

Monitoring of volatile organic pollutants in marine species of Mediterranean sea

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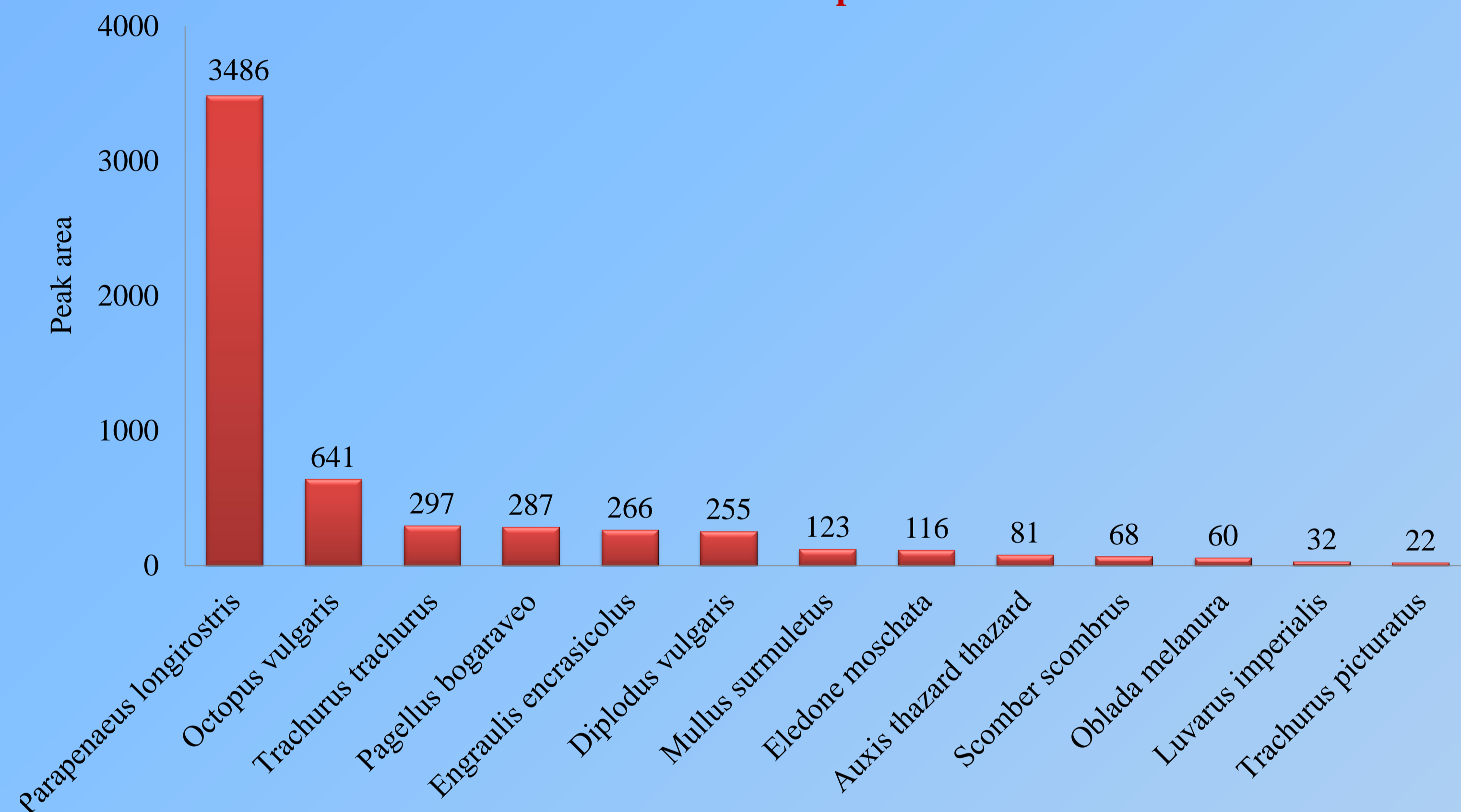
Introduction

Chemical pollution is of special concern in the Mediterranean region due to its particular ecological and socio-economic characteristics. Contamination of marine organisms from human activities can come from different sources. Contaminants such as heavy metals, PAHs, PCBs, dioxins which are known to bio-accumulate in marine organisms, were widely studied and their maximum levels in foodstuffs are set by the European Union Commission (Regulation N° 1881/2006). More volatile compounds such as benzene, toluene, xylene, styrene, short chain chlorinated paraffins (C₉₋₁₃) important to the production of polymers and numerous consumer products such as solvents, paints, pharmaceutical, etc. are less studied. In this context our research reports the results on the determination of volatile organic pollutants in several species of Mediterranean fish, crustaceans and mollusk.

Presence of volatile organic pollutants in marine species of Mediterranean sea.

	Benzene and derivatives	Hydrocarbons	Chlorinated paraffins	Phthalates
<i>Engraulis encrasicolus</i>	x	x	x	x
<i>Luvarus imperialis</i>	x	x	x	x
<i>Eledone moschata</i>	x	-	x	x
<i>Oblada melanura</i>	x	x	x	x
<i>Pagellus bogaraveo</i>	x	-	x	x
<i>Auxis thazard thazard</i>	x	-	-	x
<i>Octopus vulgaris</i>	x	x	x	x
<i>Diplodus vulgaris</i>	x	x	-	x
<i>Trachurus trachurus</i>	x	x	-	x
<i>Scomber scombrus</i>	x	x	x	x
<i>Mullus surmuletus</i>	x	x	x	x
<i>Parapenaeus longirostris</i>	x	x	x	x
<i>Trachurus picturatus</i>	x	x	-	x

Content* of BTX identified in marine species of Mediterranean sea.



Content* of benzene and its derivatives identified in marine species of Mediterranean sea.

	Benzene	Toluene	Ethylbenzene	p-Xylene	m-Xylene	o-Xylene	Ethyltoluene	Styrene	Phenol	Trimethylbenzene
<i>Engraulis encrasicolus</i>	6	79	18	43	100	-	14	7	-	-
<i>Luvarus imperialis</i>	11	13	4	2	-	-	1	1	-	-
<i>Eledone moschata</i>	3	41	23	21	9	-	13	5	-	-
<i>Oblada melanura</i>	-	19	14	17	-	-	8	-	-	-
<i>Pagellus bogaraveo</i>	3	262	4	16	-	-	1	1	-	-
<i>Auxis thazard thazard</i>	4	24	15	24	-	-	6	7	-	-
<i>Octopus vulgaris</i>	30	518	62	-	-	-	-	2	5	24
<i>Diplodus vulgaris</i>	5	37	41	11	126	25	6	3	-	-
<i>Trachurus trachurus</i>	11	90	43	21	96	-	24	12	-	-
<i>Scomber scombrus</i>	6	37	10	4	-	-	5	6	-	-
<i>Mullus surmuletus</i>	51	36	8	17	-	-	7	4	-	-
<i>Parapenaeus longirostris</i>	-	432	159	695	1897	131	-	91	18	64
<i>Trachurus picturatus</i>	1	15	6	-	-	-	-	-	-	-

* Arbitrary scale, peak area.

Conclusions

The HS-SPME-GC-MS technique allowed to monitor the content of organic contaminants in various marine species of the Mediterranean Sea. The species analyzed are part of the human diet and the identified pollutants, it is well-known, are suspected to cause cancer and other serious health effects. The research represents an important step toward a more comprehensive understanding and evaluation of human health risks associated with these pollutants exposures via marine fish consumption. Research along this line is currently in progress.

Materials and Method

Sampling

Thirteen species of fish caught in the Ionian and Tyrrhenian Sea in 2013, purchased directly from local dealers, were analyzed.

The species were:

- *Engraulis encrasicolus* (European anchovy);
- *Luvarus imperialis* (luvar);
- *Eledone moschata* (musky octopus);
- *Oblada melanura* (saddled seabream);
- *Pagellus bogaraveo* (blackspot seabream);
- *Auxis thazard thazard* (frigate tuna);
- *Octopus vulgaris* (common octopus);
- *Diplodus vulgaris* (common two-banded seabream);
- *Trachurus trachurus* (Atlantic horse mackerel);
- *Scomber scombrus* (Atlantic mackerel);
- *Mullus surmuletus* (surmullet);
- *Parapenaeus longirostris* (shrimp);
- *Trachurus picturatus* (blue jack mackerel).

Volatiles Extraction: HS-SPME

The extraction of the volatile fraction was conducted using a DVB/CAR/PDMS fiber with 50/30 μm film thickness. For the analysis 4.5 g of fish samples finely crumbled with 14 ml of a saturated aqueous solution of NaCl were placed in a vial of 40 ml. The vial was kept in a water bath at 35 °C. The HS-SPME extraction was performed exposing the fiber in the headspace of the sample in the following experimental conditions:

Equilibration time: 30'

Extraction time: 30'

After the extraction, the SPME fiber was introduced into the splitless injector of GC/MS and maintained at 260 °C for 3 minutes.

Volatiles Analysis: GC-MS

A Varian 3800 gas chromatograph directly interfaced with a Varian 2000 ion trap mass spectrometer (Varian spa, Milan, Italy) was used. The analysis conditions were as follows: injector temperature, 260 °C; injection mode, splitless; capillary column, CP-Wax 52 CB, 60 m, 0.25 mm i.d., 0.25 μm film thickness (Chrompack Italy, s.r.l. Milan, Italy); oven temperature, 45 °C held for 5 minutes, then increased to 200 °C at a rate of 5 °C/minute, to 240 °C at 3 °C/minute and held for 20 minutes; carrier gas was helium used at a constant pressure of 10 psi; transfer line temperature, 220 °C; acquisition range 40–400 m/z; scan rate, 1 μscan/second. Each compound was identified using mass spectral data, NIST'11 library (NIST/EPA/NIH Mass Spectra Library, version 2.0g USA), linear retention indices (LRIs), literature data and the injection of standards where available.

Results and Discussion

The following pollutants were quantified: chloroform, dichloromethane, benzene and its derivatives such as toluene, ethylbenzene, trimethylbenzene, ethyltoluene, styrene, xylenes and phenol, linear hydrocarbons from C₆ to C₁₆, chlorinated paraffins and phthalates.

The results showed that the classes of organic pollutants always represented in the sea species analyzed were benzene and its derivatives, and phthalates. These compounds showed the largest amount in crustaceans and mollusk.

In fish species *Auxis thazard thazard* (frigate tuna) and *Scomber scombrus* (Atlantic mackerel) chlorinated paraffins and linear hydrocarbons were the most representative classes of pollutants.

The BTX (benzene, toluene, xylenes) were found to be higher in *Parapenaeus longirostris* (shrimp) than in the other samples analyzed, especially for the amounts of *m*-xylene and *p*-xylene. Toluene was the compound most responsible for the high amounts of BTX in *Octopus vulgaris* (common octopus).

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