Bog Iron Formation in the Nassawango Watershed, Maryland

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Introduction

Bog iron deposits occur at a number of localities in the Pocomoke River basin (Figure 1) (Singewald, 1911). The most extensive deposits are situated along Nassawango Creek northwest of Snow Hill, a town on the Pocomoke River. After the discovery of these deposits an iron furnace was built in 1830 on the west side of Nassawango Creek, five miles northwest of Snow Hill, at a location known as the Furnace. The furnace exclusively smelted bog iron obtained along Nassawango Creek for a mile or so north of the furnace site; iron was produced from 1830 to 1850 at a rate of approximately 700 tons per year. Smelting technology of that period used mollusc shells for lime flux and locally burned charcoal for fuel; they were unable to remove phosphorous and the iron was rendered brittle when cold ("cold short") because of the high phosphorous content inherited from the ore. For that reason, and because of the limited size of the deposits and the discovery of the much larger and higher quality ore deposits in other parts of the country, production ceased about 1850. The bog iron deposits have been forming throughout the Holocene and are still forming today. Singewald (1911) stated, that their chief interest today lies in the fact that the deposits are now forming and at such a rate as to be observable. "Deposits which were once exhausted are again workable after an interval of a few years" (for more on rate of formation of bog ore at different locations see Starkey, 1962 and Moore, 1910). In general, bog ores consist primarily of iron oxyhydroxides, commonly goethite ($FeO(OH)$). The ores in the Nassawango, in addition to goethite and other ferric oxyhydroxides, contain a significant amount of magnetite.

Fig. 1 Index map showing location of Pocomoke River watershed on the Delmarva Penninsula of the Atlantic Coastal Plain (derived from an unpublished map of the surficial geology and geomorphology of the Altantic Coastal Plain by W.L.Newell and others, 2002)

Field Study

Figure 2 shows the surficial deposits in the Pocomoke River watershed. Sandy, quartz-rich barrier beach type deposits occupy east (ocean) side of the watershed. To the west are organic-rich fine sand to clayey silt estuarine/back bay deposits.

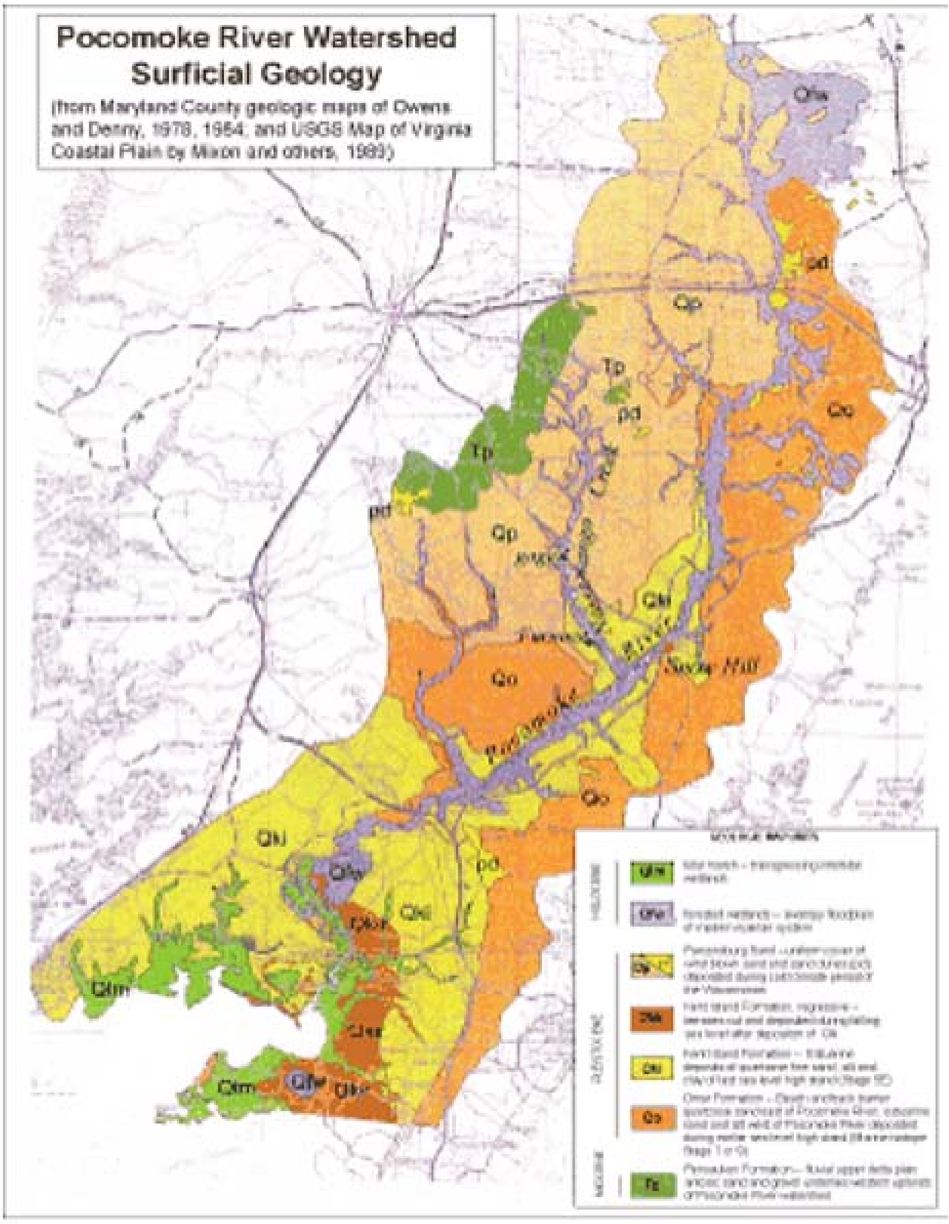


Fig. 2 The Pocomoke River drains a former barrier island-back bay complex. Sandy, quartz-rich barrier beach type deposits are to the east (ocean side) and organic-rich - fine sand to clayey silt estuarine/back bay deposits are to the west. The western divide is part of the old Delmarva Peninsula uplands adjacent to the Pleistocene coastal deposits. The barrier beach deposits are coarser and better drained than the finer grained bay deposits. Wind blown and sand dunes are distributed across the older deposits.

Figure 3 is a map showing the distribution and extent of ditching in the Pocomoke River basin. Drainage ditches have been dug since colonial times. However, most of the ditches were dug during the middle of the 20th century and are actively maintained. There is more ditching in the areas of fine grained sediment where natural drainage is poorer. The water table in the basin before ditching was close to the surface and interfered with agricultural practices. Ditching lowered the groundwater table, but caused bypassing of the natural riparian wetlands, swamps and tidal marshes where processing of nutrients and trapping of sediment occurred. Prior to ditching, there were approximately 800 miles of natural drainage through areas that permitted long contact time of water with environmental materials. Ditching created an additional 1200 miles of water ways and substantially decreased the contact time for the waters with natural materials that mitigated nutrient concentrations and trapped sediment. The shorter residence time may limit the concentration of dissolved iron.

By contrast, the Nassawango Creek has long reaches with natural channeling and limited ditching along the tributaries. This original configuration may result in the apparent higher concentration of dissolved iron and the thicker present day accumulation of ore.

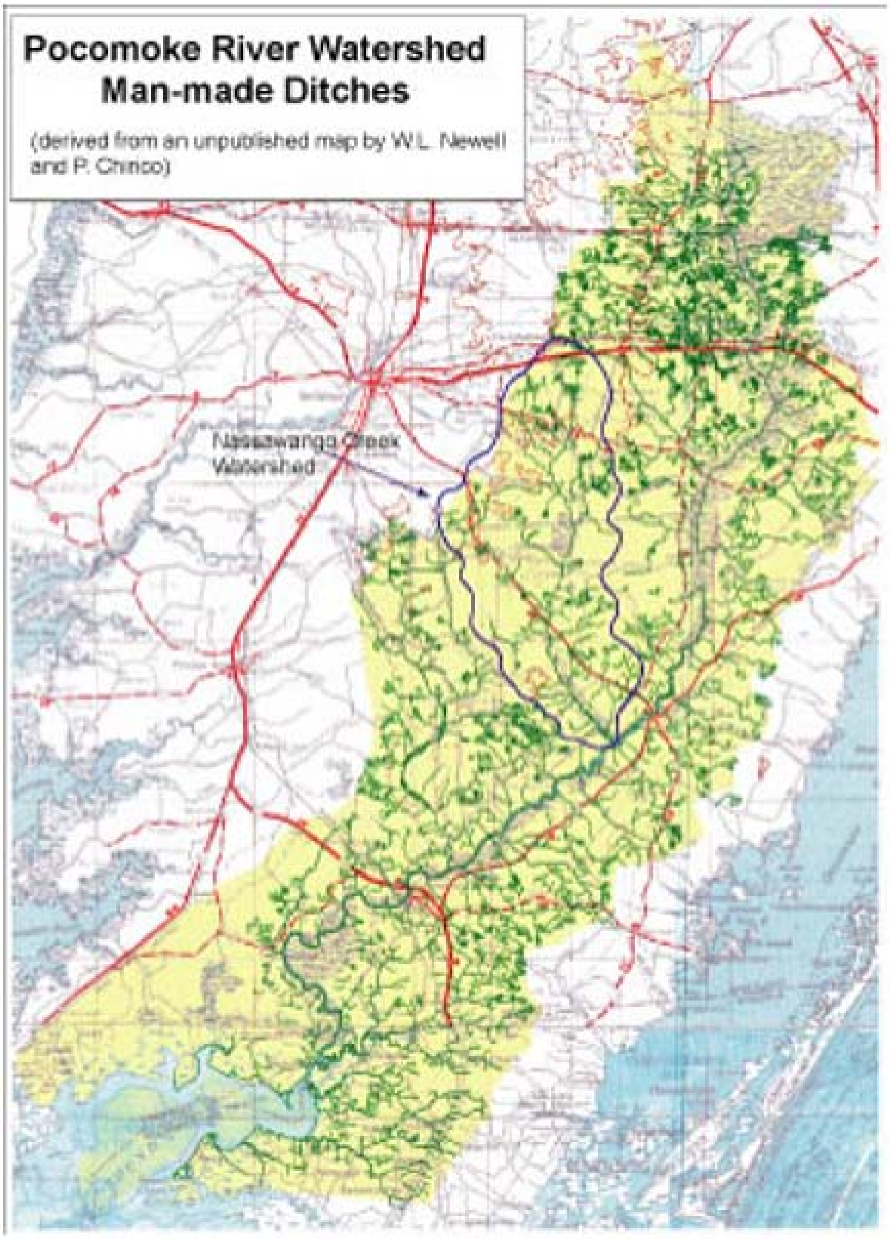
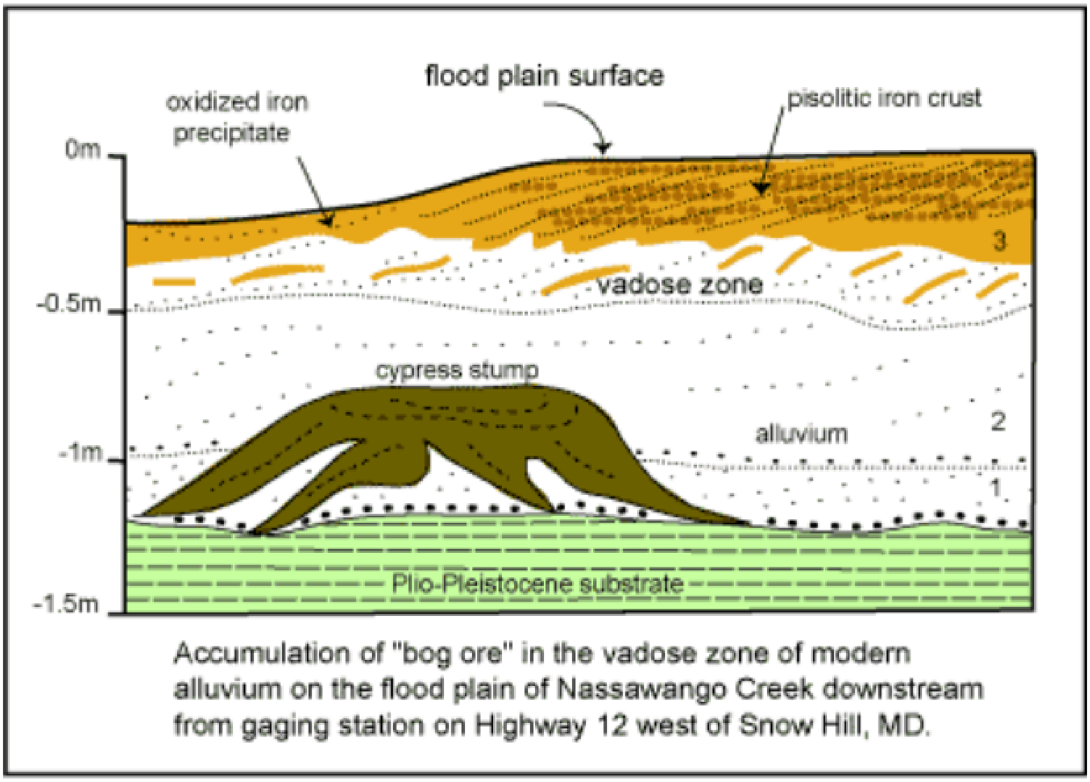


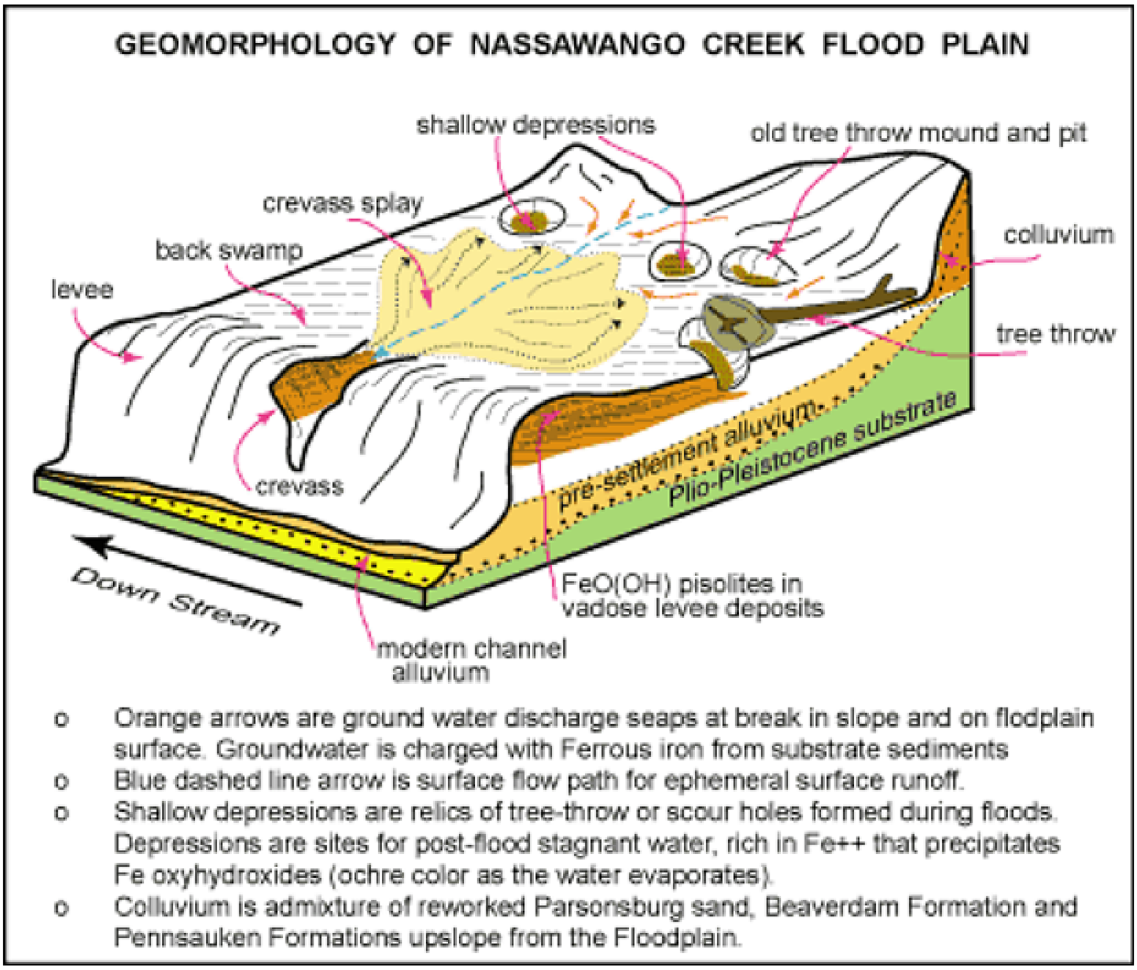
Fig. 3 Map showing the distribution and extent of ditching in the Pocomoke basin

Geomorphological models of bog iron accumulation in the Nassawango Creek watershed are shown in Figure 4.



Accumulation of "bog ore" in the vadose zone of modern alluvium on the flood plain of Nassawango Creek downstream from gaging station on Highway 12 west of Snow Hill, MD.

Fig. 4a Cross section of stratigraphic details of Nassawango Creek flood plain alluvium down stream from gaging station (see fig.2)



- Orange arrows are ground water discharge seaps at break in slope and on flodplain surface. Groundwater is charged with Ferrous iron from substrate sediments
- Blue dashed line arrow is surface flow path for ephemeral surface runoff.
- Shallow depressions are relics of tree-throw or scour holes formed during floods. Depressions are sites for post-flood stagnant water, rich in Fe++ that precipitates Fe oxyhydroxides (ochre color as the water evaporates).
- Colluvium is admixture of reworked Parsonsburg sand, Beaverdam Formation and Pennsauken Formations upslope from the Floodplain.

Fig. 4b Schematic diagram of geomorphology of flood plain along Nassawango Creek where bog iron deposits occur.

Fig. 4c Exposure of Nassawango Creek flood plain stratigraphy during extended period of near record low flow (July-September, 1999). Bank is about 1m high. Normal discharge during late summer low flow would produce 0.5m stage height higher than shown. Discharge during late winter to early spring commonly covers entrire floodplain. Details of stratigraphy are shown in Figures 4a and 4b.

Fig. 4d Iron-rich groundwater discharge form spring on Nassawango Creek floodplain. Groundwater discharge from springs is charged with Fe^{++} that oxidizes and precipitates as colloidal iron oxyhydroxide.

Fig. 4e Alluvium at water's edge of Nassawango Creek during period of low flow shows angular, platy pebbles to 2cm of goethite-limonite eroded from cemented bars and levees of floodplain. Orange "mud" is newly precepitated iron oxyhydroxide. Sweet gum leaf at top of photo is about 6cm wide.

Iron-bearing groundwater typically emerges as a spring (Figure 5). The iron is oxidized to ferric hydroxide upon encountering the oxic environment of the surface. "Bog ore" often combines goethite, magnetite and vugs or stained quartz. It is not clear whether the magnetite precipitates upon first contact with oxygen, then oxidizes to ferric compounds, or whether the ferric compounds are reduced when exposed to anoxic conditions upon burial beneath the sediment surface and reoxidized upon exhumation at the surface (Figure 6).

Fig. 5a Picture of typical iron-bearing ground water emerging as a spring. The iron is oxidized to ferric hydroxide upon encountering the oxic environment of the surface. A large number of these springs and seeps on the flood plain provide the iron for bog iron deposits..

Fig. 5b Samples of "bog ore" from Nassawango Creek show vugs lined with goethite around massive "ochre".

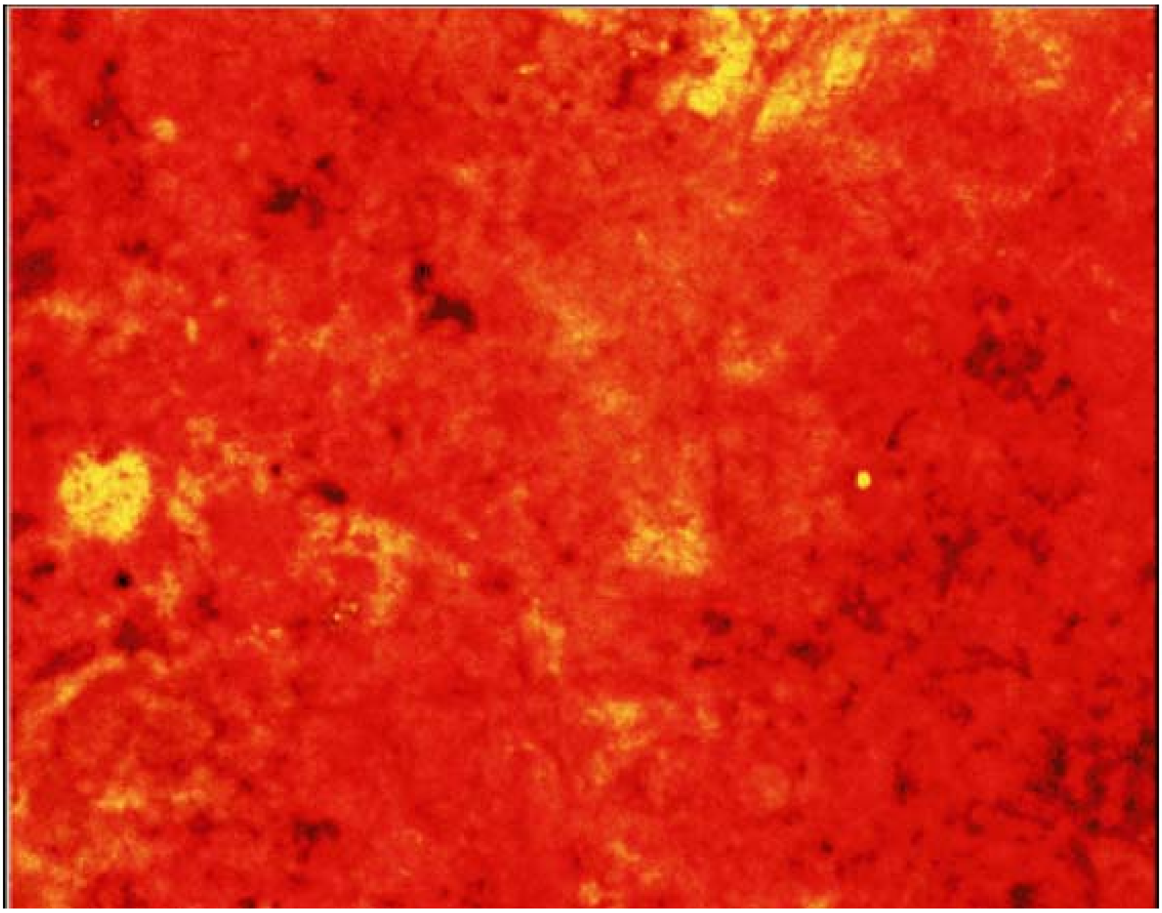
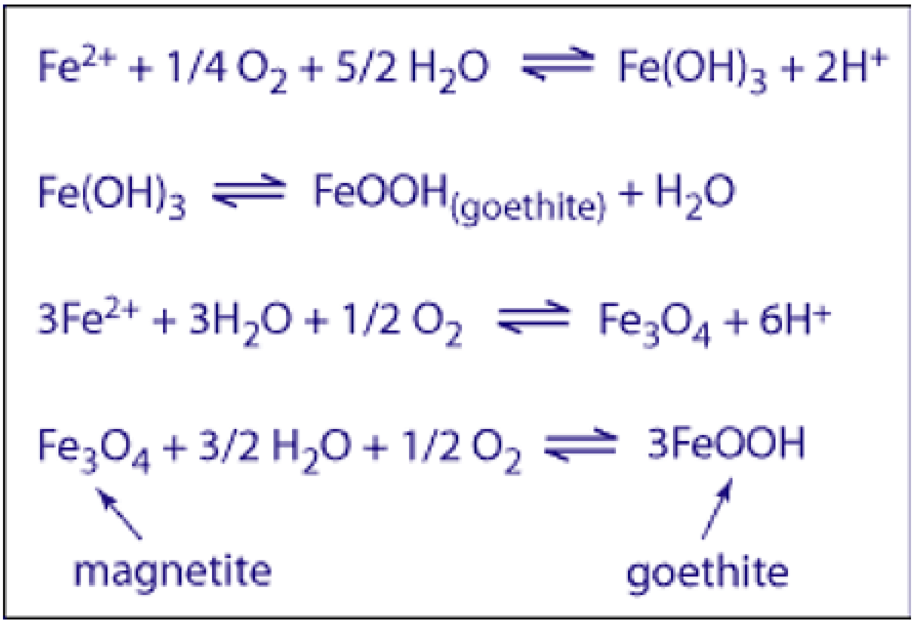


Fig. 5c Transmitted light photo-micrograph is about 0.5cm on the vertical axis. Black areas of goethite may include magnetite that has been identified by X-ray diffraction of powdered ore. Light areas may be vugs or stained quartz.



$$Fe^{2+} + 1/4\,O_2 + 5/2\,H_2O \rightleftharpoons Fe(OH)_3 + 2H^+$$

$$Fe(OH)_3 \rightleftharpoons FeOOH_{(goethite)} + H_2O$$

$$3Fe^{2+} + 3H_2O + 1/2\,O_2 \rightleftharpoons Fe_3O_4 + 6H^+$$

$$Fe_3O_4 + 3/2\,H_2O + 1/2\,O_2 \rightleftharpoons 3FeOOH$$

Fig. 6 Reactions postulated to be taking place in the emerging spring waters. It is not clear whether the magnetite precipitates upon first contact with oxygen, then oxydizes to ferric compounds, or whether the ferric compounds reduced when exposed to anoxic conditions upon burial beneath the sediment surface and reoxidized upon exhumation at the surface (we suspect latter).

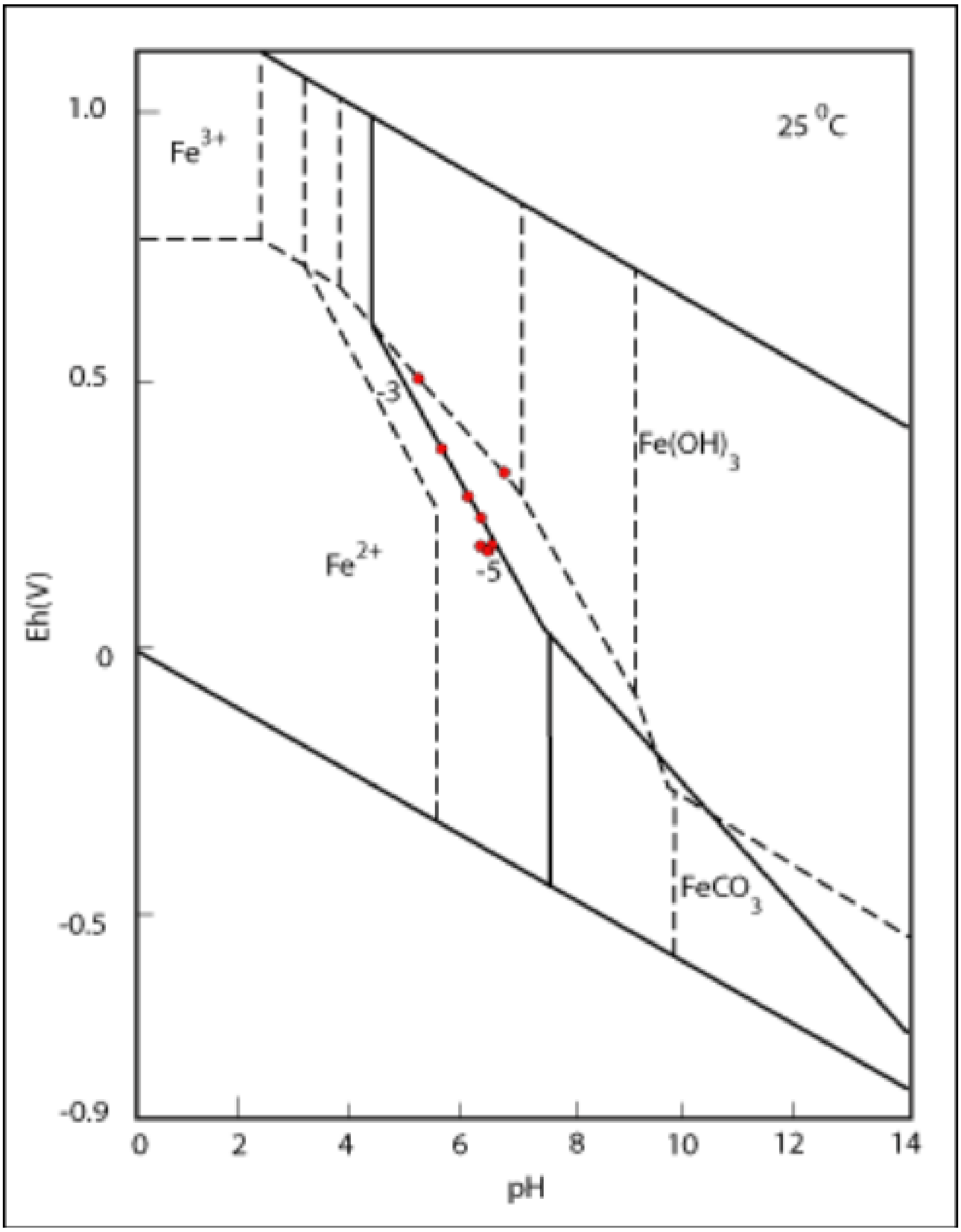


Fig. 7 Eh-pH diagramm showing measurements of a number of spring waters. Most waters are consistent with equilibrium between dissolved ferrous iron and solid ferric hydroxide (log K=-37.1). Two of the measurements are consistent with equilibrium between dissolved aqueous iron species. It is not known why the electrode responded to the dissolved species in these two cases rather than the dissolved-solid equilibrium that most measurements reflected, since all of the springs looked similar in physical characteristics.

Study of the reduction-oxidation potential of spring waters in the watershed showed that most waters are consistent with equilibrium between dissolved ferrous iron and solid ferric hydroxide (log K=-37.1). Two of the measurements (Figure 7) are consistent with equilibrium between dissolved aqueous iron species. It is not known why the electrode responded to the dissolved species in these two cases rather than the dissolved-solid equilibrium that most measurements reflected, since all of the springs looked similar in physical characteristics.

The study has shown that Pocomoke River tributaries in the central part of the watershed exhibit turbidity even during dry years (Figure 8). The turbidity results primarily from iron oxyhydroxide floc due to precipitation of ferric compounds as ferrous-rich ground water emerges as river base flow. Note that the internal generated turbidity has nothing to do with runoff and sediment transport from upland areas.

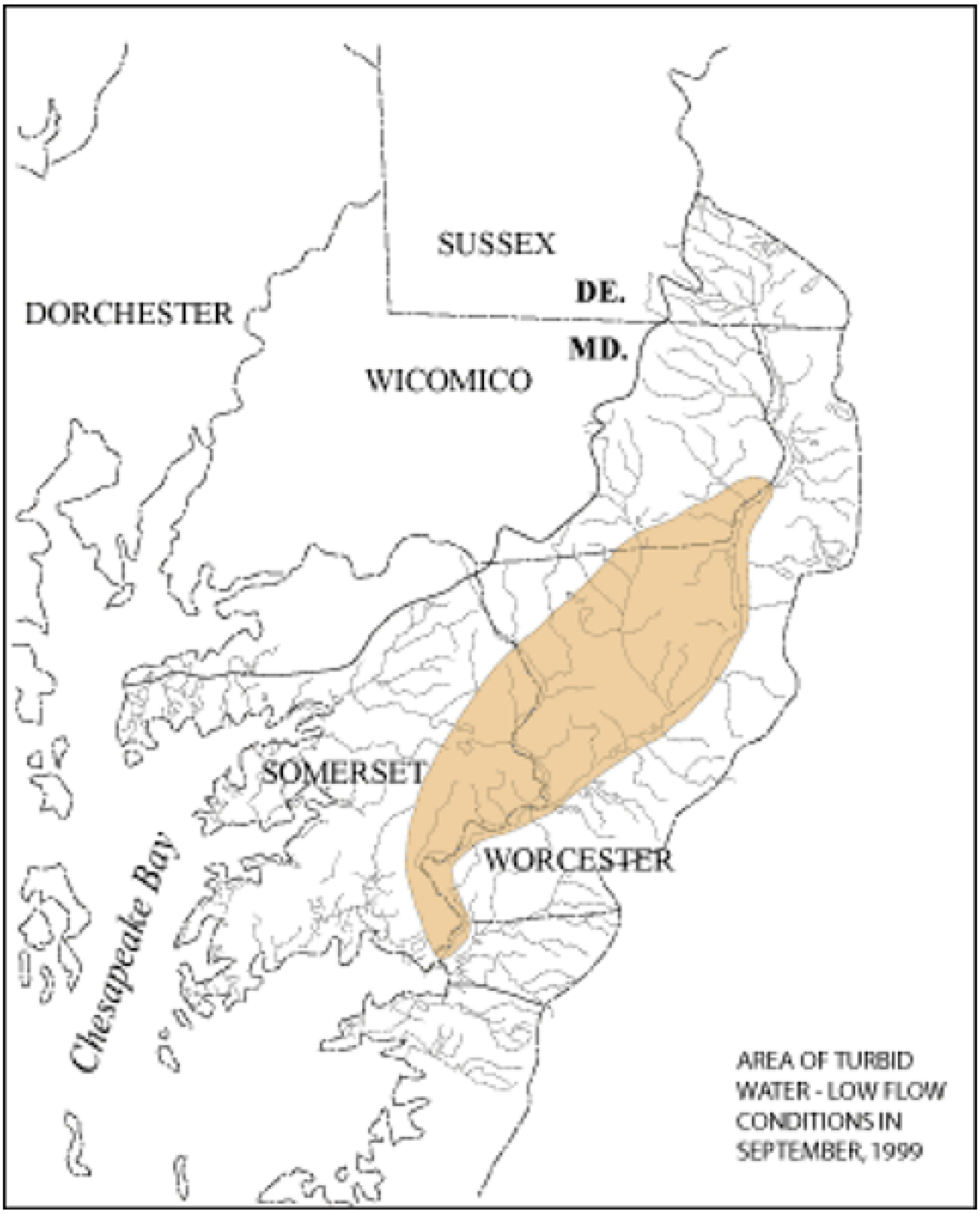


Fig. 8a

Area exhibiting turbid waters in the fall of the year when there had been no runoff of sediment-rich waters into the rivers. The turbidity results primarily from iron oxyhydroxide floc due to precipitation of ferric compounds as ferrous-rich ground water emerges as river base flow.

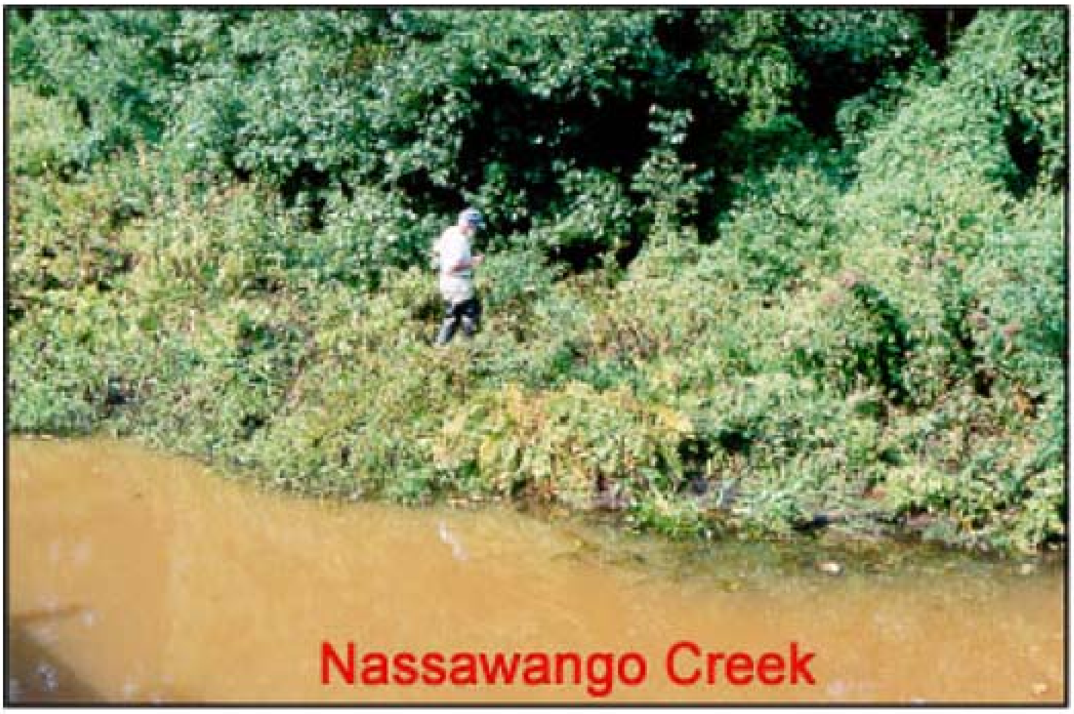


Fig. 8b

Turbid base flow discharge of Nassawango Creek during extended period of near record low flow (July-September, 1999). Turbidity in Creek is suspended floccules of iron oxyhydroxide.

Summary

The ground water of the Pocomoke basin is rich in reduced iron. This is particularly true in the Nassawango sub-basin where bog iron deposits along the flood plain of Nassawango Creek were dug in the mid-1800's to supply an iron smelter near the town of Snow Hill. The rate of bog iron formation was so rapid that areas could be re-mined in a matter of few years (Singewald, 1911). Bog iron is still forming in this area, and in other parts of the Pocomoke basin. Ground water has been measured with ferrous iron concentrations in excess of 20 ppm. When this water emerges at the surface or is discharged into the river system it rapidly oxidizes to an amorphous particulate iron oxyhydroxide which in time crystallizes to goethite. The iron in this system is important for at least two reasons: 1) iron oxyhydroxides strongly sorb phosphorous and many trace metals. Early reports on the composition of the Nassawango bog ore indicate that it commonly contained 10% P which made the pig iron smelted from this ore brittle when cold (Singewald, 1911); 2) the iron precipitating in the rivers causes turbidity which reduces light penetration to rooted aquatic vegetation and may impact other organisms, for instance, by coating gills and interfering with oxygen transfer. The first effect will play a role in the behavior and cycling of P in the system, while the second effect will impact biota in the system. In the fall of very dry years (1999 and 2001), we found the rivers in the central part of the Pocomoke basin quite turbid although there had been no storms to wash sediment-laden runoff into the rivers. Samples of the particulate matter creating the turbidity were iron-rich and displayed a weak x-ray diffraction pattern of goethite. There also seemed to be some organic material, probably algae, contributing to the turbidity, but this has not yet been investigated. Whatever the mix of materials that cause the turbidity, they are authigenic in the rivers and are not contributed by runoff. If all of the sediment erosion and runoff could be eleminated, it would have no effect on the turbidity generated by these chemical processes. Any practice recommended to reduce suspended sediment in these waters must take authigenic precepitates into consideration. Best management practices for sediment control in the watershed will have no effect on the turbidity resulting from oxidation of ferrous ions. Our project studies at other locations in the Chesapeake Bay have observed that vivianite ($Fe_3(PO_4)_2 * 8H_2O$) is forming in sediment at heads of tributary estuaries where tidal water is non-saline and anoxic. Presumably, the phosphates originate from degradation of organic materials in the anoxic environment. Vivianite is commonly encountered in modern sediments we have cored from similar depositional environments. Vivianite in the estuarine sediments of the Kent Island Formation and Omar Formation may be the source of phosphates in early bog iron that was first mined in Nassawango Creek.

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