## Copper stress induces biosynthesis of octadecanoid and eicosanoid oxygenated derivatives in the brown algal kelp Laminaria digitata

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## Abstract

• To better understand the toxicity and the orchestration of antioxidant defenses of marine brown algae in response to copper-induced stress, lipid peroxidation processes were investigated in the brown alga Laminaria digitata.

• The expression of genes involved in cell protection and anti-oxidant responses were monitored by semi-quantitative reverse transcriptase polymerase chain reaction and the lipid peroxidation products were further characterized by profiling oxylipin signatures using high-pressure liquid chromatography–mass spectrometry.

• Exposure to copper excess triggers lipoperoxide accumulation and upregulates the expression of stress related genes. It also increases the release of free polyunsaturated fatty acids, leading to an oxidative cascade through at least two distinct mechanisms. Incubations in presence of inhibitors of lipoxygenases and cycloxygenases showed that in addition to the reactive oxygen species-mediated processes, copper stress induces the synthesis of oxylipins through enzymatic mechanisms. Among complex oxylipins, cyclopentenones from C18 and C20 fatty acids such as 12-oxo-PDA and prostaglandins were detected for the first time in brown algae, as well as unique compounds such as the 18-hydroxy-17-oxo-eicosatetraenoic acid.

• These results suggest that lipid peroxidation participates in the toxic effects of copper and that lipid peroxidation derivatives may regulate protective mechanisms by employing plant-like octadecanoid signals but also eicosanoid oxylipins which are absent in vascular plants.

Key words: brown algae, copper, heavy metal, kelp, Laminaria digitata, oxylipins, prostaglandins, stress.