Importance of PCDD/F molecules' polarizability and steric hindrance on their adsorption onto zeolites in a standard EN1948-1 sampling device for incinerator emission monitoring

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Abstract

Currently, polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/F) monitoring at stationary sources uses short- and long-term sampling methods compliant with EN1948 standard. The XAD-2 resin is exposed to gas stream for 3-4 weeks (long term), and subsequently analysed in an accredited laboratory for 2 weeks. With the aim of developing an on-line mass spectrometer device using adsorption onto a set of different zeolites as specific adsorbents prior to mass analysis, the paper proposes to firstly test zeolites within the methods compliant with EN1948 standard.

In addition to the non-specific external surface adsorption, zeolites possess micropores for adsorbing molecules specifically. Zeolites allowing selective adsorption of only tetra- and penta-chlorinated toxic congeners (TeCDD/F, PeCDD/F) were exposed to the gas flow of a household waste incinerator. As the extraction method of EN 1948 standard does not allow us to discern the two types of adsorption, the adsorbents have been tested at a sampling point located before the last filter. With high congener concentrations, it is expected that the dynamic adsorption properties of the zeolites can be deduced from the breakthrough of some congeners.

The electronic interactions between zeolite surface area and PCDD/F involve the polarizability of the molecules. Thanks to the congener breakthrough comparing two zeolite structure types, it has been deduced that toxic TeCDD/F and PeCDD/F were adsorbed in the micropores of FAU-NaX zeolite due to steric compatibility of these congeners. Moreover, the partition of congeners between the condensate and gas phase was elucidated by considering the polarizability of PCDD/F molecules.

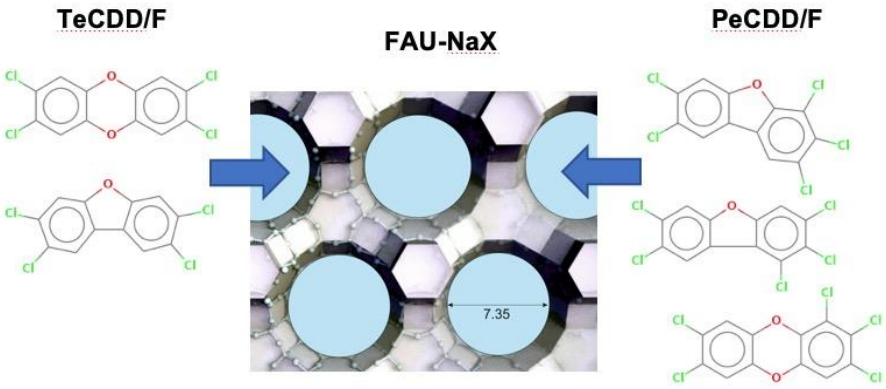
Keywords

Zeolite; POP; PCDD/F; selective adsorbent; emission monitoring; waste incinerator

Highlights

- Zeolites are non-conventional adsorbent for PCDD/F adsorption
- Zeolites are exposed to incinerator gas flux
- PCDD/F polarizability governs congener partition between condensates and gas phase
- Electronic interactions between FAU-NaX and PCDD/F involve molecule polarizability
- TeCDD/F and PeCDD/F congeners are adsorbed in FAU-NaX micropores

Graphical Abstract



1 Introduction

The term "Dioxins" is often used to refer to the family of structurally and chemically related polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzo furans (PCDF). Only 17 of these (with chlorine atoms in positions 2, 3, 7 and 8) have a significant toxicity with a toxic equivalency factor (I-TEF) assigned by WHO and NATO, 2,3,7,8-TeCDD being the most toxic [1,2].

Waste incineration results in dioxin formation with large gas volumes released permanently. Stringent laws have been promulgated to greatly reduce dioxin emission at stationary sources because dioxins are widely distributed throughout the environment, persistent and bio-accumulated. The European Union legislation has set a limit value (ELV) of 0.1 ng/m^3 I-TEQ for dioxin emission from

64 waste incineration plants [3]. In Europe, monitoring of dioxin emission at stationary sources is in
65 accordance to EN 1948 standard [4–6].

66 In 2000, Belgium was the first country worldwide which demanded the long-term sampling of
67 dioxins in municipal waste incinerators. Then, long-term sampling has been gradually implemented.
68 Since 2010, France has been the first country where a nation-wide legislation requires its use [7]. The
69 gas stream is isokinetically sampled for 4-6 week period with particle- and gas-phases collected on
70 XAD-2 resin [8–10]. This single solid support is then analysed in laboratory according to the parts 2
71 and 3 of EN 1948 standard. The European Committee for Standardization (CEN) is currently
72 finalising a standard for long-term sampling of PCDD/Fs and dioxin-like PCBs [11]. However, long-
73 term sampling involves a time-integrated exposure of the adsorbent, and then off-line analysis.
74 Consequently, short-term variation of information may be lost.

75 A continuous monitoring providing indicative dioxin levels every 8-24 hours would be relevant in
76 term of emission transparency and incineration process control, in addition to the standard method
77 with accurate levels of detection as reference. For instance, with the aim of designing an on-line
78 device, the use of a set of adsorbents (such as zeolites) having different adsorption specificities
79 according to toxicity of dioxin congeners in a sample enrichment device can increase the sensitivity
80 level of detection of a field mass spectrometer.

81 Zeolites are adsorbents at molecular scale with large surface area and possible selective
82 adsorption onto micropores [12–14]. Few papers relate the use of zeolite in remediation of dioxins
83 from incineration gases [15–18]. Jäger *et al*. demonstrated a selective adsorption of dioxins onto
84 zeolites, with dioxins thermally desorbed from incineration ashes [19]. Adsorption properties of
85 dioxins onto zeolites and energy of desorption were determined by temperature programmed
86 desorption (TPD) due to dioxin low volatility [20–24].

87 Authors of this study have proposed to determine the adsorption properties of zeolites with
88 solutions of dioxins in isooctane. Adsorption isotherms showed that 2,3-DCDD has been adsorbed in
89 the micropores of FAU-NaX zeolite with very high affinity, regarding the adsorbent micropore size
90 and dynamic molecule size, while the adsorption of 1,2,3,4-TeCDD has been limited to the external

surface [25]. Furthermore, the authors explained that the nature of the charge compensating cations could have an influence on the congener adsorption in the micropores [26]. The exchange of Na^+ cation by trivalent cation La^{3+} in FAU-type X-zeolites has led to the adsorption of 1,2,3,4 TeCDD [27,28].

Besides the size compatibility, the electronic interactions play a key role in adsorption. The toxic PCDD/F congeners possess quadrupolar moments and large polarisabilities inducing electrostatic and dispersion interactions responsible of the interactions with the aryl hydrocarbon receptor (AhR) with regards to their specificity of interaction and toxicity [29–34]. Same electronic interactions should be involved for toxic PCDD/F congeners adsorption onto zeolites. Dispersion interactions also occur for the adsorption of polarisable solvents [35]. Isooctane adsorption onto FAU-NaX zeolite has been demonstrated by authors of this study using Thermal Gravimetric Analysis and DNP RMN Spectroscopy with the addition of a polarization-transfer agent [28]. Hence the micropore accessibility can be greatly enhanced using PCDD/F in the presence of isooctane.

Thermal-desorption is a relative simple method to recover compounds from adsorbents of a sample enrichment device, for instance. Zeolites have good mechanical and thermal stabilities, so that they can be heated at high temperatures to ensure that the adsorbent is free of contamination prior to sampling and to recover the greater number of adsorbed molecules for subsequent identification and quantification. However, in the case of sampling at incineration process, a degradation mainly by dechlorination and dioxin formation could occur at temperatures higher than 300 °C due to the presence of ashes and other compounds in the adsorbents [36]. As a consequence, false levels of dioxin could be detected.

Recently, in a laboratory-scale experiment, authors of this study have shown a low effectiveness of the gas-phase dioxin adsorption onto faujasite beads at room temperature. It was mainly due to the large bead diameter reducing micropore accessibility. A new recipe to synthesise beads with smaller diameters has been then proposed by authors of this study. These beads have mechanical performances high enough for implementation in an on-line adsorption process [37]. The beads should be able to sustain the load they will be subjected to gas sampling at full-scale in an incineration process.

In this paper, two structure types of zeolite with two bead diameters have been exposed to gas fluxes of a waste-to-energy plant in a sampling device compliant with EN 1948-1 standard. The sampling device has been modified so that two different adsorbents can be tested in parallel with the same gas fluxes and a breakthrough be measured. The toxic congener concentrations adsorbed by the adsorbents have then been measured by a certified laboratory using the methods of EN 1948 standard. The adsorption properties of the zeolites have been then determined taking into account the electronic interactions between the materials and toxic PCDD/F congeners.

2 Materials and Methods

2.1 Preparation of zeolite beads

Powder of FAU-NaX (octahedron micro-crystal of 2-3 μm) and of *BEA-H (nano-crystal agglomerate of 2 μm) have been purchased from Sigma-Aldrich® and Clariant®, respectively. *BEA-H zeolite has been partly ion-exchanged with Na cations leading to *BEA-Na.

The beads have been obtained by shearing the zeolite powder in the presence of water and sodium metasilicate as inorganic binder (5 wt %). The two zeolite structures have been used for gas sampling in various bead sizes: FAU-NaX beads of 0.5-0.8 mm in diameters, FAU-NaX beads of 0.25-0.4 mm in diameters and *BEA-Na beads of 0.25-0.4 mm in diameters.

2.2 Sampling device

The sampling device refers to EN 1948-1 standard [4] using the filter/condenser method, with flow division and solid adsorbent downstream of the condenser. This sampling method ensures a constant flow in adsorbent even if the flow of the main line varies. The base of the device is a continuously dust sampling train from a gas duct under isokinetic conditions (from Cleanair Europe, La Penne-sur-Huveaune, France). A special glassware set (from La Verrerie Villeurbannaise, Villeurbanne, France) completes the dust sampling train, comprising XAD-2 resin cartridge, condenser, condensate container and different connectors and lines.

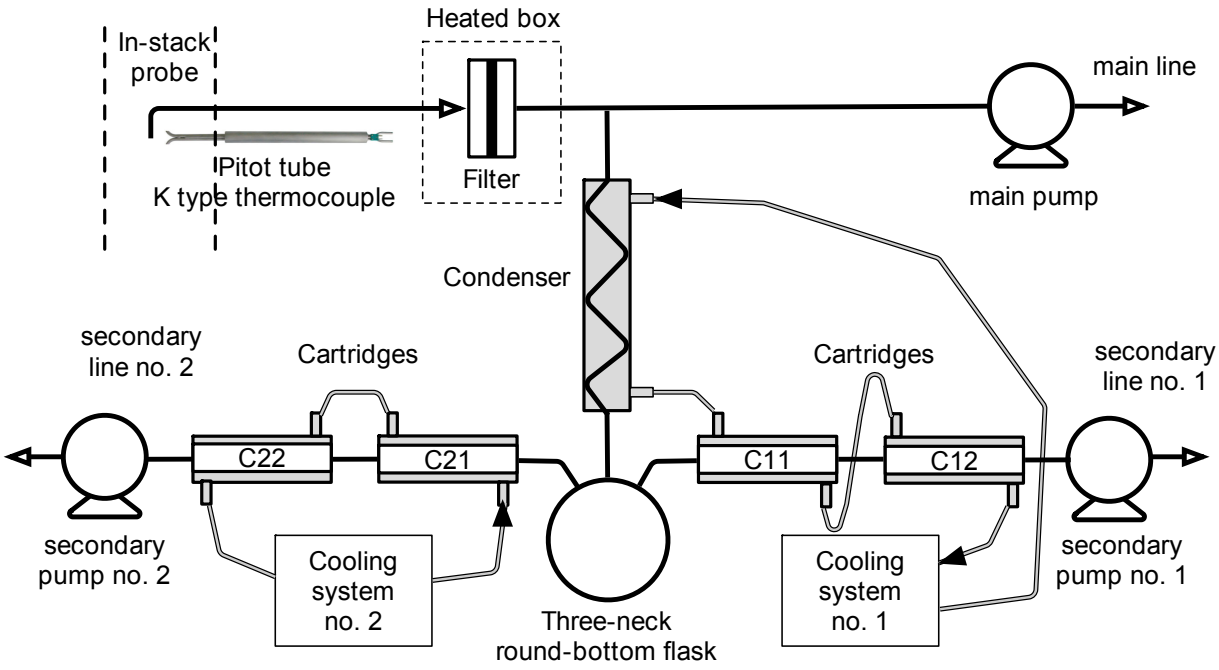


Fig. 1: Sampling train and adaptation of the glassware set for testing adsorption with selective materials according to EN 1948-1 standard. The cartridges C11 and C21 are filled with the testing adsorbents; the cartridges C12 and C22, or backup cartridges, are filled with XAD-2 resin.

The sampling probe is heated and equipped with a Pitot tube and K type thermocouples (Fig. 1). Particles are collected on a filtration media placed in a heated box. The sample flow rate is adjusted by means of the pumps in the main and secondary lines. The glassware set is modified for testing of zeolite adsorption properties. A second gas-sampling line with adsorbent cartridge is added in parallel with the first one, requiring a three-neck balloon for recovering condensate. It is then possible to compare adsorption properties of two different materials with the same incineration gas flux. Furthermore, each line has two adsorbent cartridges in series: the first cartridge is filled with the testing adsorbent, while the second, filled with XAD-2 resin, is the backup cartridge for PCDD/F breakthrough determination. In each line after the cartridges, a secondary pump (denoted as secondary pumps no. 1 and 2) aspirates the gas through a drying line filled with silica gel and a counter measures the volumetric flow rate of dry gas. The first cooling system supplies the condenser and the jackets of the both cartridges of the secondary line no. 1. An additional cooling system supplies the both cartridges of the secondary line no. 2. The temperatures of the cooling devices have been adjusted so that the temperatures of the first cartridges of lines no. 1 and 2 are identical. However, a discrepancy has been observed: higher temperature has been measured in cartridge C11 than in cartridge C21.

2.3 Sampling campaign

Sampling campaign has been performed in the same waste-to-energy plant for 3 days. Therefore, the samplings are denoted as: D1, D2 and D3. SUEZ Environnement (France), as delegated owner of the waste-to-energy plant, has coordinated the campaigns. The waste-to-energy plant is equipped with one line including: electrostatic precipitator (ESP), fabric filter (FF) and DeNOx catalyst (for instance, see ref. [38]). Typically, the incinerator gas fluxes are sampled in a long straight vertical section of tubing (in the stack). In this study, the sampling point has been chosen between the ESP and FF in order to reach high concentrations of congeners. This is an unusual place with a turbulent stream flow. As a consequence, measurement is not representative of the particle phase and of dioxin concentrations emitted by incinerator, even with isokinetic sampling [39]. However, with high concentrations of PCDD/F congeners, the breakthrough of certain congeners must occur with the adsorbents.

The glass cartridges C11 and C21 have been filled with 30 g of beads of zeolites as follow: for D1 sampling, with XAD2 and with FAU-NaX beads of 0.5-0.8 mm diameters; for D2 sampling, with FAU-NaX beads of 0.25-0.4 mm diameters and with FAU-NaX beads of 0.5-0.8 mm diameters; and for D3 sampling, with FAU-NaX beads of 0.25-0.4 mm diameters and with *BEA-Na beads of 0.25-0.4 mm, respectively. After packing, the zeolites have been conditioned: they have been heated to 300 °C under a nitrogen stream and kept at these conditions for about 24 h. The backup cartridges C12 and C22 have been filled with 30 g of XAD-2 resin. XAD-2 has a particle size of 20-60 mesh (*i.e.* 0.25-0.84 mm) with an apparent porosity between the grains (90 Å mean pore size). Then, the adsorbents have been spiked with PCDD/F standards (a mixture of ^{13}C-labelled toxic PCDD/F in toluene) before exposition to the incineration gas flux.

All of the samples have been collected for 6 hours. The volumetric flow rates have been maintained constant during sampling and compliant with the isokinetic conditions required by EN 1948 standard. The sampled volumes have been measured 3-3.1 m^3 in the main line and 2-2.7 m^3 in the two secondary lines with 13-15 % moisture, depending on the sampling day. The inlet temperature of the bulk gases at the probe has be measured at almost 198 °C, while in the filter box the temperature at 110 °C. The ice water has circulated at 2-5 °C in the jackets of the condenser and cartridges.

2.4 Concentration measurement

The glassware set, condensates and adsorbent supports have been then analysed in CARSO laboratory according to parts 2 and 3 of EN 1948 standard. A solution of ^{13}C-labelled PCDD/F has been injected on adsorbents before extraction. The toxic PCDD/F have been Soxhlet extracted with toluene from adsorbents. The extract has been purified on silica/modified silica and alumina columns. Quantitative analysis has been performed by isotopic dilution on high-resolution gas chromatograph/mass spectrometer Autospec ULTIMA from Waters [40].

The PCDD/F concentration (ng/Nm^3) has been calculated from the PCDD/F quantity (ng) measured in the filter, condenser and cartridge divided by the sampled volume of gas. However, we are not allowed to disclose the true values of concentrations. It is for that raison that they are expressed in α ng/m^3, keeping the same value for α to be able to make comparisons between absolute quantities adsorbed onto zeolites. $C_C(c)$ and $C_P(c)$ are the concentrations of congener c measured in the condensate and in the particulate phase, respectively. The concentration denoted as $C_G(c)$ is the concentration of congener c in the gas phase and corresponds to the sum of the concentrations measured in the four adsorbent cartridges. The total concentration of congener c is calculated from: $C_T(c) = C_P(c) + C_C(c) + C_G(c)$.

3 Results and Discussion

3.1 Testing the analytical method

The limit of detection (LOD) and limit of quantification (LOQ) have been determined as described in EN 1948-2 §3.8 and 3.9 by using the mean analytical blank plus x times the standard deviation of the analytical blank (Tab. 1). A concentration value that falls between the LOD and LOQ is assigned the value of the LOQ. A concentration value that falls below the LOD is assigned a value of zero.

The percent uncertainty of measured quantity for each toxic congener has been calculated using NF ISO 11352 standard [6].

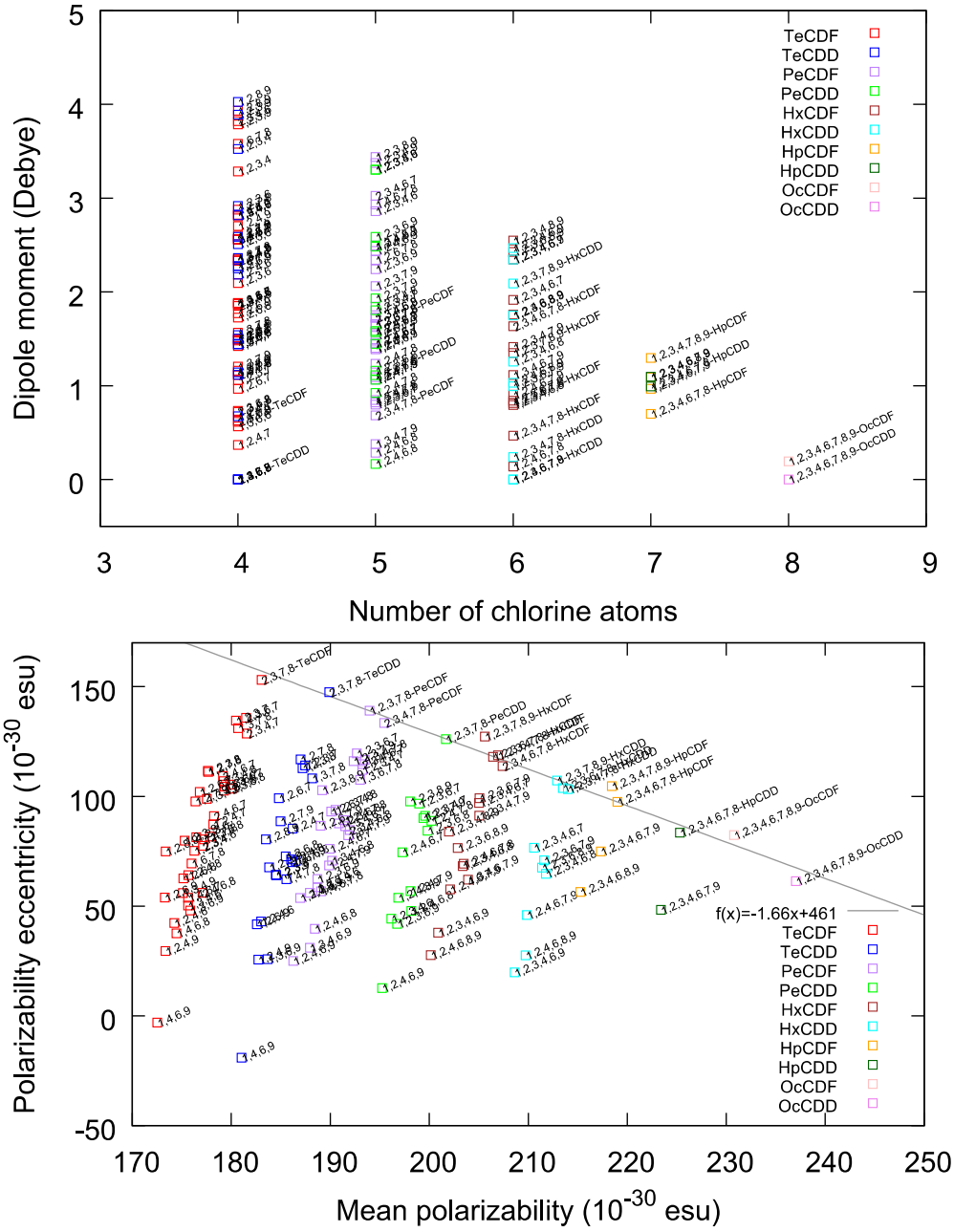
The recovery rates of ^{13}C-labelled PCDD/F standards from XAD-2 resin and three different used zeolites have been compared (Tab. 1). The recovery rates have been almost identical and sufficiently high to be accepted. This result proves Soxhlet extraction method using toluene as the extraction solvent can be applied to zeolites.

Tab. 1: Limit of detection (LOD), limit of quantification (LOQ), blank, uncertainty and examples of recovery rates of PCDD/F toxic congeners from XAD-2 and zeolites. The sampling volumes can be different, however the values of LOD and LOQ are independent of the sample volume according to calculation.
(*) A concentration value that falls between the LOD and LOQ is assigned the value of the LOQ. (**) A concentration value that falls below the LOD is assigned a value of zero. (***) For instance, D3-C11 stands for sampling D3 and cartridge C11 according to Fig. 1.

PCDD/F	LOD (pg per sample)	LOQ (pg per sample)	Blank (ng per sample)	Uncertainty (%)	Recovery rate D1-C21 (***) XAD-2 (%)	Recovery rate D3-C11 (***) FAU-NaX beads of 0.25-0.4 mm diameters (%)	Recovery rate D2-C21 (***) FAU-NaX beads of 0.5-0.8 mm diameters (%)	Recovery rate D3-C21 (***) *BEA-Na beads of 0.25-0.4 mm diameters (%)
2,3,7,8-TeCDD	0.83	1.2	<0,00120 (**)	30	95	98	94	92
1,2,3,7,8-PeCDD	0.81	1.2	<0,00120 (**)	30	81	78	81	95
1,2,3,4,7,8-HxCDD	1.1	1.5	<0,00150 (**)	30	89	79	84	79
1,2,3,6,7,8-HxCDD	1.1	1.5	<0,00150 (**)	40	80	74	78	75
1,2,3,7,8,9-HxCDD	1.1	1.5	<0,00150 (**)	60	-	-	-	-
1,2,3,4,6,7,8-HpCDD	3.9	10	<0,01000 (*)	30	89	80	83	87
OcCDD	13	25	<0,02500 (*)	60	64	61	64	75
2,3,7,8-TeCDF	1.0	1.5	<0,00150 (**)	40	84	82	82	80
1,2,3,7,8-PeCDF	0.68	1.2	<0,00120 (**)	30	86	76	56	71
2,3,4,7,8-PeCDF	0.70	1.2	<0,00120 (**)	30	75	71	73	85
1,2,3,4,7,8-HxCDF	0.71	1.2	<0,00120 (**)	30	84	78	80	73
1,2,3,6,7,8-HxCDF	0.73	1.2	<0,00120 (**)	30	88	81	82	78
2,3,4,6,7,8-HxCDF	0.72	1.2	<0,00120 (**)	30	93	84	88	83
1,2,3,7,8,9-HxCDF	0.81	1.5	<0,00150 (**)	30	81	70	50	68
1,2,3,4,6,7,8-HpCDF	2.2	5.0	<0,00500 (**)	30	69	73	72	81
1,2,3,4,7,8,9-HpCDF	0.84	1.5	<0,00150 (**)	30	88	74	60	50
OcCDF	3.9	10	<0,01000 (**)	30	65	57	61	63

3.2 Spatial structure and electrical properties of PCDD/F

Prior to sampling result interpretation, the spatial structure and electrical properties of PCDD/F must be developed. PCDD/F are quasi-planar molecules in the x0y plane, with the long axis aligned along the x-direction. The molecule size in the y-direction defines the steric compatibility with the zeolite micropore diameter sizes for specific adsorption. For instance, the molecule sizes in the y-direction are: 7.4 Å for DD, DF, 2,3,7,8-TeCDF and 2,3,7,8-TeCDD; 8.6 Å for 1,2,3,7,8-PeCDD, 1,2,3,7,8-PeCDF and 2,3,4,7,8-PeCDF; and 9.9 Å for OcCDD and OcCDF [19,41].



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233 Fig. 2: (top graph) Dipole moment as a function of the number of chlorine atoms and (bottom graph)
234 mean polarizability as a function of polarizability eccentricity of tetra- to octa-chlorinated PCDD/F
235 congeners. The plotted values are simulated values obtained with same simulation tools and collected
236 from data tables of ref. [32,42,43]. The values of the toxic congeners have been linearly interpolated
237 by the straight line of equation: $y = -1.66\,x + 461$. In both graphs, the toxic congeners are
238 referenced by their full name, *e.g.* 2,3,7,8-TeCDD, while the non-toxic by the position of the chlorine
239 atoms merely, *e.g.* 1,2,3,4.

240 Gu *et al*. have examined the electronic interactions between PCDD/F and AhR to establish the
241 main factor in predicting the PCDD/F toxicology [32,43]. They have determined the electronic
242 structures of all the PCDD/F using ab initio quantum chemical calculations. Then the polarizability

values have been calculated using the Density Functional Theory (DTF) and optimized globally without any *a priori* symmetry. Concomitantly, the values of the dipole moment have been calculated by Yang *et al*. using the same methods and tools [42]. From these simulation results, it is then possible to have a set of comparable values of the dipole moment and polarizabilities for all toxic and non-toxic PCDD/F congeners (Fig. 2). The electric polarizability tensor of toxic PCDD/F is quasi-diagonal with diagonal terms denoted as: α_{xx}, α_{yy} and α_{zz} in the x-, y- and z-directions, respectively. The mean polarizability is expressed as: $\overline{\propto} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$ and polarizability eccentricity in the plane x0y as: $\epsilon = \alpha_{xx} - \alpha_{yy}$. For the toxic PCDD/F the diagonal term α_{zz} ranges over low values (from 63 to 79 x10^{-30} esu), as the molecules are quasi-planar.

In Fig. 2, the toxic congeners are referenced by their full name, *e.g*. 2,3,7,8-TeCDD, while the non-toxic ones by the position of the chlorine atoms merely, *e.g*. 1,2,3,4. The dipole moment and polarizability units are expressed in Debye and electrostatic unit (esu), respectively, where esu is expressed as 1.112 x 10^{-16} C^2 x m^2 x J^{-1} in terms of CGS units.

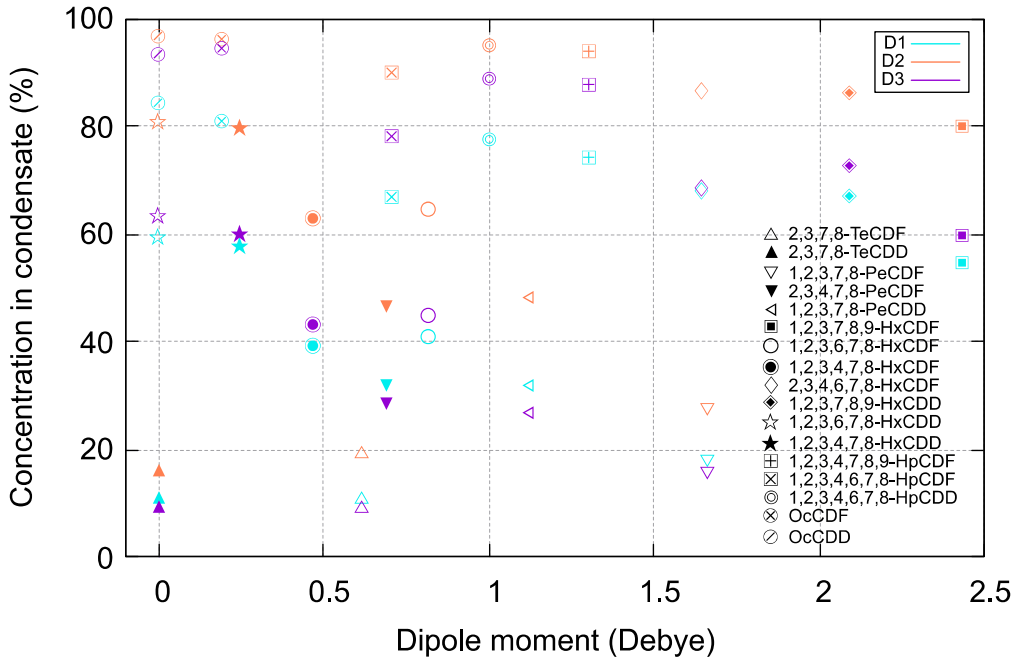
Only the polarizability could separate toxics from non-toxics of each family, as the toxic isomers have higher polarizabilities than the non-toxic ones. The differences of polarizability eccentricity between toxics and non-toxics are higher than those of mean polarizability. The polarizability values of the toxic congeners can be interpolated in the system of coordinates "mean polarizability" and "polarizability eccentricity" by the straight line of equation: $y = -1.66\,x + 461$ (Fig. 2). As a consequence, the polarizability of the toxic congeners increases quasi-linearly when the volume occupied by electrons increases, while the polarizability eccentricity decreases (from TeCDD/F to OcCDD/F congeners).

3.3 PCDD/F concentration in the condensates

Similar concentrations of the toxic congeners have been measured in the particulate phase, condensates and gas phase for the samplings D1 and D2, while for the sampling D3 the concentrations have been twice higher for more than half of the congeners. The toxic congeners have been measured in negligible quantities in the particulate phase.

The relative concentrations of toxic PCDD/F measured in the condensates, $C_C(c)(\%) = 100 \times \frac{C_C(c)}{C_T(c)}$, are plotted as a function of the dipole moment and mean polarizability of the congeners (Fig. 3). The relative quantities trapped in the condensates increase with the number of chlorine atoms of the congeners, from 10-20 % for TeCDD/F to 85-95 % for OcCDD/F. Quasi-similar relative concentrations have been measured for the samplings D1 and D3 while for the sampling D2, the relative concentrations are slightly higher for all the congeners. This is due to different temperatures of the ice water supplied by the cooling system no. 1 measured at 5 °C for the samplings D1 and D3 and at 3 °C for the sampling D2.

Consequently, the relative concentrations in the condensates and gas phase depend on the temperature in the condenser. The heat transfers between the ice water and molecules in the gas flow depend on the volumetric flow rate of the gas. To a lesser extent, the volumetric flow rate could influence the measured quantities. Reproducible relative concentrations in both the condensates and flow passing through the adsorbents can be achieved by maintaining constant the values of the operating parameters. The ratio of PCDD/F concentrations measured in the condensates and gas phase $p(c) = \frac{C_C(c)}{C_G(c)}$ is sampling device dependant and can be estimated from some samplings. Insuring same operating conditions, the emitted total concentration can be then calculated from the concentration measured only in the adsorbent by: $C_T(c) = C_G(c) + C_C(c) = C_G(c)\big(1 + p(c)\big)$.



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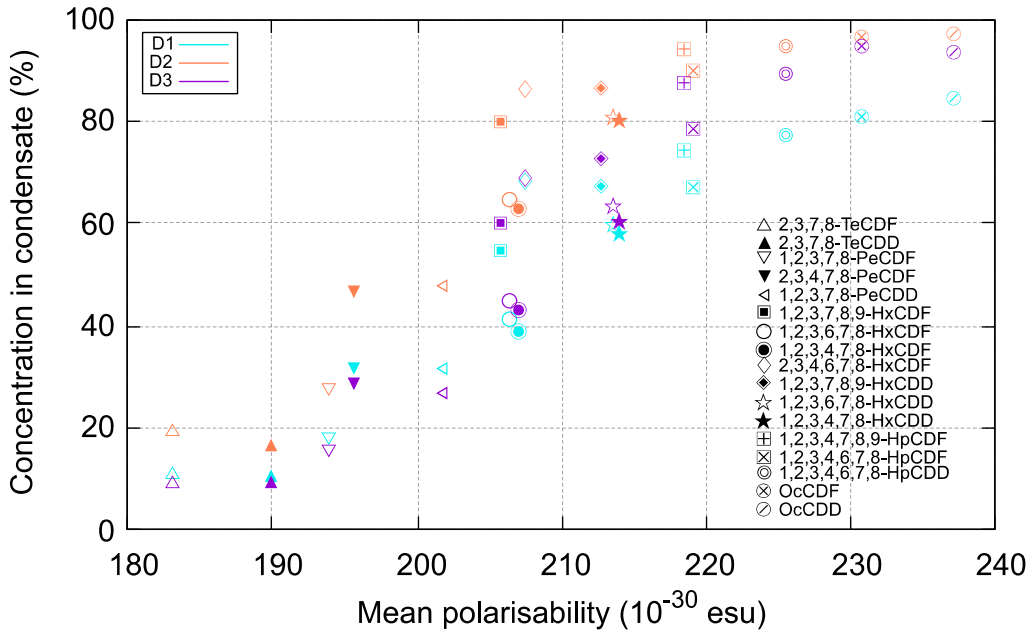

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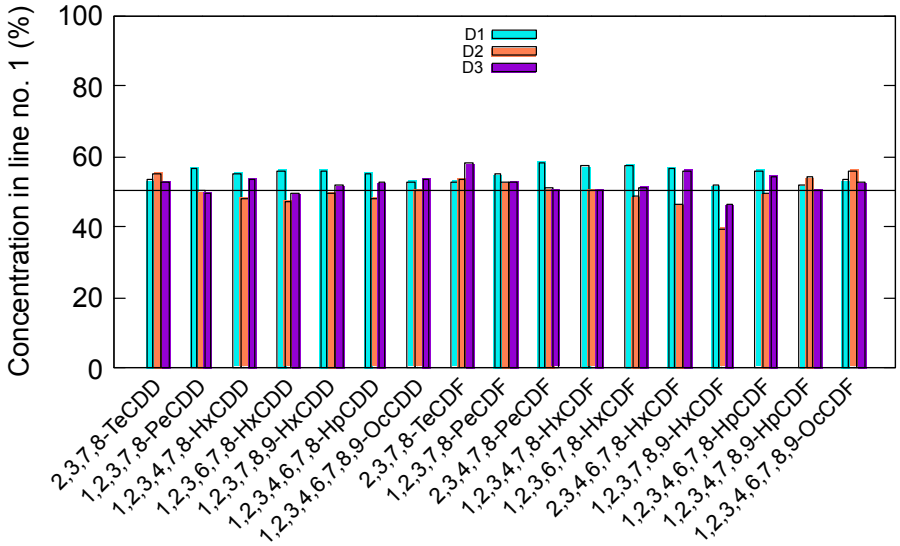
293 Fig. 3: Relative concentrations of toxic PCDD/F measured in the condensate for the samplings D1, D2
294 and D3 as a function of (top graph) dipole moment and (bottom graph) mean polarizability.

295 Furthermore, on the one hand, no relations can be deduced between the relative concentrations of
296 toxic PCDD/F measured in the condensate and the values of the dipole moment (top graph of Fig. 3).
297 On the other hand, the interaction between the PCDD/F and water in the condenser mainly depends on
298 the PCDD/F polarizability (bottom graph of Fig. 3). The more the congener polarisable, the more the

299 congener adsorbed by physisorption by water droplets falling then by gravity into the condensate
300 flask. Induced dipole-permanent dipole interaction exists between PCDD/F congeners and water.

301 **3.4 PCDD/F concentration in the two gas lines**



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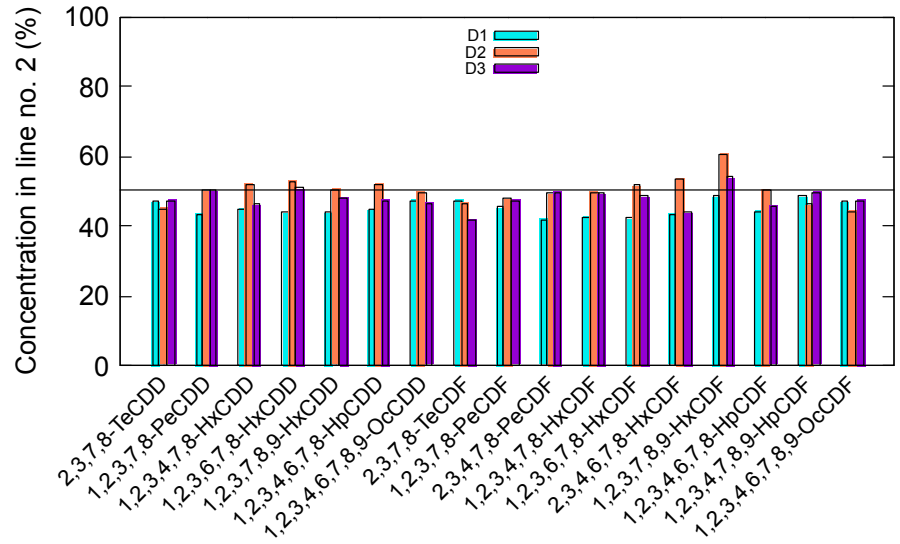

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304 Fig. 4: Relative concentrations of toxic PCDD/F measured in secondary lines no. 1 (top graph) and 2
305 (bottom graph) for the samplings D1, D2 and D3.

306 The relative concentrations in the gas lines no. 1 and 2 have been calculated from the relations:

307 $C_{L1}(c)(\%) = 100 * \frac{C_{G11}(c)+C_{G12}(c)}{C_G(c)}$ and $C_{L2}(c)\ (\%) = 100 * \frac{C_{G21}(c)+C_{G22}(c)}{C_G(c)}$, respectively, with for

instance, $C_{G21}(c)$ the concentration of congener c measured in the adsorbent packed in the first cartridge of the secondary line no. 2. The comparison of the values measured between the two secondary gas lines shows an acceptable measurement reproducibility (Fig. 4). The slight discrepancy between the two lines is due to a temperature difference between the two line inlets. The higher the temperature, the higher the concentration in the line.

3.5 Zeolite structure types

Prior to adsorption result interpretation onto zeolites, their structure types and adsorption properties must be discussed. Zeolites are microporous crystalline aluminosilicate solids. Their inorganic framework (Si-O-Al) can be described as an assembly of TO_4 tetrahedra for which T stands for silicon or aluminium atoms and each oxygen atoms, located at the vertices, is shared by two tetrahedra. These assemblies design channels and/or cavities of molecular dimensions with precisely defined sizes [14]. These arrangements define structure types. Two zeolite structure types have been submitted to gas flux: FAU-NaX and *BEA-Na. FAU-NaX has supercages of tetrahedral symmetry of 11.24 Å in diameter with interconnectivities (micropores) of 7.35 Å in diameter. The size of micropore apertures of *BEA-Na is 6.68 Å in diameter and micropore cavity 5.95 Å.

FAU-NaX and *BEA-Na crystallize in cubic and tetragonal unit cells, respectively. Confirmed by TEM imaging [44,45], the outer surface area of micro crystals (giving the external surface area and external porosity) of FAU-NaX and *BEA-Na can be represented for the three directions of the coordinate system by: for FAU the surface perpendicular to [111] direction, and for *BEA surfaces perpendicular to [100], [010] and [001] directions, respectively. As for a tetragonal crystal system, zeolite *BEA surfaces perpendicular to [100] and [010] directions are identical.

The external surface roughness and porosity of a FAU-NaX crystal perpendicular to [111] direction (from Clarian® youtube video) and those of *BEA-Na crystal perpendicular to [100] and [001] directions (from the web tool provided by the database of the International Zeolite Association [46]) are shown in Fig. 5. For *BEA-Na, the red balls represent the oxygen atoms of the framework

Si-O-Al on the external surface, and the internal surface areas of the micropores are represented in blue.

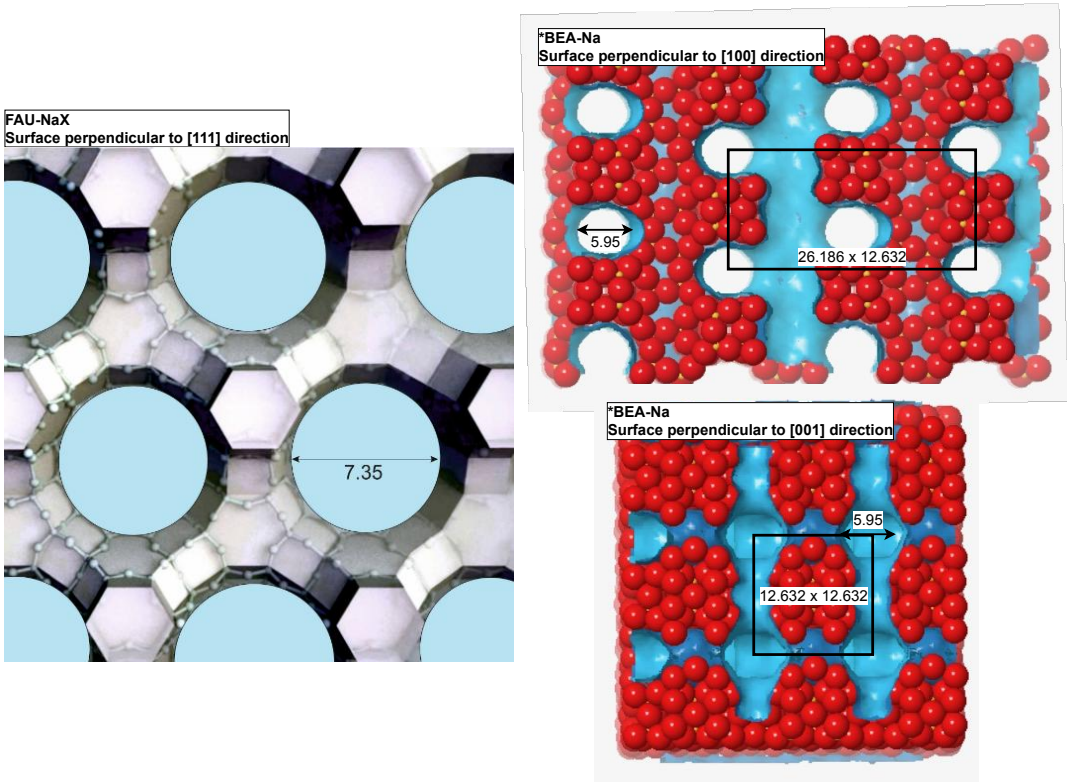


Fig. 5: External surface roughness and porosity of a FAU-NaX crystal perpendicular to [111] direction (left) and *BEA-Na crystals perpendicular to [100] or [010] (right top) and [001] directions (right bottom). The pictures are extracted from Clarian® youtube video for FAU and web tool of ref. [46] for BEA. Note that for the FAU (111) surface the 1 x 1 surface repeat unit is 17.13 x 17.13 Å [47] in contrast to the cubic 24.35 Å unit cell dimensions.

According to [47] the outer surface of FAU-NaX octahedral crystals comprise partially the walls of the super cages but also sodalite cages and 6 membered rings which contribute to the surface roughness. Probably those of *BEA nano crystals do show walls of the micropore channels that are parallel to the outer surface. The external surface of both zeolites is an oxygen-terminated, hydroxylated and partially water saturated polar surface (see scheme 1 showing interaction between adsorbed DD dioxin and zeolite in ref. [24]). So, it can be assumed that the outer surfaces of both crystals have quasi-identical physical-chemical properties.

3.6 Adsorption of PCDD/F onto zeolite beads

The adsorption of PCDD/F onto zeolites can be summarized by: (1) non-selective adsorption of the whole of the congeners onto the external surface and (2) specific adsorption into the micropores of the zeolites, when the steric hindrance is limited so only certain congeners can enter the micropores.

Not any of the PCDD/F congeners can enter the micropores of the *BEA-Na. The micropore size of FAU-NaX allows only the admission of 2,3,7,8-TeCDD and 2,3,7,8-TeCDF congeners among the toxic congeners. The toxic PeCDD/F isomers can be only adsorbed at the micropore entrances of FAU-NaX, thus blocking the access to the remainder of the micropore volume of the crystal.

When the beads are packed in a cartridge, it exists a macroporosity between the beads, in addition to the one between the crystals and binder in each bead, where the gas can pass through. However, it can be assumed that the main interactions between the gas and zeolites occurs on the external surface area of the beads, as gas velocity is higher inside the macroporosity of the bead due to higher flow hindrances. In consequence, the same adsorption properties are expected for the external surface area of *BEA-Na and FAU-NaX beads of identical diameter.

With the best arrangement of spherical beads packed in a given volume of the cartridge, when the bead diameter is doubled, the surface area of all the beads is divided by 2 and the weight of the beads does not change. As a consequence, the micropore accessibility is dived by two, if it is assumed that the interactions between the gas flow and zeolite occur mainly on the external surface area of the beads.

Authors of this study have characterised the synthesized zeolite beads used in the sampling device. Nitrogen adsorption-desorption isotherms have been performed at 77 K with Micromeritics ASAP 2420 MP Instruments. Before each measurement, the samples have been outgassed to a residual pressure of less than 0.8 Pa at 150 °C for 15 h for the beads. Specific surface area, denoted as S_{BET}, has been calculated according to the BET method ($10^{-6} < p/p^0 < 0.05$) and compared to external surface, denoted as S_{ext}, associated to intra- and inter-particular mesoporosities [48]: S_{BET} is equal to 700 and 410 m^2/g, and S_{ext} to 5 and 100 m^2/g for FAU-NaX (beads of 0.25-0.4 mm in diameters) and *BEA-Na (beads of 0.25-0.4 mm in diameters), respectively. The external surface of *BEA-Na beads is 20 times

larger than those of FAU-NaX beads, as the external surface of *BEA-Na beads is composed of the surface of the nano-crystals, mesoporosity between the nano-crystals of agglomerates and macroporosity between the agglomerates, while the external surface of FAU-NaX beads is limited to the surface of the micro-crystals and macroporosity between the micro-crystals

3.7 PCDD/F concentration adsorbed onto zeolites

The concentrations of toxic congeners adsorbed onto FAU-NaX beads of 0.25-0.4 mm and 0.5-0.8 mm diameters for the sampling D2 are given in Fig. 6. The breakthrough of 2,3,7,8-TeCDD/F, 1,2,3,7,8-PeCDF and 2,3,4,7,8-PeCDF has occurred with the beads of 0.5-0.8 mm diameters. The same congener quantities have been measured in the two gas lines, when the concentrations of the first and second cartridges are added.

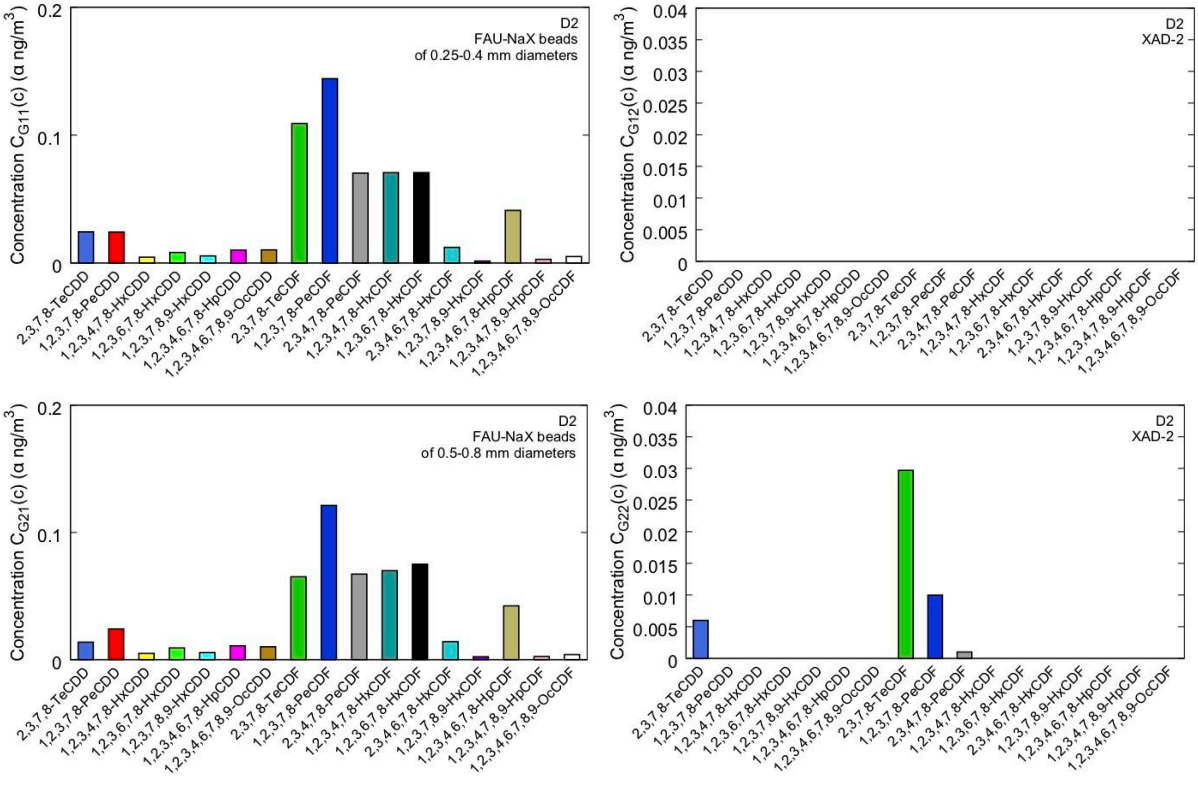


Fig. 6: Concentrations of toxic PCDD/F adsorbed the sampling day D2 in cartridges packed with FAU-NaX beads of 0.25-0.4 mm diameters and XAD-2, respectively (top figures, line no. 1) and in cartridges packed with FAU-NaX beads of 0.5-0.8 mm diameters and XAD-2, respectively (bottom figures, line no. 2).

In the following results, two different zeolite structure types have been tested in parallel. The concentrations of toxic congeners adsorbed onto FAU-NaX and *BEA-Na beads of 0.25-0.4 mm diameters are compared for the sampling D3 in Fig. 7. The breakthrough of 2,3,7,8-TeCDD/F, 1,2,3,7,8-PeCDF and 2,3,4,7,8-PeCDF has occurred with the *BEA-Na beads. The same congener quantities are measured in the two gas lines, when the quantities of the first and second cartridges are added.

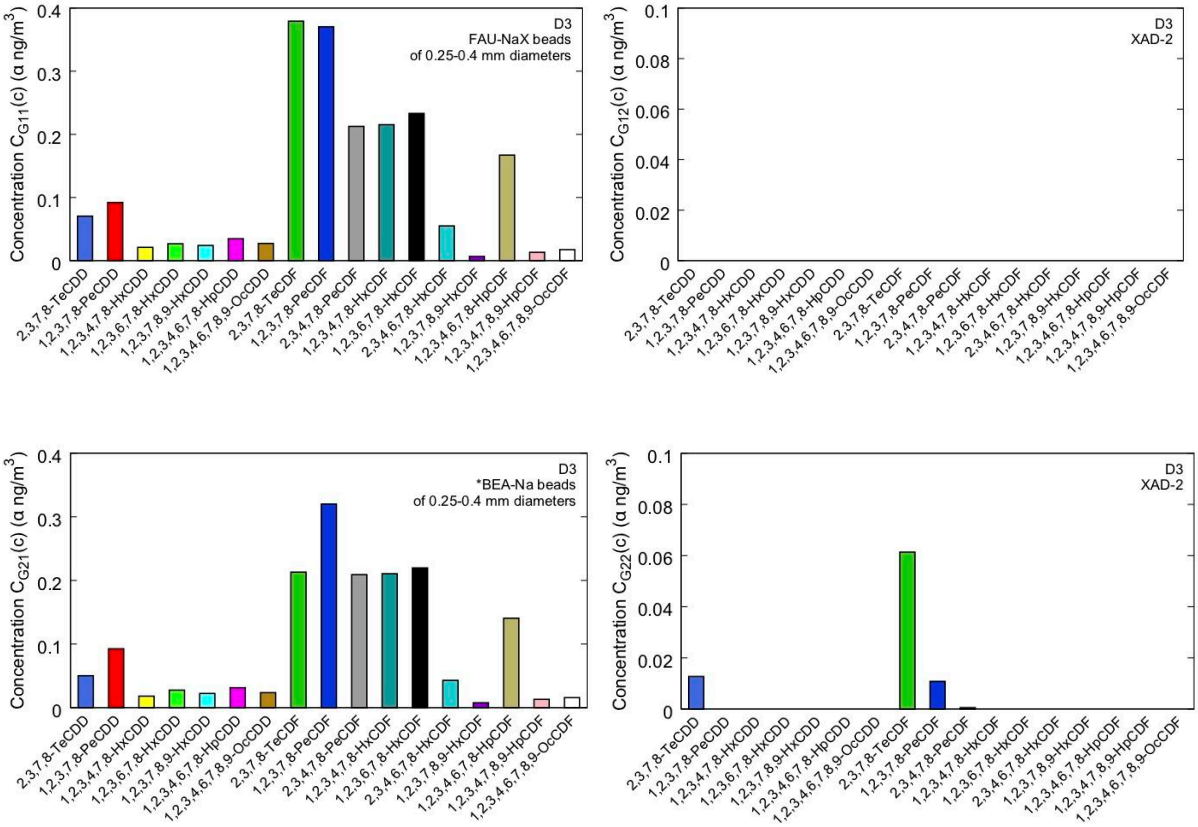
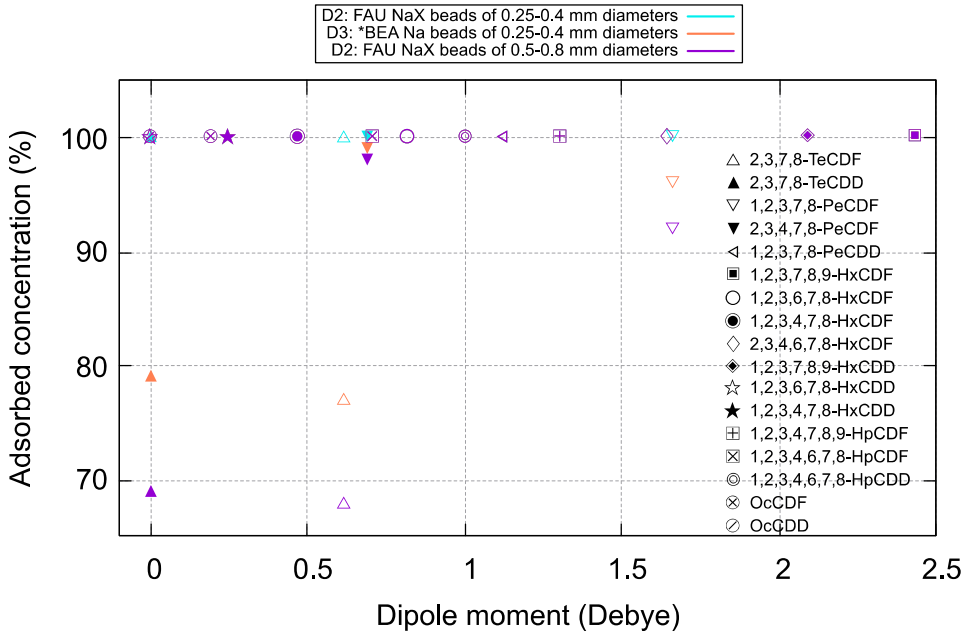


Fig. 7: Concentrations of toxic PCDD/F adsorbed the sampling day D3 in cartridges packed with FAU-NaX beads of 0.25-0.4 mm diameters and XAD-2, respectively (top figures, line no. 1) and in cartridges packed with *BEA-Na beads of 0.25-0.4 mm diameters and XAD-2, respectively (bottom figures, line no. 2).

The relative concentration (%) adsorbed onto an adsorbent is relative to the total concentration measured in the gas line. For instance, the relative concentration adsorbed in the first cartridge of the line no. 1 is expressed by: $C_{G11}(c)\ (\%) = 100 * \frac{C_{G11}(c)}{C_{G11}(c)+C_{G12}(c)}$. In Fig. 8, the relative concentrations of the toxic PCDD/F adsorbed onto FAU-NaX and *BEA-Na beads of 0.25-0.4 mm diameters, and FAU-NaX beads of 0.5-0.8 mm diameters are compared as a function of the dipole moment and

polarizability of the congener. A relative adsorbed concentration different from 100 % indicates a breakthrough of the congener.



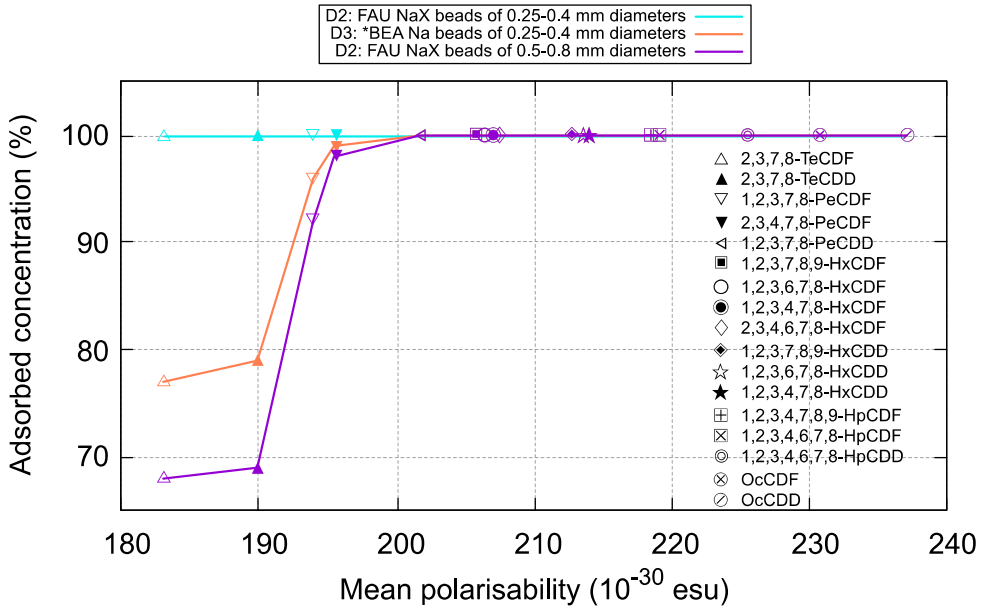


Fig. 8: Relative concentration of toxic PCDD/F adsorbed on different zeolites as a function of dipole moment (top graph) and of mean polarizability (bottom graph).

The breakthrough occurs only for the toxic TeCDD/F and PeCDF with the *BEA-Na beads of 0.25-0.4 mm diameters and FAU-NaX beads of 0.5-0.8 mm diameters. There are no correlations between the breakthrough (or quantities adsorbed) and the value of the dipole moment of the

419 congeners (top graph of Fig. 8), while the breakthrough increases when the value of the polarizability
420 diminishes (bottom graph of Fig. 8).

421 None of the toxic PCDD/F can be adsorbed by the micropores of the *BEA-Na zeolite. So, the
422 breakthrough observed with *BEA-Na beads of 0.25-0.4 mm diameters describes the interactions
423 between the congeners and the external surface area of the *BEA-Na zeolite. As the beads have same
424 diameters and external surface area of the *BEA-Na is larger than that of FAU-NaX, it is expected
425 that a breakthrough occurs also with the FAU-NaX. However, all the toxic PCDD/F congeners have
426 been adsorbed by the FAU-NaX beads having the same diameter range than the *BEA-Na beads. In
427 addition, those that have been adsorbed by the FAU-NaX and not by the *BEA-Na can enter the
428 micropore of the FAU-NaX, only. Therefore, this proves that toxic TeCDD/F and PeCDD/F have been
429 adsorbed into the micropores of FAU-NaX zeolite.

430 The FAU-NaX beads of 0.25-0.4 mm diameters have an external surface twice larger than the
431 beads of 0.5-0.8 mm diameters. As a consequence, it could be assumed that a large amount of 2,3,7,8-
432 TeCDD/F have been adsorbed by the FAU-NaX beads of 0.25-0.4 mm diameters. Furthermore, the
433 micropore accessibility is twice higher with the smallest beads. Considering this, it can be also
434 assumed that a part of 2,3,7,8-TeCDD/F measured in breakthrough of the FAU-NaX beads of 0.5-0.8
435 mm diameters have been adsorbed into the micropores and/or at the entrance of the micropores of the
436 FAU-NaX beads of 0.25-0.4 mm diameters.

437 # 4 Conclusions

438 If keeping the process parameters (condenser temperatures and gas flows) at the same values, a
439 constant and reproducible distribution of congeners between the condensate and gas phases can be
440 insured. Doing that, the total emitted concentrations of toxic congeners can be calculated from only
441 the concentrations measured in the adsorbent. If a set of adsorbents placed in parallel is required in the
442 forthcoming monitoring device, the adsorption temperature must be set to a same value in each
443 adsorbent to ensure same concentrations passing through the adsorbents.

In addition, the temperature of adsorption plays an important role to favour specific micropore adsorption. In the laboratory, a device generating gas stream with synthetic air, moisture vapour, PCDD/F and solvents in adjustable concentrations is being mounted. This gas stream generator will supply an EN1948-1 sampling device. By means of this device coupling, the optimal set of values of the sampling parameters must be estimated in order to specifically adsorb onto zeolites the greatest and stable amounts of targeted PCDD/F congeners.

These very-promising first results prove that FAU-NaX type zeolites can be operated as adsorbent for sampling the incinerator gas flow. They show the specific adsorption of the toxic TeCDD/F and PeCDD/F congeners in the micropores of FAU-NaX despite the presence of significant amounts of moisture and other large amounts of incineration compounds. In a next field campaign, Faujasite X type zeolites modified by cation exchanges [27,28] will be used in order to adsorb in the micropore volume larger-size congeners up to OcCDD/F.

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