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Can volatile organic compounds be markers of sea salt?

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ABSTRACT

Sea salt is a handmade food product that is obtained by evaporation of seawater in saltpans. During the crystallisation process, organic compounds from surroundings can be incorporated into sea salt crystals. The aim of this study is to search for potential volatile markers of sea salt. Thus, sea salts from seven north-east Atlantic Ocean locations (France, Portugal, Continental Spain, Canary Islands, and Cape Verde) were analysed by headspace solid-phase microextraction combined with comprehensive two-dimensional gas chromatography–time-of-flight mass spectrometry. A total of 165 compounds were detected, ranging from 32 to 71 compounds per salt. The volatile composition revealed the variability and individuality of each salt, and a set of ten compounds were detected in all samples. From these, seven are carotenoid-derived compounds that can be associated with the typical natural surroundings of ocean hypersaline environment. These ten compounds are proposed as potential volatile markers of sea salt.

1. Introduction

The demand for handmade food products from natural sources has increased considerably in recent years. Emotions evoked by handmade products mainly enhance the pleasure of buying, owning, and using them. More recently, food-elicited emotion is increasingly becoming critical for product differentiation as many food products are produced with similar characteristics, packaging, and price (Jiang, King, & Prinyawiwatkul, 2014). Thus, focus should be taken on the establishment of objective parameters that contribute to product differentiation, contributing to consumer information and helping companies and producers to gain a competitive edge.

Sea salt is a handmade food product obtained from seawater in saltpans that are often man-made systems where the salt is produced by crystallisation due to the combined effects of wind and sunlight. Before sea salt crystallisation, seawater circulates along a series of successive ponds with increasing levels of salinity due to continuous water evaporation. Contact with the surrounding environment is a potential source of volatile compounds that may affect the sea salt composition.

The presence of volatile compounds in sea salt was demonstrated in 2009 using headspace solid-phase microextraction (HS-SPME) combined with gas chromatography–quadrupole mass spectrometry (GC–qMS) methodology (Silva, Rocha, & Coimbra, 2009). More recently, a high-resolution methodology based on comprehensive two-dimensional gas chromatography was applied (GC × GC–ToFMS), which enabled the tentative identification of a greater number of volatile compounds from sea salt (Silva, Rocha, Coimbra, & Marriott, 2010). In the meantime, other studies reporting the presence of volatile compounds in sea salt have been published (Donadio, Bialecki, Valla, & Dufossé, 2011; Serrano, Nácher-Mestre, Portolés, Amat, & Hernández, 2011; Silva, Rocha, & Coimbra, 2010). Volatiles identified were distributed over the chemical groups of hydrocarbons, aldehydes, esters, furans, haloalkanes, ketones, ethers, alcohols, phenols, terpenoids, norisoprenoids, and lactones. Among these, the norisoprenoid β-ionone (a carotenoid-derived aroma compound), which exhibits a violet odour descriptor, was considered a potential contributor to sea salt aroma (Silva, Rocha, & Coimbra, 2010). Carotenoids are significant potential sources of volatile compounds in nature.

Several sources were reported for the volatile compounds identified in sea salt, such as algae (Donadio et al., 2011; Silva, Rocha, & Coimbra, 2009, 2010; Silva, Rocha, Coimbra, & Marriott, 2010), the surrounding bacterial community (Donadio et al., 2011; Silva, Rocha, et al., 2009; Silva, Rocha, & Coimbra, 2010; Silva, Rocha, Coimbra, & Marriott, 2010), and environmental pollution as a consequence of anthropogenic activities (Donadio et al., 2011; Serrano et al., 2011; Silva, Rocha, et al., 2009; Silva, Rocha, & Coimbra, 2010; Silva, Rocha, Coimbra, & Marriott, 2010). The presence of norisoprenoids in *fleur de sel* (first crystals of sea salt formed at the water surface of saltpans) was related to the concentration of the microalgae *Dunaliella salina* (Donadio et al., 2011). Different species of plants, animals, algae, bacteria, and other organisms, may be present, according to saltpan location; however,

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a typical biota exists associated with the hypersaline environments. Several studies focused on the flora of hypersaline environments identified in different geographical areas, such as halophytes, namely *Salicornia europaea*, *Halimione portulacoides* (Meziane, Bodineau, Retiere, & Thoumelin, 1997), *Sarcocornia fruticosa* (Válega et al., 2008), *Spartina maritime* (Silva, Dias, & Caçador, 2009), *Limoniastrum monopetalum*, and *Spartina densiflora* (Simões, Calado, Madeira, & Gazarini, 2011), and algae, namely *Fucus serratus* (Beauchêne, Grua-Priol, Lamer, Demaimay, & Quémeneur, 2000), *Polysiphonia denudata*, and *Laurencia papilosa* (Kamenarska et al., 2006). This typical biota may contribute to the volatile composition pattern of sea salt, i.e., the existence of potential sea salt volatile markers.

In the last decade, an increased consumption of sea salt has been observed. At the same time, there is a growing interest for protection, and recognising the value of saltpans intrinsically associated with the quality of sea salt. From 2005 to 2007 the project SAL – Salt from Atlantic (*Re-valorisation of the Atlantic traditional saltpans identity. Recovery and promotion of the biological, economical, and cultural potential of the humid zones from the coast*), supported by the European Commission (INTERREG IIIB Programme), focused on this natural food product (Silva, Rocha, et al., 2009; Silva, Rocha, Coimbra, & Marriott, 2010). Volatile components present in sea salt could play an important role in differentiating this handmade food product from industrial salt, and valuing sea salt as a distinct and desirable product. Therefore, the present work aims to search for potential volatile markers of sea salt. To fulfil this objective, north-east Atlantic Ocean salts from 7 geographical origins were analysed by a methodology previously described (Silva, Rocha, Coimbra, & Marriott, 2010). In addition, the potential impact of the saltpan environment as a source of volatiles is discussed.

2. Materials and methods

2.1. Sea salt samples

Sea salt samples from several geographical origins were analysed in this study (Fig. 1). The samples, produced in 2007, were collected (*ca.* 2–5 kg per sea salt) at different locations of the north-east Atlantic Ocean: Île de Ré (IR), on the west Coast of France; Aveiro (AV) and Figueira da Foz (FF), on the north coast of Portugal; Castro Marim (CM), in the Algarve, south Portugal with Mediterranean influence; Cádiz (CD), in Andalucia, south-western Spain, also with Mediterranean influence; La Palma Island (LP), in the Canary Islands; and Sal Island (S), in Cape Verde. With the exception of sea salt from Cape Verde, obtained from a local store, all the other samples were supplied by the participants of project SAL – Salt from Atlantic, supported by the European Commission (INTERREG IIIB Programme).

Four saltpans are located in estuarine areas: (i) Aveiro saltpan (AV) is located in Vouga river margins (Ria de Aveiro), 8 km from the sea; (ii) Figueira da Foz saltpan (FF) is located on Murraceira Island, in Mondego river margins, 3 km from the sea, (iii) Castro Marim saltpan (CM) is located in Guadiana river margins, 5 km from the sea, and (iv) saltpan of Cádiz (CD) is located on the Island of Léon, in Zurraque river margins, 7 km from the sea. Three saltpans are located on north-east Atlantic Ocean islands: (v) Île de Ré saltpan (IR) is located 1 km from the ocean; (vi) La Palma (LP) saltpan is located 2 km from the ocean, and (vii) Sal Island saltpan (S) is an inland saltpan located 2 km from the ocean. These two last saltpans are located in arid zones, i.e., surrounded by much less vegetation than the others. The reported distances were estimated from local maps.

For a comparative study two salts from an inland origin, far from the sea (>200 km), were also analysed. These samples were collected in saline aquifers of the Murray Darling Basin, in Australia, near Mildura, in the north-west Victoria. These samples, identified as Coarse Gold (CG) and Pink Flakes (PF), were produced in 2008 and supplied by the Australian trading company SunSalt.

All samples were stored in sealed glass bottles in the dark and at room temperature until analysis.

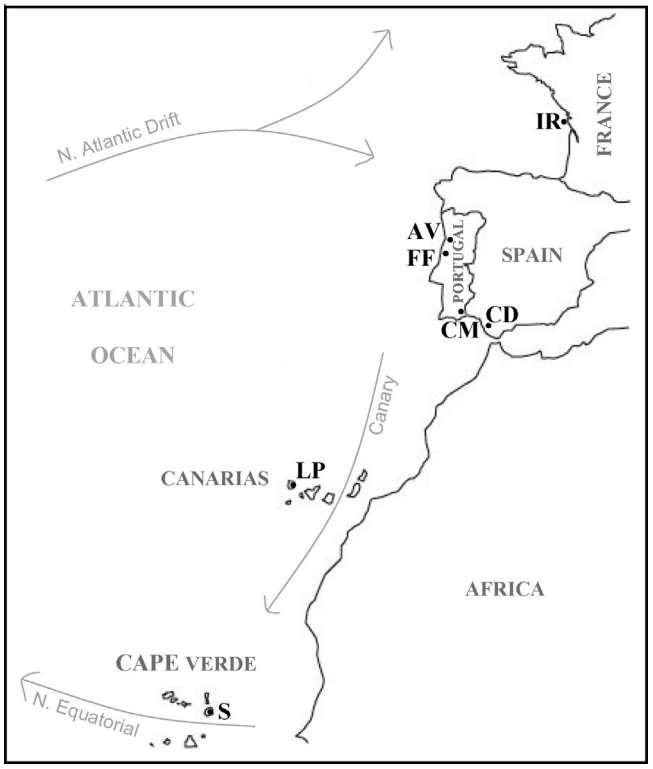

Fig. 1. Map showing the sea salt sampling sites in the North-east Atlantic Ocean. Île de Ré – IR; Aveiro – AV; Figueira da Foz – FF; Castro Marim – CM; Cádiz – CD; La Palma island – LP; Sal island – S. The Atlantic Ocean currents are also highlighted: North Atlantic Drift, Canary, North Equatorial.

2.2. Sea salt volatile determination by HS-SPME/GC × GC–ToFMS

The HS-SPME/GC × GC–ToFMS methodology used in this research study was based on previous work developed by Silva, Rocha, et al. (2009), Silva, Rocha, Coimbra, and Marriott (2010). Briefly, ~6 g ($1/\beta = 0.5$) of sea salt were added to a 22-mL vial. The vial was capped with a PTFE septum and an aluminium cap (Chromacol, Fisher Scientific, Loughborough, UK), and the sample was thermostated overnight using a dry heat block adjusted to 60.0 ± 0.1 °C. The SPME fibre coated with 1 cm divinylbenzene/Carboxen/polydimethylsiloxane (DVB/CAR/PDMS, 50/30 μm; Supelco, Bellefonte, PA) was then manually inserted into the sample vial headspace for 60 min. In order to avoid any cross-over contamination, blanks, corresponding to analysis of the coated fibre not submitted to any extraction procedure, were run between sets of three analyses.

The SPME fibre with sorbed sea salt volatile compounds was manually introduced into the GC × GC injection port at 240 °C and desorbed for 5 min in splitless mode. The desorbed volatile compounds were separated using a GC × GC–ToFMS system comprising of an HP 6890 (Agilent Technologies, Burwood, Australia) gas chromatograph and a Pegasus III time-of-flight mass spectrometer (LECO, St. Joseph, MI,). To implement the modulation process, a longitudinally-modulated cryogenic system (LMCS; Chromatography Concepts, Doncaster, Australia) was used, operated at a modulation period of 5 s with a cryotrap temperature of −20 °C. The ToFMS was operated at a storage rate of 100 Hz,