SAPIENZA
UNIVERSITÀ DI ROMA

Studio di adsorbenti innovativi finalizzati alla determinazione di microinquinanti organici in matrici ambientali

Study of innovative adsorbents aimed at investigating organic micropollutants in atmospheric matrices

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To my sister, Teresa

Dream BIG, because dreams DO HAPPEN.

Abstract

The following PhD study aims to understand how the Activated Carbon Fiber adsorbent can be used in analytical chemistry for the study of Persistent Organic Pollutants (POPs). After a deep bibliography research, the importance of choosing an ACF typology depending on its raw material, industrial process and chemical physical properties comes to light. This was the starting point for establishing the suitability of ACF-F-2000 as the best adsorbent for this purpose after physical chemical characterization and extraction tests. To study persistent POPs in the atmosphere, it is mandatory to consider their distribution between gaseous phase and dry and wet depositions (rain and snow). For this reason, the study took into consideration both the air and water matrix, the latter as rain and snow. Thanks to its versatility, the ACF is well suited to be used in several currently existing sampling methods. The ACF-F-2000 has previously been validated for sampling of air for PCDD/F and PCB analysis. This thesis describes the work of further validating the ACF-F2000 to be suitable for sampling of pesticides (PeCB and HCB) in air, according to the criteria of the EPA TO4A reference standard method. The material was also validated as a passive adsorbent in water for PCDD/Fs and PCBs according to EPA standard methods 1613B and 1668B. The work led to the definition of a sampling method for snow and the extraction of POPs from melted snow.

This extraction method, which uses ACF-F-2000 as the adsorbent, has been validated for PCDD/Fs, PCB, PeCB, HCB, α-HCH, γ-HCH, p,p'-DDE, o,p-DDT, according to EPA 1668B, 1613B, TO-4A, 1699. The sampling and extraction systems were demonstrated in field by real sampling of snow in the Svalbard Islands, Arctic region, and at Terminillo Mount, Italy, where parallel sampling of ambient air and snow were conducted. Parallel sampling allowed for the study of the scavenged effect. In addition, the GC-Orbitrap high accuracy acquisition allowed for non-target screening, which was also used to further

study the scavenged effect, and to identify classes of compounds for future validation and inclusion in the ACF-F-2000 sampling strategy.

CONTENTS

INTRODUCTION AND AIM OF THE THESIS

The following research work arises from the promising results obtained during the internship of Master's Degree thesis in Analytical Chemistry at the Sapienza University of Rome, carried out at the Institute for Atmospheric Pollution Research of Italian National Research Council (CNR-IIA) in Montelibretti (Rome). The title was *Study of activated carbon fiber filters for the sampling of semi-volatile organic micropollutants in air and GC-MS/MS determination* [1].

The MD thesis focused on the evaluation of an activated carbon fiber felt (ACF-F-2000) as an adsorbent for sampling of semivolatile organic compounds (SVOCs) in ambient air. Among these, polychlorodibenzo-p-dioxins (PCDDs), polychlorodibenzofurans (PCDFs) and dioxin like polychlorobiphenyls (PCBs) were investigated.

To validate the sampling method, the IPR (Initial Precision Recovery) and QC (Quality Control) criteria defined in the standard reference methods were used: ISO DIS 16000-13 and 14 and EPA TO-4A and TO-9A, for indoor and ambient-air sampling respectively.

Once validated, parallel samplings (Reference vs ACF-F-2000 methods) on real samples were carried out to compare quantitative data and performance.

Since the volatility of PCDD/Fs and PCBs extends over a wide range within the classes, the homologues are spread between the particulates and the gaseous phase. For this reason, the reference sampling method involves the use of two in series sorbents: a Quartz Fiber Filter (QFF) and a polyurethane foam (PUF) for the trapping of the pollutants fraction in the particulate and in the gaseous phase, respectively. The experimental internship thesis demonstrated and verified that a filter in ACF-F-2000 is able to replace the double system QFF + PUF, keeping an equivalent or even higher sampling efficiency without showing phenomena of breakthrough, even for extended sampling over time, meeting the criteria required in ISO and EPA reference methods. Given the positive

results obtained for the air-ambient sampling, the use of the ACF adsorbent could be extended to other classes of pollutants and to different environmental matrices.

On completion of the MD work, some critical issues emerged, which have been the starting point of the doctoral project.

During the internship, ACF-F-2000 was also tested for polycyclic aromatic hydrocarbons (PAHs) sampling and analysis, but despite having applied three extraction techniques (solvent elution, sonication and Soxhlet extractor), the recovery rates of perdeuterated standards never satisfied the ISO 12884 requirements [2].

A brief literature review highlighted that surface and porosity characteristics (hence adsorption) of ACFs are closely related to the raw material and the activation process [3–6]. Unfortunately, the technical specification provided by the manufacturer lack properties necessary to choose a product rather than another depending on the analytical purposes. It means that it cannot be excluded that other types of ACFs could be suitable for PAHs.

That being said, the research work of this Doctorate involved as first step a literature review on the following topics:

- Which and how the raw material and the industrial manufacturing process influence the characteristic properties of ACFs.
- Which chemical-physical tests are the most performed to characterize ACFs in scientific literature.
- Industrial applications of ACF as an abatement system, in order to identify classes of compounds to be studied from an analytical point of view.
- In-depth studies on the interactions between PAHs and ACF, to assess which sorbent could solve the extraction problems experienced during previous studies.
- Review of all the current sampling and extraction techniques for different environmental matrices, in order to decide how the ACF sorbent can be fitted.

Essential condition is the commercial availability of ACF (packaging, industrial production and starting material).

Each type of ACF selected was chemically and physically characterized and their interaction whit POPs was evaluated. For each matrix selected in this thesis work (air, water) both the reference analytical method and the developed one were decided; the latter was subsequently validated. The procedure involves the evaluation of IPR through simulated samples in the absence of a matrix and by native and label Standards. Once the method was validated in the laboratory, it was also applied to real samples through targeted measurement campaigns. This procedure was followed each time the ACF was applied to a different matrix or compound and for each modification of the standard reference method. This allows to assess compliance with the QC criteria of the method selected as reference. Real samples were analysed by Gas-Chromatography coupled to High Resolution Mass Spectrometry (GC-Orbitrap). By applying the Deconvolution plug-in of the instrument software, it was possible to start a qualitative analysis of the Unknown analytes present in the sample. This would allow to define additional classes of analytes (e.g. emerging pollutants) towards which the use of the ACF can be addressed.

1 BACKGROUND

The evaluation of the diffusion of organic micropollutants in the atmosphere should not be only limited to air but it should take into account atmospheric depositions, too. Hence, the sampling of a class of pollutants should include the gaseous phase and both dry (PM particulate) and wet (rain and snow) atmospheric depositions.

In this chapter, the importance and the interactions of the different phases in the atmosphere will be studied in depth for a complete monitoring of a class of pollutants. First of all, a general overview of current techniques for sampling and extraction of all the phases in which a class of pollutants can be found, taking into account the advantages and disadvantages, will allow to define how the ACF filter can be fitted. Persistent organic pollutants (POPs) are ubiquitous contaminants that can be found in sediments, soil, fish, wildlife, human adipose tissue, whey and milk [7–10]. They are mainly characterized by their persistence, bioaccumulation, semi-volatility and toxicity [8]. POPs migrate from tropical and subtropical latitudes to the poles due to their semi-volatility, described by the theory of global fractionation and condensation. In tropical and subtropical areas POPs are emitted directly into the atmosphere and resuspension and evaporation are favoured; while in the regions of the poles and at high altitudes condensation occurs, which results in high concentrations due to accumulation [11]. The monitoring of their presence in the air is critical since the most important means for their global redistribution is the air, due to the low solubility in water [12].

1.1 SCAVENGING EFFECT OF THE ATMOSPHERE

Persistent Organics Pollutants are removed from the atmosphere by wet and dry deposition; in the first case through snow and rain, while in the second through the particulate matter and the gaseous phase. The scavenging of contaminants from the atmosphere is the result of a combination of both processes which vary according to the

physical and chemical properties of the contaminants [13]. The greater affinity of a chemical species for a deposition depends on the properties of the species, its concentration, the environmental conditions, and the concentration of the depositions (wet and/or dry). To this end, it is important to understand (1) the distribution of chemical species between the two phases and (2) the prevailing deposition process as a function of the distribution. The distribution and equilibrium calculations are performed using specific partitioning coefficients (K). POPs coefficients describe the distribution of chemical species in a two-dimensional coordinate system in which they move from air to wet and dry deposition, depending on the temperature: $K_{Rain/Air}$ and $K_{Particle/Air}$ are used for temperature above zero, $K_{Snow/Air}$ and $K_{Particle/Air}$ for temperature below freezing point. $K_{Rain/Air}$ defines the ratio between equilibrium concentrations of a compound in rain droplets (mol m^{-3} water) and in atmospheric gas (mol m^{-3} air); likewise, $K_{Snow/Air}$ defines the ratio between equilibrium concentrations of a compound in snow (mol m^{-3} melt water) and in atmospheric gas (mol m^{-3} air). $K_{Particle/Air}$ defines the ratio between equilibrium concentrations in particles (mol m^{-3} particles) and gaseous phase (mol m^{-3} air) [14]. The equilibrium for each compound depends on the pressure of the subcooled liquid vapour of the chemicals and/or the octanol/air partition coefficient (K_{OA}) [15].

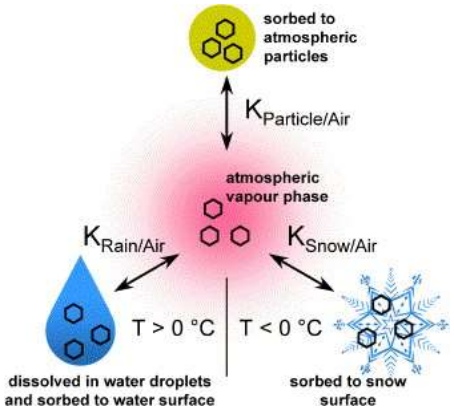


Figure 1 Schematic representation of the equilibrium phase distribution of an organic chemical substance at temperatures above and below the freezing point. $K_{Particle/Air}$; $K_{Rain/Air}$ e $K_{Snow/Air}$ are the distribution coefficients between particles and air, rain droplets and air, and snows and air, respectively.

Image Source: *Lei et al. (2004)* [14]

Focusing on the samples collected in areas of high altitude and extreme latitudes, i.e. areas characterized by temperatures ≤ 0 °C, the POPs coefficients considered are the snow/air ($K_{snow/Air}$) and particle/air ($K_{particle\ /\ air}$) ratios (Figure 1).

As stated earlier, rain and snow are two atmospheric cleaning agents, and of the two, the snow has a more powerful effect than the rain. For this reason, underestimate its monitoring even in our latitudes is to commit a big mistake. Wania et Lei (2004) showed that among all the depositions taken into consideration, the one with the greatest scavenging effect of chemical products is snow [14]. The study graphically represents the change in the distribution of an organic chemical substance as a function of its distribution coefficient within a cloud, considering the chemical concentration constant and the temperature as the only variable (cold for the snow and hot for the rain). Furthermore, Wania's study compared the scavenging efficiency of rain and snow in relation to different types of compounds.

Generally, PAHs and lighter PCBs tend to sorb to dry gaseous depositions; at temperatures above freezing, five-ring PAHs, (such as benzo[a]pyrene) will be deposited mostly by particle deposition while most PCBs will be deposited by a combination of dry gaseous and wet and dry particle deposition processes. Mists and more generally humid vapours have an insignificant impact on PCBs due to their low solubility in water. As the molecular weight increases, both PAHs and PCBs are deposited by frozen wet deposition (hail, ice) and particulates [14]. Figure 2 reports part of the study conducted by Lei and Wania (2004) on the distribution of different classes of pollutants between the various phases present in the atmosphere as temperatures vary.

The pink areas in the upper left corner indicate substances that partitioning predominantly (>90%) in the atmospheric vapour phase. The yellow areas to the upper right highlight substances that are expected to sorb mostly onto the atmospheric particles, whereas the blue areas to the lower left correspond to substances that are strongly associated with liquid or frozen hydrometeors in the atmosphere.

Quick glance at the graph in Figure 2 shows that decreasing temperature reduces dry gas deposition while increasing wet precipitation removal efficiency, due to a rebalancing of the distribution between the gaseous phase and the condensed phases in the atmosphere and the high surface extension of the snow.

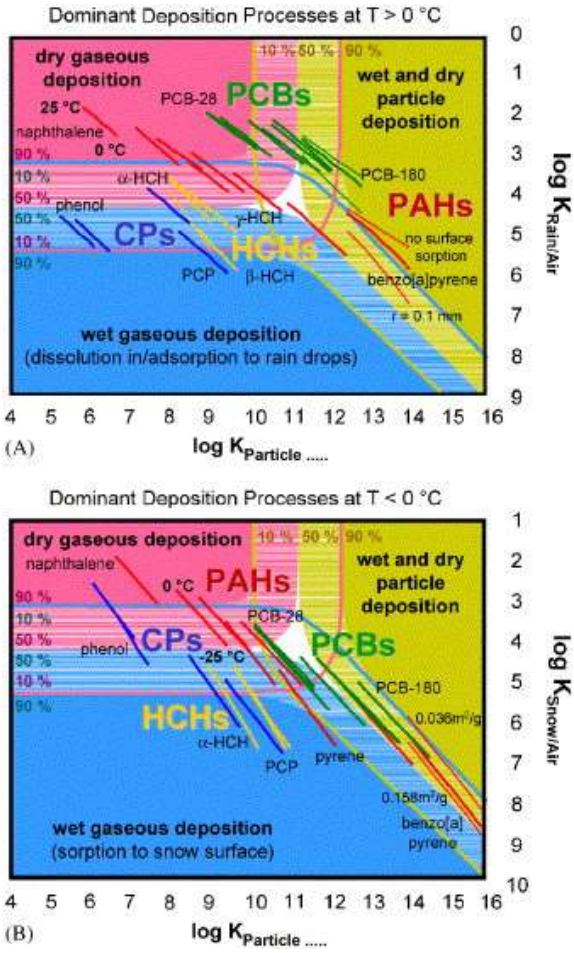


Figure 2 Dominant atmospheric deposition processes PCBs, PAHs, CPs and HCHs at temperatures above (A) and below (B) freezing as a function of its particle–air distribution coefficient $K_{Particle=Air}$, its rain–air distribution coefficient $K_{Rain=Air}$ and its snow–air distribution coefficient $K_{Snow=Air}$ The volume fraction of particles is assumed to be 10^{-12}, that of water 3×10^{-7}. The lines indicate the partitioning properties of selected PCBs (green), PAHs (red), HCHs (yellow) and chlorinated phenols (blue) in the temperature range +25°C to 0°C (A) or 0°Cto -25°C (B). When calculating the lines corresponding to specific chemicals, a droplet radius *r* of 1 mm (A) and a specific snow surface A_i area of 0.1 m^2g^{-1} (B) were assumed to apply. Image Source: *Lei et al. (2004)* [14].

In a real situation, rainfall is not constant; when it does not snow or rain, particulate matter and the gas phase are the only scavenging agents [14]. The borderline between one event and another is blurred and clearly distinguishing one type of deposition from another makes no sense. For this reason, we cannot ignore the consideration of particulate matter in a general system of wet depositions and a correct evaluation of the depositions requires the measurement of both (dry and wet) as a single system.

Furthermore, it is not possible to generalize the tendency to spawn all POPs in a single behaviour. Several variables are needed to calculate the exact values of the phase composition (specific snow surface, content of particles in the atmosphere), kinetic parameters (deposition rate, precipitation rate, particle wash ratio) and temperature [16]. Another element that binds all the phases to be considered as a single system is the fact that particulate matter constitutes the nucleation center for snowflakes and raindrops in the atmosphere: pure water droplets without nuclei do not form ice crystals at temperatures above -38 °C [17]. The surface of a particle serves as a catalyst to initiate the crystallization process. The particles can have different sizes and compositions. The deposition of pollutants can occur on the surface of the particles regardless of its size before nucleation [17]. Furthermore, pollutants adhere to the snow crystal [18].

During snow conditions, the gaseous compound is removed from the atmosphere and other aerosol particles can be incorporated into the snowflakes until final deposition. After the deposition, the temperatures and pressures due to the upper layers of snow change the structure of the flakes, this combined with the melting processes can further concentrate these contaminants are not released until the spring during dissolution. Franz's study (1994) compared the concentration of pollutants during parallel sampling in the atmosphere and in melted snow [16]. The study shows that after sampling the snow, new balances are establish between the contaminated and the melt water exactly as it happens in the spring period at high altitudes and latitudes. Franz concluded that the two events (particulate deposition and snow scavenging) cannot be treated separately unless the kinetics of adsorption and desorption of pollutants from / to the particulate matter in cold water are slow enough during the melting phase. However, there is no precise method to distinguish the action of the two events as they are related to each other [16].

The third aspect to consider is the chemical and physical behaviour of the class of compounds under consideration. K_{OW} (n-Octanol/Water Partition Coefficient) describes

the solubility of the compounds in water and the distribution of each chemical [15]. It indicates how much an organic compound tends to accumulate in the lipid fraction rather than in the aqueous phase. According to literature, compounds with a K_{OW} greater than 3.9, should to be considered dangerous for the environment [19]. The most soluble compounds with low K_{OW}, such as HCHs, can be eluted directly with the first melted snow. Those less soluble or hydrophobic, e.g. PCB and DDT [15,20] enrich the remaining fraction of the snowpack which includes particulate matter [16].

For the analysis of snow, the lack of standardized methods for sampling suggests that it is necessary to take into account both matrices, i.e. snow and particulate matter, for a correct study of POPs. The importance of the inclusion of the particle in the analysis of melting snow was highlighted by Daub (1994) and Simmleit (2004) [21,22].

Among the aspects that influence the distribution of micropollutants, there is certainly altitude: if for some pesticides such as organo phosphates (OPP) concentrations decrease with increasing altitude, DDT, α-HCH and HCB have also been detected in high altitudes in Japan. Temperature and sun exposure are two other factors that influence the distribution and presence of chemical compounds in snow. HCH, a blend of several stereoisomers, is characterized by high volatility, so its deposition is dominant in the cold and wet season, and it is usually associated with particulates. They are compounds that rapidly degrade by exposure to light by photochemical reaction, and for this reason low concentrations are found even in winter if the sample was collected from a surface exposed to direct solar radiation. This phenomenon does not affect HCB since it is stable even when exposed directly to the sun. The highest concentrations are found during the dry season and adsorbed on the particulates, given its greater affinity for the organic phase [23]. Long-distance transport of HCB through particulate matter is prevented only by wet depositions that "clean" the atmosphere [24].

For this reason, separating the particulate from the aqueous phase (rain and snow) and from the gaseous phase would lead to estimation errors during sampling. The

development of optimal sampling and extraction methods focused on identifying the technique that includes both the gas / aqueous phase and the particulate matter in the estimation of the compounds of interest.

1.2 SAMPLING OF THE ATMOSPHERE

1.2.1 Air

When the gaseous pollutant is present in the air in concentrations compatible with the limit of detection of the instrumental technique, we speak of "*direct sampling*" since the air is taken as it is and then brought to the laboratory and analysed. When the concentrations of gaseous pollutants in the air are very low, it is necessary to perform an enrichment trapping species by absorption, adsorption or change of state (at low temperatures condensation). These samplings can be defined *indirect*, due to the presence of a trapping medium dedicated to the pollutant.

Active samplers, often used for this purpose, include air inlet, a particulate filter, the trapping medium, a suction pump and a flow meter. The regulation of air flow and volume are essential in this type of instrument. An excess of air flow or volume (sampling scheduled for too many days) causes the more volatile analytes to be lost by breakthrough (saturation of the trapping medium or incompatibility with adsorption kinetics). Conversely, volumes and flows that are too low could make the sample invalid due to a collection concentration that is too low and insufficient for it to be processed and quantified.

Absorption based trapping media include a chemical interaction between the medium and the analyte (ex. impingers, denuder tubes, colorimetric tubes)

Adsorption based trapping media include a physical interaction between the medium and the analyte through weak surface forces, i.e. Van der Waals, dipole-dipole, dipole-induced dipole forces (ex. active carbon, silica gel, porous polymers).

The adsorbent, chosen based on its surface extension and its chemical nature, is packed in glass or stainless steel tubes. The choice of the adsorbent also depends on the volatility of the analyte under investigation. The analytes are extracted by thermal or chemical desorption, so it is essential to choose an adsorbent that allows easy extraction.

Particulates and aerosols can be of different chemical nature, be carriers of pathogens, adsorb and absorb atmospheric pollutants acting as a nucleus for the coagulation of water and cause fog and rain. The size of the particle discriminates the penetrability it has in the respiratory tract where, based also on its nature, it can accumulate and cause serious diseases. It is therefore essential perform an adequate sampling.

Active Particulate Matter (PM) Samplers are divided according to the air flow rate and geometry of the sampling heads.

Based on the flow rate of the pump, they are distinguished in **low** (up to 10 L/min), **medium-low** (up to 150 L/min), **medium-high** (up to 600 L/min) and **high** (up to 1200 L/min) volume samplers.

Medium-high and high volume samplers use a combination of a filter and a membranes and/or adsorbent media, in order to collect lighter volatile compounds in vapour phase that can be desorbed by the particulate matter retained by the filter above.

The **sampling head** includes cyclone systems or impactors consisting of nozzles that convey air by impacting the particulate on the walls. Based on the principle of inertia, for both the particles will be selected based on their mass and therefore on their equivalent aerodynamic diameter. The sampling heads mainly used are of the impactor type. The tortuous path determined by the nozzles, their diameter and the distance from the impact surface determines the range of sizes of the particles that are blocked. Based on the length and diameter of the nozzles, a specific cut of the sampled PM can be reached. Furthermore, depending on the interested cutting of the PM and therefore on the sampling head adopted, the flow rate is regulated. Cascade impactors are equipped with several stages (up to 12) in which particles of progressively decreasing size are captured.

When the aerosol substance is distributed into the cascade impactor, the substance enters a series of discs designed to collect solids and different particulate matter. The substance is thus collected as it passes through the disc series. Each disc is set in sequence with both the prior and the previous disc. The size of the discs is graduated as well, to properly determine the size of the particulate matter at each stage of the impactor.

As for the choice of the filter, it is determined by the particle size retention range of interest, the nature of the particulate, the compatibility with the laboratory analyses to be followed subsequently on the particulate. For example, hygroscopic cellulose esters with regular porosity are suitable for asbestos determination in AAS; non-hygroscopic quartz and glass fiber, characterized by mechanical resistance; PVC with regular porosity and low hygroscopicity suitable for metals; hydrophobic PTFE suitable for aerosols, acids and for outdoor gravimetric determination; regular porosity silver suitable for silica resistant to chemical attack.

1.2.2 Water

Atmospheric depositions represent the means through which atmospheric pollutants (dust, particulate containing heavy metals, polycyclic aromatic hydrocarbons, dioxins, furans, sulphates, nitrates, etc.) are transferred to terrestrial and aquatic ecosystems.

The samplers used to assess the atmospheric deposition may be divided into three types depending on which deposition is collected: *dry* (in the absence of precipitation), *wet* (the sampler collects only during rain or snow) and *bulk* (dry and wet depositions are collected together).

The conventional **bulk water collector system** (deposimeter), basically consists of a cylindrical funnel (25 cm ± 10% diameter, 1:1 ratio between height and diameter, short stem) and a sample collection vessel (5 or 10L capacity, depending on the expected rainfall), and are widely used to collect PAHs and metals.

The height of the cylindrical vertical section should be sufficient to avoid sampling losses due to the wind, and the diameter for the aperture area and the volume of the collector should be chosen in order to collect all precipitation for the required sampling duration. The amount of wet deposition collection is estimated through the weight. To protect the sample from exposure to light and heat, resulting in the formation of algae, the bottle and funnel are housed in an opaque plastic case whose upper edge is at the height of the edge of the funnel. To minimize the heating of the collected sample, the case must be light in colour and there must be an air gap between the tube and the plastic collection system. The upper part of the case may be equipped with an outer ring for protection from animals and, in particular, to prevent birds from using the edge of the sampler as a perch. Using a support, the deposimeter is positioned so that the upper edge of the funnel is at a height of about 180 cm [25] or more generally above 1.5 m [26], in order to prevent contamination from soil during heavy rains.

The samples, at any stage of treatment after sampling, are stored in the refrigerator at a temperature below 6 °C. If heavy rainfall is expected, when the volume inside the vessel reaches 2 L, the sample is immediately transported to the laboratory and filtered with a clean filter paper. If snow or frost is expected at the sampling site, the collecting funnel and container can be equipped with heating devices.

The fundamental difference in the sampler for PAHs and metals is in the material the sampler is made of. The analysis of metals requires a funnel and a vessel made of plastic (ie. HDPE) and that no metal or glass part of the deposimeter is in contact with the sample; PAH analysis requires the sampler in borosilicate yellow glass or Pyrex or Duran (or equivalent) and that no part in contact with the sample is made of polymeric material (ex. PTFE) [25].

Another bulk water collector system is the *tipping bucket rain gauge*: it has the advantage over the classic deposimeter of automatically marking the amount of deposition. Once a

certain volume of water has been reached, the collection swing empties by sending an electric signal that activates an arm with a pen [27].

Different adsorbents can be housed inside the funnels, in order to collect and filter directly the water retaining only the compounds of interest.

Quartz fiber thimbles were used on steel funnels for PCDD/Fs and PCBs [28]; amberlite cartridges in the stem of the funnel [29,30] and IRA-743 o XAD-2 resins connected to borosilicate glass funnels [26].

Steel buckets [29] or *steel plates* [31] were also used as bulk water collectors, by evaluating the evaporation of water during winter and summer with the addition of glycol for the colder periods.

Li et al. (2009), describes a water sampler for PAHs: a stainless steel funnel was attached to a glass filter setup [28]. The funnel was placed horizontally, 1.2 m above the ground. After about 30 days, the inner surfaces of the stainless steel funnels were wiped with precleaned cotton. The cotton and filter were combined together as particle-bounded deposition fluxes of PAHs.

An unconventional method was described by Longinelli et al. (1978) who used a 2 m^2 plastic sheet ending with a siphon to minimize evaporation [32].

As for **wet depositions**, automatic *wet-only collectors* can be used to collect samples only during the precipitation events [33]; they are suitable for both rain and snow.

In addition, it is possible to collect dry and wet depositions separately, using two sampling devices consisting of two vessels equipped with a rain sensor capable of triggering the cover, so as to protect the dry sample and collect the wet deposition in the other container. The sampler contains a humidity sensor which controls the lid of wet and dry collector compartments automatically. During the wet deposition events, the sensor moves the lid onto the dry collector and after the sensor surface becomes dry, the lid on the dry collector goes onto the wet collector [34,35].

1.2.3 Snow

Snow is certainly related to very specific altitudes and latitudes and for this reason it does not seem to be of general interest. However, what can be achieved from the analysis of snow matrix? During the winter, the air flows and particulate matter transport the contaminants to colder areas (high altitude and latitude) where this matrix is enriched with contaminants. During the summer, however, when it melts it tends to release them into the soil and watercourses. For this reason, it represents a concentrated source of micropollutants.

Sampling and extraction of POPs from snow does not have a standardized procedure, unlike air, water and rain. There is also a lack of unanimous consensus regarding the sampling methodology among scientists and researchers.

Literature review shows that sampling procedure depends on the class of pollutants. Temperature and altitude are the parameters that are constantly recorded and collected in all studies. In some studies, this information was integrated with stratigraphic data of the snowpack, measuring the physical parameters of temperature, snow density, morphology of crystals and hardness. GPS coordinates and the sampling area (length, width and depth) are recorded [23].

A common protocol for snow sampling is the **collection of surface** snow. Samples are collected manually with a pre-cleaned shovel or using other means that are often not specified [23,36,37]. Downwind samples should be collected and powder-free latex gloves should be worn to avoid contamination, but this is not always possible [38,39].

There is no common procedure even on the depth of snow collection: in some cases the first layer (3 cm) is excluded, while in others it is collected [23,40].

Another sampling method adopted consists in carrying out **core drilling** at different depths. The sample can consist of a single core [41–45] or be a composite sample consisting of several cores performed in a defined area [46]. Generally, this type of

sampling is associated with stratigraphic studies aimed at evaluating the trends of atmospheric pollution during extended periods. This is done through the identification and quantification in the different layers of the micropollutants trapped in the gaseous inclusions of the frozen snow or more simply of the micropollutants scavenged from the snow [37].

In more recent studies, cores have been used only for snow collection without the need to associate sampling with a stratigraphic study, since the collected samples are taken to the laboratory and melted before analysis [46,47].

The collection volume varies greatly, depending on the type of site and the expected concentration of contaminants. If the site is close to emission sources of the pollutant class taken into consideration (e.g. rural or urban area), it is advisable to collect volumes of snow that give 1-2 L of melted snow [23,39]. The remote areas, however, require greater volumes of melted snow (between 10 and 40 L), especially if it includes the analysis of trace compounds, and depends on the limit of detectability of the analytical technique adopted [48]. It is also not possible to define containers with a standardized volume since the volume of water in the melted snow depends very much on the texture of the snow itself. There is no uniformity even for the type of material of the container for the same class of pollutant: pre-cleaned barrels of aluminium, steel, amber bottles, Teflon bottles or bags, canisters or polyethylene bottles [23,49,50], provided that cleaning procedures are included [47].

Given the complexity of the snow system already highlighted above, the "material" parameter constituting the collection container should not be neglected, since the distribution equilibrium between one phase and another of the species under investigation can vary, giving underestimates or overestimates [51].

The samples are then transported to the laboratory covered with a light aluminium film which prevents photochemical interactions with short wave radiation [38] and are then melted for analysis. There are no standard guidelines at this stage either and the

methodology varies by research group: Talovskaya et al. (2018) for example runs it at room temperature (24h) [52], others in in a dark room [40] or at 60 °C for 20-40 min[53]. This step is prone to errors due to the volatilization of the compounds during the snow melting procedure, and it is especially true for the lighter compounds with a higher Henry's law constant as evidenced in the studies of Herbert (2004) [49].

Since there are no defined procedures for extracting POPs from snow, it can be assumed that once the snow has melted, the sample can be treated as rainwater.

1.3 EXTRACTION TECHNIQUES OF ATMOSPHERIC MATRICES

1.3.1 Air

The methods of extraction of the sampled media are distinguished into two categories: *thermal* and *solvent* extraction.

Thermal desorption is mainly used for Volatile and Semivolatile Organic Compounds [54,55]. Compared to extraction with solvents, heat absorption is simpler and is often automated through equipment, and it also shows sometimes superior performance and greater sensitivity.

Unfortunately, the thermal desorption of POPs is difficult to use. In fact, these compounds often interact with the adsorbent with bonds that can only be broken by a solvent and not by simple loosening of the bonds by heating.

Solvent extraction is mainly applied when sampling, active or passive, is performed through the enrichment of adsorbent/absorbent membranes. The extraction of analytes from the adsorbent/absorbent membranes takes place through an ultrasonic bath, used above all for PAHs, microwaves for example for metals, or through solvents at controlled temperature and/or pressure such as Accelerated Solvent Extraction (ASE) and Soxhlet.

Among the solvent extraction methods, we also include the Solid Phase Extraction (SPE), in which the compounds are eluted from the stationary phase using different solvents based on the affinity with the compound of interest. In this way, in addition to obtaining an extraction of the analytes, there is a simultaneous clean-up. The adsorbent packed in the cartridge can vary according to the class of pollutants being studied. All particle and aerosol samplings for POPs are included in solvent extractions (EPA TO-13A, [56], [57].

A clarification is required: to avoid erroneous results, as previously explained in *Scavenging Effect*, it is not possible to separate the compounds adsorbed on the particulate from those present in the gaseous phase, assuming that they are two separate systems. Since the two phases tend to interact not only in the atmosphere but also once deposited,

in the water (or when the snow melts) and during extraction, these two are not static systems [14,58,59]. It should not be forgotten that during air sampling or water filtration, the fraction of POPs adsorbed on the particulate matter (defined as a characteristic of dry deposition) can be stripped from the flow in proportion to their molecular weight for a class of compounds: the lighter compounds will be those to undergo the greatest stripping. Excluding the particulates, however, implies underestimating both the fraction of the heavier POPs that may not have been completely desorbed and all compounds not adsorbed by the particulate on the filter during sampling.

1.3.2 Water

Snow does not have a defined Standard Extraction method or common procedures accepted by the entire scientific community. Since once sampled, the extraction and purification analysis are carried out on melted snow at room temperature, the reference procedures for water can be followed. A snow sample consists of three parts: melt water, particulate matter and vapor phase (headspace of the sample vessel). These should be combined to have the total concentration of a given compound. The vapor phase, normally consists of the lighter compounds, with higher volatility Volatile Organic Compounds (VOC).

The extraction of the compounds from water (and indirectly snow) can be performed in two different ways: (1) direct extraction of the compounds from water into a solvent by **liquid/liquid extraction** and (2) extraction of an adsorbent medium used to trap the compounds **filtering** the water by a multistage extraction. The Liquid/Liquid (L/L) extraction method is the least used and even if most direct among the techniques listed above and is prescribed in some official methods (EPA 1668b and 1613). The balance of the analyte concentrations between the two phases (water and solvent) defines the principle on which it is based. The method involves the extraction of an aliquot from the water sample adding nonpolar organic solvent and shaking or stirring the water.

The solvent is collected and the whole procedure is repeated two more times [60,61]. The extracts are then combined and represent the total sample. Especially for snow, where the compounds are present in traces and it is necessary to treat the entire sampled volume, this method is laborious and prone to errors, in addition to the considerable use of solvents. Furthermore, if the water contains organic particles, an emulsion can form which complicates the extraction. Moreover, if the particulate does not come into contact sufficiently with the solvent it is extracted with low efficiency.

Solid phase extraction (**SPE)** is a faster technique than L/L extraction, but the system can cause cartridge-clogging problems when handling samples with high amounts of particulate and organic material, such as wet depositions. There are several stationary phases, among which C18 and Florisil are the most common in PAHs analysis [46,49]. Using solvents with different polarity it is also possible to purify a sample and elute the compound in different fractions.

If the expected concentration of the analytes is not consistent with the instrumental limits, it is necessary to extract the whole volume of water by filtration and subsequent extraction of the filter through solvent (Soxhlet, microwave, ultrasonic bath, ASE, elution), carrying out the so-called **enrichment** of the sample.

The deposition water is filtered either by gravity or by using pumps. The filtration method allows for the collection of the particulate and the extraction of the filter medium is the answer to the problem of the total analysis of an analyte, when the particulate extract is added to the water analysis. The best technique for filtering is to collect from the bottom of the container through a filter medium. Gravity acts on the particulate by depositing it directly on the filter; sometimes a pump is used to speed up the flow of water, eg. the millipore filtration system [53]. It is preferable to avoid sucking the water through the pipes from the bottom up, because the surface water is collected while the particulate and the high K_{ow} compound are concentrated at the bottom.

As with air, the particulate matter contained in water and snow plays an active role in the balance of analytes between the phases (melted snow, water and particles) therefore, if they were excluded, the analysis would underestimate the concentrations of the compounds. Wania, Mackay e Hoff (1999) demonstrated that the adsorption of PAHs on particles depends on the molecular weight of the analyte and physico-chemical characteristics of the particulate. Moreover, carrying out two samplings of the same volume in parallel (air and snow deposition) they demonstrated that particulate matter is more abundant in wet depositions than in air. [58].

1.4 ACTIVATED CARBON FIBERS

Activated Carbon Fibers (ACFs) is a material that combines the adsorbing properties of activated carbon with the technological mechanical resistance of carbon fibers. Activated carbon (AC) is made from treated carbon, which has a large number of easily accessible pores. Pores with high volume (> 1 cm^3/g) and high superficial area (> 2.5 m^2/g) make it an excellent means for adsorption of micropollutants into fluids. Carbon fibers (CF), on the other hand, are considered an engineering material thanks to the possibility of coupling mechanical properties of graphite to those of the strength of the fibers: low density (~2.26 g cm^3) and high Young's Modulus (~1 TPa). This type of carbonaceous structure can also work in non-oxidizing environments at high temperatures (> 3000 °C), in chemically inert environments with high electrical and thermal conductivity [62,63].
The main properties of the ACF are summarized below:

- A high apparent surface of absorption;
- Fibers with a diameter between 10 and 40 μm, characteristic required by new applications where the density of the material is fundamental, as in gas storage. The reduced diameter limits, also, the transfer of the mass which is mainly adsorbed-desorbed;
- It is a lightweight material, easily packable in fabrics, cloths, felts or paper;
- The dimensional distribution of the pores is compact and uniform even in the case of a mesoporous distribution. General porosity of the order of micropores;
- It can be used as a reducing agent to regenerate precious metals;
- It has anti-acid and alkaline properties;
- it can be easily regenerated without reducing its adsorbing properties;
- it can be used for combustion cell electrodes;
- It can be easily reduced to powder without causing secondary pollution [63].

This material is widely used in various fields thanks to its characteristics: removal of heavy metals [64,65], biomedical applications [62,66], as capacitors [67], as vapour

detectors [62,68], as refrigerants [69,70], as catalysts [71], for electrochemical applications [72,73], for the storage of natural gas and biogas [74], as a carbon molecular sieve [75,76], as electrodes [77,78].

1.4.1 Characteristics

Specific Surface Area (SSA)

Similar to many other carbonaceous materials with graphite structure, ACFs are composed of anisotropically stacked microcrystalline graphite structures that make their surface rough. The main feature of ACF is the high SSA due to the density of the pores. SSA can get to 2000 m^2/g, with a theoretical upper limit e 2630 m^2/g, even if there is evidence of ACF with SSA 3000 m^2/g [4].

The high adsorbent/absorbent power is primarily due to the edges of the surfaces, which have the same characteristics as the rest of the material. Furthermore, the structure of the nanographic and graphite walls, with their weak chemical interaction (sp2 - sp2), allows the heteroatoms to insert themselves between the graphene layers, increasing their adsorbing capacity. These pores can be produced with or without etching agents. In the second case, the genesis of the pores occurs only by volatilization of degraded by-products. The distribution of the pore sizes is mainly of the order of microns (< 2 nm) and the interconnections between them increase the complexity of the system.

Porosity

The pore system evolves according to the conditions of the process applied to the fibers. SSA is highly dependent on pore size distribution. It was observed that ACFs with low SSA (<1000 m^2 / g) have a pore size distribution centred around 1 nm, with an almost non-existent mesoporosity; while ACFs with high SSA (> 1200 m^2 / g) have a larger pore size distribution. However, whatever the SSA, most of the porous distribution is within the 0.33-10 nm range. Most of the time, this distribution is characterized by only one typology

which remains below 2 nm. Consequently, microporosity is a prevalent feature of ACFs. Hence, in order to develop a true mesopore system, the activation process must be significantly extended after the first appearance of the micropores. [79].

Packaging

ACF felt is characterized by having large meshes due to a smaller number of crossings, which give less resistance to traction and elongation. The connections, being slower and more fragile, are subject to breakage and tend to dust on the surface. Compared to ACF fabric, felt has the following advantages:

a) High porosity of the fiber (about 80%) and low impedance to fluids.
b) Larger contact area and greater absorption.
c) Ability to adapt to different ranges of thicknesses given the malleability

PAN and rayon fibers are normally the precursors for this type of product.

At the same density, fabric ACF is finer than felt ACF and the surface area does not exceed 1300 m^2/g. To increase the SSA, the thickness and consequently the stiffness of the fabric must be increased. In general, the properties of the product depend on those of the raw material but may be increased thanks to fabric reinforcement techniques. It has been shown that the plain weave having more crossing points between the weft and the warp increases the physical resistance properties of the product.

Compared to felt, ACF fabric has the following characteristics [80]:

a) Greater strength
b) Greater flexibility
c) It is not pulverized
d) It is not easily stratifiable
e) Lower apparent density.

1.4.2 Precursors

ACF is commercially produced by pyrolysis of carbonaceous materials of synthetic polymers (PAN, PVA, polyaramide and phenolic resins), synthetic fibers (e.g. viscose rayon and lignin), petroleum and pitch, tar, coal and natural fibers (e.g. cotton and sisal), followed by an activation process. Today, products already spun from biomass are widely used among the precursors. Each type of precursor has its own characteristics and limitations and, in turn, each one has its own specific field of industrial application and is used and an abatement system for specific classes of pollutants. It is well demonstrated that there is a relationship between the surface and microstructural characteristics of the ACF and the precursors used [81]. The most used precursors are PAN, cellulose, phenolic resins and pitch thanks to the combination of their low cost and mechanical capabilities. In this study, the attention was focused on the fibers coming from phenolic resins.

ACF based on phenolic resins has good plasticity and greater tensile strength. This type of fiber is difficult to graphitize, resulting in low modules. Non-graphitable carbon is a benefit for the growth of the pore structure. It is relatively soft and easy to spin, which is why it is used in clothing fabrics.

Table 1 ACF characteristics according to the raw material

Properties	**ACF**			
	Phenolic resins	**Polyacrylonitrile PAN**	**Pitch**	**Ryon**
Fiber diameter (μm)	9-11	10-14	6-11	15-18
Tensile strength (MPa)	300-400	200-500	100-180	70-100
Young's Modulus (GPa)	10-30	70-80	4-6	10-20
Elongation %	2.5-2.8	<2	2.4-2.8	2-3
SSA BET (m^2/g)	1000-3000	1000-2000	700-2000	1000-1500
Volume of micropores (mL/g)	1.0-1.2	0.2-0.7	1.5-2.0	0.2-0.7
Micropores diameter (Å)	5-30	20-30	15-45	10-16
Formula	$[C_{63}H_{55}O_{11}]_n$	$[C_3NH_3]_n$	$[Cl_{24}H_{80}NO]_n$	$[C_6H_{10}O_5]_n$

1.4.3 Production

The heat treatment transforms the fibrous precursors into carbon fibers. The process can be divided into 4 phases that include stabilization through an oxidative process, carbonization, graphitization and activation (see *Appendix A*).

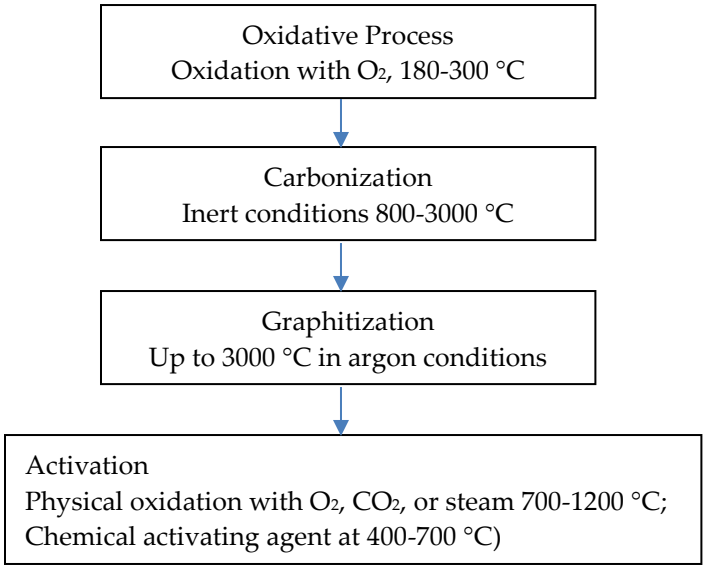


Figure 3 Step of Pyrolysis. Image Source *Jiménez et al. (2016)* [6]

Each type of precursor has its own characteristics and limitations, and for this reason, each has its own specific field of industrial application and in the removal of classes of pollutants. It is well demonstrated that there is a relationship between the surface and microstructural characteristics of the ACF and the precursors used [81]. However, PAN, cellulose, phenolic resins and pitch are the most used precursors, thanks to the combination of low cost and mechanical capabilities. In this study, fibers from a single precursor were studied and used, both for the ease of finding the material and for its characteristics: the phenolic resins Kynol.

Kynol® today it is the largest producer of ACF adsorbents in Europe as well as in Latin America, Africa and the Middle East [80].

After carbonization and activation, the precursors that have not yet undergone spinning can be transformed into different types of fabrics (paper, felt, fabrics). The primary source is wool or felt in rayon fibers.

1.4.4 Phenolic fibers

Phenolic fibers (Kynol) are used when a high tensile strength is required and they are often used to replace pitch derivatives. High temperature stability, flame and corrosion resistance and high thermal insulation characterize this product. Phenolic fibers are produced by catalyzed acid-base reactions of formaldehyde with phenol. The parameter that most influences the structure is the formaldehyde/phenol ratio, which can give rise to two different polymers: Novolac and Resole.

Two types of phenolic resins can be used to obtain ACF:

a) the first is obtained from phenol-hexamine polymer which, before carbonization, must not be stabilized in air. Hexamine, in fact, allows crosslinking already at 140°C during carbonization [82].
b) While the second is the Kynol Novaloid fiber (used in this work) highly cross-linked. This is the precursor of the fiber of the homonymous ACF felts and fabrics [83,84].

The novolac fiber or phenol-formaldehyde, if not polymerized, is weak, glassy and amorphous after spinning. Polymerization starts by heating the novolac fiber in an acidic environment in the presence of liquid or gaseous formaldehyde. The coil of phenolic fibers is immersed at room temperature in an aqueous solution of 18% HCl and 18.5% formaldehyde and the temperature is increased up to 100 °C. The formaldehyde spreading in the fiber reacts to form thermosetting structures. First, the temperature is raised to 150 °C and then oxidation is carried out at 250-450 °C, then carbonization and activation are carried out. Alternatively, Kynol fiber fabrics with surfaces up to 2800–3000 m^2/g can be obtained by proceeding directly to carbonization [79].

The production is divided into three steps. The first consists in the addition of formaldehyde to phenol, the second in the formation of the polymer, and the third

corresponds to growth. The addition reaction results in a three-dimensional cross-linked structure whose polymerization, represented by an exothermic condensation, leads to a tightly meshed structure and cross-linked resins [6].

Physical activation

Once carbonized, phenolic fibers are activated with vapour at 750-1000 °C and as times and temperatures increase, specific surface areas greater up to 2500-3000 m^2/g are obtained[82].

One of the parameters that influences the porous distribution is the activation temperature through the balance between the gasification and diffusion speed within the porosity of the coal. In fact, through a slow gasification, the activation process is uniform, and the porous distribution will be more homogeneous and of the order of a micron. Its morphological and resistance characteristics remain such as long as the process is not excessively extended. The pore size distribution, as shown in Figure 4, is significantly different and depends heavily on the activation parameters [79,85].

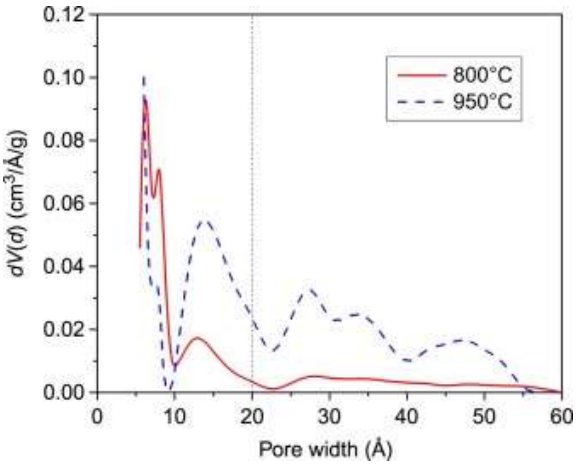


Figure 4 Pore size distribution of isotropic pitch-based ACFs activated with CO2+H2O for 3 h at 800 °C and 950 °C, respectively. Image Source: *Yue et al. (2016)* [79]

Chemical activation

The chemical activation is in detail stated in *Appendix A.4*, below there are only the information relating to phenolic resins. The phenolic fiber, once carbonized at 850 °C, is treated with KOH at 600-900 °C; at the maximum temperature produces an ACF with SSA of 1893 m^2/g [82].

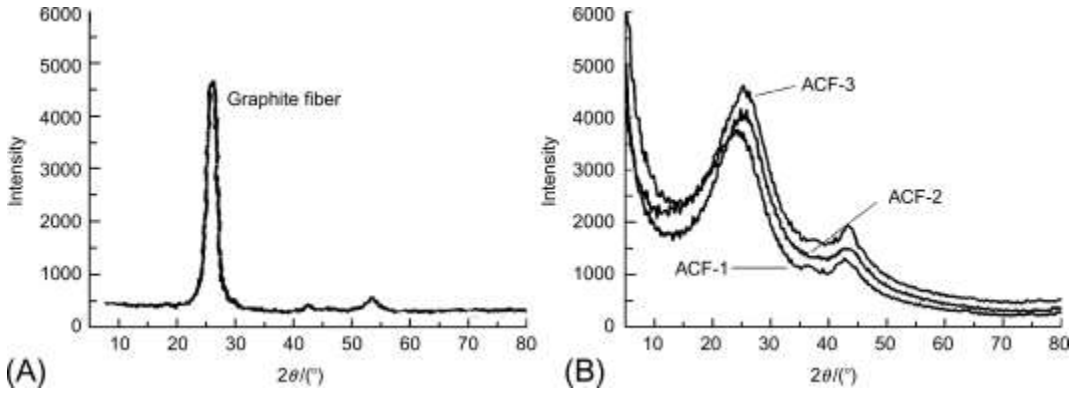


Figure 5 XRD Profile s of (A) graphitic fiber and (B) ACF. Image Source: *Li et al. (2016)* [5]

2 METHOD

Part of the work of the first year of the PhD was aimed at understanding the causes of the different behaviour of the ACF-F-2000 towards the classes investigated thus far (PCDD/Fs, PCBs, PAHs). The project started from an in-depth characterization of the material aimed at its analytical use and therefore not limited to the simple industrial information provided by the company. The study of the literature has shown that, depending on the type of raw material and the carbonization and activation processes, the final ACF has different adsorbent and affinity properties. Firstly, it was necessary to evaluate whether the batch at our disposal was consistent with the specifications declared by the supplier. Simultaneously we proceeded to test other types of ACFs and other extractive techniques for PCDD/Fs, PCBs and PAHs.

2.1 CHARACTERIZATION OF ACF

In order to use an adsorbent designed primarily for industrial use in analytical chemistry, multiple aspects must be taken into account. First of all, the cleaning of the adsorbent, i.e. the possibility of having blanks without an excessive quantity of interferents for the classes of analytes investigated. Next, the repeatability and reproducibility are maintained between one batch and another with no decrease of sensitivity in the results, which must fall within the order of magnitude of the trace compounds. The starting point was the technical information available from the manufacturers through which an initial indicative evaluation can be made to distinguish the most suitable type of material on the market.

For Kynol® fabrics and felts the data sheets are limited to the information on density (g/m^3), thickness (mm), coil size and SSA (m^2/g). The latter, perhaps the most useful information for our purposes, is too general since only the lower limit is given (e.g. > 800 > 1300 > 1800). Only for non-spun activated carbon fibers additional information is

provided relating to the absorption of iodine, benzene (Wt%) and dry and wet weight (kg/carton) because the ACF is highly hygroscopic.

Again, the information provided only indicates the lower limit.

To demonstrate the variability of the material properties, the information provided by Kynol® on the non-activated carbon fibers (the starting material, on which the properties of the finished material depend) are reported in Table 2 [86].

Table 2 Technical data sheet on non-activated carbon fibers from Kynol®. For two denier fibers, 51 mm and 70 mm fibers are also available with high-crimp (HCRC). Milled fiber; length shown is average length. Table Source: *kynol.de* [86].

	Article No.	**Single fiber**		**Fiber dia.**	**Tenacity**	**Fiber length**	**Elongation**	**Weight**	**Typical packing**
		(dTex)	Denier	(µm)	(mN/D)	(mm)	(%)	(g/m)	
Textile Fibers	KF-0251	2.2	2	14	12.8	70	30	-	40 kg/bale
	KF-0270	2.2	2	14	12.8	70	30	-	40 kg /bale
	KF-0351	3.3	3	18	12.8	51	30	-	40 kg /bale
	KF-0370	3.3	3	18	12.8	70	30	-	40 kg /bale
	KF-0570	5.6	5	23	9.8	70	20	-	40 kg /bale
Chopped Fibers	KF-0206T	2.2	2	14	12.8	6	-	-	25 kg/carton
Milled Fibers	KF-02BT	2.2	2	14	12.8	0.2	-	-	16 kg/carton
	KF-05BT	5.6	1	23	9.8	0.3	-	-	25 kg/carton
	KF-10BT	11	10	33	6.9	0.3			45 kg/carton
Tow	KT-2800	2.2	2	14	12.8	-	30	100	25 kg/carton

From the tabulated data, it can be deduced that "*textile fibers*" corresponds to the starting material for the ACF yarns. The length and diameter of the fibers between one product and another are different as well as the elongation and toughness, probably the differences are due to different carbonization and stabilization treatments. Since there is no further information on ACF yarn products, it is not possible to assess which type of fabric, in addition to the felt already used, is more suitable for analytical tests.

For this reason, it is necessary to identify the chemical-physical characteristics of the material before carrying out any experimental tests.

Four ACF products were chosen: two felts and two fabrics.

ACF-F-2000

Felt

ACF-F-2000B

Felt

ACF-C-2000

Fabric

ACF-C-800

Fabric

Table 3 Characteristics available from the data sheets provided by the selected ACF products industry.

	Manufacturer	**SSA**	**Thickness (mm)**	**Yarn**
ACF-F-2000	Kynol®	> 1800 m^2/g	1.4	Felt
ACF-F-2000B	Other	> 1800 m^2/g	1.4	Felt
ACF-C-2000	Kynol®	> 1800 m^2/g	0.55	Fabric
ACF-C-800	Kynol®	> 800 m^2/g	0.65	Fabric

ACF-F-2000 is the adsorbent used in previous studies (see *INTRODUCTION*) in which it was validated for PCDD/Fs and PCBs sampling. The ACF-F-2000B is a second felt by another manufacturer whose technical characteristics indicated are the same as those of the ACF-F-2000.

It was also decided to test the fabrics as ACF felt tends to pulverize on the surface and is more fragile to handle. Moreover, given the issue encountered during previous studies on the extraction of PAHs from ACF-F-2000, it was decided to verify whether the poor recovery rates of this class of pollutants could depend on the high porosity and the surface area of the material. According to the technical data sheets, the ACF-C-2000 is a fabric with the SSA (Specific Surface Area) comparable to the ACF-F-2000 but of lower thickness. ACF-C-800 fabric is the fourth product chosen, with lower SSA. It was not possible to perform the same tests on an ACF felt with SSA> 800 m^2/g (to compare the results with the ACF-C-800 fabric), due to the unavailability of the material by Kynol®. However, its evaluation is planned in the light of the results obtained with the selected

materials. The characterization tests performed are based on what is reported in the literature and on the ISO 21340 method (Test *methods for fibrous activated carbon*).

In particular, the ISO-21340 for the characterization of ACF provides the definition of the SSA using the Brunauer-Emmett-Teller (BET) method and the measurement of the porosity through the adsorption volume for a relative nitrogen pressure of 0.995 of the adsorption isotherm. Physical properties include fiber diameter (through a laser oscillator) and the tensile strength; in addition, loss on drying, pH, total ash content, adsorption performance of toluene, methylene blue[1] and iodine[2] are included [87].

Most scientific work aimed at the analytical use of ACF includes the following analyses: BET determination of SSA and pore volume [88–90], zero charge point or PZC to determine the general acid-base character of the material due to active groups [91,92], Bhoem analysis to identify the chemical class of active groups [91] and elemental analysis [84].

The following paragraphs outline the results of the physical and the chemical characterization of ACF, and are extracted from Cerasa et al., 2020 [93].

2.1.1 Physical

SSA, Porosity

According to literature, SSA and pore size distribution (PSD) play an important role in the characterization of the material [4]. The SSA was determined according to the BET method by Nitrogen adsorption. The two felts with SSA > 1800 m^2/g (ACF-F-2000 and ACF-F-2000B) have shown to have the same results; the results obtained for the ACF-F-2000 are reported as an example. Figure 6 shows BET isotherm of N_2 adsorption.

[1] Active sites

[2] Double bonds

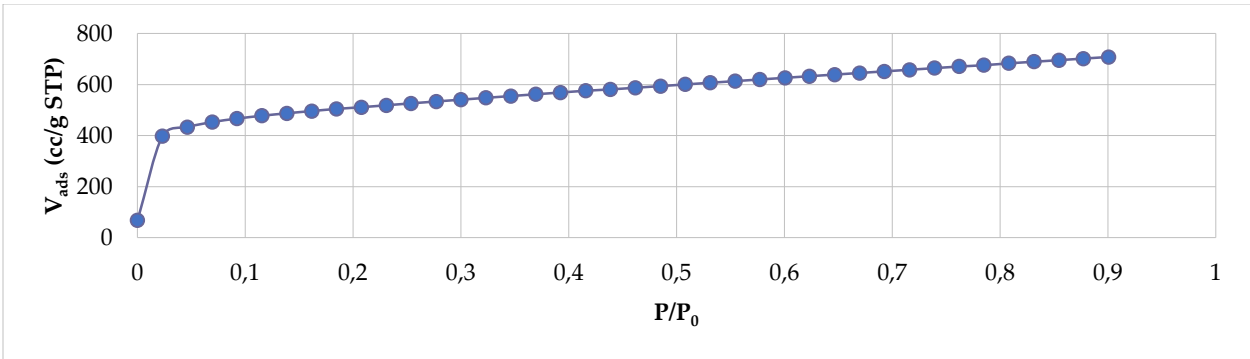


Figure 6 BET isotherm of N_2 adsorption at 77 K of the ACF-F-2000. Type I isotherm is the representative of gas adsorption in microporous adsorbents. V_{ads} = volume adsorbed; P/P_0 = Relative pressure. Image Source: *Cerasa et al. (2020)* [93]

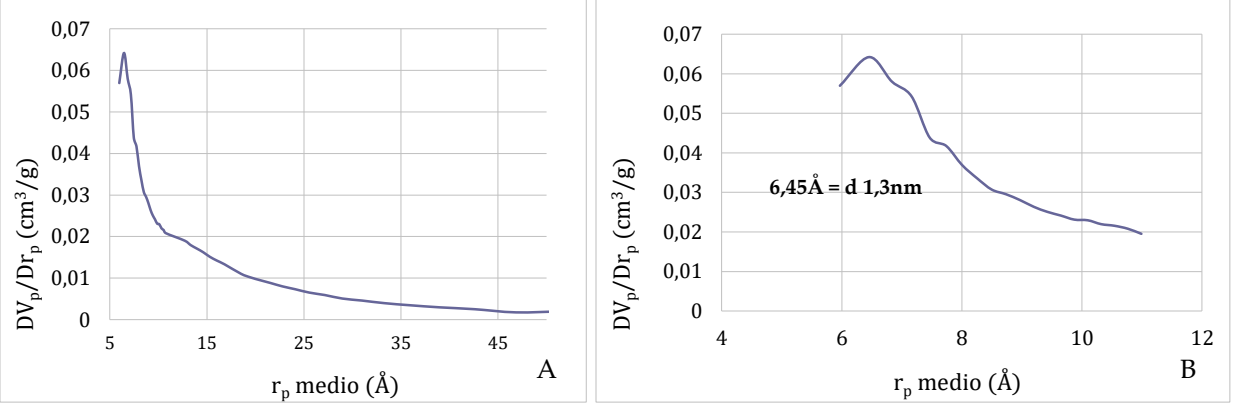


Figure 7 Pore size distribution BJH method of the ACF-F-2000. DV_P/Dr_P is the pore size distribution expressed in cm^3/g. V_P = volume of N_2 adsorbed by pores, r_P = pore radius. A) porous distribution with radius from 5 to 50 Å; B) magnification of A, from 4 to 12 Å. Image Source: *Cerasa et al. (2020)* [93].

It can be observed that the volume adsorbed (V_{ads} in cc/g STP. STP, Standard Temperature and Pressure, 1 atm and 273 K) by the ACF-F-2000 increases rapidly with the increase of the relative pressure (P/P_0) and the resulting isotherm corresponds to a type I Langmuir curve. Type I isotherm displays a curve beyond which the material reaches a plateau, meaning that it cannot adsorb after increasing partial vapor pressure. This graph known as "Langmuir curve" is associated with microporous solids (e.g. activated carbon, zeolite

molecular sieves and some porous oxides) with a relatively restrained external surface [94,95].

The Langmuir curve describes the sorption process, once the active sites define pores, they are completely covered by a first layer of molecules and the ongoing gas adsorption slows down up to the solid exhaustion. The process stops after the monolayer overlaps. The determined SSA is about 2468 m^2/g Figure 7 demonstrates the pore size distribution (PSD) of the adsorbent [4]. The average pore radius is approximately 6 Å (= 0.6 nm), that corresponds to a pore diameter of approximately 1.2 nm. In the IUPAC classification micropores are defined as "pores of width < 2nm", confirming what the BET had pointed out [96]. The same analysis was performed on the ACF-C-800 sample whose SSA was found to be ~ 757 m^2/g according to the BET analysis for a porous diameter of 1.3 nm. The results obtained show that the information provided by the technical data sheets are not always reliable as the data was at SSA> 800 m^2/g. Although the Langmuir isotherm is also type I in this case, microporous prevalence, a slight mesoporosity is also observed as shown in Figure 8. (mesoporousness - diameter between 2 and 50 nm).

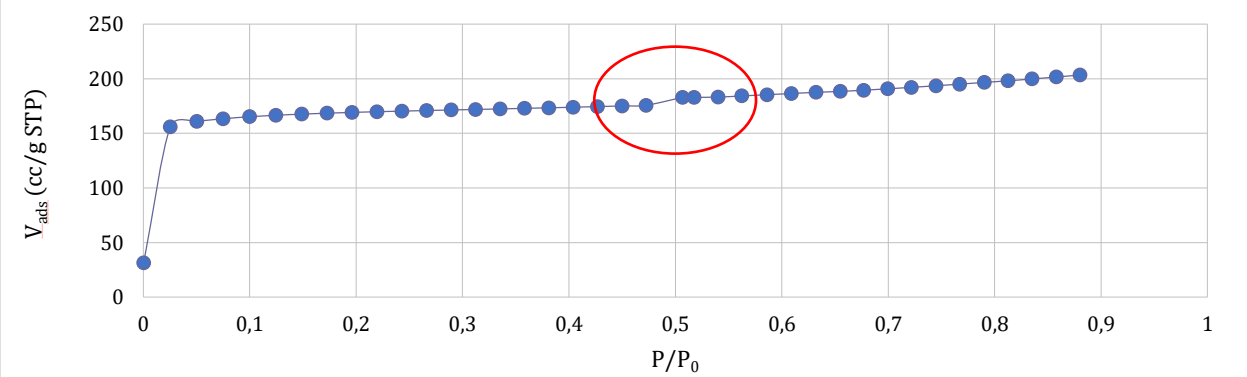


Figure 8 BET isotherm of N_2 adsorption at 77 K of the ACF-C-800. Type I isotherm is the representative of gas adsorption in microporous adsorbents. V_{ads} = volume adsorbed; P/P_0 = Relative pressure

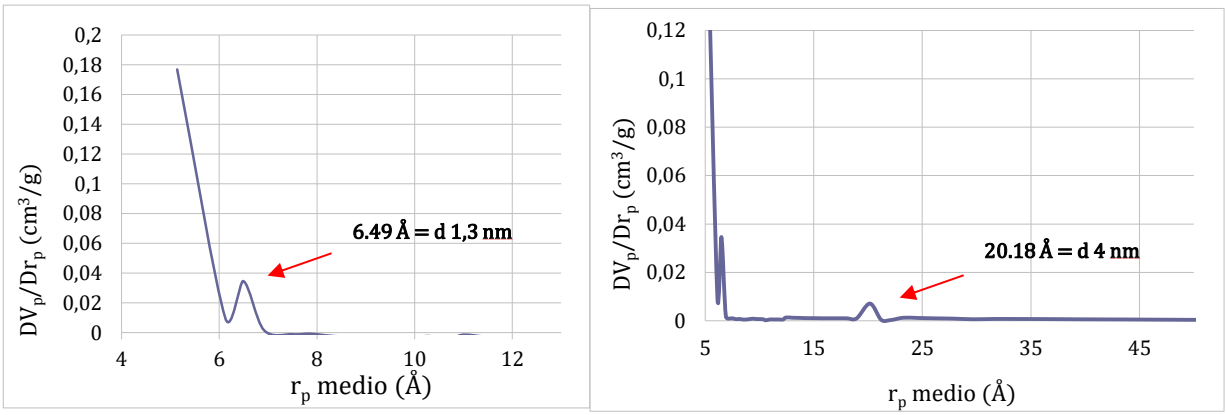


Figure 9 Pore size distribution BJH method of the ACF-C-800. Left micropore distribution; right mesopore distribution. DV_P / Dr_P is the pore size distribution expressed in cm^3/g. V_P = volume of N_2 adsorbed by pores; r_P = pore radius

Figure 9 demonstrates the porous distributions attributable to microporosity (left) and mesoporosity (right); the latter corresponds to the hysteresis highlighted on the BET isotherm in Figure 8. A coexistence of micro and meso porosity was also observed for the ACF-C-2000 fabric; the SSA according to the BET isotherms was of ~2010 m^2/g, much lower than that of the corresponding felt. Fabrics, therefore, have a different structure compared to felt and it is natural to trace it back to the different processes undergone during production.

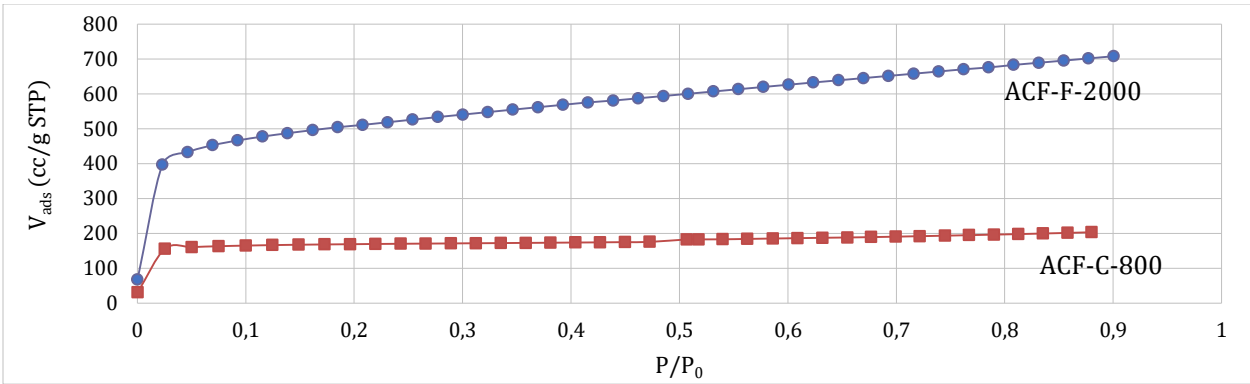


Figure 10 The absorbed N_2 was measured with a porosimeter and the results analysed using the BET method and the Langmuir equation. Before the measurements, the samples were degassed under N_2 flow at 120-150 °C overnight. The total volume of pores V_t was estimated through absorption at different relative pressures P/P_0 for variations of 0.9.

2.1.2 Chemical

Since ACFs may either have acidic and basic features and high surface charge distribution, the second stage consisted in chemical surface characterization by Boehm titration [97–99]. Basically there are three kinds of interaction mechanisms of micropollutants on activated carbons, namely π-π dispersions, formation of H bonds and electron donor-acceptor complexes [100–102]. The evaluation of the acid and basic groups present on the two felts (ACF-F-2000 and ACF-F-2000B) and on the fabric with lower SSA ACF-C-800 has been carried out following the titration method, which is based on acid-base titration of carbon acidic or basic centres. It is a method of selective neutralization, consisting in neutralizing the oxygen groups according to their acid strength [98,103–106]. The total number of acidic sites was calculated assuming that: (i) sodium hydroxide (NaOH) neutralizes carboxyl, phenolic and lactonic groups, (ii) sodium carbonate (Na_2CO_3) neutralizes carboxyl and lactonic groups while (iii) sodium bicarbonate ($NaHCO_3$), only the carboxyl groups. The number of surface basic sites was calculated by the direct titration with hydrochloric acid (HCl) [91,94]. For this purpose, 1 g of prewashed and dried ACF-F-2000 was placed in four different 50 mL vials with the following 0.05 N solutions: NaOH, Na_2CO_3, $NaHCO_3$, and HCl. The vials were sealed and

stirred for 24 h, 5 mL of each filtrate was pipetted, and the excess of base and acid was titrated with HCl and NaOH, respectively. The indicator used was methyl red with a pH ranging from red to yellow between 5 and 6, using 25 ± 0.1 ml burettes.

Table 4 Surface functional groups (in 10^{-6} meq/m^2) obtained through Boehm Titration. Table Source: *Cerasa et al. (2020)* [93]

	ACF-F-2000B	***ACF-F-2000***	***ACF-C-800***
Carboxylic groups	***76***	***8***	***205***
Lactonic groups	***3***	***1***	***55***
Phenolic groups	***57***	***31***	***161***
Pyronic groups	***111***	***119***	***305***
Acidic groups	***126***	***40***	***310***

As thoroughly explained above, the acidic and basic characteristics of ACFs and the high distribution of surface charges are obtained during the activation process by pyrolysis. It is for this reason that the second stage was the chemical characterization through the Boehm titration, intended to typify its surface carbon groups. This information is important to guarantee the repeatability and reproducibility of the interaction with the molecules of interest. Indeed, it is a known fact, that in carbons with same SSA and porous structure, changes in adsorption are attributed to differences in functional group concentrations (which influence the electronic structure of the graphene layers) rather than to small changes porosity [100]. Table 4 shows the functional groups (in 10^{-6} meq/m^2) identified on the fibers. ACF-F-2000 displays a strong acidic component, especially linked to carboxyl groups and a strong basic component due to pyrone groups, whose oxygens confer a negative charge to the material (Figure 11).

Guo et al. (2016) supposed that the adsorption reaction between chlorinated hydrocarbons and the carbon surface is due to the lactone groups. PCDD/Fs and PCBs are polychlorinated compounds, and the ACF-F-2000 has few lactone groups [107]. It is reasonable to assume that desorption of these compounds is related to the proportion between the acid and the basic component. It is also interesting to underline that the

acidic groups are related to adsorption ratio that is directly proportional to pH values [108].

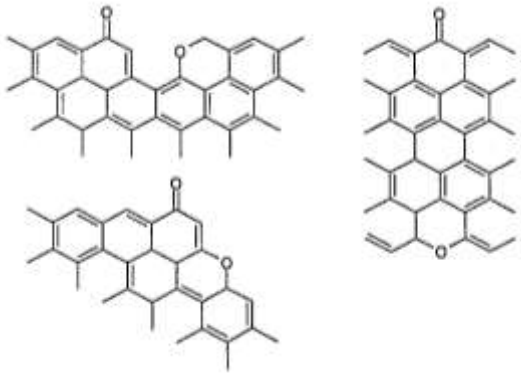


Figure 11 Possible structures of basic surface sites on a graphene layer, derived from the y-pyrone structure. Image Source: *Boehm (1994)* [109].

The chemical characterization of the materials allows for the evaluation of the type of ACF to choose for analytical purposes. In analytical chemistry, the objectives set include the use of the adsorbent not only for air but for water as well. Leng et al. (1997) have conducted studies on the phenol adsorption by ACF and they observed that the carboxylic acid content of the material promotes the absorption of water at the expense of phenol [110]. Another factor that influences the occupation of the active sites of the ACF by water is the presence of metals, thus it is suggested to wash with HCl before use [110].

The results obtained would confirm the choice of ACF-F-2000 with 8 10^{-6} meq/m^2 carboxyl groups, against 205 of ACF-C-800 and 76 of ACF-F-2000B.

2.2 EVALUATION OF EXTRACTION METHODS

Once the chemical-physical characteristics of the adsorbents had been defined, the desorption tests of PCDD/Fs, PCBs and PAHs from the different materials were carried out, by adding a known quantity of Standard containing the isotopically labelled ^{13}C and Deuterated congeners. As explained in the introduction, in the previous studies the ACF-F-2000 was validated for the adsorption/desorption of PCDD/Fs and PCBs classes according to the ISO 16000 and EPA methods. Briefly, different extraction techniques were compared: Soxhlet with toluene for 24h (as indicated by the ISO and EPA methods), the ultrasonic bath using different mixtures of solvents and extraction times and elution with solvents of increasing polarity. Among these, Soxhlet proved to be the most efficient method for PCDD/Fs and PCBs, while none of the previously listed methods allowed recovering PAHs in a satisfactory manner. The extent of adsorption/desorption is dependent on the molecular diameter of the analyte and the porous diameter of the adsorbent.

Starting from this premise, in this chapter are described the analyses carried out to evaluate:

- The extractive efficiency of further techniques for the classes already investigated (PCDD/Fs and PCBs but especially PAHs).
- The desorption capacity of ACF fabric-felts based on chemical characteristics, SSA and porous distribution in relation to pollutant classes.

The chosen extraction techniques were tested and the results evaluated based on the process speed, the environmental impact, reducing the use of solvents as much as possible and meeting the minimum requirements imposed by the methods (if any). In particular, Accelerated Solvent Extraction (ASE: Dionex ASE 200 accelerated solvent extractor) and Microwaves (Milestone Srl - ETHOS A - Microwave Digestion/Extraction Labstation) were selected.

Considering the molecular size of the PAHs and the characteristics of the materials, in addition to ACF-F-2000, ACF-C-800 (fabric with slight mesoporosity) and ACF-C-2000 (micro and mesopososity fabric with SSA similar to ACF-F-2000) were tested. Furthermore, the same tests were carried out on a Quartz Fiber Filter considered as a reference for total desorption.

Filters with a 47 mm diameter were made of the three materials, which were prepared by pre-cleaning them in Soxhlet with toluene for 24h and left to dry overnight at 150 °C under N_2 flow. An Extraction Standard Solution (ES Solution) 10 pg/μL with the ^{13}C congeners of PCDD/Fs and PCBs and PAHs (i.e. EN 1948-ES, WP-LCS and L429 RS, Wellington Laboratories) was prepared, 100 μl was added to each filter and after 10 minutes the extraction was performed. The extraction efficiency of the tested techniques was evaluated through the recovery percentages (R%) of the ^{13}C labelled compounds of the ES Solution defined by the reference method. The ranges of the PCDD/Fs labelled standards, according to ISO 16000-14, for tetra, penta and hexa PCDD / PCDF must be between 50% and 130%, while for hepta and octa between 40% and 130%. The extraction efficiency of the tested techniques was assessed through the recovery percentages (R%) of the labelled compounds of the ES Solution defined by the reference methods. According to ISO 16000-14, the R% of the ^{13}C-PCDD/Fs must be between 50% and 130% for substituted tetra, penta and hexa and between 40% and 130% for hepta and octa. While the R% for each ^{13}C-DL-PCB congeners added must be at least 40% and must not exceed 120%. In exceptional cases, recoveries between 20% and 150% are accepted, when the contribution of a single congener in the TEQ dl-PCB is less than 10% considering the WHO-TEF [111].

Regarding PAHs, both the EPA TO-13A method and ISO 12884 method were taken into account [2,112].

In neither of the two cases Sampling Standard Solution (SS Solution) is provided, except for method validation. Furthermore, the ISO 12884 method does not provide any

indication about the surrogates to be used for the different phases. The ISO 12884 range has been adopted as reference range, as it is more restrictive than the corresponding Indoor method (EPA TO 13A) [2,112].

Table 5 QC Acceptance criteria for labelled compounds in samples according to ISO 12884 and EPA TO 13 A methods. Sampling Standard Solution (SS Solution). Extraction Standard Solution (ES Solution). [2,112].

EPA TO 13 A	**R%**
SS Solution	
D10-Fluoranthene	60-120
D12-Benzo(a)pyrene	60-120
ES Solution	
D10-Fluorene	60-120
D10-Pyrene	60-120

ISO 12884	**R%**
SS Solution	75-120
ES Solution	75-120

2.2.1 Accelerated solvent extraction - ASE

All extractions were performed in 11 mL stainless-steel cells, with 40 mL of toluene at 100 atm pressure by three static cycles. The vessels were rinsed at 70% of the rinse volume. The static ASE extraction was conducted at 200 °C for 5 minutes. All extractions were conducted in triplicate. The extracted analytes were purged from the sample cell using pressurized nitrogen for100 s.

The collected fractions were concentrated under N_2 flow in a thermostatic bath between 40 and 48 °C (depending on the solvent) and before the injection to the GC-MS/MS (see *Appendix B.1*), 1000 pg of the Injection Standard Solution (IS Solution; WP-ISS, EN-1948IS and L429 RS), S was added. All the tests were carried out in triplicate and the results relating to the average of the three tests are shown (in Figure 12).

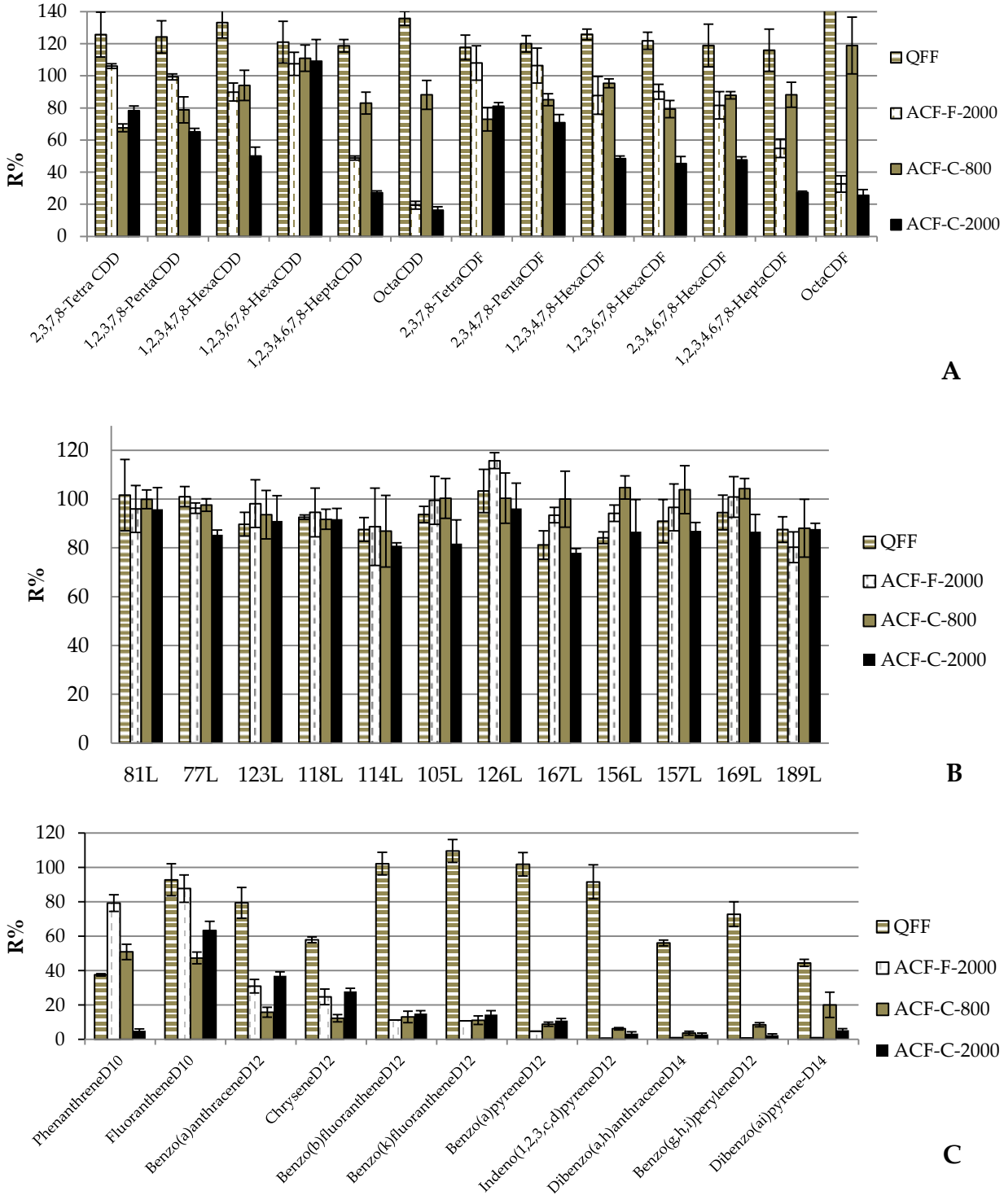


Figure 12 Average percentage recovery (R%) of the ES Solution of the three tests and STD by ASE. Quartz Fiber Filter. ACF-F-2000, ACF-C-800, ACF-C-2000. A) PCDD/Fs ^{13}C labelled compounds; B) PCBs ^{13}C labelled compounds. Suffix "L" indicates labelled compound. C) PAHs deuterated labelled compounds.

According to Figure 12A, the felt (ACF-F-2000) for dioxins maintains R%s between 90 and 100% up to the hepta class where R%s drop to 45%, reaching just 20% for the octa. For the furans the situation seems to be slightly better given that between the tetras and the hexas the recoveries are maintained between 80% and 110%, with regards to the hepta the results are at 55-60% and 35% for the octa. About the fabric with SSA slightly lower than felt, ACF-C-2000, there are no particularly satisfactory in PCDD/Fs R%s: they are all between 80% and 16%: passing from tetras to octas chlorinated the R%s progressively decreases as the molecular weight increases.

As for ACF-C-800, the second fabric with lower SSA, the R%s of ^{13}C-PCDD/Fs appear to be the best. Namely, all of them fall between 62 and 119% except for 1,2,3,7,8,9-EsaCDF equal to 53%.

As concerns ^{13}C-PCBs, the R%s for all types of ACF are > 80% Figure 12B.

On the contrary, for PAHs, no fabric can be considered valid given for any type the R%s reach the minimum values. In fact, the R%s plunged as the number of aromatic rings increased. In particular, the phenomenon occurs starting from Benzo(a)anthracene. All recoveries with a value lower than 1 are associated with a high inaccuracy, as confirmed by the RSD% which is near 100%. Therefore, such R% s are not considered as they are lost in accuracy and precision (*Appendix D*).

In simultaneously considering the results obtained with ASE, the ACF-C-800 is the best for PCDD/Fs and PCBs classes. This fabric showed narrow ranges and high R% values, thus overall, it is better than the ACF-F-2000 for which ISO 16000 13 and 14 and EPA TO 4A and 9A methods have already been validated. In general, the repeatability of data for the ASE is variable, so much so that some values are not considered valid because they are out of range (e.g. OCDF R% of ACF-C-800). However, comparing the results shown here with those of the previous tests (Master Degree results), the ACF-F-2000 combined with the toluene Soxhlet extractor is the most performant [1]. Comparing the results reported here with those of the previous tests (*Master Degree Results*, *Appendix C*), the

ACF-F-2000 combined with the Soxhlet extractor with toluene extracts about 15% more of the total PCDD/Fs, while the PCBs a 4% less. Despite the slight increase in recoveries of PCBs with ASE, the advantage using Soxhlet extractor over PCDD/Fs is greater.

2.2.2 Microwave

Microwaves are recognized as regions of the electromagnetic spectrum, with a range between 0.001 and 1 m (between infrared radiation and radio waves), corresponding to frequencies between 300 and 0.3 GHz.

Dielectric heating refers to heating by high-frequency electromagnetic radiation, namely radio frequency waves and microwaves. In fact, when the component of the electric field of electromagnetic radiation interacts with the charged particles of some materials, they can heat up. The heat produced by this interaction is mainly due to two different effects:

- In polar molecules (such as water), permanent dipoles and induced dipoles rotate when trying to align themselves with the alternating microwave electric field (2.45 billion times per second). This molecular motion creates friction between the rotating molecules, and energy is consumed as heat (dipolar polarization).
- In solid dielectric materials, charged particles can move freely in a limited area of the material (for example, π electrons in carbon materials) and generate an induced current in phase with the electromagnetic field.

The increase of heat is due to the Maxwell-Wagner effect: electrons are not able to couple to phase change in the electric field and the surplus of energy is dissipated as increment of temperature [113,114].

Microwave absorbers are materials that interact with microwaves generating heat. The heating ability of a material in the presence of a microwave field is determined by its dielectric loss tangent: $\tan\delta=\varepsilon''/\varepsilon'$. The dielectric loss tangent is composed of two parameters, the dielectric constant (or real permittivity) ε', and the dielectric loss factor (or imaginary permittivity) ε''; that is, $\varepsilon=\varepsilon'-i\varepsilon''$, where ε is the complex permittivity. The

ε' determines quantitatively the reflected and the absorbed energy, while ε" measures the dissipation of electrical energy in the form of heat in the material.

High values of tanδ, i.e. low values of ε 'with high values of ε' is present in an optimal situation where microwave energy is efficiently converted into thermal energy. Microwave reflection is a characteristic of electrical conducting materials, graphite and highly graphitized materials, thanks to the 4 electrons that can migrate in the plane, are considered electrically conductive material. For this reason, it can reflect most of the radiation in this wavelength.

In addition, in a carbon atom, delocalized π electrons move freely, and other very interesting phenomena can occur. The kinetic energy of some electrons can increase to the point where they are emitted from the material and tend to ionize the surrounding atmosphere. This phenomenon will produce small sparks visually, and microplasma will be formed microscopically. An intensive generation of these microplasmas may have an important impact on the process involved.

The microwave heating of dielectric materials by converting electromagnetic energy into heat in the irradiated material has many advantages over conventional heating, such as: (a) non-contact heating; (b) transfer of energy instead of heat; (c) Rapid heating; (d) the materials are selectively heated; (e) Volume heating; (f) Quick start and stop; (g) Heating of the material from the core outwards; (h) Higher level of safety and automation [113,114]. In order to obtain the best microwave energy coupling, moderate values of ε' and high value of ε'' (that correspond to the high value of tan δ) should be combined to convert microwave energy into heat. Therefore, although some materials do not have a high enough loss factor to allow dielectric heating (i.e. they are transparent to microwaves), while other materials (such as certain inorganic oxides and most carbon materials) are exceptional absorbers of microwaves.

Due to these advantages, microwaves are utilized in various technological and scientific fields in order to heat diverse materials [113,115,116].

Furthermore, solid materials with a high dielectric loss factor, namely microwave absorbers, can be subjected to different treatments based on microwave heating. Carbons generally are excellent microwave absorbers, thus they can be easily produced or transformed by microwave heating. Furthermore, to indirectly heat materials which are transparent to microwaves carbon materials can be used as microwave receptors. Consequently, carbon materials have been utilized as microwave receptors in the pyrolysis of biomass and organic wastes, in soil remediation processes, catalytic heterogeneous reactions, and so forth. Table 6 illustrates the high ability of carbon materials to absorb microwave energy and convert it into heat, which lists the dielectric loss tangent values of different carbons. It is evident that the loss tangents of most of the carbons, except for coal, are higher than that of distilled water (tanδ of distilled water = 0.118 at 2.45 GHz and 298 K). Searching and summarizing these data is not an easy task. Even if this parameter is essential to the study of microwave heating, only a few research groups have determined the dielectric loss tangents of carbons and the data that can be found is scattered throughout bibliography [117].

Table 6 Dielectric loss tangents for different carbon materials at a frequency of 2.45 GHz and room temperature, ca., 298K.aActivated carbon at a mean temperature of 398 K. Table Source: *Menéndez et al. (2010)* [117]

Carbon Material	tanδ = ε''/ ε'
Coal	0.02-0.08
Carbon Foam	0.05-0.20
Charcoal	0.11-0.29
Carbon Black	0.35-0.83
Activated Carbon	0.57-0.80
Activated Carbon	0.22-2.95
Carbon nanotube	0.25-1.14
Csi nanofibers	0.58-1.00

In our case, microwaves were used precisely because the ACF adsorbent has a high dielectric loss tangent value and can heat apolar solvents, transparent almost completely

to the microwaves, transferring the heat absorbed by the microwaves to the solvent in which it was immersed. A temporary reduction of π- π adsorption bonds was also expected due to the phenomenon of delocalization of electrons that are free to move.

The extraction was carried out with a Microwave (Milestone Srl - ETHOS 1 - Microwave Digestion/Extraction Labstation) in toluene. The program temperature was set as follows: Initial temperature and hold 19 °C for 0 s; initial ramp to 120 °C @ 20 °C per minute (800 W); second hold 120 °C for 20 minutes (800 w); 10 minutes of ventilation (0W). The collected fractions were concentrated under gentle N_2 flow in a thermostatic bath between 40 and 48 °C and before the injection to the GC-MS/MS (see *Appendix B.1*), 1000 pg of the IS Solution was added. Each test was performed in triplicate.

Regarding the PCDD/Fs and PCBs classes, microwave extraction (Figure 13) performed worse than ASE in Figure 12. Concerning the two types of fabrics (ACF-C-800 and ACF-C-2000), it seems that for PCDD/Fs an opposite trend was verified in the ASE extraction, i.e. lower R%s for the lighter classes compared to those with higher molecular weight (80-90%). While the ACF-F-2000 has R%s between 10 and 50% except for the 1,2,3,6,7,8-EsaCDD. The R%s of ACF-F-2000 and ACF-C-800 for PCBs seem to have the same trend while it appears to plunge for ACF-C-2000 fabric. Although the method is quite reproducible for PCDD/Fs (low STD and RSD%), the R% s do not meet the requirements imposed by the reference methods. Furthermore, the average R% s vary according to the congener as shown by the STD of the total recovery equal to 30%. If the higher recoveries obtained with the extraction in Soxhlet compared to the ASE for PCDD/Fs justified the preference of the former, the advantage is even greater when compared to Microwave: the Soxhlet extracts about 63% more PCDD/Fs than the Microwave technique, with a variability on the total Rs of PCDD/Fs of only 8%.

A phenomenon that was verified during the extraction was the high temperature in point-like areas, at the borders of the ACF membranes to be extracted, which produced cracks in the microwave Teflon cells. Probably because locally the temperatures reached

were higher than those of PTFE degradation, namely above 270 °C despite the ACF being immersed in toluene (boiling point 110 °C). This can be explained by the fact that not all the extractions were performed in a homogeneous way: the boiling reached by the solution lifted the adsorbents out of the solution itself, and therefore was unable to transfer the thermal energy to the extraction solvent.

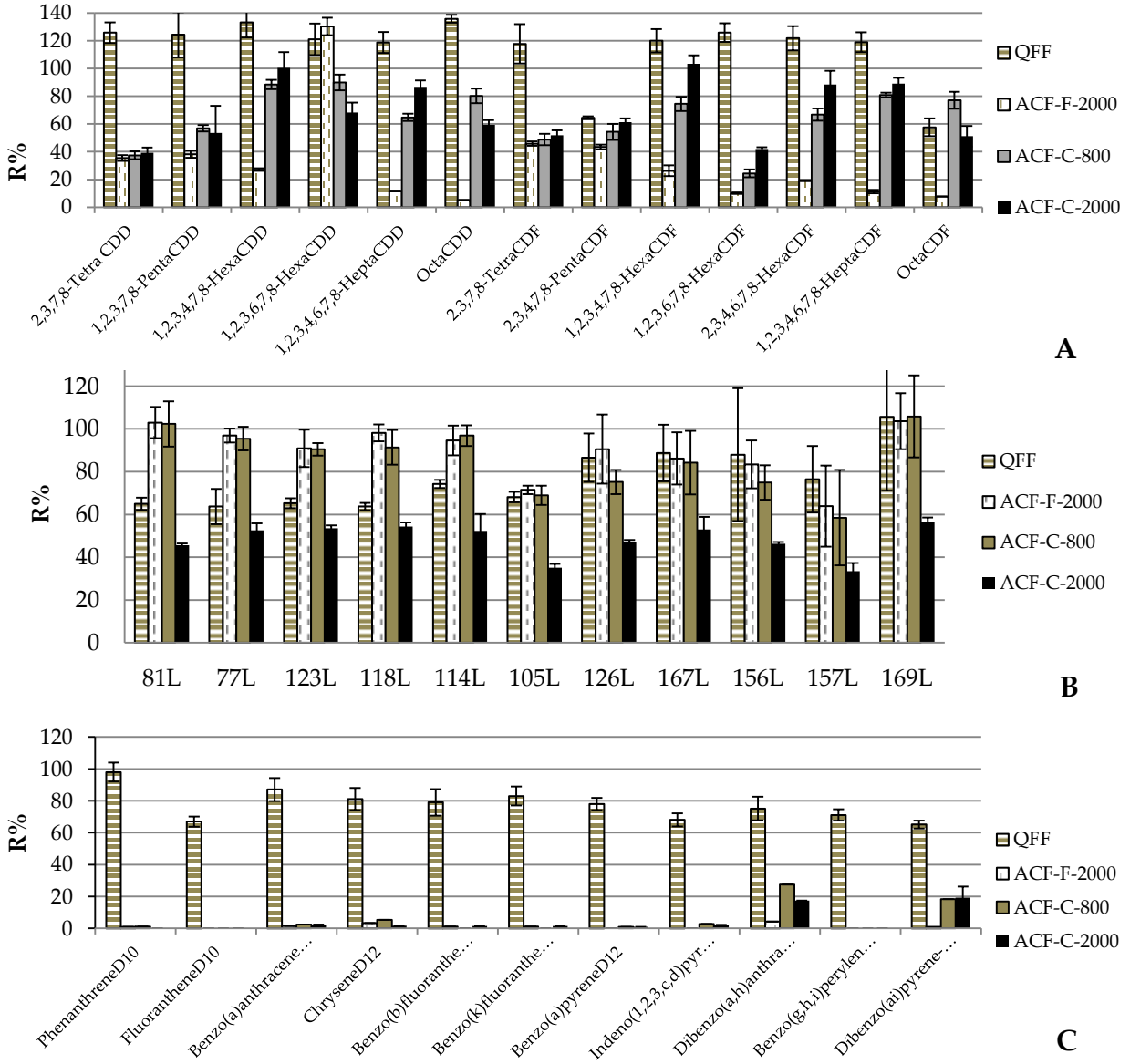


Figure 13 Average percentage recovery of the three tests (R%) with STD through Microwave of the ES Solution. QFF: Quartz Fiber Filter. ACF-F-2000, ACF-C-800, ACF-C-2000. A) ^{13}C-PCDD/Fs labelled compounds; B) ^{13}C-PCBs labelled compounds. Suffix "L" indicates labelled compounds. C) Deuterated PAHs labelled compounds.

Not even this extraction method produced satisfactory results for PAHs for any type of material tested, with R%s lower than 20% (Figure 13 C). Furthermore, during the extraction the high temperatures reached led to the degradation of the ACF adsorbents and the production of native PAHs. Figure 14 shows the comparison between the fullscan chromatograms of the QFF extract with that of the ACF-F-2000 for m/z 228, where Benzo(a)anthracene, cyclopenta(cd)pyrene and chrysene are at 18.76, 18.85 and 18.91, respectively.

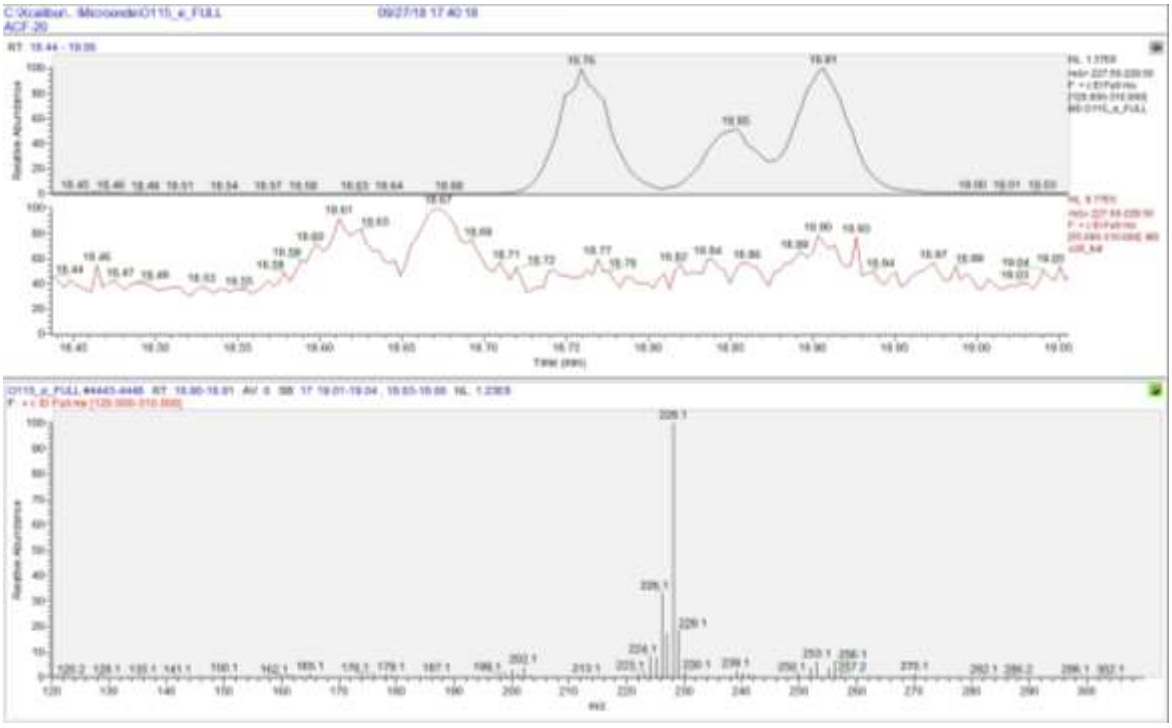


Figure 14 Comparison of the FullScan chromatograms of the QFF extract (upper chromatogram) with that of ACF-F-2000 (lower chromatogram) for mass 228. Benzo(a)anthracene, Cyclopenta(cd)Pyrene and Chrysene (18.76, 18.85 and 18.91 respectively). The spectrum is relative to the Chrysene tr. 18.9-18.91

Despite the laborious and slow technique, the recoveries qualify once again the Soxhlet extraction as the most efficient. Among the different types of ACF studied, the felt with the highest SSA (ACF-F-2000) is confirmed as the best adsorbent in terms of adsorption/desorption. It must also be considered that fabric is normally used in protective devices as a passive adsorbent. Using the fabrics actively (as it happens for the felts) by forcing a flow to cross them, it is not possible to guarantee the homogeneity of

contact due to the weaving of the fibers. For this reason, the chosen adsorbent material turned out to be ACF-F-2000.

2.2.3 Why is there no desorption of PAHs?

At this point of the study, it is possible to examine why the ACF-F-2000 is more suitable for some classes rather than for others. According to the literature, when considering large organic molecules such as PCDD/Fs and PCBs, the reversibility of the adsorption on ACF-F-2000 is possible because the pore width (about 1.2 nm) is narrower than the adsorbed molecules. Furthermore, pore shape does not allow these planar molecules to be trapped in the micropores of the material [5]. Although the structure of PCBs differs according to the number of chlorine substitutions, the molecular size is approximately 1.4 nm along the major axis and 0.8 nm along the minor axis and 0.4 and 0.8 nm thick. The study by Kawashima et al. demonstrated that materials with an SSA of 700 and 1200 m^2/g and a pore diameter of approximately 0.7 and 0.8 nm are suitable for adsorption of PCBs [108]. According to Li et al., however, the pore diameter of the adsorbent should be of the mesopore order (2 and 5 nm) to completely remove PCDD/Fs (whose diameter is approximately 0.35 and 1.37 nm) and PCB [96,118]. In addition to the porous diameter, its distribution and pore type is the second aspect to be evaluated for molecules desorption. Therefore, if the porosity is deeply branched and the pores have different sizes, the compounds can penetrate and can be trapped in the larger pores. This is the reason why ACF-F-2000 has a good reversible adsorption on both PCDD/Fs and PCBs. The pores have a diameter of 1.3 nm and are evenly distributed on the surface, which does not allow these compounds to penetrate deeply, favouring surface adsorption [93]. As far as the two ACF fabrics (ACF-C-800 and ACF-C-2000) are concerned, the detected mesoporosity (4 nm in diameter) and the irregular porosity does not allow predicting exactly which interactions and with which compounds will be established. Moreover, the

texture greatly influences the contact points so that the adsorption sites can increase according to the armour. Adsorption/desorption are phenomena that depend not only on physical but also chemical interactions. Unsaturated carbon atoms with unpaired electrons characterize the basal planes of the ACF surface. Oxygen-containing heteroatoms are usually bonded to these electrons.

As regards the organic aromatic compounds, 3 important adsorption mechanisms on activated carbon are identified in the literature:

- π-π dispersions
- H bonds formation
- Electron donor-acceptor complexes [119].

Aromatic compounds are adsorbed on activated carbon surfaces through π-π dispersion interactions with graphene layers. The functional oxygen groups at the edges of these layers provide sites for the adsorption of hydrophilic species and can affect the adsorption of the hydrophobic compounds on the graphene layers. This is exactly what happens to PCDD/Fs and PCBs: the carboxyl groups tend to attract the p-electrons of the graphene basal plane, which by reducing the donation of the π-π electrons, reduce the adsorbate-adsorbent interaction strength. The lower the SSA, the more the π-π interactions (involved in electron donation from carbon to aromatic adsorbate) are weakened by the functional groups at the head of the graphene layers. The enthalpy of adsorption augments for higher surface coverage, because it influences the π-π adsorbate-adsorbate interactions. An increase in the size of the adsorbate strengthens the interaction as shown for the adsorption of benzene and naphthalene on graphite. Therefore, molecules with a planar conformation such as dioxins and dioxin like compounds, have higher adsorption ratios [100]. PAHs and ACFs materials have practically identical structures for this reason the interaction is stable and increases as the number of rings increases. Regarding the greater desorption of PCDD/Fs and PCBs compared to that of PAHs, an answer is found in the work of Streat and Horner (2000)

on the adsorption of benazolin on the ACF [120]. As it is well known, chlorine is characterized both by a weak resonance effect (which makes the electronic pair of the halogen able to interact with the electronic system of the benzene ring) and by a more important and prevalent inductive effect which depletes the aromatic system. The predominant electron withdrawing group (EWG) nature of the chlorine, makes the interaction between the graphene layers and the PCDD/Fs and PCBs weaker, justifying their greater desorption [120]. Since the PAHs do not have Cl atoms, it is possible to hypothesize that they are irreversibly absorbed by the ACF planes, becoming part of its structure. Zhang et al., (2010) evaluating the 3 molecular dimensions of Phenanthrene (PNT), 2-Phenyl phenol (2-PP) and Biphenyl (BP) defines the type of adsorption on carbonaceous materials and identifies as fundamental the role of the planarity, the pore size and the polarity. Indeed, for PNT, a planar and non-polar molecule, its second smallest size is comparable to the diameter of the ACF micropores and once inside, the forces between the graphene and the plane of the compound prevent its desorption. While for the 2-PP and the BP, the non-planarity simplifies the entrance into the irregular pores. The compounds, once adsorbed, interacting with the carbon remain bound and can no longer leave the pores (Figures 15) [121].

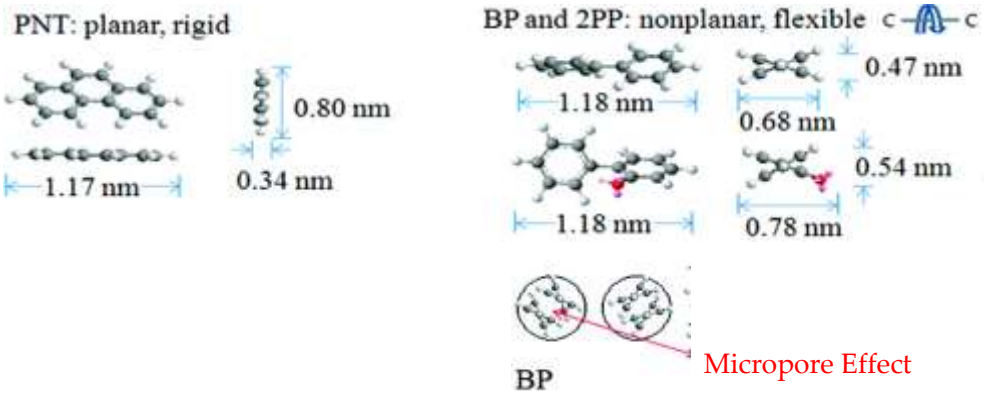


Figure 15 Right: Phenanthrene (PNT), polar and planar. 3 molecular dimensions and comparison with the diameter of an ACF micropore. Left: Above Biphenyl (BP), below 2-Phenylphenol (2-PP), non-planar and flexible. 3 molecular dimensions and comparison with the diameter of an ACF micropore. Image Source: *Zhang et al. (2010)* [121]

For all PAHs with a number of rings greater than 3 the adsorption is mainly on the surface of the ACF. As far the ACF-C-800 is concerned, according to Pinto and Leg (1997), the action of two contemporary factors is observed: a) the presence of oxygenated groups on the carbon surface (1036 10^{-6} meq/m^2) and the lower SSA reduce the adsorption of aromatic compounds favouring their extraction; b) the mesopores allow the ACF-C-800 to trap the PAHs given the diameter [110]. This does not happen for the ACF-F-2000 and the ACF-F-2000B (the 2 felts) which having SSA of about 2000 m^2/g and respectively 199 10^{-6} and 373 10^{-6} meq/m^2 of oxygenated groups have a greater interaction with PAHs.

2.3 VALIDATION OF PESTICIDE ANALYSIS IN AIR

Once the ACF-F-2000 has been characterized for analytical use, the research proceeded by applying the chosen adsorbent to another class of pollutants included in the standard methods considered, namely pesticides (EPA TO-4A). In particular, the analytes examined were hexachlorobenzene (HCB) and pentachlorobenzene (PeCB). The evidence presented will be briefly reported, applying the validation method already developed during the Master Degree studies on PCDD/Fs and PCBs [1].

2.3.1 Evaluation of PeCB and HCB extraction

Before beginning a study on the ACF-F-2000 for the sampling of any analyte, it is essential to verify if the material is able to adsorb the compounds and subsequently if the phenomenon is reversible. Technical applications well describe its industrial use as an abatement system for HCB and PeCB, so their adsorption, but not their desorption from the material.

Furthermore, investigating different extraction methods allows optimizing time and volumes of the solvents to use. In this case, the following 4 extraction techniques were tested: the ASE seen previously, and those verified during the studies of the Master Degree thesis (solvent elution, ultrasonic bath and Soxhlet extractor). First, it was necessary to confirm the results that had already been obtained, but the main aim was to evaluate whether the Soxhlet extraction was extendable to these compounds.

According to the EPA TO 4A method, a sample to be considered quantifiable, the % extraction recoveries (R%) of the isotopically labelled congeners of Standard solution must be between 60 and 120% [56].

A solution containing $^{13}C_6$-pentachlorobenzene and $^{13}C_6$-hexachlorobenzene was prepared and added to the 47mm diameter ACF-F-2000 filters, pre-washed as described above. According to the extraction technique used, the samples are concentrated up to about 200 μL and 100 μL of the Injection Standard Solution (IS Solution; $^{13}C_{12}$-PCB at

10pg/μL WP-ISS, Wellington Laboratories, Canada) is added before the GC-MS/MS analyses (see *Appendix B.1*). All tests were performed in triplicate.

The test of extraction by **elution** was performed using the AccuPrep MPS ™ automated instrument (J2 Scientific, USA), which minimizes errors and ensures the reproducibility of the extraction. The experiment has been conducted on an elution flow of 5 mL / min. and the sample was added to the cartridge from the autosampler at a flow of 3.5 μL / min. The elution solvent solution consisted of 10 mL of Toluene: Methanol 90:10 (v / v). The extracts were pre-concentrated with a Rotary evaporator up to about 5 ml, transferred into a test tube and finally brought to about 0.5 ml in a thermostatic bath at 48 °C under a gentle N_2 flow. The three eluates were then spiked with the IS Solution and analysed by GC-MS/MS (see *Appendix B.1*).

The extraction by solvent elution cannot be considered suitable for these compounds since the average R% both PeCB and HCB reach a maximum of 24%.

The **ultrasonic** extraction was performed by placing the filters previously spiked with the $^{13}C_6$-PeCB and $^{13}C_6$-HexaCB Solution, in about 20 ml of Toluene and sonicated for 10 minutes. The supernatant was collected and filtered with paper (Whatman qualitative, 125 mm, cat No. 1004 125). All the steps were repeated two times more on the same filter collecting all the fractions together. The 60 ml of the extracts, as before, were concentrated with a Rotary evaporator before and under a gentle N_2 flow in a Thermostatic bath at 48°C subsequently. The IS Standard was then spiked into the extracts before proceeding to the GC-MS/MS analyses (see *Appendix B.1*). The extraction by sonication, although better than that by elution, still proved unsatisfactory for the goal set. While the HCB reaches average R%s greater than 70%, the one of PeCB does not exceed the 5%.

The **Soxhlet extractor** was used following the indications given by the EPA methods and already validated for PCBs and PCDD/Fs, i.e. 36 h of extraction with toluene. The $^{13}C_{12}$-PeCB and $^{13}C_6$-HCB solution was added to the ACF-F-2000 filters prior to extraction. The extracts were then concentrated, as explained above, and the IS solution was added prior

to the GC-MS/MS analysis (see *Appendix B.1*). A second Soxhlet extraction was performed on the same filters to confirm the complete recovery of the labelled compounds.

The ASE extraction was performed as reported in the previous chapter, while it was preferred not to execute the microwave one. Given the high temperatures recorded in previous tests, the compounds would surely have been lost due to volatility.

All extraction methods are compared in Figure 16 and it is clear that Soxhlet extraction is the only one that can be used for both compounds as shown by the R%s.

All data and Relative Standard Deviation percentage (RSD%) are detailed in the *Appendix E* - Table 45.

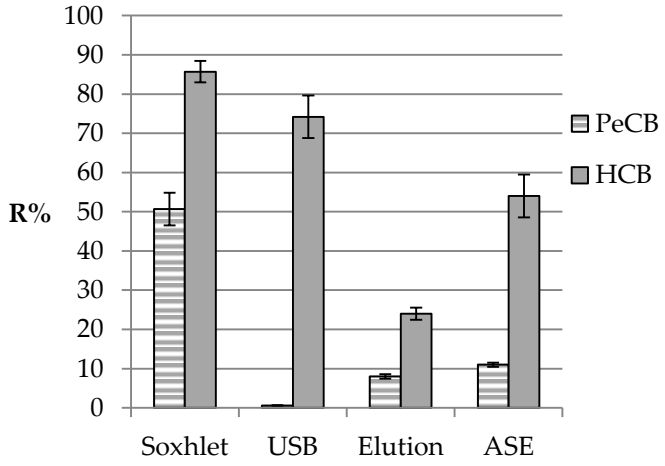


Figure 16 Average recovery percentage (R%) and STD of $^{13}C_6$-PeCB and $^{13}C_6$-HCB of triplicates performed for each extraction technique applied to ACF-F-2000.

2.3.2 Sampling - Using the ACF filter as PUF

Once Soxhlet was verified and defined as an extractive technique, the efficiency of ACF-F-2000 as an adsorbent instead of PUF was tested. The ambient-air sampling, as explained, in the introduction was performed with a High Volume PM10 Sampler equipped on the sampling head with a Quartz Fiber Filter (QFF) and a PUF. The latter has the task of adsorbing the micropollutants in the vapor phase and the compounds that could be stripped from the particulate sampled on the QFF. In fact, during sampling, a vacuum is created between the QFF and the PUF due to the pump located in the downstream of the system.

This test was performed using three different Labelled Standards Solutions:

- The Sampling Standard Solution (SS Solution) used before starting the sampling
- Extraction Standard Solution (ES Solution) spiked on the adsorbent before starting the extraction
- Injection Standard Solution (IS Solution) spiked in the sample before the instrumental analysis

According to EPA TO 4A as reported previously, sample is considered valid (quantifiable), if the ES solution recovery % is within acceptance limits of 60-120% [56]. In the test the ES solution used is a mixture of ^{13}C-PCB, for this reason the QC extraction criteria extrapolated from the ISO 16000 method are also reported. "*The recovery rate for each of the individual congeners of the 13C12-labelled dioxin-like PCB congeners added before extraction shall be at least 40% and should not exceed 120%. In exceptional cases, a recovery rate of 20% to 150% can be accepted for the field sample, if the contribution of an individual congener to the WHO-TEQPCB is less than 10%.*"

The table 7 summarizes the QC criteria adopted for the breakthrough test, which have been extrapolated from the standard reference methods [56,111].

Table 7 QC acceptance criteria of R% Labelled Standards according to EPA TO 4A. Suffix "L" means labelled compound

Compound		R%
SS Solution		
$^{13}C_6$-PeCB		65-125
$^{13}C_6$-HCB		65-126
ES Solution		
$^{13}C_{12}$-3,4,4',5-TetraCB	81L	60-120
$^{13}C_{12}$3,3',4,4'-TetraCB	77L	60-121
$^{13}C_{12}$2',3,4,4',5-PentaCB	123L	60-122
$^{13}C_{12}$2,3',4,4',5-PentaCB	118L	60-123
$^{13}C_{12}$2,3,4,4',5-PentaCB	114L	60-124
$^{13}C_{12}$2,3,3',4,4'-PentaCB	105L	60-125
$^{13}C_{12}$3,3',4,4',5-PentaCB	126L	60-126
$^{13}C_{12}$2,3',4,4',5,5'-HexaCB	167L	60-127
$^{13}C_{12}$2,3,3',4,4',5-HexaCB	156L	60-128
$^{13}C_{12}$2,3,3',4,4',5'-HexaCB	157L	60-129
$^{13}C_{12}$3,3',4,4',5,5'-HexaCB	169L	60-130
$^{13}C_{12}$2,3,3',4,4',5,5'-HeptaCB	189L	60-131

Evaluation of the breakthrough

The procedure reported here is the same followed for validation in the Master Degree thesis for the validation of the ACF-F-2000 for the PCDD/Fs and PCBs samplings.

The filter efficiency in ACF-F-2000 functioning as a PUF can be expressed in terms of the evaluation of the volume of the breakthrough. The breakthrough volume (saturation) is defined as the volume of known air that can be passed through an adsorbent before the concentration of the analytes eluting from the adsorbent reaches 10% of the applied test concentration [122].

For this purpose, simulated samplings were performed at the CNR (National Research Council) area of Montelibretti. Two pre-washed ACF-F-2000 filters were positioned between the Quartz Fiber Filter (QFF) and the PUF as shown in figure. Considering the air inlet flow, the two overlapping filters will be called ACF-F-2000 A and B respectively. The ACF-F-2000 B filter was used as the backup of the upper one (ACF-F-2000 A) to

measure breakthrough. All samplings were performed at a flow rate of 200 L/min, but by varying the sampling times (24h, 72h, 7 days) to increase the total sampling volume.

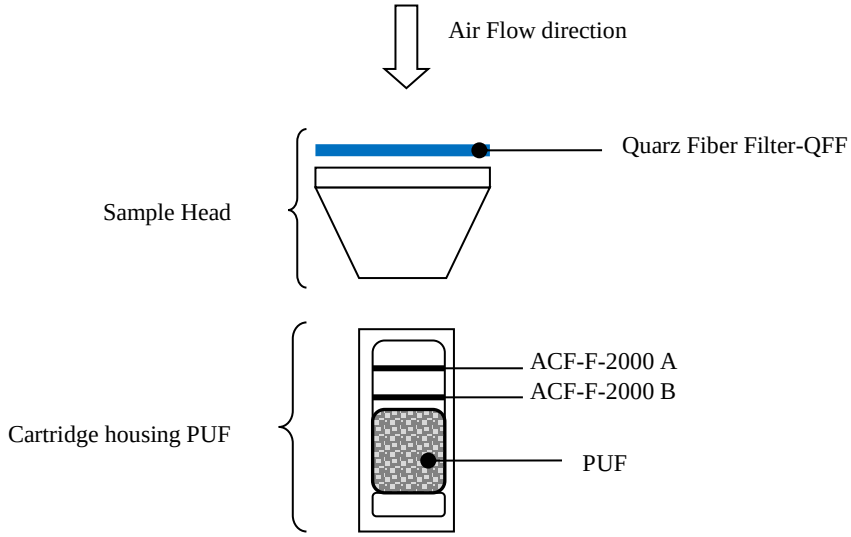


Figure 17 Schematization of the head of a High Volume sampler. Configuration for breakthrough evaluation

Prior to each test, the QFF was labelled with 1000 pg of the SS Solution containing $^{13}C_6$-PeCB and $^{13}C_6$-HCB (Wellington Laboratories, Canada). Once carried out the sampling, each adsorbent (QFF, ACF-F-2000, ACF-F-2000 A, ACF-F-2000 B and the PUF) was separately extracted separately by Soxhlet with toluene for 36 h, after adding 100 µL pg of the ES Solution (10 pg/µL of WP-LCS, Wellington Laboratories, Canada). The sample was then concentrated through Rotary evaporators to approximately 2 mL and transferred into a tube with Hexane and Dichloromethane to clean the extraction flask. The sample was purified by a multi-layer silica column[3] with 150 mL of n-hexane, after it was concentrated to almost 200 µL and 50 µL of the IS Solution (20 pg/µL P-48-SS, Wellington Laboratories, Canada) was added before GC-MS/MS analyses (see *Appendix B.1*). The arrangement of the high volume sampler head was defined to understand the extent of efficiency of the filters in ACF-F-2000 in collecting PeCB and HCB compounds

[3] Na_2SO_4 anhydrous, silica, 10% $AgNO_3$ activated silica w/w, activated silica, 44% H_2SO_4 activated silica w/w, activated silica, Na_2SO_4 anhydrous eluted with 150 mL of Hexane

without breakthroughs. If the ACF-F-2000 A filter (the first one inserted in the sampling line) quantitatively collects the volatile compounds of the SS Solution added on the QFF without exceeding the breakthrough volume, there should be less than 10% of the $^{13}C_6$ -PeCB and $^{13}C_6$ -HCB R%s (The initial Solution) on the ACF-F-2000 B filter. Therefore, the presence of the labelled micropollutants in each adsorbent of the sampling system was evaluated by extracting them separately.

For these tests, in addition to the 24 h standard sampling, the volume of air going through the adsorbents was increased, extending the sampling period. The samplings performed lasted 24h, 72h and 168h (3 and 7 days, 850 and 1850 m^3 respectively) and each test was performed in triplicate.

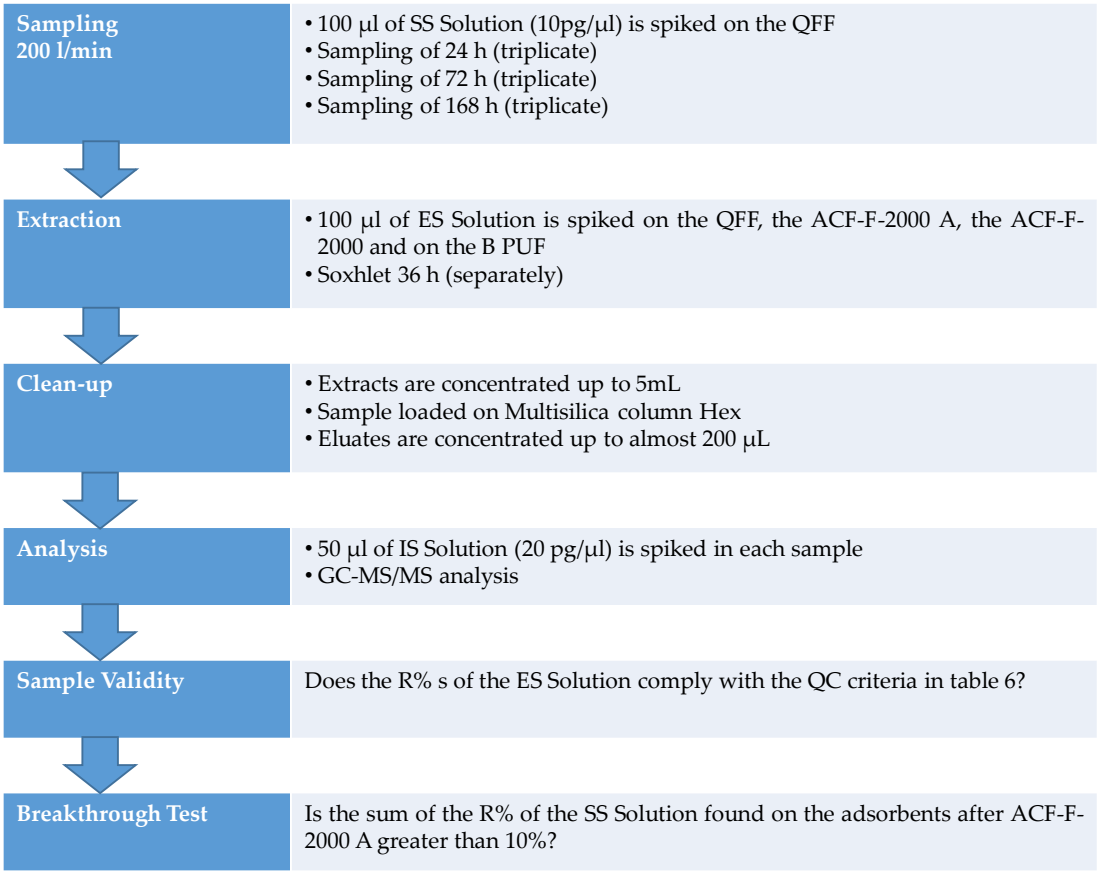


Figure 18 Schematization of all the steps of the Breakthrough Test. The following procedure was performed in triplicates for each time sampling.

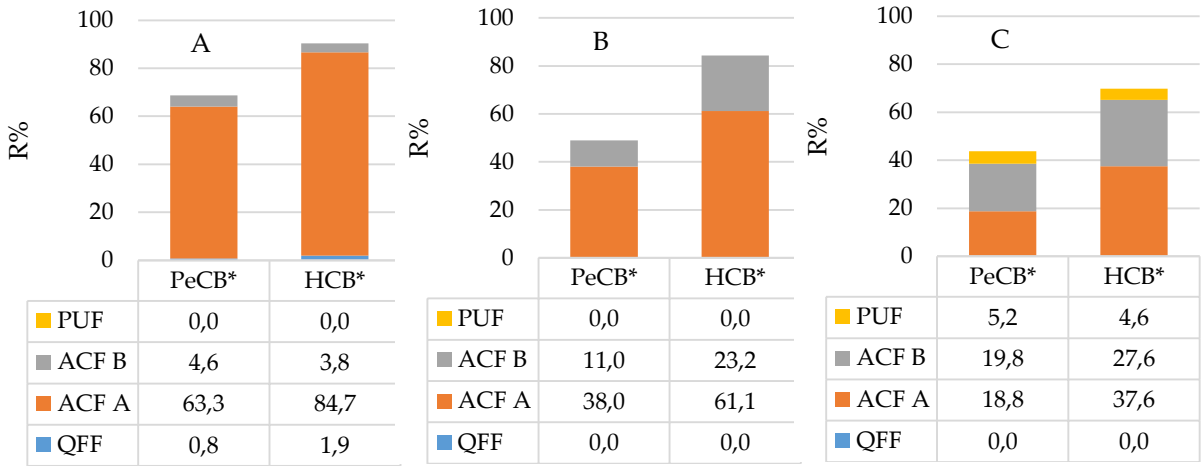


Figure 19 R%s of the SS Solution from the different adsorbents. A) 24 h Sampling; B) 72h Sampling; C) 168 h Sampling

Due to their high volatility, the CBs are little retained by the QFF and are stripped by the air flow to the underlying adsorbents. In fact, there is a R% of just 0.8% for the $^{13}C_6$-PeCB and 1.9% for the $^{13}C_6$-HCB. Both compounds cross the ACF A filter reaching the ACF B filter (even if in traces) already after 24h. Despite this, the acceptance criteria required by the Standard Reference Method are fulfilled: the R%s are 63.3% for $^{13}C_6$-PeCB and 84.7% for $^{13}C_6$-HCB by ACF A. The ISO/DIS -16000 13 method requires that the R%s of each labelled compound of the initial solution is between 50 and 150%; the CBs are significantly eluted down to the ACF B filter already after 72 h. In fact, it is observed that on the filter in ACF B there is 22.0% of the PeCB, which at 168h reach the 46%. It can therefore be deduced that the PeCB can be sampled at 24h with a single ACF-F-2000 filter, while for sampling at 72h and 168h, at least two ACF-F-2000 filters must be used. The HCB, on the other hand, can be sampled with a single filter in ACF up to 72h, beyond which the breakthrough volume is reached. It should be noted that the method adopted ISO / DIS 16000-13 is specific for the classes of PCBs from tetra chlorine to substituted deca chlorine, thus excluding the lighter ones. In addition, the EPA TO-4A, which includes pesticide analysis including HCB, allows sampling up to 24h. It is therefore

understandable that for sampling longer than 24h there may be problems in recovering the CBs, a problem easily solved by increasing the thickness of the ACF-F-2000 adsorbent. Data of average R%s and RSD% of the SS Solution from the different adsorbents, shown in Figure 19, are reported in *Appendix E* - Table 46.

2.4 VALIDATION OF PCDD/Fs AND PCBs ANALYSIS IN WATER

In the Introduction it was explained how in the MD thesis the ACF-F-2000 had been validated for the sampling of PCDD/F and PCBs in air, according to ISO 16000-13 and 14 and EPA TO 4A and 9A; the same procedure was followed for the water samples which will be summarized here. As explained in *BACKGROUND* chapter, the wet deposition is a matrix that must absolutely be evaluated for atmospheric monitoring of POPs. Due to their very low, although toxicologically relevant levels in natural waters, direct determination of their concentration is challenging with common analytical techniques. Moreover, the low solubility of these POPs in water bodies requires high enrichment by extracting large sample volumes to obtain sufficient amount for quantification. Several passive samplers, such as polyoxymethylene strips, silicone rubber [123], low density polyethylene (LDPE) [124], and semi-permeable membrane devices (SPMDs) [125] have been commonly used in monitoring organic compounds in aquatic environment [126].

The ACF-F-2000 was tested in water as a passive sampler for PCDD/Fs and PCBs. To assess its efficiency, the requirements of standard methods EPA 1613B and EPA 1668B [127,128] were evaluated. The following paragraph outline the results of the tests and are extracted from Cerasa et al., 2020 [93].

2.4.1 Validation Method

The laboratory tests performed were primarily aimed at verifying the adsorbing capacity of the ACF-F-2000 given a known quantity of the classes of compounds under examination in water. Secondly to verify its desorption capacity giving a minimum recovery percentage (R%) for all classes of PCDD/Fs and PCBs to evaluate if the adsorbent was suitable for the EPA methods (1613B and 1668B). The reference parameter was the Recovery percentage (R%) of the Quality Control (QC) acceptance criteria for labelled compounds (Table 8 A and B).

Table 8 QC acceptance criteria of A) ^{13}C-PCBs US EPA 1668b (2008) and B) of ^{13}C-PCDD/ Fs US EPA 1613b (1994). Suffix "L" means labelled[127,128]

A) Compound		R%
$^{13}C_{12}$-3,4,4',5-TetraCB	81L	57-100
$^{13}C_{12}$-3,3',4,4'-TetraCB	77L	57-101
$^{13}C_{12}$-2',3,4,4',5-PentaCB	123L	66-103
$^{13}C_{12}$-2,3',4,4',5-PentaCB	118L	65-102
$^{13}C_{12}$-2,3,4,4',5-PentaCB	114L	57-100
$^{13}C_{12}$-2,3,3',4,4'-PentaCB	105L	66-101
$^{13}C_{12}$-3,3',4,4',5-PentaCB	126L	67-100
$^{13}C_{12}$-2,3',4,4',5,5'-HexaCB	167L	74-103
$^{13}C_{12}$-2,3,3',4,4',5-HexaCB	156L	61-100
$^{13}C_{12}$-2,3,3',4,4',5'-HexaCB	157L	61-100
$^{13}C_{12}$-3,3',4,4',5,5'-HexaCB	169L	66-103
$^{13}C_{12}$-2,3,3',4,4',5,5'-HeptaCB	189L	68-10

B) Compound	R%
$^{13}C_{12}$-2,3,7,8-Tetra CDD	25-164
$^{13}C_{12}$-2,3,7,8-TetraCDF	24-169
$^{13}C_{12}$-1,2,3,7,8-PentaCDD	25-181
$^{13}C_{12}$-1,2,3,7,8-PentaCDF	24-185
$^{13}C_{12}$-2,3,4,7,8-PentaCDF	21-178
$^{13}C_{12}$-1,2,3,4,7,8-HexaCDD	32-141
$^{13}C_{12}$-1,2,3,6,7,8-HexaCDD	28-130
$^{13}C_{12}$-1,2,3,4,7,8-HexaCDF	26-152
$^{13}C_{12}$-1,2,3,6,7,8-HexaCDF	26-123
$^{13}C_{12}$-2,3,4,6,7,8-HexaCDF	29-147
$^{13}C_{12}$-1,2,3,7,8,9-HexaCDF	28-136
$^{13}C_{12}$-1,2,3,4,6,7,8-HeptaCDD	23-140
$^{13}C_{12}$-1,2,3,4,6,7,8-HeptaCDF	28-143
$^{13}C_{12}$-1,2,3,4,7,8,9-HeptaCDF	26-138
$^{13}C_{12}$-OctaCDD	26-138

Prior to follow the procedure, ACF-F-2000 (Kynol®) has been cleaned using a Soxhlet extractor for 24 h with toluene, then was washed with methanol and dried at 130 °C for 12 h. The prewashed ACF-F-2000, was cut into 8x5 cm rectangles (0.56 ± 0.02 g) and inserted in a cellulose tea bag filter (ChaCult GmbHe Germany) pre-washed in DCM. The bag filter was suspended in the water sample by a cord of inert material (PTFE). Tap water samples were collected from the Rome supply system (average conductivity of 546 μS/cm at 20 °C and a TOC of 0.6 mg/L). 100 μL in nonane, containing a known amount of WP-LCS and EPA-1613LCS standards (Mix Solution; 10pg/μL; $^{13}C_{12}$-Standards Wellington Labs - Canada), for PCBs and PCDD/Fs respectively, was diluted to 5 mL with acetone (to make it soluble in water sample) and added into a glass tank containing 24 L of tap water. The sample was shaken and left to stand for 24 h before sampling with the ACF-F-2000 filter, as to grant a uniform distribution of standards between water and suspended particulate matter. An inert magnetic stir bar (PTFE coated) was added to the

tank, and it was spun at 300 rpm in order to simulate a continuous mixing. The passive sampler was left in the water sample for 48 h to enrich. 48 h could be considered as an overextended time, but the optimizing of this time will be object of future studies [88]. During this first step, the ionic strength of aqueous sample has not been increased using NaCl, with the aim of assessing the efficiency of direct extraction without altering the sample. At the end of the sampling and before the extraction, the ACF-F-2000 is dried at room temperature overnight. Na_2SO_4 is added to the sample in order to avoid water in the extract and then36 h Soxhlet extraction with toluene is performed. Since liquid/liquid extraction was taken into account as the "reference" method, another 24 L water sample was spiked with the same amount of labelled standards and extracted by dichloromethane. Due to the large volume, the sample is L/L extracted in 3 L aliquots (9 aliquots in total), in a funnel, for three times with 300mL of dichloromethane after the addition of 40 g NaCl (Figure 20).

Figure 20 Left: Reference method: LLE; Right: ACF method

The extracts (both from Soxhlet and from LLE) were then subjected to clean-up procedure by a multi-layer silica column (extract eluted with hexane) and an alumina microcolumn to separate PCDD/Fs from dl-PCB [93]. The eluate was concentrated and the Injection Standard Solution (IS Solution) was spiked (WP-ISS and EPA1613-ISS $^{13}C_{12}$-PCBs and $^{13}C_{12}$-PCDD/Fs, respectively (Standards Wellington Labs – Canada)) [129]. The

instrumental analyses were performed by a triple quadrupole gas chromatograph/mass spectrometer (Trace 1310 GC/TSQ 8000 Evo, Thermo) and the chromatographic separation was performed by a DB-XLB column (60m x 0.25 mm, 0.25 mm I.D., Agilent J&W) (see *Appendix B.1*) [130]. In figure 21 it is shown a schematization of all phases of the validation process and the comparison between the Reference and the ACF method.

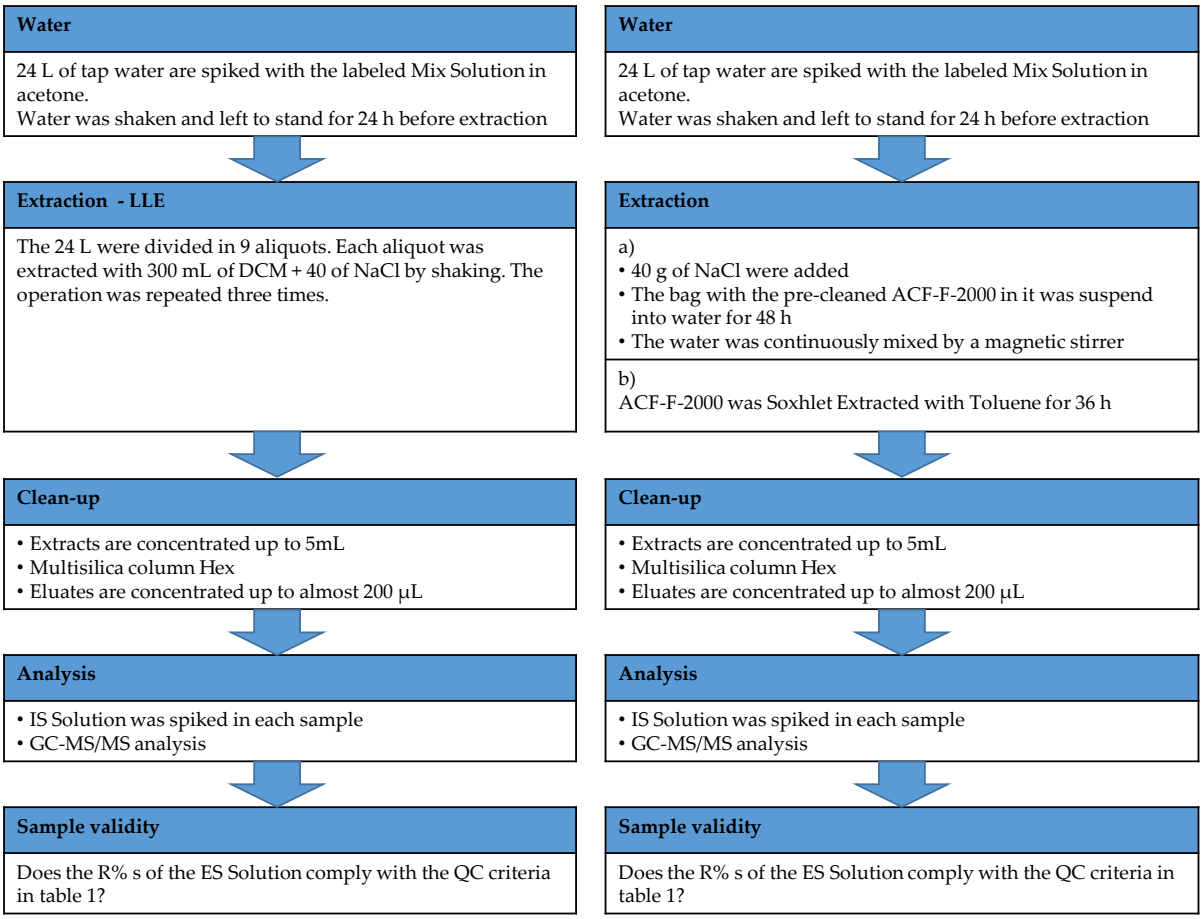


Figure 21 the step diagram for method validation. Right reference method; Left proposed method with ACF-F-2000

Fig. 22 A and B show the average R%s of the triplicate tests of $^{13}C_{12}$-labelled compounds WP-LCS and EPA 1613-LCS for both PCBs and PCDD/Fs, respectively, for both the extraction methods (carbon fibers and liquid/liquid extraction). As it can be seen from the

figures, the R%s of PCDD/Fs and PCBs increase with the number of chlorinated substituent for both methods. The R% ranges are 44-124% and 63-99%, for PCDD/Fs and PCBs respectively, that are within the limits of EPA methods (Method 1613B, 1994; Method 1668B, 2008). Although the R% of the standards is slightly lower for the method that uses ACF-F-2000 adsorbent compared to LLE extraction, the repeatability of the first one is always better than the second one. Each test had triplicated, and the relative standard deviation (RSD %) on percentage recovery for each compound is within 6% for ACF method, whereas it reaches even 13% for LLE method. In addition, a paired t-test for each compound was done; the calculated P-value is 0.0017 and 0.00013 for PCBs and PCDD/Fs, respectively, showing a statistical significance. This implies that the proposed method has the advantage of being more precise than the LLE, this also because it is not affected by the organic phase in water that leads to the formation of an emulsion between the organic solvent and the water whose quantity it is not constant. In practical terms, the use of ACF for the extraction of large volumes of water can be considered a "semi-automatic method". In fact, the use of a magnetic stirrer bar for the extraction does not require the constant presence and an active work of the operator, unlike the liquid/liquid extraction method. In economic terms, there is a great saving of used and wasted solvents Compared to manual method. In the reference method (LLE) a small amount of NaCl is added to increase the ionic strength of the water and therefore to facilitate the breakdown of the micro organic pollutants in the organic phase, as previously stated, the R% are slightly lower for the extraction with ACF-F-2000 adsorbent where no additive has been added. This means that adding NaCl could improve R%s of the ^{13}C-labelled congeners of PCDD/Fs and PCBs, even if they are already satisfactory. The obtained results show a possible dual use of the ACF-F-2000: (i) As an extracting medium of collected water samples in the laboratory, avoiding the LLE technique, much more laborious and less constant in the results; (ii) as a passive sampler for averaged time samplings in situ, like river's water sampling, after further specific studies.

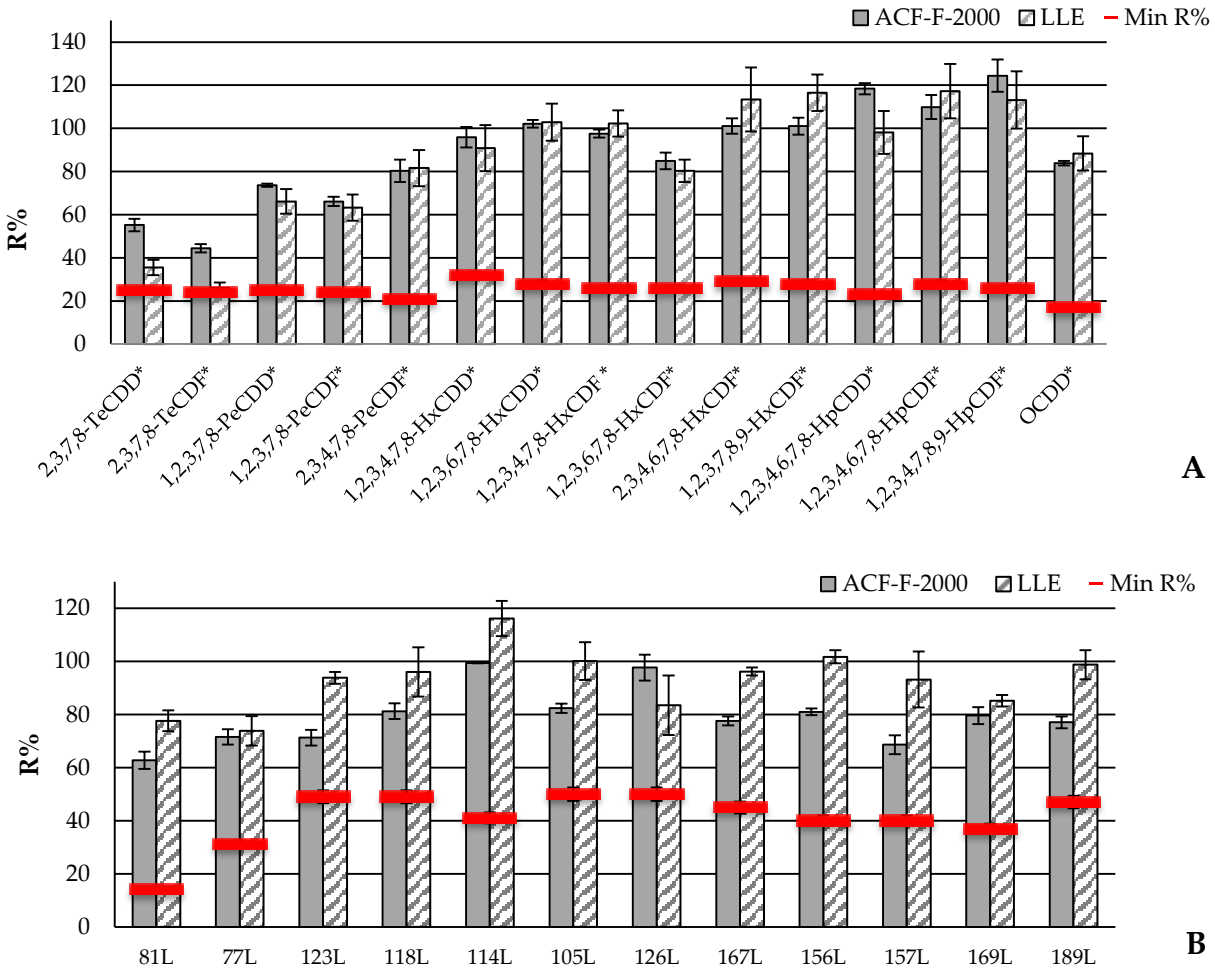


Figure 22 A: Comparison of average percentage recoveries (R%) of $^{13}C_{12}$-labelled compounds EPA 1613-LCS of triplicate tests; B: Comparison of average percentage recoveries (R%) of $^{13}C_{12}$-labelled compounds WP-LCS of triplicate tests. Red line: minimum recovery rate (min R%) required by EPA 1613B and 1668B [93,127,128]

The results showed that ACF-F-2000 fulfils the requirements defined by EPA methods and it shows a higher efficiency compared to the LLE (the reference method). Therefore, it can be used as an extraction medium for PCDD/Fs and PCBs from collected water samples. Compared to the LLE, the ACF-F-2000 method is less laborious and time-consuming in all the analytical procedure, from the extraction to the clean-up step. With a more complete kinetic adsorption study, firstly based on the variation of the adsorption time, it will be possible to optimize the sample amount and the extraction time. Since each sample undergoes through enrichment and purification, it would possibly be able to

carry out the two steps simultaneously in order to reduce analysis time and cost. Another future prospective is to try a selective extraction of PCBs and PCDD/Fs or to avoid the simultaneous adsorption of the interfering substances (e.g. sulphur compounds) by different surface modification. In this study, the material, i.e. ACF-F-2000, has been deeply characterized in most of its physical-chemical properties. Considering the amphoteric characteristics of this adsorbent, it is possible to extend its use to other classes of compounds such as those included in the EPA 625 method dedicated to base/neutrals and acids organic micro- pollutants in water. The findings of this study could be considered as the starting point for a complete laboratory sampling validation study of this material as a potential use as passive sampler.

2.5 VALIDATION OF PCDD/Fs, PCBs AND PESTICIDE ANALYSIS IN SNOW

As described in the previous chapter, the studies carried out so far have led to the validation of ACF-F-2000 as a passive adsorbent for PCDD/Fs and PCBs in water according to ISO 1613B and EPA 1668B reference methods, for wet rain depositions (see *Validation of PCDD/Fs and PCBs analysis in water*). Since from an analytical point of view, the "snow" matrix can be treated like the water matrix, the next step of the research was to evaluate the use of ACF-F-2000 for the determination of the aforementioned compounds also in snow. Together with the rains, snow is one of the agents that have the most pronounced scavenging effect in the atmosphere, especially at high altitudes and latitudes. In fact, selected persistent organic pollutants (POPs) are transported to and distributed within the Arctic region by long-range transboundary transport (atmosphere and/or ocean currents)[131,132]. For some POPs, the Arctic environment may even serve as sink with considerable potential for accumulation in the sensitive Arctic marine food chain [133]. After atmospheric long range transport, snow is considered as effective scavenger and deposition medium for atmospheric POPs (gas & particle phase) [14,16,134]. As explained in *Sampling of the atmosphere* and *Extraction techniques of the atmosphere matrices* chapters, there is no standard reference methods for snow; therefore, it was taken as "reference method" the validated procedure that is normally used by the University Centre in Longyearbyen, Svalbard, Norway (UNIS), where this part of the research has been carried out. The research carried out at UNIS was focused not only on the analysis of PCBs but also on the analysis of some chlorinated pesticides (α-HCH, γ-HCH, p,p'-DDE, o,p-DDT e HCB), compounds already studied in that laboratory. The review of the state of sampling and extraction of micro pollutants from the snow made it possible to develop and adapt the system used at UNIS laboratories to use the ACF-F-2000.

The validation for pesticides described in this study was carried out through the EPA 1699 method [135]. In order to support the results obtained, $^{13}C_{12}$-PCBs labelled standards

were added to evaluate the R% based on the ranges defined by the EPA 1668B method (Table 8A) [127].

For the EPA 1699 method, the sampling of aqueous solutions must be within 1 L but, considering the snow matrix in remote areas, as explained in Snow sampling, the sampled volumes are very variable and must be extended in order to determine compounds in ultratraces.

The next step after validating the method in the laboratory was the evaluation of the matrix effect through the analysis of two real samples. The analyses were performed with the use of gas chromatography coupled with High Resolution Mass Spectrometry (GC-Orbitrap) (see *Appendix B.2*). Furthermore, as an additional step, a procedure was defined for the study of unknown compounds present in real samples. This was possible through the dedicated software that allowed the deconvolution of the non-targeted peaks of the chromatograms obtained from the real samples.

2.5.1 EPA 1699 Pesticides in water

EPA 1699 states that *"each time a modification is made to this Method, the laboratory is required to follow the procedure of Initial Precision Recovery - IPR. If the detection limit of the Method will be affected by the change, the laboratory is required to demonstrate that the MDLs (Method Detection Limits) are lower than one-third the regulatory compliance level or the MDLs in this Method, whichever are greater"* [135]. In addition, EPA 1699 requires a literary research that justifies the change of the method.

"Results from all quality control (QC) tests comparing the modified method to this Method, including: a) Calibration b) Calibration verification c) Initial precision and recovery d) Labelled compound recovery e) Analysis of blanks f) Accuracy assessment"[135].

The results defined by points a) and b), which refer to common good laboratory practices, have not been reported here, while the results of points c), d), e), and f), which represent the true validation, are described.

In this case, considering that the matrices come from atmospheric wet depositions, snow and rainwater, the "IPR" section relating to samples with low content of suspended solids of EPA 1699 was chosen. The IPR for the low content of suspension in water, considers four 1 L aliquots of water free of native components to which 1 mL of native and labelled Std Solution is added in acetone according to the concentrations reported in Tables 9. The samples containing the Standard Solutions (native and labelled) extracted and subsequently eluted have to be concentrated to obtain the concentrations shown in table 9. The labelled standard solution available in the lab also had D_6-α-HCH compound in it. EPA 1699 method does not require the use of this compound, so there are no reference values. In order to use also D_6 α-HCH as a reference, the values of $^{13}C_6$- γ-BHC in the table 9 and 10 have been associated with it.

Table 9 Concentrations of native and labelled pesticides in stock solutions, spiking solutions, and final extracts. Table Source: *EPA Method 1699 (2007)* [135].

	Stock (ng/mL)	Spiking solution (pg/mL)	In 20 μL extract (ng/mL; pg/μL)
Hexachlorobenzene (HCB)	800	800	40
α-HCH	1200	1200	60
γ-HCH (Lindane)	1200	1200	60
2,4'-DDT	600	600	30
4,4'-DDE	600	600	30
$^{13}C_6$-HCB	1800	1800	90
D_6-α-HCH	*2600*	*2600*	*130*
$^{13}C_6$-γ-HCH	2600	2600	130
$^{13}C_{12}$-p,p-DDE	1600	1600	80

The labelled Standard Solution (which is included in the Sampling Standard Solution - SS Solution) is added to each sample to evaluate the performance of the method at the IPR, on the blank and on the sample matrix by calculating its R%s.

"All steps of sample processing, including preparation, extraction and cleaning, must be included in this test. Using results of the set of four analyses, compute the average percent recovery ($\bar{R}$%)

of the extracts and the relative standard deviation (RSD) of the concentration for each compound, by isotope dilution for pesticides with a labelled analog, and by internal standard for pesticides without a labelled analog and for the labelled compounds"[135]. For each labelled pesticide and compound, compare RSD and $\bar{R}$% with the corresponding limits for initial precision and recovery (IPR) in Table 10. If RSD and $\bar{R}$% for all compounds meet the acceptance criteria, system performance is acceptable, and the analysis of blanks and samples can begin.

Table 10 QC acceptance criteria for IPR and samples based on a 20 μL extract final volume. Table Source: *EPA Method 1699 (2007)* [135]

Pesticide	IPR $\bar{R}$% Limits	IPR RSD	Recovery in samples (%)
o,p'-DDT	55 - 108	30	
p,p'-DDE	55 - 108	30	
α-HCH	55 - 108	30	
γ-HCH (Lindane)	55 - 108	30	
Hexaclorobenzene (HCB)	55 - 108	30	
SS Solution			
D_6-α-HCH	*6 - 112*	*62*	*11 - 120*
$^{13}C_6$-γ-HCH	6 - 112	62	11 - 120
$^{13}C_{12}$-p,p-DDE	29 - 152	43	47 - 160
$^{13}C_6$-HCB	6 - 108	70	5 – 120

According to EPA 1699, analyses of method blanks are required to demonstrate freedom from contamination. "*The matrix for the Method blank must be similar to the sample matrix for the batch, e.g., a 1-L reagent water blank. Spike 1.0 mL each of the Labelled spiking solution into the Method blank. Prepare, extract, clean-up, and concentrate the Method blank.*

If any pesticide (Table 11) is found in the blank at greater than the minimum level (Table 11) or one-third the regulatory compliance limit, whichever is greater; or if any potentially interfering compound is found in the blank at the minimum level for each pesticide in Table 11 (assuming a response factor of 1), analysis of samples must be halted until the sample batch is re-extracted and the extracts re-analysed, and the blank associated with the sample batch shows no evidence of

contamination at these levels. All samples must be associated with an uncontaminated Method blank before the results for those samples may be reported or used for permitting or regulatory compliance purposes."[135].

Table 11 Names, CAS Registry numbers, and ambient water quality criteria for pesticides determined by isotope dilution and internal standard HRGC/HRMS. Table Source: *EPA Method 1699 (2007)* [135]

Pesticide	CAS Number	Labelled analog	Ambient Criterion (pg/L)	Water (pg/L)	
				MDL	ML
o,p'-DDT	789-02-6	$^{13}C_{12}$-o,p-DDT		2	30
p,p'-DDE	72-55-9	$^{13}C_{12}$-p,p-DDE	11	6	30
α-HCH	319-84-6	$^{13}C_6$-HCH, alpha	2600	7	60
γ-HCH (Lindane)	58-89-9	$^{13}C_6$-HCH, gamma	160000	9	60
Hexaclorobenzene (HCB)	118-74-1	$^{13}C_6$-Hexachlorobenzene		4	40

In this work, all the above criteria of the EPA 1699 have been met, considering those of Table 10 as validation intervals.

2.5.2 EPA 1668B PCBs in water

For PCBs, the EPA 1668B method was followed, according to which the use of the ACF-F-2000 in water has been validated as a passive adsorbent in water. The IPR procedure of the 1668B method fits well with the one of EPA 1699 for pesticides described above, and it was performed in the same way on 4 replicates.

In the previous chapter, the LLE reference method was compared with ACF-F-2000 as a passive adsorbent, therefore only the Extraction Standard Solution (into the water) was used. For this reason, the QC criteria of the R%s of a single labelled standard was reported. For the IPR procedure, the same mix of ^{13}C-PCB congeners (WP-LCS, Wellington Laboratories) will be part of the SS Solution together with the labelled pesticides. A second standard of ^{13}C-PCB called Extraction Standard Solution (P-48SS, Wellington Laboratories) is added to the ACF-F-2000 filter before filtering the water. All the congeners of the SS Solution refer to this standard for the calculation of the recovery percentages (pesticides included). Finally, an Injection Standard Solution (IS Solution) of ^{13}C-PCB (WP-ISS, Wellington Laboratories) is added to the samples before instrumental analysis.

In this case, three ^{13}C isotopically marked Standards will be used:

- Sampling Standard Solution (SS Solution), spiked with the Labelled Solution of the pesticides;
- Extraction Standard Solution (ES Solution) added before water processing using the ACF-F-2000 and to which the Pesticides will also refer.
- Injection Standard Solution (IS Solution) added before instrumental analysis.

Table 12 shows the concentrations of labelled chlorinated biphenyls in stock solutions, spiking solutions, and final extracts defined by EPA 1668B.

Table 12 Concentrations of labelled chlorinated biphenyls in stock solutions, spiking solutions, and final extracts. Table Source: *Method 1668B (2008)* [127]

		Solution Concentration		
		Stock (ng/mL)	Spiking (ng/mL)	Extract (ng/mL)
SS Solution	Labelled Toxics/LOC/window-defining			
3,4,4',5-TetraCB	81L	1	2	100
3,3',4,4'-TetraCB	77L	1	2	100
2',3,4,4',5-PentaCB	123L	1	2	100
2,3',4,4',5-PentaCB	118L	1	2	100
2,3,4,4',5-PentaCB	114L	1	2	100
2,3,3',4,4'-PentaCB	105L	1	2	100
3,3',4,4',5-PentaCB	126L	1	2	100
2,3',4,4',5,5'-HexaCB	167L	1	2	100
2,3,3',4,4',5-HexaCB	156L	1	2	100
2,3,3',4,4',5'-HexaCB	157L	1	2	100
3,3',4,4',5,5'-HexaCB	169L	1	2	100
2,3,3',4,4',5,5'-HeptaCB	189L	1	2	100
ES Solution				
2,4,4'-TetraCB	28L	1	2	100
2,3,3',5,5'-PentaCB	111L	1	2	100
2,2',3,3',5,5',6-HeptaCB	178L	1	2	100

Table 13 shows RSDs and $\bar{R}$%s with the corresponding limits for IPR. Having used in the ES Solution labelled congeners other than those proposed by the EPA 1668B, the ranges of the recoveries of the congeners with the same degree of chlorination of the CB will be associated.

Table 13 QC Acceptance criteria for IPR, RSD% and labelled compounds in samples. Table Source: *Method 1668B (2008)* [127]

	IPR Recovery (%)	**RSD%**	**Recovery Labelled Compounds in Samples (%)**
SS Solution			
81L	57 - 100	33	14-127
77L	57 - 100	35	31-109
123L	66 - 103	32	49-116
118L	65 - 102	33	49-111
114L	57 - 100	41	41-121
105L	66 - 101	31	50-111
126L	67 - 100	29	50-106
167L	74 - 103	24	45-118
156L	61 - 100	35	40-120
157L	61 - 100	35	40-120
169L	66 - 103	33	37-117
189L	68 - 100	28	47-116
ES Solution			
60L	43-106	63	14-131
127L	75-102	23	57-112
159L	78-117	30	57-125

2.5.3 UNIS procedure

Snow samples

Snow/ice samples (deposited and subsequently frozen snow) are collected using the shovel technique. The surface and depth temperatures of the snowpack are measured, and the GPS coordinates and dimensions of the sampling area are recorded. During sample collection, the operator must physically place himself downstream of the wind to avoid contaminating it. Sampling is carried out in 50 L barrels (pre-cleaned with methanol) which, once filled with snow, are transported to the laboratory. The samples are then melted slowly under controlled conditions at about 20 °C for 24 h. Each sampling always includes a Field Blank, consisting of 1 L of MilliQ water, which is brought into the field during sampling and exposed to the atmosphere during the sample collection.

Extraction and clean-up

Once the snow sample has melted, the analytes are extracted by filtering the water with a solid phase that adsorbs them. Field blanks and samples undergo the same procedures. UNIS provides that the melt water is filtered through a system consisting of two holders in series connected to a pump: the first holder contains a Quartz Fiber Filter (QFF) for the particulates, the second holder houses an Empore® disk for the analytes present in the aqueous phase (Figure 23).

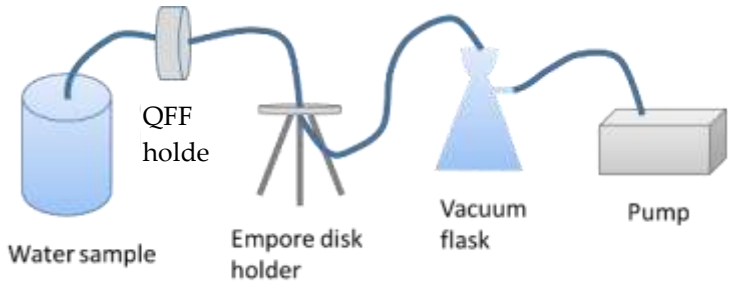


Figure 23 Schematic picture of the UNIS system for the filtration of the water sample

Before processing the sample, the two filters are cleaned with 50 mL of an acetone: n-hexane mixture (1:1, v:v) which is kept in the system for 1 minute; turning on the pump the solvent will be removed completely. The next step involves conditioning the Empore® disk, which is left to soak in 20 mL of methanol for 3 minutes. The solvent is removed by turning on the pump. The operation is repeated twice. The whole system is rinsed with 500 mL of MilliQ water. At this point, the sample is loaded. The QFF filter must be replaced whenever it becomes clogged due to particulate matter, all QFFs must be collected together. After the sample has been filtered, approximately 500 mL of MilliQ water is added (and collected) to the barrel to rinse its inner walls and set system ducts. The Empore® disk is dried by sucking air into the system, switching on the pump for at least 10 minutes. Once the entire melted water has been filtered, the Internal Standard is added to the filters before proceeding with their extraction in an ultrasonic bath (USB extraction) with hexane: acetone (1:1, v:v) for 10 minutes. The extract is transferred to a pre-cleaned separating funnel and the whole operation is repeated two more times, each time collecting all the extracts together. The separator funnel is used to remove any water present before cleaning: a known amount of n-hexane is added to force phase separation (an excess of acetone may occur which causes an increase in the solubility of water in the solution). During the shaking, n-hexane washes the compounds from the aqueous phase and also removes water from the organic phase. The organic phase is transferred to a round-bottomed flask and the operation is repeated two more times. The addition of Na_2SO_4 in excess allows the removal of any last traces of water. Leave overnight (if possible) at room temperature. The supernatant is then withdrawn and the volume is reduced to 5 mL through Turbovap®. A column of Na_2SO_4 is prepared through which the sample is eluted. The beaker walls of the Turbovap® system are rinsed twice with 10 mL of hexane, which is collected, eluted on the column and collected in the same flask. The sample is reduced to 0.5 mL and eluted with 50 mL n-hexane:toluene (65:35, v:v) on a column of 8% deactivated silica and Na_2SO_4 (if there is any residual moisture) for the

clean-up. The sample undergoes a solvent change by reducing its volume through Turbovap® and adding approximately 3 mL of n-hexane at the end of concentration (approximately 1 mL residual). The operation is repeated 3-5 times. Finally, evaporation is carried out under a nitrogen flow up to about 200µl and the Internal Standard is added before the GC-MS analysis.

2.5.4 Applying ACF-F-2000 on UNIS procedure

The performed method is an adaptation of the above reference method. The snow sampling will be performed as indicated in the UNIS procedure, and the changes made are reported in the section below relating to real samples.

As regards the analyte extraction phase, several changes were made in order to improve the system where possible. As required by the EPA 1699, each change was justified.

Starting from the extraction system in figure 23, the first step was to adopt materials that interfere as little as possible with the analytes, i.e. Teflon tubes and steel or glass collection containers. As explained in the chapter *Sampling of the atmosphere - Snow*, the water-particulate system cannot be split, since it is in a continuous state of rebalancing, and the two filter membranes (QFF and Empore® disk) cannot be analysed separately. During the Master's Degree thesis work the ability of the ACF-F-2000 to replace the combined system QFF + PUF for air sampling was demonstrated and validated (see *Introduction and aim of the thesis*). The same was done in the chapter *Validation of pesticides analysis in air*, validating the adsorbent for PeCB and HCB air sampling up to 24 h. On the same principal, it was therefore thought to also replace the combined QFF + Empore® disk system with an ACF-F-2000 disk, after demonstrating the absence of breakthrough. The extraction of the snow samples was performed through a specifically designed sandwich arrangement, where the ACF-F-2000 was placed between two Quartz Fiber Filters

(QFF/ACF-F-2000/QFF – 102 mm diameter). Figure 24 shows the general outline of the extraction procedure:

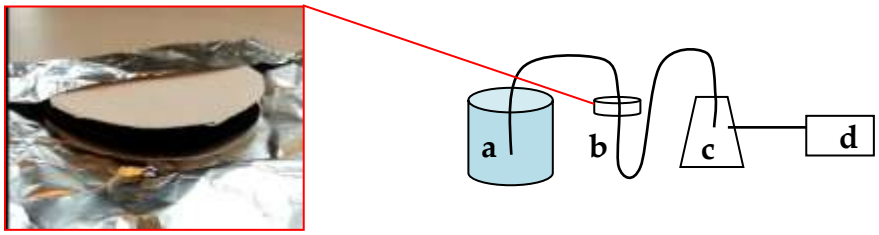


Figure 24 Custom designed extraction system for ACF-F-2000 based SPE extraction for meltwater samples derived from Svalbard snow: a) sample container (50L container; meltwater); b) QFF/ACF-F-2000/QFF Holder 47 mm; c) Vacuum flask; d) Pump.

This type of arrangement allows the replacement of the first QFF in case of particulate obstruction during water filtration. Among the various advantages in this replacement, the main one is the lower impedance of the water adsorbents. Differently from the Empore® disk, in fact, the ACF-F-2000 has zero impedance. Prior to sample extraction, the SPE sandwich arrangement is conditioned with MilliQ water. 1000 pg of SS Solution including ^{13}C-dl-PCBs and ^{13}C and perdeuterated pesticides are added to 1 mL of acetone and spiked in to the melted snow (tables 9 e 12). QFF/ACF-F-2000/QFF system is spiked with 1000 pg of the ES Solution prior to start the water filtration. Once the filter has been placed inside the holder, the system was conditioned with 500 mL of MilliQ water. A magnetic stirrer continuously shaked the water sample in the bottle, so that the analytes and the SS solution were evenly distributed. The meltwater was pumped with a piston vacuum pump at a flow rate of approx. 1 L/min through the QFF/ACF-F-2000/QFF filter. After water extraction, the QFF/ACF-F-2000/QFF system was extracted placing them in a thimble for 36h in a 200 mL Soxhlet with toluene.

Na_2SO_4 was added inside the thimble to remove any excess water resulting from the filter. The extract was concentrated and purified using a basic alumina column for purification with 15 mL of n-hexane:DCM (94:6). All samples were concentrated, and the IS Solution was spiked in them prior the GC-Orbitrap analysis (see *Appendix B.2*).

An obvious advantage in replacing the UNIS extraction procedure with the proposed one is the simplicity of the process and fewer steps (and thus reduce the possibility of errors and sample losses).

The IPR required by the EPA method 1699 is performed as follows.

Laboratory recovery tests: four pre-cleaned barrels are filled with 15 L of MilliQ water. According to the EPA requirement for the concentrations of the IPR solution, a mix with native α-HCH; γ-HCH; p,p'-DDE; o,p'-DDT and SS Solution (table 10 and 13) is added to 1 mL of acetone and spiked in to the MilliQ water. The QFF/ACF-F-2000/QFF was spiked with 1000 pg of ES Solution (table 13).

Laboratory Blank: a pre-cleaned barrel is filled with 15 L of MilliQ water that was spiked whit the SS Solution. The QFF/ACF-F-2000/QFF was spiked with the ES Solution prior to the water filtration.

The following table below shows the average recoveries % and the RSD%s of 4 tests

Table 14 $\bar{R}$% of 4 Laboratory Tests and RSD%

	IPR $\bar{R}$%	IPR RSD%
α-HCH	87	18
γ-HCH	72	4
HCB	103	3
p,p,-DDE	81	1
o,p'-DDT	90	8
α-HCH D_6	94	4
γ-HCH $^{13}C_6$	98	5
p,p'-DDE $^{13}C_{12}$	65	27

As can be seen from the results, the method fulfils all the ranges imposed by the EPA 1699 method and the use of QFF/ACF-F-2000/QFF up to 15 L of water volume has been validated. In addition, the $\bar{R}$%s in Table 14 demonstrate that the suction system is able to withdraw all of the analytes from the sampling vessel, without loss for surface adhesion on the walls.

The IPR described by the EPA 1699 method did not require the use of the ES Solution but only the mix of the natives and the SS Solution added to the water. During the sampling of the snow, it is not possible to define a priori the volume of water that will be obtained, since a lot depends on its texture. The tests were carried out on 15 L of water, being on average of the maximum volume obtained for sampling in remote areas with 60 - 40 L barrels of compacted snow. The validation procedure was also aimed at verifying whether the system was able to adsorb the compounds of interest on the QFF/ACF-F-2000/QFF without exceeding the Breakthrough volume. For this reason, despite the fact that the suction system was consolidated by the usual use by UNIS, the ES Solution was added to the sandwich filter at time t = 0. Already by $\bar{R}$% results shown in Table 14 of ^{13}C labelled pesticides can be seen which has not been exceeded the breakthrough volume of the QFF/ACF-F-2000/QFF. As further confirmation, it can be seen in Figure 25 that even the average R%s of the $^{13}C_{12}$-PCBs of the four replicate of the ES Solution added to the QFF/ACF-F-2000/QFF respect the ranges defined by 1668B.

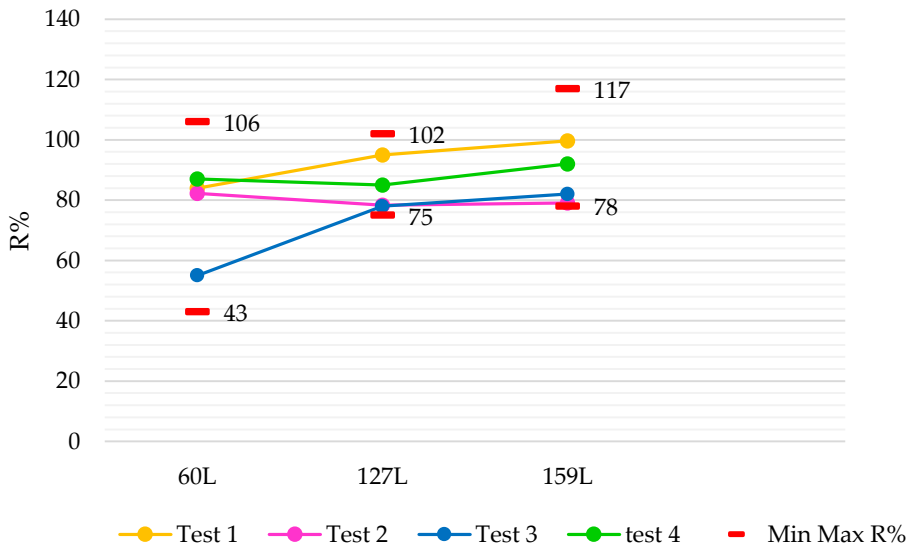


Figure 25 R% of PCBs ES Standard in the four Test for the IPR. Suffix "L" indicates labelled compound. R% = Recovery Percentage. Minimum and Maximum R%s according to EPA methods for IPR Tests (%) table 13: 43 <60L< 106; 75 <127L< 102; 78 <159L< 117

3 DEMONSTRATIONS ON REAL SAMPLES

3.1 SVALBARD - ANALYSIS OF PCB AND PESTICIDES

ACF-F-2000 has been validated for the extraction of POPs from Arctic surface snow collected at Spitsbergen (Svalbard, Norwegian Arctic). For our study, ACF-F-2000 adsorbent was tested to be used for solid phase disk extraction (SPDE) of dioxin like-polychlorinated biphenyls (PCBs) and organochlorine pesticides from Svalbard ice/snow samples and the subsequent quantitative ultra-trace analysis with gas chromatography and mass selective detection. A complete method validation was performed, including the determination of compound specific recovery rates, detection and quantification limits as well as non-linear matrix effects for real sample quantification.

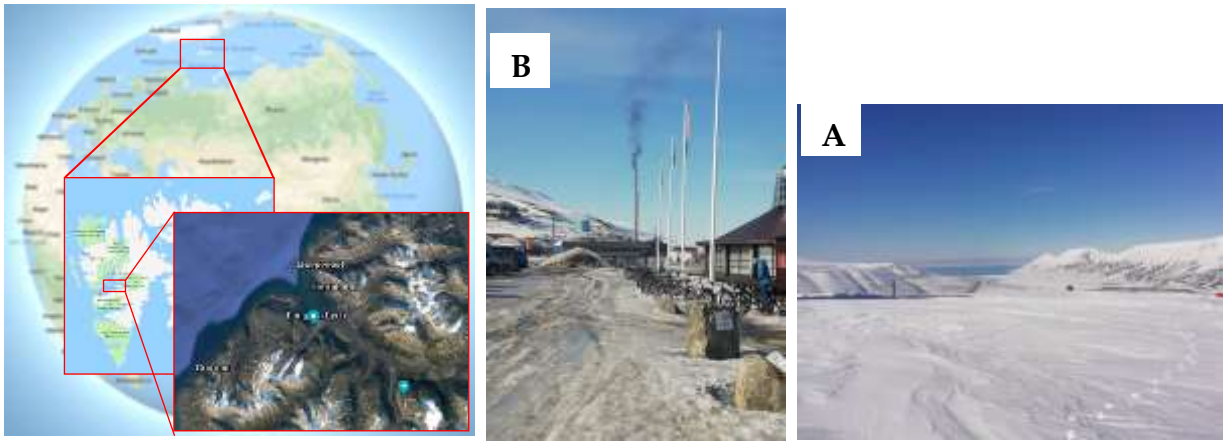


Figure 26 Sampling sites. Longyearbyen, Svalbard. A) Remote area, Sample A; B) Small town area, Sample B.

After the complete method validation, two snow surface samples were collected (Figure 26). **Sample A** (50L volume) was collected in a remote area, in the surroundings of Longyearbyen, 78°08'49.8"N 16°01'57.0"E (May 10, 2019) at 1:46 pm at 536 m a.s.l. , in a 1 x 1.3 m area, 5±1 cm depth. Surface temperature: -3±0.1 °C, Temperature in depth - 7±0.1 °C. **Sample B**, was collected in the small town of Longyearbyen (Svalbard), 78°13'01.3"N

15°36'41.8"E (May 10, 2019) at 16:50 at 16 m a.s.l. being aurban site, 1 L of volume was sampled, as suggested by literature data, in an area of 41 x 13 cm, 4-5 cm depth. Surface temperature: 2.3 ±0.1 °C, temperature in-depth - 3.1 ±0.1 °C.

The respective field blanks of the two samples (Field Blank A and Field Blank B) were brought to the sampling site, the bottles remained open throughout the sampling and closed at the end. After carefully melting at temperatures of ca. 24±1 °C in a gas tight sampling container for 2 days, the samples were prepared for extraction.

For the Snow samples the meltwater volume was determined between 0.5 (Sample A) and 17,1 L (Sample B).

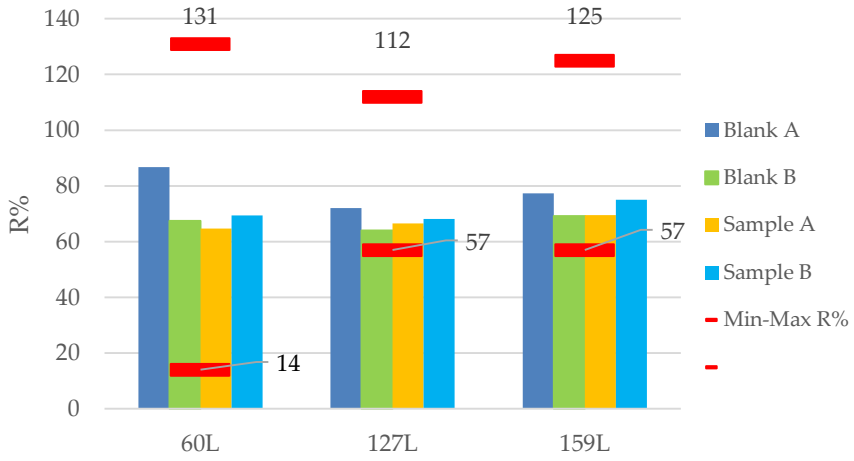


Figure 27 R% of ^{13}C-PCBs ES Solution of Sample A and Field Blank A, Sample B and Field Blank B. Suffix "L" indicates labelled compound. R% = Recovery rate. Minimum and Maximum R%s according to EPA methods in Samples (%) Table 13: 14<60L<131; 57<127L<112; 57<159L<125.

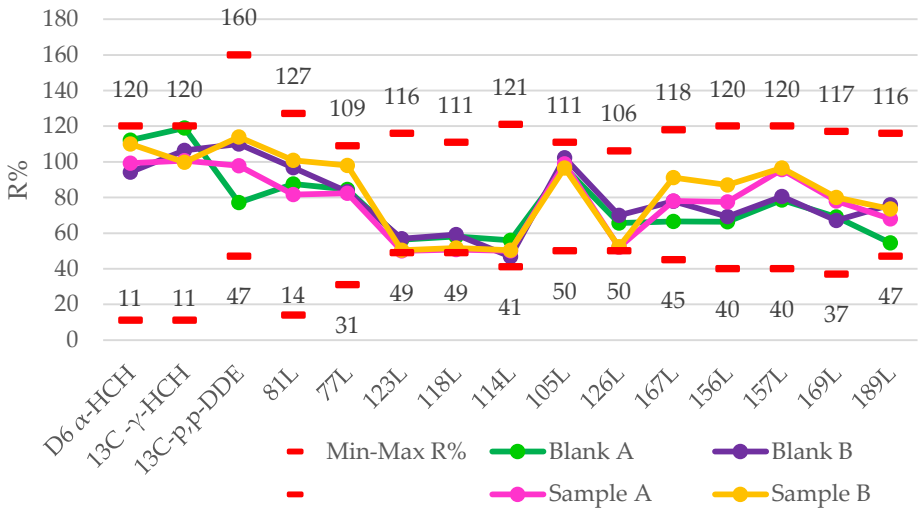


Figure 28 R% of ^{13}C-PCBs and Pesticides labelled SS Solution of Sample A and Field Blank A, Sample B and Field Blank B. Suffix "L" indicate labelled compound. R% = Recovery percentage. Minimum and Maximum R%s according to EPA in Samples (%) Table 13.

The sampling and clean-up standard R%s here expose fulfil the requirements of EPA Method 1668B and 1699 also for the real samples. The matrix effect evaluation in real samples from Arctic region has a key rule due to the low concentration of the analytes and the possible presence of interfering compounds. Since the R%s of the sample and blanks results are within the given limits, we consider the general control criteria of the tested ACF-F-2000 method as acceptable. The use of the three labelled solutions (SS, ES and IS) during the analytes extraction from the MilliQ water and from the melted snow, before the QFF/ACF-F-2000/QFF water filtration and before the injection allowed a sample specific method validation.

Table 15 Concentrations (pg L^{-1}) of organochlorine pesticides in the snow samples.

	Sample A (17.7 L) pg/L	Sample B (0.5 L) pg/L
α-HCH	6.7	68.3
HCB	19.8	1063.5
γ-HCH	3.7	105.9
p,p-DDE	115.4	417.5
o,p-DDT	15.6	355.1

Table 15 shows the concentrations in pg L^{-1} of the chlorinated pesticides for the sample collected in the remote area (sample A) and in the small town area (Sample B). Concentrations of PCBs were all found to be below the LoD, and therefore were not reported. The concentrations detected in the two samples are clearly different, which confirms that it is not possible to ignore the type of sampling location to decide the volumes of snow to be collected so that they are consistent with the instrumental limits. While for Sample B collected in the urban area of Longyearbyen it was sufficient to sample 1 L of snow, in the remote area (Sample A) 50 L of snow were needed. Despite this, the values found are 1 or 2 orders of magnitude greater in Sample B because it is richer. The values of α-HCH and γ-HCH in Sample A are 10 times lower than the literature data; it can be reasonably assumed that the environmental conditions in which the snow was collected have influenced. The compounds under examination are photosensitive and in the period in which the sampling was carried out (May) there were 24 hours of daylight in that region, so degradation is assumed. This means that the values found in Sample B have either a local source or that the quantities found are underestimated (despite of the high values).

As highlighted in numerous papers, HCB is one of the compounds, along with p, p-DDE and o, p-DDT which, given their persistence, tend to accumulate in non-source regions such as the Arctic [136]. It can be assumed that the different concentrations between Sample A and in Sample B is due to the sources: contribution of Long Range Transport in the first site and local pollution in site B. Given the high concentrations, especially of

HCB, it cannot be excluded that the citizen itself represents a source and that Sample A is not affected by it. Just two samples are not enough to be able to draw environmental conclusions; however, it can be asserted that the proposed method using the ACF-F-2000 is valid both for extremely concentrated samples (Sample B, low volumes) and for samples with trace compounds (Sample A, high volumes).

3.1.1 Non-target screening

In the analysis of complex matrices, there is often the coelution of compounds of interest or the coelution of analytes with interferences due to the matrix.

The TraceFinder 4.1 software with the deconvolution plug-in allows the automatic deconvolution of coeluted chromatographic peaks into multiple components through the alignment of mass spectral peaks in accordance with the infinitesimal differences in retention times. In addition, the software performs an automatic search and comparison within the libraries and databases. By combining this software application with the "unknown screening" function it is possible to perform a cross comparison of the same analyte within different samples at a concentration well below the conventional concentrations used by a quadrupole with unit mass resolution.

Table 16 Automatic steps of plug-in deconvolution software. Table Source: *Technical note10624, Thermofisher.*

STEP	Summary
1	Ion extraction (nominal mass) and ion chromatogram production
2	Identification of each peak of the ion chromatogram
3	Collection of all the most intense peaks (for each RT and every m/z)
4	Elimination of all the peaks that are inside the Parameter % of the "Ion overlap Window" (for example: 99% of the height) and, if considered, inside the TIC threshold.
5	Research of the component in the library
6	Repetition from step 3 to 5 for subsequent peaks of maximum intensity until they are no longer detected.

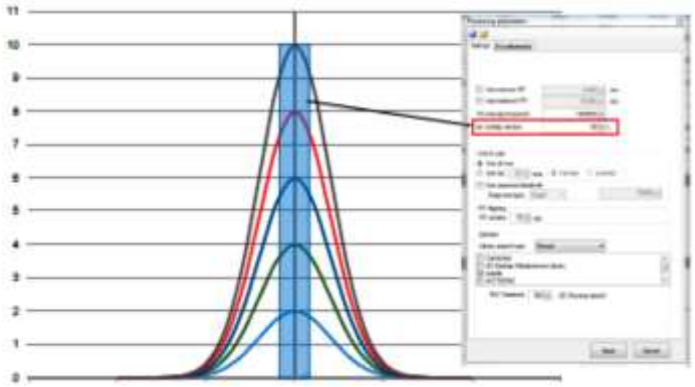


Figure 29 Example of an Ion overlay window of 90%. Image Source: *Technical note10624 Thermofisher.*

In order not to lose information during the clean-up, the samples on which the deconvolution was performed were injected into the GC-Orbitrap "raw", immediately after extraction (see *Appendix B.2*).

The signals of the chromatograms with a TIC intensity threshold equal to at least 1000 (being samples with trace compounds) were deconvoluted with an Ion overlap window of 98%, RT aligning of maximum 3 s, SI Threshold of 500. Subsequently (step 5) the cross search within all the libraries was set and defined the Unknown compounds obtained from the deconvoluted chromatograms. Regarding the processing of the Unknowns, a minimum MS Signal Threshold 105 has been adopted, and a maximum of 107, Min Pick width 0.50 and a max of 1.00, RT Shift of 0.50 minutes.

At this point, the blank was subtracted from the list of identified compounds.

It was necessary to define two levels of reliability for identification.

a) <u>High level</u> It includes only the compounds with a Score > 90% in both Sample A and Sample B. The Score represents the correspondence between the deconvolved spectrum and the library search and is expressed in percentage units. It combines several parameters including the SI (Index score (0-999) for each detected compound returned by the search within the NIST library) and the HRF score (High-Resolution Filtering Score - The percentage of all ions of the chromatogram of which it is possible to identify the

formula through the library). A pattern of theoretical ions is created that can be generated by the chemical formula according to all combinations. For example, C_2H_2 could produce H^+, H_2^+, C^+, CH^+, CH_2^+, C_2^+, C_2H^+ e $C_2H_2^+$ ions. It is verified that each peak of the deconvolved spectrum falls within the mass tolerance limits set for each ion belonging to the original chemical formula. When the intensity of an experimental ion corresponds to at least one possible ion with the original chemical formula, the latter is divided by the total ionic current of the deconvolved experimental spectrum to provide HRF score.

b) Medium Level It includes all compounds with an Average Score rate (AVG Score %) > 90%. The AVG Score of a compound is the weighted average by intensity of a compound's match score across the batch.

For each compound listed in the table, a bibliographic research was performed, in order to verify its origin, toxicity and previous studies.

The analysed batch comprehended Field Blank A, Sample A, Field Blank B and Sample B. 4695 total deconvoluted peaks were identified; a % identification score was associated to each one. Through retention time alignment (after injection of alkanes with the same chromatographic method) the software searches for the compounds identified in each sample, aligning their RTs and associating an AVG Score defined by the individual sample identification scores.

The criteria established for the identification levels were applied to the batch under analysis. The identified compounds were then analysed, excluding all those that were unequivocally false positives due to fragmentation, retention times and type of compound. Once the substances in the lists were identified, we continued by analysing which compounds were typical of the Arctic area because they are present in both samples Sample A and B, which are typical of remote and urban areas. This type of analysis gives the possibility not only to study the area, but also to extend the use of the ACF-F-2000 for sampling (targeted) to other classes of pollutants. Table 17 shows the compounds that are common to the remote and urban areas, after selection at the second

stage. Having carried out two-point samplings, it is not possible to define whether the compounds identified were transported from Northern Europe and condensed in the Arctic or whether the source is the town of Longyearbyen. The identified substances have been divided by classes, defined by use, emission, relevance, literature data, as specified below: Yellow - incomplete combustion; Green - personal care; Orange - Natural Products; Blue - Agricultural Products (fertilizers/pesticides/fungicides); Purple - Industrial Products; Grey - drugs.

Table 17 Compounds Common to Sample A and Sample B. High level of identification Score% > 90%; Absence of peak in Blank B and Blank A. The identified substances have been divided by type as specified below: Yellow = Incomplete Combustion; Green = Personal Care; Orange = Natural Products; Blue = Agricultural Products (Fertilizers/pesticides/fungicides); Purple = Industrial Products; Grey = Drugs

Chemical Name	**CAS**	**Reference**
Tetracosamethyl-cyclododecasiloxane	18919-94-3	[137,138]
Dicyclohexyl phthalate	84-61-7	[139]
D:A-Friedooleanan-28-al, 3-oxo-	14440-40-5	
Ether, 3-methyl-2-butenyl o-tolyl	23446-47-1	
Cyclohexanecarboxylic acid, 2-phenylethyl ester	37139-88-1	
2,2'-Dimethylbiphenyl	605-39-0	[140]
Benzene, 3-hexenyl-	35008-86-7	
2-(Phenylmethyl)phenol, trimethylacetate		
4-Biphenyl methyl carbinol	3562-73-0	
2-Methylhexacosane	1561-02-0	
Phenanthrene, 2,4,5,7-tetramethyl-	7396-38-5	
Benzene, 1-methyl-4-(phenylmethyl)-	620-83-7	
Octacosane, 2-methyl-	1560-98-1	
Benzyl alcohol	100-51-6	[141]
1-(2,3-Dimethylphenyl)ethanone	2142-71-4	

From the analysis of data in Table 17, it can be observed that most of the identified substances belongs to the class of natural substances. This class includes aromatic esters, sesquiterpenoids, terpenes and molecules of similar structure, which cannot be

associated with the other classes. Many of these compounds can also be considered in the personal care class, given that some of them (e.g. essential oils) are also often used in the cosmetics industry and some essences are used in the food industry [142]. As already highlighted in several studies, there are compounds belonging to Personal Care (Green class) that are also found in remote areas, and they are mainly the characteristic compounds of cosmetic products. Benzyl Alcohol is an aromatic organic compound that occurs naturally in various plants, and in particular, it is the component of some essential oils such as jasmine, neroli, violet and ylang-ylang. Given the price for the extraction, the equivalent of synthesis is often used in cosmetics. There is a whole section dedicated to products of natural origin, in orange while yellow indicates the class of products from incomplete combustion such as hydrocarbons or PAH and derivatives. The class of "industrial products" (purple) includes solvents and plasticizers attributable to packaging, which tend to be released over time (Tetracosamethyl-cyclododecasiloxane) [143]. The following table shows the compounds included by the High level of identification reliability, present only in Sample B, i.e. the one collected in the urban area of Longyearbyen (table 18). The city was originally born around a coalmine whose activity has represented the island's main resource for years. Surely, today it has been replaced by tourism, but the activity still remains (the mine supplies the local coal-power plant with about 30.000 tons of coal annually, while another 80.000 tons are exported to customers in the European metallurgical and chemical industry). Sample B was collected about 1.2 km from the coal-power plant, which was active that day. It can therefore be assumed that part of the compounds that enrich Sample B represent combustion products and can be traced back to the plant.

Table 18 Sample B High level of identification Score% > 90%; Absence of peak in Field Blank B. The identified substances have been divided by type as specified below: Yellow = Incomplete Combustion; Green = Personal Care; Orange = Natural Products; Blue = Agricultural Products (Fertilizers/pesticides/fungicides); Purple = Industrial Products; grey = Drugs

Chemical Name	**CAS**	**Reference**
Carbonic acid, heptyl phenyl ester		
Pentanediamide, N,N'-di-benzoyloxy-		
Bicyclo[2.2.1]heptane, 2-(phenylmethyl)-	37794-91-5	[144]
2,4,6-Cycloheptatrien-1-one, 2-hydroxy-	533-75-5	[145,146]
Vanillin, isopropyl ether		[147]
4-(t-Butyl)benzaldehyde	939-97-9	[148]
Butanoic acid, 2-methyl-, 2-phenylethyl ester	24817-51-4	[149]
1H-Indene, 3-ethyl-1-(1-methylethyl)-	111400-85-2	
Benzene, 1-(1-buten-3-yl)-4-pentyl-		

In addition, in this case we find the large classes defined previously of Personal Care, Industrial Products, Natural Products to which a new category is added: Drugs. However, the boundary of this classification is very blurred since the same compound can belong to several categories. For example, Benzyl alcohol despite was classify as a Personal Care is both a natural and synthetic product, and it is used in detergents/solvents thanks to its disinfectant effect. This means that it could be included in the class of natural products, but also of personal care as well as industrial products. Another example is represented by Phthalates, known plasticizers inserted as industrial products but which can also be found in Personal Care or Natural products. Clearly, the research presented here represents only a qualitative assessment, and the next step should be to select a class of compounds and start a targeted search. The certainty that the ACF-F-2000 is able to sample also the compounds mentioned above cannot be given by the simple detection through Unknown search, but a real validation should be started through dedicated Standards in order to have the certainty of the identifications and quantifications.

3.2 ITALY - PARALLEL SAMPLING OF AIR AND SNOW

Thanks to its versatility, the ACF-F-2000 is suitable to be used as an adsorbent for both air and wet precipitation monitoring. Snow monitoring is not only important for areas at extreme latitudes, but also for those at high altitudes. As previously explained, cold areas such as mountains, Arctic and Antarctica area represent the tank of numerous pollutants that condense here due to low temperatures. In mountain areas, it is mainly concerned with water stored in reservoirs and needed for agricultural, livestock and even domestic uses. As for humans, the intake through drinking water is negligible compared to the consumption through nutrients, especially fish, which leads to the accumulation in lipids and tissues. Another factor is the negative impact on the ecosystem that motivates the need to improve sampling and monitoring strategies. In particular, predators are the ones at the highest risk being at the top of the food chain. Some examples are eagles, ospreys and vultures, lynxes, bears, wolves and pumas whose habitat is precisely that of mountainous regions.

As reported by Daly, the accumulation of POPs does not just affect predators. Going down the food chain we have the amphibians whose population has decreased in the Californian Sierra Nevada due to micropollutants, or the phytotoxic effect that halogenated hydrocarbons and its derivatives can express on alpine plants [150].

The mountains are representative of large changes in the composition of the ecosystem on a small scale due to the great variability of the climate and exposure with altitude. They safeguard an enormous amount of animal and plant species that have found refuge here over time, even following climate change. ACF-F-2000 was applied to a real case for the monitoring of atmospheric events that will allow its use for both air and wet precipitation. The concentrations of PCDD/Fs, PCBs and pesticides was evaluated through ambient-air and snow deposition samplings. The validity of the samples was assessed through the R% of the ^{13}C labelled and perdeuterated standards with reference to ISO 16000 13 and 14, EPA TO-4A and 9A for air and EPA 1668B, 1613B and 1699 for

snow. The next step was the evaluation of scavenging effect where concentration of the pollutants allowed it.

Furthermore, the study of the Unknown compounds, already carried out for the snow samples of the Svalbard Islands, was conducted according to the same criteria explained in the chapter "*Snow*". By extending the study also to ambient air samples, it was possible to eventually carry out a qualitative evaluation of the Snow scavenging action on the Unknowns compounds.

3.2.1 EPA 1613B Dioxins and Furans

In this chapter, the validation studies of the ACF-F-2000 for the sampling of PCDD/Fs using ^{13}C labelled standards Solutions are presented. The standard method referred to is EPA 1613B - *Tetra-through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS*, which establishes an IPR (Initial Precision Recovery) method as in the previous chapter to which reference is made for the procedure. That is, the evaluation of the average percentage recoveries of isotopically labelled Sampling Standard Solution (SS Solution) spiked in 1 mL of acetone and added in 4 aliquots of 15 L each of MilliQ water. All steps of sample processing (including preparation, extraction and cleaning) must be included in this test. System performances are accepted if both s (standard deviation of the concentration) and X (average of the concentration) are in the corresponding limits for IPR in Table 19.

Table 19 Acceptance criteria for performance tests when all CDDS/CDFs are tested. Table Source: *Method 1613B (1994)* [128]. All specifications are given as concentration in the final extract, assuming a 20 μL volume.

	Test Conc. (ng/mL)	**IPR[2,3]**	
		s (ng/mL)	**X (ng/mL)**
$^{13}C_{12}$-2,3,7,8-Tetra CDD	100	37	28-134
$^{13}C_{12}$-2,3,7,8-TetraCDF	100	35	31-113
$^{13}C_{12}$-1,2,3,7,8-PentaCDD	100	39	27-184
$^{13}C_{12}$-1,2,3,7,8-PentaCDF	100	39	27-184
$^{13}C_{12}$-2,3,4,7,8-PentaCDF	100	38	16-279
$^{13}C_{12}$-1,2,3,4,7,8-HexaCDD	100	41	29-147
$^{13}C_{12}$-1,2,3,6,7,8-HexaCDD	100	38	34-122
$^{13}C_{12}$-1,2,3,4,7,8-HexaCDF	100	43	27-152
$^{13}C_{12}$-1,2,3,6,7,8-HexaCDF	100	35	30-122
$^{13}C_{12}$-1,2,3,7,8,9-HexaCDF	100	40	24-157
$^{13}C_{12}$-2,3,4,6,7,8-HexaCDF	100	37	29-136
$^{13}C_{12}$-1,2,3,4,6,7,8-HeptaCDD	100	35	34-129
$^{13}C_{12}$-1,2,3,4,6,7,8-HeptaCDF	100	41	32-110
$^{13}C_{12}$-1,2,3,4,7,8,9-HeptaCDF	100	40	28-141
$^{13}C_{12}$-OctaCDD	200	95	41-276
$^{13}C_{12}$-OctaCDF	*200*	*95*	*41-276*

[2]s = standard deviation of the concentration on the 4 tests. [3]X = average concentration, that must fall in the range.

Despite EPA 1613B method does not consider $^{13}C_{12}$-OctaCDF congener, it is included in table 19 because it is included in the Standard solutions used. IPR and test concentrations were associated with values of $^{13}C_{12}$-OctaCDD, the congener with the same degree of chlorination. Once the procedure was validated, the percentage recoveries of the standards, extraction before and sampling after, of the real samples were verified according to the QC criteria (table 20). Again, the values referring to $^{13}C_{12}$OctaCDD have been extended to $^{13}C_{12}$OCDF.

Table 20 Labelled compound recovery in samples when all PCDDs/Fs are tested. Table Source: *Method 1613B (1994)* [128].

	Test Conc. (ng/mL)	Labelled Compound Recovery (ng/mL)[1]	(%)
$^{13}C_{12}$-2,3,7,8-Tetra CDD	100	25-164	25-164
$^{13}C_{12}$-2,3,7,8-TetraCDF	100	24-169	24-169
$^{13}C_{12}$-1,2,3,7,8-PentaCDD	100	25-181	25-181
$^{13}C_{12}$-1,2,3,7,8-PentaCDF	100	25-181	25-181
$^{13}C_{12}$-2,3,4,7,8-PentaCDF	100	21-178	21-178
$^{13}C_{12}$-1,2,3,4,7,8-HexaCDD	100	32-141	32-141
$^{13}C_{12}$-1,2,3,6,7,8-HexaCDD	100	28-130	28-130
$^{13}C_{12}$-1,2,3,4,7,8-HexaCDF	100	26-152	26-152
$^{13}C_{12}$-1,2,3,6,7,8-HexaCDF	100	26-123	26-123
$^{13}C_{12}$-1,2,3,7,8,9-HexaCDF	100	29-147	29-147
$^{13}C_{12}$-2,3,4,6,7,8-HexaCDF	100	28-136	28-136
$^{13}C_{12}$-1,2,3,4,6,7,8-HeptaCDD	100	23-140	23-140
$^{13}C_{12}$-1,2,3,4,6,7,8-HeptaCDF	100	28-143	28-143
$^{13}C_{12}$-1,2,3,4,7,8,9-HeptaCDF	100	26-138	26-138
$^{13}C_{12}$-OctaCDD	200	34-313	34-313
$^{13}C_{12}$-OctaCDF	*200*	*34-313*	*34-313*

[1] Specification given as concentration in the final extract, assuming a 20-µL volume.

3.2.2 ACF-F-2000 method on snow and air

The procedure used for the IPR follows the same method explained in the *Snow* chapter.

A modification has been made with respect to the extraction system in Figure 23 (used for system validation for PCBs and pesticides) as shown below in Figure 30.

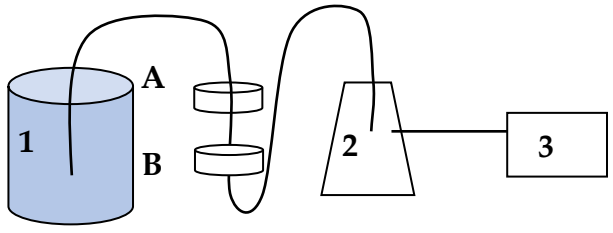


Figure 30 Custom designed extraction system for ACF-F-2000 based SPE extraction for meltwater samples derived from Terminillo Mountain snow: 1) sample container (50L container; meltwater); A) QFF/ACF-F-2000/QFF Holder; B) QFF/ACF-F-2000/QFF Holder; 2)Vacuum flask; 3) Vacuum Pump.

A second QFF/ACF-F-2000/QFF filter is placed in series with the first, respectively ACF A and ACF B; the latter was used as a backup filter for ACF A, in order to control the eventual Breakthrough. Before starting the tests, the water is spiked with Snow Standard Sampling Solution (Snow SS Solution 10 pg/μL) diluted in 1 mL of acetone. This solution contains ^{13}C and perdeuterated labelled congeners of pesticides ($^{13}C_6$-HCB, $^{13}C_6$-PeCB, $^{13}C_6$-γ-HCH, D_6, $^{13}C_{12}$-α-HCH, $^{13}C_{12}$-p,p-DDE), ^{13}C-PCBs (P-48SS, Wellington Laboratories) and $^{13}C_{12}$-PCDD/Fs (EN-1948 SS, Wellington Laboratories) prepared according to Standard solution concentration defined by EPA 1699, 1668B and 1613B methods (tables 9 and 12). The Extraction Standard Solution (ES Solution), consisting of EN-1948 ES and WP-LCS (Wellington Laboratories) $^{13}C_{12}$-PCDD/Fs and $^{13}C_{12}$-PCBs (100 μL; 10 pg / μL) respectively, is added to the first filter. Any detection of Snow SS or ES Solution labelled congeners on the ACF B indicates that it has exceeded the breakthrough. The breakthrough limit is defined as quantities greater than 10% of the Snow SS and ES Solutions added at time t = 0. The two filters are then extracted separately in Soxhlet with Toluene for 36 h. The extract is concentrated up to about 5 mL with a rotary evaporator (40 °C and 40 torr) and subsequently up to 200μl under a gentle flow of nitrogen in a thermostatic bath (40 °C).

Finally, the IS Solution (EN 1948 IS and WP-ISS, $^{13}C_{12}$-PCDD/Fs and $^{13}C_{12}$-PCBs respectively) is added prior to GC-Orbitrap analysis to quantify the R%s of the Snow SS and ES Solutions from the ACF A and ACF B (see *Appendix* B.2).

Table 21 shows the compositions of all the used solutions (Snow SS, ES and IS Solution). As regards for the acceptance criteria of R% in real samples, one can refer to Table 10 and 13 in the *Snow* chapter, paragraph *EPA-1699* and *EPA-1668B* for pesticides and PCBs respectively, and to Table 20 of the previous paragraph for PCDD/Fs.

Table 21 Composition of the Snow SS Solution, ES Solution and IS Solution. Suffix "L" means labelled PCBs

Pesticides	PCBs	PCDD/Fs
Snow SS Solution		
D_6-α-HCH	60L	$^{13}C_{12}$-1,2,3,7,8-PentaCDF
$^{13}C_6$-γ-HCH	127L	$^{13}C_{12}$-1,2,3,7,8,9-EsaCDF
$^{13}C_{12}$-p,p-DDE	159L	$^{13}C_{12}$-1,2,3,4,7,8,9-HeptaCDF
$^{13}C_6$-HCB		
ES Solution		
	81L	$^{13}C_{12}$-2,3,7,8-Tetra CDD
	77L	$^{13}C_{12}$-2,3,7,8-TetraCDF
	123L	$^{13}C_{12}$-1,2,3,7,8-PentaCDD
	118L	$^{13}C_{12}$-2,3,4,7,8-PentaCDF
	114L	$^{13}C_{12}$-1,2,3,4,7,8-EsaCDD
	105L	$^{13}C_{12}$-1,2,3,6,7,8-EsaCDD
	126L	$^{13}C_{12}$-1,2,3,4,7,8-EsaCDF
	167L	$^{13}C_{12}$-1,2,3,6,7,8-EsaCDF
	156L	$^{13}C_{12}$-2,3,4,6,7,8-EsaCDF
	157L	$^{13}C_{12}$-1,2,3,4,6,7,8-HeptaCDD
	169L	$^{13}C_{12}$-1,2,3,4,6,7,8-HeptaCDF
	189L	$^{13}C_{12}$-OCDD
		$^{13}C_{12}$-OCDF
IS Solution		
	70L	$^{13}C_{12}$-1,2,3,4-TetraCDD
	138L	$^{13}C_{12}$-1,2,3,7,8,9-EsaCDD
	111L	

EPA methods do not require the analysis of trace compounds and as well as for pesticides and PCBs, the concentrations reported by the reference methods are far from to be comparable (because higher) with the quantities found in the snow according to the literature. For this reason, the concentrations to be used have been significantly reduced, the range of which is reported in Tables 19 and 20 and is six orders of magnitude lower than that of EPA 1613B (pg/L instead of ng/mL).

The average concentrations of the R%s of the Snow SS and ES Solutions of the 4 tests are reported below (table 22).

Table 22 Average of the concentrations of $^{13}C_{12}$- PCDD/Fs recoveries from the 4 Tests for the evaluation of IPR. All specifications are given as concentration in the final extract, assuming a 20 μL volume. [2]s = standard deviation of the concentration of the 4 tests. [3]X = average concentration

	Test Conc. (pg/L)	IPR[2,3] s ACF A (pg/L)	IPR[2,3] X ACF A (pg/L)
SS Solution			
$^{13}C_{12}$-1,2,3,7,8-PentaCDF	66.7	3	68
$^{13}C_{12}$ -1,2,3,7,8,9-HexaCDF	66.7	6	70
$^{13}C_{12}$ -1,2,3,4,7,8,9-HeptaCDF	133.3	23	144
ES Solution			
$^{13}C_{12}$ -2,3,7,8-Tetra CDD	66.7	6	62
$^{13}C_{12}$ -2,3,7,8-TetraCDF	66.7	2	54
$^{13}C_{12}$ -1,2,3,7,8-PentaCDD	66.7	5	59
$^{13}C_{12}$ -2,3,4,7,8-PentaCDF	66.7	3	57
$^{13}C_{12}$ -1,2,3,4,7,8-HexaCDD	66.7	6	60
$^{13}C_{12}$ -1,2,3,6,7,8-HexaCDD	66.7	9	56
$^{13}C_{12}$ -1,2,3,4,7,8-HexaCDF	66.7	2	57
$^{13}C_{12}$ -1,2,3,6,7,8-HexaCDF	66.7	6	54
$^{13}C_{12}$ -2,3,4,6,7,8-HexaCDF	66.7	3	53
$^{13}C_{12}$ -1,2,3,4,6,7,8-HeptaCDD	133.3	15	112
$^{13}C_{12}$ -1,2,3,4,6,7,8-HeptaCDF	133.3	4	118
$^{13}C_{12}$ -OctaCDD	133.3	3	122
$^{13}C_{12}$ -OctaCDF	*133.3*	*25*	*138*

Although concentrations of approximately 6 orders of magnitude of SS and ES Solution lower than those indicated in Table 19 have been used, all values of *X* (pg/L) tested on 15 L and the relative *s* are within the predetermined values. It means that the ACF-F-2000 reversibly adsorbs the analytes, it can therefore be considered that all the requirements of the IPR are met.

The results relating to ACF B have not been tabulated, as they are all lower than the LOD, which confirms that despite the 15 L of MilliQ water, the breakthrough volume has not been exceeded. Real Samples – Mount Terminillo. The real air-ambient and snow samples were collected in an open field located on Mount Terminillo (Rieti, Italy; 42°26'43.5"N 12°59'36.2"E) at a higher altitude (1536 m asl) than those of the Svalbard Islands (16 m and 500 m asl).

Two events were monitored, each consisting of a High Volume ambient-air sampling and a snow sampling. Ambient air sampling was programmed in the absence of wet depositions, which, however, had to start at the end of the air sampling and within a maximum time span of 3h. The snow collected belonged to the snowfall immediately following the air sampling. Both events were planned by monitoring the weather forecast from the Italian Air Force site.

Ambient-air sampling was performed through two High Volume PM_{10} Samplers in parallel (HV A1 and HV B1 first event; HV A2 and HV B2 second event) at a flow rate of 200 L/min for 24 h. A 102 mm diameter QFF/ACF-F-2000/QFF sandwich filter was placed on the sampler head (figure 31 and 32). All the ACF-F-2000 filters were pre-washed and once packaged they were sealed until the moment of use.

Figure 31 Parallel High Volume PM_{10} Sampler, HV A and HV B

Figure 32 Sandwich Filter QFF/ACF-F-2000/QFF for High Volume PM_{10} Sampler 102 mm diameter

The nonane solution of the Snow SS is added (100 μl) on the QFF/ACF-F-2000/QFF filter before the start of sampling. After sampling, the filters are extracted in a Soxhlet with toluene for 36 h by adding the ES solution (100 μL). The extraction and purification procedure is exactly the one used in the *Validation of pesticide analysis in air* chapter. Before the GC-Orbitrap analysis, 1000 pg of the IS Solution are added.

The **snow samples** were performed by taking two samples for each event (Snow 1 and Snow 2 first event; Snow 3 and Snow 4 second event). Each sampling has provided the relative Field Blank consisting of a 1 L bottle of MilliQ Water opened at the beginning of the sampling and closed at its end.

From literature, it is known that some compounds such as HCHs are photosensitive and their concentration is influenced by exposure to light [23], for this reason all samplings concerned night snowfalls and were collected before sunrise.

Pre-washed fiberglass blankets were placed on the ground and secured with stakes high enough to clearly identify the sampling area. This detail allows to collect only the snowfall following the air sampling, avoiding previous snow deposits (Figure 33). Two pre-washed 50 L steel barrels were filled with snow with a pre-washed shovel, the samples were collected downstream of the wind to avoid contaminating the area of interest. The temperatures of the surface snow and the depth of sampling were taken and the snow texture was evaluated (Table 23). The samples collected were transported to the laboratory and extracted according to the procedure described in the "Snow" chapter.

Both snow samples and related Field Blank were treated in the same way.

Table 23 Snow sampling data. Event 1: Snow 1 e 2. Event 2: Snow 3 and 4. The pH was measured on melted snow.

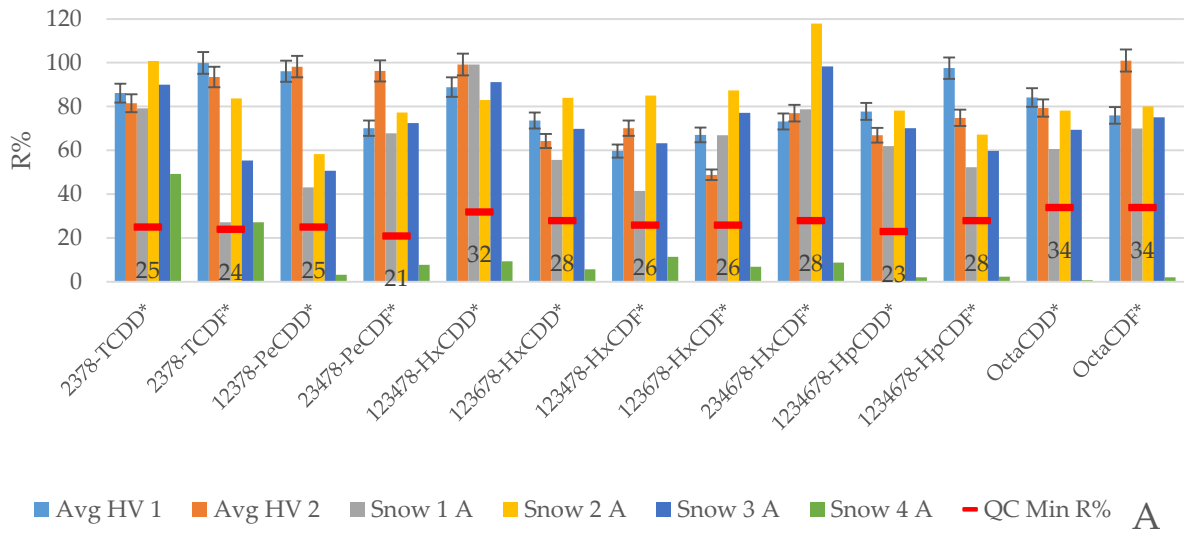
	Sampling date and time	Sampling Area and height (cm)	Temp. surface Snow (°C)	Temp. deep snow (°C)	Texture	pH	Volume of melted snow (L)
Snow 1	27/07/2020 7:00	126X360X3	-6	-7	powdery	5.85	17.7
Snow 2	27/07/2020 7:30	107x166x5	-1	-3	grainy	6	15.4
Snow 3	08/03/2020 6:49	145X147X5	-6	-1	Icy and grainy	5.9	13.8
Snow 4	08/03/2020 7:10	120x163x5	-5	-1	Icy and grainy	6.1	14.8

Table 24 HV PM_{10} ambient air sampling data. Event 1: HV A1 and HV B2; Event 2: HV A2 and HV B2. Va = Volume of air sampled.

	Sampling Date and time		Sampling time (h)	Sampling flow rate (L/min)	Va (m^3)
	Start	End			
HV A1	25/02/2020 11:00	26 /02/2020 11:00	24	200	286.816
HV B1	25/02/2020 11:00	26 /02/2020 11:00	24	200	286.884
HV A2	06/03/2020 17:16	07/03/2020 17:16	24	200	286.940
HV B2	06/03/2020 17:16	07/03/2020 17:16	24	200	287.029

Figure 33 - Sampling area of Snow. Fiberglass tarpaulin enclosed by sticks; steel barrel and shovel; Field Blank bottle

The Figure 34 shows R%s of the $^{13}C_{12}$-PCDD/Fs (Figure 34A) and $^{13}C_{12}$-PCBs (Figure 34B) congeners of the ES Solution through which it is possible to define which samples can be considered valid for quantification. Ambient air samples were collected by taking two measurements in parallel (A and B) in each event 1 and 2; since they were all valid, the results are reported as averages of the two events, HV 1 and HV 2.



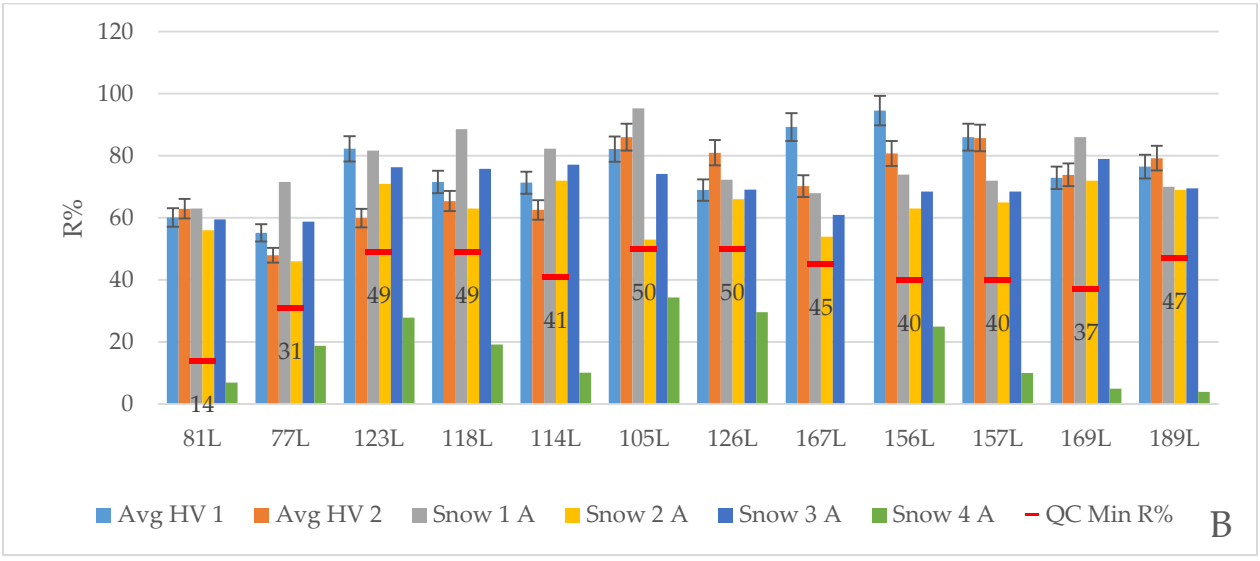


Figure 34 A) R%s of $^{13}C_{12}$-PCDD/Fs of the ES Solution. "*" = labelled compounds ^{13}C. B) R% of $^{13}C_{12}$-PCBs of the ES Solution. Suffix "L" means labelled compounds ^{13}C. Avg HV 1 = Average of the R%s of parallel air-ambient samplings (HV A1 and HV B1) of Event 1; Avg HV 2 = Average of the R%s of parallel air-ambient samplings (HV A2 and HV B2) of Event 2.

As can be seen from figure 34, the percentage recoveries of each PCDD/F and PCB congener in the air and snow samples fall within the ranges defined by EPA 1613B and 1668B except for the Snow 4 sample. A problem is assumed during the analysis; therefore, it is not taken into consideration in subsequent evaluations.

In Figure 35 the R%s of the Snow Sampling Solution with the related QC acceptance criteria defined in the EPA 1699, 1668B and 1613B methods are also reported.

All congeners respect the defined ranges, maintaining the same trend for both sample types, so the use of the QFF/ACF-F-2000/ACF sandwich system seems not to be influenced by the matrix (air or water). Furthermore, the interference of the matrix in these specific cases does not affect the recoveries of the analytes. This confirms what has already been observed for PCBs and Pesticides, and extends to PCDD/Fs.

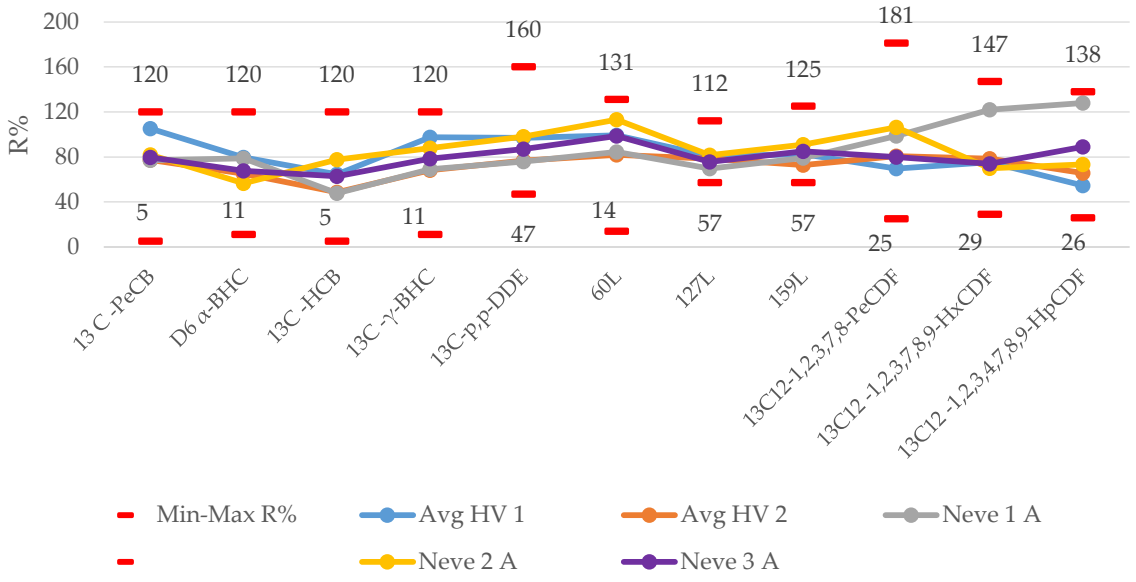


Figure 35 R% of Snow SS Solution compounds added to the melted snow before starting the extraction.

The snow sampling extraction system included a second QFF/ACF-F-2000/QFF B sandwich, used as a backup filter to evaluate the breakthrough. From the analysis, the concentrations of Snow SS Solution and ES Solution for all labelled congeners were found to be below the limit of quantification, so the results were not reported. It is therefore possible to state that the Breakthrough volume was not exceeded in any of the snow samples (Snow 1, Snow 2, Snow 3, Snow 4). This is also valid for the Snow 4 sample whose QFF/ACF-F-2000/QFF A system was excluded from the quantities. Table 25 shows the

concentration of each compound (pesticides, PCBs and PCDD/Fs) in each air and snow sample.

Table 25 Concentrations (pg m^{-3} and pg L^{-1}) of organochlorine pesticides, PCBs and PCDD/Fs in the air ambient and snow samples. All values <LOD were considered as LOD/2 for the quantitative, and identified in bold in the table; values <LOQ are identified in italic. [151].

	HV A 1 pg/m3	HV B 1 pg/m3	HV A 2 pg/m3	HV B 2 pg/m3	Snow 1 A pg/L	Snow 2 A pg/L	Snow 3 A pg/L
PeCB	148	125	103	70	**0.0032***	**0.0036***	**0.0032***
α-HCH	2.0	1.4	0.91	**0.5***	41	156	112
HCB	92	73	55	40	196	174	152
γ-HCH	10.7	8.3	5.8	1.2	160	461	476
p,p-DDE	8.8	5.8	2.8	1.8	419	100	228
o,p-DDT	68	44	21	15	175	78	**0.22***
81	0.32	0.35	0.31	0.30	**0.0021***	11	**0.0033***
77	0.71	1.1	1.4	0.20	**0.0032***	201	20
123	0.52	0.31	0.10	0.70	48	30	40
118	8.7	6.6	4.5	2.8	850	200	100
114	0.20	0.10	0.11	0.12	**0.031***	**0.030***	**0.031***
105	1.9	1.5	1.1	2.1	241	110	70
126	0.90	0.70	0.60	0.40	**0.0031***	**0.0030***	**0.0031***
167	2.9	2.5	2.1	1.5	**0.0030***	**0.0030***	**0.0032***
156	4.1	3.2	2.3	1.8	55.3	**0.010***	**0.011***
157	2.8	2.6	2.4	2.1	**0.0040***	**0.010***	**0.010***
169	0.90	0.70	0.50	**0.00022***	**0.0021***	**0.0023***	**0.0031***
189	6.7	6.5	6.3	4.1	**0.0022***	**0.0037***	**0.0032***
2,3,7,8-TeCDD	**0.0018***	**0.0018***	**0.0018***	**0.0018***	**0.0024***	**0.0027***	**0.0034***
2,3,7,8-TeCDF	**0.0011***	**0.0011***	**0.0011***	**0.0011***	**0.0015***	**0.0017***	**0.0019***
1,2,3,7,8-PeCDD	**0.0061***	**0.0060***	**0.0061***	**0.0062***	**0.0082***	**0.0094***	**0.011***
1,2,3,7,8-PeCDF	0.0012	**0.0010***	***0.***0011*	**0.0015***	**0.0013***	**0.0015***	**0.0016***
2,3,4,7,8-PeCDF	**0.00051***	**0.00054***	**0.00053***	**0.00051***	**0.00066***	**0.00065***	**0.00081***
1,2,3,4,7,8-HxCDD	**0.0019***	**0.0019***	**0.0019***	**0.0019***	**0.0025***	**0.0029***	**0.0033***
1,2,3,6,7,8-HxCDD	**0.0037***	**0.0037***	**0.0037***	**0.0037***	**0.0048***	**0.0056***	**0.0062***
1,2,3,7,8,9-HxCDD	**0.0026***	**0.0026***	**0.0026***	**0.0026***	**0.0035***	**0.0045***	**0.0044***
1,2,3,4,7,8-HxCDF	**0.0031***	**0.0031***	**0.0031***	**0.0031***	**0.0045***	**0.0046***	**0.0052***
1,2,3,6,7,8-HxCDF	**0.00061***	**0.00061***	**0.00061***	**0.00061***	**0.00082***	**0.00092***	**0.0011***
2,3,4,6,7,8-HxCDF	**0.00091***	**0.00091***	**0.00091***	**0.00091***	**0.0012***	**0.0014***	**0.0015***
1,2,3,7,8,9-HxCDF	**0.0031***	**0.0031***	**0.0031***	**0.0031***	**0.0041***	**0.0047***	**0.0053***
1,2,3,4,6,7,8-HpCDD	**0.0035***	**0.0035***	0.082	0.095	**0.046***	**0.047***	0.085
1,2,3,4,6,7,8-HpCDF	**0.0011***	**0.0011***	0.026	**0.0010***	**0.015***	**0.012***	*0.027*
1,2,3,4,7,8,9-HpCDF	0.062	0.064	0.014	**0.0010***	0.08	*0.025*	0.091
OCDD	**0.0047***	**0.0047***	11	0.69	0.062	0.093	0.18
OCDF	**0.00051***	**0.00051***	0.11	0.0063	0.0061	0.072	0.088

Analysing the concentration data shown in table 25, it can be observed that the response varies according to the class of compounds under examination. Pesticides are found at higher concentrations in snow samples than in the air. This result is confirmed by the study by Lei and Wania, who underline how for α-HCH and γ-HCH the snow scavenging ratio (total concentration in air with respect to the action that each deposition exerts on the removal class) increases with decreasing temperatures (< 0 °C) [14]. The high concentrations determined are probably also linked to the fact that the samples were collected in winter with a low presence of irradiation and before sunrise, so they underwent limited degradation. However, it is necessary to emphasize that as far as they may appear high concentrations of HCB, p,p-DDE and o,p-DDT still fall within the ranges found in remote areas of this type [59]. HCB, on the other hand, is a compound that does not undergo photodegradation and is persistent, so much, so that in mountainous areas and at high latitudes it tends to accumulate during the winter and resists until summer, when it is released following the melting of the snow. Furthermore, the lighter compounds (e.g. α-HCH, γ-HCH, PeCB and HCB) tend to undergo long-distance transport and it is easy to find them in these regions despite the low values in the air. As regards p,p-DDE and o,p-DDT, of higher molecular weight, it can reasonably be assumed that they are compounds deriving from the valley in the province of Rieti since strong winds were recorded from the south/east. The concentrations of these compounds detected in the air are significantly lower than those in snow samples. From this, it can be said that 24 hours of sampling of this type are not enough to represent the ACF-F-2000 so that it can be compared with snow. It is hypothesized that larger volumes of air are needed to enrich ACF-F-2000 more of the classes under examination, which results in longer samplings.

PeCB is detected in all ambient air samples but not in snow samples and given the R% of the $^{13}C_6$-PeCB homologue present in the Snow SS Solution between 77 and 89% for all

snow samples, the cause cannot be attributed to the analytical method. There are no comparable studies in the literature on this compound and only two events are not sufficient to draw environmental conclusions. As for PCBs, according to Lei and Wania's study, the snow scavenging ratio is directly proportional to the degree of chlorination as the temperature decreases (< 0 °C). This justifies the higher relative concentration in the snow samples compared to the air of the congeners 156, 157 and 189 (respectively Hexa- and Hepta-chlorosubstituted) compared to 123 (Penta substituted chlorine). Overall, for PCBs it was observed that despite the concentrations of ambient air samples, snow scavenging was not as efficient as for pesticides; according with the literature, this is due to the greater scavenging action of the particulate with respect to the wet depositions on this class. [14,152]. Anyway, the detected concentrations of PCBs and pesticidie coincide with the values normally detected in areas of this kind, both for air-sampling environment that snow [59,153].

As regards PCDD/Fs, from the substituted Tetras to the Hexa, the measured concentrations were lower than the detection limit of the method; for this reason the medium bound approach was followed, associating the value of the LOD/2 (Limit of Detection). It can be assumed that the environmental concentrations of this class require longer air-ambient samplings, since the recovery of the labelled standards falls within the requirements of the methods used (as for PeCB).

Hepta and octa chlorosubstituted congeners were found both in air and in snow samples. A behavior similar to that of PCBs can be hypothesized: despite the prevailing scavenging by particulate matter, the snow scavenging action increases as the degree of chlorination increases and temperatures decrease.

3.2.3 Non-target screening

All the samples related to the two events were analysed for the study of the Unknown compounds, setting the Deconvolution plug-in with the same parameters described in the *Unknown compound - Snow*. The Snow 4 sample was not processed since the R%s of Snow SS and ES Solution did not meet the minimum requirements of the methods.

4 Batches have been created:

- **Snow**: Snow 1, Snow 2, Snow 3, Field Blank 1, Field Blank 2 and Field Blank 3
- **High Volume Air**: HV A1, HV B1, HV A2, HV B2, Blank1 HV and Blank2 HV
- **Event 1**: HV A1, HV B1, Snow 1, Snow 2, Bianco1 HV, Bianco2 HV, Field Blank 1 e Field Blank 2
- **Event 2**: HV A2, HV B2, Snow 3, Bianco1 HV, Bianco2 HV and Field Blank 3

The *Snow* batch is aimed at understanding on which compounds this matrix has a greater scavenging effect. It also allows a comparison with the Unknown Compounds of the Svalbard Islands, by defining any correlation for altitude-latitude and temperature.

The *High Volume Air* batch is aimed at identifying compounds characteristic of high altitudes, present in the air, and not taken into consideration during the previous chapters.

Both the Snow as the High Volume Air batches allow to identify in the two matrices (air and snow) to which classes of compounds extend the use of the ACF-F-2000 in the future (eventually considering emerging contaminant too). The Event 1 and Event 2 batches respectively, include the samples involved in the two events and the relative blanks. They were designed to evaluate the snow scavenging action on compounds identified in the air before precipitation.

Snow

Following the deconvolution of the chromatograms and the alignment of the retention times, 5040 compounds were identified in the Snow batch, to which the relevant Scores and AVG Scores for identification in the library were associated.

The two levels of identification reliability were thus defined.

Briefly, the High Level of Identification Reliability includes only compounds with a Score > 90% in all 3 snow samples (Snow 1, Snow 2, Snow 3). The Identification Medium Confidence Level includes all compounds with AVG Score > 90%. Furthermore, for both Levels of Identification, no compound (regardless of the Score) must be present in the Field blanks. Once the two Levels had been defined, the identified compounds were analysed, excluding all those that, due to fragmentation, retention times, and type of compound, were clearly false positives.

Table 26 Compounds Common to Snow 1, Snow2 and Snow3. High and Medium Level of Identification Reliability. The identified substances have been divided into groups as specified below: Yellow = Incomplete Combustion; Green = Personal Care; Orange = Natural Products; Blue = Agricultural Products (Fertilizers/pesticides/fungicides); Purple = Industrial Products; Grey = Drugs.

	Chemical Name	**CAS**	**Reference**
Snow High Level of Identification Reliability	Dibutyl phthalate - DP	84-74-2	[154]
	3-Butenyl adipate	N.D.	[155]
	Phthalic acid, cyclobutyl pentyl ester	N.D.	[156]
	Dicyclohexyl phthalate	84-61-7	[139]
	Bis(2-ethylhexyl) phthalate	117-81-7	[156]
	Phthalic acid, cyclobutyl tridecyl ester	N.D.	[156]
	1,2-Benzenedicarboxylic acid, dinonyl ester – DNP	84-76-4	[157]
	Di-n-octyl phthalate - DNOP	117-84-0	[158]
	Diphenylmethoxy acetic acid	21409-25-6	[159]
	Pentadecanoic acid	1002-84-2	[160]
	Cytidine, 2'-deoxy-5-methyl-	838-07-3	[161]
	Decane, 2,5,9-trimethyl-	*62108-22-9*	[162]
	1,2-Dimethoxy-4-(1,2,3-trimethoxypropyl)benzene	N.D.	[163]
	Cyclohexane, (2-methylpropyl)-	1678-98-4	
	Cyclohexane, octyl-	1795-15-9	
	2-Methyltetracosane	1560-78-7	[164,165]

	2-Ethylhexyl 4-(dimethylamino)benzoate	**21245-02-3**	[166]
	1-Tetradecyne	765-10-6	
	1-Pentadecyne	765-13-9	
	Chemical Name	**CAS**	
Snow Medium Level of Identification Reliability	Phosphoric acid, tris(2-ethylhexyl) ester - THEP	78-42-2	[167,168]
	Benzyl butyl phthalate (BBP)	85-68-7	[169,170]
	Phthalic acid, 2-isopropylphenyl methyl ester	N.D.	[139,156]
	Tributyl phosphate	126-73-8	[171]
	Sulfurous acid, cyclohexylmethyl hexadecyl ester	N.D.	
	Ethanone, 2,2-dimethoxy-1,2-diphenyl-	*24650-42-8*	[172,173]
	4,4'-Dimethylbiphenyl	613-33-2	
	Benzene, (1-methylnonyl)-	4537-13-7	[174]
	9,10-Anthracenedione	84-65-1	[175]
	Anthrone	90-44-8	[175]
	4b,8-Dimethyl-2-isopropylphenanthrene, 4b,5,6,7,8,8a,9,10-octahydro-	N.D.	[176,177]
	Hexadecanamide	629-54-9	[178,179]
	1-Tetradecyne	765-10-6	
	1-Hexadecyne	629-74-3	[180]
	N-Phenethylbenzenesulfonamide	77198-99-3	[181]

The samples shown in table 25 have been divided trying to respect as far as possible the classes defined in the *Unknown Compounds - Snow* paragraph.

Most of the compounds belong to the category of Industrial Products, both in the High and Medium Level of Identification Reliability.

Among these, phthalates are dominant, a class well known for their toxicity as reported by the European Commission [182]. Phthalic acid esters ("phthalates") are used as plasticizers in many consumer products, raw materials and building materials. Phthalates, not being chemically bound to the products, are continuously emitted and leached. This implies that they can be found in high concentrations both indoors and outdoors in the gaseous phase or in the particulate matter being semivolatile compounds (SVOC). This is the case, for example, of Dibutyl Phtalate, of Di-n-octyl phthalate (DNOP) often found in indoor dust or of 1,2-Benzenedicarboxylic acid, dinonyl ester (DNP), used primarily as a plasticizer for polyvinyl chloride (PVC) to impart flexibility [154,157,158].

As plasticizing agents, phthalates are often found also in food linked above all to food and beverage packaging (eg. Dicyclohexyl phthalate o Phthalic acid, 2-isopropylphenyl methyl ester) [139].

By subjecting plastics to high temperatures, various compounds are released into the atmosphere as in the case of the 3-Butenyl adipate listed in the table. Although 3-Butenyl adipate has not been identified as a desired constituent in polymers, according to A. Naik et al., It represents a thermal degradation product of thermoplastic polyurethane (TPU)[155,183]. This compound is also a flame retardant, another class that has been included within the Industrial Products. Among these are also identified the Tributyl phosphate and the Phosphoric acid, tris (2-ethylhexyl) ester. The latter is well known as THEP has been widely used as a plasticizer, fire retardant and solvent [184]. THEP, an organophosphorus compound (OP), is also a ubiquitous pollutant found in airborne particles in the Pacific, Indian, Arctic and Southern Oceans [168] as well as often present in the dust of houses [167].

The compounds identified among the natural ones belong to vegetation, and are the same identified also in the analysis of indoor environments in the presence of real wood furniture and parquet, such as e.g. 2,2-dimethoxy-1,2-diphenyl-ethanone, a by-product of degradation emitted by parquet when it is hit by UV radiation. [172].

It is interesting to note that compounds have been identified in the Industrial Products class which, according to ECHA (European Chemical Agency), are irritating, toxic for reproduction or endocrine disruptors, regulated by REACH or even banned [182]. The BBP and the DP are certainly among the best known and most widespread, and for this reason among the most difficult to identify because they are subject to overestimates due to laboratory contamination [170].

Numerous compounds identified belong to the class of combustion products or substances associated with fuels. These compounds may already be present in the original fuel, produced during combustion, or modified by reactions in the atmosphere.

For example, in the Medium Level of Identification Reliability, two Oxy-PAHs have been identified, which may have been generated directly in the combustion of e.g. Diesel engines [185] or after PAH emission deriving from combustion (anthropogenic or natural) due to reactions in the atmosphere [186]. Also included in this class are substituted aromatic hydrocarbons, known constituents of fuels and consequently probable products of incomplete combustion PICs.

Within the Personal Care class, two compounds were identified, one present in the High Level of Identification Reliability group and the other in the Medium Level.

The first is 2-Ethylhexyl 4- (dimethylamino) benzoate, also known as Padimate O, and is a constituent of sunscreens as a UV filter. Thanks to this property, it is also used in solar panels. It has now been reduced for its effect as an endocrine disruptor and its use is regulated by a maximum of 8% in sun creams [166]. UV filters, thanks to their resistance to photodegradation, can be transported over long distances. The NILU (Norwegian Institute For Air Research Norway) identifies UV filters as a class of emerging pollutants [143]. The second compound is the Hexadecanamide used for the topical treatment of dermatitis [178,179]. Different alkynes are finally detected for which it has not found any reference in the literature, but that probably may have biogenic source.

High Volume Air

For the "HV" Batch, after the processing of the Deconvolution software, 6094 compounds were identify. As previously, the two Identification Reliability Levels (High and Medium) have been created. The High Level of Identification Reliability includes all compounds present simultaneously in HV A1, HV B1, HV A2, HV B2 whose Score is > 90% for all samples. While the Medium Level of Identification Reliability includes all compounds with AVG Score > 90%. All the compounds listed must be absent (regardless of the Score) from both Blank1 HV and Blank2 HV.

Table 27 Compounds Common to HV A1, HV B1, HV A2, HV B2. High and Medium Level of Identification Reliability. The identified substances have been divided into groups as specified below: Yellow = Incomplete Combustion; Green = Personal Care; Orange = Natural Products; Blue = Agricultural Products (Fertilizers/pesticides/fungicides); Purple = Industrial Products; Grey = Drugs.

	Chemical Name	CAS	Reference
HV High Level of Identification Reliability	2,4-Di-tert-butylphenol	96-76-4	[187]
	3-Butenyl adipate		[155]
	Tributyl phosphate	126-73-8	[171]
	Phthalic acid, cyclobutyl tridecyl ester		[3]
	Naphthalene, 1,6-dimethyl-	575-43-9	
	Decane, 2,9-dimethyl-	1002-17-1	
	[1,1'-Biphenyl]-2-ol, acetate	3271-80-5	
	Fluoranthene	206-44-0	
	2,2'-Dimethylbiphenyl	605-39-0	[140,143]
	5-Acetyl-2-methoxyphenyl acetate	60792-88-3	
	Dibenzyl	103-29-7	
	Benzyl Benzoate	120-51-4	[189]
	2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-	719-22-2	
	Valeric anhydride	2082-59-9	
HV Medium Level of Identification Reliability	**Chemical Name**	**CAS**	**Reference**
	Phthalic acid, hexyl tridec-2-yn-1-yl ester		
	Undecane, 3,7-dimethyl-	17301-29-0	
	Benzene, (1-pentylheptyl)-	2719-62-2	
	Naphthalene, 1,6,7-trimethyl-	2245-38-7	
	Heptacosane	593-49-7	[175]
	Oxalic acid, allyl nonyl ester		[190]
	Trimethoquinol		[191]
	1-Pentadecyne	765-13-9	
	Carbonic acid, eicosyl vinyl ester		[192]

The compounds identified within the Industrial Products group are different from those identified in the same group of the Snow Batch. First, a decrease in the amount of plasticizing compounds identified (phthalates) is observed. However, we find all the flame-retardants previously identified, namely 3-Butenyl adipate and Tributyl phosphate.

The compound 2,4-Di-tert-butylphenol has also been identified, identified by ECHA as dangerous and registered by REACH as very toxic to aquatic life with long-term effects, causing skin and eye irritation. This product can be found in the fuel and used in industrial applications in the packaging. *The release into the environment can take place at an industrial level in closed systems with minimal release (e.g. cooling liquids in refrigerators, oil-based electric heaters) and outdoor use in close systems with minimal release (e.g. hydraulic liquids in automotive suspension, lubricants in motor oil and break fluids)* [193]. Also, in this case PAHs are products which are often used in industry but which have been classified as Incomplete Combustion products. Those detected are two very light PAHs (substituted naphthalene) with two benzene rings which, as seen in the first chapters, are able to be adsorbed and desorbed by the ACF used as a sampling system. Linear and aromatic alkanes are included as performed above.

Comparing the *HV* batch with the one previously seen, it is interesting to note the introduction of two compounds from the groups of Pharmaceutical Products (in grey) and Agricultural Products (in blue). Benzyl Benzoate is used as a plasticizer in cellulose and other polymers, a fixative in fragrances, a food additive, a solvent, a remedy for scabies, a pesticide to kill ticks, mites, and lice, and has been used as a repellent for chiggers, ticks, and mosquitoes [189]. In reality, this last compound would be halfway between two groups, but it was decided to place it within the class of pesticides given the studies on the ACF-F-2000. Trimethoquinol is a beta-stimulating adrenergic drug, selective for bronchial receptors. This does not mean that the ACF-F-2000 is capable of quantitatively sampling all types of drugs, but that it is a class not to be excluded.

The research carried out on the two matrices considered in this PhD study presents some common classes which have a certain relevance also at a toxicological level: phthalates, flame retardants, some combustion products, UV filter, pesticides, incomplete combustion products, personal care.

Comparing scavenging effects

To complete the study, the Event 1 and Event 2 Batches are also processed. The reported data are qualitatively analysed to see if it is possible to verify the scavenging effect also through studies on Unknowns compounds. Not sure that the ACF-F-2000 is valid for each of the compounds reported in the tables for quantitative studies, no firm conclusion can be reached. The deconvolution of chromatograms and alignment of the retention times have allowed the identification of a total of 6769 compounds for Event 1 batch and 6813 for the Event 2 batch. After the meticulous reworking of each list of compounds, it was possible to build the Table 27.

Table 28 High and Medium Level of Identification Reliability.for Event 1 and Event 2 batches. The identified substances have been divided into groups as specified below: Yellow = Incomplete Combustion; Green = Personal Care; Orange = Natural Products; Blue = Agricultural Products (Fertilizers/pesticides/fungicides); Purple = Industrial Products; Grey = Drugs

	Chemical Name	**CAS**	
Event 1 High Level of Identification Reliability	Benzaldehyde, 3-hydroxy-4-methoxy-	621-59-0	[194,195]
	Phosphoric acid, tris(2-ethylhexyl) ester	78-42-2	[167]
	Dibutyl phthalate - DP	84-74-2	[154]
	Phthalic acid, cyclobutyl tridecyl ester		[156]
	Fluoranthene	206-44-0	
	Apocynin	498-02-2	[196]
	Dibenzyl	103-29-7	
	Dodecanoic acid, 1-methylethyl ester	10233-13-3	[197]
	Benzyl Benzoate	120-51-3	[189]
Event 2 High Level of Identification Reliability	Ethyl 4-dimethylaminobenzoate	10287-53-3	[198]
	Cyclooctane, 1,4-dimethyl-, trans-	13151-98-9	
	7-Tetradecene	10374-74-0	
	cis-Calamenene	72937-55-4	
	2,2'-Dimethylbiphenyl	605-39-0	[140]
	4,4'-Dimethylbiphenyl	613-33-2	[140]
	3,5-di-tert-Butyl-4-hydroxybenzaldehyde	1620-98-0	
	Chemical Name	**CAS**	
Event 1 Medium Level of Identification Reliability	Phthalic acid, 2-isopropylphenyl methyl ester		[139,156]
	Phthalic acid, heptyl pentyl ester		[157]
	Phthalic acid, pentyl tridec-2-yn-1-yl ester		[157]
	Decane, 2,4,6-trimethyl-	62108-27-4	
	Oxalic acid, 2-ethylhexyl hexyl ester		

	Methyl 2,4-dihydroxy-3,6-dimethylbenzoate	4707-47-5	[199]
	Ethyl 2-benzoylheptanoate	24317-97-3	
	1,14-Tetradecanediol	19812-64-7	[200]
Event 2 Medium Level of Identification Reliability	Diethylene glycol acetate propionate		[201]
	2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-	719-22-2	
	Nonadecane	629-92-5	
	4,4'-Dimethylbiphenyl	613-33-2	[140]
	Methanone, (2-methylphenyl)phenyl-	131-58-8	[202,203]
	Carbonic acid, eicosyl vinyl ester		[192]

First of all, it can be observed that there are some apparent inconsistencies between the compounds listed here and those reported in the previous tables relating to *Snow* and *HV* batches It is important to remember that for each event only the compounds present simultaneously in all the samples of the same event were selected. Furthermore, the criteria defined previously for the High and Medium Level of Identification Reliability and the removal of Blanks are respected. For example, the tris (2-ethylhexyl) external Phosphoric acid, is included in the High Reliability Level of Identification of the Event 1 batch and in the Medium Level of the Snow Batch, but absent from the HV Batch. The compound in question has been identified with a Score > 90% in HV A1, HV B1, Snow 1, Snow 2 (and absent in all the blanks) for this reason it is included in the High Level in table 27. The compound in the Snow 3 sample has a Score < 90%, but the AVG Score of the batch is equal to 90.623% and for this reason it is included in the Medium Reliability Level of the Snow batch. Finally, Phosphoric acid, tris (2-ethylhexyl) ester is absent in HV B2 sample, and for this reason excluded from the batch table relating to ambient air sampling.

Table 29 Phosphoric acid, tris (2-ethylhexyl) ester R%s in each sample.

	HV A1	HV B1	HV A2	HV B2	Snow1	Snow2	Snow3	HV 1 e 2 Blank	Field Blank 1, 2, 3
Score %	> 90%	> 90%	< 90%	ND	> 90%	> 90%	< 90%	ND	ND

Among the Industrial Products, many compounds already seen and belonging to phthalates (plasticizers) have been identified. This means that the lower detection of this class in air (HV batch table 26) is not attributable to an inefficiency of the ACF-F-2000 adsorbent, but that the phthalate contamination detected was specific of the Event 1. Also, since they were in the snow but not in the air of Event 2, it could be due to suspended materials being transported during the snowy night (Snow 3). This result is supported by the large number of phthalic acid esters found in Event 1 compared to Event 2 in all Levels (Table 27). This data highlights the importance of atmospheric stability, the presence of winds and vertical mixing as parameters to be considered when studying the Scavenging effect of depositions.

Among the specific compounds of Event1, Benzaldehyde, 3-hydroxy-4-methoxy-, better known as Isovanillin, was identified. It is found in many plastic objects (e.g. toys) even if it is not a specific component used for its construction. It is irritating to the eyes and skin and causes serious irritation to the respiratory tract [195].

Moreover, two compounds used as additives for paints have been identified in Event 2 batch: Ethyl 4-dimethylaminobenzoate [54] and Diethylene glycol acetate propionate [201]. Two days before the start of the air-ambient sampling of Event 2, some balustrades were painted not far from the sampling site. This implies a positive confirmation of the truthfulness of the data collected, given the absence of these compounds in Event 1.

Among the Personal Care, two constituents of detergents, household cleaning products and therefore particularly present indoors have been identified (ex. Methyl 2,4-dihydroxy-3,6-dimethylbenzoate [199,204]).

Between the unclassified compounds there is (2-methylphenyl) phenyl-Methanone, for which there is no specific literature data. It could be included in personal care since there are a number of Benzophenones used as UV screens in sunscreens [203].

This screening made it possible to identify and confirm some families of compounds against which the ACF-F-2000 will certainly be tested in the future. To what has already

been listed above, detergents, adhesives and additives for paints are therefore added, all classes of compounds that the ACF-F-2000 was able to adsorb and desorb both in air and in water. The next step will be to address validation studies to understand whether the adsorption and desorption are quantitative and reproducible. In all cases, this represents only a preliminary screening since this type of approach is not enough to carry out the study of Unknown compounds through High Resolution. The injection of reference standards in the same analytical sequence and possibly in two orthogonal analyses can be mandatory for identifications with utmost certainty [205].

4 SUMMARY

The countless characteristics of Activated Carbon Fibers allow the wide use of this material in the industrial field for the abatement of micropollutants. In this PhD work the potential of the ACF in this area has also been investigated in the analytical field.

An in-depth bibliographic study has clearly shown that there are many variables that influence the efficiency and characteristics of the ACF. First of all, the production process and the type of starting material. Using the ACF as an adsorbent for analytical purposes on the basis of the simple technical specifications given is inconceivable.

For this reason, it was essential to perform a characterization of this adsorbent aimed at analytical use. After a physico-chemical characterization of 4 types of ACF and adsorption / desorption efficiency tests, the ACF-F-2000 turned out to be the best. It is a material derived from phenolic fibers also known as Kynol.

The SSA was determined according to the BET method by Nitrogen adsorption and was found to be about 2468 m^2 / g. The average pore radius is approximately 6 Å (= 0.6 nm), that corresponds to a pore diameter of approximately 1.2 nm. The resulting isotherm corresponds to a type I Langmuir curve, i.e. a material whose homogeneous microporosity is distributed on the surface.

Through the Boehm Titration it was possible to define that ACF-F-2000 displays a strong acidic component, especially linked to carboxyl groups and a strong basic component due to pyrone groups, whose oxygens confer a negative charge to the material.

In order to use any adsorbent to sample organic micropollutants, it must first of all be able to adsorb and subsequently desorb them.

The many industrial applications found in the bibliography demonstrate the adsorption of POPs, so we proceeded directly to verify the reversibility of adsorption in a quantitative way.

The study then continued to test various extraction techniques through the use of isotopically marked standards, evaluating the percentage recovery. Soxhlet extraction with Toluene for 36h was found to be the most suitable technique for PCDD/Fs, PCBs, PeCB and HCB.

Another result achieved was the deepening of the analysis of PAHs: regardless of the type of extraction and type of ACF, no test gave satisfactory results. Therefore, the class of PAHs was excluded from subsequent evaluations.

Due to their structure, in fact, they establish an interaction with the ACF such that the force is proportional to the increase of the benzene rings.

During the Master's thesis, the ACF-F-2000 filter had been validated for indoor and ambient sampling of PCDD/Fs and PCBs both in the gaseous phase and adsorbed on the particulate according to the standard reference methods ISO 16000-13 and 14, EPA TO 4A and 9A. Both methods (EPA and ISO) to meet the same efficiency require a double absorbing system for this type of sampling: a Quartz Fiber Filter (for the particulate matter) plus PUF (for the gas phase).

Since the re-extraction of PeCB and HCB from ACF-F-2000 has been verified, in this work we proceeded to complete the master's thesis studies by validating the adsorbent for the air-environment sampling of these classes according to the EPA method TO4A. It has been demonstrated that the material is suitable for sampling in the absence of breakthrough up to 24 h.

An in-depth study of POPs in the atmosphere cannot be limited only to the air matrix. Dry and wet depositions have a decidedly not negligible scavenging effect on POPs. The impact of a deposition with respect to another is highly dependent on the temperatures at which they perform the monitoring. The following research aimed at validating the use of the adsorbent ACF-F-2000 also for wet depositions, i.e. rain and snow.

According to the literature, the most widely used method for the extraction of PCDD/Fs and PCBs from rainwater samples is liquid/liquid extraction (LLE) and the associated

methods are EPA 1613B and 1668B. Using isotopically labelled standards, the results of LLE were compared with those obtained by the ACF-F-2000 used as a passive adsorbent. This led to the validation of the proposed method to extract up to 24 L of water by adopting the QC criteria EPA 1613B and 1668B.

As for the snow matrix, there are no reference methods for POPs analysis. An extensive bibliography research has made it possible to first define a sampling method and subsequently an extraction method. The analysis of micropollutants from snow involves the use of melted snow; therefore, it was decided to use the QC criteria of the methods for the water matrix for the validation of the ACF-F-2000.

Through the EPA 1613B and EPA 1699 methods it was possible to validate a new extraction system, modifying the one usually adopted by the University Center in Longyearbyen (Svalbard). The modified system involves the use of a suction pump for melted snow and sees the ACF-F-2000 as an adsorbent filter for the extraction of PCBs and pesticides (α-HCH, γ-HCH, p, p'-DDE, o, p-DDT, HCB and PeCB). once validated, the sampling and extraction system was applied in the field on real samples performed in the Svalbard Islands.

The ACF-F-2000 was finally used for the simultaneous and parallel sampling of ambient air and snow of PCDD/Fs, PCBs, α-HCH, γ-HCH, p, p'-DDE, o, p-DDT, HCB and PeCB, carrying out samples at Mount Terminillo. It can therefore be said that the ACF-F-2000 adsorbent, given its characteristics, has proved to be validated for all the classes of compounds listed above both in the air and water/snow matrix.

The advantage of this material is due to its ability to reversibly trap POPs, both the gas phase/dissolved in water and the phase adsorbed on the particulate. These two phases cannot be separated from each other regardless of the sampled matrix for the total quantification of POPs, given that their distribution between one phase and another is continuously rebalancing. The material, in addition to being easy to handle, is easy to adapt to existing extraction techniques. Its use in all the above techniques has led to a

saving of time and solvents. Among the various advantages of the ACF, there is precisely the non-specificity of adsorption which led to perform some further tests to define the future possible uses of the ACF-F-2000.

On the real samples of ambient air collected on Mount Terminillo and snow collected both on Mount Terminillo Svalbard that it was possible to carry out the study of Uknown compounds, through the use of a plug-in of the used GC-Orbitrap instrument software.

The research carried out on the two matrices considered in this doctoral work highlights the presence of some common classes that have a certain relevance also at a toxicological level: phthalates, flame retardants, some combustion products, UV shielding, pesticides, personal care. To what has already been listed above detergents, adhesives and additives for paints are also added, all classes of compounds that the ACF-F-2000 was able to adsorb and desorb both in air and in water.

The next step will be to undertake validation studies to understand whether the adsorption and desorption of these classes of substances are quantitative and reproducible. In all cases, this represents only a preliminary screening since the use of ad hoc Standards is required to carry out the study of Unknown compounds.

Table 30 Main objectives achieved and future perspective.

	Air	**Water**	**Snow**
Compounds			
PCDD/Fs	Indoor and ambient air sampling up to 7 days ISO 1600 13 and 14 EPA TO 4A and 9A	ACF passive sampler for samples of 24 L EPA 1613B	SPE-ACF: Samples up to 17 L EPA 1613B *In matrix*
PCBs	Indoor and ambient air sampling up to 7 days ISO 1600 13 and 14 EPA TO 4A and 9A	ACF passive sampler for samples of 24 L EPA 1668B	SPE-ACF: Samples up to 17 L EPA 1668B *In matrix*

HCB and PeCB	Indoor and ambient air sampling up to 24 h EPA TO 4A		SPE-ACF: Samples up to 17 L EPA 1699 *In matrix*
α-HCH, γ-HCH, p,p'-DDE, o,p-DDT and HCB	Ambient Air samples up to 24 Through ^{13}C Standard quantified on PCBs *In matrix*		SPE-ACF: Samples up to 15 L EPA 1699
Unknown	Plasticizers, UV screens in sunscreens, flame retardants, combustion products, pesticides, personal care, drugs, detergents, adhesives and additives for paints. Development of a method for studying the Unknowns		

Sampling	Efficient in adsorbing both the Vapor and Particulate phase without Breakthrough. Replacement of the current double QFF + PUF system	Passive adsorbent sampler	Development of a sampling method
Extraction	Soxhlet extraction of ACF-F-2000	Snow can be considered as water once it has melted. 1) Development of 2 extraction methods: - passive adsorbent - SPE: specific designed sandwich arrangement QFF / ACF-F-2000 / QFF 2) Soxhlet extraction of ACF-F-2000	

Future Perspective

- Verification of the robustness of the methods validated through inter-laboratory tests.
- Perform studies to validate the ACF-F-2000 for the classes of untargeted compounds in all matrices through Standard.
- Develop analytical methods for the defined Untargeted compound classes
- Quantify the atmosphere scavenging of snow and rain on POPs (both of the already validated compounds and of the classes of unknown compounds defined).

APPENDIX

APPENDIX A: PYROLYSIS

A.1 Oxidative stabilization

The first step of pyrolysis is oxidative stabilization that leads to the formation of a conjugated scale structure and is expressed through chemical reactions of cyclization, dehydrogenation, aromatization, oxidation and crosslinking [206]. Given the high number of reactions, this is considered a very delicate phase. During this step, many characteristics of the ACF essential for the carbonization and activation steps (the shape and strength of the fibers, porosity, carbon yield and graphite structure), are conferred. By skipping this phase, the ACF subjected to high temperatures can undergo melting, degradation and even decomposition.

In general, the chemistry of the stabilization process consists in the cyclization of the nitrile groups and in the cross-linking of the molecules of the chain in the form of –C = N-C = N. The triple bond of one nitrile group turns into a double bond and the nitrogen of the nitrile group forms a bond with the carbon of the next nitrile group. The heat treatment involved in this phase is usually performed in the range of 180-300 °C [207]. If the temperature is too high, the fiber can overheat and melt or even burn; conversely, if the temperature is too low, the reactions are slow and may result in incomplete stabilization, which reduces the properties of the fiber [206].

The most common oxidizing agent during stabilization is air: oxygen reacts with fibres through an exothermic reaction and at the same time forms groups containing oxygen such as OH, CO_2 and CO through direct oxidation [208].

The high temperature carbonization treatment can also be carried out using an inert gas in the presence of a polymer containing external oxygen groups that provides greater stability to support the treatment itself [209,210].

During this step, two reactions take place on which the chemical structure of the fiber depends. Dehydrogenation is responsible for the formation of double bonds that make the carbon chains more stable, and cyclization is responsible for the formation of rings. Several studies have shown that oxygen is an initiator for the formation of an activated center for cyclization due to the increased activation energy [6].

A.2 Carbonization

Fundamental changes in both chemical composition and physical properties can be observed at this stage. The pre-treated fibers are heated in a reducing or inert environment to be carbonized until a disordered graphite structure is obtained. Temperatures are brought up to 800-3000 °C by removing the volatile fraction and favoring the increase of the aromatic structure (Ko et al., 1993). The maximum carbonisation temperature varies depending on the precursor and the use of the finished product. During carbonization the diameter of the fiber is reduced losing about half of the weight in the form of H_2, CH_4, N_2, H_2O, CO, CO_2, NH_3 [83].

At 1000 °C fibers with a low modulus are made, while at 1500 °C the intermediate ones (type II)[211,212].

During this phase, closed and open porosities are formed, due to the removal of non-carbonaceous atoms following dehydration, dehydrogenation, rearrangement, condensation, hydrogen transfer and isomerization. Depending on the nature of the precursor, the final temperature of the pyrolysis controls the degree of carbonization, the carbon content and the size of the pores, as well as the degree of disorder of the structure. The heating rate, the final temperature and the processing time are the carbonization parameters that determine the quality and yield of the fibers.

A.3 Graphitization

It represents the process by which carbonaceous structures are transformed into ordered graphite structures. Graphitization is carbonization at elevated temperatures. During this step 90% of the precursor polymers are transformed into carbonaceous structures: the carbonized fibers are treated at temperatures above 3000 °C with argon. At the end of the process, the structure increases its order, and therefore the thickness is reduced following the elimination of empty spaces.

A.4 Activation

It is a thermal process in which the fibers (already carbonized) are heated up to temperatures between 700 and 1200 °C, thus increasing the porosity of the material by removing the carbon atoms with greater reactivity. There are two different procedures: physical activation through hot gases, supercritical fluids or plasma and chemical activation through the incorporation of chemical reagents into the fibers [6].

A.5 Physical Activation

Physical activation uses oxidizing gases at high temperatures (500 - 1200 °C) to remove selectively carbon atoms. In this way, new pores are created, the micropores accessible to the gas are enlarged and closed pores open. The most common oxidizing gases are CO2 and water vapor, which can be used individually, in a mixture, or through an inert carrier gas [85]. Since physical activation is a heterogeneous reaction with a rate determined by the diffusion of the gas, the degree of surface activation of the fiber is usually greater than the internal one. The development of porosity is a function of the characteristics of the precursor and of the fiber at the end of the carbonization process, of its carbon structure and of the presence of catalytic impurities. Much, however, also depends on the type of gas used for activation, on its pressure, temperature and flow rate and on the activation time.

According to various studies, in fact, CO_2 tends to produce mainly microporosity without widening the pores and gives the final product a lower resistance to traction. The water vapor, on the other hand, produces adsorbents with a less homogeneous porous distribution since it mainly acts on the enlargement of the pores [79,85].

A.6 Chemical Activation

Chemical activation is considered as a solid-solid reaction between a raw material and a chemical substance (even if the latter is a liquid at room temperature). Raw materials can be spun fibers, stabilized, semi-carbonized or carbonized. The process is usually performed by impregnating or mixing the raw material with a certain chemical reagent (called activation) followed by a heat treatment (300-900 °C). In most cases, the carbonization (removal of non-carbonaceous elements) and activation (porosity formation) steps proceed simultaneously in the presence of activation reagents. After activation, it is necessary to wash carefully the fibers with ad hoc products (e.g. acid and basic solutions) to remove the activation reagents. The most commonly used chemical activation reagents in the preparation of ACF are: phosphoric acid (H_3PO_4), Zinc chloride ($ZnCl_2$), Potassium hydroxide (KOH). Chemical activation, compared to physical activation, implies lower temperatures and shorter activation times, greater carbon yield, irregular pore size and distributions, as well as specific surface group properties [213].
Also for this type of activation, the result (in terms of porosity) largely depends on the nature of the precursor and on the treatments that the fiber has undergone (yarning, stabilization, semi-carbonization or carbonization). For example, potassium is inserted between the graphene to form intercalation compounds that separate the lamellae as the heat treatment increases; once the potassium salts and carbon atoms are removed, microporous structures are created. At temperatures between 350 °C and 750 °C, the ACF treated with H3PO4 shows a decrease in the BET surface; exceeding 750 °C, the phosphorus species react with the carbon and release gaseous elemental P causing an

increase in the BET surface area. The latter seems to grow as a function of the concentrations of the activation reagents. Once the plateau is reached, concentrations that are too high, however, tend to negatively affect the properties of the fiber. In particular, phenolic fiber carbonized at 850 °C, is successfully treated with KOH at 600–900 °C, that at the maximum temperature produces an ACF with a SSA of 1893 m^2/g [82].

A.7 Pyrolysis of Phenolic Resins

During the pyrolysis of formaldehyde, a phenolic resin fiber characterized by carbon with a glass structure is formed. At temperatures above 100 °C, low molecular weight molecules and water are released, while above 500 °C CO, CH_4 and H_2 are released. Below 500 °C the cross linking of the aromatic units occurs due to the formation of aliphatic bridges. Above 500 °C, the polymer structure is destroyed in favour of hexagonal carbon planes. Above 850 °C the content of hexagonal planes increases thanks to the formation of amorphous carbon in the fibers. The precursors of Kynol fibers have several advantages: carbon yields are > 50%, they have a high carbonization rate and finally an adjustable degree of activation. Yue et al work shows the variation of the specific surface (BET) and the degree of carbonization as a function of the temperature [82]. At temperatures > 500 °C the surface open porosity is formed which increases up to 600 - 900 °C; at 1000 °C the pores collapse or remain closed.

Carbonized phenolic fibers are activated with vapour at 750–1000 °C and as times and temperatures increase, more SSA are obtained, up to 2500–3000 m^2/g [82]. One of the parameters that influences the porous distribution is the activation temperature through the balance between the gasification and diffusion speed within the porosity of the coal. In fact, through a slow gasification the activation process is uniform, and the porous distribution will be more homogeneous and of the order of a micron. However, if the

process is excessively extended, the fiber will lose its morphological and resistance characteristics [79,85].

The pore size distribution, is significantly different and strongly depends on the activation parameters [79,85,214].

APPENDIX B: GC MS/MS Methods

B.1 Air – Water GC/QQQ MS Conditions

GC/QQQ MS ThermoScientific Trace 1310, TSQ 8000 Evo

Column ThermoScientific TG-XLBMS, Length: 60 m; I.D. 0.25 mm; Film: 0.25 μm

Carrier gas H_2 @ 3 mL/min

	PeCB, HCB and PCB	**PCDD/Fs**
GC conditions Injector		
PTV mode	Splitless	Splitless
Injection Initial T °C Hold (min)	150 0.1	150 0.1
Transfer initial ramp (°C/min) Final T (°C)	14.5 320	14.5 320
Isotherm (min)	1.00	1.00
Cleaning ramp (°C/min) Final T (°C)	5.00 350	5.00 350
Isotherm (min)	5.00	5.00
Splitless time (min) Splitless flow (mL/min)	1 100.00	1 100.00
GC Temperature program		
Initial temperature (°C) and hold (min)	140 1	150 1
Initial ramp (°C/min) Final T (°C)	6.00 200	20.00 210
Isotherm (min)	5.00	0.00
Second hold (°C/min) Final T (°C)	6.00 245	3.0 275
Isotherm (min)	10.00	12.00
Third hold (°C/min) Final T (°C)	6.00 325	15.00 300
Isotherm (min)	3.00	1.00
Final hold (°C/min) Final T (°C)	NO	25.00 330
Isotherm (min)		3.00
Mass spectrometer conditions		
Source temperature °C	300	350
Transfer line °C	280	300
Electron energy (eV)	70	70
Emission current (μA)	50	50
Ionization mode	EI+	EI+
Collision gas argon (mTorr)	1.5	1.5

Table 31 Inclusion List of PCDD/s target SIM. Suffix "*" means labelled

List of Target SIM							
Name	**RT**	**Ion Polarity**	**Window**	**Mass**	**Product Mass**	**Collision Energy**	**Dwell Time Priority**
1234-TCDD *	16.68	Positive	1	331.9	268	18	Normal
1234-TCDD *	16.68	Positive	1	333.9	270	18	Normal
2378-TCDF *	17	Positive	1	315.9	252	26	Normal
2378-TCDF *	17	Positive	1	317.9	254	26	Normal
2378-TCDF	17.01	Positive	1	303.9	240.9	26	High
2378-TCDF	17.01	Positive	1	305.9	242.9	26	High
2378-TCDD *	17.48	Positive	1	331.9	268	18	Normal
2378-TCDD *	17.48	Positive	1	333.9	270	18	Normal
2378-TCDD	17.49	Positive	1	319.9	256.9	18	High
2378-TCDD	17.49	Positive	1	321.9	258.9	18	High
12378-PeCDF *	20.6	Positive	1	349.9	285.9	26	Normal
12378-PeCDF *	20.6	Positive	1	351.9	287.9	26	Normal
12378-PeCDF	20.61	Positive	1	337.9	274.9	26	High
12378-PeCDF	20.61	Positive	1	339.9	276.9	26	High
23478-PeCDF *	21.71	Positive	1	349.9	285.9	26	Normal
23478-PeCDF *	21.71	Positive	1	351.9	287.9	26	Normal
23478-PeCDF	21.72	Positive	1	337.9	274.9	26	High
23478-PeCDF	21.72	Positive	1	339.9	276.9	26	High
12378-PeCDD *	21.9	Positive	1	365.9	301.9	18	Normal
12378-PeCDD *	21.9	Positive	1	367.9	303.9	18	Normal
12378-PeCDD	21.91	Positive	1	353.9	290.9	18	High
12378-PeCDD	21.91	Positive	1	355.9	292.9	18	High
123478-HxCDF *	25.07	Positive	1	383.9	319.9	26	Normal
123478-HxCDF *	25.07	Positive	4	385.9	321.9	26	Normal
123478-HxCDF	25.08	Positive	4	371.8	308.9	26	High
123478-HxCDF	25.08	Positive	4	373.8	310.9	26	High
123678-HxCDF *	25.22	Positive	4	383.9	319.9	26	Normal
123678-HxCDF *	25.22	Positive	4	385.9	321.9	26	Normal
123678-HxCDF	25.23	Positive	4	371.8	308.9	26	High
123678-HxCDF	25.23	Positive	4	373.8	310.9	26	High
234678-HxCDF *	26.02	Positive	4	383.9	319.9	26	Normal
234678-HxCDF *	26.02	Positive	4	385.9	321.9	26	Normal
234678-HxCDF	26.03	Positive	4	371.8	308.9	26	High

234678-HxCDF	26.03	Positive	4	373.8	310.9	26	High
123478-HxCDD *	26.12	Positive	4	399.9	335.9	18	Normal
123478-HxCDD *	26.12	Positive	4	401.9	337.9	18	Normal
123478-HxCDD	26.13	Positive	4	387.8	324.9	18	High
123478-HxCDD	26.13	Positive	4	389.8	326.9	18	High
123678-HxCDD *	26.29	Positive	4	399.9	335.9	18	Normal
123678-HxCDD *	26.29	Positive	4	401.9	337.9	18	Normal
123678-HxCDD	26.3	Positive	4	387.8	324.9	18	High
123678-HxCDD	26.3	Positive	4	389.8	326.9	18	High
123789-HxCDD *	26.64	Positive	4	399.9	335.9	18	Normal
123789-HxCDD *	26.64	Positive	4	401.9	337.9	18	Normal
123789-HxCDD	26.65	Positive	4	387.8	324.9	18	High
123789-HxCDD	26.65	Positive	4	389.8	326.9	18	High
123789-HxCDF*	27.22	Positive	4	383.9	319.9	26	Normal
123789-HxCDF*	27.22	Positive	4	385.9	321.9	26	Normal
123789-HxCDF	27.24	Positive	4	371.8	308.9	26	High
123789-HxCDF	27.24	Positive	4	373.8	310.9	26	High
1234678-HpCDF*	29.6	Positive	4	419.8	355.9	26	Normal
1234678-HpCDF*	29.6	Positive	4	421.8	357.9	26	Normal
1234678-HpCDF	29.61	Positive	4	407.8	344.8	26	High
1234678-HpCDF	29.61	Positive	4	409.8	346.8	26	High
1234678-HpCDD*	31.82	Positive	4	435.8	371.9	18	Normal
1234678-HpCDD*	31.82	Positive	4	437.8	373.9	18	Normal
1234678-HpCDD	31.84	Positive	4	423.8	360.8	18	High
1234678-HpCDD	31.84	Positive	4	425.8	362.8	18	High
1234789-HpCDF*	33.13	Positive	4	419.8	355.9	26	Normal
1234789-HpCDF*	33.13	Positive	4	421.8	357.9	26	Normal
1234789-HpCDF	33.15	Positive	4	407.8	344.8	26	High
1234789-HpCDF	33.15	Positive	4	409.8	346.8	26	High
OCDD *	39.13	Positive	4	469.8	405.8	18	Normal
OCDD *	39.13	Positive	4	471.8	407.8	18	Normal
OCDD	39.14	Positive	4	457.7	394.8	18	High
OCDD	39.14	Positive	4	459.7	396.8	18	High
OCDF *	39.48	Positive	4	453.8	389.8	26	Normal
OCDF *	39.48	Positive	4	455.8	391.8	26	Normal
OCDF	39.49	Positive	4	441.8	378.8	26	High
OCDF	39.49	Positive	4	443.8	380.8	26	High

Table 32 Inclusion List of PCBs and Pesticides target SIM. Suffix "*" means labelled

List of Target SIM							
Name	**RT**	**Ion Polarity**	**Window**	**Mass**	**Product Mass**	**Collision Energy**	**DwellTimePriority**
PeCB	15	Positive	4	249.8	141.9	25	High
PeCB*	15	Positive	4	255.8	147.9	25	Normal
HCB	20	Positive	4	283.8	213.8	25	High
HCB*	20	Positive	4	289.8	219.8	25	Normal
TriPCB	22	Positive	10	256	186	25	High
TriPCB*	22	Positive	10	268	198	25	Normal
TetraPCB	29	Positive	16	289.9	220	25	High
TetraPCB	29	Positive	16	291.9	222	25	High
TetraPCB-*	29	Positive	16	301.9	231.9	25	Normal
TetraPCB-*	29	Positive	16	303.9	234	25	Normal
PentaPCB	33	Positive	16	323.9	253.9	25	High
PentaPCB	33	Positive	16	325.9	255.9	25	High
PentaPCB-*	33	Positive	16	335.9	265.9	25	Normal
PentaPCB-*	33	Positive	16	337.9	267.9	25	Normal
HexaPCB	37	Positive	19	357.8	287.9	25	High
HexaPCB	37	Positive	19	359.8	289.9	25	High
HexaPCB-*	37	Positive	19	369.9	299.9	25	Normal
HexaPCB-*	37	Positive	19	371.9	301.9	25	Normal
HeptaPCB	41	Positive	12	393.8	323.8	25	High
HeptaPCB-*	41	Positive	12	405.8	335.8	25	Normal

B.2 Snow GC-Orbitrap conditions

GC- Orbitrap MS ThermoScientific Trace 1310, Exactive GC

Column Agilent DB-XLB, Length: 60 m; I.D. 0.25mm; Film: 0.25 μm

Carrier gas He

	Pesticides and PCBs	**PCDD/Fs**
GC conditions Injector		
PTV mode	CT Splitless w/Surge	Splitless
Injection Initial T °C	200	150
Hold (min)	-	0.05
Transfer initial ramp (°C/min)	-	5.00
Final T (°C)	-	300
Isotherm (min)	-	2.00
Cleaning ramp (°C/min)	-	14.00
Final T (°C)	-	320
Isotherm (min)	-	5.00
Splitless time (min)	0.80	1
Splitless flow (mL/min)	100	50.00
Carrier mode	Programmed Flow	Constant 1.1 mL/min
Flow (mL/min)	1.200	-
Hold (min)	30.00	-
Rate (mL/min)	0.400	-
Flow (mL/min)	1.300	-
Hold (min)	30.00	-
GC Temperature program		
Initial temperature (°C)	130	150
and hold (min)	1	1
Initial ramp (°C/min)	30.00	20.00
Final T (°C)	170	210
Isotherm (min)	5.00	0.00
Second hold (°C/min)	7.00	3.0
Final T (°C)	190	275
Isotherm (min)	2.00	12.00
Third hold (°C/min)	5.00	15.00
Final T (°C)	245	300
Isotherm (min)	12.00	1.00
Final hold (°C/min)	7.00	25.00
Final T (°C)	325	330
Isotherm (min)	10.00	15.00
Mass spectrometer conditions		
Source temperature °C	300	300
Transfer line °C	280	280
Transfer line 1 and 2 °C	280	280

Electron energy (eV)	70	70
Emission current (μA)	50	50
Ionization mode	EI+	EI+
Properties of Full MS		
Resolution	60,000	60,000
AGC Target	1e6	1e6
Maximum IT	Auto	Auto
Scan Range	50 to 500 m/z	50 to 500 m/z
Properties Target SIM		
Resolution	30.000	30.000
AGC Target	5e5	5e5
Maximum IT	auto	auto
Isolation window m/z	10.0	8.5

Table 33 Inclusion List of PCDD/s target SIM. Suffix "*" means labelled

Inclusion List of Target SIM				
Mass [m/z]	**Polarity**	**Start [min]**	**End [min]**	**Comment**
305	Positive	23.00	25.00	TetraCDF
320	Positive	23.00	25.00	TetraCDF* TetraCDD
337	Positive	23.00	31.00	TetraCDD* PentaCDF
353	Positive	27.50	31.00	PentaCDF* PentaCDD
370	Positive	29.50	40.50	PentaCDD* HxCDF
387	Positive	34.80	40.50	HzCDF* HxCDD
405	Positive	36.80	44.00	HxCDD* HpCDF
421	Positive	40.00	44.00	HpCDF* HpCDD
435	Positive	41.50	43.00	HpCDD*
443	Positive	45.50	47.00	OCDF
457	Positive	45.50	47.00	OCDF* OCDD
471	Positive	45.20	47.00	OCDD*

Table 34 Inclusion List of PCBs and Pesticides target SIM. Suffix "*" means labelled

Inclusion List of Target SIM				
Mass [m/z]	**Polarity**	**Start [min]**	**End [min]**	**Comment**
185	Positive	7.00	22.00	α-HCH* γ-HCH*, α-HCH, γ-HCH
235	Positive	22.00	39.00	o,p'-DDT
248	Positive	22.00	39.00	p,p'-DDE
253	Positive	10.00	20.00	PeCB* PeCB
258	Positive	22.00	39.00	o,p'-DDE*
266	Positive	15.00	26.00	TCN
287	Positive	10.00	20.00	HCB* HCH
292	Positive	24.00	36.00	TetraCB
304	Positive	22.00	36.00	TetraCB*
326	Positive	25.00	40.00	PentaCB
338	Positive	23.00	40.00	PentaCB*
360	Positive	30.00	47.00	HexaCB
372	Positive	30.00	47.00	HexaCB*
394	Positive	36.00	47.00	HeptaCB
406	Positive	36.00	47.00	HeptaCB*

APPENDIX C: MASTER DEGREE RESULTS

C.1 Extraction

C.1.1 Elution Extraction

Table 35 Extraction test of PCBs by solvents elution. Average of the percentage recoveries (R%) and RSD% of the triplicates of N° fractions. "-" = RSD% > 90%. "L" = ^{13}C labelled compounds [1]

	10mL **HEX** **N°1**		10 mL **DCM:MeOH** **N° 3**		10 mL **DCM:MeOH** **N° 4**		10 mL **TOL:MeOH** **N° 5**		10 mL **TOL:MeOH** **N° 6**	
	R%	RSD %	R%	RSD %	R%	RSD %	R%	RSD %	R%	RSD %
PCB 81L	*< 1*	-	*< 1*	-	*< 1*	-	*46*	*20*	*4.1*	*26*
PCB 77L	*< 1*	-	*< 1*	-	*< 1*	-	*47*	*15*	*3.9*	*71*
PCB 123L	*< 1*	-	*8.5*	*70*	*2.3*	-	*26*	*10*	*< 1*	-
PCB 118L	*< 1*	-	*6.5*	*54*	*3.2*	-	*31*	*15*	*< 1*	-
PCB 114L	*< 1*	-	*15*	*48*	*5.3*	-	*17*	*15*	*< 1*	-
PCB 105L	*< 1*	-	*12*	*43*	*4.1*	-	*23*	*4*	*< 1*	-
PCB 126L	*< 1*	-	*< 1*	-	*< 1*	-	*36*	*12*	*10*	*23*
PCB 167L	*< 1*	-	*4.5*	*45*	*1.7*	-	*37*	*10*	*1.8*	*17*
PCB 156L	*< 1*	-	*10*	*50*	*3.4*	-	*33*	*3*	*< 1*	-
PCB 157L	*2.6*	-	*8.2*	*35*	*4.6*	-	*32*	*4*	*1.7*	*64*
PCB 169L	*< 1*	-	*< 1*	-	*< 1*	-	*28*	*1*	*14*	*49*
PCB 189L	*< 1*	-	*4.4*	*26*	*2.0*	-	*38*	*5*	*1.9*	-

Table 36 Extraction test of PCDD/Fs by solvents elution. Average of the percentage recoveries (R%) and RSD% of the triplicates of fractions 11 and 12 of the three tests (A. B. C). Elute with 10 mL of Tol: MeOH 90:10. "-" = RSD% >90%. "*" = ^{13}C labelled compounds [1]

	10 mL TOL:MeOH Fraction N° 5		**10 mL TOL:MeOH Fraction N° 6**	
	R %	**RSD %**	**R %**	**RSD %**
2.3.7.8-TetraCDD*	4.12	11,0	2.77	26
1.2.3.7.8-PentaCDD*	2.56	4,0	3.34	13
1.2.3.4.7.8-HexaCDD*	1.21	24,0	1.08	0.8
1.2.3.6.7.8-HexaCDD*	< 1	-	< 1	-
1.2.3.7.8.9-HexaCDD*	< 1	-	< 1	-
1.2.3.4.6.7.8-HeptaCDD*	< 1	-	1.06	39
OCDD*	< 1	-	< 1	-
2.3.7.8-Tetra CDF*	9.33	6,0	8.19	-
1.2.3.7.8-PentaCDF*	< 1	-	19.93	-
2.3.4.7.8-Penta CDF*	2.92	43,0	1.07	-
1.2.3.4.7.8-HexaCDF*	1.34	5,0	1.59	69
1.2.3.6.7.8-HexaCDF*	1.02	36,0	1.02	38
2.3.4.6.7.8-HexaCDF*	1.16	4,0	1.08	34
1.2.3.7.8.9-HexaCDF*	< 1	-	< 1	-
1.2.3.4.6.7.8-HeptaCDF*	< 1	-	< 1	-
1.2.3.4.7.8.9-HeptaCDF*	< 1	-	< 1	-
OCDF*	< 1	-	< 1	-

C.1.2 Sonication Extraction

Table 37 Average recoveries % (R%) and RSD% of the ES Solution of the three tests performed at 5 and 10 minutes of Ultrasonic bath Extraction. "*" and "L" = ^{13}C labelled compounds. Left: PCBs; Right: PCDD/Fs. [1]

PCB	ACF 1 5Minutes		ACF 2 10 Minutes	
	R%	**RSD %**	**R%**	**RSD %**
PCB 81L	*60*	*2*	*73*	*5*
PCB 77L	*64*	*26*	*73*	*3*
PCB 123L	*61*	*4*	*75*	*11*
PCB 118L	*78*	*2*	*86*	*4*
PCB 114L	*56*	*4*	*68*	*14*
PCB 105L	*81*	*3*	*79*	*0.4*
PCB 126L	*64*	*3*	*67*	*2*
PCB 167L	*81*	*9*	*92*	*4*
PCB 156L	*75*	*4*	*85*	*5*
PCB 157L	*97*	*4*	*122*	*18*
PCB 169L	*83*	*2*	*83*	*5*
PCB 189L	*75*	*5*	*80*	*1*

PCDD/F	ACF1 5 Minutes		ACF2 10 Minutes	
	R%	**RSD %**	**R%**	**RSD %**
2378-TetraCDD*	*24*	*2*	*17*	*18*
12378-PentaCDD*	*16*	*21*	*15*	*17*
123478-HexaCDD*	*8.2*	*13*	*6.9*	*26*
123678-HexaCDD*	*7.5*	*17*	*7.4*	*33*
123789-HexaCDD*	*4.0*	*63*	*3.1*	*55*
1234678-HeptaCDD*	*2.2*	*38*	*1.8*	*62*
OCDD*	*5.1*	*43*	*2.4*	*76*
2378-Tetra CDF*	*36*	*8*	*35*	*6*
12378-PentaCDF*	*15*	*9*	*13*	*11*
23478-Penta CDF*	*22*	*7*	*19*	*12*
123478-HexaCDF*	*9.0*	*9*	*9.3*	*15*
123678-HexaCDF*	*9.4*	*14*	*6.7*	*25*
234678-HexaCDF*	*6.9*	*20*	*5.9*	*24*
123789-HexaCDF*	*3.0*	*71*	*3.0*	*66*
1234678-HeptaCDF*	*4.6*	*50*	*3.9*	*22*
1234789-HeptaCDF*	*7.2*	*42*	*3.4*	*50*
OCDF*	*4.6*	*37*	*2.2*	*85*

C.1.3 Soxhlet Extraction

Table 38 Average recoveries % (R%) and RSD% of the ES Solution of the triplicate tests. Extraction with Toluene for 36h by Soxhlet. "*" and "L" = ^{13}C labelled compounds. Left: PCBs; Right: PCDD/Fs [1].

PCB	R%	RSD%	**PCDD/F**	R%	RSD%
PCB 81L	99	6	2378-Tetra CDD *	83	5
PCB 77L	106	1	12378-PentaCDD *	87	8
PCB 123L	89	12	123478-HexaCDD *	100	5
PCB 118L	90	12	123678-HexaCDD *	103	2
PCB 14L	88	13	1234678-HeptaCDD *	99	1
PCB 105L	84	10	OCDD *	99	1.5
PCB 126L	95	18	2378-TetraCDF *	78	12
PCB 167L	96	1.3	23478-PentaCDF *	80	8
PCB 156L	95	10	123478-HexaCDF *	98	1
PCB 157L	98	8	123678-HexaCDF *	99	3
PCB 169L	89	13	234678-HexaCDF *	102	2
PCB 189L	74	3	1234678-HeptaCDF*	98	3
			OCDF *	97	4

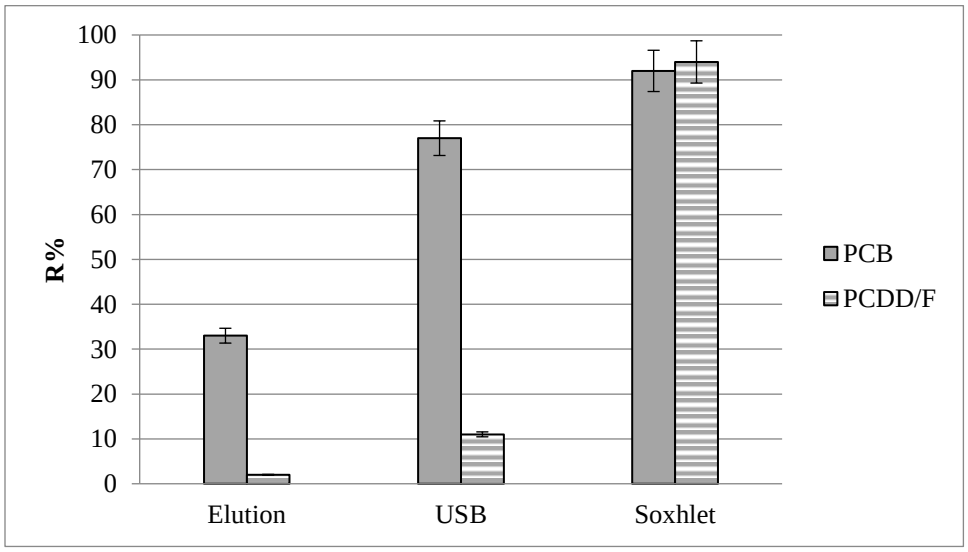
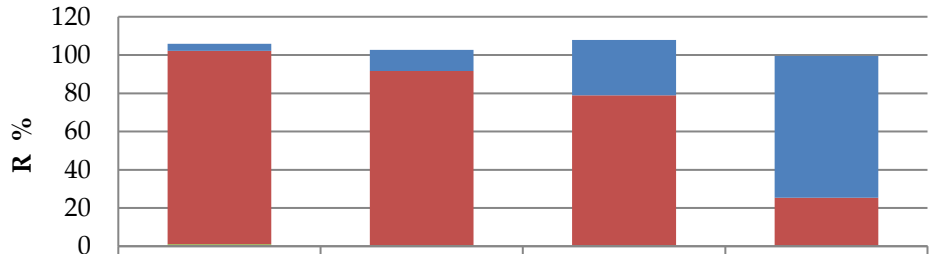


Figure 36 Comparison between the total percentage recoveries (R%) and STD of PCBs and PCDD/Fs obtained from the three extraction techniques used [1].

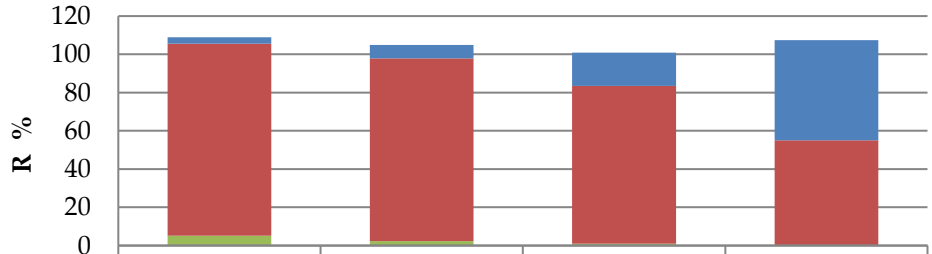
C.2 Sampling – Evaluation of ACF efficiency as PUF

Samplings were performed at the CNR area of Montelibretti (Rome) by arranging the ACF-F-2000 filters between a Quartz Fiber Filter and the PUF (figure 17) at different sampling times (24h, 72h, 7 days). Before each test, the QFF was labelled with a known quantity of isotopically labelled Standards of PCDD/Fs and PCBs. The distribution of the classes on the adsorbents is shown below, and it is expressed as average of R%s on the triplicate of the total classes.



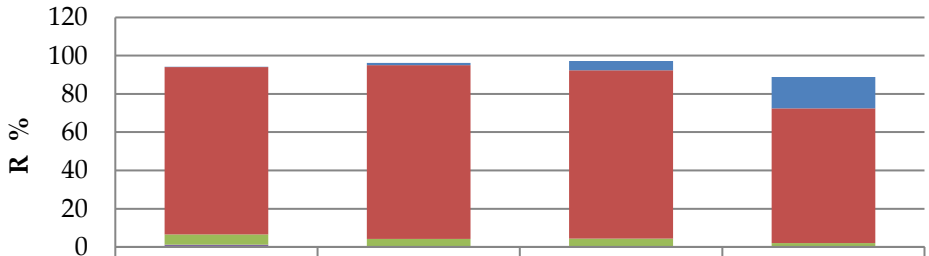
	TetraCB	PentaCB	HexaCB	HeptaCB
QFF	4	11	29	74
ACF-F-2000 A	101	91	79	25
ACF-F-2000 B	1,1	0,60	0,47	0,10
PUF	0,0	0,0	0,0	0,0

A



	TetraCB	PentaCB	HexaCB	HeptaCB
QFF	3,3	7,1	17	52
ACF-F-2000 A	101	96	82	55
ACF-F-2000 B	5,0	2,1	0,93	0,007
PUF	0,11	0,21	0,08	0,00

B

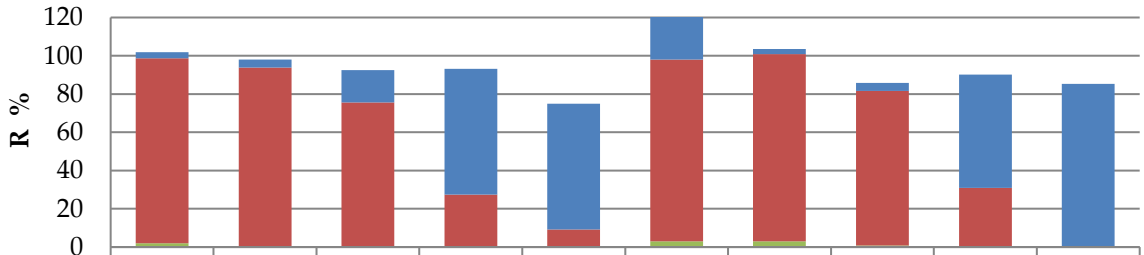


	TetraCB	PentaCB	HexaCB	HeptaCB
QFF	0,11	1,2	4,8	16
ACF-F-2000 A	88	91	88	70
ACF-F-2000 B	5,3	4,1	4,2	2,1
PUF	1,2	0,087	0,17	0,011

C

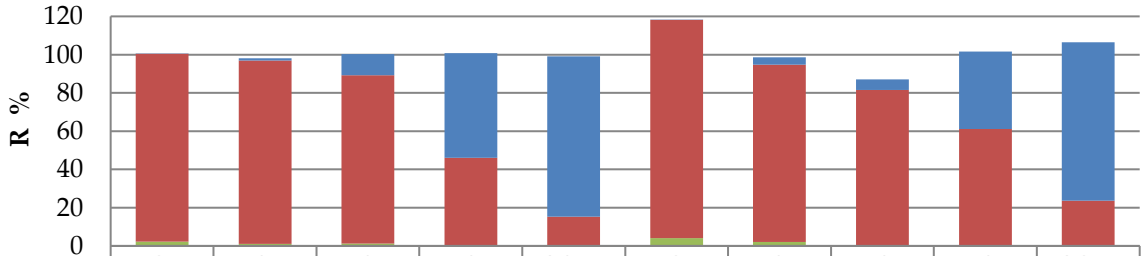
Figure 37 Average of R%s and RSD% of the SS Solution from the different adsorbents of triplicate test at different sampling extension time. 24 h Sampling; 72h Sampling; 168 h Sampling. "*" = ^{13}C labelled compounds [1].

A



	TeCDD	PeCDD	HxCDD	HpCDD	OCDD	TeCDF	PeCDF	HxCDF	HpCDF	OCDF
QFF	3,07	4,25	16,86	65,75	65,75	65,75	2,75	4,29	59,155	85,17
ACF-F-2000 A	97	94	76	27	9,2	95	98	81	31	0,049
ACF-F-2000 B	2,03	0,010	0,010	0,010	0,010	3,0	3,0	0,78	0,010	0,010
PUF	0,010	0,010	0,010	0,010	0,010	0,010	0,010	0,010	0,010	0,010

B



	TeCDD	PeCDD	HxCDD	HpCDD	OCDD	TeCDF	PeCDF	HxCDF	HpCDF	OCDF
QFF	0,010	1,12	11,07	54,58	83,77	0,010	3,93	5,6675	40,465	82,77
ACF-F-2000 A	98,25	95,9	88,0633333	46,12	15,36	114,1	92,655	81,455	61,175	23,7
ACF-F-2000 B	2,19	1,05	1,17333333	0,010	0,010	4	2,02	0,010	0,010	0,010
PUF	0,010	0,010	0,010	0,010	0,010	0,010	0,010	0,010	0,010	0,010

C

	TeCDD	PeCDD	HxCDD	HpCDD	OCDD	TeCDF	PeCDF	HxCDF	HpCDF	OCDF
QFF	0,010	0,010	2,1	39,0	70,1	0,010	0,010	3,0	31,8	73,2
ACF-F-2000 A	94,2	91,5	97,8	66,2	33,2	102,8	98,6	90,4	75,7	40,4
ACF-F-2000 B	4,1	2,1	0,7	0,010	0,010	7,0	4,6	2,9	0,9	0,010
PUF	0,010	0,010	0,010	0,010	0,010	0,010	0,010	0,010	0,010	0,010

Figure 38 Average R%s and RSD% of the SS Solution for the different adsorbents in triplicate test at different extended sampling time: 24 h; 72h and 168 h. "*" = ^{13}C labelled compounds. Values < LOD are = 0.010 [1].

APPENDIX D: EVALUATION OF EXTRACTION METHODS

D.1 Accelerated Solvent Extraction - ASE

Table 39 PCDD/Fs ASE Test. Average of Recoveries % and RSD% of the ES Solution of triplicates test. (R%). "-" = RSD% >90%. "*" = ^{13}C labelled compounds.

	QFF		ACF-F-2000		ACF-C-800		ACF-C-2000	
	R%	RSD%	R%	RSD%	R%	RSD%	R%	RSD%
2,3,7,8-Tetra CDD*	126	11	106	1.4	68	3.7	78	3.7
1,2,3,7,8-PentaCDD*	124	8.1	99	1.8	79	10	65	3.1
1,2,3,4,7,8-HexaCDD*	133	7.2	90	6.3	94	10	50	11
1,2,3,6,7,8-HexaCDD*	121	11	108	6.7	111	7.4	109	12
1,2,3,4,6,7,8-HeptaCDD*	119	3.3	49	2.6	83	8.1	27	3.9
OctaCDD*	136	3.2	19	12	88	10	16	12
2,3,7,8-TetraCDF*	118	6.5	108	9.9	73	10	81	2.8
2,3,4,7,8-PentaCDF*	120	4.3	106	10	85	4.3	71	7.1
1,2,3,4,7,8-HexaCDF*	126	2.7	88	13	95	2.9	48	3.4
1,2,3,6,7,8-HexaCDF*	122	4.4	90	5.2	79	6.7	45	9.6
2,3,4,6,7,8-HexaCDF*	119	11	82	10	88	2.5	48	4.1
1,2,3,4,6,7,8-HeptaCDF*	116	11	55	10	88	8.8	27	2.8
OctaCDF*	185	4.0	33	16	119	15	26	14

Table 40 PCBs ASE Test Average Recoveries % and RSD% of the ES Solution of triplicates test. (R%). "-" = RSD% >90%. "L" = ^{13}C labelled compounds.

	QFF		ACF-F-2000		ACF-C-800		ACF-C-2000	
	R%	RSD%	R%	RSD%	R%	RSD%	R%	RSD%
81L	102	14	96	9.6	100	3.9	96	8.9
77L	101	4.1	96	2.2	98	2.6	85	1.9
123L	90	5.4	98	9.8	94	9.9	91	10
118L	93	1.0	95	10	92	4.1	92	4.4
114L	88	5.5	89	16	87	15	81	1.2
105L	94	3.5	100	9.8	100	8.2	82	9.6
126L	103	8.6	116	3.3	100	10	96	10
167L	81	7.2	93	3.1	100	11	78	1.7
156L	84	2.9	94	3.4	105	4.7	87	13
157L	91	9.7	97	9.6	104	9.9	87	3.4

	QFF		ACF-F-2000		ACF-C-800		ACF-C-2000	
	R%	RSD%	R%	RSD%	R%	RSD%	R%	RSD%
169L	95	7.5	101	8.3	104	4.2	87	7.1
189L	88	6.0	80	6.3	88	12	88	2.3

Table 41 PAHs ASE Test. Average Recoveries % and RSD% of the ES Solution of triplicates test. (R%). "-" = RSD% >90%.

	QFF		ACF-F-2000		ACF-C-800		ACF-C-2000	
	R%	RSD%	R%	RSD%	R%	RSD%	R%	RSD%
PhenanthreneD10	93	1.8	88	6.2	47	8.8	63	22
FluorantheneD10	79	10.0	31	9.1	16	7.3	37	8.3
Benzo(a)anthraceneD12	58	11.2	25	13	12	18	28	6.0
ChryseneD12	102	2.9	11	18	13	17	15	6.2
Benzo(b)fluorantheneD12	110	6.5	11	-	11	25	14	12
Benzo(k)fluorantheneD12	102	6.1	4.8	-	8.8	22	11	15
Benzo(a)pyreneD12	92	6.7	< 1	-	6.3	14	3.4	12
Indeno(1,2,3,c,d)pyreneD12	56	10.8	< 1	-	3.7	11	3.0	34
Dibenzo(a,h)anthraceneD14	73	3.0	< 1	-	8.6	31	2.5	25
Benzo(g,h,i)peryleneD12	53	9.9	29	-	34	15	33	31
Dibenzo(ai)pyrene-D14	45	4.7	< 1	-	20	37	5.4	17

D.2 Microwave

Table 42 PCDD/Fs Microwave Test. Average Recoveries % and RSD% of the ES Solution of triplicates test.(R%). "-" = RSD% >90%. "*" = ^{13}C labelled compounds.

	QFF		ACF-F-2000		ACF-C-800		ACF-C-2000	
	R%	RSD%	R%	RSD%	R%	RSD%	R%	RSD%
2,3,7,8-TetraCDD*	126	6.0	35	6.1	37	7.4	39	9.8
1,2,3,7,8-PentaCDD*	124	13.1	38	6.9	57	4.1	53	36.9
1,2,3,4,7,8-HexaCDD*	133	8.2	27	3.5	88	3.8	100	11.4
1,2,3,6,7,8-HexaCDD*	121	9.3	130	4.9	90	6.3	68	10.3
1,2,3,4,6,7,8-HeptaCDD*	119	6.4	12	2.4	65	4.0	87	5.3
OctaCDD*	136	2.1	5	-	80	6.5	59	5.7
2,3,7,8-TetraCDF*	118	12.1	46	3.6	49	8.3	52	6.7
2,3,4,7,8-PentaCDF*	64	1.7	43	4.0	54	10.6	61	4.6
1,2,3,4,7,8-HexaCDF*	120	7.0	26	15.1	74	6.8	103	5.9
1,2,3,6,7,8-HexaCDF*	126	5.4	10	5.2	24	11.6	42	3.2
2,3,4,6,7,8-HexaCDF*	122	7.2	19	1.7	67	6.6	88	11.2
1,2,3,4,6,7,8-HeptaCDF*	119	6.1	11	11.0	81	2.1	89	4.8
OctaCDF*	58	11.1	8	-	77	7.9	51	14.5

Table 43 PCBs Microwave Test. Average of Recoveries % and RSD% of the ES Solution of triplicates test. (R%). "-" = RSD% >90%. "L" = ^{13}C labelled compounds.

	QFF		ACF-F-2000		ACF-C-800		ACF-C-2000	
	R%	**RSD %**	**R%**	**RSD %**	**R%**	**RSD %**	**R%**	**RSD %**
81L	101	8.2	78	1.8	93	1.4	50	6.2
77L	65	4.5	103	7.1	102	10.3	46	1.7
123L	64	13.0	97	3.4	95	5.8	53	6.1
118L	65	3.6	91	9.6	90	3.3	54	2.3
114L	64	2.7	98	4.1	91	8.9	54	3.7
105L	74	2.6	95	7.4	97	5.0	52	15.1
126L	68	3.6	71	2.8	69	6.5	35	5.2
167L	87	13.1	91	17.8	75	7.5	47	1.7
156L	89	14.9	86	14.2	84	17.6	53	11.0
157L	88	35.3	83	13.5	75	10.7	46	1.7
169L	76	20.3	64	29.7	58	38.1	33	11.5
189L	106	32.7	104	12.7	106	18.1	56	3.7

Table 44 PAHs Microwave Test. Average Recoveries % and RSD% of the ES Solution of triplicates test. (R%). "-" = RSD% > 90%.

	QFF		ACF-F-2000		ACF-C-800		ACF-C-2000	
	R %	**RSD%**	**R%**	**RSD%**	**R%**	**RSD%**	**R%**	**RSD%**
PhenanthreneD10	98	6,1	1,1	-	1,2	-	<1	-
FluoranthèneD10	67	4,8	< 1	-	<1	-	<1	-
Benzo(a)anthraceneD12	87	8,3	1,6	-	2,5	-	2,5	-
ChryseneD12	81	8,6	3,4	-	5,4	-	1,8	-
Benzo(b)fluorantheneD12	79	10,6	1,1	-	<1	-	1,6	-
Benzo(k)fluorantheneD12	83	7,2	1,2	-	<1	-	1,6	-
Benzo(a)pyreneD12	78	4,9	<1	-	1,0	-	1,1	-
Indeno(1,2,3,c,d)pyrene D12	68	6,1	<1	-	3	-	2,2	-
Dibenzo(a,h)anthracene D14	75	9,8	4,3	-	28	-	18	-
Benzo(g,h,i)peryleneD12	71	5,0	<1	-	<1	-	<1	-
Dibenzo(ai)pyrene-D14	65	3,9	1	-	18	-	19	36,1

APPENDIX E: VALIDATION OF PESTICIDE ANALYSIS IN AIR

E.1 Evaluation of PeCB and HCB extraction

Table 45 Average recovery percentage (R%) and RSD% of ^{13}C-Pentachlorobenzene and ^{13}C-Hexachlorobenzene of triplicates performed for each extraction technique applied to ACF-F-2000. "-" = RSD% > 90%. "*" = ^{13}C labelled compounds.

	PeCB*		HCB*	
	R%	**RSD%**	**R%**	**RSD%**
Soxhlet	51	8.2	86	3.2
USB	< 1	-	74	7.3
Elution	8	7.3	24	6.5
ASE	11	-	54	10.1

E.2 Evaluation of the breakthrough

Table 46 Average R%s and RSD% of the SS Solution from the different adsorbents of triplicate test at different extended sampling time. 24 h; 72h and 168 h. "*" = ^{13}C labelled compounds.

	PeCB*		HCB*	
	R%	**RSD%**	**R%**	**RSD%**
24 h				
QFF	< 1	-	1.9	12
ACF A	63	8.9	85	8.8
ACF B	4.6	12	3.8	-
PUF	< 1	-	<1	-
72h				
QFF	< 1	-	<1	-
ACF A	38	21	61	26
ACF B	11	47	23	46
PUF	<1	-	<1	-
168h				
QFF	<1	-	<1	-
ACF A	19	72	38	60
ACF B	20	26	28	15
PUF	5.2	32	4.6	46

APPENDIX F: VALIDATION OF PCDD/Fs AND PCBs ANALYSIS IN WATER

Table 47 Average percentage recoveries (R%) and RSD% of ^{13}C-PCDD/Fs compounds EPA 1613-LCS of four replicates. Liquid Liquid extraction vs ACF-F-2000 passive adsorbent.

	ACF-F-2000		LLE	
	R%	RSD%	R%	RSD%
2,3,7,8-TetraCDD*	55	5.2	36	9.9
2,3,7,8-TetraCDF*	44	4.3	26	9.6
1,2,3,7,8-PentaCDD*	74	1.1	66	8.6
1,2,3,7,8-PentaCDF*	66	3.3	63	9.6
2,3,4,7,8-PentaCDF*	80	6.5	82	10
1,2,3,4,7,8-HexaCDD*	96	5.0	91	12
1,2,3,6,7,8-HexaCDD*	102	1.7	103	8.4
1,2,3,4,7,8-HexaCDF *	98	1.9	102	5.9
1,2,3,6,7,8-HexaCDF*	85	4.6	80	6.4
2,3,4,6,7,8-HexaCDF*	101	3.6	113	13
1,2,3,7,8,9-HexaCDF*	101	3.9	117	7.3
1,2,3,4,6,7,8-HeptaCDD*	118	2.2	98	10
1,2,3,4,6,7,8-HeptaCDF*	110	5.1	117	11
1,2,3,4,7,8,9-HeptaCDF*	124	6.0	113	12
OCDD*	84	1.3	88	9.0

Table 48 Average percentage recoveries (R%) and RSD% of ^{13}C-PCBs compound EPA 1613-LCS of four replicates. Liquid Liquid extraction vs ACF-F-2000 passive adsorbent.

	ACF-F-2000		LLE	
	R%	RSD%	R%	RSD%
81L	63	5.2	78	5.0
77L	72	4.0	74	7.5
123L	71	4.2	94	2.4
118L	81	3.7	96	9.6
114L	99	0.13	116	5.7
105L	82	2.1	100	7.1
126L	98	5.0	83	13
167L	78	2.2	96	1.5
156L	81	1.6	102	2.4
157L	69	5.1	93	11
169L	80	4.0	85	2.5
189L	77	2.9	99	5.5

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