Occurrence of plastic additives in outdoor air particulate matters from two industrial parks of Tarragona, Spain: Human inhalation intake risk assessment.

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1. Introduction

Plastic additives include several kinds of natural and synthetic chemicals that have various applications in commodities and industrial products. They are commonly used in the processing of plastics and other products to improve their properties (mechanical, optical, thermal, among others) and shelf life by preventing the effects of deterioration which can lead to the oxidation, degradation or alteration of the final product [1]. There are several kinds of plastic additives (for example, plasticizers, flame retardants, pigments, thermal stabilizers and foaming agents, among others) and the present study focuses on UV stabilizers (Tinuvins) and phenolic and aromatic antioxidants which are relatively cheap, widely used and chemically stable [2,3]. For this reason, they are present in a wide range of materials including cosmetics, personal care products and pharmaceuticals [4,5], food [6–10], paints [11–13], surface coatings [14], building materials [15–17] and all sorts of plastic-based products [18–22].

Because of their extensive use, they can migrate to the environment and humans are therefore exposed to these compounds. Plastic additives can be introduced into the environment because they are used and produced in industrial processes and because they can also be released from the matrix of the final product over time [6,12]. Many studies have shown that they are present in such environmental compartments as natural waters [23–27], drinking water [20], influent and effluent waters of wastewater treatment plants (WWTPs) [11,23,27], sewage sludge [6,14,24] and indoor dust [17,28–31] with concentrations ranging from part-per-trillion (ppt) to part-per-million (ppm) [4,24]. Plastic additives have also been found in food because they migrate from the preserving and packaging materials [8,10,18,21,32]. Therefore, human exposure to these contaminants via ingestion or dermal contact is obvious, and is also being confirmed by their detection in human urine samples [33,34]. However, ambient inhalation is another possible pathway by which humans can be exposed, although little is known about it. As far as we know, no information is available about the occurrence of these compounds in outdoor environments. Even so, because of the moderate molecular weights, octanol-water coefficients and low vapour pressures of some of these compounds, they are expected to be mainly associated with suspended particulate matter in the air [15].

For all these reasons, in recent years, these groups of emerging pollutants have been raising increasing concern due to their reported toxic effects [23,30,35,36]. It has been reported that direct contact with materials treated with Tinuvins can have effects such as dermatitis and skin irritation [15,23]. Moreover, some antioxidants may cause allergic reactions such as asthma and hives and they can also act as endocrine disruptors [37]. Besides, data on the bioaccumulation of Tinuvins in birds and aquatic organisms [38,39] suggest that continuous exposure may lead to concentrations in the human body [15]. Although data regarding the ecotoxicological risks of both types of antioxidant are scarce [5], some animal laboratory tests have already demonstrated that, at high doses, butylated hydroxy-toluene (BHT) may act as a carcinogenic agent [5]. Among other antioxidants, 3(2)tert-butyl-4-methoxyphenol (BHA) has been reported to be a tumour promoter, an endocrine disruptor, and a carcinogen [35]. Furthermore, attention must be paid to their degradation products, which also present an environmental and human health risk [6,24]. The European Chemicals Agency (REACH) has reported that target compounds such as BHT, UV320 or UV328 may have toxic effects on human health and the environment [40]. Therefore, new analytical data are required to support assessments of human health risks associated with different kinds of exposure to these pollutants.

In this regard, reliable analytical methods are required that can simultaneously determine several plastic additives and some of their degradation products in outdoor air and thus be able to assess the exposure and risk to the population. Various analytical methods have been developed to determine some of these additives. The most common of which are based on liquid chromatography (LC) coupled to mass spectrometry (MS) or tandem mass spectrometry (MS/MS) because of the properties of the target compounds selected [1,8,21]. However, Tinuvins are poorly ionised in the electrospray source in LC-MS systems [14]. Nevertheless, gas chromatography (GC) coupled to MS or MS/MS could be a useful alternative for multi-residue analysis which evaluates the presence of several types of polymer additive [3,16,31,41].

Regarding the collection of particulate matter samples, quartz fibre filters (QFFs) and glass fibre filters (GFFs) can be used. QFFs are the most commonly used because GFFs may present higher blank levels of some compounds [42,43]. Filters are most often extracted with an organic solvent using an extraction technique such as ultrasound-

assisted extraction (UAE), microwave-assisted extraction (MAE), solid-liquid extraction (SLE), Soxhlet extraction or pressurised liquid extraction (PLE) [6,18,19,21,39]. Among these extraction techniques, PLE consumes less solvent, has shorter extraction times, and presents good recovery values, although it requires specific equipment [15].

The main objectives of the present study are (1) to develop an analytical method based on PLE followed by GC-MS to simultaneously determine 12 polymer additives (7 light stabilizers, 2 aromatic antioxidants, 3 phenolic antioxidants) and 5 of their degradation products, (2) to evaluate the presence of these compounds in PM_{10} outdoor air samples from two locations influenced by industry, and (3) to assess the non-dietary human exposure to these compounds through outdoor air inhalation for several age groups (infants, children, and adults) in the two locations studied for two different exposure scenarios. To the best of our knowledge, this is the first study to show the occurrence of several plastic additives in particulate matter from outdoor air and to assess human exposure via ambient inhalation. Consequently, the methodology developed will be useful for future research into the origin of these compounds, their distribution, fate, accumulation and the range of concentration levels found in locations affected by industry.

2. Experimental part

2.1. Reagents and standards

The solvents used to extract the analytes from QFFs and to prepare the standard solutions were methanol (MeOH), ethyl acetate (EtAc), dichloromethane (DCM) and n-hexane, all of which were GC grade with purity >99.9% from J.T. Baker (Deventer, the Netherlands). Dimethylformamide (DMF) was used to prevent the compounds from volatilizing in the evaporation step and was obtained from Sigma-Aldrich (St. Louis, USA). The nitrogen gas for the PLE instrument and the helium gas for chromatographic analysis with a purity of 99.999% were sourced from Carburos Metálicos (El Morell, Tarragona, Spain).

The target compounds were: three phenolic antioxidants (PAs): 2,6-di-tert-butyl-4-methylphenol (BHT), 3(2)-tert-butyl-4-methoxyphenol (BHA) and 2,4-di-tert-butylphenol (2,4-DTBP), and five of their degradation products: 3,5-di-tert-butyl-4-hydroxybenzaldehyde (BHT-CHO), 3,5-di-tert-butyl-4-hydroxybenzoic acid (BHT-COOH), 2,6-di-tert-butylcyclohexa-2,5-diene-1,4-dione (BHT-Q), 2-6-di-tert-butyl-4-(hydroxymethyl)phenol (BHT-OH) and 2-tert-butylbenzene-1,4-diol (TBHQ); two aromatic antioxidants (AAs): octadecyl3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (Irganox 1073) and tris(2,4-di-tert-butylphenyl) phosphate (Irgafos 168); and seven ultraviolet stabilizers (Tinuvins): 2-(3,5-di-tert-butyl-2-hydroxyphenyl)-2H-benzotriazole (UV320), 2-tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl)-4-methylphenol (UV326), 2,4-di-tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl)phenol (UV327), 2-(2H-benzotriazol-2-yl)-4,6-di-tert-pentylphenol (UV328), 2-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol (UV329), 2-(2-hydroxy-5-methylphenyl)benzotriazole (UV P) and 2-(2H-benzotriazol-2-yl)-4-methyl-6-(2-propenyl)phenol (Allyl-BZT). They were all purchased from Sigma-Aldrich except BHT-CHO and UV320 which were obtained from LGC standards (Barcelona, Spain). Their chemical structures and physico-chemical properties are shown in Table S-1. Internal standard calibration was performed using acenaphtene-d_{10} (ACP-d_{10}) and phenantrene-d_{10} (PNT-d_{10}) from Sigma-Aldrich. Individual stock solutions of 4000 mg L^{-1} and an intermediate mixture solution of each compound group at 500 mg L^{-1} were prepared in ethyl acetate and stored at -20ºC. For daily work, a mixture solution of all target compounds was prepared in ethyl acetate at 10 mg L^{-1} and stored at 4ºC in the dark.

2.2. Sampling sites

The region of Tarragona is a coastal area in southern Catalonia (Spain) and has one of Europe's largest chemical hubs. There are two important industrial parks, called North and South (Figure 1), which comprise more than 30 chemical companies in an area of 1,200 ha that also has harbour facilities. Every year, these complexes produce almost 21 million tonnes of products, mainly fuels and plastics, more than 50% of which are exported to other countries from Tarragona harbour [44].

The sampling sites were in the village of Constantí and Tarragona harbour (Figure 1) because they are both in the industrial complexes mentioned above. Constantí is less

than 3 km south-west of the North complex which consists of chemical factories and a petrochemical industrial park. It is also next to an urban waste incinerator. Tarragona harbour is next to the South Park, which mainly produces plastics, and has a small refinery, a WWTP and storage facilities for chemical products.

2.3. Sampling conditions

PM_{10} samples were taken on the rooftops of governmental automatic measurement stations about 3 metres from the ground at the two sampling sites described in section 2.2. The sampling campaign was conducted from November 2017 to March 2018. During this period, ten samples were collected at both locations.

Samples were taken using two high volume air samplers: MCV-PM_{10} (MCV S.A., Collbató, Barcelona, Spain) in Constantí and TE-6070 PM_{10} (Tisch Environmental Inc., Village of Cleves, Ohio, USA) in Tarragona harbour. All the samples were collected after a period of 24 h working at a flow-rate of approximately 30 $m^3\ h^{-1}$ in Constantí and 50 $m^3\ h^{-1}$ in Tarragona harbour. Therefore, around 720 m^3 and 1,200 m^3 of air were collected in each sampling, respectively. A PM_{10} QMA micro-fibre quartz filter (diameter 102 mm) supplied by Whatman (Maidstone, UK) was used to collect the PM_{10} samples. In Constantí, the filter was 150 mm Ø and in Tarragona harbour it was 8 in. × 10 in.

Once the filters had been sampled, they were wrapped in aluminium foil, placed in a glass amber jar with a screw top, and kept at -20 ºC until they were analysed.

2.4. Extraction procedure

Plastic additives were extracted from filters using an ASE 350 Accelerated Solvent Extraction system (Dionex, Sunnyvale, Ca, USA). The QQFs were cut in small pieces and were added after a cellulose filter and 1 g of diatomaceous earth (DE) into 11 mL stainless steel extraction cells. The solvent used was EtAc. PLE was conducted in a single cycle extraction with a 5 min preheat time, an extraction temperature of 80 ºC, an extraction pressure of 1,500 psi, a nitrogen purge time of 120 s and a flushing volume of 100%. An extract of *ca.* 15 mL was obtained. To this extract, an aliquot of 400 µL of

DMF was added to prevent evaporation to dryness, and it was then concentrated using a miVac Duo concentrator (Genevac, Ipswich, UK) to a volume of *ca*. 200 µL. Subsequently, 10 µL of the internal standards mix at 100 mg L^{-1} were added and finally it was reconstituted to a final volume of 1 mL with EtAc and injected into the GC-MS system.

2.5. Chromatographic analysis

Samples were analysed in a GCMS-QP2010 Ultra High Performance Gas Chromatograph equipped with an automatic injector and a Mass Spectrometer with an EI ionization source and a quadrupole analyser (Shimadzu Corporation, Izasa S.A., Madrid, Spain). The chromatographic column was a capillary column Zebron ZB-50, 50% phenyl-50% dimethylpolysiloxane (30 m x 0.25 mm i.d.; 0.25 µm film thickness), from Phenomenex (Torrance, CA, USA). For the analysis, a volume of 1 µL was injected in splitless mode, at a flow-rate of 1.2 mL min^{-1} of helium as carrier gas. The injector was set at a temperature of 300 ºC. The GC oven temperature was initially 80 ºC and it was increased to 250 ºC at 10 ºC min^{-1}, then to 275 ºC at 5 ºC min^{-1} and finally to 320 ºC at 20 ºC min^{-1}, where it was held for 5 min.

The mass spectrometer acquired data in selective ion monitoring (SIM) at an electron impact energy of 70 eV. The ion source and GC-MS interface temperatures were set at 230ºC and 280ºC, respectively. The compounds were quantified by internal standard method. Table 1 summarises the retention times, the internal standards and the quantifier and qualifier ions selected for each compound.

2.6. Quality assurance/quality control (QA/QC)

To minimize cross contamination, all the processes were carried out using only glassware that had previously been washed and solvent rinsed. Moreover, the QFFs were conditioned at 600 ºC for 4, covered with aluminium foils and stored in the freezer until they were used. Method blanks, equipment blanks, solvent blanks and standard controls were included during the GC-MS batches for QA/QC. Triplicates were carried out for all experiments tested. The analytes were quantified using an internal standard calibration method. Eleven calibration levels (varying from 1 µg L^{-1} to 10,000 µg L^{-1},

for most of the compounds) were injected for the instrumental calibration, and the linearity of the calibration curve (r^2) was >0.990 for each analyte. Repeatability and reproducibility were expressed as percent relative standard deviation (%RSD) and were calculated as the percent ratio between the standard deviation and the arithmetic mean of the values obtained for the tests done inter-day or intra-day, respectively. Recovery values for each analyte were calculated as the percent ratio between the observed value and the actual value with the following equation (Eq. (1)):

$$\text{Recovery (\%)} = \frac{x_i - x_0}{x_{ss}} \times 100 \qquad \text{Eq. (1)}$$

where x_i and x_0 are the GC-MS responses of each analyte in the spiked and blank samples, respectively, and x_{ss} is the response of each analyte in the standard solutions.

2.7. Calculations to assess human exposure via inhalation

To estimate human exposure, estimated daily intake (EDIs, in ng kg_{bw}^{-1} day^{-1}) via ambient inhalation was calculated as shown in Eq. (2) [45]:

$$\text{EDI (inh.)}_{a_p} = \frac{C_{a_p} \times IR \times RR \times ABS_a \times ET \times EF \times ED}{BW \times AT} \qquad \text{Eq. (2)}$$

where $EDI\ (inh.)_{a_p}$ is the average daily dose for each compound *a* via ambient inhalation in the microenvironment studied *p* (ng kg_{bw}^{-1} day^{-1}), C_{a_p} is the concentration of *a* in the samples of microenvironment *p* (ng m^{-3}), *IR* and *BW* are the inhalation rate (m^3 day^{-1}) and body weight (kg), respectively, *RR* is the retention rate of inhaled air (%), ABS_a is the percentage of compound *a* absorbed into the bloodstream (%), *ET* is the exposure time (h day^{-1}), *EF* is the exposure frequency (days $years^{-1}$) and *ED* is the exposure duration (years). *AT* is the average time (period in days over which exposure is averaged), in the case of these compounds, for non-reported carcinogenic effects of human exposure via inhalation. *AT* is *ED* per 365 days $year^{-1}$.

Therefore, human exposure to each kind of plastic additive was reported using the sum of concentrations for each group in each microenvironment. Different subpopulation

groups, classified according to age (infant, children and adult) and divided into off-site workers and off-site residents, schools and by-passers for adults were taken into account. Moreover, with the obtained concentrations, two exposure scenarios –low (based on geometric mean) and high (95^{th} percentile)– were simulated for each microenvironment. For non-detected or non-quantified compounds, the USEPA criteria [46] were followed considering half of the method detection limit (MDL) or method quantification limit (MQL), respectively.

2.8. Statistical analysis

An experimental design based on a multifactorial design of $3^2 2^1$ was used to optimise the PLE extraction conditions. Statistical analysis for the calculation of standardised effects was carried out with STATGRAPHICS Centurion XVII v.17.2.00 from StatPoint Technologies, Inc. (Warrenton, VA, USA). The statistically significant bound at the 95% confidence level of the Pareto charts was also calculated using the software mentioned above. Moreover, response surface graphs for each compound were created with Minitab® 18 statistical software from Minitab Inc. (State Collage, Pennsylvania).

3. Results and discussion

3.1. Method optimization

3.1.1. Chromatographic optimization

EtAc was chosen as the solvent for standard preparation because it gave better results than MeOH, DCM and n-hexane (higher peak area and better repeatability). Moreover, a keto-enol tautomerism of TBHQ was observed when n-hexane was used with a ratio of approx. 3, causing two peaks to appear for this compound. Several temperature programs were tested to optimise the separation using a Zebron ZB-50 capillary column. Finally, the optimum chromatographic parameters are the ones described in section 2.4.

Once the separation had been optimized (Figure S-1), instrumental validation parameters were evaluated. Internal standard calibration was used with acenaphthene-

d_{10} and phenanthrene-d_{10} as internal standards. As far as the linearity range was concerned, the lowest point of the calibration curves was the instrumental quantification limit (IQL) and its signal was more than 10 times the signal to noise ratio. These values ranged from 5 µg L^{-1} for 2,4-DTBP, UV320 and UV328 to 100 µg L^{-1} for Irganox1076 and UV P. The lowest instrumental detection limit (IDL), calculated as 3 times the signal-to-noise ratio, was 1 µg L^{-1} and the highest was 25 µg L^{-1} for the same compounds. The calibration curves were linear up to 10 mg L^{-1}, except for TBHQ which was 5 mg L^{-1}. For BHT-COOH, sensitivity was low when GC-MS was used and its detection limit was 2.5 mg L^{-1}. Therefore, the compound was not taken into account for further tests. This may be due to the presence of the carboxylic acid group which causes a bad peak shape and a long tail (see Figure S-1). Instrumental repeatability and reproducibility, calculated at 0.1 mg L^{-1} (n=3) and expressed as relative standard deviation (%RSD), did not exceed 5% (except 6% and 7% for TBHQ and UV329, respectively), while the %RSD values for reproducibility between days were lower than 10%, which corresponds to TBHQ.

3.1.2. PLE optimization

Initial PLE experiments were carried out to select the optimal extraction solvent. Taking into account the solubility of the target compounds, the solvents tested were: DCM, EtAc, MeOH and n-hexane. Prior to PLE optimisation, the evaporation step for the various solvents tested was evaluated using miVac Duo Concentrator. In all cases, losses were observed for the more volatile compounds. Therefore, 400 µL of DMF was added prior to the evaporation to prevent the compounds from volatilizing [43]. This approach improved the results, and the losses were less than 5%.

Once the evaporation procedure had been checked, the extraction solvent was optimised. Several QFFs (150 mm Ø) spiked with 100 µL of a standard solution at 10 mg L^{-1} for all the compounds were extracted at 80 ºC and 1.500 psi in a single cycle of 5 min for all the extraction solvents tested. In all the experiments, the flush volume and purge time were set to 100% and 120 s, respectively. Non-spiked filters were also analysed for each test and the signal of the target compounds was taken into account. PLE extracts were mixed with 400 µL of DMF and evaporated to a volume of *ca.* 200

µL. Then, 10 µL of the internal standards solution at 100 mg L^{-1} was added. Finally, this mixture was adjusted to 1 mL with EtAc and analysed by GC-MS.

During these solvent optimisation tests, various compounds were observed in the filter blanks at concentrations below 70 µg L^{-1}, depending on the solvent used. The target compounds found were the following: BHT-Q, BHT, Irgafos168 and Irganox1076 (of which BHT-Q presented the highest concentrations). Therefore, conditioning tests for QFFs and DE were carried out in order to decrease the concentrations found in the filter blanks. QFFs and DE were separately conditioned at 600ºC during 4 h and PLE extractions were done with each extraction solvent. Subsequently, it was observed that conditioning DE did not decrease the signal but conditioning QFFs reduced the blank signals to <MQL and even eliminated (<MDL) some compounds (BHT and Irgafos168). Therefore, QFFs needed to be conditioned before being sampled.

The results obtained for the optimisation of the extraction solvent are summarised in Figure 2. In general, the results were best when EtAc was used to extract the target compounds. Therefore, it was used as the extraction solvent thereafter.

Following the PLE optimisation, the effects of extraction temperature, extraction time and number of cycles were evaluated using a multifactorial design $3^2 2^1$ composed of 18 randomised experiments. Table 2 summarises the factors and levels selected for the experimental design.

In all of these randomised experiments, the pressure was set to 1500 psi, flush volume to 100% and purge time to 120 s. By way of example, the calculated standardised effects for the three factors and the 2-factor interactions for BHT-OH and Irgafos 168 are shown in the Pareto charts in Figure S-2. The standardised effect is obtained by dividing the estimated effect by its standard error. The vertical line indicates the statistically significant bound at the 95% confidence level.

The temperature factor was statistically significant for most of the compounds. As an example, Figure S-2 shows that increasing the temperature from 80 to 120 ºC had a negative effect on the extraction efficiency of polymer additives. The extraction time

and the number of cycles did not have an important effect at the levels studied, and were statistically insignificant for all the compounds.

As far as 2-factor interactions are concerned, the effect of the interaction between temperature and the number of cycles (AC) was only significant for BHT-Q. Therefore, the effect of increasing the temperature in the extraction process is different depending on the number of cycles.

Response surface graphs of the factors studied were fitted for each compound. As an example, Figure S-3 shows the fitted response surface for BHT-CHO at 1 cycle. Results were similar for most of the target compounds. In general, extraction times up to 10 min increase extraction recoveries, except for BHT whose recoveries were higher when the extraction time was shorter. For all the PA compounds, recoveries were clearly higher at low temperatures. Meanwhile, for some Tinuvins and AAs the increase in the recoveries at lower temperatures was only a little higher. The number of cycles did not improve the recovery values, so one extraction cycle was chosen.

Finally, from the results obtained for all the compounds, we set an extraction temperature of 80 ºC, an extraction static time of 10 min and 1 cycle. Table 1 shows the recovery results for blank filters spiked for a final concentration of 2.5 mg L^{-1} and their repeatability expressed as the relative standard deviation (%RSD, n=3). As it can be seen, the recovery values were quite high, most of them being around 100%, with the exception of BHT and Irgafos 168, which were about 75%.

3.2. Method validation

Once the PLE parameters had been optimised, the whole method was validated. The optimal PLE/GC-MS method was applied to sampled filters previously conditioned to evaluate the recoveries in real air samples. Therefore, sampled QFFs (150 Ø) were divided into two parts. One of these parts was spiked at low or high concentration level, (i.e. 0.3 and 6.9 ng m^{-3}, respectively) and the other part was used as blank sample to subtract the concentration level of the compounds, in order to calculate the recovery values. These values ranged from 66% (Irgafos 168) to 119% (UV326) for both concentration levels with method repeatability values (intra-day precision), expressed as

%RSD (n=3), between 1 and 13% (see Table 1). Method reproducibility (inter-day precision) was evaluated at 6.9 ng m^{-3}, and was found to be between 2 and 19% (%RSD, n=3). The recovery values obtained for the spiked blank filters and the spiked sampled filters were quite similar, therefore, the analytes were quantified by internal standard calibration and the recoveries were used to calculate the final sample concentration.

The MDL and MQL were calculated with their IDL or IQL and taking into account the sampling volume and the recoveries obtained. For the samples taken in Constantí (720 m^3), MDLs ranged from 1.0 pg m^{-3} (2,4-DTBP, UV320 and UV328) to 41 pg m^{-3} (UV P) and MQLs were between 6.8 pg m^{-3} (2,4-DTBP) and 162 pg m^{-3} (UV P). All of the validation results are shown in Table 1. For the Tarragona harbour samples (1,200 m^3), the MDLs ranged from 0.8 to 24 pg m^{-3} and MQLs were between 4.0 and 97 pg m^{-3}.

3.3. Polymer additives in PM_{10} outdoor air samples

The PLE/GC-MS method was used to analyse the PM_{10} outdoor air samples from Constantí and Tarragona harbour. Table 3 shows the arithmetic mean, the concentration range (in pg m^{-3}) and the detection rate (in %) of each compound for the samples collected at both sampling points, as well as the sum of the compounds belonging to each family.

The results obtained at both sampling points show that AAs were detected in all samples (DR = 100%) at higher concentrations than the other compounds. Irgafos 168 and Irganox 1076 are two of the most manufactured and/or imported compounds in the European Economic Area (EEA), in excess of 100,000 tonnes per year [40]. Furthermore, several authors have reported their presence in packaging or food packaging at levels of high μg g^{-1} [8,18] and they are expected to occur in the environment because of their widespread use in several commodities and industrial processes. Moreover, the highest concentrations were found in Tarragona harbour, maybe because of the nearby plastic industries. As an example, a chromatogram obtained from a Tarragona harbour sample is shown in Figure 3.

In contrast, Tinuvins were the least detected compounds in both locations, with detection rates of 30% and 40% in Constantí and Tarragona harbour, respectively. The Tinuvins detected were as follows: UV P, UV320, UV328 and UV327. Of these, UV P was the most detected with the largest concentrations in Tarragona harbour, which reflects the fact that it is more commonly used than the others (1,000-10,000 tonnes per year vs. 100-1,000 tonnes per year in the EEA) [40]. Moreover, in comparison to other compounds, Tinuvin concentrations were 10 times lower at both sampling points. These results are in line with those obtained by Carpinteiro et al. [15], Kim et al. [47] and Rani et al. [38], who reported that concentrations (ng g^{-1}) of these contaminants were lower in indoor dust from different compartments (private houses, vehicle cabins, administrative buildings, etc.) and countries (Philippines, South Korea and Spain), and in plastic marine debris and new products than the levels of aromatic and phenolic antioxidants.

As far as PAs are concerned, the parent antioxidants are BHT, BHA and 2,4-DTBP, which can also come from the degradation of bulky structured Irganoxes while products are being processed [38]. The rest of the target antioxidants are transformation products (TPs) of the parent compounds obtained by different transformation pathways [5,10,28]. The precursors BHT and 2,4-DTBP were found in all samples, with mean concentrations of 121 and 310 pg m^{-3} for Constantí and 100 and 163 pg m^{-3} for Tarragona harbour, respectively. However, the other precursor BHA was not detected in any sample from either location. This may be because its $\log K_{ow}$ is lower than those of the other precursors (see Table S-1), which means that it is less likely to be adsorbed onto the atmospheric particles. In addition, BHA is less used and consequently less produced (100 - 1,000 tonnes per year in the EEA [40]) compared with the other compounds. These results are in line with those obtained by Wang et al. [17], who reported the detection of BHA in house dust from China, in contrast to the other elevel countries studied, where this compound was not found in any samples. However, Liu et al. [4] found a high detection frequency of BHA but with a low average proportion (14.2 – 73.8 ng g^{-1}) in urban and rural house dust samples also in China (Jinan city).

BHT-Q and BHT-CHO were the only TPs found (DR = 100%), with BHT-Q being the most abundant, whereas TBHQ and BHT-OH were not found at either of the sampling points. This fact could be explained by the absence of BHA, the major transformation product of which is TBHQ [5]. Moreover, the lack of BHT-OH might be due to its

possible oxidation to BHT-CHO in ambient conditions via photodegradation mechanisms as suggested by Fernandez-Alvarez et al. [28]. In addition, the non-detected PAs are those with the lowest logK_{ow} (see Table S-1), which may be another reason why they have not been detected in any sample. 2,4-DTBP may be present because it has long been used as a chemical intermediate for the synthesis of Tinuvins, antioxidants and other chemical intermediates [16]. Finally, between 10,000 and 100,000 tonnes of BHT are manufactured in the EEA every year and it is one of the most used plastic additive, so it is only to be expected that it will be found in the environment. However, as mentioned above, Fernandez-Alvarez et al. [28] made a study of UV irradiation to BHT to elucidate its TPs. They showed that in less than 20 min BHT completely photodegraded into its TPs, which explains why it was found in lower concentrations than BHT-Q. Zhang et al. [30] also reported the ubiquitous detection in indoor dust of BHT in Nanjing (China), the prominent transformation product of which is BHT-Q followed to a lesser extent by BHT-CHO and BHT-OH. This order may be also explained due to their hydrophobicities (log K_{ow} = 5.10, 4.42, 4.20 and 3.68, respectively).

3.4. Human exposure via outdoor inhalation

Several factors can influence the extent to which humans are exposed to air contaminants (in vapour or the particulate phase), such as the concentration of chemicals at the location, human breathing rate, human activity pattern, duration and frequency of exposure, gender and body weight, among others [45]. Therefore, it is important to take into account all these parameters when calculating EDIs via ambient inhalation. Table S-2 shows the values for the parameters used in Eq. (1) recommended by [45] for PM_{10} ambient inhalation. Moreover, the retention rate of inhaled air (*RR*) and the percentage of chemicals absorbed into the bloodstream (ABS_a) were assumed to be 100% for all the compounds in all cases and scenarios. To the best of our knowledge, this is the first study to provide multi-case exposure assessment for such a wide variety of polymer additives based on outdoor air samples from two locations influenced by different industrial activities. However, the limited number of samples and their representativeness is a major source of uncertainty in these intake values.

Figure 4 shows the EDIs for each group of plastic additives and the different subpopulation groups in each microenvironment studied. In general, EDIs were higher for infants and children than for adults, and also higher for adult residents than adult workers because they spent more time in outdoor environments. This suggests that children may be at higher risk because they are more sensitive during the developmental stage. The EDIs in high exposure scenarios were calculated on the basis of the 95th percentile concentrations of the compounds, while the EDIs in low exposure scenarios were calculated using the geometric mean (GM) concentrations. In addition, human exposure to all compounds was greater in Tarragona harbour than in Constantí. In the worst case exposure scenario, the ∑PAs EDIs for Tarragona harbour varied from 113.6 to 320.0 pg kg_{bw}^{-1} day^{-1} (Table S-3). In comparison with the EDIs of food in Korea (40 µg kg_{bw}^{-1} day^{-1}) and America (0.39 mg kg_{bw}^{-1} day^{-1}) [10], the ambient inhalation exposure was much lower. On the other hand, in comparison with exposure through the ingestion of indoor dust for urban and rural residents in China, similar values can be seen for adults who reside in rural areas (ranging from 0.06 to 0.94 ng kg_{bw}^{-1} day^{-1} based on the GM of the concentrations) [6].

Unlike the PAs and AAs in Tarragona harbour, the EDIs of Tinuvins were lower than in Constantí. As can be seen in Table S-3, the Tinuvins values in Constantí ranged from 21.2 (job-adult) to 59.7 pg kg_{bw}^{-1} day^{-1} (children) for the worst case of exposure, which was 2 times higher than the values in Tarragona harbour. Kim et al. [47] calculated the EDIs for some Tinuvins through house dust ingestion in the Philippines. In the worst exposure scenario, they calculated EDI values between 0.009 (UV234) and 0.3 ng kg_{bw}^{-1} day^{-1} (UV320) for adults and between 0.2 and 6.3 ng kg_{bw}^{-1} day^{-1} for children. Therefore, the results obtained in the present paper and those obtained in the study mentioned above show that exposure to these compounds was slightly higher through dust ingestion. These results demonstrate that house dust ingestion is more significant as an exposure pathway to these contaminants for the population than ambient inhalation. However, inhalation intake has to be considered as one of the possible human exposure pathways.

Finally, due to the low toxicological information, only data on chronic effects such as the non-observed adverse effect level (NOAEL) values were available for UV328 (15 mg kg_{bw}^{-1} day^{-1} for rats) [47], UV320 (0.1 mg kg_{bw}^{-1} day^{-1} for male rats and 2.5 mg kg_{bw}^{-}

^{1} day^{-1} for female rats) [39] and BHT (25 mg kg$_{bw}^{-1}$ day^{-1} for rats) [10]. These NOAELs were used to estimate the reference dose value (RfD) for each compound. The RfDs were calculated by dividing NOAEL by a safety factor of 10,000 as described by Kim et al. [47] to minimize the toxicological risks for compounds. The RfDs for infants, children and adults were as follows: UV328=0.024, 0.044 and 0.105 mg day^{-1}; UV320=0.16, 0.29 and 0.7 µg day^{-1}; and BHT=0.04, 0.07 and 0.18 mg day^{-1}, respectively. Therefore, comparing the EDIs obtained in this study with the RfDs, it can be observed that ambient inhalation exposure is not dangerous for the human population that are close to the sampling points. However, more detailed information is required for other exposure pathways, because ambient inhalation is supplemented with other exposure pathways, such as ingestion of different foods and beverages, indoor inhalation and dermal absorption.

4. Conclusions

A simple and sensitive analytical method to simultaneously determine 16 plastic additives including their transformation products using PLE followed by GC-MS has been developed, validated and applied to real samples of particulate matter from outdoor air. The method extracts most of the target compounds with recoveries above 85% and can detect and quantify them even at low pg m^{-3} levels.

Samples collected from two locations influenced by different types of industrial emissions showed the presence of these compounds, the most commonly detected of which were the aromatic antioxidants (680-826 pg m^{-3}, DR=100%) and phenolic antioxidants (670-937 pg m^{-3}, DR=57%) compared to Tinuvins (69 – 132 pg m^{-3}, DR < 40%). The only PAs detected, where the 2,4-DTBP, BHT and their transformation products (BHT-Q and BHT-CHO). Nearly all of the Tinuvins were determined in one sample from both sampling sites, with UV328 being the most detected compound.

The results show that these polymer additives are released into the atmosphere, possibly due to their widespread use in the plastic industry and their presence in several daily use products. Hence, humans are shown to be subject to chronic exposure via ambient inhalation. The EDIs for the various population age groups were low for ambient air inhalation. In the worst case scenario, 0.51 ng kg$_{bw}^{-1}$ day^{-1} was the highest EDI for

children, which is five times lower than the intake calculated for urban indoor dust. Therefore, the results derived from this study suggest that human exposure to these plastic additives via ambient inhalation do not pose an immediate health risk to the population of the Tarragona region.

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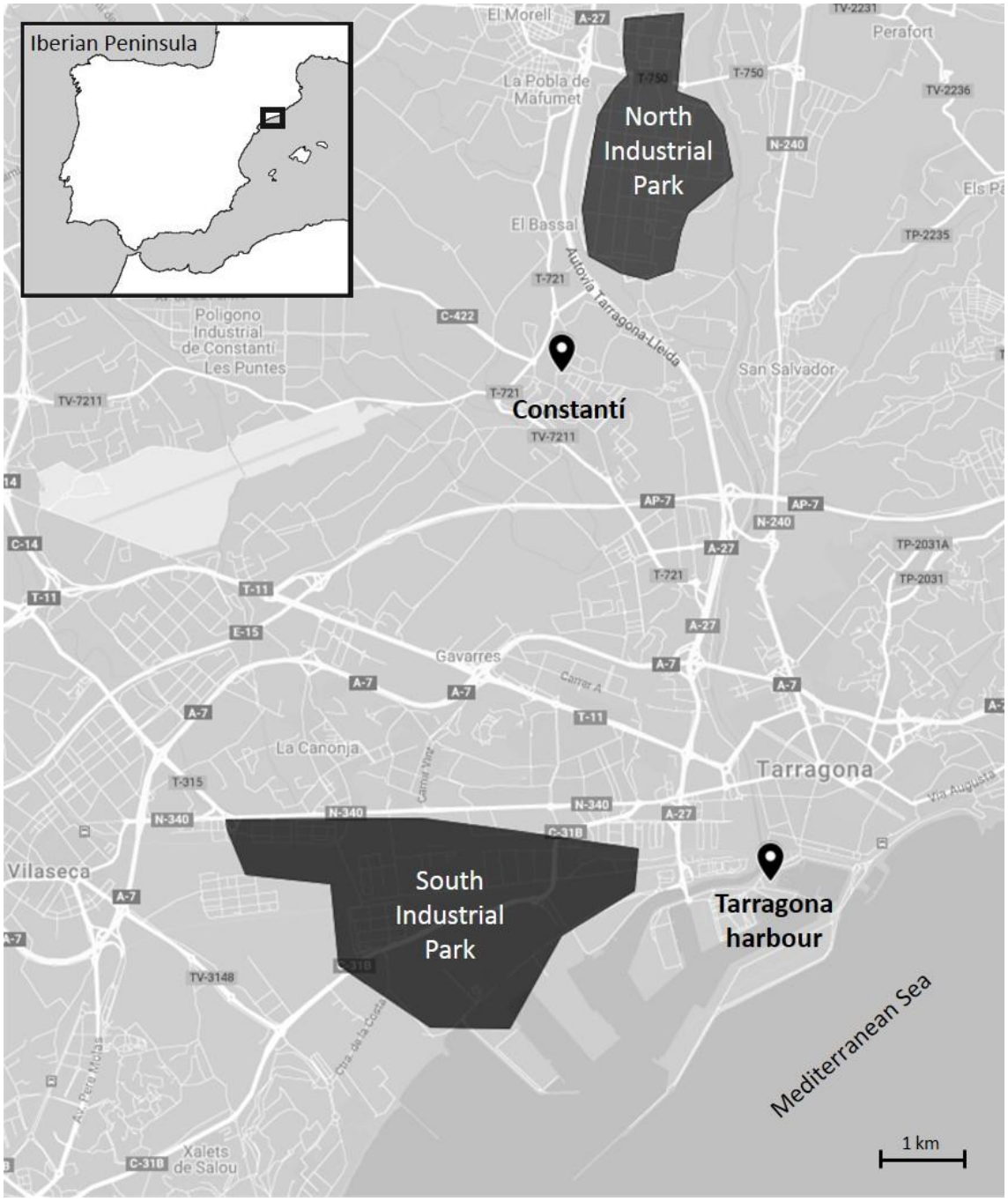

Figure 1. Map of Tarragona region showing the location of the sampling points and the Industrial Parks.

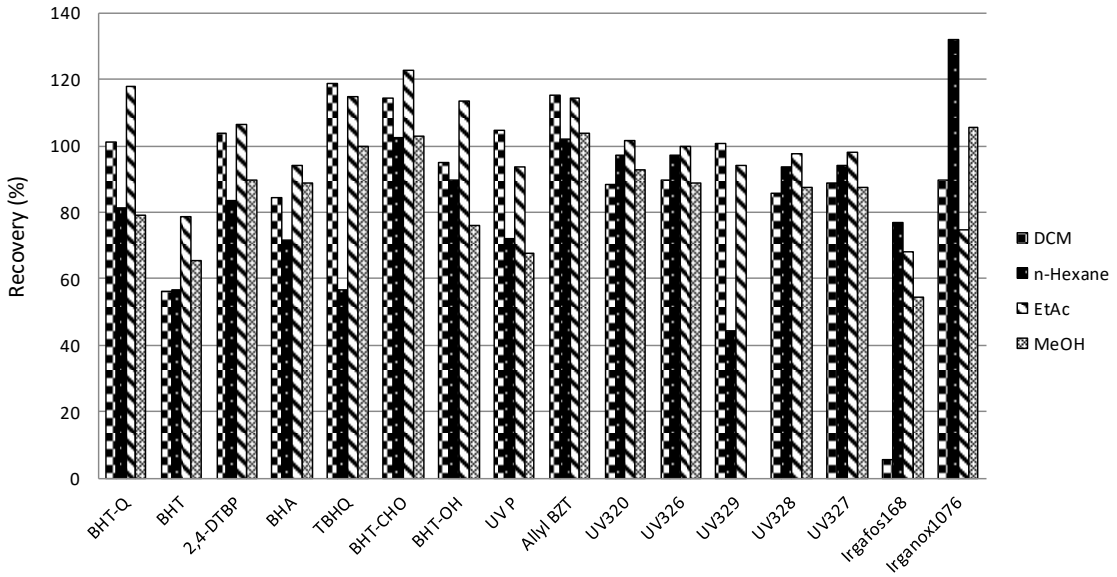

Figure 2. Influence of the solvent on the efficiency of the extraction process (n=3, Mean±SD).

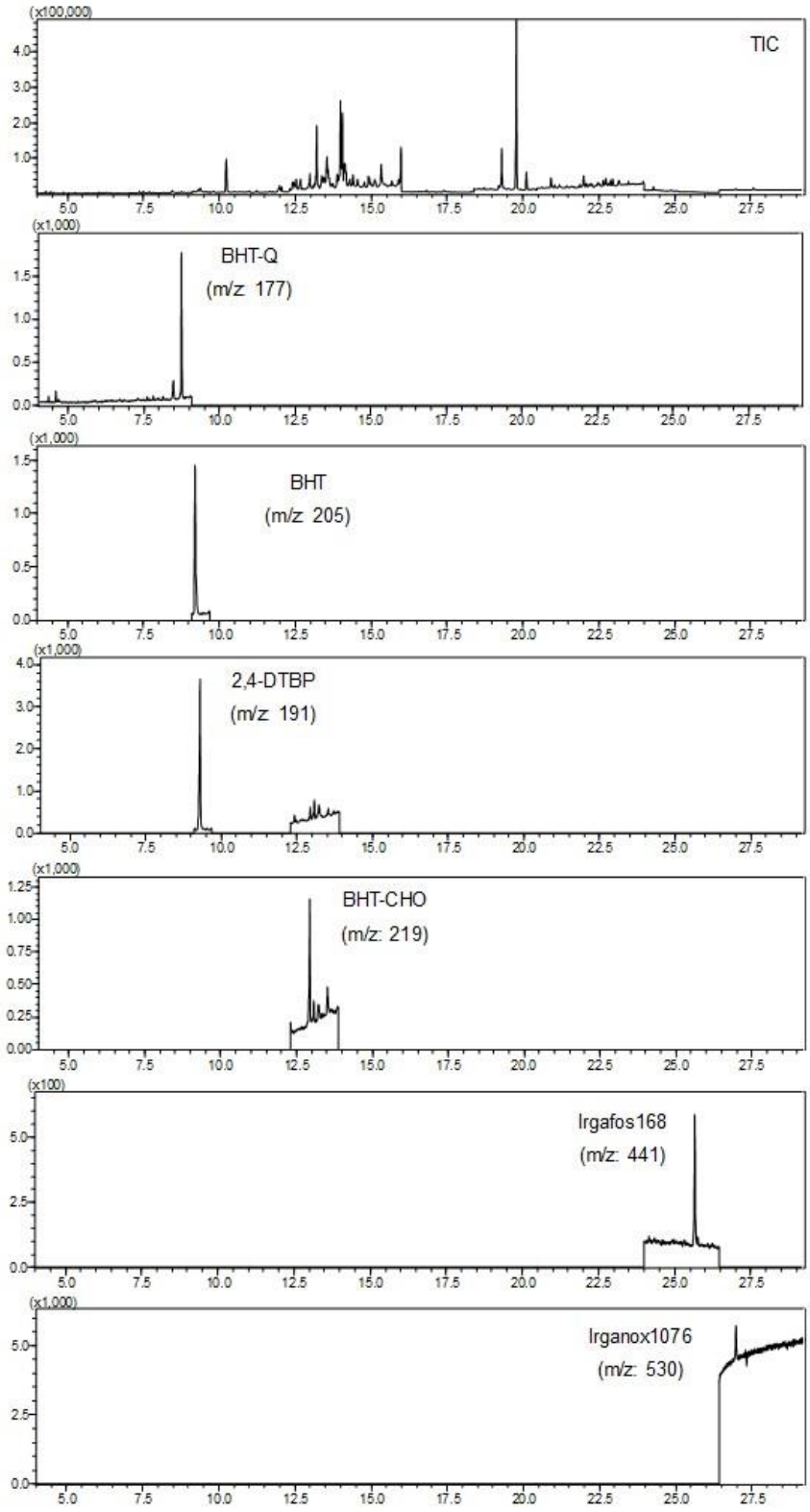

Figure 3. A total ion chromatogram (TIC) from Tarragona harbour sample and the extracted ions of the compounds detected.

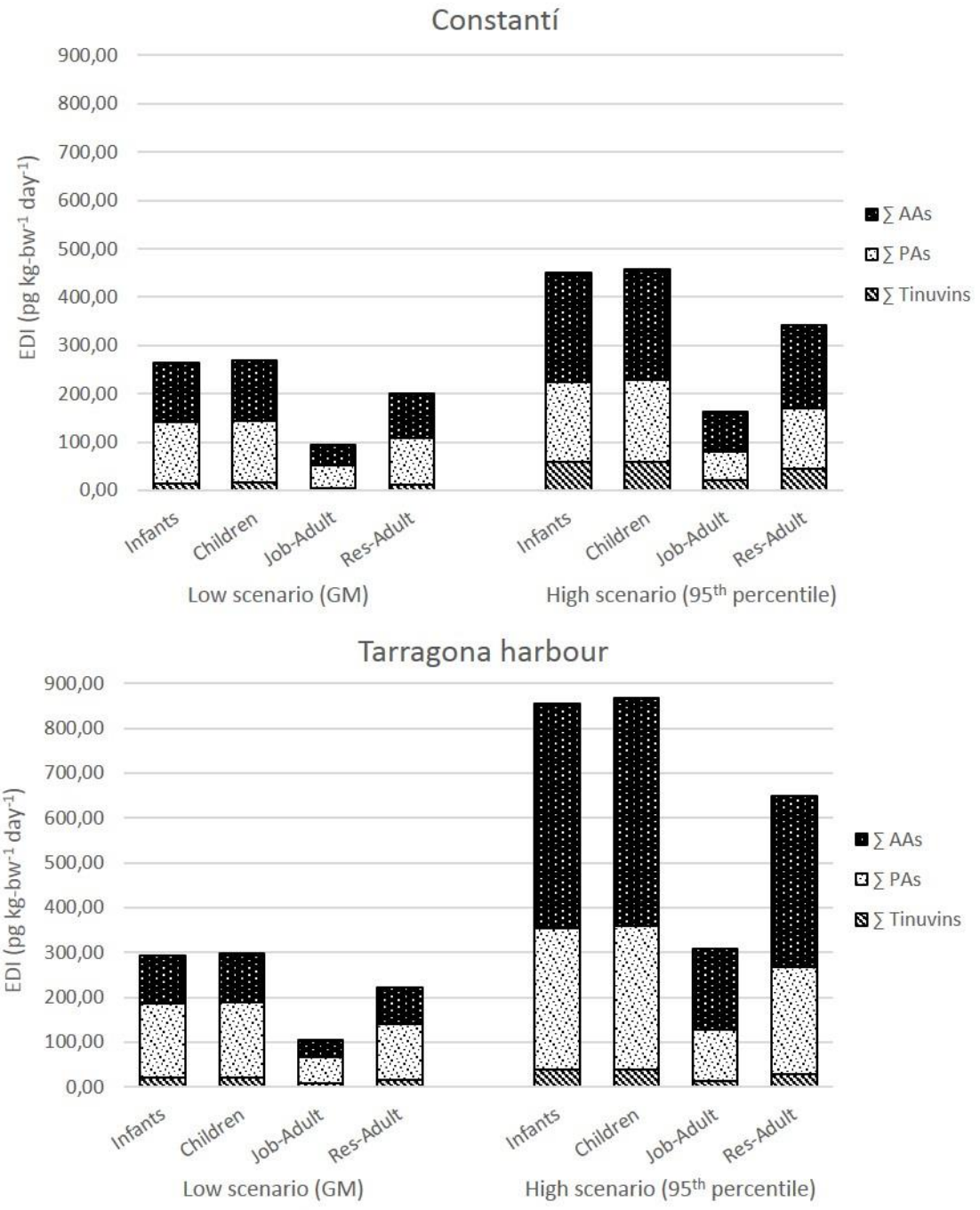

Figure 4. EDIs for each group of contaminants via outdoor air inhalation.

Table 1. Retention times, quantifier and qualifier ions and their relative abundance, method detection limits (MDL) and method quantification limits (MQL) expressed in pg m^{-3}, apparent recoveries (%) and their repeatability (%RSD, n=3) in brackets of blank and sampled filters for each target compound.

Compound	t_R (min)	Quantifier ion	Qualifier ions[a]	MDL[b] (pg m^{-3})	MQL[b] (pg m^{-3})	Recovery (%)		
						Blank filters (%RSD, n=3)	Sampled filters (%RSD, n=3)	
						6,9 ng m^{-3}	0,3 ng m^{-3}	6,9 ng m^{-3}
BHT-Q (1)	8,85	177	135(76); 220(69); 67(51)	3,3	15	108 (4)	91 (8)	92 (3)
BHT (1)	9,29	205	220(27); 57(23); 145(13)	3,8	18	76 (2)	79 (6)	69 (4)
2,4-DTBP (1)	9,37	191	57(35); 206(19); 192(14)	1,0	6,8	94 (1)	103 (4)	96 (1)
BHA (1)	9,98	137	165(92); 180(41); 77(13)	13	64	92 (2)	108 (8)	93 (1)
TBHQ (2)	11,24	123	151(81); 166(33); 77(12)	14	68	103 (7)	101 (3)	112 (7)
BHT-CHO (2)	13,04	219	191(29); 234(24); 57(18)	9,0	45	77 (1)	78 (5)	87 (2)
BHT-OH (2)	13,11	221	57(19); 236(21); 131(10)	16	80	80 (2)	86 (2)	78 (4)
BHT-COOH (2)	14,59	235	207(28); 250(21); 57(15)	-	-	-	-	-
UV P (2)	16,96	225	66(17); 226(16); 65(14)	41	162	79 (2)	86 (5)	84 (4)
Allyl-BZT (2)	19,33	265	250(99); 92(38); 117(31)	13	66	102 (1)	105 (5)	107 (2)
UV 320 (2)	19,85	308	323(28); 309(27); 57(9)	1,0	7,1	106 (3)	98 (5)	111 (1)
UV 326 (2)	21,06	300	315(44); 119(27); 302(34)	6,8	34	119 (2)	103 (6)	89 (1)
UV 329 (2)	21,33	252	253(18); 133(12); 105(7)	14	71	98 (2)	97 (6)	117 (4)
UV 328 (2)	21,66	322	323(28); 351(13); 133(7)	1,0	7,3	102 (1)	96 (6)	82 (1)
UV 327 (2)	21,71	342	344(34); 357(24); 57(21)	3,2	15	96 (1)	94 (7)	87 (1)
Irgafos 168 (1)	25,74	441	57(71); 442(34); 147(20)	22	108	68 (8)	66 (13)	71 (11)
Irganox 1076 (1)	27,10	530	57(96); 515(64); 531(48)	32	125	105 (2)	111 (9)	98 (7)
ACP-d_{10}	10,33	164	162(90); 160(40); 80(39)	-	-	-	-	-
PNT-d_{10}	14,22	188	80(23); 94(20); 189 (16)	-	-	-	-	-

[a] Relative abundance in brakets.
[b] MDL and MQL calculated for a sampling volume of 720 m^3 and taking into account the method recoveries.
(1) ACP-d_{10} is used as IS.
(2) PNT-d_{10} is used as IS.

Table 2. Factors and levels selected for the $3^2 2^1$ experimental design.

Factors	**Levels**		
Temperature (ºC)	80	100	120
Time (min)	5	10	15
Number of cycles	1	-	2

Table 3. Mean concentration, detection rate and concentration range of the target compounds in particulate phase of outdoor air collected in each sampling point (n=10 for both).

Compounds	Constantí			Tarragona harbour		
	Arithmetic mean (pg m^{-3})	DR[a] (%)	Concentration range (pg m^{-3})	Arithmetic mean (pg m^{-3})	DR[a] (%)	Concentration range (pg m^{-3})
BHT-Q	177	100	63 - 350	621	100	162 - 1126
BHT	12	100	43 - 251	100	100	68 - 159
2,4-DTBP	310	100	180 - 412	163	100	148 - 209
BHA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
TBHQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BHT-CHO	78	100	<MQL - 131	53	100	30 - 116
BHT-OH	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
UV P	n.d.	n.d.	n.d.	129	90	n.d. - 196
Allyl-BZT	<MQL	10	n.d. - <MQL	n.d.	n.d.	n.d.
UV 320	17	70	n.d. - 39	5.4	90	n.d. – 7.2
UV 326	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
UV 329	294	10	n.d. - 294	n.d.	n.d.	n.d.
UV 328	20	70	n.d. - 43	14	100	6.5 - 21
UV 327	38	50	n.d. - 68	n.d.	n.d.	n.d.
Irgafos 168	202	100	<MQL - 293	544	100	<MQL - 2860
Irganox 1076	559	100	295 - 981	500	100	224 - 1854
∑ Tinuvins	69	30	n.d. - 384	132	40	<MQL - 221
∑ PAs	670	57	307 - 898	937	57	452 - 1806
∑ AAs	680	100	303 - 1218	826	100	276 - 3274

[a] Detection rate.
[b] n.d. = <MDL

Supplementary Material

Occurrence of plastic additives in particulate matter from outdoor air. Estimation of the human inhalation intake.

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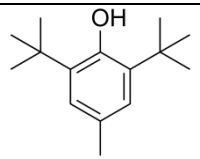
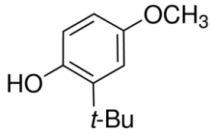
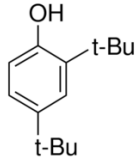
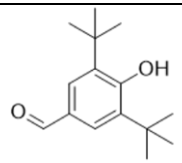
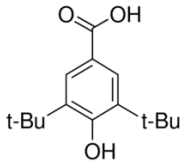
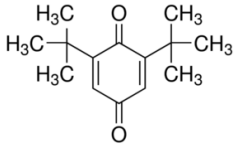
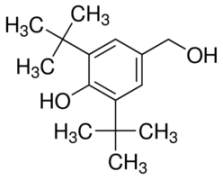
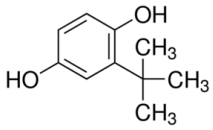
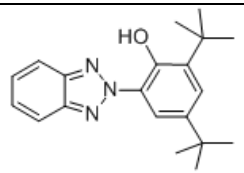
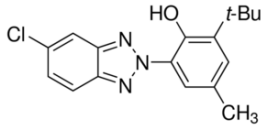
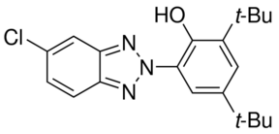
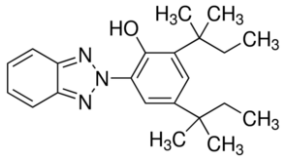
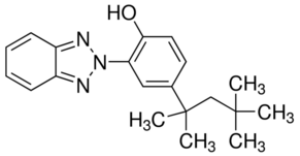
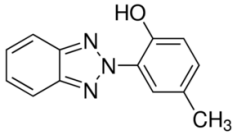
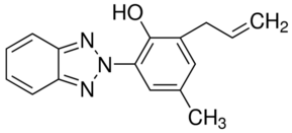
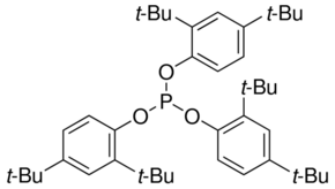
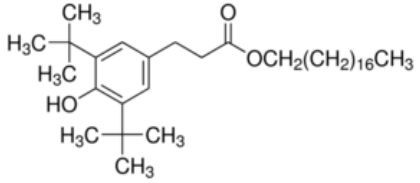
57 **Table S-1.**

Family	Compound	Acronym	Structure	CAS	BP (ºC)	Log K_{ow}
Phenolic antioxidants	2,6-di-tert-butyl-4-methylphenol	BHT		128-37-0	265	5,17
	3(2)-tert-butyl-4-methoxyphenol	BHA		25013-16-5	268	3,50
	2,4-di-tert-butylphenol	2,4-DTBP		96-76-4	264	4,61
Phenolic antioxidants transformation products'	3,5-di-tert-butyl-4-hydroxybenzaldehyde	BHT-CHO		1620-98-0	289	4,15
	3,5-di-tert-butyl-4-hydroxybenzoic acid	BHT-COOH		1421-49-4	341	4,18

	2,6-di-tert-butylcyclohexa-2,5-diene-1,4-dione	BHT-Q		719-22-2	285	3,77
	2-6-di-tert-butyl-4-(hydroxymethyl)phenol	BHT-OH		88-26-6	306	3,50
	2-tert-butylbenzene-1,4-diol	TBHQ		1948-33-0	291	2,26
Tinuvins	2-(3,5-di-tert-butyl-2-hydroxyphenyl)-2H-benzotriazole	UV 320		3846-71-7	444	6,85
	2-tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl)-4-methylphenol	UV 326		3896-11-5	460	6,81
	2,4-di-tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl)phenol	UV 327		3864-99-1	469	7,54

	2-(2H-benzotriazol-2-yl)-4,6-di-tert-pentylphenol	UV 328		25973-55-1	469	7,87
	2-(2H-Benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol	UV 329		3147-75-9	472	7,42
	2-(2-Hydroxy-5-methylphenyl)benzotriazole	UV P		2440-22-4	225	4,30
	2-(2H-Benzotriazol-2-yl)-4-methyl-6-(2-propenyl)phenol	Allyl BZT		2170-39-0	451	5,22
Aromatic antioxidants	tris(2,4-di-tert-butylphenyl) phosphite	Irgafos 168		31570-04-4	594	13,7
	octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate	Irganox 1076		2082-79-3	568	13,5

58

59 **Table S-2**. Values used in Equation 1.

Parameter	Infants (1-6 years)	Children (6-12 years)	Adults	
			Off-site residents, schools and by-passers	Off-site workers
Average body weight (BW, kg)	16	29	70	70
Average lifetime exposure period (ED, years)	5	6	58	58
Inhalation rate (IR, $m^3\ h^{-1}$)	0.25	0.46	0.83	0.83
Retention rate of inhaled air (RR, %)	100	100	100	100
Frequency of PM_{10} inhalation (EF, days $year^{-1}$)	365	365	365	260
Duration of PM_{10} inhalation (outside) (ET, h day^{-1})	12	12	12	8
Period over which exposure is averaged (AT, days)	1825	2190	21170	21170

60
61

Table S-3. Estimated daily intakes (EDI_{outinh}, pg kg_{bw}^{-1} day^{-1}) of ∑Tinuvins, ∑PAs and ∑AAs through inhalationof particulate matter from outdoor air from two sampling sites for several age groups for different exposure scenarios.

Sampling site	Compounds	EDI_{outinh} (pg kg_{bw}^{-1} day^{-1})							
		Low exposure scenario (GM[a])				High exposure scenario (95th percentile)			
		Infants	Children	Job-Adult	Res-Adult	Infants	Children	Job-Adult	Res-Adult
Constantí	∑ Tinuvins	15,1	15,4	5,5	11,5	58,8	59,7	21,2	44,6
	∑ PAs	126,8	128,8	45,7	96,3	166,4	168,9	60,0	126,3
	∑ AAs	121,8	123,6	43,9	92,4	224,6	228,0	80,9	170,4
Tarragona harbour	∑ Tinuvins	20,1	20,4	7,3	15,3	38,5	39,1	13,9	29,3
	∑ PAs	165,9	168,5	59,8	125,9	315,2	320,0	113,6	239,2
	∑ AAs	106,5	108,1	38,4	80,8	500,8	508,4	180,5	380,0

[a] Geometric mean.

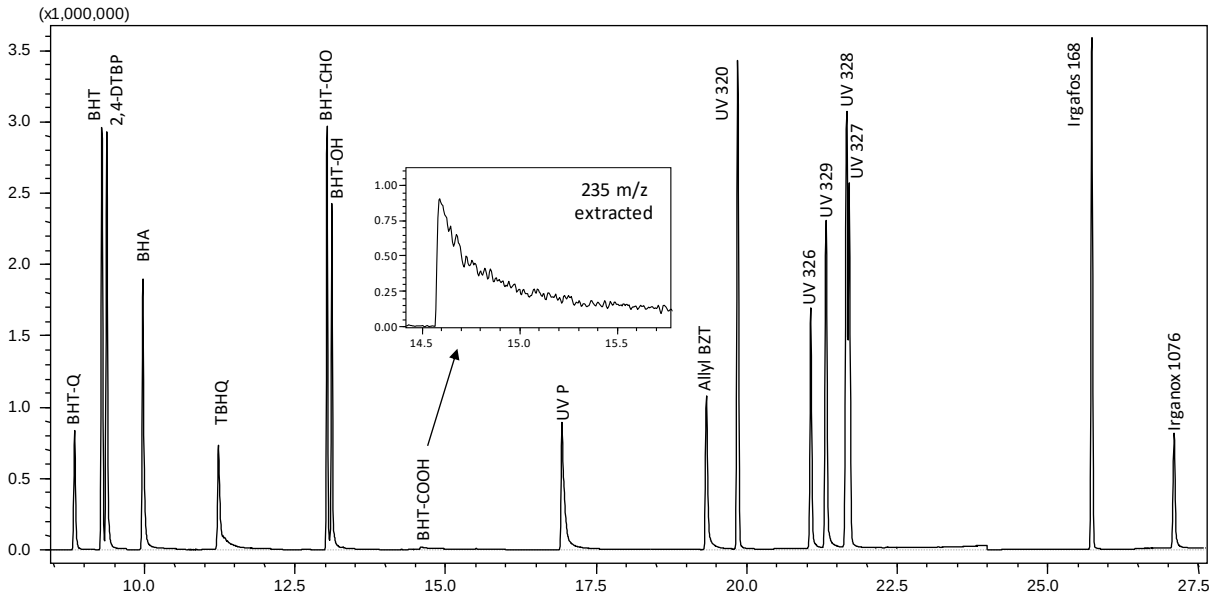


Figure S-1. Chromatogram obtained from a standard solution of 2.5 mg L^{-1} for all the target compounds.

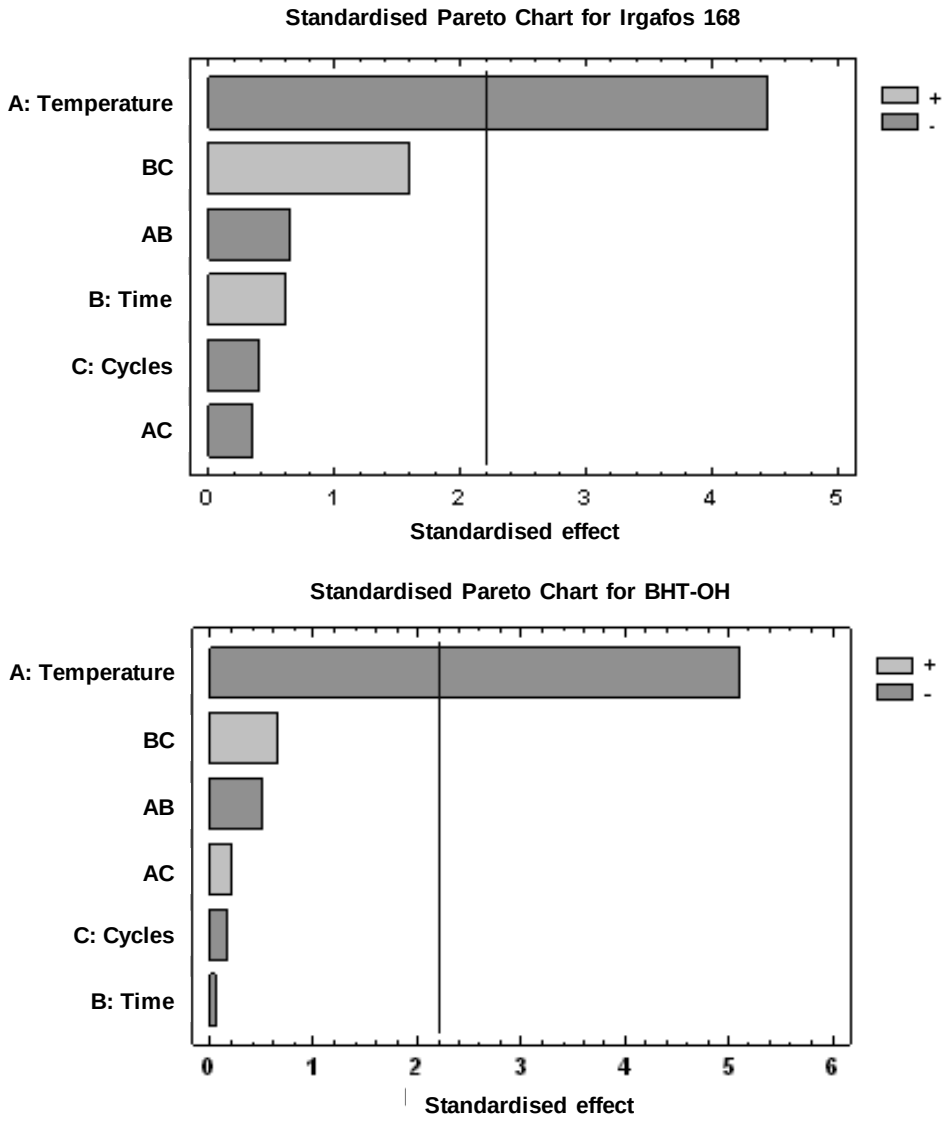


Figure S-2. Standardised Pareto charts for the mean and 2-factor effects interactions of the multifactorial design for Irgafos 168 and BHT-OH.

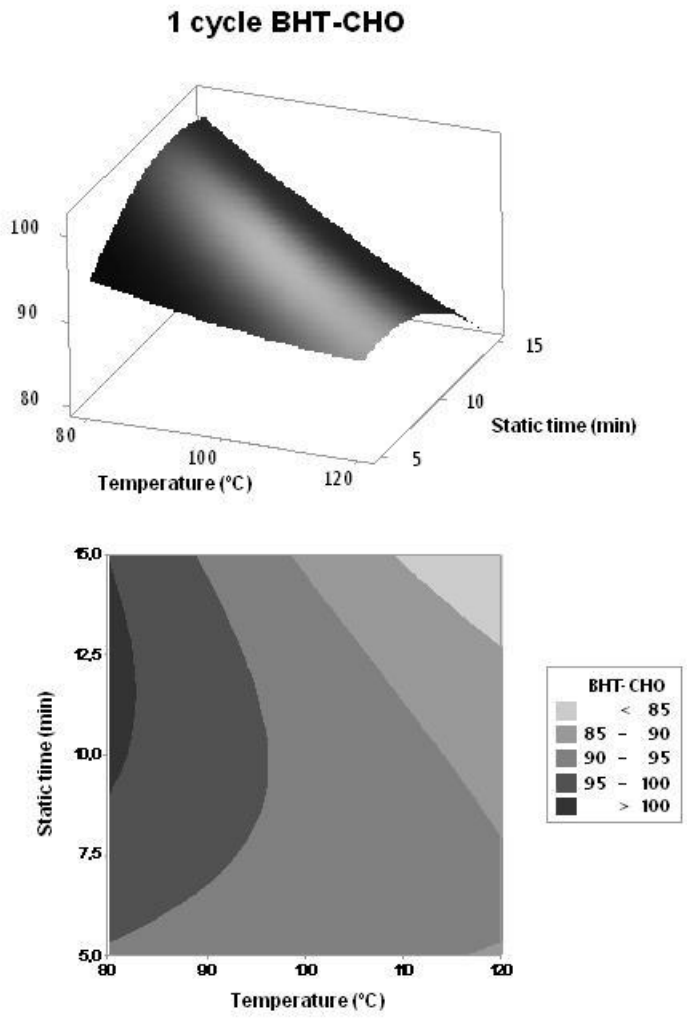


Figure S-3. BHT-CHO response surface for the extraction temperature against the extraction time (1 cycle)