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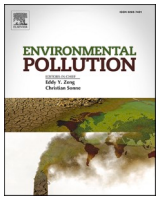

Environmental formation of sulfonated-PCBs and OH-sulfonated-PCBs: Is it greater under aerobic or anaerobic conditions?☆

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ABSTRACT

The aerobic and anaerobic degradation of PCBs is well documented in literature. On the other hand, OH-sulfonated- and sulfonated-PCBs are newly discovered metabolites, therefore, little information is known about their fate in the environment. For instance, their formation in anaerobic conditions was never investigated. In the current paper, aerobic, anaerobic-aerobic (two steps mode) and anaerobic treatments were set up to compare for the first time the OH-, OH-sulfonated- and sulfonated-PCB production in different oxic and anoxic conditions. For this purpose, leaves of *Quercus ilex* were used as microbial inoculum in 40 mL vials spiked with PCB 155 used as individual contaminant. In general, all three classes were produced in every condition. The aerobic treatment was the best one, as the highest concentrations and number of congeners were detected. Then, the more oxygen decreases, the lower the concentration of metabolites formed: aerobiosis > anaerobiosis-aerobiosis > anaerobiosis. In addition, the same chlorination families for each class were formed, except for the anaerobiosis-aerobiosis treatment, where a hexa-Cl-sulfonated-PCB was also detected.

1. Introduction

The manufacture of polychlorinated biphenyls (PCBs) was globally banned in 2001 by the Stockholm Convention, since these chemicals were classified as persistent organic pollutants (POPs) (UNEP, 2001). However, due to their recalcitrant nature, PCBs are still present in the environment and are well known for the toxic effects they can induce on both humans and the environment (Humphrey et al., 2000; IARC, 2016). Their use in many industrial applications led to their release into the environment, causing soil, sediment and water contamination worldwide. PCBs persist in these compartments due to slow degradation processes involving organisms and microorganisms (Borja et al., 2005). It is commonly assumed that PCBs can be degraded both anaerobically and aerobically. Anaerobic microbes degrade PCBs with more chlorine atoms through reductive dechlorination, preferentially removing chlorines in *meta*- and *para*-position (Abramowicz, 1995). On the other hand, aerobic microorganisms attack the lower chlorinated PCBs with oxidative processes, using these chemicals as a carbon and energy source. PCBs are thus converted to chlorobenzoic acid, which in turn can be converted to carbon dioxide, water, chloride and biomass (Borja et al., 2005; Field and Sierra-Alvarez, 2008). Several studies demonstrated the efficiency of two types of approaches coupling these two PCB degradative pathways (Chen et al., 2014; Evans et al., 1996; Long et al., 2015; Master et al., 2002; Pathiraja et al., 2019; Payne et al., 2013). One approach involves an initial step in anaerobiosis and a second step in aerobiosis. The other approach consists of alternating these two conditions.

In the current work, the two steps mode is one of the conditions chosen to test the degradation of PCB 155 and the resulting formation of sulfonated-polychlorinated biphenyls (sulfonated-PCBs) and hydroxy-sulfonated-polychlorinated biphenyls (OH-sulfonated-PCBs), two newly discovered classes of environmental contaminants. The PCB 155

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was selected for several reasons. First, it is a hexa-chlorinated congener, and the hexa-PCB family is one of the most abundant. Furthermore, it was already used as a model compound in previous experiments (Palladini et al., 2025a, 2025b, 2022) and, being a symmetrical congener, the potential formation of isomers is reduced. Therefore, the metabolites detected are more likely to be related to the parent compound. For instance, if one of the H-atoms in the free 4 meta-positions is substituted by the -SO3H group, just one type of sulfonated-hexachloro biphenyl can be formed (Palladini et al., 2025b).

Sulfonated-PCBs were identified for the first time in polar bear serum (Liu et al., 2018) and, shortly after, they were detected, together with the OH-sulfonated-PCBs, in agricultural soil samples collected from a heavily PCB contaminated site (SIN Brescia-Caffaro) located in Northern Italy (Bagnati et al., 2019). Following studies focused on the environmental fate of these new contaminants, highlighting their ability to bioaccumulate in earthworms (Palladini et al., 2022) and plant roots and their persistence as well as their higher mobility through percolating water in soil, owing to their higher polarity than the respective parent compounds (Palladini et al., 2023). No information exists on their ecotoxicological and toxicological properties, although it was shown there are present in the environment as newly discovered PCB metabolites (Bagnati et al., 2019; Palladini et al., 2023). In addition, the role of microorganisms in their formation was also investigated (Li et al., 2021; Palladini et al., 2025a, 2025b). Palladini and colleagues (Palladini et al., 2025a, 2025b) showed that both classes can be produced from PCBs under aerobic conditions through the degradative action of different microbial inocula. However, experiments in which PCBs are biotransformed into sulfonated- and OH-sulfonated-PCBs under anoxia are scarce in the literature, especially on the role of oxygen level in the production of metabolites. The aim of the current study is therefore to test three different conditions: anaerobiosis, aerobiosis and anaerobiosis-aerobiosis, with leaves of *Quercus ilex* used as microbial inoculum, in the degradation of PCB 155. No attempts were made to identify microbial species or consortia, specific metabolite concentrations nor pathways. The inoculum from leaves of *Quercus ilex* was chosen as it efficiently formed PCB OH-, OH-sulfonated- and sulfonated-PCBs in two previous experiments (Palladini et al., 2025a, 2025b).

2. Materials and methods

2.1. Experimental design and setup

Vials (n = 36) were filled with 20 mL of sterilized mineral medium (MM), spiked with PCB 155 and added with one fresh leaf of *Quercus ilex* each. The mineral medium had the following composition: 900 mg L^{-1} KH_2PO_4, 100 mg L^{-1} K_2HPO_4, 80 mg L^{-1} $CaCl_2$, 100 mg L^{-1} NH_4NO_3, 100 mg L^{-1} $MgSO_4{\cdot}7\ H_2O$, 2 μgL^{-1} $Na_2B_4O7{\cdot}10\ H_2O$, 2 μgL^{-1} $MnSO_4{\cdot}H_2O$, 2 μgL^{-1} $CuSO_4{\cdot}5\ H_2O$, 1.4 μgL^{-1} $Na_2MoO_4{\cdot}2\ H_2O$, 2 μgL^{-1} $ZnSO_4{\cdot}H_2O$, and 10 μgL^{-1} $FeCl_3{\cdot}6H_2O$ (Terzaghi et al., 2021). The spike solution was prepared by dissolving 172 mg of PCB 155 in 100 mL of acetone, resulting in a concentration of 43 μg/mL in each vial. The reason for such high concentration lies in the need of guaranteeing a reasonably high bioavailable concentration to assure metabolite production in the relatively short experimental time. 12 vials for the aerobic treatment were sealed with a cap, whose septum was replaced with a 0.45 μm filter, to prevent microbial contamination, and placed on a shaker to be continuously stirred for 20 days. On the other hand, 12 vials for the anaerobic treatment were sealed with a septum cap that was pierced with a syringe to inject N_2 and make the environment anoxic. Then, each cap was covered with parafilm. These vials were maintained under static conditions for the entire duration of the experiment. Anoxia was verified by setting up 3 more vials under the same conditions with the Resazurin Anaerobic Indicator. The other 12 vials were used for theanaerobic-aerobic treatment. In the first half of the experiment, vials were kept under the same anaerobic conditions described above. In the second half, however, aerobiosis was restored. In addition, two sterilized flasks (250 mL) were used as sterile controls to assess abiotic degradation in dark/light conditions. All operations were performed in a presterilized laminar flow hood. Each flask was filled with 100 mL of sterilized mineral medium (MM) and spiked PCB 155 at the same concentration as the treatments. The experimental setup is illustrated in Fig. 1.

On the 7th and 21st day, 6 vials at a time (pooled two by two for a total of 3 replicates for each sampling time and treatment) were sacrificed and thoroughly extracted to remove potentially formed metabolites.

2.2. Chemicals and reagents

Cyclohexane and ethyl acetate were purchased from Honeywell (Carolina, USA). HPLC solvents and reagents were of pesticide or LC-MS grade: water (in house Milli-Q apparatus), acetonitrile and acetone, (Honeywell) methanol, formic acid and ammonium acetate (Chem-Lab NV). OH-PCB pure standard (4-hydroxy-2,2′,3,4′,5,5′,6-Heptachlorobiphenyl, OH-PCB-187) was purchased from Wellington Laboratories (Guelph, ON, Canada) and had a purity of ≥99 %. A hexa-Cl -sulfonated-PCB standard (corresponding to the sulfonated-PCB 155, or 2,2′ 4,4′ 6,6′-hexachloro-[1,1′ -biphenyl]-3-sulphonic acid) was synthesized by our group and described in a companion paper (Maspero et al., 2023), as well as the PCB 155 (purity of 99 %) used in the experiment. Supelclean ENVI-18 3 mL cartridges were purchased from Merck (Darmstadt, Germany). Mineral medium salts were obtained from several suppliers: $FeCl_3$ (≥98 %, Fisher scientific); $MnSO_4$ (98 %, BDH Laboratory Supplies); $ZnSO_4 \cdot 7$ H2O (≥99 %, Sigma-Aldrich); $Na_2MoO_4 \cdot 2$ H2O (>99 %, Acros organics); KH_2PO_4 (>99.5 %, Fisher scientific); K_2HPO_4 (≥99 %, Fisher scientific); $MgSO_4 \cdot 7$ H2O (99.5 %, Acros organics); NH_4NO_3 (≥98 %, Fisher scientific); $CaCl_2$ (99 %, BDH Laboratory Supplies); $CuSO_4$ (≥99 %, Fisher chemicals), $Na_2B_4O_7 \cdot 10$ H2O (≥99.5 %, Sigma-Aldrich). Plate Count Agar (PCA) and Sabouraud Dextrose Agar (SGA) were purchased from Fisher scientific.

2.3. Extraction and analysis of OH-, OH-sulfonated and sulfonated-PCBs

Mineral medium. The analytical method used to extract mineral medium samples was presented in (Palladini et al., 2023) as the first method setup for the extraction of sulfonated and OH-sulfonated-PCBs from the aqueous phase. Briefly, the extraction was performed with the ENVI-C18 SPE cartridges by acidifying the samples with 0.1 % formic acid. Methanol and cyclohexane were used to elute the cartridges.

Leaves. Leaf extraction was performed by sonicating samples with 40 mL of a mixture of Acetone:MilliQ water (95:5 v/v) solution added with 1 % formic acid for 1 h and later with 40 mL of cyclohexane:ethyl acetate (1:1 v/v).

Vials. The vials were first rinsed with 15 mL of a mixture of Acetone: MilliQ water (95:5 % v/v) solution containing 1 % formic acid solution and then with 15 mL of a mixture of Cyclohexane:Ethyl acetate (1:1 v/v) solution. These solvents were then mixed with the previously extracted mineral medium.

After being extracted, all samples were concentrated with a rotary evaporator, further evaporated under nitrogen and reconstituted with 1 mL of acetonitrile before being injected in a Thermo Fisher Scientific HPLC-HRMS, a Vanquish LC system coupled to an Orbitrap Exploris 120 high resolution mass spectrometer, run at 30,000 resolution. More details on the analytical procedure are given in **Text SI-1**. In all treatments, concentrations are referred to the sum of extracted leaf and mineral medium.

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

OH-PCB-187 and sulfonated-PCB 155 were used to quantify the detected metabolites (more information on the quantitative analysis are given in **Text SI-1**). To evaluate possible cross-contamination,

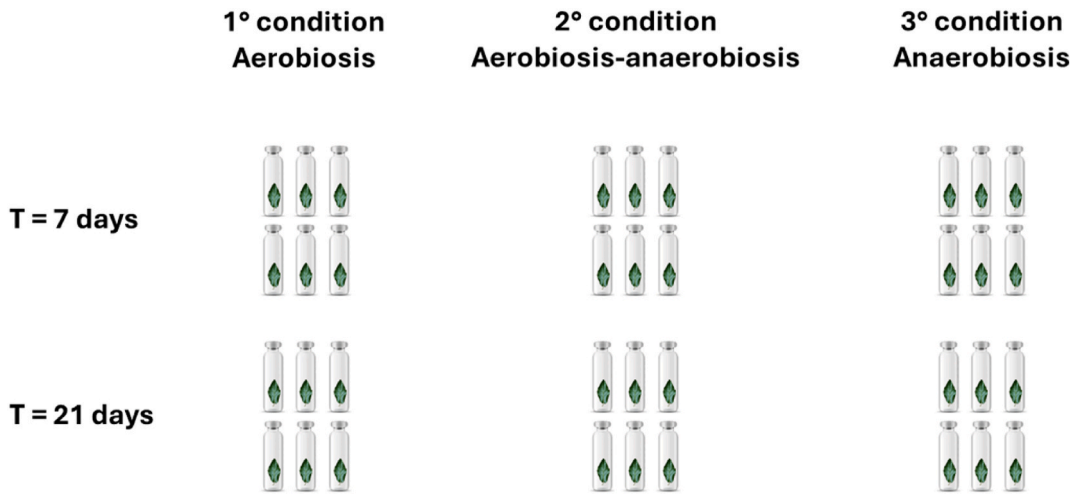

Fig. 1. – Experiment setup. Three conditions (aerobiosis, anaerobiosis-aerobiosis and anaerobiosis) and two sampling times (T7 and T21).

laboratory blanks (solvents) were included at a rate of one per sample batch and extracted following the same procedures as for samples. The extraction recovery of internal standard from the aqueous phase was complete (139 ± 15 %) (Palladini et al., 2023), whereas it was 75 ± 10 % for leaves (Bagnati et al., 2019). The spike solution was also analyzed for metabolites and, if found, they were subtracted from those in the

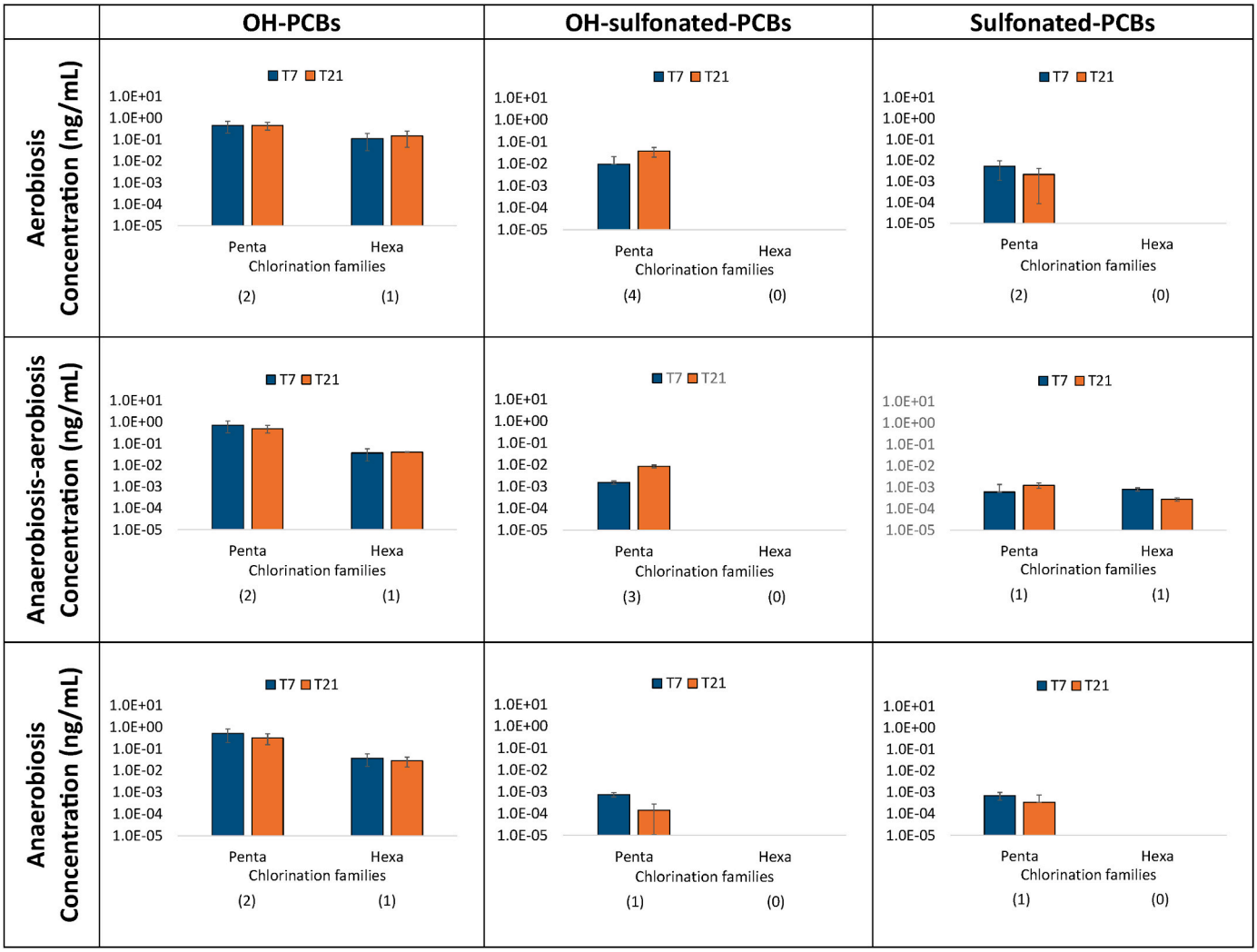

Fig. 2. – Average concentration (ng/mL) on a log scale of OH-PCBs, OH-sulfonated-PCBs and sulfonated-PCBs in each treatment (aerobiosis, anaerobiosis-aerobiosis and anaerobiosis). The number in brackets below each box plot indicates the total number of congeners detected for each class. Error bars represent standard deviation. No significant differences ($p < 0.05$) were found between pairs of the same chemical class between T7 and T21, for all treatments.

experimental samples.

2.5. Plate counting

The initial colony forming units (CFUs) were determined for leaves before the start of the experiment by serial dilutions (from 10^{-1} to 10^{-8}) and the spread plate method. The first dilution (10^{-1}) was obtained by diluting the pellet sample deriving from leaf extraction (60 leaves extracted in 400 mL of *0.1 M potassium dihydrogen phosphate buffer* that was subsequently centrifuged) in some mL of physiological solution reaching a total volume of 10 mL. From this dilution, an additional seven subsequent dilutions were obtained. Then 200 μL of each of these diluted solutions were plated in Plate Count Agar (PCA) and Sabouraud Dextrose Agar (SDA) plates to evaluate the microbial abundance of leaves before the start of the experiment. After 4 days of incubation at 20 ± 1 °C, results were expressed as CFU per cm^2 of leaves.

2.6. Statistical analysis

Principal component analysis (PCA) and ANOVA were performed using Xlstat 2023.1.2 (Lumivero Inc., Denver, CO, USA) on all the metabolites formed by each treatment at both sampling times (T7 and T21). PCA was also performed including data from (Palladini et al., 2025b) to compare the results.

3. Results and discussion

The initial bacterial and fungal cultivable fraction associated to *Quercus ilex* leaves was 6.5 × 10^3 CFU cm^{-2} and 6.4 × 10^3 CFU cm^{-2} respectively. No metabolites were formed in control samples. As for aerobic, anaerobic-aerobic and anaerobic treatments, different results were obtained, as shown in Fig. 2. In general, OH-PCBs was the most produced class in terms of concentration (~1-10^{-1} ng/mL), followed by OH-sulfonated-PCBs (10^{-1}-10^{-4} ng/mL) and sulfonated-PCBs (10^{-2}-10^{-4} ng/mL). In all treatments, penta- and hexa-OH-PCBs were detected at comparable concentrations, that did not vary between 7 and 21 days. However, the level of the penta-family was higher than that of the hexa-family, by up to an order of magnitude. On the other hand, for OH-sulfonated-PCBs, only penta-congeners were found, and at decreasing concentrations as the available oxygen decreased: aerobiosis > anaerobiosis-aerobiosis > anaerobiosis. Their level did not change over time ($p > 0.05$). As for sulfonated-PCBs, penta-congeners were detected in aerobiosis, penta- and hexa-in anaerobiosis-aerobiosis and penta-in anaerobiosis. Even in this case, the concentration of penta-sulfonated-PCBs decreased with oxygen availability, therefore, under anoxia their production was lowest. They also did not appreciably change with time. Interestingly, a hexa-Cl-sulfonated-PCB only appeared in the two-step treatment.

In general, the aerobic treatment prevailed over the others, also when looking at the number of congeners formed for each family within each class (mainly penta-OH-sulfonated-PCBs).

The type of inoculum used in this experiment was selected from a previously published work which investigated the ability of different microbial inocula to form OH-sulfonated- and sulfonated-PCBs (Palladini et al., 2025a). In this study, 3 fresh leaves of Quercus ilex were exposed to a native PCB mix (10 μg/mL) in aerobic conditions, and this inoculum showed the ability to form the highest concentration of OH-sulfonated-PCBs (~1 ng/mL) and sulfonated-PCBs (~10^{-2} ng/mL). Instead, the level of OH-PCBs was comparable to that produced by the other experimental inocula (around 10^{-1} ng/mL). In the current paper, the same inoculum showed different results, also when compared to those obtained in aerobiosis. OH-PCBs was the most produced class (almost 1 ng/mL), followed by OH-sulfonated-PCBs (~10^{-1} ng/mL), and sulfonated-PCBs (~10^{-2} ng/mL). Only the latter corresponds to the level detected in the previous work (Palladini et al., 2025a). This is probably due to the different experimental conditions of the two studies, especially the different type and number of PCB congeners to which the inoculum was exposed. In both studies PCB 155 was used, but the microbial community may vary depending on the exposure to a PCB mix or a single congener, giving different results in terms of degradation products (Correa et al., 2010). In addition, the leaves used in the previous study (Palladini et al., 2025a) were collected in Lombardy, northern Italy, whereas the leaves used in the current study were sampled in Lancaster in the north-west of England. This is important, since the microbial community constituting the phyllosphere depends on several factors, including the plant location (Leveau, 2019). In fact, the results obtained also differ on some aspects from a similar experiment, where *Quercus ilex* leaves were exposed in aerobiosis to PCB 155 used as an individual congener. Here, considering the closest sampling time (T40), OH-PCBs were the most abundant (between 10^{-2} and 10-1 ng/mL), then sulfonated-PCBs (almost 10^{-2} ng/mL) and OH-sulfonated-PCBs (10^{-3} ng/mL). Concerning the number of congeners, two more penta-OH-sulfonated-PCBs were detected in the present study, and one penta-sulfonated-PCB instead of the hexaCl-sulfonated-PCB. However, the other measured congeners do correspond, as they have the same retention time (see Table SI–1).

In Fig. 3, a Principal Component Analysis was performed, considering all metabolites produced by each treatment at every sampling

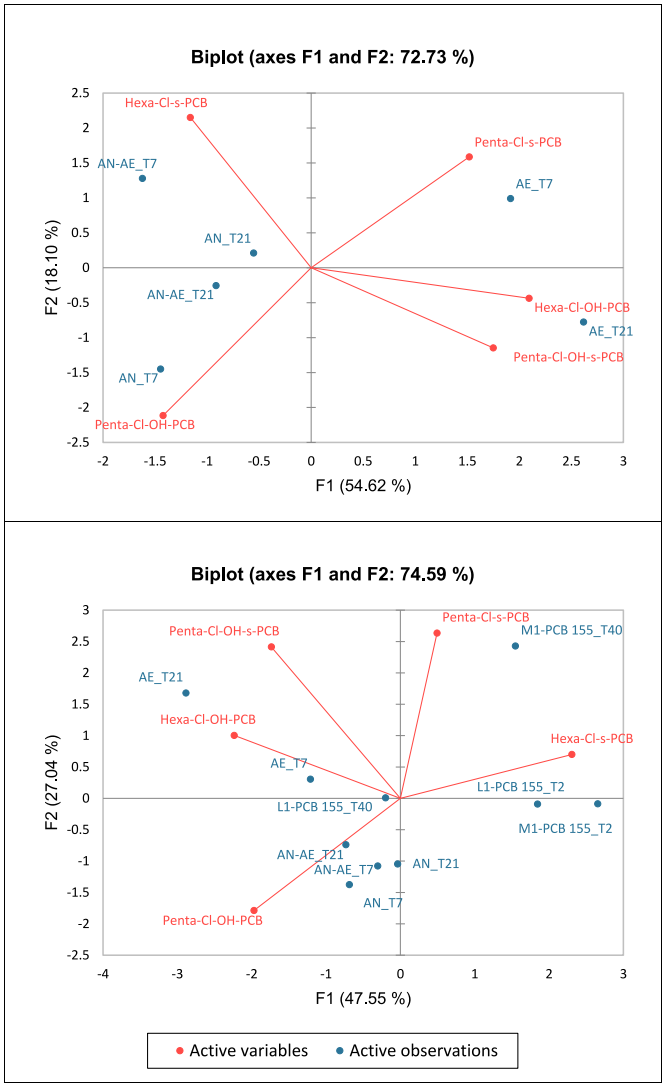

Fig. 3. PCA analyses for OH-, OH-sulfonated- and sulfonated-PCB metabolites considering all samples and metabolite classes together (above) and comparing the results with those from (Palladini et al., 2025b) (below).

time. Most of the variance (54.62 %) is explained by the first component, driven by the Hexa-Cl -OH-PCB on one end and a combination of hexa-Cl -s-PCB and penta-OH-PCB. It shows that the aerobic treatment is quite different from the anaerobic-aerobic and the anaerobic ones, being more focused on the production of hexa-Cl-OH-PCBs, penta-OH-sulfonated-PCBs and penta-sulfonated-PCBs. In fact, these congeners formed at the highest level.

In the same Fig. 3, the results obtained were also compared with those from (Palladini et al., 2025b). For all treatments, the same picture appears. Anaerobic-aerobic and anaerobic samples are grouped, while the aerobic treatment differs from the others, except for the treatment with *Q. ilex* leaves (L1-PCB 155_T40) (Palladini et al., 2025b). In fact, in both samples the hexa-Cl-OH-PCBs were more concentrated than in the others.

3.1. Degradation products

All metabolites produced in aerobiosis, anaerobiosis-aerobiosis and anaerobiosis are listed in Fig. 4. All of them appeared from the 7th day of the experiment, at variable concentrations and number of congeners. PCB 155 is a symmetric molecule from which only 1 hexa-Cl-sulfonated isomer can be formed, as the -SO3H group can only replace one of the 4 H atoms in meta positions. In fact, no more than 1 hexa-Cl-sulfonated-PCB was detected in the samples. Its chemical identity was also confirmed by the standard (sulfonated-PCB 155) synthetized by our group (Maspero et al., 2023). The same applies for the hexa-Cl-OH-PCB, where the OH-substitution probably occurs in the available meta positions as well. On the other hand, a higher number of congeners was detected for the penta-chlorinated family of each class. This may occur through dichlorination Thus, the meta position is no longer the only one available, allowing for congener diversification. Similar considerations were drawn in the previous study on the production of sulfonated-PCBs by the leaf-associated inoculum (Palladini et al., 2025b). The number of congeners formed is comparable for almost all chlorination families, except for penta-OH-sulfonated-PCBs, whose maximum number in the aerobic treatment of the current study is 4 (Fig. SI–1) instead of 2 (Palladini et al., 2025b). This can be explained by assuming that both the OH-group and the SO_3H-group can replace a chlorine atom, as hypothesized for the formation of the octa-OH-sulfonated-PCB from the deca-PCB by Palladini and coworkers (Palladini et al., 2025a). In addition, concerning this metabolite class, there is still an open debate on its identity. Indeed, the same fragmentation pattern of OH-sulfonated-PCBs obtained by the HPLC-HRMS (Orbitrap) was also found by Liu and coworkers (Liu et al., 2018), who attributed the fragmentation ions to sulfated-PCBs. Hence, it cannot be stated whether they are OH-sulfonated-PCBs, sulfated-PCBs or a mixture of the two. From the experiment performed by Palladini and coworkers (Palladini et al., 2025b), it seems more likely to be OH-sulfonated-PCBs, but further research is needed to confirm this hypothesis.

4. Conclusions

The aerobic, anaerobic-aerobic, and anaerobic conditions resulted in different outcomes in terms of PCB metabolite formation. First, all three classes were produced in all conditions. The aerobic treatment was the most effective, as it resulted in the highest concentrations and number of congeners. In general, concentrations decreased as the available oxygen decreased: aerobiosis > anaerobiosis-aerobiosis > anaerobiosis. The same chlorination families of OH-, OH-sulfonated- and sulfonated-PCBs formed, except for the anaerobiosis-aerobiosis treatment, where a hexa-Cl-sulfonated-PCB was detected. Thus, it appears that these new environmental contaminants can also form in situations where oxygen is lacking, for instance, in anoxic microenvironments in soil or in the gastro-intestinal tract of earthworms. Further studies could be directed to identify the species of degrading microorganisms under oxygenated and anoxic conditions as well as verify whether a shift in the

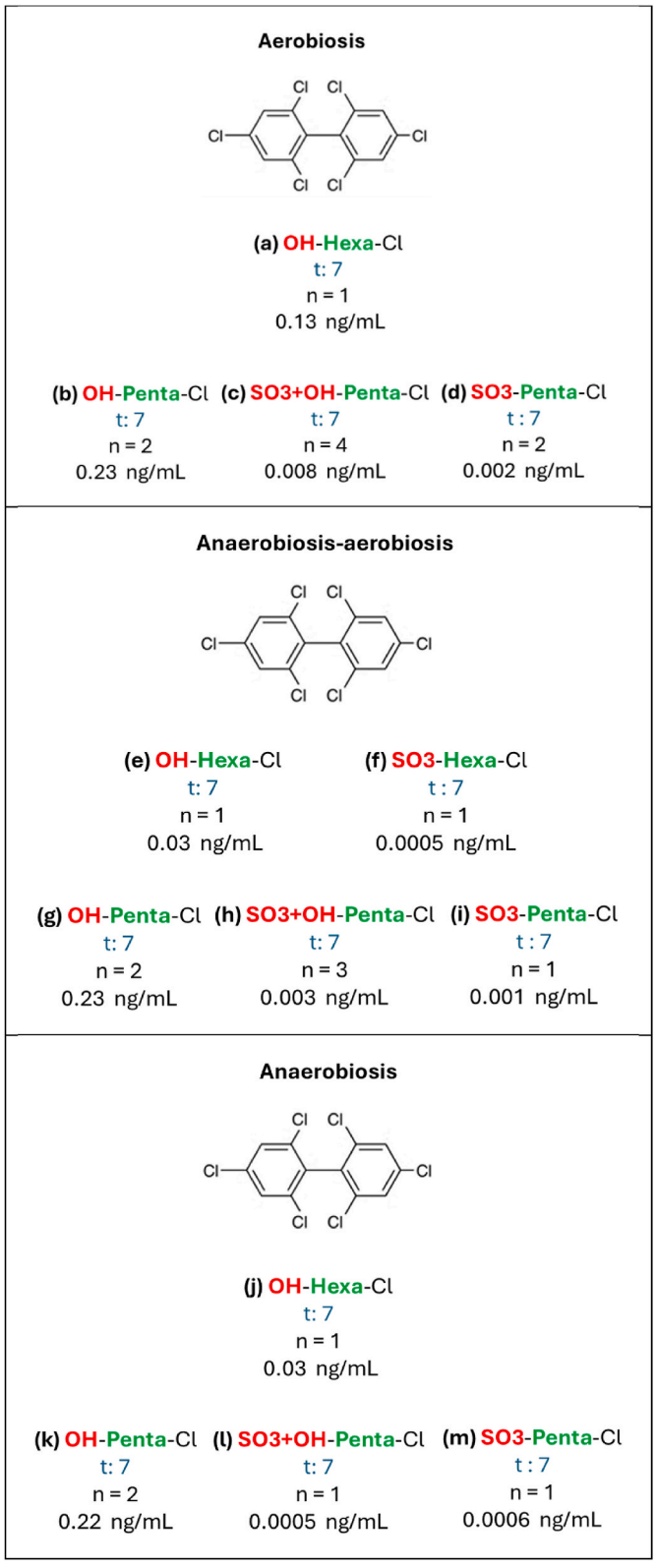

Fig. 4. –Degradation products in all treatments (aerobiosis, anaerobiosis-aerobiosis and anaerobiosis). t is time in days, n is the number of isomers formed. Concentrations are average for isomer family.

communities or their relative abundance would change according to oxygen availability.

CRediT authorship contribution statement

Jessica Palladini: Writing – original draft, Methodology, Investigation, Data curation. **Bhushan P. Gandhi:** Methodology. **Kevin C. Jones:** Resources, Investigation, Conceptualization. **Elisa Terzaghi:** Writing – review & editing, Methodology, Investigation, Conceptualization. **Elisabetta Zanardini:** Resources, Conceptualization. **Giovanni Palmisano:** Methodology, Investigation. **Renzo Bagnati:** Formal analysis, Conceptualization. **Alice Passoni:** Methodology, Investigation. **Kirk T. Semple:** Writing – review & editing, Supervision, Methodology. **Antonio Di Guardo:** Writing – review & editing, Supervision, Resources, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2025.126735.

Data availability

Data are attached in SI

References

Abramowicz, D.A., 1995. Aerobic and anaerobic PCB biodegradation in the environment. Environ. Health Perspect. 103 (Suppl. 5), 97–99. https://doi.org/10.1289/ehp.95103s497.

Bagnati, R., Terzaghi, E., Passoni, A., Davoli, E., Fattore, E., Maspero, A., Palmisano, G., Zanardini, E., Borin, S., Di Guardo, A., 2019. Identification of sulfonated and hydroxy-sulfonated polychlorinated biphenyl (PCB) metabolites in soil: new classes of intermediate products of PCB degradation? Environ. Sci. Technol. 53, 10601–10611. https://doi.org/10.1021/acs.est.9b03010.

Borja, J., Taleon, D.M., Auresenia, J., Gallardo, S., 2005. Polychlorinated biphenyls and their biodegradation. Process Biochem. 40, 1999–2013. https://doi.org/10.1016/j.procbio.2004.08.006.

Chen, C., Yu, C., Shen, C., Tang, X., Qin, Z., Yang, K., Hashmi, M.Z., Huang, R., Shi, H., 2014. Paddy field – a natural sequential anaerobic–aerobic bioreactor for polychlorinated biphenyls transformation. Environ. Pollut. 190, 43–50. https://doi.org/10.1016/j.envpol.2014.03.018.

Correa, P.A., Lin, L., Just, C.L., Hu, D., Hornbuckle, K.C., Schnoor, J.L., Van Aken, B., 2010. The effects of individual PCB congeners on the soil bacterial community structure and the abundance of biphenyl dioxygenase genes. Environ. Int. 36, 901–906. https://doi.org/10.1016/j.envint.2009.07.015.

Evans, B.S., Dudley, C.A., Klasson, K.T., 1996. Sequential anaerobic-aerobic biodegradation of PCBs in soil slurry microcosms. Appl. Biochem. Biotechnol. 57–58, 885–894. https://doi.org/10.1007/BF02941769.

Field, J.A., Sierra-Alvarez, R., 2008. Microbial transformation and degradation of polychlorinated biphenyls. Environ. Pollut. 155, 1–12. https://doi.org/10.1016/j.envpol.2007.10.016.

Humphrey, H.B., Gardiner, J.C., Pandya, J.R., Sweeney, A.M., Gasior, D.M., Schantz, S. L., 2000. PCB Congener profile in the serum of humans consuming Great Lakes fish. Environ. Health Perspect. 108, 167–172. https://doi.org/10.1289/ehp.00108167.

IARC, 2016. Polychlorinated biphenyls and polybrominated biphenyls. IARC Working Group on the Evaluation of Carcinogenic Risks to Humans, 107. International Agency for Research on Cancer, p. 510. https://publications.iarc.fr/_publications/media/download/7436/4402c95e826a3f01686a3acf3129d790fa013b36cb3.pdf.

Leveau, J.H., 2019. A brief from the leaf: latest research to inform our understanding of the phyllosphere microbiome. Current Opinion in Microbiology, Environmental Microbiology 49, 41–49. https://doi.org/10.1016/j.mib.2019.10.002.

Li, X., Liu, Y., Martin, J.W., Cui, J.Y., Lehmler, H.-J., 2021. Nontarget analysis reveals gut microbiome-dependent differences in the fecal PCB metabolite profiles of germ-free and conventional mice. Environ. Pollut. 268, 115726. https://doi.org/10.1016/j.envpol.2020.115726.

Liu, Y., Richardson, E.S., Derocher, A.E., Lunn, N.J., Lehmler, H., Li, X., Zhang, Y., Cui, J. Y., Cheng, L., Martin, J.W., 2018. Hundreds of unrecognized halogenated contaminants discovered in polar bear serum. Angew. Chem. Int. Ed. 57, 16401–16406. https://doi.org/10.1002/anie.201809906.

Long, Y.-Y., Fang, Y., Zhang, C., Du, Y., Shentu, J., Shen, D.-S., 2015. Degradation of polychlorinated biphenyls by sequential anaerobic–aerobic composting. Water Air Soil Pollut. 226, 44. https://doi.org/10.1007/s11270-015-2333-6.

Maspero, A., Vavassori, F., Penoni, A., Galli, S., Palmisano, G., Bagnati, R., Passoni, A., Davoli, E., Palladini, J., Terzaghi, E., Di Guardo, A., 2023. Synthesis of a new sulfonated-hexachlorobiphenyl standard for environmental analysis, ecotoxicological, and toxicological studies. Sci. Total Environ. 882, 163445. https://doi.org/10.1016/j.scitotenv.2023.163445.

Master, E.R., Lai, V.W.-M., Kuipers, B., Cullen, W.R., Mohn, W.W., 2002. Sequential anaerobic−aerobic treatment of soil contaminated with weathered aroclor 1260. Environ. Sci. Technol. 36, 100–103. https://doi.org/10.1021/es001930l.

Palladini, J., Bagnati, R., Passoni, A., Davoli, E., Lanno, A., Terzaghi, E., Falakdin, P., Di Guardo, A., 2022. Bioaccumulation of PCBs and their hydroxy and sulfonated metabolites in earthworms: comparing lab and field results. Environ. Pollut. 293, 118507. https://doi.org/10.1016/j.envpol.2021.118507.

Palladini, J., Terzaghi, E., Bagnati, R., Passoni, A., Davoli, E., Maspero, A., Palmisano, G., Di Guardo, A., 2023. Environmental fate of sulfonated-PCBs: soil partitioning properties, bioaccumulation, persistence, and mobility. J. Hazard Mater. 457, 131853. https://doi.org/10.1016/j.jhazmat.2023.131853.

Palladini, J., Terzaghi, E., Zanardini, E., Palmisano, G., Bagnati, R., Passoni, A., Di Guardo, A., 2025a. First evidence of environmental formation of sulfonated PCBs. Environ. Sci. Technol. Lett. https://doi.org/10.1021/acs.estlett.5c00139 acs.estlett.5c00139.

Palladini, J., Terzaghi, E., Zanardini, E., Palmisano, G., Bagnati, R., Passoni, A., Di Guardo, A., 2025b. Sulfonated-PCBs and OH-sulfonated-PCBs: an insight into their environmental formation and identification. Submitted to Science of the Total Environment.

Pathiraja, G., Egodawatta, P., Goonetilleke, A., Te'o, V.S.J., 2019. Effective degradation of polychlorinated biphenyls by a facultative anaerobic bacterial consortium using alternating anaerobic aerobic treatments. Sci. Total Environ. 659, 507–514. https://doi.org/10.1016/j.scitotenv.2018.12.385.

Payne, R.B., Fagervold, S.K., May, H.D., Sowers, K.R., 2013. Remediation of polychlorinated biphenyl impacted sediment by concurrent bioaugmentation with anaerobic halorespiring and aerobic degrading bacteria. Environ. Sci. Technol. 47, 3807–3815. https://doi.org/10.1021/es304372t.

Terzaghi, E., Posada-Baquero, R., Di Guardo, A., Ortega-Calvo, J.-J., 2021. Microbial degradation of pyrene in holm oak (Quercus ilex) phyllosphere: role of particulate matter in regulating bioaccessibility. Sci. Total Environ. 786, 147431. https://doi.org/10.1016/j.scitotenv.2021.147431.

UNEP, 2001. Stockholm Convention - Home Page [WWW Document]. URL. http://www.pops.int/. (Accessed 27 February 2020).