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Microbial fuel cells with polychlorinated biphenyls contaminated soil as electrolyte: energy performance and decontamination potential in presence of compost

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HIGHLIGHTS

- Single chamber TMFCs with PCBs and compost were assembled and tested.
- TMFCs with a low PCB contamination showed good energy performance.
- High PCB concentration negatively affected microbial activity.
- 20 % PCB degradation did not imply dioxine-like PCB formation.
- Internal resistance is strongly related to soil contamination.

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ABSTRACT

The electrical performance of Terrestrial Microbial Fuel Cells (TMFCs) with soil as the electrolyte was tested with two concentrations (150 or 250 ng/g soil) of PCBs (Polychlorinated biphenlys) and compost (3 % w/w) in an experiment lasting 60–80 days. Energy output levels were recorded daily by varying the external resistance for detecting the best operating conditions. PCB concentrations and microbiological analyses (total microbial abundance and activity) were performed at the start and end of the experiment. The highest power generation (207 ± 80 mW/m^2 at 112.5 Ω) was recorded in the presence of compost with the lowest PCB concentration, when compared to TMFCs without compost (1.5 ± 0.2 mW/m^2 at 300.8 Ω). The results demonstrated that the power generation was correlated with a lower internal resistance and a higher microbial activity. Moreover, chemical results indicated a possible threshold of PCB concentration for the concurrently electricity production and PCB degradation. In fact, PCB removal was obtained only in the cells with high PCB concentration, achieving a reduction of 21 % and 16 % with and without compost, respectively. The microbiological results showed that an additional organic carbon source (methanol or compost) promoted microbial activity and abundance. A positive correlation was found between microbial activity and TMFC electrical output only in the case of PCB low concentration, in the presence of compost. No previous studies addressed the performance of TMFCs with different levels of PCBs in terms of soil decontamination and electricity production. Although a longer experiment is needed, considering PCB persistence in soils, this experiment provided useful information and a new insight on the TMFC effectiveness for soil decontamination and electricity production. The results presented here support considerations about soil resilience through microbial communities and orient further research on contaminant degradation by TMFCs.

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1. Introduction

The EU objectives of reaching net zero emissions by the middle of the 21st century and the targeted reduction at 2030 (Fit for55[1]; Repower EU[2]) can only be achieved through a systematic adoption of renewable energy sources. Although new technologies are available for use, the recovery of contaminated soils remains a significant challenge, at least in the next few decades – EU Soil Strategy 2030 [1–3]. Bioelectrochemical systems (BES) represent a promising solution in terms of both electricity production and decontamination potential, with low installation and maintenance costs. Among the BES family, microbial fuel cells (MFCs) are a reliable solution that can generate electricity from a variety of waste materials, e.g., organic matter, from the metabolism of microbial communities, growing as biofilms on electrode surfaces. Electroactive bacteria convert chemical energy from organic compounds to electrical energy through catalytic reactions [4], in a low-cost and carbon-neutral energy manner [5]. They have also been used for biodegradation/removal of a range of contaminants, including chlorinated samples [6]. Persistent contaminants, in particular, such as polychlorinated biphenyls (PCBs), require aerobic and anaerobic conditions for their degradation; the latter are necessary for reductive dehalogenation in the presence of electron donors (organic compounds), which is a key step for their removal [7].

Even though traditionally MFCs work with wastewater [8], an increased number of experiments with soils and sediments have more recently been reported [9,10]. In terrestrial MFCs (TMFCs) soil acts as the electrolyte for the degradation of organic compounds [10]. Soil is a complex substrate characterized by a variable and abundant microbial community, including electrogenic bacteria, needed to convert chemical energy into electrical energy and for electron transport [11–14]. In addition, soil is a material rich in complex compounds and nutrients, accumulated from plant and animal material decomposition. TMFCs proved to be a low-cost technology able to work also for long periods [15,16], and used, among others, for remote sensing [11,17,18]. TMFC technology is still at an early stage of development, therefore there are still some technical and operational constraints, such as low power density and reliability that currently limit the potential of MFCs [15,17–19]. Despite the low instantaneous power, the huge availability of wastewater and polluted soils could be exploited using innovative methods of energy production, allowing a simultaneous bioenergy generation and bioremediation of substrates, at low set-up costs.

To assess the potential of TMFCs, key parameters should be properly analyzed. Soil moisture is essential for microbial activity, as it ensures substrate dissolution and maintains soil electric characteristics. Temperature is also a key factor, affecting pollutant removal and microbial behavior, including those of Electrochemically Active Bacteria (EAB) [20,21]. Furthermore, soil is rich in microorganisms (bacteria, fungi) which have a key role in transforming inorganic substances and degrading organic compounds, including persistent and toxic contaminants, such as PCBs [22]. Similarly, impedance matching (Jacobi's law) is essential for maximum power transfer in MFCs [23–25]. Because TMFCs, in addition to energy production, can transform contaminants, they represent a promising technology for soil bioremediation [26]. The presence of exogenous organic additives, such as compost, has been also found useful to enhance activity of soil microorganisms and PCB degradation [27,28].

PCBs are halogenated aromatic hydrocarbons primarily used for their insulating properties in various applications, including electrical equipment [29]. Because they are persistent organic pollutants with a high degree of chemical stability and lipophilicity, they can bioconcentrate in different compartments, mainly in soils and sediments [30,31]. PCBs consist of 209 congeners, based on the position of chlorine atoms on the biphenyl rings, which are subdivided into ten isomeric classes (congeners with an equal number of atoms of chlorine: mono-CB, di-CB, to deca-CB). Dioxin-like PCBs (DL-PCBs) include 4 non-ortho (PCB-77, PCB-81, PCB-126 and PCB-169) and 8 mono-ortho (PCB-105, PCB-114, PCB-118, PCB-123, PCB-156, PCB-157, PCB-167 and PCB-189) substituted congeners which exert a number of toxic responses similar to those observed for 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), the reference substance for calculating PCB toxicity [32,33]. These DL-PCB congeners, "bulky" substituents in the ortho position that would sterically interfere with the rotation of the rings around the biphenyl bond, can bind to aromatic hydrocarbon receptors, transcription factors involved in xenobiotic metabolism [32]. Several toxic effects of PCBs have been detected in humans, experimental animals, and cell cultures. Due to their relevant toxicity, DL-PCB congeners must be searched for in soil for ensuring a detailed PCB pollution assessment.

The complex PCB degradation processes, which involve both aerobic and anaerobic biodegradation phases, rarely occur naturally. The absence or scarcity of end-terminal electron donors can further decrease removal efficiency of their biodegradation or even prevent it [34]. MFCs were found to be a useful tool for PCB remediation in previous studies using river sediments, obtaining encouraging results with an Aroclor1254 removal efficiency of about 45 % after 60 days [35,36]. Cao et al. [37] studied the degradation of a hexachlorobenzene, an organic chlorine compound similar to PCBs, using a soil microbial fuel cell. They observed that TMFC promoted growth in electrogenic bacteria, which also favoured hexachlorobenzene removal efficiency. However, applications of TMFCs for PCB degradation using soil as the electrolyte are still scarce [38]. The presence of high amounts of toxic compounds, such as PCBs, could negatively affect TMFC efficiency [39,40], because they can hamper microbial activity. However, there is no knowledge on TMFC efficiency if operating at different PCB concentrations, similar to those found in real cases [41]. Substrate depletion or low carbon source can decrease TMFC performance [42]. Recently, compost was found to be a suitable carbon source for stimulating microbial activity [43] favouring persistent organic pollutant degradation [44–46]. In fact, since compost can have a high organic carbon content (up to 26 % or more), it can improve dechlorination acting as an electron donor [47]. The benefits of adding compost for persistent organic contaminant like PCBs has also been previously found in other experiments [44,48,49].

In the present study, the performance of single chamber TMFCs using PCB contaminated soils as the electrolytes has been tested. The influence of two different PCB concentrations (High: 250 ng/g or Low: 150 ng/g) and compost were assessed on energy performance and microbial community activity.

To the best of the authors' knowledge, no previous studies addressing the performance of TMFCs with different levels of toxic contaminants, taking into consideration both soil decontamination and electricity production, have been reported. The results presented here can support further considerations of soil resilience, by shedding light on the internal mechanisms of resistance to contamination, with a possible solution to counteract soil degradation.

2. Materials and methods

2.1. Soil sampling, soil moisture, water holding capacity and compost addition

An overall amount of 12 kg of clay soil (48 % clay, 24 % silt, 28 % sand) with a neutral pH was used for the TMFC experiment. It was manually sampled (0–30 cm depth) from an uncultured land in Central Italy located close to Rome. The soil used in this experiment did not contain PCBs (PCB concentration: <LOD). Before the experimental set-up, the soil was air-dried (approximately at 25 °C) and sieved (5 mm mesh). The organic carbon and total nitrogen, measured by a CHNS

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[1] https://www.consilium.europa.eu/en/policies/green-deal/fit-for-55/.

[2] https://commission.europa.eu/strategy-and-policy/priorities-2019-2024/european-green-deal/repowereu-affordable-secure-and-sustainable-energy-europe_en.

analyzer (Carlo Erba NA 1500 series 2 C/H/N/O/S, Milan, Italy), were 1.47 % and 0.16 %, respectively. The soil used for this work was from an abandoned agricultural site where a previous experiment on dichlorodiphenyldichloroethylene (DDE), a chlorinated organic compound, showed the presence of natural microbial populations able to degrade it [10]. To perform the experiments, a municipal solid waste compost (3 % w/w dry soil, quantity frequently used as an organic amendment in agriculture), supplied by Progeva Spa, was added and mixed to an aliquot (4.8 kg) of soil. The compost was an ISO/IEC 17025 certified material whose main characteristics have been previously described in depth [27]. The compost had a 26 % organic carbon content, whereas the compost-amended soil contained 1.9 % organic carbon and 0.22 % total nitrogen. The maximum water content (water holding capacity, WHC) of soil and soil with compost was 58.8 and 62.1 %, respectively. The TMFCs were set up with a soil moisture of about 34 % (which corresponds to about 60 % of WHC), which is considered a suitable soil moisture for enhancing microbial activity [50,51].

2.2. *Chemicals and soil spiking*

A standard solution (PCB-Mix 3) containing a mixture of seven PCBs with a different chlorine content [52] (six PCB markers and one dioxin-like, see Table 1) was purchased from LGC Standards (Teddington, Middlesex, UK). Aliquots (150 μl or 250 μl) of standard solution were dissolved in 200 ml of MilliQ water and Methanol (MeOH) (Honeywell, LC/MS CHROMASOLV) and used to add PCBs to soil for obtaining two different concentrations of PCBs, named in the present experiment Low (for 150 ng/g) or High (for 250 ng/g).

The spiked PCB amounts corresponded to more than 2-fold and 6-fold respectively the Italian regulatory limit of 60 ng/g for PCBs in soil (Italian Environmental Law [47,53,54]). These concentrations are also in the rage of those found in a historically contaminated soil of Southern Italy (about 270 ng/g soil, [41]) and those detected in several Countries (150 ng/g as ΣPCB, [55]).

Soil was spiked using a peristaltic pump (Minipuls 3, Gilson) set at 11 mL/min flow. To homogenize the soil to which PCBs were added, soil samples were previously air-dried for 3 days, spiked with the PCB solutions, and then placed for 3 days in glass jars (1 L Volume) on a rotary stirrer (built ad hoc at IRSA-CNR lab). Finally, to test the possible effect of methanol added for spiking PCBs on TMFC efficiency and microbial activity, 350 μL of methanol alone were added to some soil samples. The experimental conditions are listed in Table 2.

2.3. *TMFC setup*

Single chamber TMFCs consisted of borosilicate cylindrical containers (diameter: 11.5 cm; height: 12 cm). Anode and cathode electrodes were graphite felt with a 0.5 cm thickness [10]. TMFCs were set up with soil with a 34 % moisture, in accordance with Borello et al. (2021) [44] (see Supplementary Materials, Fig. S1). The anode and cathode of each cell were connected through an external electrical circuit with a measurement device [44]. The equipment was used to continuously measure electrical output and, to perform the polarization experiments, modulate the operating conditions (switching between open and closed-circuit conditions by varying the external resistance) so as to achieve maximum power transfer. The operating parameters were accurately controlled to guarantee a proper assessment of TMFC performance variation along the experimental period. All TMFCs were maintained in a thermostatic chamber (Fig. S1) at a constant temperature of 25 °C ± 1 °C. TMFCs were set up in triplicates for each soil condition (Table 2).

Table 1
List of PCBs analyzed (12 dioxin-like PCBs, 6 markers and 13 non-dioxin-like PCBs). In bold: PCBs contained in the PCB-Mix 3 used in this experiment.

PCB type	PCB Congeners
Dioxin-like PCBs	77, 81, 105, 114, **118**, 123, 126, 156, 157, 167, 169, 189
Marker PCBs	**28, 52, 101, 138, 153, 180**
Non-dioxin-like PCBs	81, 77, 105, 114, 118, 123, 126, 156, 157, 169, 16, 189

Table 2
TMFC experimental conditions.

TMFC	Electrolyte
Soil + High PCBs	Soil spiked with PCB mix, 250 ng/g soil
Soil + Low PCBs	Soil spiked with PCB mix, 150 ng/g soil
Soil + Compost + High PCBs	Soil + compost + high PCB, 250 ng/g soil
Soil + Compost + Low PCBs	Soil + compost + low PCB, 150 ng/g soil
Soil + methanol (Control TMFC)	Soil spiked with only methanol

Soil moisture was maintained during the experimental period. The required amount of distilled water (ca. 6–7 mL in TMFCs with High PCBs concentration and ca. 9.5 mL in TMFC with Low PCBs and without compost) was daily added to compensate evaporative losses. The TMFCs were kept for 60 days, except for *Soil + Compost + Low PCBs* which were maintained for 80 days due to the higher electrical performance recorded throughout the entire experimental period. Microbial and chemical analyses were performed on soil samples collected from each TMFC at the start (t0: 0 day) and end of the experiment (t1: 60 or 80 days). The whole set-up, including all experimental conditions, is depicted in Fig. 1.

2.4. *Electrical measurements*

Electrical measurements were carried out daily after refilling with water, (added for maintaining the soil moisture), to assess TMFC performance. TMFCs were kept in open circuit (OC) conditions for most of the time. Since the electric measurements tests were carried out to assess the best conditions for the energy harvesting and to ensure a peak power useful for sensoring (so small electric devices). The homemade measurement device [56] was connected with the TMFCs to monitor the operating conditions such as open (OC) and closed circuit (CC). The tests (outputs recorded twice a day, at 9 a.m. and at 6 p.m.) consisted in OC (charge phase) and current measurements, when the circuit was closed (CC, discharge phase). OC and CC phase periods were set at 900 s and 15 s, respectively. During the CC phase, several resistances were applied, such as 112.5, 300.8, 530.8, 990.6, 2983.3, 4976.0 and 9957.7 Ohm. This wide range of resistances was selected to obtain the maximum power output, produced when the internal resistance is equal to external one (Jacobi's Law [25]). The power output was calculated according to Ohm's Law [57].

Since the ohmic resistance strongly influences energy output, in order to obtain more accurate values, these were also calculated from the linear fit of the ohmic region of each polarization curve. The values were derived from the slope of the polarization curves [58]. The internal resistance was analyzed at the end of the experiment at day 60 (or day 80 for the *Soil + Compost + Low PCBs* only). Moreover, an analysis of the closed-circuit performance was carried out focusing on the best performance conditions.

2.5. *PCB analyses*

Soil samples at t0 and t1 of the experiment were dried at 30 °C for 2 days and pulverized in a ball mill (Retsch MM301 Mixer Mill, Haan, Germany) with zirconium oxide jars to have the suitable particle size (about 200 μm). The PCB extraction was performed using 1 g of soil (in duplicates) for each sample, with an Accelerated Solvent Extractor (ASE 350 Dionex, Thermo Scientific) and using hexane, as reported in detail in Ancona et al., 2017 [41]. More details are included in Supplementary Materials.

To assess the degradation of the spiked PCB congeners (see Table 1) and their possible transformation to other congeners, the PCB quantitative analysis in soil samples was performed using a PCB standard

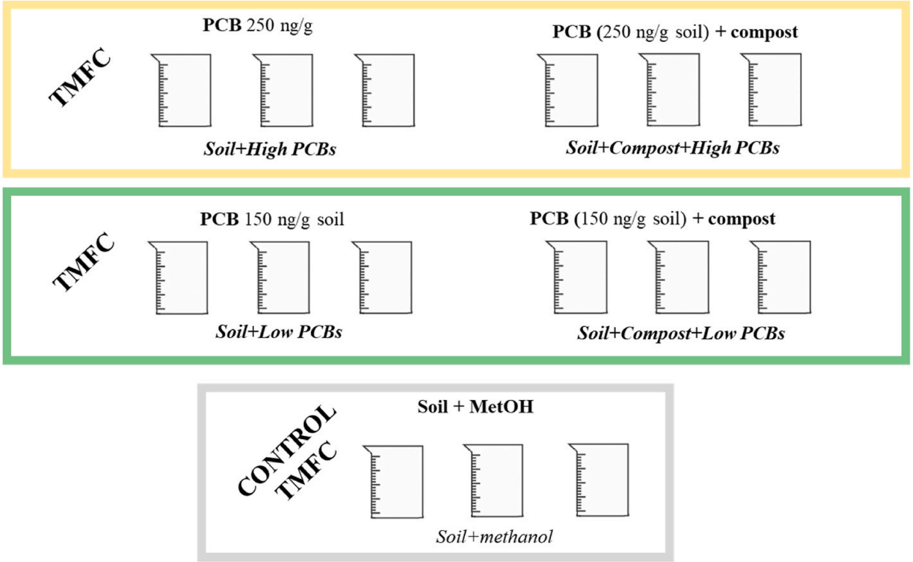

Fig. 1. Experimental set-up.

mixture containing a total of 31 congeners (Analytical Standards). The PCB congeners analyzed (Table 1) were 12 dioxin-like PCBs, 6 markers and 13 non dioxin-like PCBs. Results are reported as average values expressed as the sum of the entire 31 PCB congeners analyzed ng/g (**Σ**PCB; see Table 1).

2.6. Soil microbial community

Microbiological analyses (microbial abundance and activity) were performed at the start (t0) and at the end (t1) of experiment in all conditions. Total microbial abundance (No. cell/g soil) was assessed using DAPI (4',6-diamidino-2-phenylindole) for the direct count of the microbial cells under an epifluorescence microscope (Leica DM 4000 B fluorescence microscope, Leica Microsystems GmbH, Wetzlar, Germany), following the method described in Barra Caracciolo et al. [59]. Microbial activity was measured with the dehydrogenase assay. It reflects the overall microbial respiration rate and, therefore, the biological oxidation of organic matter [60]. However, it can be affected by the presence of toxic pollutants (e.g. PCBs) [61]. The soil dehydrogenase activity was expressed as μg of triphenylformazan (TPF)/g dry soil. More details on microbiological analyses are included in Supplementary Materials.

2.7. Statistical analysis

The statistical analysis for assessing differences in PCB concentration, dehydrogenase activity and microbial abundance between the different conditions was performed using the Kruskal-Wallis One Way Analysis of Variance on Ranks, with significant differences at the $p < 0.05$ level. Moreover, correlations were performed between microbial activity and TMFC electrical output (power generation).

A multivariate statistical analysis (Principal Component Analysis, PCA) was performed to better correlate electrical outputs (Power density), PCB concentrations (PCB marker and dioxin like), dehydrogenase activity (DHA), microbial cell counts (DAPI) in soil samples. The PCA was performed with R software, using the packages *FactoMineR* and *factoextra*. The dataset was normalized by the *scale* function.

3. Results and discussion

The end (t1: 60 or 80 days) of the experiment for each TMFC condition was defined on the basis of electrical output reduction. Because the TMFCs with compost and low PCB content (*Soil* + *Compost* + *Low PCBs*) had still good electrical outputs after 60 days (corresponding to the end of the experiment for the other TMFCs), these TMFCs were maintained for further 20 days.

3.1. PCB analyses

The concentration of the added PCBs determined in each TMFC at t0 and t1 (end of the experiment: 60 or 80 days) are reported in Table 3. The GC/MS analyses revealed that the total amount of PCBs in all soil samples was attributable to the seven congeners used in the spiking procedure (6 markers and 1 dioxin–like, see Table 1).

A partial PCB removal (21 % and 16 % in *Soil* + *High PCBs* and *Soil* + *Compost* + *High PCBs*, respectively, Table 3) was achieved when the PCBs were spiked at the highest concentration. The decrease in PCBs was significant ($p < 0.05$) only in the presence of compost (*Soil* + *Compost* + *High PCBs*). PCB amount in TMFCs with a low PCB content (*Soil* + *Low PCBs* and *Soil* + *Compost* + *Low PCBs*) remained in the same range of the initial one (considering the standard errors). PCB degradation requires very complex aerobic and anaerobic processes, and acts as a strong selective selection for resistant microorganisms to their toxic effects or able of biotransform them [62]. The decrease in high PCB concentration observed in *Soil* + *High PCBs* + *Compost* can be ascribed to a reductive dechlorination (the first step for PCB degradation). The addition of compost introduced organic carbon which presumably provided microorganisms and electron donors, as found in other works [41,44]. However, some microbial populations were affected by the high PCB concentration, as highlighted by the lower initial cell abundance in the

Table 3
PCB concentration at the start (t0) and at t1 (end of the experiment: 60 days in all experimental conditions and 80 days for *Soil* + *Compost* + *Low PCBs* condition). PCBs are reported as sum of the entire 31 congeners analyzed (ΣPCB; see Table 1). Results are reported with their standard errors. The symbol * indicates that the PCB removal was significant ($p < 0.05$).

TMFC	ΣPCB t0 [ng/g dry soil]	ΣPCB t1 [ng/g dry soil]	PCB removal %
Soil + *Low PCBs*	127.77 ± 19.91	141.99 ± 10.37	–
Soil + *High PCBs*	203.08 ± 31.07	160.32 ± 22.13	21.06
Soil + *Compost* + *Low PCBs*	108.77 ± 40.71	132.55 ± 11.73	–
Soil + *Compost* + *High PCBs*	250.49 ± 10.72	210.38 ± 20.56	16.01*

High PCBs + *Compost* than *Low PCBs* + *Compost* conditions (Fig. 5A, section 3.3 Microbiological results). Overall, PCBs (low/high amounts) and absence/presence of compost affected the natural soil microbial community, electrical performance, and contaminant degradation in different ways.

Finally, at the end of the experiment no significant transformations in other PCB congeners beyond those spiked, were observed (Table 4), among those analyzed.

In fact, among the 12 DL-PCB analyzed, only PCB118 was found and all Marker PCBs added to soil (28, 52, 101, 153, 138 and 180) were detected. Finally, all the Non-DL-PCBs were below the instrument detection limit (0.5 μg/kg).

There are no previous reports regarding TMFCs with PCB contaminated soil as the electrolyte so far, and there are only few studies reporting PCB degradation in sediments. For example, 30 % of PCBs (Aroclor 1254, initial concentration: 6 mg/kg sediment) degraded in 60 days in a sediment microbial fuel cell, although no deep analysis of the congeners was performed [35]. A reduction in hexachlorobenzene (another chlorine persistent contaminant, which requires a reductive dechlorination for its degradation) was found in a soil microbial fuel cell with an initial concentration of 40 mg/kg.

3.2. Electrical performance

Electrical parameters, such as open circuit voltage (OCV) and power density, were measured in all experimental conditions (Table 2) during the entire experimental period. The average open circuit voltage values are shown in Fig. 2.

In general, an increase in the open circuit (OC) voltage indicates beneficial redox environmental conditions for electricity generation [63] and possibly favorable conditions for organic carbon degradation in the TMFCs. This increase was evident only in the *Soil* + *Compost* + *Low PCBs* and control TMFC (*Soil* + *methanol*) setups (Fig. 2), and this could be due to anodic electroactive biofilm development [36,64]. The prompt voltage increase in the presence of methanol (black symbols, Fig. 2) was probably due to the absence of PCBs, which have been found to be toxic for microorganisms in MFCs [65], and the capability of electroactive bacteria to use methanol as an organic source. For this reason, in methanol presence, the microbial community did not require an adaptation period and a faster response was measured (about 40 days in advance). In the case of *Soil* + *Compost* + *Low PCBs*, a significantly higher open circuit voltage was observed from day 28, compared to the other TMFCs, reaching a maximum voltage of 580 ± 8.3 mV at day 65. This suggests that the PCB concentration (ca. 150 ng/g soil) initially affected the electrical performance because soil and compost microbial populations were selected [66] before being adapted to the experimental condition. However, in these TMFCs any significant PCB degradation was observed.

Table 4
Concentrations of various PCB groups (DL-PCB: Dioxin like; Marker PCB; Non DL-PCB: Non-Dioxin like) expressed as a sum of congeners in different TMFC experimental conditions. The congeners with concentrations < the instrument detection limit are reported in *italics*. The symbol * indicates the congeners detected within the Dioxin like or Marker PCB groups.

TMFC	Days	DL-PCB	Marker PCB
		81, 77, 123, 114, 118*, 105, 126, 167, 156, 157, 169, 189 (ng/g)	28*, 52*, 101*,153*, 138*, 180* (ng/g)
Soil + *Low PCBs*	0	21.62 ± 4.55	106.15 ± 15.36
	60	18.44 ± 3.40	123.55 ± 6.97
Soil + *High PCBs*	0	33.53 ± 6.55	169.55 ± 24.52
	60	27.03 ± 5.85	133.29 ± 16.28
Soil + *Compost* + *Low PCBs*	0	16.99 ± 5.45	91.78 ± 35.26
	80	21.76 ± 1.85	110.79 ± 9.88
Soil + *Compost* + *High PCBs*	0	40.57 ± 1.55	209.92 ± 9.22
	60	32.47 ± 1.80	177.91 ± 18.76

In all the other configurations (*Soil* + *Low PCBs*, *Soil* + *High PCBs* and *Soil* + *Compost* + *High PCBs*), only a low OCV level was reached, confirming that PCB contamination (in the absence of compost or at high PCBs concentration) did not result in redox conditions that would favor the growth of electroactive bacteria.

Specifically, the *Soil* + *Compost* + *High PCBs* configuration showed an OCV trend similar to that of the TMFCs without compost and containing only PCB contaminated soil (High and Low), recording voltage values between 30 mV and 90 mV.

In a previous work [10], a comparison among the performance of TMFCs with and without compost and contaminated with a persistent pollutant (DDE) was performed. The TMFC + DDE showed OC values (300 mV) similar to those found in the present work. On the other hand, the compost presence also increased the TMFC performance (up to three times when considering the OCV values). This behavior confirmed that PCBs had a detrimental effect on the soil and compost microbial populations. The overall microbial community of TMFC required a longer time for adapting to the contaminant and, consequently, to produce electricity.

The TMFC performance reported as the maximum power density value measured when varying the external resistance is reported in Fig. 3. The maximum values were measured with external resistances varying between 112.5 and 9957.7 Ohm. TMFCs without compost (Fig. 3a) showed power density values ranging between 0.01 and 1 mW/m^2, with peaks of about 1.5 mW/m^2, indicating that, without any organic carbon addition, the activity of electroactive bacteria was limited and, consequently, cation transport across the soil was not efficient for obtaining good electrical output levels, as already found by other authors [67].

Fig. 3 a shows that during the first experimental period (about 21 days), the *Soil* + *Compost* + *High PCBs* condition showed performances comparable to that produced by TMFCs with PCBs in absence of compost (*TMFC Soil* + *PCBs High* and *TMFC Soil* + *PCBs Low*, Fig. 3a), suggesting that compost did not stimulate electroactive bacteria growth when PCB was in the high concentration. However, as shown in Fig. 3 b, starting from the fourth week of the experiment, the *Soil* + *Compost* + *Low PCBs* TMFCs produced a higher power output, similar to that measured for control TMFCs (soil not spiked with PCBs, containing only methanol). *Soil* + *Compost* + *Low PCBs* TMFCs reached their maximum power output (207 ± 80 mW/m^2) at day 65, which outperformed that of the control TMFC (maximum Power output: 126 ± 28 mW/m^2 at day 21). This trend was maintained until the end of the experimental period (day 80).

Wu et al. (2019) [68] measured a maximum power density (78.87 mW/m^2) with microbial fuel cells with sediment contaminated with PCBs lower than that found in the present study. Another study performed by Cao et al. [69] also obtained a lower maximum power output (77.5 $mW/m^{2)}$ with a soil MFC spiked with hexachlorobenzene (HCB), a high chlorinated compound like PCBs. Although the experimental operating conditions of these previous studies were different (the MFC electrolytes were contaminated by PCBs or HCB at concentrations two-three orders higher than in the current study), overall, the power recorded was three-fold lower than that obtained in the present experiment. This can confirm our results, although further investigations are necessary to fully understand and improve this aspect.

Moreover, the results here reported showed a possible threshold level of PCBs that can have a substantial impact on the growth of electroactive bacteria and energy generation. Further research is needed to confirm this issue, because literature is still lacking on this topic. For example, additional experiments could be conducted to test different PCB concentrations (among those tested in this work) to verify the existence of an intermediate concentration of PCBs that can simultaneously maximize the degradation of the pollutant and the electricity generation.

To further investigate the potential for electricity production, MFC

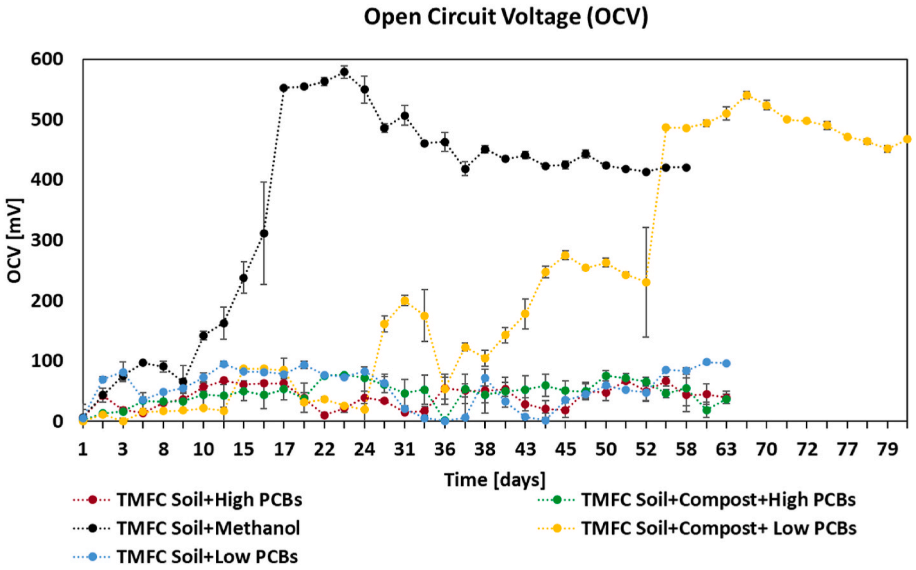

Fig. 2. Open circuit voltage measurements (mV) in all experimental conditions (see Table 2) during the entire experimental period.

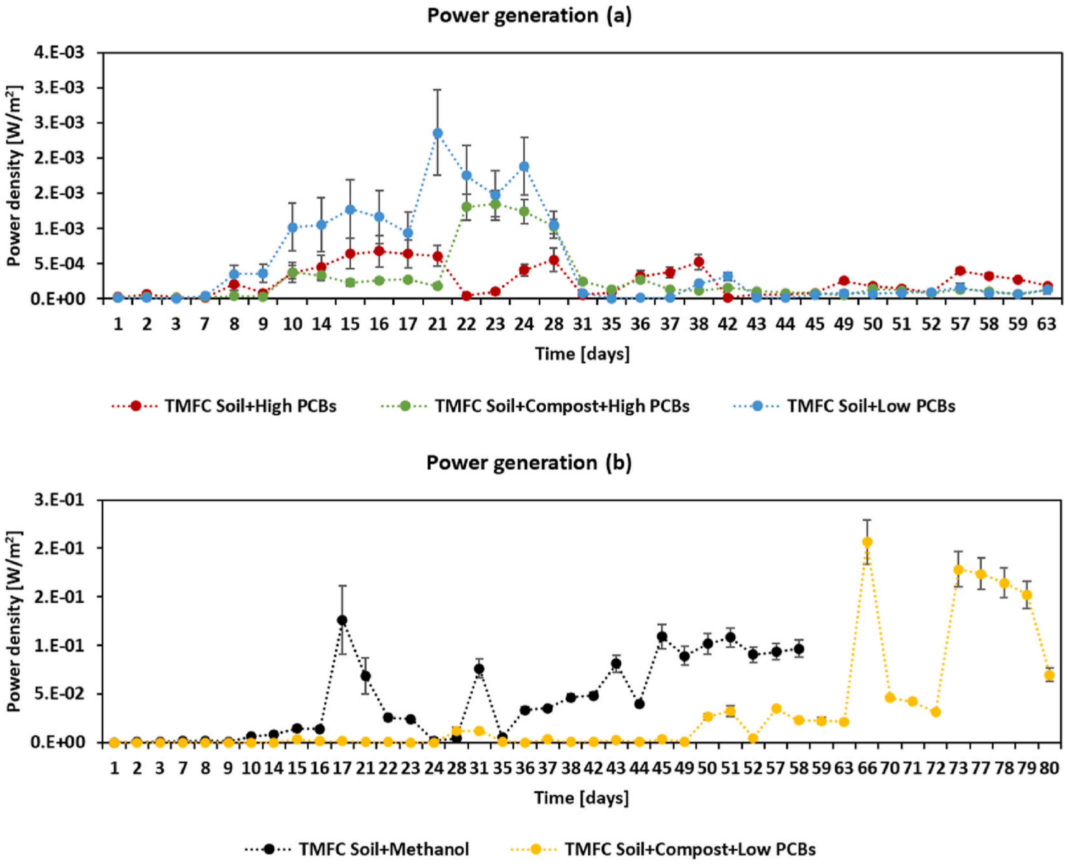

Fig. 3. Maximum power density curves in all experimental conditions: a) TMFCs with high or low PCB concentration in absence of compost and TMFC with high PCB concentration in presence of compost; b) TMFCs with low PCB concentration in presence of compost and in control TMFCs (with only methanol).

output was measured across variable external resistances. These were selected assuming that the maximum power was obtained when the external resistance is equal to the internal one (Jacobi's Law [25]). The internal resistance of the TMFCs was obtained by analyzing the slope of the polarization curves at the end of the experiment at day 60 (day 80 for the *Soil* + *Compost* + *Low PCBs* only). Moreover, an analysis of the closed-circuit performance was carried out focusing on the best performance conditions (Supplementary Material Fig. S2).

The polarization curves obtained at the end of the experiment as a function of current density or external resistance for the *Soil* + *Compost* + *Low PCBs* and *Soil* + *Compost* + *High PCBs* TMFCs are shown in Fig. 4a, b,c,d. The corresponding calculated values of the internal resistance for all conditions are reported in Table 5. The same data, reported as power density generation in CC, are reported in Supplementary Materials,

Table 5
– Internal resistance of TMFCs calculated at the end of the experiment from the slope of the TMFCs polarization curves.

Experimental condition	Resistance (Ohm)
Soil + Low PCBs	152
Soil + High PCBs	1052
Soil + Compost + Low PCBs	99.8
Soil + Compost + High PCBs	2802.1
Soil + MeOH	26

Fig. S2. A wide ohmic region for *Soil + Compost + Low PCBs* is shown in Fig. 4 a, where the slope indicates an internal resistance of ca. 100 Ohm (Table 5). The results of the power and polarization curves obtained at the end of the experiment as a function of external resistance for *Soil + Compost + Low PCBs* (Fig. 4b) confirm this finding indicating that the maximum power (and current) was obtained when the external resistance was equal to 112.5 Ohm (Table 5). In Fig. 4c and 4d, the same plots are reported for the *Soil + Compost + High PCBs* TMFCs.

The internal resistance can be attributed to slow molecular kinetics, tardy transfer of cations across the electrolyte (soil) and electrons through resistive media and materials. These results were probably due to the insulating property of PCBs [29]. An internal resistance of ca. 1000 Ohm (similar to those found for *Soil + High PCBs* and *Soil + Compost + High PCBs* conditions, Table 5) was measured by Cao et al. [69] that tested a contamination level much higher than the low PCB condition, thus confirming that the higher the contamination present, the higher the internal resistance occurs.

The external resistance values corresponding to the maximum electrical power generation in all conditions are reported in Table 6. These results, combined with those from the polarization curves at the end of the experiments (Supplementary Materials, Fig. S3) confirm that the maximum power was obtained for the external resistance value closest to the internal one (Table 5). At the end of the experiment, the maximum power generation was obtained with different external resistance values (Table 6): 100 Ω for TMFCs with low PCBs concentration (both with/without compost) and for Control TMFCs (with methanol), 1000 Ω for TMFCs with high PCBs concentration, without compost; 3000 Ω for TMFCs with compost and high PCBs concentration.

The recorded electrical performance was achieved under suboptimal conditions. Further experiments with the TMFCs continuously connected to the external resistance (Closed Circuit), generating electricity, could be performed for better assessing contaminant degradation.

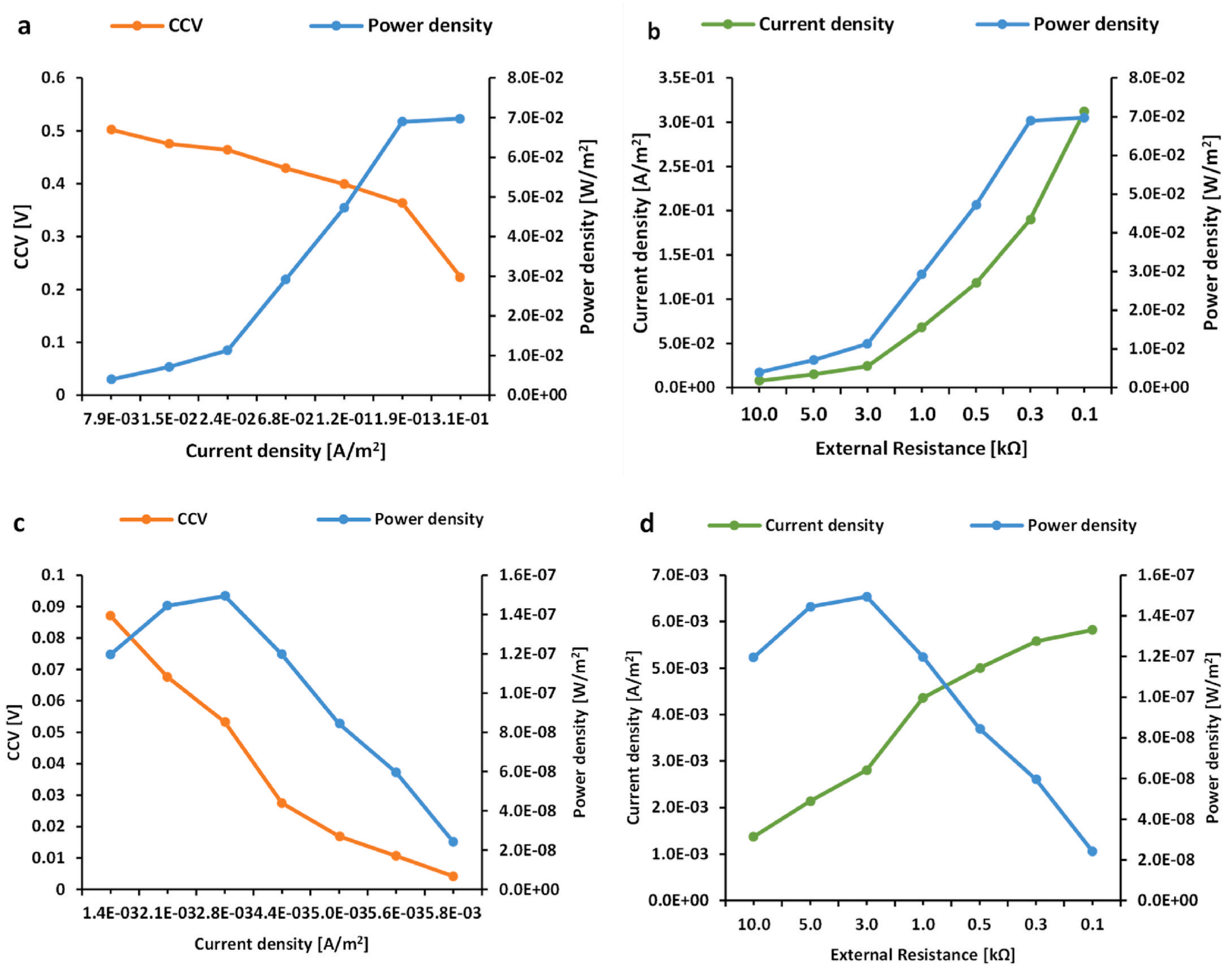

Fig. 4. Power and polarization curves obtained at the end of the experiment as a function of current density (a and c) or external resistance (b and d) for TMFCs treated with PCBs and compost (a and b: *Soil + Compost + Low PCBs*; c and d: *Soil + Compost + High* PCBs). CCV: closed circuit voltage.

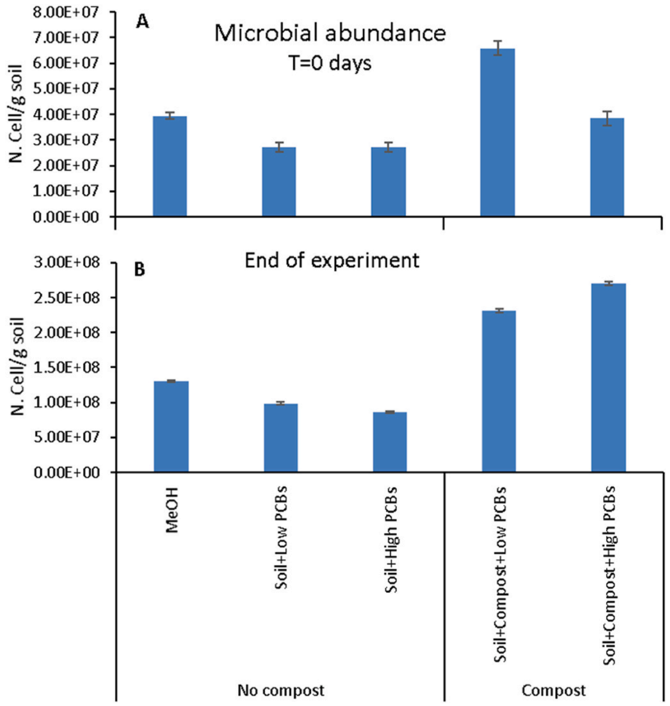

Fig. 5. Total microbial abundance in the various experimental conditions at the start (A) and at the end of the experiment (B). Conditions: MeOH (methanol), *Soil* + *Low PCBs* (without compost), *Soil* + *High PCBs* (without compost) on the left; *Soil* + *Low PCBs* (with compost), *Soil* + *High PCBs* (with compost) on the right.

Table 6
External resistance values required to obtain the maximum electrical power generation from TMFCs.

Experimental condition	Resistance (Ohm)
Soil + *Low PCBs*	112.5
Soil + *High PCBs*	990.6
Soil + *Compost* + *Low PCBs*	112.5
Soil + *Compost* + *High PCBs*	2983.3
Soil + *MeOH*	112.5

3.3. Microbiological results

The microbial abundance at the start of the experiment in soil spiked with PCBs without compost (*Soil* + *Low PCBs*; *Soil* + *High PCBs*) was ca. 2×10^7 cells/g soil (Fig. 5A, left side). The addition of compost resulted in a prompt increase in cell abundance and a significant ($p < 0.01$) higher value (about 6×10^7 cells/g soil) was found at the low concentration of PCBs (Fig. 5A, right side). This was due to the introduction of microbial populations with compost, as already found in previous studies [27,28]. The relatively lower increase in microbial abundances in the *Soil* + *Compost* + *High PCBs* condition was presumably due to an initial toxic effect of the added chemicals on some microbial populations. Evidently, at the end of the experiment (Fig. 5B), the microbial abundance which increased ($p < 0.01$) in all TMFCs, had significantly higher values ($p < 0.05$) in both *Soil* + *Compost* + *Low PCBs* and *Soil* + *Compost* + *High PCBs* conditions. This indicates how PCBs allowed for selection of bacterial cells capable of growing under those conditions, with eventual PCB degradation, whilst preventing the growth of electroactive bacteria at high PCB concentration.

The microbial activity measured by the dehydrogenase method (DHA) is reported in Fig. 6. In line with the microbial abundances, the highest activity values were found in the presence of compost in both initial (Fig. 6A) and final (Fig. 6B) samples, showing how compost introduced both microbial cells and organic carbon which promoted microbial activity, as found in other works [43,47].

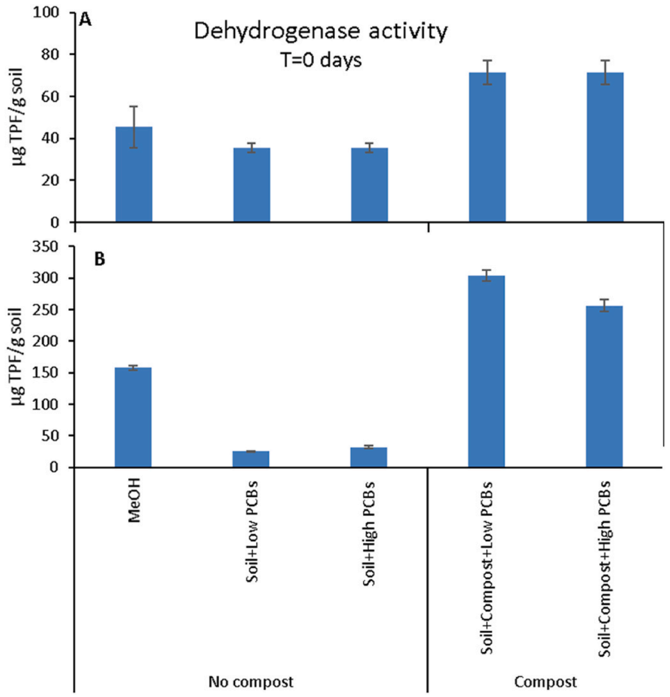

Fig. 6. Microbial activity in the various experimental conditions at the start (A) and at the end of the experiment (B). Conditions: MeOH (methanol), *Soil* + *Low PCBs* (without compost), *Soil* + *High PCBs* (without compost) on the left; *Soil* + *Low PCBs* (with compost), *Soil* + *High PCBs* (with compost) on the right.

At the start of the experiment, the increase in DHA was higher in the presence of Low than High PCB concentration, because these pollutants had a toxic effect on some microbial populations ([61]). A microbial activity increase was found in all conditions (including those without compost addition) at the end of the experiment (when compared to the initial ones), but significant higher values ($p < 0.01$) were found in *Soil* + *Compost* + *Low PCBs*, *Soil* + *Compost* + *High PCBs* and *Soil* + *MeOH* conditions (303.54 ± 8.42 µg TPF/g dry soil, 256.39 ± 9.63 µg TPF/g dry soil and 58.15 ± 3.44 µg TPF/g dry soil, respectively) compared to the conditions without compost. Moreover, matching the microbial activity at the end of the experiment (Fig. 6B) and the internal resistance (Table 5), a higher resistance and lower microbial activity was detected in compost absence. On the other hand, in the case of *Soil* + *Compost* + *Low PCBs* the high microbial activity can be ascribed to the low value of internal resistance.

The overall results confirm how an additional organic carbon source (in particular compost) promoted microbial activity and TMFC performance when PCB is present at a Low concentration. Indeed, dehydrogenase activity, reflecting overall oxidative capabilities of a microbial community during the degradation of organic compounds, can improve electrical outputs of microbial fuel cell systems [70]. For example, a recent study on terrestrial MFCs (set up with soil without any pollutant content) has demonstrated how, in compost presence, microbial activity and electrical measurements were significantly correlated, thanks to an increase in electroactive bacterial performance [43]. In the present study, a positive correlation ($p < 0.05$) between microbial activity and TMFC electrical outputs was found only in the case of the *Soil* + *Compost* + *Low PCBs* and *Soil* + *MeOH* conditions, showing how a high PCB amount suppressed electroactive bacteria and selecting degradative populations [12]. Additionally, in the case of *Soil* + *Compost* + *High PCBs*, the microbial activity did not lead to low resistance values. This fact confirms that the presence of PCBs suppressed mainly electroactive bacteria, as also found by other studies [71].

The PCA considering overall microbiological, chemical and electrical results support how above mentioned (Fig. S4). In fact, the first two principal components (which explain nearly 90 % of the total variance) can accurately represent overall data. The first principal component shows high positive values for DAPI, DHA and power density and the values for PCBs are relatively negative.

Contrasting results on the role of electroactive bacteria in the degradation of contaminants are reported in recent works [72] and the role of the anode-associated microorganisms is sometimes difficult to clarify [73], considering also that only a few electroactive bacterial species in soil have been identified. The higher microbial activity found in this work did not reflect a reduction in internal resistance and increase in performance in the presence of PCBs, in all cases. However, when the contamination was low (*Soil* + *Compost* + *Low PCBs*), adding organic matter (compost) exceeded the deteriorating effects (insulating properties and toxic effects on microbial community) of PCBs. On the other hand, the fact that PCBs decreased in the *Soil* + *Compost* + *High PCBs* confirmed that a strong selection of resistant and degrading PCB microbial populations possibly occurred in these conditions.

4. Conclusions

The electrical performance of Terrestrial Microbial Fuel Cells was assessed in the presence of both compost and persistent organic pollutants (PCBs) at two different concentrations. Open and Closed-Circuit configurations with variable resistances were considered. Compost had an overall positive effect on electroactive bacteria and TMFC performance only in the cell set-up with a relative Low PCB concentration (150 ng/g).

On the other hand, in the High PCB concentration (250 ng/g), the soil microbial community was negatively affected by these contaminants. In this case, the microbial activity increase observed in compost presence was mainly due to a selection of PCB resistant bacteria which contributed to their overall decrease. In terms of electrical performance, the low voltage and power output levels observed, were presumably due to inhibitory effects of High PCB concentration on electroactive bacteria.

Overall results suggest a threshold level of PCBs, which can significantly affect electroactive bacteria development and energy production, even in the presence of compost. Further investigations are necessary to confirm these findings. Due to the fact that in this experiment the TMFCs were kept in open circuit (OC) condition for most of the time (electrical monitoring apparatus operation), other experiments with the TMFCs continuously connected to the external resistance (CC), could be performed for testing further PCB degradation, also in the case of high contaminant concentrations. Moreover, steady state tests, stacked TMFCs and different PCB concentrations could be evaluated to better understand the factors - including the presence of a contaminant - which can improve TMFC performance, favoring PCB degradation by soil microbial communities. This will provide a deeper understanding of all chemical-biological phenomena enabling tests that can verify this technology for contaminant degradation on both large laboratory-scale experiments and field tests in real scale applications.

CRediT authorship contribution statement

G.G. Gagliardi: Writing – original draft, Methodology, Investigation, Formal analysis. **D. Borello:** Writing – review & editing, Supervision, Investigation, Conceptualization. **C. Cosentini:** Writing – original draft, Investigation, Data curation. **A. Barra Caracciolo:** Writing – review & editing, Supervision, Investigation, Conceptualization. **G. Aimola:** Writing – original draft, Investigation, Formal analysis, Data curation. **V. Ancona:** Writing – review & editing, Supervision, Methodology, Investigation, Conceptualization. **I.A. Ieropoulos:** Writing – review & editing, Supervision. **G.L. Garbini:** Investigation, Formal analysis, Data curation. **L. Rolando:** Investigation, Formal analysis, Data curation. **P. Grenni:** Writing – review & editing, Supervision, Methodology, 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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jpowsour.2024.234878.

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