Rheological properties of exopolymeric secretions in HABs may be functions of length scale

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Abstract

Measurements have been made of the rheology of seawater, algal cultures and HABs by two methods. The first used concentric cylinders separated by a gap of 500 µm, while the second used fish-gills of pore size ~25-35 µm. More recently the yield stress of lumpy, organic floc suspension has been shown to depend strongly on the length scale of the measurements. Measuring the rheology of HABs and natural waters at different length scales now has the potential to elucidate the scales of polymer structures associated with bioengineering by plankton, particularly in HABs.

Introduction

Many planktonic algae secrete exopolymers, which form networks, directly or by spontaneous assembly (Chin et al 1998). These structures can locally thicken, and even gel, the water. We have argued earlier (Jenkinson & Wyatt 1995, Wyatt & Ribera 2006,) that rheological changes wrought by these polymers alter physical and chemical processes in the local environment, and can thus be viewed as engineering tools in the sense pioneered by Jones et al (1994). Local thickening is generally correlated with phytoplankton biomass (Jenkinson 1986, 1989, Jenkinson and Biddanda 1995, Seuront 2006), and may be uniform or quasi-fractal. Observed and measured by different techniques, this patchiness in both phytoplankton and exopolymer abundance is evident from ocean-basin (10^6 m) down to macromolecular (10^{-9} m) scales (refs in Jenkinson & Biddanda 1995; in Passow 2000; in Higgins et al 2003; in Wyatt and Ribera 2006; in Žutić and Svetličić 2006).

Attempts have previously been made to model the effects of this rheological thickening on ocean turbulence (Jenkinson 1986, 1993b). Although care was taken to match the length scales used for measurement to those of the turbulence as closely as possible (mm-scale), however, it was not then known how strongly the polymeric component of the rheological properties might vary with length scale.

The aim of this communication is to illustrate how the hierarchically flocculated nature of algal exopolymers leads to any measured rheological property of being a function of the characteristic length-scale of the geometry of the flow system used to measure it.

We hope that such better understanding of rheological thickening and of the aggregation scales in slimy harmful algal blooms (HABs) will help research into the mitigation of its harmful effects.

Methods

Like seawater, but in more concentrated form, sewage sludge is a suspension of flocculated exopolymers (Li & Ganczarczyk, 1986) so its physical structure is closely comparable. Yield stress Y in sewage sludge was measured by the EU standard method of pouring sludge into a Kasumeter (Fig. 1), and allowing it to flow out through a capillary tube. When the flow stops, Y is measured as the height difference between the sludge-air surface and the capillary tube times the sludge density times the acceleration due to gravity. Spinosa and Lotito (2003) investigated the effects of both capillary diameter and sludge concentration on Y.

To investigate the effects of polymeric thickening in water on ventilation-flow in fish, an ichthyoviscometer was used to measure rheological properties, including Y, in seawater, algal cultures and intertidal organic fluff. This apparatus resembles the Kasumeter, except that a dead fish replaces the capillary tube, and the water is directed through its gill passages. The range of hydrostatic pressure imposed spans that produced by the same fish in life, thus minimising any mismatch of scales between those in the measurement apparatus and those in the process of interest, gill ventilation (Jenkinson and Arzul, 1998; Jenkinson et al, 2007) (Fig. 2).

Results

The data of Spinosa and Lotito (2003) show that in sewage sludge, not only is Y a function of sludge concentration but that

$$Y \sim 1/D^{-2}$$

where D is the capillary tube diameter (Fig. 3).

The data of Jenkinson et al (2007), who used an ichthyoviscometer incorporating a dead ~26-g sole to measure Y in organic fluff overlying the mud on intertidal flats, at scales relevant to ventilation by living sole, showed a strong positive relationship with the particulate organic matter (POM) concentration (Fig. 4). They showed that Y would exceed the maximum hydrostatic pressure developed by 26-g soles, ~30 Pa, thus preventing the sole from ventilating, at a POM concentration of 3 to 4 g.L^{-1}.

Jenkinson and Arzul (1998), using an ichthyoviscometer with 100-200-g largemouth bass or trout and a culture of 27,000 cells.mL^{-1} of the ichthyotoxic dinoflagellate, *Karenia* (as *Gymnodinium) mikimotoi,* found Y equal to 50 to 90 Pa in fresh culture and 400 to 600 Pa in culture that had stood for 12 h. Extracellular organic matter concentrations in these cultures are likely to have been ~3 orders of magnitude less than in the organic fluff, yet they gave higher values of Y.

Finally, Jenkinson and Arzul (2002) used an ichthyoviscometer with dead ~80-g seabass to measure the effect of cysteine compounds on Y values produced by two ichthyotoxic dinoflagellates *K. mikimotoi* and *Gymnodinium* cf *maguelonnense*, isolated from southern Tunisia. At concentrations of 21,000 and 23,000 cells.mL^{-1}, *K. mikimotoi* gave Y values of 33 and 38 Pa respectively, while at a concentrations of 10,000 and 21,000 cells.mL^{-1}, *G.* cf *maguelonnense* gave respective values for Y of 7 and 22 Pa. Addition of 0.01 mM acetyl cysteine (= ethyl L-cysteine ester) reduced Y values in these cultures by 65% to 84%.

Discussion and Conclusions

Scales used in measurement should be matched to those of the environmental processes of interest as closely as possible. However, if these two length scales plus the function relating the particular rheological value to length scale are known, the value acting at the length scale of a process can be predicted from the value measured at a different (but not too distant) length scale. This case illustrates how a rheological property, in this case Y, of a lumpy material can show a very strong negative relationship with a critical length scale in the measurement apparatus.

The critical length scale for ventilation-flow is likely the gill-pore size. Even if water can be diverted into larger channels around the gills, such diverted water will not ventilate the respiratory surfaces. Pore widths for 26 to 200-g seabass range from 25 to 35µm (Langille et al, 1983), and were thus those pertinent to the ichthyoviscometer experiments mentioned above.

By comparison, Jenkinson (1986, 1993a,b) and Jenkinson and Biddanda (1995) used a gap width of 500 µm (~15 times larger) in a rotary (Couette) system to measure the properties of algal cultures and seawater. Comparative measurements are thus required on the same blooms and cultures using measurement systems incorporating such different length scales.

That organic fluff of POM content several g.L^{-1} showed Y values comparable to those of *Karenia mikimotoi* and *Gymnodinium* cf *maguelonnense* cultures ~3 orders of magnitude poorer in extracellular organic matter (POM/DOM) suggests that the structure of the polymers in the fluff may have been far smaller than those in *Karenia* and *Gymnodinium* cultures. Light microscopy of cultures and blooms stained with Alcian Blue might help resolve whether this is so.

Allelopathic action of *Karenia mikimotoi* may act through labile polyunsaturated fatty acids (PUFAs) diffusing out from the cell. As the PUFAs decay, it is proposed this gives a radius of action, here ~175 µm. However, PUFAs secreted by *K. mikimotoi* (Gentien, this conference) may be mechanically linked to the secreted exopolymers.

Phytoplankton can secrete hierarchically aggregated polymers that modify the viscosity of the surrounding water as a function of their composition, their concentration and length scale. Polymer abundance and its correlation with phytoplankton abundance are scale-dependent, and can also vary with the stage of the life cycle. Exopolymers may be tools by which genes engineer niches by managing their physical environment. In addition, secondary effects may result, such as air-sea surface reinforcement and increased vertical flux

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References

Chin, W.-C., Orellana, M.V., Verdugo, P. (1998). Nature, 391, 568-572.

Higgins, M.J., Sader, J.E., Mulvaney, P., Wetherbee, R. (2003). J. Phycol., 39, 722-734.

Jenkinson, I.R. (1986). Nature, 323, 435- 437

Jenkinson, I.R. (1989). In: Okaichi, T., Anderson, D.M., Nemoto, T., eds. Red Tides, Elsevier, New York, pp. 435-438.
Jenkinson, I.R. (1993a). In: Toxic Phytoplankton Blooms in the Sea, Smayda, T.J., Shimizu, Y., eds, Elsevier, Amsterdam, pp. 757-762.
Jenkinson, I.R. (1993b). Oceanol. Acta, 16, 317-334.
Jenkinson, I.R., Arzul, G. (1998). In: Harmful Algae, Reguera, B., Blanco, J., Fernandez, M.L., Wyatt, T. eds. UNESCO, Paris, pp. 425-428.
Jenkinson, I.R., Arzul, G. (2002). In: Harmful Algal Blooms 2000, Hallegraeff, G.M., Blackburn, S.I., Bolch, C.J., Lewis, R.J. eds., Unesco, Paris, pp. 461-464.
Jenkinson, I.R., Biddanda, B.A. (1995). J. Plankt. Res., 17, 2251-2274.
Jenkinson, I.R., Wyatt, T. (1995). In: Harmful Marine Algal Blooms, Lassus, P., Arzul, G., Erard, E., Gentien, P., Marcaillou-Le Baut, C. eds., Lavoisier, Paris, pp. 603-608.
Jenkinson, I.R., Claireaux, G., Gentien, P. (2007). Mar. Biol., 150, 471-485.
Jones, C., Lawton, J., Shachak, M. (1994). Oikos, 69, 373-386.
Langille, B.L., Stevens, E.D., Antantaraman, A. (1983). In: Fish Biodynamics, Webb, P.W., Weihs, D. eds, Praeger, New York, pp. 92-139.
Li, D.-H., Ganczarczyk, J.J. (1986), Crit. Rev. env. Control 17, 53-87.
Passow, U. (2000). Mar. Ecol. Prog. Ser., 192, 1-11.
Seuront, L., Vincent, D., Mitchell, J.G. (2006). J. mar. Sys., 61, 118-133.
Spinosa, L., Lotito, V., (2003). Adv. env. Res., 7,: 655-659.
Wyatt, T., Ribera d'Alcalà, M. (2006). CIESM Workshop Monographs, 28, 13-24.
Žutić, V., Svetličić, V. (2006). CIESM Workshop Monographs, 28, 45-48.

Legends

Fig. 1. The Kasumeter (yield-stress viscometer).

Fig. 2. An ichthyoviscometer. (From Jenkinson et al., in press)

Fig. 3. Yield stress of sewage sludge for different sludge concentrations (%) as a function of tube diameter. Note the difference in log scales on the x- and y-axes. (Drawn from data in Spinosa and Lotito, 2003.)

Fig. 4. Yield stress of intertidal organic fluff (Pa) vs. POM concentration ($g.L^{-1}$) measured with an ichthyoviscometer incorporating a dead juvenile sole (Jenkinson et al, in press)

Author's note *post scriptum*, "Jenkinson et al (in press)" is now published as "Jenkinson, Claireaux & Gentien, *Marine Biology*, 150, 471-485"

Figure 1

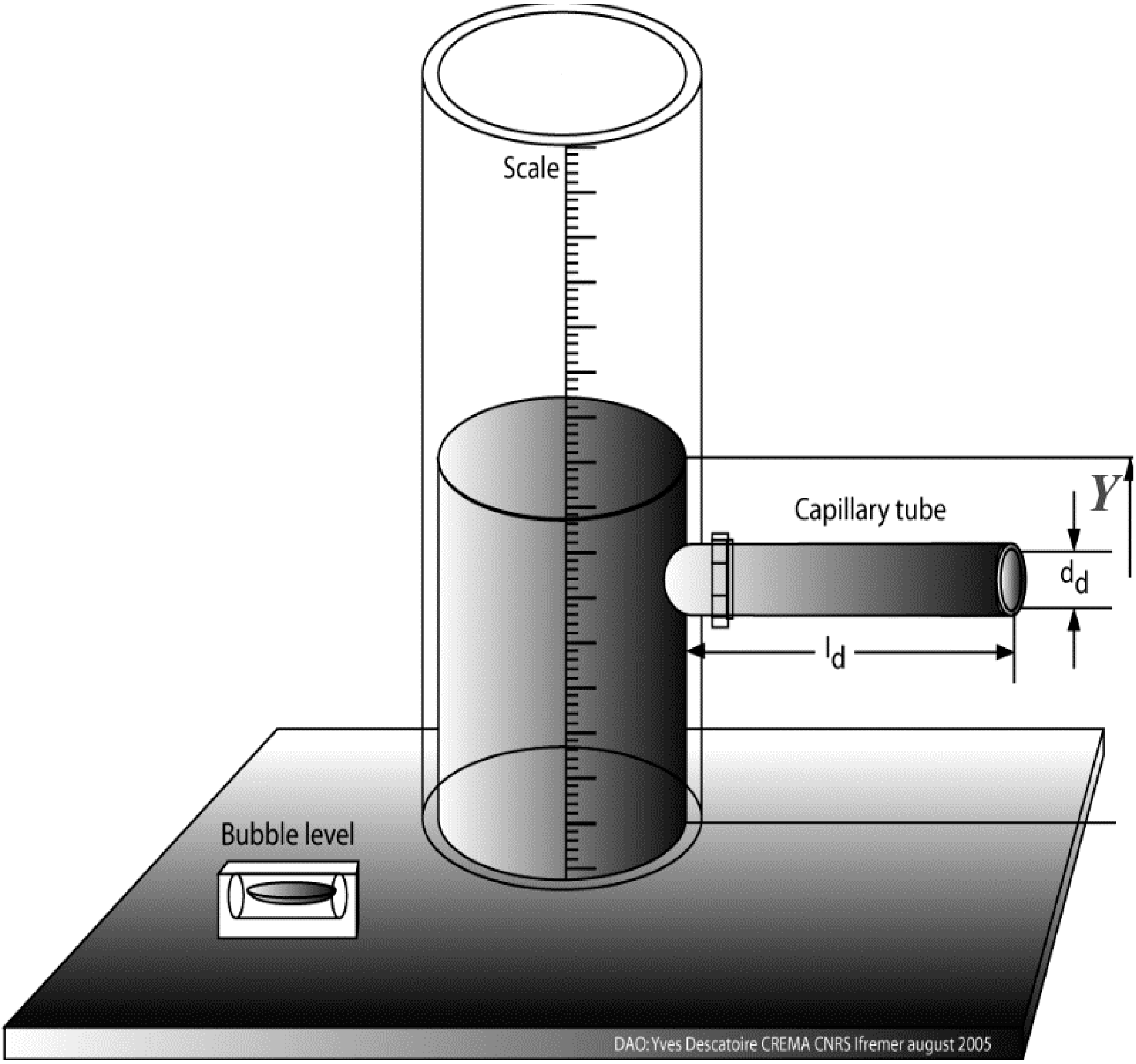
Scale
Capillary tube
Y
d_d
l_d
Bubble level
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Figure 2

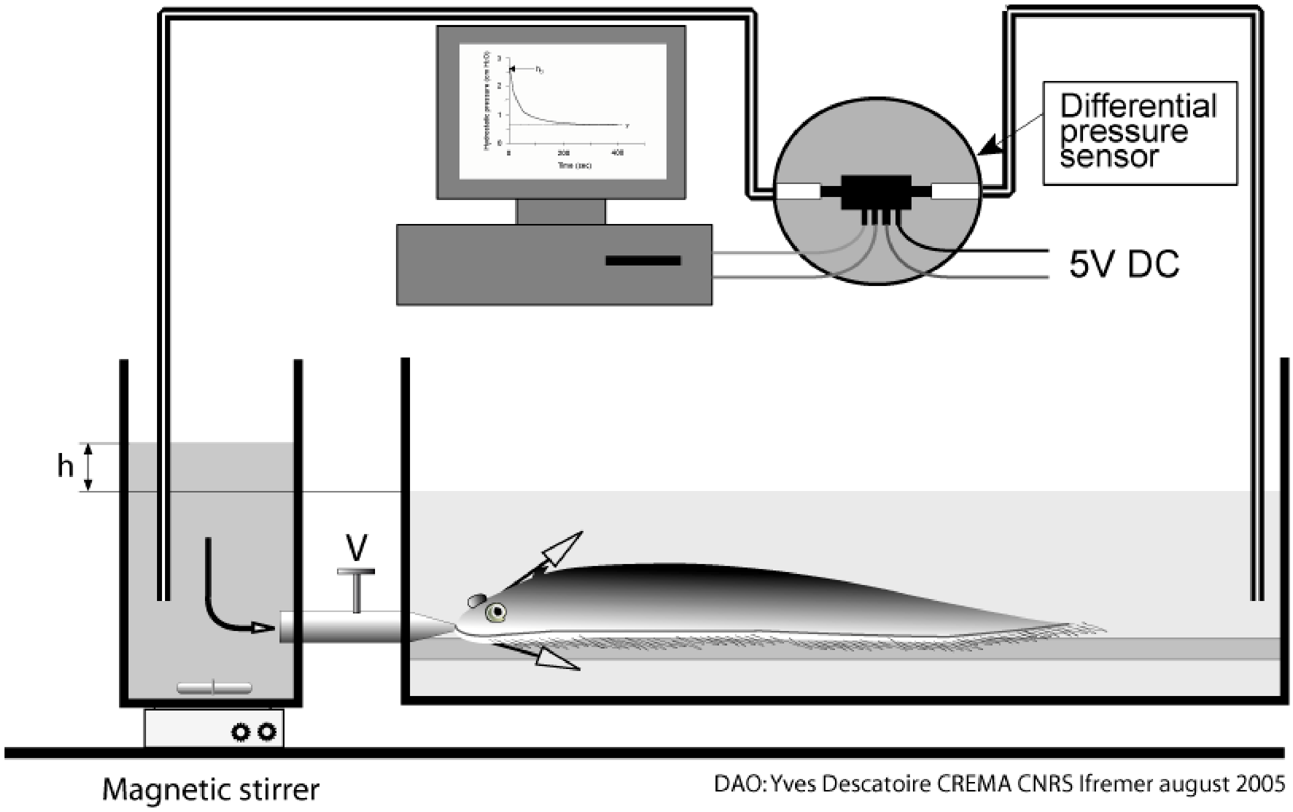

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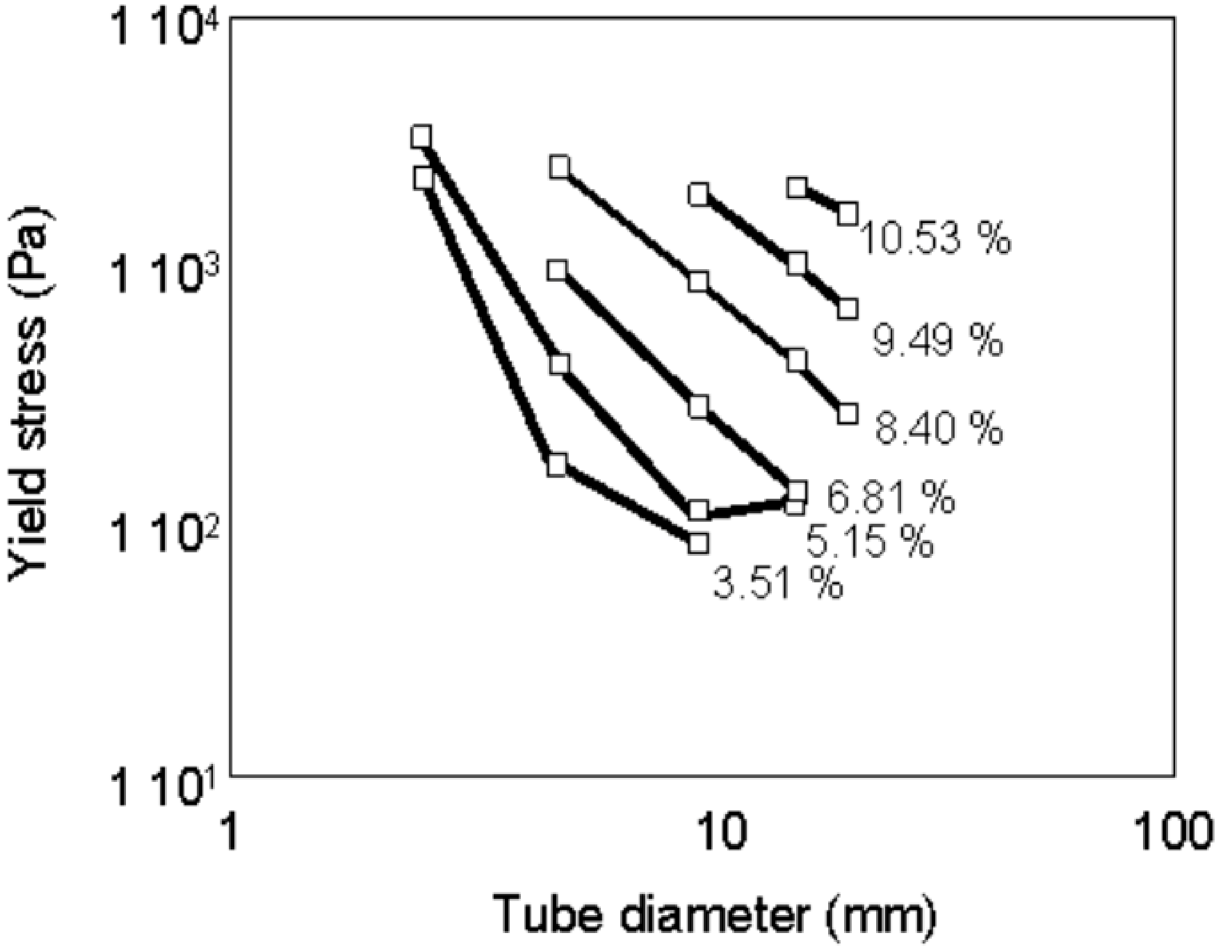
Figure 3



1 10⁴
1 10³
1 10²
1 10¹
1
10
100
Yield stress (Pa)
Tube diameter (mm)
10.53 %
9.49 %
8.40 %
6.81 %
5.15 %
3.51 %

Figure 4