In a single sample taken from the Suwannee River as it left the Okefenokee, Co, Pb and Fe appeared in the suspended state. Co and Pb were not observed in any other water samples. Results of this study are only preliminary and further expansion will be forthcoming in another paper.

7. Relatively high concentrations of such metals as Hg, Pb, Cr and Cd are usually taken as indications of pollution due to human activities. At the Minnie’s Lake site the levels of these constituents did not vary with depth. At this site the movement of water is quite slow and in many cases the water cover is intermittent. At the Chesser Prairie site, where water is continually flowing over the peat except in times of severe drought, Hg and Pb levels seemed to decrease with depth. Whether this is related to the proximity of Chesser Prairie to Trail Ridge (the only major watershed in the area) is not clear. While the Minnie’s Lake core showed no trend of Hg with depth, the levels found were 3 times higher (1 ppm) than the mean for Chesser Prairie (0.3 ppm). Thus there is no compelling reason for supposing that Okefenokee Swamp is as yet being polluted by metals released by human activities.
8. It is worth noting here that Casagrande and Erchull (1975) found that certain metals, including iron, are concentrated in certain fractions of the peat such as humic acids. This will have an effect on the manner in which metals are retained after coalification.

ACKNOWLEDGMENTS

The authors acknowledge the Earth Science Section of the National Science Foundation and Governors State University for their support of this work. Drs. Arthur Cohen and Peter Gunther are thanked for their help in identifying botanical specimens, and they and Messers. C. Berschinski, R. Conti and Refuge Manager, John Eadie, and his staff are thanked for their cooperation in the field endeavors. Ms. K. Siefert and Ms. N. Sutton are acknowledged for their review of the manuscript.

REFERENCES CITED


—1974b, Possible influence of sub-peat topography in sediment type upon the development of the Okefenokee Swamp, Georgia: Southeastern Geology, v. 15, No. 3, p. 141-151.


FIGURE CAPTIONS  (D. J. Casagrande & L. D. Erchull)

Figure 1. INDEX MAP OF OKEFENOKEE SWAMP.
Figure 2. TAXODIUM AT MINNIE'S LAKE SITE.
Figure 3. SAMPLING SITE AT CHESSER PRAIRIE.
Figure 4. ANALYTICAL PROCEDURES.
Figure 5. MEAN DISTRIBUTION OF MAJOR METALS AT THE MINNIE'S LAKE SITE.
Figure 6. MEAN DISTRIBUTION OF MAJOR METALS AT THE CHESSER PRAIRIE SITE.
Figure 7. ASH YIELD OF PEAT AS A FUNCTION OF DEPTH.
Figure 8. DISTRIBUTION OF MAJOR METALS AS A FUNCTION OF DEPTH IN THE MINNIE'S LAKE CORE.
Figure 9. DISTRIBUTION OF MAJOR METALS AS A FUNCTION OF DEPTH IN THE CHESSER PRAIRIE CORE.
Figure 10. MEAN DISTRIBUTION OF TRACE METALS IN THE MINNIE'S LAKE CORE.
Figure 11. MEAN DISTRIBUTION OF TRACE METALS IN THE CHESSER PRAIRIE CORE.