RED SLIME, BLACK COATS, AND OILY FILMS: THE IRON AND MANGANESE CYCLES AT HUNTLEY MEADOWS WETLAND, FAIRFAX COUNTY, VA

Field Trip Guidebook for
Geological Society of Washington

by

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The iron and manganese cycles in the Huntley Meadows (Fig. 1) wetland in Alexandria, VA, are the result of many interacting processes. Coring has shown that the Huntley Meadows wetland lies in an old meander of the ancestral Potomac River (Froelich and others, 1978). This meander, which was active between 100,000 and 30,000 years ago, is now called Hybla Valley. It filled first with gravel, and later with clay and peat. The clay forms an impervious subsurface that focuses Fe- and Mn-bearing ground water to discharge primarily along the outside edges of the meander.

The sediments and sedimentary rocks into which the meander cut (Fig. 2) are the Cretaceous and Tertiary units of the Atlantic Coastal Plain. These were formed, in part, by the weathering of Fe- and Mn-bearing crystalline Piedmont rocks (Drake and others, 1979). It is easy to find places in the Washington, D.C. metro area where Piedmont rocks are weathering red from oxidation of the iron minerals (Reed and Obermeier, 1982).

In some places, such as around Laurel, Md., the Mn-rich iron was mined as bog iron ore (Singewald, 1911). In the 1700s the French bought this ore from the American colonies because it had excellent metallurgical properties. No metallurgists were present at that time to explain that the value of the ore rested on the presence of Mn which turned the pig iron into steel.

Fe and Mn are typically found together because they are stable under similar Eh-pH conditions (Hem, 1985). Their kinetics do not match exactly, however, as we will see during the field trip. Under circumneutral conditions such as at Huntley Meadows, Fe and Mn exhibit two oxidation states. Under oxidizing conditions, Fe exists as ferric ion --Fe(III)-- and Mn exists as manganic ion --Mn(IV). Under reducing conditions, Fe exists as ferrous ion --Fe(II)-- and Mn as manganous ion --Mn(II).

The microbial cycles of Fe and Mn are well known (Ghiorse, 1984; Ghiorse and Ehrlich, 1992; Nealson, 1983) and will be the focus of this field trip. Three groups of microorganisms interact with these cations. The aerobes, or oxidizers, are bacteria that function where oxygen is present. The anaerobes, or reducers, function where oxygen is absent. In the zone between them, the microaerophiles function where only a small amount of oxygen is present, on the order of 0.1-2 mg/L. The so-called "iron bacteria" oxidize Fe and Mn and live where oxygen is low or abundant, so they are aerobes and microaerophiles.

Both aerobes and microaerophiles oxidize Fe and Mn. Such chemical reactions occur for a variety of reasons. One of the iron bacteria derives energy by oxidizing the Fe(II) to Fe(III); <u>Gallionella</u> gains an electron in this process representing energy worth somewhere between 1,000 and 10,000 cal/mole of Fe (Robbins and others, 1987; Ehrlich, 1990). Most of the iron bacteria are thought to oxidize Fe and Mn as byproduct processes from unrelated metabolic reactions. The iron mineral known to be precipitated by the bacteria is ferrihydrite, a hydrated iron oxide mineral that can dehydrate to later form hematite (Chukhrov and others, 1974). The oxidation of Mn by the bacteria may also serve as a detoxification mechanism; whether or not energy is available from the oxidation is debated (Nealson, 1983).

The iron bacteria collected here (Robbins and Norden, 1994) are (Figure):
Leptothrix ochracea (look like sausages or thinly coated straws)
L. cholodnii (look like thickly coated straws)
Gallionella ferruginea (look like braids)
Siderocapsa sp. (look like globules with "two peering eyes")
Sidercystis sp. (primarily coat algae; said to look like little corn cobs)
[Toxothrix trichogenes (look like ladders) has not been collected here yet. It should be present because the entire suite of iron bacteria tend to co-exist.]

One other iron bacterium here plays a big role in the Mn cycle and also makes the oily-looking films on water. Leptothrix discophora look like doughnuts with holes in the middle of holdfasts that hold onto the air-water interface (thereby making oily films) or hold onto rocks in riffles (thereby precipitating Mn). (Riffles are places in creek where water runs swiftly over rocks.)

On this field trip, we will observe places where ground water discharges into the wetland and where iron bacteria precipitate Fe and Mn. We will collect bacteria and Mn nodules and Mn coated rocks in riffles. The objective of these observations and collections is to understand metal cycles in our environment.

IN TRANSIT DIRECTIONS (Fig. 1):
START at Huntley Meadows Park parking lot
PILE lots of people into few cars
DRIVE North on Harrison Lane (up the hill)
TURN left at the light on South Kings Highway
OBSERVE As you drive down the hill, observe S. Kings Highway retaining wall on right (look at weep holes in the retaining wall - how many have running water and bright red precipitates?)
TURN left into Huntley Meadows back parking lot (near the 7-11) at intersection of S. Kings Highway with Telegraph Rd. - PARK

(BEWARE: Poison ivy--three leaves--is abundant here spring, summer, and fall; a proven method for avoiding reactions to it is to spread antiperspirant containing Al chlorhydrate on your hands and arms; the Al binds the offending poison ivy protein. It is best to wash as soon as you touch poison ivy. When you get home, take a shower and wash off with cool water; i.e. don't open your pores.)

STOP 1: BACK ENTRANCE AT HUNTLEY MEADOWS PARK TO OBSERVE THE IRON CYCLE

WALK along the street towards the Dogue Creek bridge, scoot left under the railing, climb down the rocks, and go under the bridge:

OBSERVE bright red patches and oil slicks. TAKE pH, air temperature, and water temperature. This is a circumneutral pH wetland.

The bright red patches are places where anoxic (=no oxygen) ground water discharges into oxygenated water. The red color is iron oxide-coated (rust) sheaths of a variety of iron bacteria. Different bacteria dominate at different times of the year.

COLLECT a sample of the iron floc in a vial using an eyedropper, if you wish (record date of collection on vial). Be very careful to collect only in the bright red places or else you will collect reducing bacteria along with the oxidizing bacteria. If this happens, your vial of bright red Fe will turn brown and then black within a week.

The water chemistry here is as follows (Robbins and others, 1992):

	Fe (mg/L)	Mn (mg/L)	pH
surface water	0.65	0.02	
aquifer water	34.2	0.49	5.9

The oil slicks are formed by Leptothrix discophora. This colorless rod-shaped bacterium has a holdfast which attaches to the air-water interface. It then procedes to secret extracellular proteins and carbohydrates; the refraction of light off the holdfasts and secretions look like an oil slick. COLLECT a sample of the slick by sliding a microscope slide under the film, if you wish (record write date of collection on back of slide).

WALK up tributary creek - OBSERVE red color in the north bank of the stream. These are undoubtedly places where ground water has discharged in the past.

If we are lucky, we may OBSERVE the redox boundary (=zone between reduction and oxidation) for reduced and oxidized Fe in the water column. This will appear as red flocculate floating in the water above black sediment. (At other times of the year, the redox boundary is in the sediments and must be dug out to observe it.)

Stick the eyedropper into the mud or sand and see what color the Fe is underneath the places having bright red Fe at the surface. Is it black? If so, this is the color of reduced Fe and this is the place where iron reducing bacteria are living in anoxic water. If you would like to watch your red colony turn black over time, add some reducers to your vial.

These different bacteria can be studied in two ways. Put a drop on a microscope slide under a cover slip and look under the microscope (at least 100x) to see what bacteria are there. Or place the vial on a windowsill and observe what changes over several years. (My kitchen windowsill holds my collection and these are my pet bacteria which are good for laughs with my friends who have cats and dogs for pets.)

STOP 2: NORTH UP DOGUE CREEK TO OBSERVE THE MANGANESE CYCLE

WALK through the culvert under Dogue Creek bridge

OBSERVE the rusting pipe. The pipe is made of steel, which contains reduced Fe. I think that the iron oxidizers may oxidize it (rust) to obtain energy. A cool project to do with students would be to set up some experiments to discover if bacteria cause rust. (No one has ever done this before, to my knowledge.)

OBSERVE the black encrustations on the cobbles in the riffles. (Riffles are places in creek where water runs swiftly over rocks; the opposite of riffles are pools, where water moves slowly - pools are the best places for finding wily old fish.) The black encrustations are Mn oxide. Another word for this is "wad" -- in days long gone, the old-time prospectors would scrape off the wad to determine its chemical composition. They did this because economic metals such as Ag, Ni, Co, and Mo are coprecipitated with Mn.

The wad is formed by Leptothrix discophora. This is the same bacterium that makes the oil films. In the case of Mn, these bacteria are colonizing the water/rock interface and are precipitating the black Mn by using a very specific protein. The ultimate reason for doing this may be detoxification because Mn may be toxic to certain metabolic reactions. BREAK open cobbles (**WATCH EYEBALLS PLEASE**) to see that the Mn is only a rim.

OBSERVE the Mn precipitated on microscope slides that were left attached to roots. This is the best method to observe the bacteria - those of us working on the Mn cycle leave these slides in the water for 6 weeks and then take them back to the lab and observe what has precipitated. The collecting technique involves making slide sandwiches - write date on two slides, put slides together, tie them together with telephone wire, and affix the wire to a tree root (best method) or to a bamboo skewer or a pencil.

STOP 3: MITTENDORFF SPRING

WALK across Dogue creek to other side.

This spring is perennial but the flow rate varies at times. OBSERVE either the different communities of bacteria or the thick deposits of Fe oxide. Note the black leaves where Fe has been reduced and the red leaves that are coated with Fe oxide. If the spring is flowing, collect iron bacteria. Or keep walking upsream until seeps are present.

The water chemistry here is as follows (Robbins and others, 1992):

	Fe (mg/L)	Mn (mg/L)	pH
surface water	25.8	0.44	6.0
aquifer water	17.3	0.51	6.0

IN TRANSIT DIRECTIONS:
PILE into cars.
TURN right onto S. Kings Highway.
TURN right at first street (Deer Run Dr.).
TURN right at first street (Deer Run Ct), and PARK on Deer Run Court.

STOP 4: MANGANESE NODULES IN DEER RUN (A RENEWABLE RESOURCE)

WALK along the path, down the hill, to Deer Run.

OBSERVE the manganese nodules in the creek. These are made of a mixture of a Ba-Mn oxide mineral called romanechite and an Fe-oxide mineral called ferrihydrite (Robbins and others, 1992). Manganese nodules can be broken by hand when they are still moist. (Doing this when they are dried breaks fingernails.)

OBSERVE the Mn precipitated on the microscope slides attached to the tree roots. These show that Mn-oxidizing bacteria are active in the water.

OBSERVE the Mn nodules in the soil profile. (CAUTION: if you fall into the pit dug for a soil profile, it was only one meter deep.) The soil here is classified as a Typic Ochraquult belonging to the Othello series (Porter and others, 1963). I put slides into the soil (method of Perfiliev and Gabe, 1961) and discovered that Mn-oxidizing bacteria are active in the soil.

This is a very important field site because those of us who have published on these manganese nodules could not agree if the nodules were forming in the creek, or if they were forming in the soil and washing into the creek (Robbins and others, 1982). I showed that there are Mn-oxidizing bacteria in the creek where the nodules are, and therefore the nodules are forming in the creek. Professor Del Fanning, soil scientist at Univ. Maryland, thinks the nodules are forming in the soil similar to those he published in Germany (Schwertmann and Fanning, 1976) and washing into the creek as the creek meanders over time. By arduously digging the pit, he showed that the nodules occur in nests and concentrate at -40 cm depth in a zone overlying a very impervious clay. I showed that there are Mn-oxidizing bacteria in the soil, so this is reasonable. John D'Agostino, retired economic geologist with the USGS, took the intermediate position that the nodules were forming both in the creek and in the soil (he's been happily married for a very long time). We are still looking for ideas and students to resolve this issue.

The nodules are zoned, which suggests they grow with the aid of processes that act periodically. Dorothy Keough (1992), now with the Corps of Engineers at Fort Belvoir, took a monthly hydrological profile for more than a year and showed that the water table is very close to the surface in the winter, but plunges precipitously to -80 cm as soon as leaf-out occurs in the spring. This suggests that the pumping action of leaves control the water table level and thus may also control the periodic availability of Mn in the soil profile.

IN TRANSIT DIRECTIONS:
PILE back into cars.
TURN left on Deer Run Dr.
TURN right on S. Kings Highway
PARK on Vantage Lane
CROSS highway (it's dangerous, BE CAREFUL)

OPTIONAL STOP 5: IRON BACTERIA IN WEEP HOLES OF RETAINING WALL

OBSERVE iron bacteria in the weep holes and Mn staining in the ditch. Fairfax County put this wall up perpendicular to the direction of water transport, so they had to leave holes to allow ground water to seep through. This is a normal engineering technique to solve such a problem, and you will begin to notice this other places you travel (my favorite place was the weep holes in a wall in Martinique). The ground water behind the wall is obviously anoxic; this water is a great source of Fe and Mn, and as you can see, where it discharges, there is plenty of evidence for healthy microbial activity and metal precipitation.

IN TRANSIT DIRECTIONS:
PILE back into cars
CONTINUE east on S. Kings Highway
TURN right on Harrison Lane
TURN into Huntley Meadows Park, the largest park in Fairfax County (1261 acres).

LUNCH:
STOP at cars and pick up your lunch.
FOLLOW the trail to the main wetland in the Park. Pick a place to sit and eat.

This is a wetland complex composed of forested wetland (red maple, green ash, swamp chestnut oak), shrub wetland (button bush and swamp rose), emergent wetland (lizard's tail, rushes, sedges), and submergent wetland (pondweed) (Robbins and Taft, 1985). Walk along the boardwalk and observe red patches of iron bacteria on the ground. If you keep walking, there is a tower that looks out over the main wetland. Peat is actively being deposited along Deer Trail that leads away from the tower. This peat and peat obtained from a nearby boring concentrates both Mn and Fe (Robbins and others, 1992), thereby showing that metal accumulation also occurred in the past history of this wetland.

MICROSCOPIC OBSERVATIONS FOLLOWING LUNCH:
WALK into Visitor's Center to room where microscope is set up for us to make observations. We will put drops of floc onto microscope slides, cover them with cover slips, and observe the different populations (compare to Figure).

REFERENCES

Chukhrov, F.V., Zvyagin, B.B., Goshkov, A.I., Yermilova, L.P., and Balachova, V.V., 1974, Ferrihydrite: International Geology Reviews, v. 16, p. 1131-1143.

Drake, A.A., Jr., Nelson, A.E., Force, L.M., Froelich, J.A., and Lyttle, P.T., 1979, Preliminary geologic map of Fairfax County, Virginia: U.S. Geological Survey Open-File Report 79-0398.

Ehrlich, H.L., 1990, Geomicrobiology, 2nd Ed.: New York, Marcel Dekker, 646 p.

Froelich, A.J., Johnston, R.H. and Langer, W.H., 1978, Preliminary report on the ancestral Potomac River deposits in Fairfax County, Virginia: U.S. Geological Survey Open-File Report 78-544, 37 p.

Ghiorse, W.C., 1984, Bacterial transformations of manganese in wetland environments, in Klug, M.J., and Reddy, C.A., eds., Current Perspectives in Microbial Ecology: Washington, D.C., American Society of Microbiologists, p. 615-622.

Ghiorse, W.C., and Ehrlich, H.L., 1992, Microbial biomineralization of iron and manganese: Catena Supplement 2, p. 75-99.

Hem, J.D., 1985, Study and Interpretation of the Chemical Characteristics of Natural Water, 3rd Ed.: U.S. Geological Survey Water-Supply Paper 2254, 263 p.

Keough, D.E., 1992, An evaluation of the practicality of using the "rusty rod" technique to estimate groundwater levels in constructed wetlands in northern Virginia: MA Thesis, Hood College, Frederick, MD.

Nealson, K.H., 1983, Microbial oxidation and reduction of manganese and iron, in Westbroek, P., and deJong, E.W., eds., Biomineralization and Biological Metal Accumulation: New York, D. Reidel, p. 459-479.

Perfiliev, B.V. and Gabe, D.R., 1961, Capillary methods of studying the microorganisms (in Russian). Akad Nauk SSSR, 534 p.

Porter, H.C., and others, 1963, Fairfax County Soil Survey: U.S. Department of Agriculture-Soil Conservation Service, 103 p.

Reed, J.C., Jr., and Obermeier, S.F., 1982, The geology beneath Washington, D.C.--The foundations of a nation's capital: Geological Society of America, Reviews of Engineering Geology, v. 5, p. 1-24.

Robbins, E.I., D'Agostino, J.P., Ostwald, J., Fanning, D.S., Carter, V., and Van Hoven, R.L., 1992, Manganese nodules and microbial oxidation of manganese in the Huntley Meadows wetland, Virginia: Catena Supplement 21, p. 179-202.

Robbins, E.I., LaBerge, G.L. and Schmidt, R.G., 1987, A model for the biological precipitation of Precambrian iron formation: B) Morphological evidence and modern analogs, in Appel, P.W.U., and LaBerge, G.L., eds., Precambrian Iron Formations: Athens, Greece, Theophrastus Press, p. 97-139.

Robbins, E.I., and Norden, A.W., 1994, Microbial oxidation of iron and manganese in wetlands and creeks of Maryland, Virginia, Delaware, and Washington, D.C., in Chiang, S.-H., ed., 11th Annual International Pittsburgh Coal Conference, Proceedings, "Coal-Energy and the Environment", Vol. 2, p. 1154-1159.

Robbins, E.I. and Taft, L.K., 1985, Huntley Meadows wetland of Fairfax County, Virginia: National Wetlands Newsletter, v. 7, p. 14-16.

Schwertmann, U., and Fanning, D.S., 1976, Iron-manganese concretions in hydrosequences of soils and loess in Bavaria: Soil Science Society of America Jour. 40, 731-738.

Singewald, J.T., Jr., 1911, The iron ores of Maryland: Maryland Geological and Economic Survey, Special Publication 9, Part 3, 337 p.

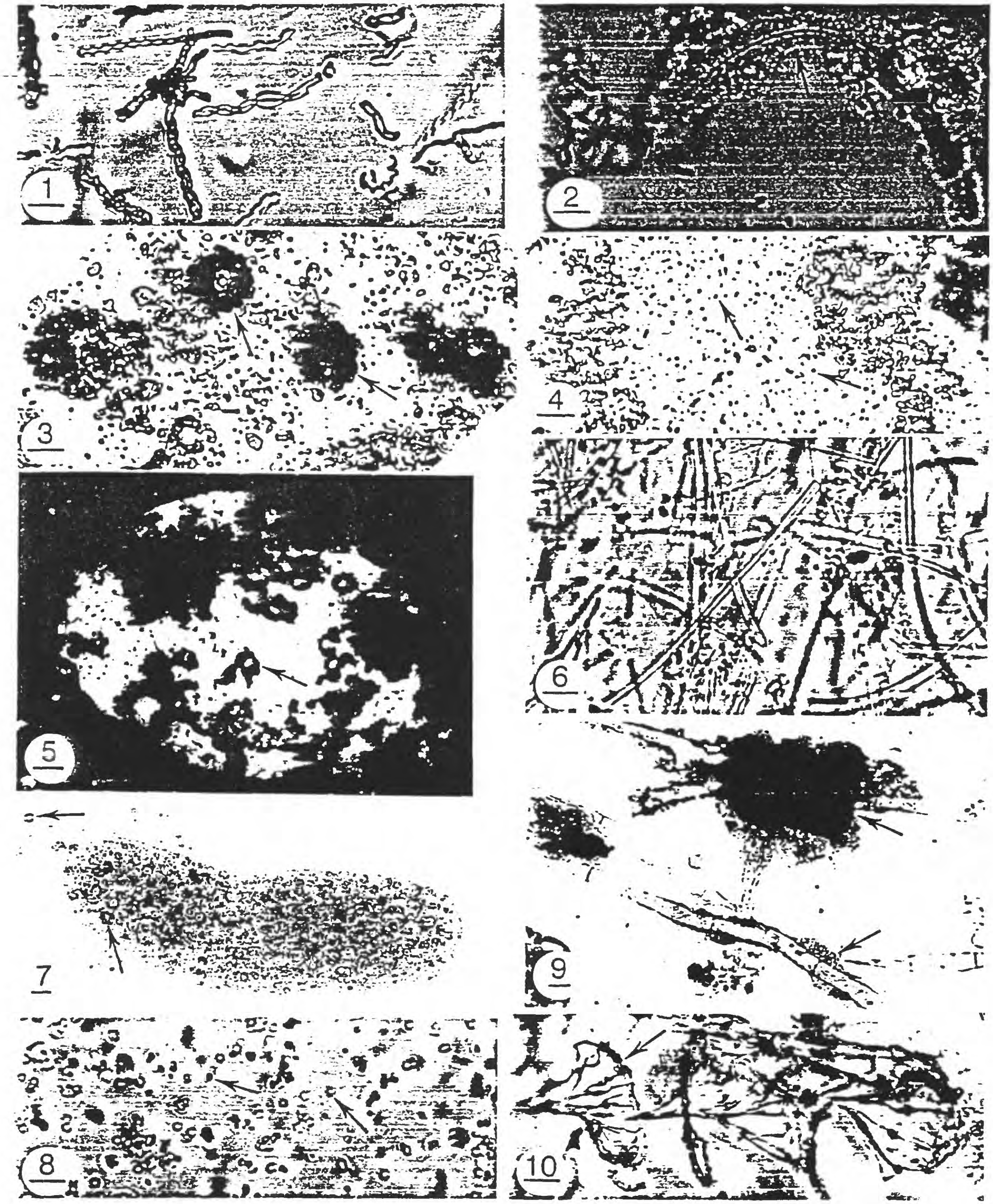


Fig. 1. Photomicrographs of iron bacteria in flocculates or on microscope slides. (Scale bar 10 μm)

1. Gallionella ferruginea [braid-like] in floc - Rhode River tributary, 3/92
2. L. cholodnii [sausage-like] (arrow) in floc - Sugarland Run 7/92
3. L. discophora fresh rounded holdfasts [doughnut-like] (arrows) on microscope slide - Barnyard Run tributary 5/14-23/88
4. Leptothrix discophora [dots] on film on water - Pomonkey Creek swamp 8/90
5. L. discophora dehydrated holdfasts within hole on Mn-coated microscope slide - Dogue Creek tributary 5/2-7/12/89
6. Leptothrix ochracea [drinking straw-like] in floc - Oxon Run 5/89
7. Siderocapsa sp. [globular] (arrows) colonizing fecal pellet in floc - Dogue Creek tributary 2/87
8. Siderococcus sp. [dot-like] (arrows) in floc - Calvert Cliffs 11/87
9. Siderocystis sp. [agglomerations] (arrows) coloning dead alga in floc - Barnyard Run 3/87
10. Toxothrix trichogenes [ladder-like] (arrow) in floc - Severn River tributary 8/90

(from Robbins and Norden, 1994)

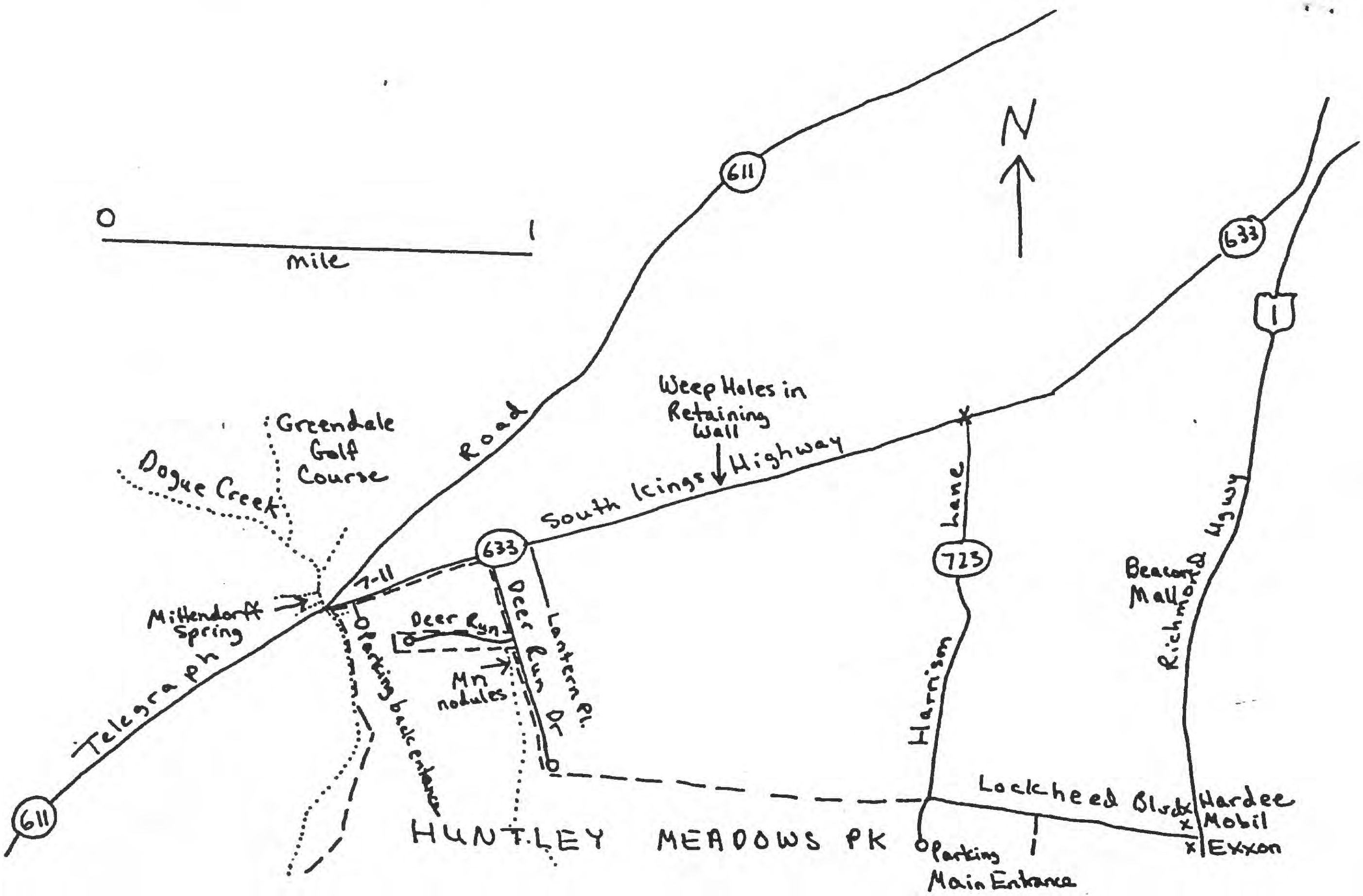
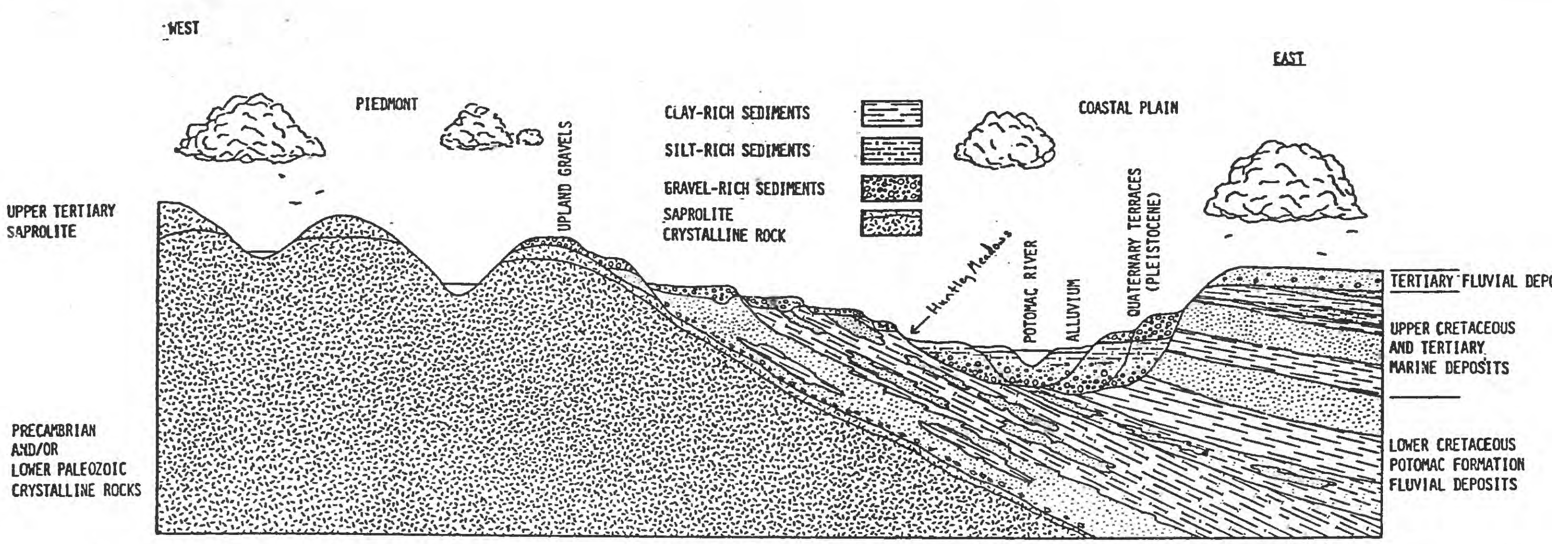


Figure 1. Locality map showing highways, creeks, park, and collecting sites at Huntley Meadows.



(Reed & Obermeier, 1982)

Figure 2. Geological cross section from Virginia to Maryland across the Potomac River showing location of Huntley Meadows wetland.