The Role of The Tannin –Sapropel Cycle in Habitat Reversals
The Western Connecticut Habitat Failure for Blue Crabs, August 2011
A Capstone Proposal – Case History Discussions
Leaves and Brown Waters Hurricane Irene
Tropical Storm Lee
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So many times in reviewing the history of fisheries I come across periods of dought followed by tremendous rainfalls and then the appearance of chocolate or "brown waters." The most famous incident is perhaps the upper Narragansett Bay Brown Water – Black Water Fish Kill and marine die off of August 1898. Dr. Scott Nixon wrote up the event in an extensive historical review called the "An Extraordinary Red Tide and Fish Kill in Narragansett Bay." Coastal and Estuarine studies Vol 35, pg 429 to 447, 1992.

Heavy rains on July 13, 1898 into the Providence River Watershed occurred before an intensive heat wave August 18 to September 5th 1898. A record rainfall contributed to a tremendous watershed removal of tannin – the final breakdown of wood tissues and in our area mostly leaves. Tannins (three major types) are brown and gives wood its typical brown hues. The New England region recorded intense heat waves in much warmer than average summers between 1895 and 1901 Narragansett Bay (Rhode Island of 1898) had climate enhanced algal blooms – frequently called chocolate tides or red waters. One event in particular was very severe and known as the Great Bay fish kill (Narragansett Bay Rhode Island). In July to September (1898) climatic events combined to produce a major toxic fish kill fueled by heavy rains that washed a huge organic wave of debris (human sewage also) down stream into upper Narragansett Bay. In July – August it was very hot and little wind or storm energy as this organic matter presumably putrefied. (It must be noted that relatively dry conditions before most likely lowered moisture in leaf litter and forest humis called duff). When heavy rains occurred this organic matter was "light" and therefore could quickly be moved into transport waterways. Fishers on Cape Cod called this light organic debris oatmeal or chaff.

Professor A. D. Mead of Brown University wrote up the 1898 event in an article titled "An Investigation of the Plaque which destroyed multitudes of fish and crustacean during the fall of 1898" and later submitted his article for Science

Magazine (S. Nixon Coastal and Estuarine Studies – Novel Phytoplankton Blooms Vol 35, pg 430 1992). The description of Professor Mead (1898) details the appearance of chocolate waters which signifies Tannin in huge amounts, followed by harmful algal blooms (HABS) and then sulfide induced toxicity from low oxygen conditions. Sulfide toxicity is often rapid and prevents the "flee factor" of declining oxygen levels – fish can move if the transition is slow but if quick fish and crabs often perish. One indication of sulfide events (other than the stench of sulfur) is the "Jubilee factor" blue crabs climbing out of the water which according to Professor Dr. Meads's account did occur. Dr. Nixon repeated Dr. Mead's account and his description which is still very valid today following a second very warm period in New England 1974-2004 is included below. A century later it is still valid and is repeated here.

Upper Narragansett Bay Fish Kill of 1898 – A Classic Tannin/Sapropel Case History

After heavy July 1898 rains – Dr. Mead Reports the following:

> "During the last two months the inhabitants of Rhode Island witnessed the following remarkable phenomenon. The water of a considerable portion of the Bay became thick and red, omitting an odor almost intolerable to those living near by. The situation became alarming when, on the 9th and 10th of September {1898}, thousands of dead fish, crabs and shrimps were found strewn along the shores or even piled up in windrows.
>
> During the last of August, throughout September and a part of October streaks of red or 'chocolate' water were observed from near Quonset Point and Prudence Island, north to Providence, and, on the flood tide, up to Seekonk River, nearly to Pawtucket, a range of about fifteen miles. In other parts of the Bay, as far as could be learned, the phenomenon had not been observed.
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> On the 8th and 9th of September the water became extremely red and thick in various localities from East Greenwich to Providence, and the peculiar behavior of the marine animals attracted much attention. Myriads of shrimps and blue crabs, and vast numbers of eels, menhaden, tautog and flatfish came up to the surface and to the edge of the shore as though struggling to get out of the noxious water. Indeed, the shrimp and crabs were observed actually to climb out of the water upon stakes and buoys and even upon the iron cylinders which support one of the bridges and which must have been very hot in the bright sun."

The initial beginning of many fish kills is now likely rain swept Tannin contamination. Tannins are themselves not the direct cause but start a process for lack of a better term – The Tannin – Sapropel Cycle. Tannin acts to over load organic matter reduction processes and helps them become part of the Sulfur Cycle.

Three things need to happen to put the Tannin – Sapropel cycle "in play" for significant habitat change, a huge influx of Tannin dissolved or in leaf matter following a heavy rain, hot temperatures and low energy post signaling event. In simple terms the oxygen dependent bacteria that naturally breakdown organic matter – recycling it so to speak are just completely overwhelmed. The Tannins drive suspended organic matter out of the water making the situation even worse – high temperatures reduce available oxygen even more – further (oxygen inverse solubility law) and the bottom waters become oxygen depleted, then anoxic.

At the same time sulfides form near the bottom and the killing begins – slowly at first (those crabs and fish that can flee the area will do so) and if a storm comes it is enough to break up the sulfide layer (in the warm stratified waters layers of The Narrow River upper ponds – Pettaqaumscutt lake shores Rhode Island, Arthur Gaines reported sulfide levels 10 times that of the Black Sea (Maritimes Vol 35 #2, May 1991) and introduce cooler more oxygen containing waters, if not a bottom sulfide kill turns into a general system wide (especially in restricted coves and bays) fish kill. Greenwich Bay in Rhode Island suffered a Tannin – Sapropel sulfide fish kill in 2003 – also following hot weather and heavy rains.

Probably the most common acidic (also termed astringency) form of household tannins most people know (or did a century ago) is a product called Witch Hazel. The center for Witch Hazel production for a century or more was the Dickerson factories of Essex – Deep River area of Connecticut. It is traced to the area Native Americans boiling the roots of the Hamamelis - virginiana plants to obtain topical treatments.

In the riverine environment tannins are termed a "natural clarifier" that is its acidic character tends to cling to proteins and amino acids. As a wash therefore it left skin topical treatments feeling "clean" and refreshed. (No trade or product endorsement implied).

In the marine environment Tannin also cleans the water and causing dead algae (fresh or marine) to clump and drop to the bottom. Some recent papers refer to this as marine snow. If I continue this analogy – heavy rainfalls then create blizzards of dead organics falling to bay and cove bottoms, and Tannins jumpstart the Sapropel Cycle in warm low oxygen waters.

Fishers Make the First Tannin – Sapropel Connections

At the turn of the century it was alewife fishers and fishery managers, then called Alewife wardens, walked streams checking on alewife runs. The Great Heat 1880-

1920, a climatic period of low rainfall and high heat, organic matter both manmade (refuse) and natural (leaves) filled many alewife runs. This is the result of low habitat energy – slow, murky waters carry less organic matter to the sea – a problem that has plagued dike and canal builders since the start of recorded time. Over time these low energy waterways filled with organic matter which then turned into Sapropel. Some of the most visible impact of Tannin contamination was in the Alewife fisheries of Maine. Fishers and residents living along rivers and streams noticed the impact of saw dust (from lumber mills) entering water courses over a century ago. Tannins would quickly leech from sawdust staining waters brown and precipitate woody tissue to the bottoms (Tannin today are still referred to as nature's precipitate). As heat continued, toxic sulfides formed and ruined alewife runs.

In the twenty-eighth report of the Commission of Sea and Shore Fisheries of the State of Maine (1903-1904, August 1905 – Kennebec Journal Print) contains the comments of Alewife Warden, S.P. Cousins, on page 61 in the alewife section the following excerpts:

The report for the State of Maine has a division devoted to alewife fisheries a species of both value and concern. The report concludes that many of Maine's alewife fishways were hopelessly filled with organic debris (1903) and some had" no connection with the water" (sea) and takes aim at the organic matter increase from mills that had in many communities filled to block fish passage. On page 61 stating, " refuse from the mills obstruct the fishways and make them useless." The report now includes the report by Alewife Warden Cousins and his observations (Impact of Tannins – Reduction low pH).

"There are many who now assert that sawdust is not injurious to fish life, and naturally those are frequently mill owners, and their assertions have weight in that those most interested don't take the trouble to investigate the question and authoritatively refute these statements."

The question of sawdust pollution of fish streams has been, I will say, so conclusively determined by scientific experiment and investigation as to leave no doubt from interest or lack of information, I give the result of careful investigations of the effect of sawdust upon fish made by Dr. A.P. Knight, professor of Animal Biology, Queens University, Kingston, Canada, which sets at rest the question and conclusively proves how fatal to life is sawdust when allowed to enter fish streams (I now quote Dr. A.P. Knight):

> "When sawdust was allowed to lie in still water, or in very slowly running water, the most disastrous effects, followed the immersion of different animals in the poisonous mixture. Not merely did adult fish die in it, but fish eggs, fry, aquatic worms, small anthropods, animalcules and water plants. Nor was the

cause of death due to suffocation from lack of oxygen because when air was made to bubble rapidly through the solution the final results were the same, the only difference being that death was somewhat delayed. No one could paint too vividly the deadly effects of this solution. Adult fish died in two or three minute, fish eggs in a few hours, fry and minnows in from ten to fifteen minutes, aquatic worms and insects, eight to twenty-four hours- aquatic plants in a few days. Every living thing died in it and if one were to judge of the effects by laboratory experiments above then the prohibitory legislation need no better defense" (referring to Canadian statues forbidding the throwing of sawdust into streams).

It was most likely the Bay scallopers who first noticed the "deadlines" in coves and bays. This was often described as a line on moving chains below which all marine life suddenly disappeared. The chain was devoid of life no barnacles, mussels and at times even algae. Instead the chain was often stained black and clean. Below which was often "foul smelling black bottoms" (John Farrington, personal communication, Borne Sandwich Shell Fishermens Meeting, Cape Cod, early 1980s). A shellfish survey in Centerville River found an abandoned Christmas tree from the year before while towing a hand hauled oyster dredge – the top branches were heavy set of bay scallops – below which the branches were stained black with no set. Shellfish nets hung from shellfish floats in Falmouth also showed above the bottom "deadlines" below certain layers seed shellfish perished (George Sousa, Falmouth Shellfish Officer, Personal Communication, 1982).

This describes the killing of marine life when hydrogen sulfide is dissolved into seawater. In summer, warmer temperatures blocked oxygen pathways into bottom waters and now rich in sulfide became poisonous and killed millions of bay scallop sets. In saline areas the hydrogen sulfide levels from toxic more dense sulfide waters below surface fresh waters. In times of rain, strong tides or storms this heavier black water or sulfide water comes to the surface killing fish and bringing with it the strong odor of sulfur.

These black waters still occur today in coastal coves and rivers. Some recent photographs picture black sulfide water as river under a river. In most cases, brown waters proceed black waters and the presence of Tannins, a sulfide trigger. Shellfishers on Cape Cod consistently noted the best areas for seed quahogs were those areas already covered by "shell hash" (Pleasant Bay Study, 1968, Massachusetts Marine Fisheries Bulletin). These bottoms were often described a "sweet" slightly alkaline which oysters and clams need so they do not dissolve on low pH bottoms. Sulfide/Sapropel bottoms contained no shellfish. The Tannin acidic role in hydrogen sulfide formation has been known for quite some time. The largest Tannin source in our New England area are Oak leaves. That is why after heavy rains, high energy streams turn brown – leaves rolled and pounded to release the brown Tannins, which can then jumpstart the Sapropel cycle.

This is a recent Wikipedia™ description, which fits the description of Blackwater a century ago frequently after brown water or chocolate water events:

> "The leaching of highly water soluble Tannins from decaying vegetation and leaves along a stream may produce what is known as a blackwater – water flowing out of bays has a characteristic brown color from dissolved peat tannins. The presence of tannins (or humic acid) in well water can make it smell bad."

Under the right conditions brown waters can be turned into iron sulfide (black) waters containing the deadly sulfide wash downstream or generating a sulfide block to returning Shad, herring and alewife.

Sulfide water in the 1960s was to kill crops in irrigated fields in southern states during warm weather. H.W. Ford and D.V. Carvert of the University of Florida Indian River Field Laboratory Fort Pierce (which I was to tour in 1973) produced a paper (Florida Experiment Station Journal Series #2509) titled "Induced Anaerobiosis Caused by Flood Irrigation with Water Containing Sulfides" pertaining to sulfide damaging citrus roots, often killing the plant. They observed much the same as Connecticut farmers noticed a century before – sulfides could kill most crops.

On page 107 of their report contains this statement after massive planting kills – "A heavy accumulation of gelatinous black insoluble iron sulfide had formed under the furrows. The layer was found to restrict the movement of water. Hydrogen sulfide released when the layer slowly oxidized could kill roots above the water table." This description is very similar to the explanation of eelgrass death rings in the North Sea. Eelgrass patches started on sandy marine soils as the meadow grew Sapropel formed (organic matter trapped between the blades of eelgrass) and increased hydrogen sulfide until it became lethal to the first "set" of eelgrass forming huge rings as sulfide killed the oldest eelgrass first.
(See Denmark Coasts Eelgrass Rings Jens Borum University of Copenhagen and Marianne Holmer University of Southern Demark).

In the 1980s as Sapropel covered previously hard and shelly bay bottoms. Winter flounder fishers also complained about bottoms becoming foul, leave covered and from time to time emitted strong smells. The 1972 to 2004 period would see huge habitat transitions from primarily harder firm shell containing bottoms to Sapropel which now covered shellfish beds – in terms of feet. It would proceed the winter flounder fishery collapse as critical sanding/shelly habitats reversed to those which rot the fins and caused necrotic lesions.

Fishers frequently report brown waters if the temperature is high enough and energy low (minimum tidal flushing or restricted flushing) can often lead to "black water" conditions and some of the most horrific fish kills. But heavy rains almost always proceed brown water events and this is the "flood waters release of tannins" was observed by so many western CT blue crabbers in August/September of 2011. The river most impacted by organic matter tannins both dissolved and hard forms (leaves) now appears to be the Saugatuck River in Western, CT.

Locked in the molecular weight of tannins are the waxes that give the slow reduction of it sapropel its shine. It is also the substance that reduces pore water circulation in marine soils and creates acidic conditions fatal to shellfish veligers and fish eggs. It is nearly always fatal to fish eggs. Earth Watch a local environmental organization who has been study water quality issues in western CT for decades noticed the old brown color in western CT Rivers after Irene and Lee adding that leafy build up on river beds is "uninviting" for bottom dwelling fish. Richard Harris commented in a Westport News Article (Not All Is Looking Up On The Saugatuck's Bottom," Oct 23, 2011) referring to now heavy leaf accumulations in the Saugatuck is quoted "It fouls the bottom, so the fish and lay eggs such as flounder and other bottom –dwellers can't use the bottom to raise their young use it as a nursery – "Basically once the bottom turns into that kind of condition for them its kind of hands off for them."

As a natural flocculant tannins contribute to oxygen depletion in bottom waters in regions of low tidal exchange concurrently as oxygen levels drop, sulfide levels rise. This happens in the shallow and most important habitats for many fin and shellfish species of "value" and that includes the blue crab. Tannins locked in organic matter (the leaves) can be released for days or months after a heavy rainfall). This brown water happens in freshwater lakes also as warm surface waters forms a barrier – a thermocline and isolates the bottom water from oxygen in air. As the summer progresses the bottoms of lake and reservoirs become extremely oxygen poor even anoxic or without oxygen. In the fall cool nights cause surface waters to cool quickly the surface waters to sink below (more dense) pushing the bottom oxygen poor water to the surface which can now appear brown or black. It is black because it contains sulfate of iron and hydrogen sulfide itself, the infamous rotten egg odor of the Great Heat 1880-1920.

Fall "over turn" or exchange of bottom sulfide waters (toxic to fish) if quick enough or continues under ice can cause a winter fish kill. The toxic sulfide wash or exchange can be just a few minutes to several hours and be gone leaving the dead fish behind with no apparent explanation other than it got really cold really quick and dead fish now float to the surface. Tides or river flows disperse the sulfides over time leaving no indication of the damage. Sulfide washes can occur after heavy rains which dislodge rotting leaves in brooks, and can block (if severe enough) returning shad and alewife – in this case it is termed a chemical or sulfide block.

Blue Crabs and Brown Waters – The Case of the "Jubilee"

Brown waters down south a century ago proceeded blue crab jubilees – in hot stagnant weather and following heavy rains (tannin input dissolved or hard) often caused a brown water event – low oxygen then sulfide resulting in the Blue Crabs fleeing the water (the excitement associated with the jubilee is that you could run to the shore and just pick up the blue crabs huddled on the beaches) itself. This is nearly always associated by the sulfide rotten egg odor hours to days later. As bacterial sulfur reducers now set into reducing nearly arrived tannins and leaves water turned black killing most living organisms. These fish kills could last for weeks as ammonia levels then increased creating red or brown algal blooms now (called Tides) which when dead continued the oxygen depletion by Tannins precipitating them now strengthening the sapropel cycle. Usually a strong storm, waves, or colder temperatures would introduce enough oxygen to stop the Tannin – Sapropel cycle but by then it was often too late, killing of fish and shellfish happens and if long enough even clams and oysters would die. Today such events evoke a manmade cause but frequently that is not the case. We can contribute no doubt (sewage overflows) but such sewage is high in nitrate which ironically helps buffers the sulfate reducing process. In other words nitrate in this case is the "good" nitrogen that can help break the Tannin – Sapropel cycle.

Available nitrate buffers or holds the sulfur bacteria reducers off – the oxygen reducing bacteria will go to nitrate (oxygen) compounds first for reducing organic matters, once oxygen is depleted bacteria that need oxygen look to oxygen compounds and nitrate is one of them. Once nitrate runs out the sulfate bacteria step in and simply put the oxygen dependant bacteria reducers now die and the far more damaging sulfur reducers now step up to finish the job by accessing sulfate. The oxygen dependent bacteria populations perish while sulfur reducing bacteria increase. The Tannin – Sapropel cycle by way of oxygen depletion and sulfur increases has killed more shellfish and finfish than we could ever do and it does it silently and out of view. Many fishers may observe or see it but until now lacked a name.

Observations of Fishers

Some of the first fishers to report about these The Tannin Sapropel event were eastern brook trout fishers. As waters warmed (1890s) bad smells emanating from trout brooks raised the first alarm – bells a century ago. As the climate warmed brook trout suffered a series of habitat extinction events. Fishery managers grew concerned and soon asked for the US Fish Commission for assistance with trout hatcheries at that time. They complied and many states built trout hatcheries but with the growing heat brook trout populations continued to decline. Several researchers now wrote about sewage fungus growing on rotting leaves and the smell of sulfur long before the development of the Saprobien classification system in 1909. The sewage fungus we call today sulfur reducing bacteria. As the years of heat continued the US Fish Commission suggested that Northeastern states introduce more heat tolerant species of Brown and Rainbow trout – which they did in the late 1870s and 1880s. As the heat continued many New England stream waters often became black and acidic as trout died by the thousands.

The Two Sides of Sapropel – A Public Policy Dilemma for Fishery Managers

Natural Sapropel is a substance that has two sides, one with oxygen it is a marine compost – a neutral to alkaline pH and black surface usually thanks to dissolved iron in seawater. Blue crabs crawl in it and fish swim over it, fish also hid almost submerged aquatic vegetation growing in it and although not the richest habitat type in regards to biodiversity it frequently has mud snails, an occasional blue mussel, and grazers shrimp and crustaceans such as green crabs. Thin patches help nourish submerged aquatic vegetation such as eelgrass making it a productive habitat for Blue Crab Megalops. Although not the best substrate for oysters if mixed with sand it can support dense sets of the soft shell clam called steamers especially after moderate storm events.

Oak leaves contain a hard to digest wax from the leaf itself and gives it a shine. This is what also gives Sapropel its often "greasy" description in the historical fisheries literature. When oxygen is short (limited) from biological or chemical oxygen demands restricted circulation or very hot water temperatures create low dissolved oxygen levels or when hypoxia occurs Sapropels other side comes out, the one with a sulfur. This side is a deadly as any toxic pollutant.

Sapropel Can Transition Habitat Value

What does Sapropel consist of and why is it important? In the marine environment adjacent to shore in quiet coves, bays and lagoons it is detrital remains (mostly leaves) that collect and overtime decompose simply put they rot. Other than some species of shrimp terrestrial organic matter in seawater is "different" often "tough to digest" and without oxygen warms and bacteria conduct the "reduction process" over much longer periods; it reduces organic matter back to molecules created by the plant tissue. In simple terms bacteria slowly "eat it," and in the process release chemical compounds, in the presence of oxygen – nitrates, amino acids (weak acidity) and long chain carbon molecules that are hard to digest – leaving them for other processes. These hard to digest molecules include waxes – belonging to a hydrocarbon classification called paraffin.

When oxygen is very short (limiting) a different process comes into view – sulfur reducing bacteria that utilize sulfate – not nitrate and in the process produce sulfides of iron not oxides. In this sulfuring reducing pathway comes a powerful toxin called hydrogen sulfide (10 times more toxic than cyanide) H2S which is very deadly to marine organisms and enclosed air spaces even to us. That is that rotten egg smell in hot temperatures that often just proceeds a large fish kill most often reported in the fisheries literature. As the process continues sulfide levels can increase especially as Sapropel deepens – the paraffin (waxes) form a film (it gives Sapropel its shine and its greasy feel) and seals off the oxygen from sulfate organic matter. The waxes clog the circulation in the Sapropel itself overtime increasing sulfide levels that kills eelgrass. Beyond tidal turbulence or restricted circulation Sapropel forms (Sapro organic matter pelos meaning putrefaction Greek language roots) and becomes sulfur rich – it smells. The older and deeper it gets the more toxic with out oxygen it becomes. Now comes the worse part disturb the Sapropel – and introduce oxygen and you have a reaction that releases sulfuric acid and a dramatically lower pH then now happens – the acid dissolves estuarine bivalve shell (some times on contact). It can get down to a pH of 3 – deadly to most oxygen dependent larval forms. There is more, instead of nitrate production – Sapropel sheds ammonia and increases of that nutrient helps fuel red or brown algae blooms – robbing what little oxygen remains and the source of the black water deaths a century ago. The Tannins then remove dead brown algae as a precipitate which now strengthens the Sapropel cycle.

Sapropel can kill in three ways – a toxic substance, (gill exchanges) low pH, and oxygen depletion by way of ammonia induced algae blooms. It in the marine environment is a real habitat game changer equal to fishing as a resource based activity upon certain habitat types. Can we make Sapropel in the lab? Sapropel formation behind dams takes years so a few details for source supplies often requires these components. (I suspect large deposits of Sapropel have accumulated in the Conowingo Pond on the Susquehanna river). For laboratory use the following is needed.

1) Sea water (sulfate)
2) Organic matter source ground oak leaves, oatmeal, ground wheat – other organic compounds
3) Sulfur bacteria
4) Absence of oxygen
5) Sealable plastic tubs (3) small because of toxic gas these experiments must follow all appropriate laboratory PPE protocols.
    - Sulfur bacteria are present in small quantities under cobblestones on beaches (underside stained black a sign for absence of oxygen – better to start dried samples of concentrate (if possible) it takes years for cultures to grow in the wild.
6) An incubator for heating

Deep coastal coves of deposits can be examined for Sapropel and the deeper the core the more Sapropel evidence is often apparent.

Although Sapropel can also form in cold, it is a very slow process while heating quickens the process – drives off ammonia and hastens nitrate elimination – once all oxygen (elemental) and organic oxygen (locked in chemical compounds) is used up then sulfur reducing bacteria takes over putrefies the organic matter as it turns black in the presence of iron. Sulfur compounds increase as sulfate reducing bacteria breakdown it as a source of oxygen. Although sulfur reducing bacteria don't dominate in an oxygen sufficient time when oxygen becomes limiting they come back with a vengeance. The sulfur cycle once ruled the earth but now waits in isolated oxygen limited environments. We know those environments as coastal coves, bays and Sounds important to fisheries.

Seawater -

In the presence of iron hydrogen sulfide forms ferric sulfide and the blue/black color associated with Sapropel. Sulfate and iron compounds are not "limiting" and therefore have huge roles in the process. Iron is available as being a compound of minerals washed from land and is not generally considered "limiting." Sulfate is abundant in seawater and is also not considered limiting. Temperature and oxygen levels can and do influence bacterial organic matter reduction and establish low oxygen or anoxic waters. Most reports tend to classify the anoxic types rather than detailing the basic changes in Sapropel formation. Few studies look at changes in land patterns for organic residues (forest humis, duff and leaf falls). Connecticut forests now recovered from the last century of extensive clearing for agriculture (mostly dairy farms) a reviewed forest canopy drops huge quantities of leaves and suburban leaves that fall on paved surfaces has quickened the deluge of organic matter into smaller streams. In some cases streams are choked with organic matter - Oyster River, Old Saybrook watershed and small brooks from Madison to Branford. They often contain deep, black deposits in the tidal regions. Occasional shellfish surveys find buried oyster beds beneath them.

Overseas it seems the link between organics, water temperatures and energy (rain falls) clearly exists. This is an excerpt from a paper about Australian Rivers:

"Black water events can provide a valuable source of carbon to rivers which can stimulate fish breeding and food production, but they can also create low levels of dissolved oxygen in water which can be harmful to fish and other aquatic species.

Black water usually occurs in flooded wetlands or floodplains, which have large accumulations of organic material. It can also occur in rivers if large amounts of leafy or woody material are washed in from storms.

The two most important factors influencing the development of black water are temperature of the water and the amount of carbon (i.e. leafy litter and woody debris) present. The heightened risk of black water events is influenced by increased amounts of organic material and rising air and water temperatures.

In 2010-11, black water affected sections of the Murray River (particularly large wetland areas such as the Barmah-Millewa and Koondrock-Pericotta Forests), Edward and Wakool river systems, Lower Darling and Murrumbidgee Rivers."

Sapropel Creates Habitat Change

Estuarine habitat types such as submerged aquatic vegetation (eelgrass) first benefits from this compost deposits, but as it becomes sulfide rich can destroy it, marine soils of sand/pebbles can loose its ability to attract and sustain clam sets. Sulfide bottoms kill most larval stages upon contact. Marine soils can become clogged with waxes, becoming "sticky" or plastic when probed. Shellfish cannot set or live in Sapropel and the presence of soft muck filled bottoms has always been a concern on oyster reefs. In fact very few organisms can live in high sulfide habitats found in estuaries.

That is often perplexing to fishers and the general public – how could these soft deposits long championed as essential and occasionally be termed beneficial critical habitats for near shore species become so deadly? In general terms we opted for a short term habitat view – it appears as though habitat succession in the marine environment was forgotten. Habitats do change in the marine environment as they do on land, they are subject to destruction by energy (floods, storms hurricanes) and shifts in temperature. Species suffer habitat extinction events (called extirpation) but do so over much longer periods. There is a disconnect between today's environmental policy as well – most dredging activities are viewed in a negative regulatory view (very few publications highlight the benefits of marine dredging) because all bottom habitats are viewed as always important or necessary. As such only negative bottom in them aspects in my view have been studied while the positive energy habitat role dramatically under studied. There is a bias in the environmental literature that mirrors the bias in environmental policy. The disconnect is present with fishers following long term habitat conditions by direct observations, they often "see" the disconnect.

Fisher habitat observations are key to fully understanding marine habitat processes known as succession. One of the measures is the Tannin – Sapropel Cycle. Over time estuarine habitats in medium to low energy areas appear to "fail" for certain species. This is especially true for the areas we fish and therefore observe. Hard bottom habitats can (overtime) "reverse" and become soft or muck filled. Soft mud deposits with oxygen appear harmless and beneficial which is true but change when energy is applied they often now are termed "hard." Temperature/oxygen levels can fall and what was "good" bottoms can quickly become "foul" bottoms. You see this observation over time often in the same fishing location or spot, especially with clammers and oysters fishers. Most noticeable changes occur after energy, heavy rains or strong coastal storms.

Coastal residents often see this as well – shallow wood and leaf litter act as structure for fish and in the presence of oxygen shallow areas abound with small fish, kill fish, silver sides, small crabs, etc. At night in late August when water temperatures rise oxygen levels drop to low levels, Sapropel reduction increases and sulfate reducing bacteria generate sulfide gases and the marsh stink (smells) near dawn. But not all the sulfide comes out as a gas, some is dissolved in sea water and complexes in the soft bottom. If hot enough and long enough the smells can discolor house paints from coastal fog sulfuric acids damage car finishes and generate coastal comments long reported as – "the marsh smells" such as the Niantic Bay area in the 1970s and 1980s.

Long before sulfide kills fish and crabs they flee – clam and oysters can not and tolerate only short periods of sulfide toxicity it is only the huge long events – extreme heat, extreme low energy and "trapped" fish does the "killing" become in full view. In the morning sunlight restarts algal oxygen production and coastal residents (with smells gone) observe the shallows once again active with fish unaware of the habitat battles that occurred over night. They now contain fish and small crabs as before and the intense smell from the night before is dismissed. The habitat battle between sulfur and oxygen was out of sight and the sulfur cycle continues to be poorly understood by many coastal residents regarding these smells. Many Rhode Island Greenwich Bay residents experienced a smaller version of the 1898 Upper Narragansett Bay kill in 2003.

Organic Matter and Estuarine Habitats

The farm community a century ago recognized the danger of putrefied organic matter as fertilizer. Much different than surface composts – those exposed to oxygen reducing bacteria accumulations. The organic matter trapped by mill dams became so deadly unless it was allowed to freeze first and be treated with lime or oyster shells before application it was avoided. In the navigational dredging industry these sulfate acidic soils can ruin metal equipment. John Hammond on Cape Cod used this organic matter for growing tomatoes but mixed it with crumbly oyster shell to modify the acidity, his tomatoes patch was outstanding but farmers of the last century that utilized "marine mud" on thin glacial soils soon recognized its danger when it was allowed to age behind dams. It contained when exposed to air high amounts of sulfuric acid. Dams would collect the "fall lawn" leaves (and other woody tissue) and as the accumulation grew deeper stratifying the sediment into one with no or little oxygen sulfur compounds increased. The deeper they dug the more toxic the material became and today called sulfate acidic soil when exposed to air (Sapropel) oxidized producing huge amounts of sulfuric acid and often devastating low pH. But sometimes even green leaves – those that for some reason drought or winds deposit them into estuarine can cause sulfide toxicity. (Hurricane Gustav fish kill report and case history on the Atchafalaya Basin Keeper® website has an excellent write up.

Green Leaves and Hurricane Gustav Hits Louisiana

This case history involves a day-by-day timeline from when Hurricane Gustav hit Louisiana's coast September 1, 2008 as a strong category 2 storm, almost a category 3. This is a valuable report as it occurred in a relatively low population area and gives a detailed report on the impacts of leaves entering low energy waters.

On Monday, September 1st, huge amounts of green leaves into area waterways and forests, commonly known as the Atchafalaya Basin. Wednesday, September 4th – flooding occurs as heavy rains now enter waterways. On Thursday, September 5th, the water in wooded areas starts to smell "like raw sewage" and the writer refers to it as "the green manure effect."

September 6th finds dead and dying fish – waters are flooding with millions of gallons of green leaves now going into the basin watershed.

The report continues, "the effect of green leaves in water is very different from dry, brown autumn leaves rotting the water. Fish are coming to the surface."

September 7th reports dropping water levels but massive fish kills of shad, catfish, carp, buffalo white drum, perch (several species) and bass (all species). The only fishes that lived were garfish, bowfin and minnows.

September 8th – Pat's Bay suffers 100% kill of all fish; horrible smell starts

September 10th – Black water comes out of Sorrel Shellfield Bayou. Black water mixes with muddy water of Bayou Sorrel. Egrets observed feeding on sick fish. Black water looks black and thick and smells like raw sewage. Fish are taking refuge in Mound's Bayou.

September 13th – Hurricane Gustav makes landfall in Texas. Very strong winds push bad water back into basin worsening water quality that now has a horrible smell.

September 17th to 18th – Water quality improves. Fish again observed in some areas. Although in some areas it continues to be very bad – Shellfield.

Conclusion: “Our observations suggest that massive fish kills following hurricanes are caused by green leaves falling into the water and decaying” (Report of the Atchafalaya Basin Keeper®)

Other case histories involve the paper industry which uses a process that utilizes sulfate reducing bacteria to break down pulp wood chips (very similar to marine breakdown of leaves in the marine environment) to produce a thick, black water fluid called black liquor. Before paper industries regulated waste products (which they do today), they often discharged black water into rivers and streams. In one of the most detailed case histories (which is now available on the internet) titled “Defining a Nuisance: Pollution, Science, and Environmental Politics on Maine’s Androscoggin River.” In 2012, Wallace Scot McFarland in a paper on environmental history (Environmental History, 2012, 17(2), pages 307-335) details the social, regulating and economic issues confronting residents along the Androscoggin River, which at the time had several pulp and paper mills. It is some of the observations in the article (and this one in particular) highlights the Tannin (Brown water) Sapropel black water cycles.

This is the opening quote from the McFarland article:

“In 1941, along Maine’s fetid Androscoggin River, houses freshly painted white turned black as hydrogen sulfide rising from the water reacted with paint, a direct result of polluting from upstream pulp and paper mills. Inside Leo Good’s drugstore, the river odor was so strong that “people would order ice cream and go away without eating it.”

Water quality problems were linked to several factors, including dams “as the number of dams multiplied, they reduced the Androscoggin’s ability to process an increasing amount of organic matter and lowered dissolved oxygen levels” (The absence of “stream energy” is frequently mentioned in Saprobien System, 1909); and further, “the large amounts of organic matter in the waste that pulp and paper mills dumped into the river created a biochemical oxygen demand, lowering dissolved oxygen levels as the oxygen consuming bacteria digested the organic matter.”

This environmental problem would continue for four decades.

The Rhode Greenwich By Fish Kill of 2003

In the summer of 2003 along the western shore of Greenwich Bay Rhode Island coastal residents witnessed the return of the Tannin – Sapropel Cycle – after a century at first they could smell it. It was a hot summer and heavy rains occurred the end of July – A September 2003 Rhode Island DEM report states “many noted a rotten egg smell associated with hydrogen sulfide (toxic to organisms) being produced by sediment chemistry and bacteria processes" (pg 3).

While the report correctly identifies much of the products of the Tannin Sapropel Cycle neither is mentioned in the report. Heavy rainfalls in watersheds containing forests always have tannin leaching into waterways. It is what turns coastal river waters brown even in winter. Residential property can also shed Tannin from leaves on yards in gutters and street basins. Almost every storm water street basin – containing leaves and water start Tannins and sometimes sulfides on their way to the sea. Shellfishers on Cape Cod noticed that roadway leaves – still at the time raked to side streets before the prohibition of fall leaf burning were ground by car tires into an oatmeal (brown) paste that after heavy rains accumulated in loose waves of chaff that soon turned black in Lewis Bay Hyannis (1982-83). In fact the paving of streets have greatly speeded the time it takes for tannins to arrive – acidic and a natural clarifier settling organic matter to bay and coves bottoms.

As the fish kill intensified in deeper Greenwich Bay (2003) waters reports include depth contour band of shellfish kills, mostly likely where sulfide rich waters stagnated in place killing shellfish on the bay bottom miles from the surface chocolate or grey waters. This killing continued as shellfish meats add "fuel to the fire" and accelerates sulfur reducing bacteria. I believe that a great number of dead crabs (including blue crabs) if dredged or caught in sampling trawl nets at that time would have been stained black by the sulfide.

As many older fish kills in the fisheries literature, it is almost nearly the same observations – it is remarkable as to the similarity of these events – rainfall, high heat, low energy.

The Greenwich Bay Kill Case Review

The first part of August 2003 the Providence area was hit by heavy rains and on August 7 to 8 nearly 4 inches in 24 hours on the range of a tropical system. It had been a hot summer with little in the way of strong winds or storms. Some highly sensitive small soft shell clams had died the end of July (Large fish kill often have precursor events - many of the large kills had smaller kills two or three years before, this is believed to be linked to transition of Sapropelic bottoms) observations include increasing algal bloom peaking around August 11 to 13th. These blooms are not sustainable and low pH restricts green algae but allows for browns to survive living off ammonia from the reduction of leaves. When they die they provide more "food" for now overwhelmed bacteria that reduce organic matter by oxygen – who are displaced by sulfur reducers. As sulfate reduction strengthens hydrogen sulfide kills living organisms who again create an even greater oxygen debt. Oxygen reducers can hang on for as long as the nitrate/nitrogen compounds hold out but once that is limiting they allow sulfate reducers to thrive and the hydrogen sulfide smells begin. In this case when oxygen is limiting nitrate buffers the sulfate reduction process. This is a natural selection process between two huge groups of bacteria – those that need oxygen and those who can access it by way of the sulfur cycle. It is the sulfur reducing bacteria that eat the leaves on the bottom in oxygen limited waters. They form the basis of the Sapropel Cycle in estuarine habitat and reverses thousands of acres of habitat unsuited for most estuarine species. Between 1980 and 1990 Sapropel would become the dominant habitat type in nearshore areas between New Jersey to Maine.

The report does a good job with the oceanographic factors: the heated, stratified cove surface water, weak tidal flows (low energy) and low oxygen, but misses the impact of organic matter loadings in low oxygen conditions.

The report focuses upon inputs from domestic septic systems, but the link to rainfall is tied to overflow wastewater treatment plants, which is an immediate event, but septic system nitrate levels when often rise 15 to 30 days after rain events. Nitrate would tend to reduce sulfate reduction and underestimates the rapid release of ammonia from organic reduction. Sapropel can release tremendous amounts of ammonia, fueling brown algal blooms. In fact, the organic loadings from watershed sources seems to be underestimated, noting the primary source of nitrogen to Greenwich Bay as 51% from septic systems while just a brief mention of the Providence River or terrestrial organics. I did not find an explanation for the source of sulfur in hydrogen sulfide. Organic matter from terrestrial sources (leaves) is not mentioned as a potential nutrient source (The Greenwich Bay Fish Kill, August 2003, Causes Impacts and Responses, Rhode Island Department of Environmental Management, September 2003).

Even "green leaves" (not those from fall drop or street basins) can provide a tremendous nutrient base and sometimes is termed "green manure."

Tropical Storm Lee Western CT and Blue Crabs Kills

The remnants of Tropical Storm Lee hit the eastern seaboard on September 7, 2011 brought with it very heavy rains. This happened just a few days following Irene. The summer to date had been a hot one for Connecticut and much of the mid Atlantic states northward. When reviewing the impacts of rainfall upon blue crab habitats after July 2011 rain events the NOAA – National Climatic Data Center National review website has been a terrific help. It is possible to use this national overview site check the year and month database to look up significant weather events. The ability to cross reference blue crab observations against weather is a new field of habitat assessment and provides insight into major habitat reversals. The beginning of July was unusually dry and hot Portland Maine reached 100^{f} on July 22^{nd}. Connecticut was under a period of high heat and very dry conditions but not the entire state. Forest and leaf letter was also dry and heat weakens leaves – in long dry periods leaves will fall even when green. That would have a role with changes beginning July 26th to 29th as heavy thunderstorms rocked western CT.

A severe thunderstorm warning was issued on July 26th followed by a tornado warning at 5:57 am. The National weather service confirmed a tornado at Goshen New York 90-100 mp hour winds (NWS Public Statement 338 pm Saturday, July 30, 2011) Western Connecticut was hit the hardest, and flooded street basins (blocked by leaves) were frequent. Most of the central and eastern sections had little rain. Torrents of hot often brown water were reported by crabbers August 1st and 2nd. Several observations reported dead blue crabs and unusual smells. Rains on warmed surfaces (thermal shock) huge amounts of freshwater (salinity shock) was thought to be the cause of these dead crabs. However after a few days western blue crabbing dropped – suddenly. Irene came August 28 to 29 and Lee September 8th by September 9th some part of Connecticut had 8 inches of rain in ten days. (Burlington by August 29, 2011 8.71 inches) with much more after Lee which stalled over New York for days.

I missed the significance of a potential (July 26 to 30) huge sulfide event which after reviewing crabber observations which I do believed occurred then. After the sulfide event (I should have been suspicious from the reports of smells) then came Hurricane Irene – washing more organic matter and causing leaf fall and tree fall. Almost overnight the ground in much of Connecticut was covered in ripped leaves, bit of twigs – bark, needles and the like. Cars were covered with this organic wind blown paste and slurries of "oatmeal" ground leaves and organics clogged overflowing street basins as the heat continued. A final hit to many blue crab habitats was then Tropical Storm Lee although not as powerful as Irene a few days before bringing heavy rains to Connecticut and delivered a "broom clean" impact of sweeping much of the already down organic matter on the ground into streams. By September I was getting reports of leaves in dredged marina basins – several feet in some areas. By October large portions of the lower Saugatuck River appeared "dead" and covered in leaves. {Some of the same problems occurred in the Branford River and after Gloria (1985) and by 1988 bad smells were reported by trees and fell into the Branford River and blocked leaves National Guard Comes to Rescue, Branford Review August 10, 1988, Engineers to Remove Fallen Trees from River, New Haven Register August 5, 1988}.

Blue crabbing had been nothing short of fantastic as much of the 2010 year class (thought to be the largest since 1912) that over wintered in the lower reaches of river or dredged basins emerged in early spring. Crabbing started off slow (megalops reports 1 to 7 2011) but quickly picked up. After the reports of brown water crabbing dropped like a rock.

Hurricane Irene and Tropical Storm Lee Review

In June and early July blue crabbing was superb in western Connecticut. In July, before these two tropical systems hit the Northeast, western Connecticut sustained very heavy rains as a remnant cold front collapsed and stalled over western Connecticut for days. A "training effect" soon followed as thunderstorm after thunderstorm rode up along the stalled front for days of intermittent heavy rain. Waters turned brown and blue crabbers reported dead crabs in brown waters and the smell of sulfur. A huge wave of crabs left the Housatonic River and headed east toward New Haven (Megalops Reports, July 2011 – A write-up of these reports can be found in IMEP Habitat History Newsletter #22 found on Blue Crab Information™ 's Fishing, eeling and oystering thread). (I have followed these leaf accumulations and reports about them since). Some western Connecticut communities between the end of July thunderstorms (26 to 30) Irene August 28-29 and then Lee September 7-8 obtained more than 15 inches of rain.

I at first thought that this large movement of blue crabs was a seasonal or density dependent migration (too many crabs competing for the same habitat or interspecies competition) (July/August, 2011). I was wrong. I suspect today that what western Connecticut crabbers were reporting was a massive sulfide event brought down river by heavy rains triggers a migration out not quite a Jubilee but something close. Irene came and washed loosened organic material from watersheds after this July deluge followed by the remnants of storm Lee and by October 2011, several feet of leaves covered some blue crabbing areas. The blue crabs were long gone. Western Connecticut crab reports greatly declined and then stopped. Blue crabbing in the center and eastern parts of Connecticut slowed, but did not seem to drop that much. Western Connecticut crabbing has yet to recover from July 2011 and these rain events. Many areas I observe continue to have "black leaves" and gas discharges. Several areas in the central sections as well.

What about the Conowingo Dam and Sulfide Wash?

This dam and the organic matter trapped behind it (Conowingo Pond) has been posted on several websites. Since 1997 it looks like this will be a major case study for sulfur reduction. I have a couple of senior students interested in looking into this now. The Conowingo Pond has been in the news again lately and now shows up in many sites. The Conowingo Dam (Pond) case history will be an interesting one and perhaps as long as the public policy debates surrounding the Androscoggin River in Maine between 1889 to 1974. Fishers are correct in raising concerns about what lies under the Conowingo Pond accumulations if sulfide washes are released after heavy rains they would acidify marine soils far below the dam. Deep core sections were done in Connecticut's coastal coves (1990-94) they showed distinct layers of blue black organic matter and then layers of bivalve shell. Deep core sections behind the Conowingo could be just as interesting and any deep core sections (usually performed by the Army Corps of Engineers) would document organic (woody tissue twigs and leaves) and the sulfur cycle. In warm weather I suspect warm organic deposition sheds enormous quantities of ammonia (nitrogen) compounding the impacts down stream. Core tests and examinations may well answer many habitat impacts questions from Sapropel accumulations.

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