

Impacts from Mosquito Control-induced Sulphur Mobilization in a Cape Cod Estuary

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INTRODUCTION

The restriction of salt water from small estuaries by means of dikes and one-way valves has been a popular method of control for the Salt-marsh Mosquito (*Aedes sollicitans*) in the northeastern United States. In some instances, the resulting destruction of the salt-marsh by diking has led to the establishment of freshwater wetland vegetation and animal communities. Such freshwater marshes soon produce their own hoards of mosquitoes, however, and, on Cape Cod, drainage ditches have been dug and maintained within the freshwater wetlands to control these latter pests.

Although the effects of diking, and especially ditching, have been hotly disputed (Daiber, 1974, 1982), there is little serious question that the combination of diking with ditching leads to desiccation of the original salt-marsh soils, premature disappearance of freshwater marsh and its flora and fauna, and rapid invasion of the marsh soils by upland vegetation. In this report, we present a case-study of even more direct destruction of the marsh-dependent fauna as a result of disturbances of the biogeochemical cycles of these wetlands following diking and drainage.

STUDY-SITE

Our primary study-site is the 400-ha Herring River Basin in Wellfleet, Massachusetts, USA (Fig. 1), which has a complicated history (Portnoy & Soukup, 1982). Early local records reflect a thriving natural resource, with salt-hay farming and an American Eel (*Anguilla rostrata*) and herring (*Alosa* spp.) fishery supporting many people; however, drastic changes were apparently associated with the construction in 1909, amid much controversy, of a dike from Griffin Island to the mainland. The dike was intended to provide for agricultural use of the basin (which never materialized), and for mosquito control. Nevertheless, a continued mosquito nuisance (probably from freshwater and brackish-water species) is reflected in subsequent town-meeting minutes in which expenditures for ditching, dike repair, and pesticides, are frequently recorded.

Major vegetation changes also occurred (Portnoy & Soukup, 1982); local photographs indicate that, by the 1930s, these diked marshlands were largely vegetated by cattails (*Typha* spp.) and senescent stands of Salt-meadow or High-water Grass (*Spartina patens*). During this period major

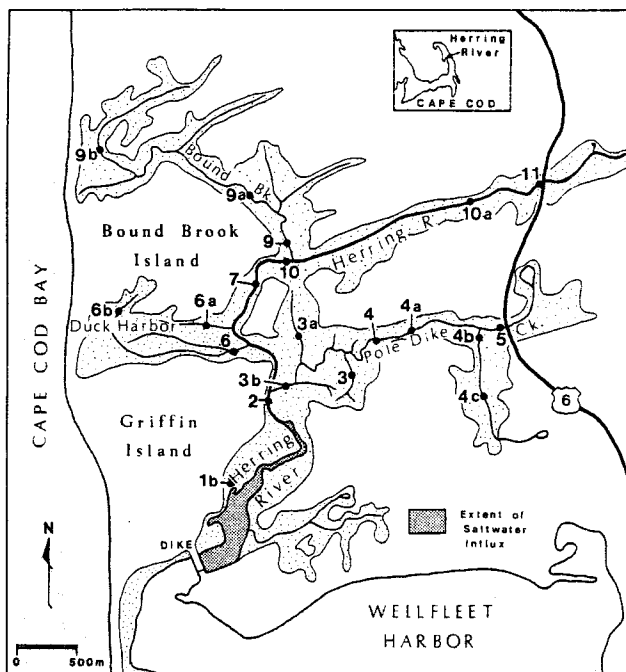


FIG. 1. Site map of the Herring River and its 100-years' floodplain (highest probable flood-water level in on average 100 years' period) below its origin at Herring Pond, Wellfleet, Massachusetts. Sampling stations and the extent of salt-water influence are also indicated. Recent fish-kills occurred from the area above tidal influence to just above Station 10 on the main channel, and in the vicinity of Stations 4, 4a, and 9.

efforts, sometimes associated with federal work programmes, were mounted to ditch remaining portions of the wetlands. Today the dike at the mouth of the River (Fig. 1) continues to restrict tidal exchange, and large-scale operations still maintain an extensive system of drainage ditches intended to control freshwater mosquito populations.

FISH MORTALITY

In the autumn of 1980, we observed a die-off of several thousand American Eels of all sizes, along with lesser numbers of other fish species, in the main (freshwater) channel and in tributary streams of the lower Herring River. Fig. 1 shows the major sites of fish mortality and sampling sta-

tions where we have subsequently monitored. Necropsy of dead Eels performed at the University of Rhode Island and National Marine Fisheries Service (Maryland) laboratories showed no detectable pathogens, although gastro-intestinal and gill lesions were observed. Eel tissue (pooled samples) was analyzed for As, Cd, Cu, Hg, Pb, Se, and Zn, by Analytical Bio-Chemistry Laboratories, Inc. (of Columbia, Missouri), and for PCBs (polychlorinated biphenyls) and organochlorines by Raltech, Inc. (of Madison, Wisconsin). No significant accumulations were found.

Moribund Eels removed from the lower Herring River and placed in cold sea-water regained vigour and survived for weeks at the National Marine Fisheries Service aquarium at Woods Hole, Massachusetts; Eels held in the Herring River at Station 7 (Fig. 1) died after 24–72 hours. Eels placed in cages in the upper Herring River (Station 11, Fig. 1) survived until they were released after 3 weeks.

Investigations in the upper reaches of the River (above Route 6, see Fig. 1) indicated a diverse fauna, with abundant fishes, herpetofauna, and invertebrates—including freshwater ectoparasites (such as *Pectinatella magnifica*), sponges, and mussels. In contrast, after substantial seining efforts, only a few individual fishes (of two species) were found in the lower reaches of the Herring River in early 1981 (K. Hartell, Museum of Comparative Zoology, Harvard University, pers. comm. 1981). Local reports also document massive die-offs of juvenile herrings (both *Alosa pseudoharengus* and *A. aestivalis*) during their autumn migrations in some previous years.

Similarly the herpetofauna, apparently represented in the lower Herring River only by the Snapping Turtle (*Chelydra serpentina*), Green Frog (*Rana clamitans*), and Painted Turtle (*Chrysemys picta*), together with the invertebrate community, had this last dominated by mosquito larvae (principally *Aedes cantator*) and was severely impoverished in the lower reaches.

ANALYSIS OF SAMPLES OF WATER AND SEDIMENT

Water and sediment samples were then examined for possible causes of the major loss of fauna. Data from determinations of pH, sulphate, and Al, are presented in Fig. 2. The water samples referred to in that table were taken on 7 January 1982, refrigerated in dark Nalgene bottles at 4°C, and analysed at latest within several days of collection. Measurements of pH were made, within 2 hours of collection, at our National Atmospheric Deposition Program station in Truro, Massachusetts, by glass KCl-filled electrode; sulphate was determined by the turbidimetric method, and aluminium (total monomeric) was determined by direct aspiration of samples (with 1 ml KCl) for atomic absorption spectrophotometry (nitrous oxide-acetylene flame; wavelength 309.3 nm; slit width = 0.7 nm). Additional samples, immediately filtered through a 0.45 µm Millipore filter and subdivided, with one-half receiving nitric acid as a preservative, were subjected to similar treatments, and yielded comparable sulphate and aluminium values.

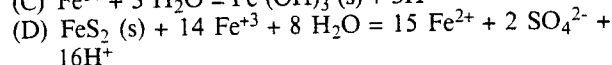
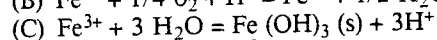
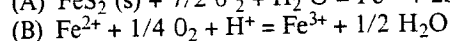
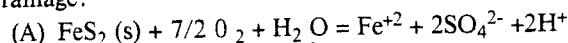
Dissolved oxygen (by Winkler titration) was found to be near to saturation in the main stream. Normal river conditions (moderate pH, low content of metals, etc.) are also reflected in data taken at the upper reaches (Stations 5 and 10), but not in the lower reaches (Fig. 2). Data are also presented in Fig. 2 for extensive segments of mosquito-

control ditches which are periodically recut and maintained throughout the River's basin. Extremely high sulphate levels occur in water emanating from these 'mosquito' ditches. Similarly, the low pHs, as well as the extreme aluminium concentrations, are found in water draining via the 'mosquito' ditches. High sulphate, acidity, and aluminium, concentrations, are diluted by the main-stream flow, but remain at toxic levels.

Similar ranges and distribution patterns were also found for those same constituents in samples that had been taken in November 1980 (and held at 4°C), and in samples taken periodically through May 1982. Maximum acidities are in the range of 500 mg CaCO₃ per litre (titration after hot peroxide pretreatment), with accompanying pH values of 2.8–3.0. For the data (n=20) shown in Fig. 2, pH varies inversely with logarithmic sulphate concentration in mg per litre ($y = 7.11 - 1.51x$; $r^2 = 0.82$; $t = 8.88$; $P < .001$).

MOBILIZATION OF SULPHUR, ALUMINIUM, AND ACIDITY

Our observations suggest that mobilization of sulphur from the oxidation of pyrite—the process of 'kattellei' formation, see below—is occurring in the Herring River as a result of drainage for nuisance-mosquito control. Stumm & Morgan (1981) have summarized the sections of the oxidation of pyrite as it occurs in the formation of acidic mine drainage:



The process occurs in coastal areas because salt-marsh sediments characteristically have high concentrations of reduced sulphur. Marine and estuarine sulphate-reducing Bacteria in anoxic marine habitats utilize the sulphate ions that are abundant in sea-water (Berner, 1970), and, in a productive salt marsh, energy equivalent to a significant portion (and perhaps the entire) net productivity can be expended in dissimilatory sulphate reduction (Howarth & Teal, 1979). Pyrite is a major reduction product in these marsh sediments (Howarth & Teal, 1979; Howarth & Merkel, 1982; Luther *et al.*, 1982).

With desiccation and aeration of estuarine sediments, the oxidation of pyrite to sulphate begins, releasing dissolved ferrous iron (equation 'A' above), which then undergoes oxygenation to ferric iron ('B'), which then hydrolyses to form insoluble 'ferric hydroxide' ('C', see Stumm & Morgan, 1981). This reaction releases more acidity, usually causing stream-beds (or in this case 'mosquito' ditches) to be coated with precipitate.

Ferric iron can also oxidize pyrite, releasing acidity (equation 'D', above). The additional ferrous iron can enter into reaction 'B', the result being one of the most acidic weathering reactions known, with a mole of pyrite yielding 4 equivalents of acid (Stumm & Morgan, 1981). Development of such conditions has resulted from many coastal reclamation attempts and is known as *kattellei* (or 'cat clay') formation (cf. Edelman & Staveren, 1958; Neely, 1958; Daiber, 1974, 1982).

Examination of spoil-piles along recently-ditched channels in the Herring River basin reveals conspicuous ma-

Mainstream				Tributary stream				Drainage ditch			
Sta	SO ₄	pH	Al	Sta	SO ₄	pH	Al	Sta	SO ₄	pH	Al
11	5	5.88	<0.3								
10a	10	5.95	<0.3								
				9	75	3.62	4.0	9a	100	3.69	5.2
								9b	60	3.71	2.6
10	30	5.05	0.75								
7	35	4.91	0.75								
								6a	780	3.26	49
				6	200	3.51	9.9	6b	150	3.38	6.6
				3b	140	3.87	8.9	3a	470	3.30	22
								3	450	3.87	30
2	70	4.15	4.0								
1	190	7.45	0.75					1b	400	3.30	23

FIG. 2. Sulphate, pH, and aluminium, data are presented for stations representing the main-stream, major tributaries, and drainage ditches, on 7 January 1982 (when samples collected); these stations are arranged to simulate the order of their confluence. Aluminium and sulphate are reported in mg per litre.

croscopic deposits of sulphur compounds, apparently including jarosite ($\text{KFe}_3(\text{OH})_2(\text{SO}_4)_4$ and coquimbite ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$). In addition we have found pools of water standing on these spoil-piles with pH values of 2.6–2.85. We are currently monitoring rainfall, flow, and acidity, to determine the seasonal characteristics of acid production and the flow conditions (such as pH shifts below 4.5), which favour the periodic destruction of fish and other fauna (Alabaster & Lloyd, 1982; Fromm, 1982) in the River's main-stream.

Production of acid also promotes mobilization of Al from local clays. For the data in Fig. 2, log Al (in ppb)* varies inversely with pH ($y = 6.86 - 0.82x$ (if Al below detection limits of 300 ppb is estimated at 100 ppb); $r^2 = 0.87$; $t = 11.71$; $P < .001$); high concentrations of Al, probably as Al^{+3} , would be expected, owing to the enhanced solubility of Al at pHs of less than 4.5 (Stumm & Morgan, 1981). However, the high concentrations of sulphate that were observed simultaneously, may form strong complexes with aluminium at low pH, so that the activity of aluminium as well as its toxic effects may be reduced (Hem, 1968; Driscoll *et al.*, 1980). Nevertheless the concentrations observed are extremely high; levels of 0.3 mg per litre are considered toxic to many fish (Driscoll *et al.*, 1980). Hence aluminium mobilization may well be a contributing factor in the fish die-offs in the Herring River. As is shown

in Fig. 2, there exists a wide range of pH and of sulphate and Al concentrations, in various parts of the system, and the locations of fish-kills coincide with those areas where the pH is < 4.5 .

DISCUSSION

Although this phenomenon has been noted in relation to wetland management in the United States (Edelman & Staveren, 1958; Neely, 1958; Calvert & Ford, 1973), and more recently in England (Gosling & Baker, 1980), the magnitude of its potential impact has not been fully appreciated, much less considered in evaluating mosquito control techniques. In the Herring River, the technique of isolating pyrite-rich sediments from tidal exchange by diking, followed by desiccation of those sediments through ditching (which also mechanically aerates and increases the reaction's surface-area along channels and spoil-piles), is promoting the formation of sulphuric acid. This acidity periodically dominates (apparently in response to heavy rainfall after dry periods) the chemistry of this poorly-buffered freshwater River system, and, in concert with acid-mobilized Al, renders this habitat untenable to anadromous, catadromous, as well as more sedentary, fish populations.

Interestingly, before the diking of this River, recorded proceeds from the Herring River Fishery Station and Pound (a community-financed project) were sufficient to pay the annual salaries of all the elected officers of the

* Parts per American billion = 1,000,000,000.—Ed.

Town of Wellfleet; currently the magnitude of the herring run is of no commercial value and reflects the depression of most of the other aquatic fauna. Ironically, the mosquito nuisance continues, with larvae of the locally predominant pest species (*Aedes cantator*) surviving well at pHs as low as 2.85 in ditches, which, due to low pH and dissolved oxygen, exclude fish and other predators (Portnoy, in press).

Because a large portion of the habitat available to anadromous and catadromous fishes along the east coast of the United States has disappeared, largely through human interference, it is extremely important that their remaining habitats be not compromised by such unnecessarily harsh methods as diking and ditching. Restoration of the Herring River estuary, a resource that was formerly prized for its abundant fauna, would provide significant ecological as well as local and offshore fishery benefits.

On Cape Cod, maintenance of dikes remains a common practice; moreover, it has recently been estimated that 1,000 miles (1,609 km) of ditches are now being maintained in the Cape's freshwater marshes (DeSista & Newling, 1979), many of which are actually diked salt marshes. Re-evaluation of these methods, and their impacts wherever they are practised, is long overdue, and could provide major benefits.

SUMMARY

Insect control programmes sometimes include environmental modification techniques such as diking and drainage. The impacts of such techniques are not often known or assessed. As a telling example having wide implications, we present an analysis of impacts in a small estuary which has been subjected to both diking and ditching—primarily for mosquito control.

The major impacts stem from *kattklei* formation. Desiccated salt-marsh sediments produce acidified leachates which result from oxidation of pyrites. Lowered pH and high (acid-mobilized) aluminium concentrations both surpass levels that are known to be toxic to aquatic fauna. Fish and invertebrate communities in the basin are impoverished, and important commercial species such as American Eels and Alewives are heavily decimated. The acid-tolerant mosquito *Aedes cantator* thrives, however. Thus a natural system of substantial economic and aesthetic value has been inadvertently devastated through application of unnecessarily harsh as well as, in this case, ineffective mosquito control methods. Their use should be re-evaluated for similar impacts wherever such application has been carried out or is being contemplated.

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