

PCDDs, PCDFs, and PCBs co-occurrence in TiO₂ nanoparticles

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Abstract In the present study, we report on the co-occurrence of persistent organic pollutants (POPs) adsorbed on nanoparticulate titanium dioxide (TiO₂). We report on the finding of polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs) on the surface of commercially available TiO₂ nanoparticles, being formed during the fabrication process of the TiO₂. Thereby, the samples comprise PCBs with higher congener numbers or, in the absence of PCBs, a high concentration of PCDDs and PCDFs. This new class of POPs on an active catalytic surface and the great range of applications of nanoparticulate TiO₂, such as in color pigments,

cosmetics, and inks, give rise to great concern due to their potential toxicity.

Keywords Persistent organic pollutants (POPs) · Polychlorinated biphenyls (PCBs) · Polychlorinated dibenzodioxins (PCDDs) · Polychlorinated dibenzofurans (PCDFs) · TiO₂ nanoparticles · Sun lotions · Pigments · Food additives · Surface bound

Introduction

Polychlorinated biphenyls (PCBs) are a class of 209 congeners (CAS number 1336-36-3), which were intentionally synthesized as dielectric and coolant fluids (Librando et al. 2013). They are persistent organic pollutants (POPs) due to their environmental persistence and toxicity. Their production was banned in 1979 by the US Congress and by the Stockholm Convention of POPs in 2001 (Porta and Zumeta 2002). PCBs cause cancer in animals and humans and exhibit endocrine disruptor effects (Jeong et al. 2008; Lauby-Secretan et al. 2013; Annamalai and Namasivayam 2015). PCBs are a class of compounds, which are similar in structure and physico-chemical properties. They exhibit low water solubility, between 0.002 and 0.42 ng/L for Aroclor mixtures, and high solubility in organic solvents, oils, and fats. Therefore, PCBs penetrate readily into skin (Cogliano 1998). Furthermore, they are chemically resistant to oxidation, reduction, addition, elimination, and electrophilic substitution (Librando et al. 2013). Therefore, PCBs do not decompose readily in the environment. Due to their chloro-substitution pattern, PCBs may be divided into two major classes: (i) coplanar non- or mono-ortho-substituted dioxins such as PCBs and (ii) multi-ortho-substituted congeners. As polychlorinated dibenzo-p-dioxins

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(PCDDs) and furans (PCDFs), the dioxin-like PCBs are agonists of the aryl hydrogen receptor (AhR) (Luthe et al. 2008).

The group of polyhalogenated organic compounds, polychlorinated dibenzodioxins (PCDDs), are significant environmental pollutants. Each PCDD molecule contains a dibenzo-1,4-dioxin skeletal structure, with 1,4-dioxane as the central ring. PCDDs bioaccumulate in humans and wildlife because of their lipophilic properties and may cause developmental disturbances and cancer (Pohjanvirta and Tuomisto 1994). The most toxic dioxin, 2,3,7,8-tetrachlorodibenzodioxin (TCDD), became well known as a contaminant of Agent Orange, an herbicide used in the Malayan Emergency and the Vietnam War (Schechter et al. 2006). Later, dioxins were found in Times Beach, Missouri; Love Canal, New York; and Seveso, Italy (Schechter et al. 2006). Dioxins also have been implicated in the poisoning of President Viktor Yushchenko of Ukraine in 2004 (Schechter et al. 2006), the Naples mozzarella crisis (Borrello et al. 2008), the 2008 Irish pork crisis (Tlustos 2009), and the German feed incident of 2010.

PCDFs are a family of organic compounds with one or several of the hydrogens in the dibenzofuran structure replaced by chlorines. PCDFs are more toxic than the parent compounds, with properties and chemical structures similar to PCDDs. These groups of PCDDs and PCDFs are together often inaccurately called dioxins. They are known teratogens, mutagens, and suspected human carcinogens (Yang et al. 2008). PCDFs tend to co-occur with PCDDs. PCDFs can be formed by pyrolysis or incineration of chlorine-containing products, at temperatures below 1200 °C. PCDFs are known POPs, classified among the dirty dozen in the Stockholm Convention on Persistent Organic Pollutants (Fiedler 2007).

Titanium dioxide (TiO₂) is an industrially highly important material with three crystal types, which can be found in nature: rutile (crystal system: tetragonal (4/mmm); space group: P4₂/mmn-D¹⁴_{4h}), anatase (tetragonal (4/mmm); I4₁/amd-D¹⁹_{4h}), and brookite (orthorhombic (mmm); Pbca-D¹⁵_{2h}). From these, only the first two are important for industrial applications, ranging from white pigment, mostly in paints, varnishes, paper, to plastics and accounting for 80 % of the global TiO₂ consumption (Ceresana 2013). Ink, fibers, rubber, cosmetic products, and food additives (E171, red-colored candy) (Fries and Simkó 2012; Shi et al. 2013; Larue et al. 2014; Jamuna et al. 2014) account for another 8 % (Ceresana 2013) of the consumption. The predominant production process of TiO₂ is the chloride process, which primarily produces the rutile form TiO₂, having the highest TiO₂ content (Fries and Simkó 2012).

In this paper, we describe the results of POP measurements in commercially available TiO₂ samples. Further, we describe a probable transformation pathway of PCBs into PCDDs/PCDFs mediated through the nanoparticulate TiO₂. We propose that PCBs, PCDDs, and PCDFs are formed in the process

of nanomaterial production of metal chlorides at high temperatures, such as titanium tetrachloride (TiCl₄). Mineral TiO₂ is purified via conversion to TiCl₄ in such chloride process. We hypothesize that lipophilic POPs, including PCBs, co-occurring with polar nanoparticles (NPs) such as TiO₂-NPs are a new class of POPs (NP-POPs) with yet unknown properties due to their mixed physicochemical properties, such as polarity.

Experimental part

Chemicals

Titanium dioxide samples

Sample A: titanium pigment (“Pigment Titaanwit”, ~1 µm; verftechnieken.nl; the Netherlands)

Sample B: titanium oxide nanopowder/nanoparticle dispersion (TiO₂ nanoparticle aqueous dispersion, rutile, 20 wt%, 30–50 nm) (stock no. US7070; US Research Nanomaterials, Inc. Houston, TX, USA)

Sample C: titanium(IV) oxide rutile 99.8 % (metals basis), 0.9–1.6 µm APS powder, S.A. 3.3–6.1 m²/g (art. no. 42681; Alfa Aesar GmbH & Co. KG, Germany)

Sample D: titanium(IV) oxide rutile 99.5 % min (metals basis) 1.0–2.0 µm APS powder (art. no. 43047; Alfa Aesar GmbH & Co. KG, Germany)

Sample E: titanium(IV) oxide rutile 99.9 % (metals basis) 3–6 µm sintered pieces (art. no. 44375; Alfa Aesar GmbH & Co. KG, Germany)

Solvents and standards

Toluene, acetone, dodecane, and dichloromethane were of “picograde” quality (LGC Promochem Wesel, Germany); GC standards: Precision and Recovery Standard Mix 17 native 2,3,7,8-PCDD/F, Art. no. EDF-7999 (LGC Promochem Wesel, Germany)

Single standards (all from Promochem Wesel, Germany): 1,2,3,4-TCDD ¹³C₁₂ isotope labeled art. no. ED-910; 2,3,7,8-TCDD ¹³C₁₂ isotope labeled art. no. ED-900; 1,2,3,7,8-PeCDD ¹³C₁₂ isotope labeled art. no. ED-955; 1,2,3,4,7,8-HxCDD ¹³C₁₂ isotope labeled Art. no. ED-946; 1,2,3,6,7,8-HxCDD ¹³C₁₂ isotope labeled art. no. ED-966; 1,2,3,7,8,9-HxCDD ¹³C₁₂ isotope labeled art. no. ED-996; 1,2,3,4,6,7,8-HpCDD ¹³C₁₂ isotope labeled art. no. ED-972; 1,2,3,4,5,6,7,8-OCDD ¹³C₁₂ isotope labeled art. no. ED-981; 2,3,7,8-TCDF ¹³C₁₂ isotope labeled art. no. EF-904; 1,2,3,7,8-PeCDF ¹³C₁₂ isotope labeled art. no. EF-952; 2,3,4,7,8-PeCDF ¹³C₁₂ isotope labeled art. no. EF-958; 1,2,3,4,7,8-HxCDF ¹³C₁₂ isotope labeled art. no. EF-963; 1,2,3,6,7,8-HxCDF ¹³C₁₂ isotope labeled art. no. EF-985; 1,2,3,7,8,9-HxCDF ¹³C₁₂

isotope labeled art. no. EF-986; 2,3,4,6,7,8-HxCDF $^{13}\text{C}_{12}$ isotope labeled art. no. EF-987; 1,2,3,4,6,7,8-HpCDF $^{13}\text{C}_{12}$ isotope labeled art. no. EF-974; 1,2,3,4,7,8,9-HpCDF $^{13}\text{C}_{12}$ isotope labeled art. no. EF-988; 1,2,3,4,6,7,8,9-OCDF $^{13}\text{C}_{12}$ isotope labeled art. no. EF-983

Instrumentation

GC-HRMS measurements were completed with a Trace GC Ultra instrument (Thermo Fisher Scientific Waltham, MA, USA) including DFS mass spectrometry. GC columns used were HT8 60 m (SGE Analytical Science, TX, USA), DB-5MS 60 m (Agilent, USA).

General procedure

The procedure implemented for all analytical PCB determinations was consistent with a procedure related to the German standard methods for the examination of water, wastewater, and sludge—sludge and sediments (group S)—part 24: determination of polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF) (DIN 38415–6 2001). This procedure is suited to the examination of samples for 17 tetra- to octa-substituted PCDD and PCDF single components with chloro-substitution in positions 2, 3, 7, and 8. The corresponding limits of detection are in the range of circa 1 to 10 ng/kg dry mass.

For sample preparation, extraction, and sample clean-dioxin-range, two separate laboratory rooms were used. Both rooms included a complete set of laboratory equipment with own glassware and all necessary technical equipment for sample pretreatment. To avoid cross-contamination between samples, the samples with a presumably higher PCDD and PCDF content were stored in a separate high-security laboratory (HSL) and the samples with a presumably lower PCDD and PCDF strain in a laboratory for low loaded samples (NL).

The homogenized, air-dried samples (1–10 g sample weight) were transferred into an extraction thimble and after addition of 20 ml extraction standard for a duration of ~17 h by Soxhlet extraction with a toluene/acetone (9:1) solvent mixture. Subsequently, the extracts were concentrated by rotary evaporation to yield final volumes of <3 ml. The residues were dissolved in iso-hexane and further purified by column chromatography using a column packed with silver nitrate/silica gel. This was followed by treatment using a column packed with aluminum oxide (DIN 38415–6 2001). Subsequently, final separation was done via capillary gas chromatography and determined with mass spectrometry utilizing the selected ion monitoring (SIM) method. Quantification was done by $^{13}\text{C}_{12}$ -labeled internal standards related to the overall procedure.

The extraction standard contains 13 to 17 $^{13}\text{C}_{12}$ -labeled 2, 3, 7, 8-congeners in dodecane. The extraction standard served

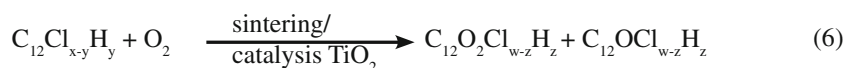
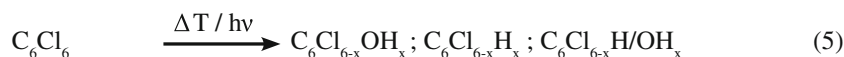
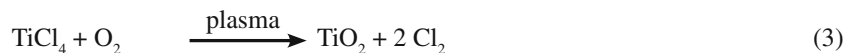
to monitor the entire sample preparation of the extraction on the extract purification to transfer into the measuring vessel. It also served to monitor the analysis of the HRGC/HRMS coupling and is the internal quantification standard for the calculation of the results.

Results and discussion

We hypothesized that surface-bound POPs, such as PCBs, PCDDs, and PCDFs, are formed and transformed during the fabrication and purification process of TiO_2 . Titanium tetrachloride (TiCl_4) is formed from the titanium-containing ore in a purification step at high temperatures (Fig. 1, Eq. 1) in the presence of carbon and molecular chlorine. The rutile and/or anatase (containing at least 70 % TiO_2) is reduced with carbon and oxidized with chlorine to produce titanium tetrachloride, i.e., carbo-thermal chlorination. Next, TiCl_4 is distilled and re-oxidized mainly in a hydrolysis (Fig. 1, Eq. 2) or in a pure oxygen flame or plasma at 1500–2000 K (Fig. 1, Eq. 3). During this carbo-thermal chlorination process, PCBs, PCDDs, and PCDFs are potentially formed (Fig. 1, Eqs. 4 and 5).

Figures 2 and 3 show examples of two samples (samples A and E): the relative mass contribution of the different PCB congeners (Fig. 2, sample A) and of the PCDD and PCDF mass contribution (Fig. 3, sample E). It is visible that a large amount of POPs can be detected in the samples. A detailed look at the PCB profile of Fig. 2 shows that the measured PCB profiles do not match any known Aroclor source (Frame et al. 2001). This is a strong indication that the PCBs are unintentionally formed during the production process and do not arise via environmental contamination. The profiles of PCDD and PCDF in Fig. 3 show a similar trend. There is an increase in the concentration to the higher chlorinated dioxins and furans. This similarity points toward a similar formation route under high temperature.

A complete list of the performed measurements and samples is shown in Table 1. Let us first concentrate on the PCBs. The first four samples (A–D) contain the following congeners: sample A contains PCB 28 and 52, <100 ng/kg; PCB 101, 282 ng/kg; PCB 138, 843 ng/kg; PCB 153, 752 ng/kg; and PCB 180, 802 ng/kg, with total PCB content of 2680 ng/kg. The dioxin-like PCBs (indicated in red in Fig. 2) are lower in concentration: PCB 77, <5 ng/kg; PCB 81, 2.5 ng/kg; PCB 105, 44.8 ng/kg; PCB 114, <50 ng/kg; PCB 118, 133 ng/kg; PCB 123, <5 ng/kg; PCB 126, <1.25 ng/kg; PCB 156, 130 ng/kg; PCB 157, 9.36 ng/kg; PCB 167, 45.8 ng/kg; PCB 169, <2.5 ng/kg; and PCB 189, 25.7 ng/kg. The PCB TEQ is 0.215 ng/kg (WHO 2005 including BG). Samples B, C, and D are TiO_2 for research purposes and contain PCBs 28, 52, and 101, <200 ng/kg; PCBs 138, 153, and 180, <400 ng/kg, with total PCB content of 1800 ng/kg. The dioxin-like PCBs



PCBs

PCDDs

PCDFs

x, y = 0 - 10 ; w, z = 0 - 8

Fig. 1 TiO₂ synthesis and origin of unintentional impurities of chlorinated POPs. TiCl₄ is produced by the chloride process, which involves the reduction of titanium oxide ores, typically ilmenite (FeTiO₃) with carbon under flowing chlorine at 900 °C (1). Around 90 % of the TiCl₄ production is used to make the pigment titanium dioxide (TiO₂) by hydrolysis (2) or direct oxidation in a plasma (3). During the TiCl₄ formation (1), unintentionally high and per-

chlorinated benzene, biphenyls, and naphthalenes can be formed (4). These POPs can be oxidized with oxygen at higher temperatures, with light in the presence of catalysts, for example TiO₂ forming ROS, and oxygen plasma combustion (5) into lower chlorinated POPs, hydroxylated ones, dioxins, and furans. Furthermore, PCBs can be oxidized with oxygen at higher temperatures in a sintering process, in the presence of catalysts like TiO₂ forming PCDDs and PCDFs (6)

are lower in concentration: PCB 77, <10 ng/kg; PCB 81, <5 ng/kg; PCB 105, <50 ng/kg; PCB 114, <100 ng/kg; PCB 118, <200 ng/kg; PCB 123, <10 ng/kg; PCB 126, <2.5 ng/kg; PCB 156, <20 ng/kg; PCB 157, <10 ng/kg; PCB 167, <20 ng/

kg; PCB 169, <2.5 ng/kg; and PCB 189, <20 ng/kg. The PCB TEQ is 0.415 ng/kg (WHO 2005 including BG). Sample E shows the least amount of PCBs (at least a factor of 3 less than in the other samples). The first four samples contain the same

Fig. 2 PCB congener distribution (in relative mass percentage %) and corresponding mass concentrations in nanograms per kilogram found in the commercial TiO₂ sample A. The dioxin-like PCBs are indicated in red (sample descriptions are included in the “Experimental part” section)

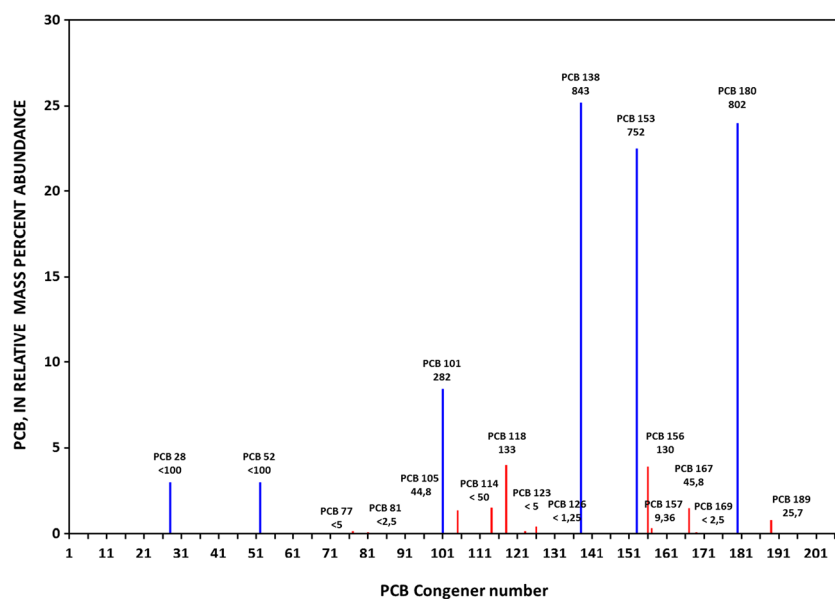
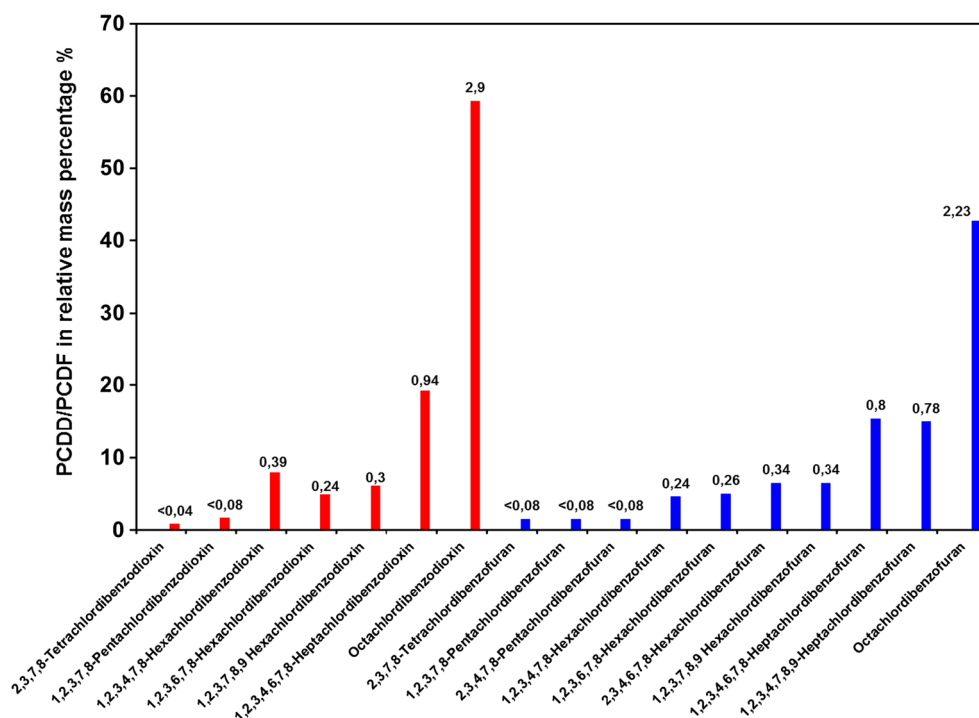


Fig. 3 PCDD and PCDF distribution (in relative mass percentage %) and respective mass concentrations (in ng/kg) found in the commercial TiO₂ sample E (sample descriptions are included in the “Experimental part” section)



PCBs and dioxin-like PCBs, but in the samples made for scientific purposes, the concentrations are on the order of two times lower, an indication of a further purification step during fabrication. The TEQ is higher in sample B, having therefore a projected higher toxicity. Penta- (PCB 101), hexa- (PCBs 138 and 153), and hepta-chlorinated (PCB 180) PCBs show the highest concentration in both samples. In the group of the dioxin-like PCBs, the same picture can be found: the penta- (PCBs 105, 114, 118, and 123), hexa- (PCBs 156, 157, and 167), and hepta-chlorinated (PCB 189) PCBs show the highest concentrations. This indicates that the concentration of chlorine in the process of formation is highly abundant due to the high chlorination degree. On the other side, substitution in the *ortho*-position is favored showing the higher concentration of non-coplanar PCBs compared to coplanar PCBs.

In the case of the PCDDs and PCDFs following picture emerges from Table 1. Samples A to D do not contain PCDDs and PCDFs with certainty, while sample E does. Concentrations of lower chlorinated PCDDs and PCDFs could not be found. The concentration of the hexa-chloro-dibenzodioxins 1,2,3,4,7,8-PCDD is 0.39 ng/kg, 1,2,3,6,7,8-PCDD is 0.24 ng/kg, and 1,2,3,7,8,9-PCDD is 0.3 ng/kg, while hepta-chlorinated PCDD clearly increases with 0.9 ng/kg for 1,2,3,4,6,7,8-PCDD and even higher for the fully chlorinated octa-PCDD at 2.9 ng/kg. The same trend is visible for the PCDFs; starting with hexa-chloro-dibenzofurans 1,2,3,4,7,8-PCDF with 0.24 ng/kg, 1,2,3,6,

7,8-PCDF with 0.26 ng/kg, 2,3,4,6,7,8-PCDF, and 1,2,3,7,8,9-PCDF showing both 0.34 ng/kg. Here, the concentration of the hepta-chlorinated 1,2,3,4,7,8,9-PCDF is also higher at 0.8 and 0.78 ng/kg for 1,2,3,4,7,8,9-PCDF. Further, the octa-chlorinated PCDF has the highest value at 2.23 ng/kg. The concentrations of the PCDDs and PCDFs are thereby comparable and, as mentioned above, indicate a similar formation route. Sample E is the only sample undergoing a sintering process. We suggest that PCBs on the TiO₂ are transformed in this sintering process in the presence of oxygen at high temperature into PCDDs and PCDFs (Fig. 1, Eq. 6), which might also explain the low and therefore uncertain concentrations of PCBs. This is an interesting result, showing that PCBs can potentially be transformed into PCDDs and PCDFs on the catalytic active surfaces of TiO₂ at high temperature and possibly under the influence of light. The absence of lower chlorinated PCDDs and PCDFs might be explained by the possible evaporation of the lower volatile congeners, being then present in the surrounding atmosphere. Furthermore, also environmental persistent free radicals could be formed from the chlorinated aromatics on the TiO₂ surface (Lomnicki et al. 2008; Patterson et al. 2013). However, we cannot with final certainty be clear about the pathway based only on our small sample size. To be able to do this, specific experiments need to be carried out to test our assumptions. These are currently ongoing, unraveling the potential formation route of PCDDs and PCDFs from PCBs.

Table 1 PCB, PCDD, and PCDF mass concentrations detected in 5 different commercial TiO₂ samples and their corresponding toxic equivalency (TEQ)

	Sample A	Sample B	Sample C	Sample D	Sample E
Polychlorinated biphenyls (PCBs) [ng/kg]					
PCB no. 28	<100	<200	<120	<160	<40
PCB no. 52	<100	<200	<120	<160	<40
PCB no. 101	282	<200	<120	<160	<40
PCB no. 138	843	<400	<240	<320	<80
PCB no. 153	752	<400	<240	<320	<80
PCB no. 180	802	<400	<240	<400	<80
Dioxin-like PCBs [ng/kg]					
PCB no. 77	<5	<10	<2	<8	<2
PCB no. 81	<2.5	<5	<1	<4	<1
PCB no. 126	<1.25	<2.5	<0.5	<2	<0.5
PCB no. 169	<2.5	<5	<1	<4	<1
PCB no. 105	44.8	<50	<30	<40	<10
PCB no. 114	<50	<100	<60	<80	<20
PCB no. 118	133	<200	<120	<160	<40
PCB no. 123	<5	<10	<6	<8	<2
PCB no. 156	130	<20	<24	<32	<4
PCB no. 157	9.36	<10	<6	<8	<2
PCB no. 167	45.8	<20	<12	<16	<4
PCB no. 189	25.7	<20	<12	<16	<4
Polychlorinated dibenzodioxins (PCDDs) [ng/kg]					
2,3,7,8-TCDD	<0.05	<0.1	<0.08	<0.12	<0.04
1,2,3,7,8-PeCDD	<0.1	<0.2	<0.16	<0.24	<0.08
1,2,3,4,7,8-HxCDD	<0.15	<0.3	<0.24	<0.36	0.39
1,2,3,6,7,8 HxCDD	<0.15	<0.3	<0.24	<0.36	0.24
1,2,3,7,8,9-HxCDD	<0.15	<0.3	<0.24	<0.36	0.3
1,2,3,4,6,7,8-HpCDD	<0.75	<1.5	<1.2	<1.8	0.94
OctaCDD	<2.5	<5	<4	<6	2.9
Polychlorinated dibenzofurans (PCDFs) [ng/kg]					
2,3,7,8-TCDF	<0.2	<0.1	<0.16	<0.24	<0.08
1,2,3,7,8-PeCDF	<0.2	<0.1	<0.16	<0.24	<0.08
2,3,4,7,8-PeCDF	<0.2	<0.1	<0.16	<0.24	<0.08
1,2,3,4,7,8-HxCDF	<0.3	<0.15	<0.24	<0.36	0.24
1,2,3,6,7,8 HxCDF	<0.3	<0.15	<0.24	<0.36	0.26
2,3,4,6,7,8-HxCDF	<0.3	<0.15	<0.24	<0.36	0.34
1,2,3,7,8,9-HxCDF	<0.3	<0.15	<0.24	<0.36	0.34
1,2,3,4,6,7,8-HpCDF	<1.5	<0.75	<1.2	<1.8	0.8
1,2,3,4,7,8,9-HpCDF	<1.5	<0.75	<1.2	<1.8	0.78
OctaCDF	<5	<2.5	<4	<6	2.23
Toxic equivalency (TEQ)					
PCB-TEQ (WHO 1997) exkl. BG	0.0906	—	0.122	0.324	0.0789
PCB-TEQ (WHO 1997) inkl. ½ BG	0.179	0.197	—	—	—
PCB-TEQ (WHO 1997) inkl. BG	0.267	0.395	0.0611	0.162	0.0395
PCB-TEQ (WHO 2005) exkl. BG	0.0117	—	0.0886	0.333	0.0831
PCB-TEQ (WHO 2005) inkl. ½ BG	0.113	0.208	—	—	—
PCB-TEQ (WHO 2005) inkl. BG	0.215	0.415	0.0443	0.166	0.0415

Sample descriptions are included in the “[Experimental part](#)” section

Conclusions

We presented our trace analysis of different standard commercially available nanoparticulate TiO₂ samples, revealing the presence of POPs, such as PCBs, PCDDs, and PCDFs. We inferred that these POPs are unintentionally formed during the fabrication process and presented the most probable pathway through the chlorination of the titanium ore. Moreover, our results point to a transformation of PCBs on the reactive surface of the TiO₂ nanoparticles to PCDDs and PCDFs under the influence of temperature, light, and oxygen. We hypothesize that lipophilic POPs including PCBs, co-occurring with polar NPs such as TiO₂-NPs are a toxicologically highly important new class of POPs (NP-POPs) with yet unknown properties due to their mixed physicochemical properties, such as polarity. Our findings pave the way to new insights in the possible toxicity of nanoparticulate TiO₂, being widely used as white color pigment in, e.g., paints and cosmetic products.

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