



Biodegradation and toxicity of vegetable oils in contaminated aquatic environments: Effect of antioxidants and oil composition



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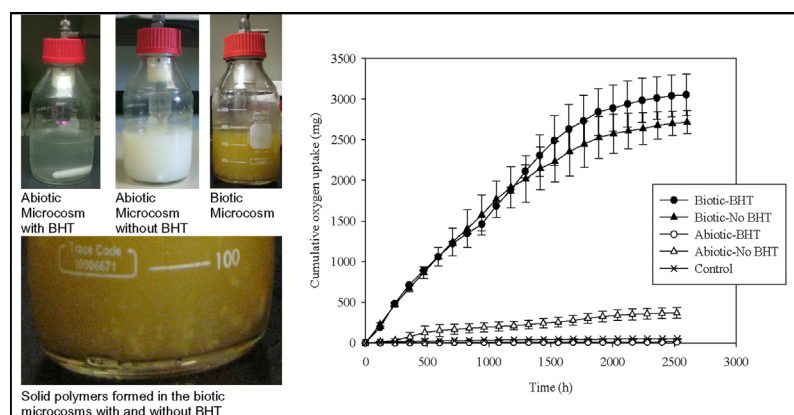
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HIGHLIGHTS

- The presence of BHT did not significantly enhance the biodegradation of canola oil.
- Intractable solid polymers were formed in the biotic microcosms.
- Toxicity was observed in the biotic microcosms with and without BHT.
- The potency of an antioxidant is dependent on the oil fatty acid composition.
- The fatty acid composition of spilled vegetable oils defines their fate and impact.

GRAPHICAL ABSTRACT



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ABSTRACT

Antioxidants may affect the oxidative rate of vegetable oils determining their fate and impact in contaminated aquatic media. In previous studies, we demonstrated the effectiveness of butylated hydroxytoluene (BHT), one of the most used antioxidants in edible oils, in enhancing the biodegradation of glyceryl trilinoleate, a pure triacylglycerol of *cis,cis*-9,12-octadecadienoic acid (C18:2 Δ), through retarding its oxidative polymerization relatively to the oil with no added antioxidant. In this study, the effect of BHT on the biodegradation and toxicity of purified canola oil, a mixed-acid triacylglycerol with high C18:1 content, was investigated in respirometric microcosms and by use of the Microtox® assay. Investigations were carried out in the absence and presence (200 mg kg^{-1}) of the antioxidant, and at an oil loading of 0.31 L m^{-2} ($333 \text{ gal acre}^{-1}$). Substantial oil mineralization was achieved after 16 weeks of incubation ($>77\%$) and was not significantly different ($p > 0.05$) between the two BHT treatments, demonstrating an important role of the oil fatty acid composition in determining the potency of antioxidants and, consequently, the fate of spilled vegetable oils. Furthermore, for both treatments, toxicity was measured at early stages of the experiments and disappeared at a later stage of incubation. The observed transient toxicity was associated with the combined effect of toxic biodegradation intermediates and autoxidation products. These results were supported by the gradual disappearance of BHT in the microcosms initially supplemented with the antioxidant, reaching negligible amounts after only 2 weeks of incubation.

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1. Introduction

The world generation of vegetable oils has increased rapidly during the past years driven mainly by a higher consumption of edible oils and an increasing interest in their use as replacements for mineral oil based products (Coyle, 2007). The likelihood of spillages of large volumes of vegetable oils in the aquatic environment, as a result of their dynamic trade on the world's market, is therefore no different from that of mineral oils. Spillages of large volumes of vegetable oils have been reported during the last 40 years and were in some cases more harmful than mineral oil spills (Bucas and Saliot, 2002).

The deleterious effects of vegetable oil spills in impacted aquatic ecosystems include oxygen depletion, smothering of surface dwelling organisms, and toxicity to aquatic fauna. The toxicity of vegetable oils is primarily due to the oil biodegradation intermediates, namely long chain fatty acids (LCFAs), and its autoxidation byproducts. The toxicity of vegetable oils and their detrimental effects in aquatic media are thoroughly reported in the literature (McKelvey et al., 1980; Groenewold et al., 1982; Mudge et al., 1995; Mudge, 1995; Rigger, 1997; Bucas and Saliot, 2002; Pereira et al., 2002; Wincele et al., 2004; Salam et al., 2012a).

The fate and impact of vegetable oils in contaminated aquatic media largely depend on their specific properties (Bucas and Saliot, 2002). Although readily biodegradable, vegetable oils can polymerize to form intractable lumps resistant to many erosional or degradation processes (Mudge et al., 1993; Mudge, 1997). Competition between biodegradation and polymerization was reported by Mudge et al. (1995) in simulated sunflower and linseed oil spills in salt marsh sediments. In the case of sunflower, the oil polymerized after 28 days resulting in the formation of a cap of reduced permeability to oxygen and water, while no polymers were formed in the case of linseed oil. Contrasting results were reported from similar spill simulations conducted by Pereira et al. (1998). In this case, spilled sunflower oil did not polymerize. Rather, it degraded slowly while linseed oil degraded at a faster rate. In a later study, the authors observed that sunflower oil persisted in an unaltered state for six months, whereas 60% of linseed oil was consumed within two months (Pereira et al., 2003a). While based on these studies the authors were not able to make a clear conclusion on what determines the fate of spilled vegetable oils, they suggested that the explanation could be found in the fatty acids composition of the oil and the environmental factors that instigate the oil biodegradation or polymerization pathways (Pereira et al., 2003b).

It has become clear that the extent of vegetable oils autoxidation depends on their degree of unsaturation (Belitz et al., 2009), oils with high content of unsaturated fatty acids being more prone to autoxidation (Sherwin, 1976). Relative oxidation rate of C18 fatty acids is reported to be 1, 100, 1200, and 2500 at 25 °C for stearic (C18:0), oleic (C18:1), linoleic (C18:2), and linolenic (C18:3) acids respectively (Belitz et al., 2009). Furthermore, the composition of vegetable oils and interaction between their constituent fatty acids significantly affects the rate of the oil oxidation (Frankel, 1980). Oleic acid is reported to initially act as a diluent for the oxidation of linoleic acid, while at advanced stages of oxidation the rate is affected by both propagation and termination reactions (Frankel, 1980). In addition, Neff et al. (1994) reported the effect of fatty acids position in the triacylglycerol (TAG) molecule on the oxidation of purified vegetable oils. The authors found a positive correlation of reduced oxidative stability with increased linoleic acid (C18:2) concentration at carbon 2 of the TAG.

Moreover, the presence of antioxidants may also affect the oxidative rate of vegetable oils (Wanasundara and Shahidi, 2005). In previous experiments conducted by our research group and investigating the effect of antioxidants on the biodegradation of spilled vegetable oils in contaminated aquatic environments (Salam et al., 2012b), we demonstrated the effectiveness of butylated hydroxytoluene (BHT), one of the most used antioxidants in edible oils, in retarding the oxidative polymerization of glyceryl trilinoleate at concentrations as low as

50 mg kg⁻¹. After 19 weeks of incubation, only about 41% of the oil was mineralized in the microcosms with no BHT, while mineralization exceeded 67% in the microcosms with added antioxidant and did not significantly increase with increasing BHT concentrations (50–800 mg kg⁻¹). Glyceryl trilinoleate, a pure triacylglycerol of cis,cis-9,12-octadecadienoic acid (C18:2 delta), was chosen in those experiments as model vegetable oil for its high susceptibility to autoxidation.

In this study, it is our purpose to extend these investigations to commonly used vegetable oils in order to quantitatively evaluate the impact of antioxidants on the biodegradability of mixed-acid triacylglycerols (different fatty acid moieties esterified to the same glycerol molecule) in contaminated aquatic media. Another main objective of this study is to determine the effect of antioxidants on the induced toxicity of spilled vegetable oils. To achieve these aims, respirometric experiments were conducted to evaluate the aerobic biodegradation and toxicity of purified canola oil in the presence and absence of BHT. Canola oil was chosen for its unique composition containing the major saturated and unsaturated LCFAs. In addition, canola oil represents the second largest oil crop globally produced (Ash, 2015) and the preferred feedstock for biodiesel production in Europe (Ajavonic, 2011).

2. Materials and methods

2.1. Canola oil purification

Refined organic canola oil (Spectrum Naturals®) was purchased from a local grocery store and was purified from tocopherols, naturally occurring antioxidants in vegetable oils, by adsorption chromatography using activated alumina (Al₂O₃). Details on canola oil purification are presented in Supporting information (SI). Analysis of the purified oil by high performance liquid chromatography (HPLC) showed no detectable tocopherols and hydroperoxides, and a percent distribution of the triglycerides comparable to the original oil. Fatty acid composition of the purified oil was determined by gas chromatography mass spectroscopy and showed a high content of oleic, linoleic, and linolenic acids (56.5, 22.6, and 12.4% w/w, respectively). The chemical analysis and characteristics of the purified oil are presented in SI.

2.2. Biodegradation experiments

Biodegradation experiments of purified canola oil with high content of oleic, linoleic, and linolenic acids (56.5, 22.6, and 12.4% w/w, respectively) were performed in computerized Comput-Ox respirometers, Model OO-244SC (N-Con Systems, Crawford, GA, USA). The biodegradation microcosms consisted of the standard 500 mL (7 cm i.d. × 17.6 cm) N-Con respirometric flasks equipped with a PTFE encased magnetic stir bar of 1 cm diameter and 6.4 cm length. The microcosms were filled with 250 mL mineral medium made of potassium phosphate monobasic buffer (KH₂PO₄) supplemented with minimal nutrients. The mineral solution composition is presented in Table S2 in the Supplementary information (SI).

Two sets of respirometric microcosms were prepared. In one set, a slick of the oil free of antioxidant was applied to the surface of the microcosms, while in the other set the oil was supplemented with 200 mg kg⁻¹ of BHT. The tested BHT concentration is commonly used in the food industry to stabilize vegetable oils (Madhavi and Salunkhe, 1995). In addition, previous conducted experiments by Salam et al. (2012b) on the effect of different levels of BHT on the biodegradation of glyceryl trilinoleate in aquatic media demonstrated minimal additional protective effect of the antioxidant above 50 and up to 800 mg kg⁻¹.

In both treatments, the oil was added under nitrogen gas at a loading of 0.31 L m⁻² (333 gal acre⁻¹) corresponding to an amount of 1.1 g per microcosm. The oil loading was selected based on reported amounts of vegetable oil spills in aquatic environments, and considering the results from previous vegetable oil biodegradation experiments conducted by

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