

# Occurrence and spatiotemporal variability of sunscreen agents along the polish part of the Baltic Sea coast

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## Abstract

UV-filters accumulate in tissues of aquatic organisms and induce negative effects on fertility and reproduction. Since they are “new emerging pollutants” general monitoring programs are rare and mainly conducted in touristic places, where high temperatures are recorded throughout the year (Spain, the Gulf of Mexico, the Mediterranean coast). This study is focused on benzophenones and derivatives of camphor. The concentration of UV-filters was monitored seasonally in core sediments collected in four Polish beaches (Ustka, Rowy, Darłowo, Czołpino) characterized by various level of touristic pressure along a transect perpendicular to the shoreline over a period of 1 year. Analysis of target compounds in sand cores was performed by means of dispersive liquid-liquid microextraction method followed by high performance liquid chromatography equipped with diode array detector (HPLC-DAD). In samples collected in the most touristic attractive location the presence of benzophenones was confirmed.

**Keywords:** sunscreen agents, river water, sludge, sand sediments, toxicity

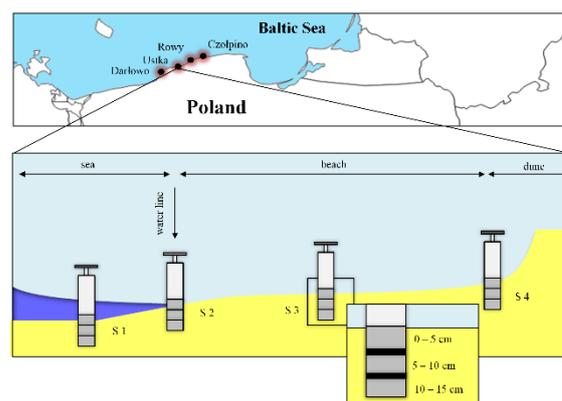
## 1. Introduction

Sunscreen agents which constitute a component of a majority of body care cosmetics are an effective protection against harmful impact of UV radiation which results in skin sunburn or premature skin ageing and skin cancer. Widespread use of UV filters raises concern about their potentially dangerous impact on the environment and human health. Sunscreen agents negatively impact on the coral reef, causing its bleaching and weathering. In the course of numerous analyses hormonal (BP1, BP2, BP3, BP4, HMS, OC, EHMC, BMDBM, 4MBC, OMC) activity of certain UV filters and their harmful impact on fertility and reproduction were proved. Inhibition of oogenesis, egg production and ripe oocytes release females and the loss of secondary sexual characteristics. Inhibition of spermatogenesis, the loss of mating behavior and cessation of reproduction in males was observed.

This research is focused on the detection of benzophenones and derivatives of camphor in beach sediments of four Polish beaches according to seasonality, vertical and horizontal transects over a period of 1 year.

## 2. Materials and Methods

Sand samples were analyzed for 5 UV-filters ((2,4-dihydroxyphenyl) phenylmethanone (BP1), bis (2,4-dihydroxyphenyl) methanone (BP2), oxybenzone (BP3), 3-benzylidene camphor (3BC), 4-methylbenzylidene camphor (4MBC)). Samples were collected seasonally (spring – prior touristic season, summer – high season, autumn – after touristic season) in 2018 along a transect perpendicular to the shoreline in Ustka, Czołpino, Darłowo and Rowy – sandy beaches situated in northern Poland. They differ in terms of the degree of anthropogenic impact. Four sampling sites were located along this transect: site S1 — was located approximately 3 m offshore, at a depth of about 1 m underwater; site S2 — was situated at the waterline (boundary between the beach and the sea); site S3 — was around halfway up the beach, 30 m from the shore; while the most distant site S4 was a sheltered place among dunes, about 60–70 m away from the shore. The sand cores, 15 cm long, were collected in three replicates and divided into 3 sections in the field (0–5 cm, 5–10 cm, 10–15 cm) (Figure 1).



**Figure 1.** Location of investigated sandy beaches along the distance of Polish coast.

Extraction of analytes from 10 g of core sediments was achieved by ultrasonic extraction using 5 ml of MeOH. Likewise, details on the extraction method can be found in Jeon et al. (2006). The separation, identification and quantification of analytes were performed using high-performance liquid chromatography (Shimadzu LC Workstation, Japan) equipped with LC-2AD pump and coupled with diode array detector (SPD-M20A DAD).

HPL-DAD analysis was carried out on a NUCLEOSIL®100-5 C18 column (250 mm x 4.6 mm i.d. x 5 µm film thickness).

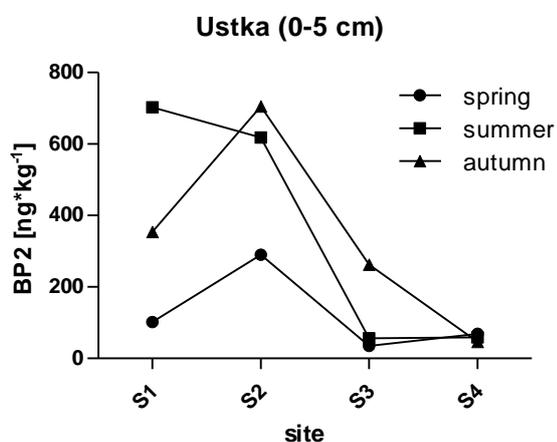
### 3. Results and Discussion

The average concentration of UV-filters in core sediments collected along the Polish coastline is summarized in Table 1. The highest concentration was determined for BP2 with values over 1450 ng kg<sup>-1</sup> on average, followed by 4MBC, BP1 and BP3. The presence of 3BC was not confirmed.

**Table 1.** Mean concentration (ng kg<sup>-1</sup>) and range of UV-filters determined in sand samples.

	N	Mean	Maximum	Minimum
BP1	10	52.7	74.2	16.0
BP2	129	296.2	1474.3	10.2
BP3	16	15.0	52.5	5.4
4MBC	19	78.3	133.0	26.4

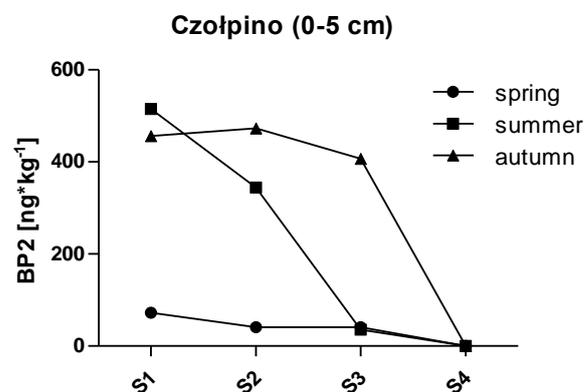
The level of BP2 reported here is within the same range than those previously published by Tarazona et al. (2014) and far less than the levels reported by Vila et al. (2018) and Benedé et al. (2018) for beach sediments collected in Spain. Regarding the occurrence of BP2 in beach sediments according to seasonality as well as vertical transects and horizontal profiles substantial variability was observed. As an example, figure 2 shows the BP2 concentration in the top layer of beach sediments collected in Ustka according to the seasonality and distance from the shore.



**Figure 2.** Seasonal variability of BP2 concentration in top layer of beach sediments collected in Ustka along the horizontal transect regarding water line.

As could be seen the highest BP2 concentration was determined on S1 and S2 (sites having permanent contact

with sea water) in the peak of touristic season. Similar dependence was observed in Darłowo and Czołpino, however in the case of the last location which is a reference place the range of BP2 concentration was lower (Figure 3).



**Figure 3.** Seasonal variability of BP2 concentration in top layer of beach sediments collected in Czołpino along the horizontal transect regarding water line.

### 4. Conclusions

The occurrence of BP2 in beach sediments of Polish coast is similar to those observed in Spain. Some differences are observed between concentration of UV-filters in beach sediments collected from places of various touristic pressure. In general, the highest distance from the water line the lower concentration of sunscreen agents.

### References

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