

CHEMICAL WARFARE BETWEEN MICROALGAE: BIOGENETIC BROMINE CYANIDE (BRCN) CONTROLS BIOFILM FORMATION AROUND A MARINE BENTHIC DIATOM

Vanelslander Bart¹, Georg Pohnert², Koen Sabbe¹ and Wim Vyverman¹

¹ Laboratory of Protistology & Aquatic Ecology, Department of Biology, Ghent University, Krijgslaan 281-S8, B-9000 Ghent, Belgium
E-mail: Bart.Vanelslander@ugent.be

² Institute for Inorganic and Analytical Chemistry, Bioorganic Analytics, Friedrich Schiller University of Jena, Lessingstrasse 8, 07743 Jena, Germany

Biofilm formation in marine habitats is a ubiquitous process and nearly all surfaces are covered with a complex community. If technical surfaces such as ship hulls are concerned in this process, termed as fouling, it can cause severe economic damage and therefore intense efforts are undertaken to control such processes (Yebra *et al.*, 2004). Among the early settlers, microalgae play a key role in the development of biofilms and especially diatoms are able to settle on even the most fouling resistant surfaces. Fundamental processes during marine biofilm formation might be regulated by chemical factors released by settling organisms in this habitat. Especially around benthic microalgae fine-scale spatial variations in species composition are often observed (Saburova *et al.*, 1995). This spatial distribution of species is characterized by non-overlapping areas of maximal density and negative correlation of species densities (Saburova *et al.*, 1995). Since these occur even in the absence of abiotic heterogeneity, species interactions mediated by allelochemicals might play a key role.

We demonstrate that a marine benthic diatom biosynthesizes and exudes novel halogenated allelochemicals with strong effects on naturally co-occurring diatoms. Using a bioassay-guided approach, we demonstrate that the diatom *Nitzschia cf. pellucida* produces a diverse mixture of iodinated and brominated metabolites including the new natural products BrCN (Bromine cyanide) and ICN (Iodine cyanide) which exhibits pronounced allelopathic properties. Allelopathic activity is highest shortly after daybreak and the labile compound obviously acts as short term signal, leading to "cleaning" daily events around the algae which suggests a highly effective novel strategy for biofilm control. We show that the production of all halogenated metabolites detected is hydrogen peroxide dependent and therefore link BrCN and ICN production to haloperoxidase enzymes (Butler and Sandy, 2009). Halogenated low molecular weight hydrocarbons are ubiquitously released from marine micro- and macroalgae (Sturges *et al.*, 1992; Paul and Pohnert, 2011) but their function is often controversially discussed. Micro and macroalgae contribute significantly to the atmospheric halocarbon budget and local maxima are often observed in coastal regions. Here we provide a novel explanation for the poorly understood role of halogenated low molecular weight molecules from microalgae (Sturges *et al.*, 1992).

References

- Butler A. and M. Sandy. 2009. Mechanistic considerations of halogenating enzymes. *Nature* 460:848-854.
- Paul C. and G. Pohnert. 2011. Production and role of volatile halogenated compounds from marine algae. *Nat. Prod. Rep.* (in press).
- Saburova M., I. Polikarpov and I. Burkovsky. 1995. Spatial structure of an intertidal sandflat micro-phytobenthic community as related to different spatial scales. *Mar. Ecol. Prog. Ser.* 129:229-239.
- Sturges W., G. Cota and P. Buckley. 1992. Bromoform emission from Arctic ice algae. *Nature* 358:660-662.
- Yebra D., S. Kiil and K. Dam-Johansen. 2004. Antifouling technology - past, present and future steps towards efficient and environmentally friendly antifouling coatings. *Prog. Org. Coat.* 50:75-104.