SUPPORTING INFORMATION

Nanoscale coloristic pigments: Upper limits on releases from pigmented plastic during environmental aging, in food contact, and by leaching

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As separate file, we provide a **movie from X-ray computed microtomography** of Fe_2O_3_PE plates weathered for 328 h (NP-02W), 1288 h (NP-08W), 1944 h (NP-12W) and 2928 h (NP-18W). The 18 weeks samples were obtained by prolonging irradiation of 12 weeks samples for 6 weeks but the water spraying frequency was reduced to 20 minutes per week. 2D slices parallel to sample surface are scanned from above the surface to 35 µm deep into the sample. Both the density of cracks and their depth increase with the aging time. The movie can be downloaded directly from Dropbox here:

https://www.dropbox.com/sh/mdbbfhxcag964ly/AACKbT5TwKvCpf4c_uqE94zDa?dl=0

MATERIAL DETAILS

Table S1. Physico-chemical properties of the organic DPP pigment and the inorganic Fe_2O_3 pigment. System-dependant properties (zeta-potential, reactivity, dissolution, dispersibility) were determined as specified for Tier 2 testing in the ECETOC grouping scheme.[1]

Abbreviations: FRAS: Ferric Reducing Ability of Serum, PSF: Phagolysosomal stimulant fluid, DMEM-FCS: cell culture medium containing 10% fetal calf serum.

	Organic DPP pigment	**Inorganic Fe_2O_3 pigment**
median particle size	43 ± 14 nm	35 ± 20 nm
specific BET surface	94 m^2/g	30 m^2/g
composition [elements in %]	C 60.9, H 2.8, N 7.8, O 9.0, Cl 19.9	Fe_2O_3, hematite
contaminations	no contaminations > 0.1%; Si, Br < 0.1%	no contaminations > 0.1%; Cr 32 ppm.
surface composition [elements in %]	C 77.1; O 10.9; N 5.9; Cl 6.1	C 50.7; 33.7; Fe 15.6
Hydrophobicity [contact angle]	135° (hydrophobic)	< 10° (hydrophilic)
Zeta-potential (pH 7, water)	-16 mV	+32 mV
Surface reactivity (FRAS)	non-oxidative	intermediate
Dissolution in PSF (pH 4.5)	0.1 ppm	<1 ppm
Dispersibilty (d50 in DMEM-FCS)	0.8 µm	0.3 µm

To simulate primary fragmentation, granules were frozen to cryogenic temperatures (at -193°C, liquid N2) to maximize their brittleness. Milling was done using an impeller breaker (Pallmann PPL 18) in which the frozen granules passed through a 0.3 mm gap between a rotor/stator impeller which rotated at 10,000 rpm (92 m/s circumferential speed).

The *iron* content was followed through all processing steps by complete acid digestion and ICP-MS analysis. The measured Fe contamination increases with each processing step, yet remains on a vanishingly low level compared to the intentionally added Fe_2O_3 nanopigments (Table S2). Another *organic* side component is introduced via the masterbatch pre-processing of pigments in LDPE wax. The composition was adjusted such that the materials had about the same content of LDPE wax (2%) although the pigment content (0.2% OrgPig vs. 1% Fe_2O_3) was different. No other contamination above 0.1% level is known for the LDPE or HDPE materials.

Table S2 Elemental analysis of bulk iron content (acid digestion + ICPMS)

Material	Fe content
PE granule (SYN)	< 3 mg/kg
PE plate (FOR)	4 mg/kg
PE_FP (USE)	35 mg/kg
Fe_2O_3_PE granule (SYN)	5,800 mg/kg
Fe_2O_3_PE plate (FOR)	5,800 mg/kg
Fe_2O_3_PE_FP (USE)	5,700 mg/kg

METHOD DETAILS

Release during and after matrix degradation by simulated sunlight (scenarios I & II)

Aging protocols

Degradation of the PE matrix induced by outdoor exposure was simulated by artificial weathering under Xenon lamps. The method used is compliant with the procedure already used and described by the *NanoRelease initiative*.[2, 3] Identical standard UV specimen intensities were applied to chosen

life cycle stages of both case studies according to ISO protocol 4892-2A (UV 300-400 nm, 50 W/m^2, dry/wet cycles: 102 min/18 min) which was found to accelerate aging compared to outdoor weathering by a factor of 8-30 in case of a closely related polyolefin (polypropylene, PP) matrix.[4] Plates of both nanocomposites (Fe$_2$O$_3$_PE_USE and OrgPig_PE_USE) and corresponding pure PE references were placed on the bottom of a climate chamber (Atlas Ci 5000). Total weathering time was 12 weeks corresponding to a UV dose of 363 MJ/m^2. For the inorganic pigment case study, time series of 4 and 8 weeks were additionally applied.

In addition, a modified weathering scheme derived from ISO protocol 4892-2A was used for the inorganic pigment case study and the pure PE reference allowing the collection of run-off waters over 12 weeks (scenario I). For this, plates of Fe$_2$O$_3$_PE and PE were placed into a weathering chamber Suntest XLS+ in 800 ml glass beakers with slanted PTFE supports to avoid sample immersion in water and promote water streaming on the surface (see Figure S1 in SI). To avoid heterogeneity in spraying distribution, a rotating plate operated on batteries was mount into the climate chamber and served as support for the beakers. Irradiation was adjusted to a nominal intensity of 35 W/m^2 resulting in 52 W/m^2 at the elevated position of plates (extra height of ca 18 cm with respect to chamber floor), thus allowing the comparison with materials weathered according to the original ISO protocol 4892-2A described above. Spray frequency and duration of wet and dry cycles were adjusted as well to avoid flooding of the beakers. ISO 4892-2 defines 2h weathering cycles, alternating dry phases of 102 minutes and 18 minutes water spray. In our configuration, samples were flooded after 3 cycles. An optimization of the weathering cycles with respect to our experimental setup was then undertaken. Spray frequency and duration were reduced and finally adjusted to 3 short spray phases (2 min) every 7 h, followed by a 2 h cycle consisting in a 110 minutes dry phase and 1 spraying event of 10 min. The test program was stopped three times a week (on Monday, Wednesday and Friday) to recover the water collected in the beakers. The modified test program is detailed in Table S3.

Moreover, FP of the iron containing nanocomposite were spread in a glass tray which was placed at the bottom of a climate chamber (Suntest XLS+). In this case, dry aging conditions were applied (UV light only, 50 W/m^2). To ensure homogenous irradiation of the whole sample, fragments were mixed with a paper comb three times a week during the whole duration of 12 weeks. An aliquot was taken out from each tray every two weeks.
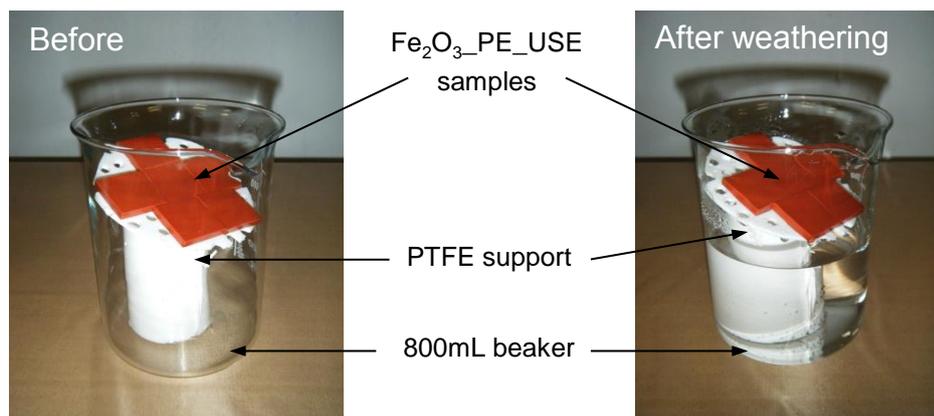
Figure S1. Beakers and PTFE supports used in weathering experiments, before being introduced in Suntest XLS+ (left) and after 46h weathering (right)

Analysis of matrix degradation

Matrix degradation was determined with emphasis on morphological, chemical and structural changes. Morphological degradation was studied by *gloss retention* measurements (measuring angle 60°), *scanning electron microscopy (SEM,* JSM 7500 TFE, Jeol or Strata 400, FEI, after 9nm Pt coating, detecting secondary electrons) and *X-ray tomography* (microXCT-400 X-ray microscope, Zeiss Xradia, 40 kV, 2501 projections x 20s, voxel size = 0.51 μm). Chemical degradation of the samples was assessed by *Fourier Transform Infrared Spectroscopy (FTIR)* in the Attenuated Total Reflectance (ATR) mode. Spectra were collected between 4000 - 400 cm^{-1} (resolution 4 cm^{-1}) on a Nicolet NEXUS spectrometer equiped with Smart Orbit ATR. These collected spectra were averaged over 64 scans. For each sample the analysis was performed on three different locations to take into account for potentially heterogeneous degradation, but on average the variability was only 25% for the three locations (error bars of Figure 5). In addition, plates of the inorganic pigment case study were weighed on a Sartorius CP 324S precision scale before insertion and after withdrawal from the climate chamber to evaluate mass loss of the specimen during aging. The accuracy of the weighing was 0.25 mg.

Release sampling

Two different sampling methods were implemented to assess spontaneous release during weathering (scenario I) and release induced by immersion and mechanical stimulation on aged materials (scenario II). Spontaneous release was only determined in the Fe_2O_3 case study. Run-off waters were collected from all beakers (containing either Fe_2O_3_PE or pure PE plates) during

weathering according to the modified ISO 4892-2A protocol (Table S3) three times a week. Release induced by immersion and mechanical stimulation on plates weathered according to the original ISO 4892-2A was investigated for both case studies. The applied release sampling method was already described in detail in the literature.[5, 6] Briefly, the aged plate surface was immersed in H_2O containing 0.5 g/l SDS (Sodium Dodecyl Sulfate) over 24 h or immersed under same conditions and sonicated afterwards over 1 hour (single determination). For both scenarios, the pure PE reference material was treated and investigated equally.

Table S3. Modified weathering scheme derived from ISO protocol 4892-2A used for plates of the inorganic pigment case study. Irradiation was adjusted to a nominal intenstity of 35 W/m^2 resulting in 52 W/m^2 at the elevated position of plates, thus allowing the comparison with materials weathered according to the original ISO protocol 4892-2A.

Weekday	Duration dry/wet (min)
Mo - Fr	415/5
	418/2
	418/2
	110/10
Fr - Mo	438/2
	438/2
	438/2
	110/10

Quantification and characterization of released fragments

Quantification of spontaneous release during weathering (scenario I)

Iron content in run-off waters was analyzed by ICP-MS (Perkin Elmer Nexion 300, operated in collision mode) to estimate spontaneous release of free Fe **(dissolved and particulate)** during the weathering procedure. The digestion of Fe_2O_3 in run-off waters was carried out beforehand in an UltraWAVE microwave digestion system. 1 ml of samples was placed in PTFE vessels with 1 ml HCl 32%-35% (PlasmaPure) and inserted into the microwave system. Temperature was raised to 250°C in 20 minutes, maintained over 15 minutes and then allowed to cool down to room temperature in 25 minutes. After digestion, yellow solutions were recovered from PTFE vessels, without any visible precipitate. 2 ml Milli-Q water were used to rinse PTFE vessels, resulting in a final sample volume of 4 ml (dilution 1:4). Iron content was determined by ICP-MS via quantitative analysis of ^{56}Fe.

Quantification and characterization of induced release after weathering (scenario II)

Detection of fragments **(dissolved, particulate, and embedded Fe)** released during immersion of plates after weathering was done by *UV/Vis spectroscopy* (Ocean Optic USB4000 spectrometer) at a wavelength of 244 nm. For very low content of scattering or absorbing particles, this wavelength offers the best signal-to-noise with our instrument. For the quantification of fragments from plates after weathering, an *Analytical Ultracentrifuge (AUC*, Beckman Ultracentrifuge type XLA with integrated absorption optics) was used, as described in detail earlier.[6, 7] Immersion waters were investigated with speed ramps from 1,000 to 20,000 rpm to ensure complete coverage of the relevant measurement interval between 1 μm down to several nm. The AUC quantification and detection limits for both pigments are 10 and 1 ppm, respectively. Pure H_2O and H_2O with 0.5 g/l SDS were studied as negative controls. In addition, released fragments in immersion waters were assessed using a *transmission electron microscope (TEM)* from FEI, Type Strata 400 DB, equipped with a field emission cathode.

Release in food contact (scenario III)

Release in food contact was estimated on granules of the inorganic pigment nanocomposite (Fe_2O_3_PE_FOR) as they comprise a higher surface area compared to plates, but still have macroscopic dimensions. Pure PE granules (PE_FOR) were used as control. 1 g of material was weighed into PP tubes and 10 ml of a food simulant (pure Milli-Q water, Milli-Q water with 10% ethanol, or Milli-Q water with 3% acetic acid) were added resulting in a final concentration of 100 g/l. All samples were prepared in triplicates and were incubated for 10 days at 40°C, according to the European Commission Directive (No. 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food. Off J Eur Comm, 2011, 828 50, 1-89.) for articles intended to be in contact with food. After incubation samples were prepared for total Fe release measurements **(dissolved, particulate, and embedded)** by evaporating the solutions (after separation of the granules) and performing microwave-assisted (Multiwave 3000, Anton-Paar) acid digestion (using 6 mL 65% HNO_3, 2 mL 40% HF, 2 mL 35% HCl). Samples were subsequently diluted with Milli-Q water and analyzed by ICP-MS (Agilent technologies, 7700x) for isotope [56]Fe.

Table S4. Instrumental settings for the detection of Fe in single particle mode (spICP-MS, Agilent 7900)

RF power	1550 W
Plasma gas flow rate	15 l/min
Carrier gas flow rate	0.98 ml/min
Makeup gas flow rate	0.19 ml/min
Nebulizer	Micromist
Isotope monitored	^{56}Fe
Integration time	5 ms
Sample flow rate	390 µl/min
Acquisition time	60 sec
Cell gas/flow rate	H_2/5 ml/min

Release by leaching in environmentally relevant media (scenario IV)

The leaching of iron from fragmented products **(dissolved and particulate)** of the Fe_2O_3 case study was assessed in three environmentally relevant media, namely Milli-Q water (DIW, pH 6.5), moderately hard EPA water (pH 7.6, a representative of fresh water containing mixture of mono- and divalent cations Na+, K+, Ca2+ and Mg2+, prepared according to the 2002 EPA guideline), and Suwannee River Humic Acid (SRNOM, 1 mg/l dissolved organic carbon (DOC), pH 8.0) by single-particle ICP-MS.[8, 9]

1 g of PE_FP and Fe_2O_3_PE_FP was weighed into PMP bottles (Nalgene) and 100 ml of leaching media was added (10 g/l). Both as-produced and aged materials were investigated. Samples were rotated end over end at room temperature for 3 months and then directly ^{56}Fe was measured by single particle Inductively Coupled Plasma Mass Spectrometry (spICP-MS, Agilent 7900 ICP-MS, Agilent Technologies, Santa Clara, CA), allowing the detection of both total Fe content and presence of Fe particles. spICP-MS is very powerful with regard of release measurements as it meets the requirements of a very high sensitivity (ng/l), high throughput, and robustness.[9] In addition, it directly detects particle number concentration and particle mass. For natural metal colloids spICP-MS was first described by Degueldre et al.[10] and further adopted for analysis of silver nanoparticles in various matrices like in waste water[11] or in enzymatic digested chicken meat.[12] In our study, hydrogen was used as a reaction gas at a flow rate of 5 ml/min to remove the polyatomic $^{40}Ar^{16}O$ interference on isotope ^{56}Fe (Table S4). Background iron concentration was measured in each pure leaching media as well and subtracted from sample data.
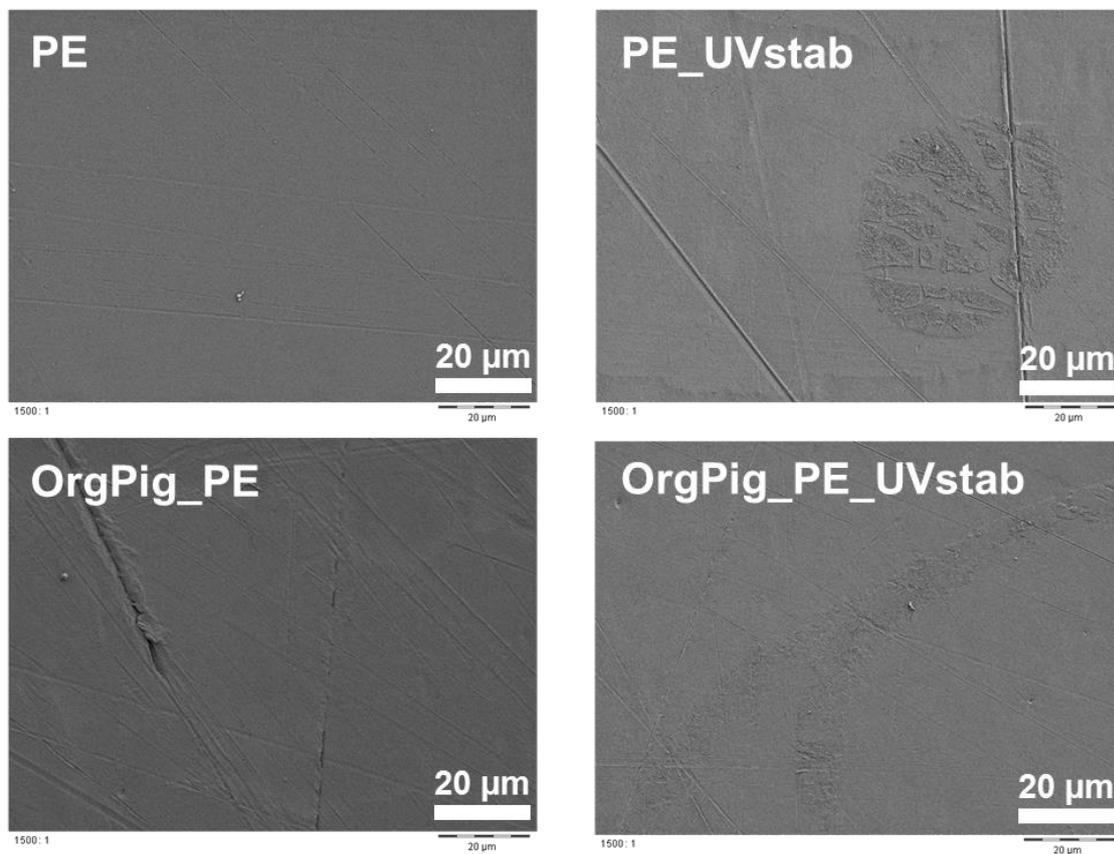
Figure S2. SEM images for pure PE and the organic pigment composite, both with and without stabilizer, after wet weathering over 12 weeks
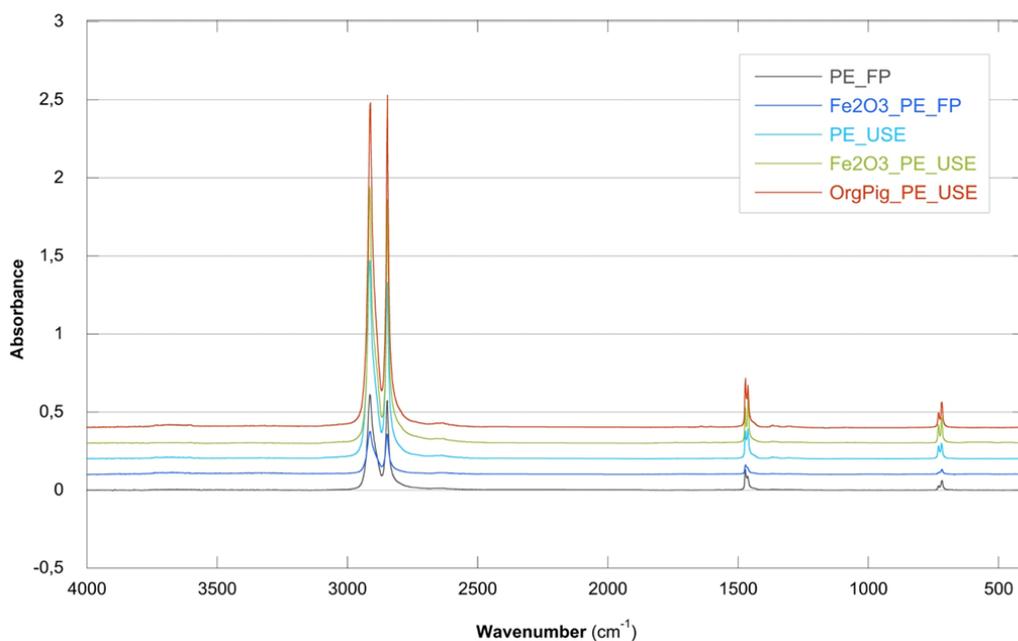
**Figure S3.** FTIR spectra recorded for as-produced materials: fragmented products of pure PE (PE_FP, gray) and Fe$_2$O$_3$_PE (Fe$_2$O$_3$_PE_FP, dark blue), plates of PE (PE_USE, light blue), Fe$_2$O$_3$_PE (Fe$_2$O$_3$_PE_USE, green) and OrgPig_PE (OrgPig_PE_USE, red).

After aging, a discrepancy is observed between the carbonyl index calculated for PE plates weathered according the two different protocols. For comparable exposure times, the original ISO protocol 4892-2A induces a stronger PE oxidation. In addition, the C=O bands of nanocomposite and reference plates weathered by the same protocol display a similar shape, while they clearly differ when comparing the original and modified protocol. The analysis of the carbonyl region by deconvolution techniques shows that conjugated ketones (1698 cm^{-1}) and esters (1735 cm^{-1}) are formed in all samples. However, carboxylic acids (1714 cm^{-1}) were only found in a significant amount on PE and OrgPig_PE plates weathered according to ISO 4892-2A. In the modified ISO protocol, ketones (1720 cm^{-1}) are preferentially produced and/or accumulated. Finally, γ-lactones (1780 cm^{-1}) can only be detected on Fe$_2$O$_3$_PE plates, maybe because of the strongest oxidation of this sample. As the presence of different oxidation products in the materials depends on the applied protocol, we assume different mechanisms of oxidation. As the main difference between the two protocols is the water spraying frequency (dry/wet cycle of 102min/18min for ISO 4892-2A versus 415min/5min for the modified protocol), hydrolysis might have contributed in a non-negligible way to PE oxidation.
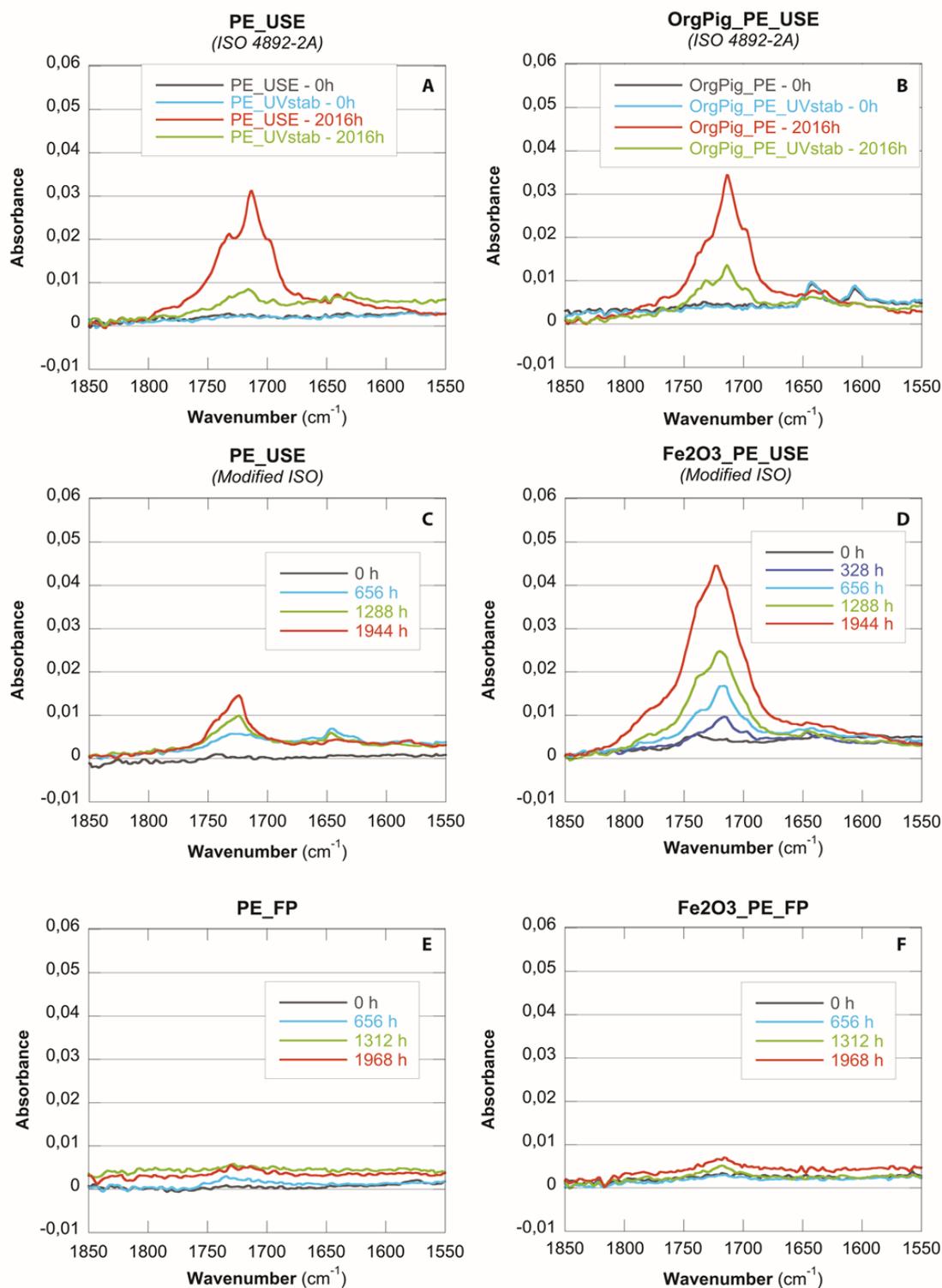
Figure S4. Evolution of the carbonyl band in FTIR spectra of (A) PE and (B) OrgPig_PE plates weathered according to ISO 4892-2A protocol; (C) PE_USE and (D) Fe$_2$O$_3$_PE_USE weathered according to the modified ISO protocol; (E) PE_FP and (F) Fe$_2$O$_3$_PE_FP weathered in Suntest XLS+ under dry conditions.
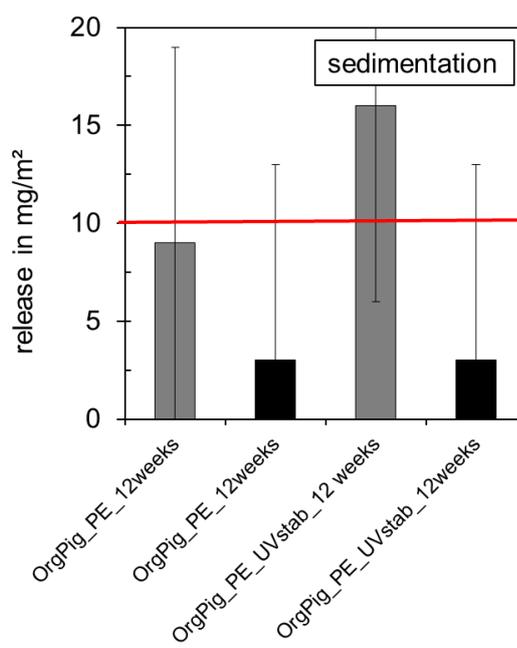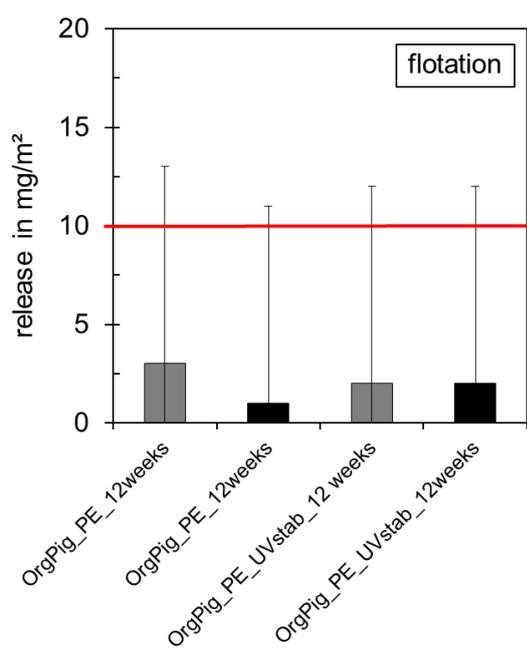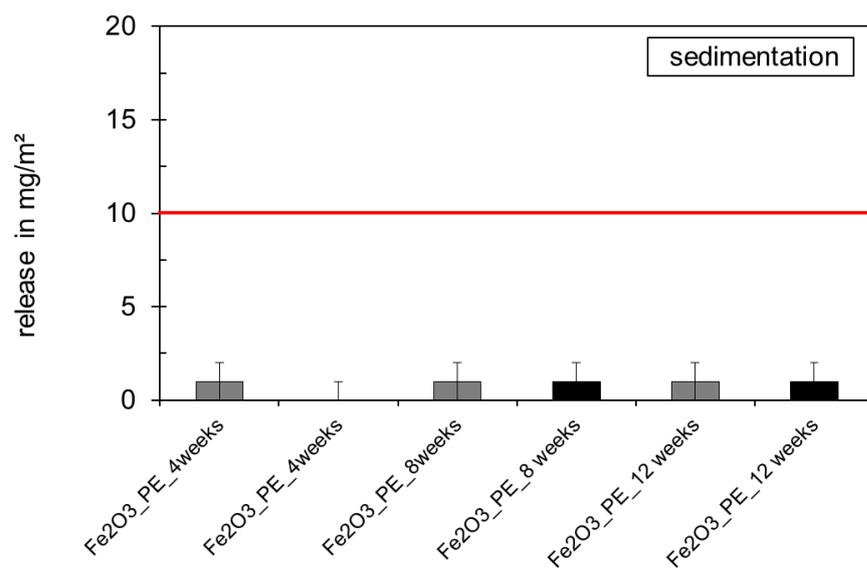
Figure S5. Results of analytical ultracentrifugation given as release in mg/m² for aged materials. Release sampling in both cases was performed by both 24h immersion (grey) and 24h immersion & 1h sonication (black).
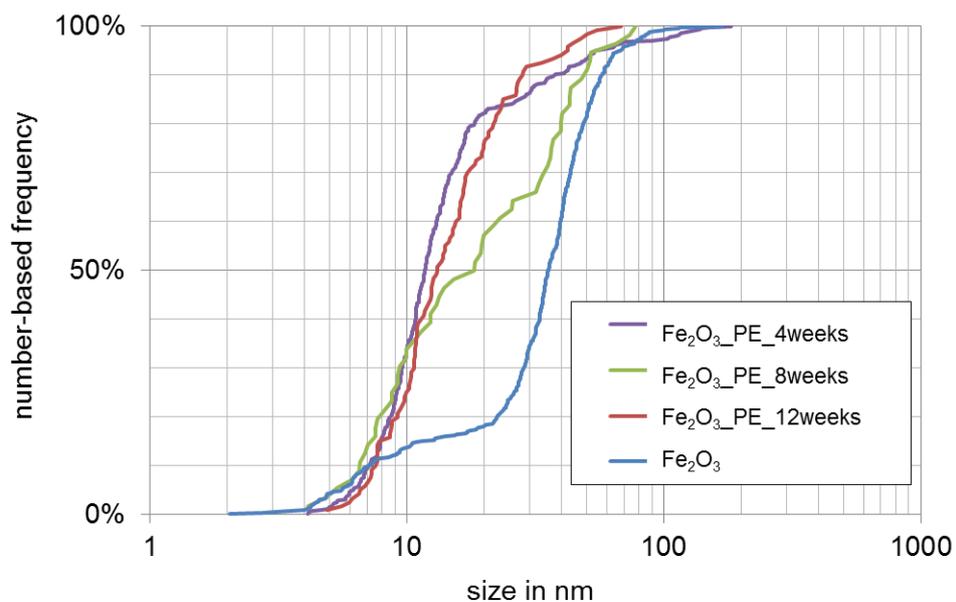
Figure S6. Size distributions determined based on TEM images for the pristine Fe_2O_3 pigment powder (blue line) and for iron-containing fragments in immersion waters of aged $Fe_2O_3\_PE$ plates. The median diameters of constituent particles are much smaller for the fragments in immersion waters (12, 18, 13 nm respectively for 4, 8, 12 weeks of aging) compared to pristine Fe_2O_3 (35 nm).
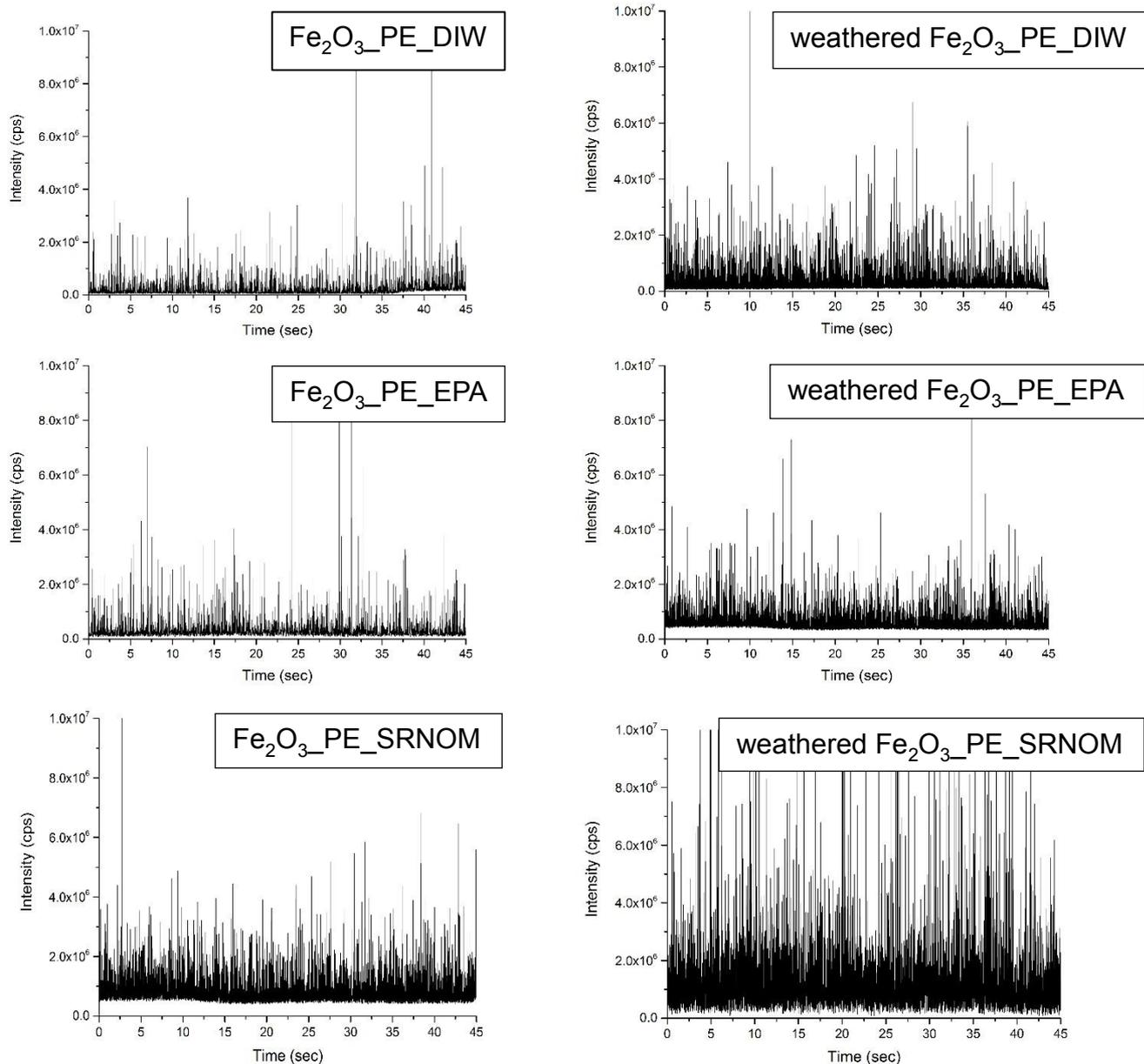
Figure S7. spICP-MS analysis elugrams of weathered and non-weathered PE_Fe_2O_3 in 3 different leaching media

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