# PENOBSCOT RIVER MERCURY STUDY

## Chapter 4

## Field Data and Experiments on *in situ* Particle Formation in the Penobscot River

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Research by many others has documented that *in situ* particle formation occurs in estuaries mainly as a result of “salting out” of dissolved organic carbon (DOC) delivered to the estuary by rivers. The extent of this reaction appears to involve less than 30% of river-borne DOC (Sholkovitz 1976; Mulholland 1981; Fox 1983; Roesler et al. 2006). Cronan (2011) recently reported that ~117,000 metric tonne per year (t/yr) of DOC are exported to the Penobscot estuary by the Penobscot River. If as much as 30% of this DOC is converted to particulate matter then 35,000 t/yr of particulate carbon (equal to ~70,000 t/yr of total suspended solids, TSS) would be produced/deposited in the estuary. This flux of TSS would be added to the 32,500 t/yr of TSS as reported by Cronan (2011) to be exported by the Penobscot River to its estuary. Penobscot River Mercury Study (PRMS) data indicate that DOC concentrations decrease conservatively (simple dilution) with increasing salinities up to about 15 parts per thousand (ppth) and then decrease non-conservatively at higher salinities (Figure 3-1). This pattern is consistent with *in situ* particle formation in the estuary but other processes, such as photochemical and microbial degradation, cannot be excluded. Optical sensor data (Roesler et al. 2008) calibrated to DOC has also shown removals of DOC, between the Eddington United States Geological Survey (USGS) station and the lower Penobscot Bay, of <10% for low flux periods and of 50% during high flux periods (Figure 3-2).

Mixing experiments were conducted in 2011 (June through September) using river water from Veazie (upstream of the lower Penobscot) and seawater from Castine (in Penobscot Bay) to assess *in situ* particle formation over a range of salinities. In addition to tracking concentrations of DOC and particulate organic carbon (POC) in the mixtures for as long as 38 hours, TSS, turbidity and color were measured as alternate indices of particle formation. Turbidity and color were too insensitive to be useful in detecting what generally proved to be a small “salting out” effect. When river water had relatively low DOC (<6 milligrams per liter [mg/L]) and TSS (<5 mg/L), *in situ* particle formation was difficult to detect, with changes in the mixtures being close to or within the measurement error. Hurricane Irene provided higher DOC (10 mg/L) and TSS (20 mg/L) values allowing reliable detection of *in situ* particle formation (Figure 3-3a). Mixtures from Irene samples with salinities in the mid-range produced POC and calculated equivalent TSS (POC x 2 =TSS) concentrations that amounted to ~2% to 8% of river end-member TSS concentrations. Kinetic study with mixtures prepared 10 days after Irene again showed maximum DOC removals at mid-range salinities (Figure 3-3b) but with higher relative percent removals of DOC (10% to 15%). Inorganic mercury (Hg) concentrations on particles that formed due to salting out in filtered mixtures of river water and seawater collected during and 10 days after Irene ranged from 0.028 to 0.204 microgram per gram(μg/g). The highest mercury concentrations (0.170 and 0.204 μg/g) were associated with mixture salinities of 13% and 16‰ (Figure 3-4).

Overall, the mixing studies suggested that *in situ* particle formation may increase TSS concentrations by about 1 to 2 mg/L. Thus, at the average discharge (400 cubic meters per second [$m^3/s$]) of the Penobscot River, *in situ* particle formation would add up to 25,200 t/yr of new particles (TSS) to the estuary. This estimate is nearly identical to the value (23,400 t/yr) derived from the annual DOC flux reported by Cronan (2011) and the optical studies by Roesler et al. (2006) suggesting that <10% of DOC (11,700 x 2 = 23,400) is removed in the estuary during low flux periods.

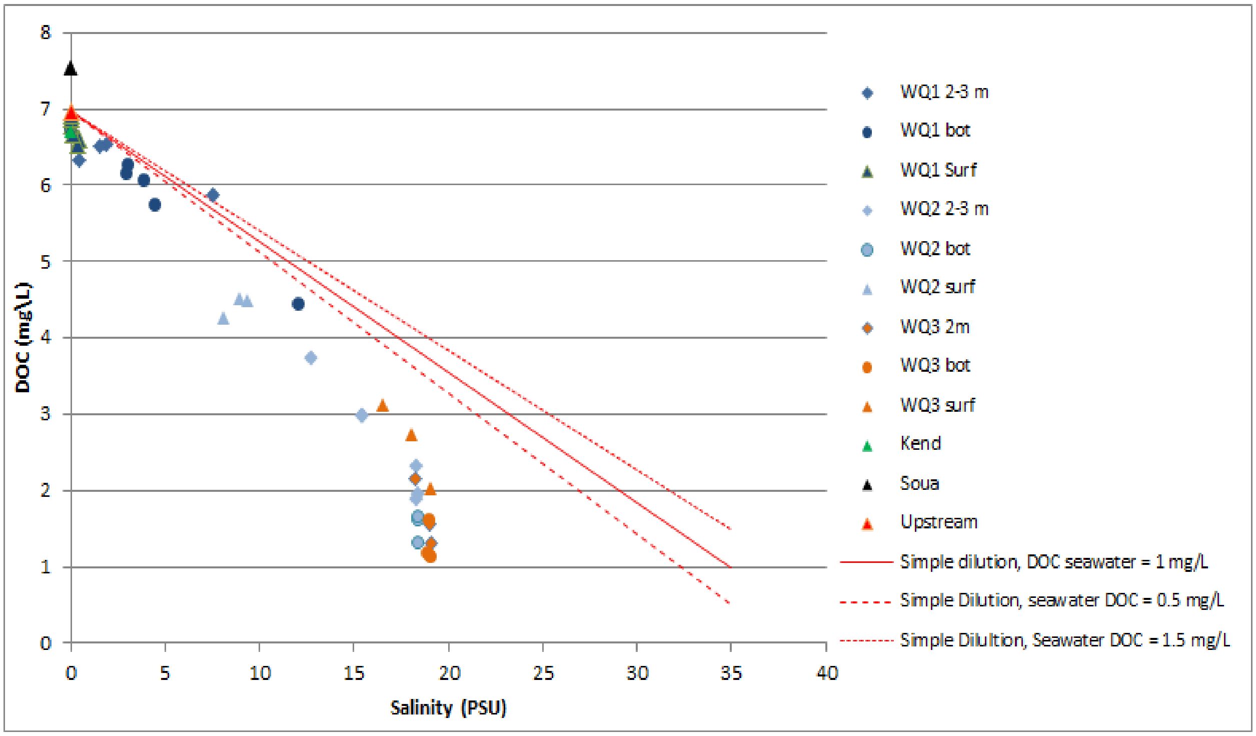


Figure 3-1a. Change in DOC concentrations over salinity gradient for September 2009 monitoring event. Data from Penobscot River Mercury Study.

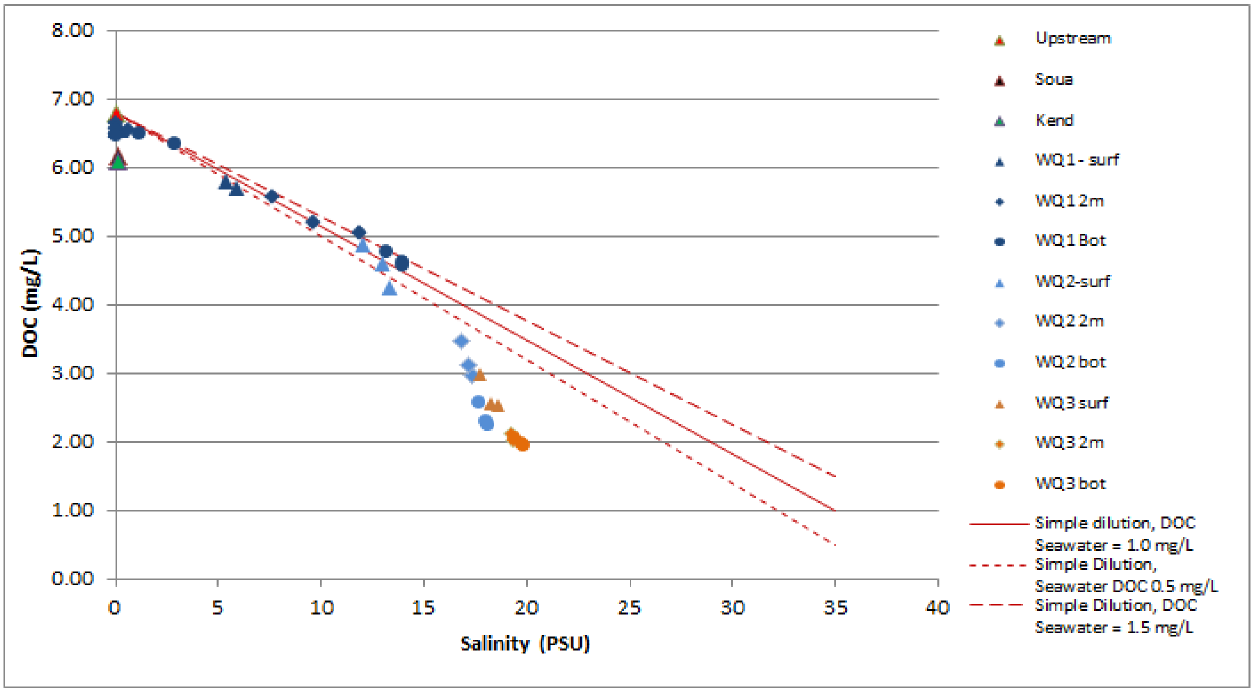


Figure 3-1b. Change in DOC concentrations over salinity gradient for July 2010 monitoring event. Data from Penobscot River Mercury Study.

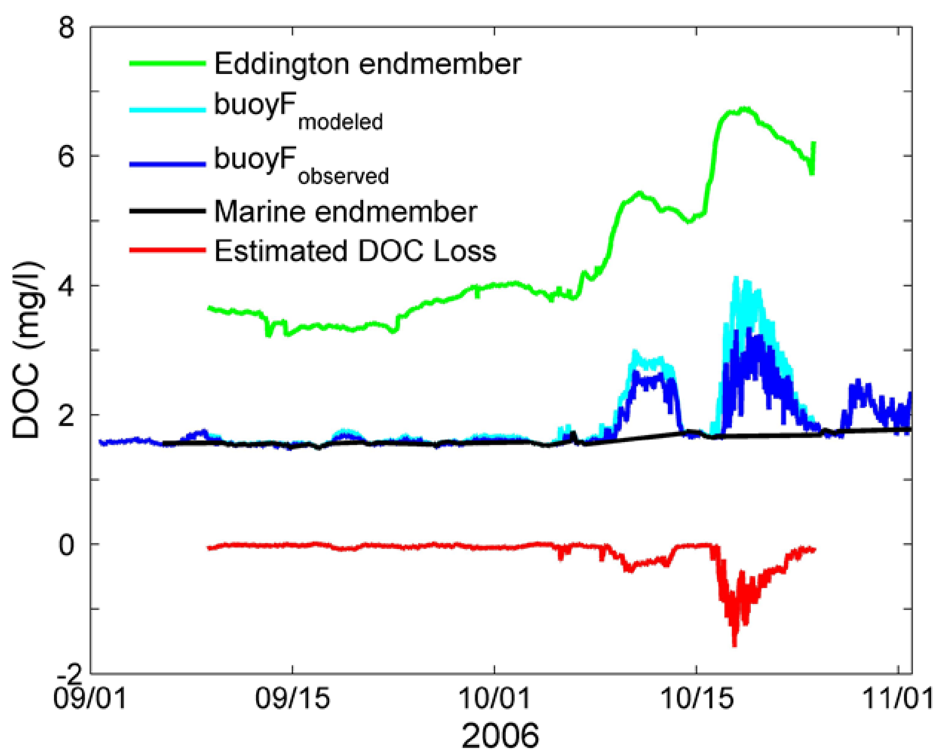


Figure 3-2. Optical sensor monitoring data from Roesler et al (2006) showing removal of DOC between river end-member (Eddington) and bouy F (lower Penobscot Bay).

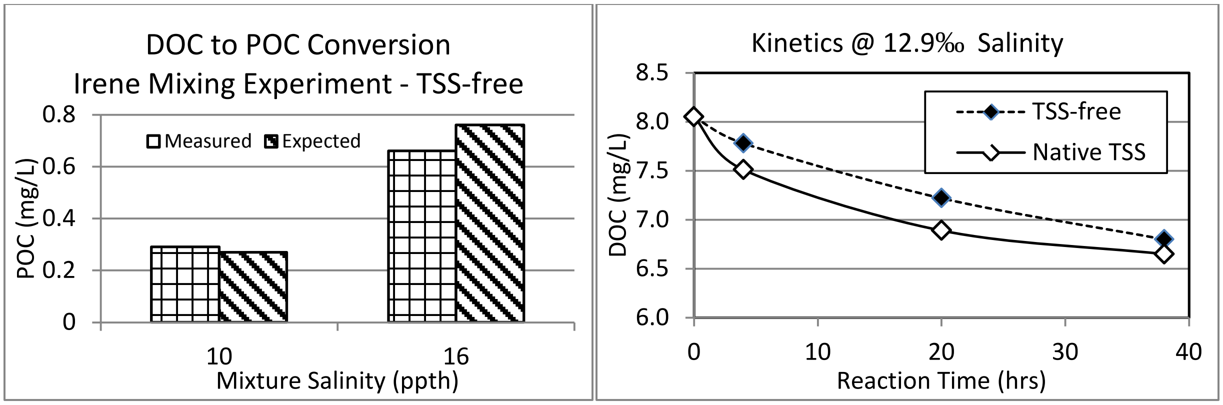


Figure 3-3a (left). Measured POC formation in mixtures of river water and seawater compared with POC formation expected from the difference in DOC between river end member and each mixture. Figure 3-3b (right). Kinetics of DOC losses in filtered and unfiltered mixtures with 12.9 ppth salinity.

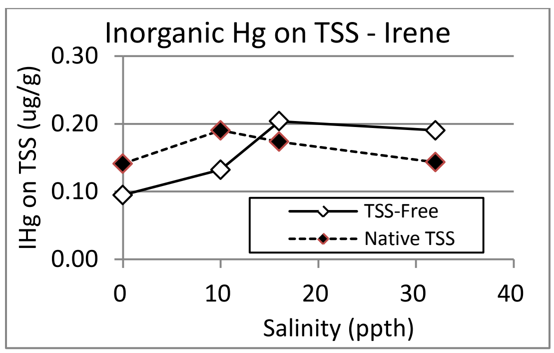


Figure 3-4. Concentrations (µg/g dry weight) of inorganic mercury on particles in mixtures of river water and seawater collected during Hurricane Irene.

# 1 REFERENCES


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