April 2, 2003

Bruce Gillman
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RE: Your long awaited results on the foam from Lake Canandaigua.

Bruce

Here are your foam results. As you can see, it turned out to be a lot more work than I initially thought. Unfortunately the results do not necessarily confirm or deny the role of zebra mussels.

1. The foam is probably originating from algal biomass in the water column. At this point in time, it is impossible to rule out a role for zebra mussels dying and releasing protein to the water. The protein content in the foam is significantly higher than the surrounding water and at a concentration high enough to cause foaming, but protein still makes up a relatively small amount (<5%) of the organic material present in the foam-water mixture.
2. Neither does it look to be a simple "algal bloom" releasing lipids that lead to foam formation. The fatty acid profile is too complex to be fresh diatom bloom, though that may be distorted by bacterial processing in the foam itself. This would be in agreement with the idea that the foam represents an "old" algal bloom, hence the reason we did not observe elevated or bloom abundance of algae in our original water sample.
3. The atomic C/N ratio and $\delta 13C$ values suggest that terrestrial runoff is not the source of the foam material.

Again, sorry for the delay

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Foam Analysis from Canandaigua Lake

On August 28th, 2002 (~10:00 am), Kevin Olveney, Bruce Gilman and myself collected foam from a mid-Lake location off Seneca Point in Canandaigua Lake. Weather was relatively calm and the water was free of any visible algal blooms, though later analysis in the lab suggested that the foam water mixture (F1) contained about ~20-30 µg/L chlorophyll and < 0.05 µg/L cyanobacterial phycocyanin. We attempted to collect the foam without any of the surface water using a vacuum apparatus. This apparatus did not work very well and we ended up with a foam-water mixture. As a control, we collected a second sample of lake water from an area free of foam north of our initial point. These samples were returned to ESF where the foam was collapsed with distilled water, and then filtered through a 934AH glass fiber filter to remove numerous small insects that were trapped in the foam material. The resulting water; ca 4.0 L of foam material (sample F1), 4.0L of the control water (F2) and a 2L filtrate rinse of the initial foam material (F3) were all lyophilized to dryness. This powder was then subjected to a number of tests as shown in Table 1.

Table 1 Tests Run and Results.

Test	F1 Foam-Water mix	F2 Water Control	F3 Foam Rinse
Lake Chlorophyll Starting sample	19 µg/L	34 µg/L	
Total dry weight (4L sample)	517 mg (130 mg/L)	721 mg (180 mg/L)	24 mg[a] (12 mg/L)
Residuals after 24 hr at 500ºC	57%[b] (74 mg/L)	72% (131 mg/L)	-[c]
Organic material (total wt – residuals)	43%	28%	-
Total Protein[b] (BCA assay)	1.0-2.5%	0.0-0.2%	3.5-8.3%
Hydrophobic Protein[b] (Bradford Assay)	0.4%	0%	1.3%
Total Carbohydrate[b] (phenol sulfuric)	3.9 %	0.7%	9.7%
Chlorophyll after filtration in the powder[b]	0.08%	0.01%	0.12%
$\delta^{13}C$	-19 ‰	Too low to measure	-
Weight percent carbon[b]	16%	6%	-
$\delta^{15}N$	+ 5 ‰	Non detectable	-
Weight percent[b] Nitrogen	1.1 %	Non detectable	-
Atomic C/N	17	-	-
Fatty acid analysis (GCMS)	long chain wax esters and bacterial fatty acids were present with a predominate even: odd ratio, few sterols	No fatty acids observed	Complex mixture

[a] Rinse sample was 2 L only. [b] All % are based on total dry weight. [c] "-" means the test was not run or the results are unavailable for that sample.

Thoughts and Analysis:

If you simply compare the foam water mixture with the control, you will see that the foam mixture is enriched in organic material including both proteinacous and carbohydrate material. I think the reason the starting lake chlorophyll and total mg dry weight are lower in F1 (foam water mix) than in the lake control (F2) has more to do with the fact that I had to add distilled water to break the foam rather than a true difference in the samples. I would have expected the lake water chemistry between the two sites to be very similar.

The most interesting results are the δ13C and the atomic C/N ratio provided by Professor Mark Teece here in the Chemistry Department. The δ13C is the atomic enrichment of C13 over C12 relative to a standard. This enrichment comes from discrimination against the heavier carbon-13 during metabolic processes. Here the F1 sample had a δ13C value of -19 ‰. This is significantly enriched in the heavier carbon-13 than expected for phytoplankton (δ13C ~ -21‰), suggesting the sample contained additional carbohydrates and proteins. This was confirmed by the bulk analysis where we found significantly more protein and carbohydrate than the water control. Interestingly, the observed δ13C value of -19 ‰ was similar to that expected for zooplankton and fish. It is unlikely to be fish since polyunsaturated fatty acids were missing from the lipid analysis. This leaves zooplankton or possibly zebra mussels. I have given Mark Teece a sample of the zebra mussel tissue collected by Web Persall from Canandaigua Lake. We might be able to tell more from a direct comparison if and when he has a chance to run it for isotope analysis.

The atomic C/N ratio of the foam material is also interesting and between that of fresh algal material and detritus. The following table gives you some benchmarks values:

Table 2: Benchmark values for C/N ratios

Pure protein	~8
Fresh Algal biomass	~10
Foam Sample F1	**17**
Detritus biomass	~20
Terrestrial Leaf material	~25

This intermediate value indicates the material had started to break down. Most importantly, it was not indicative of terrestrial runoff material, which would have a value closer to 25. This elevated atomic C/N ratio coupled with the isotope value suggests the organic material responsible for the foam originated in the water column. This elevated atomic C/N ratio is also in agreement with the higher carbohydrate percentage versus protein observed in the bulk analysis.

The most likely origin of this organic material is algae as evidenced by lipid analysis conducted by Professor Teece. He found a complex mixture of long chain fatty acids and alcohols that probably come from waxes and suggest a plant origin. The even to odd predominance of the fatty acids (i.e. fatty acid 20:0 > 21:0, 22:0 > 23:0, etc.) indicate a non-terrestrial origin and confirm what was suggested from the atomic C/N ratio. The presence of these long chain fatty acids and alcohols would be fairly hydrophobic (soap-like) and could lead to foam production.

In addition to these plant or algal fatty acids, the analysis also showed the presence of 15:0 and 17:0 fatty acids that were indicative of bacterial production and breakdown of the material. This also agrees with the atomic C/N ratio, which suggested this material was starting to degrade. In fact, the fatty acid chromatograph was extremely complex, which is usually a sign of secondary processing and modification of fatty acids. This processing could either come about from bacterial metabolism, or potentially from metabolism by zebra mussels. Dr. Teece found very few unsaturated fatty acids that might indicate a diatom bloom. He also found few sterols such as cholesterol (a marker of zebra mussel lipids) or insect sterols in the GC traces, but we would have to do further analysis before ruling out the role of zebra mussels. To date, the origin of these fatty acids in the foam are unknown though I will continue to look through the literature.

In summary,

Foam in lakes is usually thought to be due to one of several origins: terrestrial runoff, lipids from an in-lake algal (usually diatom) bloom, or elevated protein content from either a terrestrial or in-lake source. In your case:

4. The foam is probably originating from algal biomass in the water column. At this point in time, it is impossible to rule out a role for zebra mussels dying and releasing protein to the water. The protein content in the foam is significantly higher than the surrounding water and at a concentration high enough to cause foaming, but protein still makes up a relatively small amount (<5%) of the organic material present in the foam-water mixture.
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Unfortunately these results do not answer the question "Are zebra mussels responsible for the foam?" What puzzles me is that the occurrence of your foam does not appear to be tied to normal algal growth periods, suggesting a permanent 'in-lake' source. I have tried unsuccessfully to think of an easy way to determine if that source may be the zebra mussels. One approach would be to compare the fatty acid analysis obtained from zebra mussels with the fatty acid abundance in their diet. This would give you some idea if the profiles match. If you are interested in pursuing this further, you might consider supporting a student here at ESF.

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